

Conductivity Studies of the Size-Induced Metal-Insulator Transition (SIMIT) in Silver Nanoparticles

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A thesis submitted to the Department of Chemistry, University of Oxford for the Degree
of Doctor of Philosophy in Inorganic Chemistry

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The work described in this thesis was performed in the Inorganic Chemistry Laboratory, University of Oxford from February 2012 until September 2015, under the complete supervision of Professor Peter P. Edwards. All of the work is my own unless otherwise stated and has not been submitted previously for any other degree at this or any other university.

Nurul A. Che Lah

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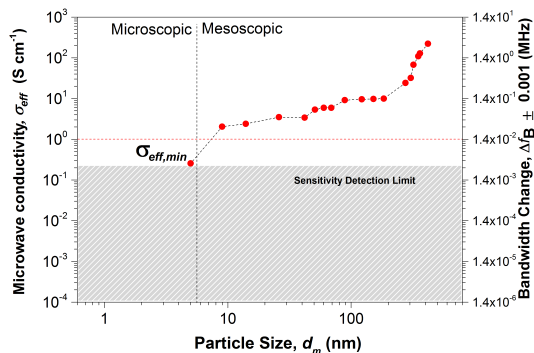
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Abstract

In his tenth decade, Professor Sir Nevill Mott, in a letter to Professor Peter P. Edwards, reminiscenced about the fundamental difference between metals and non-metals; thus he wrote of the situation at the absolute zero of temperature ($T = 0$ K) '*...there a metal conducts, and a non-metal doesn't*'. This simple – but amazingly powerful – commentary stands as a powerful abiding description of the challenge of the fascinating question as to what makes a metal conduct. Many years of experimental studies of metals and non-metals, targeted at the experimental verification in divided-metal systems ranging from transition mesoscopic metal compounds to microscopic colloidal metals, the occurrence of the electronic transition between these two canonical states of matter have always an enduring fascination where the possibility of a *Size-Induced Metal-Insulator Transition* (SIMIT) within a small particle of a bulk metal is accessed. In contrast to the situation of a discontinuous Metal-to-Insulator Transition (MIT) in macroscopic systems containing huge numbers of interacting particles and electrons (*i.e.* a doped semiconductor), the onset of the SIMIT in a single, isolated microscopic particle of a metallic element of the Periodic Table is expected to be a continuous metal-insulator transition.



A logarithmic plot of the variation of the effective microwave conductivity obtained from microwave cavity resonator measurements as a function of the mean Ag particle diameter, d_m .

Here, we report an experimental study on the microwave electrical conductivity across the possible SIMIT in particles of the most conductive of all metals in Periodic Table - silver (Ag). Particular emphasis has been placed on the development and application of a non-intrusive microwave measurement technique, taken across a broad range microwave frequencies. The aim is to look for, and interrogate the nature of the SIMIT in such ultra-fine Ag particles. We have attempted to develop a coherent description of the different dielectric responses that yield electrical conductivity over a wide range of mesoscopic and microscopic Ag particles, from which the SIMIT is identified and rationalised. We find that, at 294 K, the mesoscopic Ag particles approximately 5 nm exhibit an 'effective' microwave conductivities which is reduced by some two orders-of-magnitude below that of bulk metallic Ag.

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Chapter 1

Size-Induced Metal-Insulator Transition (SIMIT)

Silver nanoparticles are one of the most actively studied materials together with gold nanoparticles for its remarkable electrical properties. One of the current unique electrical properties is the one so-called the Mott's Metal-Insulator Transition which is really important for application in electronic device. Despite the recent progress in synthesis and characterisation of silver and other metal transition nanoparticles, it is still an open question as to-how the *Size-Induced Metal-Insulator Transition* occurs specifically on the microscopic regime. This chapter starts with a brief historical background of silver particles and their correlated terms that define their states either as nanoparticles or colloids in the **first section**. A brief introduction on this complex phenomena, particularly emphasising the idea of a 'Mott metal to non-metal transition' in silver particles systems at and below room temperature are provided in the **second section**.

1.1 Historical Perspective of Ag Nanoparticles

Colloidal silver (Ag) has been known since time immemorial and was widely used as a versatile antibacterial store vessels lining for water, wine and vinegar, which were highly valued by the Athenians, Romanians, Phoenicians and Macedonians. Alchemists in the Middle

Ages described that the discovery of a soluble form of Ag would result in a miraculous elixir called the “Blue-Bloods Tonic” which mostly found from the used of Ag utensils and goblets that if ingested would lead to eternal fortune of health life. European alchemists were noted to offer this elixir not only to the upper echelons of society but also to the whole community as a protection from the rampant plagues of those centuries [1]. Hindu Ayurvedic chemists also developed Ag tonics as a rejuvenating promoter for patients incapacitated by age or disease to these days. Over this millennium, the uses of colloidal Ag are more centred on countless medical conditions, most practically even before the consciousness of that microbes were the agents of infection.

Even though colloidal Ag was superior for ancient and medieval applications, the use of silver nitrate (AgNO_3) for medicinal purposes was overwhelmed those centuries for a long time [2]. During the early 1900’s, it was proven that Ag alone possesses low and almost no toxicity to public health, which increases the need for colloidal Ag-based synthesis formulations. The colloidal phase was observed to be the most compelling phase among other man-made Ag formulations since colloidal Ag does not possess the caustic properties of salts (*e.g.* AgNO_3) and it also demonstrates a high level of activity at very low concentrations [2]. Although Michael Faraday’s research on Ag colloids has not much been written as compared to gold (Au) colloids, the recognition of the potential uses of Ag colloids was first emphasised by him in the 1850’s when he studied the experimental relations of Au and other metals [3].

Perhaps, the true history of colloidal Ag began in the late 19th century, where the very first proper electrochemical preparation of colloidal Ag was devised in 1881 by Lea (Figure 1.1) [4]. Lea accomplished the foremost turning point in Ag chemistry when he documented the true synthesis route of colloidal Ag *via* reduction of AgNO_3 using sulphate ions. The widespread interest in colloidal Ag followed here, and a large numbers of enthusiast biochemists begins to initiated the use of colloidal Ag into technology in the late 1900s’ and

early 2000's. One of the water purification developments known as *Katadyn Silver* was reinvented by Krause in 1928 [5]. Colloidal Ag was utilised as a coating-impregnated ceramic to sterilise water in remote areas where clean water was not readily available. The *Katadyn Silver* was considered to be the state-of-the-art at the time.

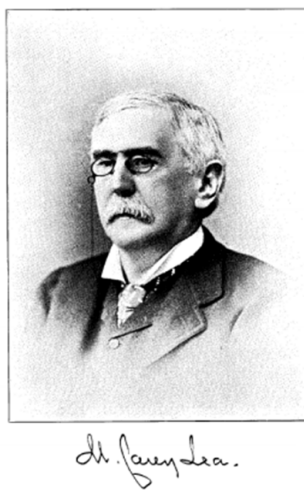


Figure 1.1: Mathew Carey Lea (1823-1897) was the first chemist who accomplished a major milestone in chemistry by preparing the Ag colloid *via* reduction of AgNO_3 (*adapted from www.historiccamera.com*).

The potential of Ag colloids was studied using scientific methods in order to unravel more of its unique applications. This was highlighted in a famous Richard Feynman's visionary and prophetic lecture, 'There's Plenty of Room at the Bottom' which initiated the concept of 'nano-world' in 1959 [6]. Following an excellence Feynman's lecture, the realisation on the importance and awareness on the implications of quantum confinement effect consisting colloidal Ag grew. The popularity of zero-valence colloidal Ag continues to grow and one of the significant discoveries was the development of immobilized Ag colloids on activated carbon for water disinfection discovered by Renn in 1965 [7]. Later, Frens and Overbeek succeeded in their consequent capping protection experiment after Lea's colloidal Ag particles with citrate ions in 1969 [8].

The influence of the term 'colloid' has grown considerably after a myriad of successful stories on the roles of Ag and Au substances in industrial applications in the 20th century. The term 'colloid' was coined by Graham, who is known as the Father of Colloid Chemistry in 1861 [9] following the year of Faraday's established works on a series of transition metals (Ag, Au, Cu, Pt, Fe, Zn, Pd, Rh, Ir and Hg). The term 'colloid' originally comes from the Greek word *kolla*, which means glue. Colloids were something new and unusual, and their properties were rather astonishing at the time. Faraday's pioneering works in observing the colour changes of thin films prepared from dried colloidal metal solutions proved that the metals suspended in colloids were able to interact with light. Hence, Faraday was the first to classify that the vivid colours of colloidal Ag were due to the small size and morphology of the Ag particles, which suggested that their dimensions were essentially the same order of magnitude as the wavelength of light right after his accomplishment work on Au colloid. Faraday discovered that the metal particles in the colloids must be very tiny enough, such that they could not be viewed with the high-powered microscopes at the time. Mie [10] was the first to provide a generic and comprehensive comparative theory which explains the strong scattering and absorption of light by small spherical particles which were later interpreted as localised surface plasmon resonance. Approximately a half of century after Lea's work, the ingredient presents in Lea's colloidal Ag were identified owing to the development of shorter wavelengths of electron microscopes. The average diameters of the Ag nanoparticles were found to range from 7 to 10 nm [8].

In the early 20th century, catalysis is another area where Ag colloids were used in catalysis reaction of methanol to formaldehyde [11]. The availability of electron microscopes have enabled scientist to examine the size and morphology of Ag and other metal colloids intensively which led to the discovery and exploitation of their unique properties.

1.2 Ag Clusters, Colloids and Nanoparticles: A Matter of Definition

The discussion above has underlined a brief historical perspective of Ag colloids over past decades. In the 20th century the intimation and all important linked areas of cluster chemistry, nano-chemistry and particularly metal colloids itself have expanded dramatically and many research journals and proposals primarily leaned to merge these three distinctive areas under the generic term **nanoscience** or **nanotechnology**. Apparently, the boundaries between these areas were neglected on purpose, even though there should be a clear distinction between them [12–14]. **Nanoscience** is the study of the phenomena and manipulation of materials at the atomic, molecular and macromolecular scales, whereby the properties of the materials differ significantly from those at a larger scale. In contrast, **nanotechnology** is the characterisation, production and application of the structures, devices and systems used to control the shape and size of the materials at the nanometer scale [15].

The essential connection between these definitions is based on the conviction: ‘*novel properties that differentiate nanoparticles from the bulk material typically develop at a critical length scale of under 100 nm*’. The possibility of attaining novel physicochemical properties along with the intriguing demarcation of the nano-size regime have been the focus of a large number of research activities over the years [14, 16–22]. This demarcation view has further emphasised the necessities and consideration conditions of the nano-size regime particles. However, the definitions of clusters, colloids and nanoparticles are rather oversimplified and thus, there is a need to distinguish the systems in a more subtle, interesting way. Therefore, it is imperative to define and distinguish the similarities and differences between these systems, while recognizing that there are some particles which will occupy an overlapping border state. At present, studies on specific physicochemical properties of nano-size dimensions have to-date indicated that the behaviour of these particles are no longer reflect their behaviour in bulk dimensions and the transition is significantly far

identical for each property. The differences between cluster, colloid and nanoparticles are presented further in the next section.

1.2.1 Cluster

Cluster (Figure 1.2) is defined as *a number of metal centres grouped close together which can have direct metal-metal bonding interactions or interactions through a bridging ligand, but are not necessarily held together by these interactions*. In simple words, clusters are mostly considered as a species, which is precisely defined in the chemical constitution and structure. The bonding of Ag molecular cluster compounds with anionic halogen ligand was established by Rabin [23–26] between 1990 and 2009. Some of the characteristics of Ag cluster features:

1. Ag clusters possess well-defined chemical compositions and structural conditions based on the collection of crystallographic and spectroscopic data.
2. Ag clusters possess well-described ligand spheres bonded to the central core atom.
3. The synthetic approach (generally the main route) used to synthesise Ag clusters usually involves a solution phase. The synthesis methods are well-defined and reproducible. For unstable Ag cluster systems, factors such as size and the number of bonded ligands influence the overall size of the cluster formed.
4. Even though Ag clusters are usually soluble in non-polar organic solvents, the functionalised ligands may be altered in order to maximise their solubility in water. Typically, the solid-solution equilibrium is a reversible system and hence the Ag compounds may tend to recrystallise when the particle size is more than 10 nm.

Thus, the reduction in cluster size to the ultra-fine microscopic scale increases the energy difference between the lowest unoccupied cluster orbital and the highest occupied cluster orbital that definitely give rise to different electronic properties. The quantum size behaviour of metal clusters has been suggested to develop spontaneously unlike nanoparticles where

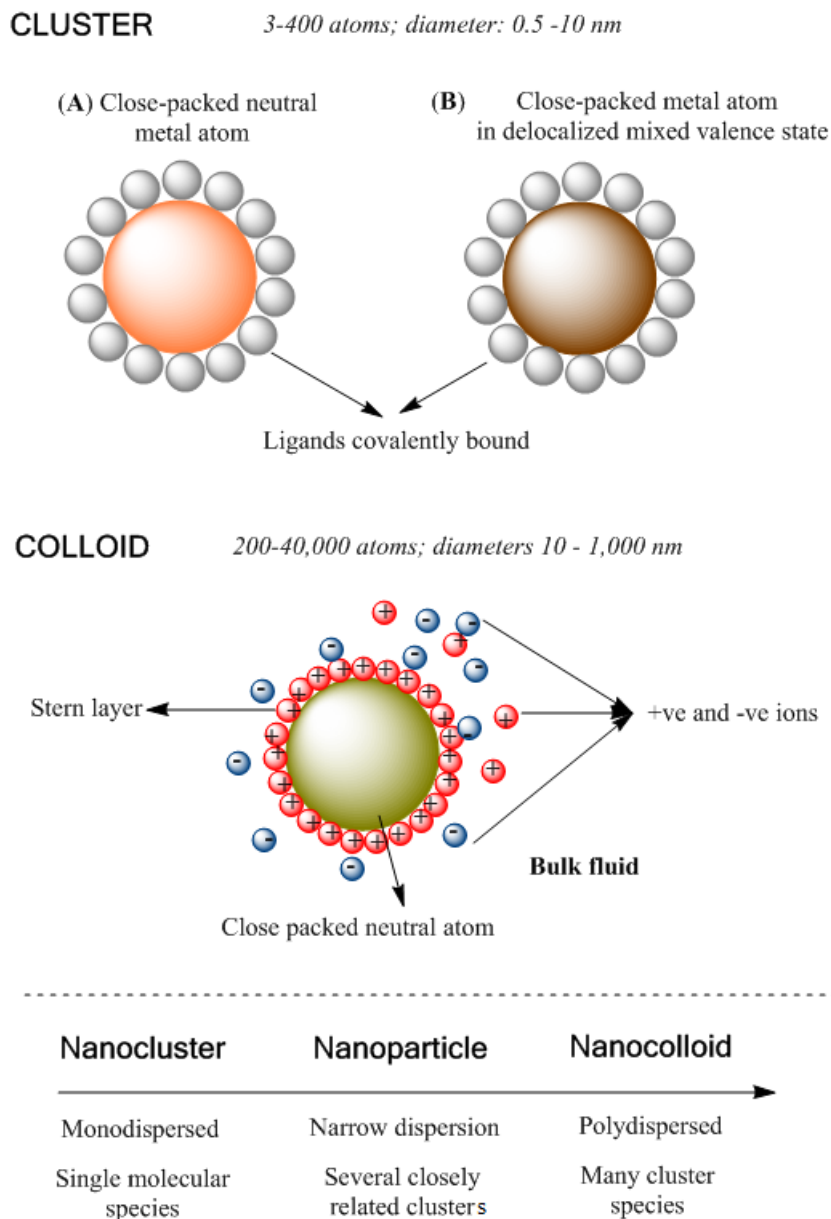


Figure 1.2: Schematic illustration of basic constituents that have been used to describe clusters and colloid structures - either 'colloidal molecule' or 'patchy particles' which hardly do any justice to their intricacy (*reproduced from Mingos [27]*). Mingos proposed that colloidal particles are first formed at soft-matter scales (nanoclusters) which then build up to form more intricate structures (nanoparticles) and consequently grow into 3-D organization of materials (nanocolloids).

the discrete behaviour occurs continuously [28]. Since this work does not involve analysing the properties of the Ag cluster, the structures and the bonding properties of them are not been discussed further. This work will only concentrate on Ag colloids and nanoparticles.

1.2.2 Colloids and Nanoparticles

Prior to reviewing the major developments on the atomic properties and metallic states, it is perhaps useful to provide the basic definition of each sub-physical terminology. Based on a review by Mingos [27], the IUPAC Gold Book [29] provides following descriptions for each definition:

Colloidal term is a state of sub-regime implicitly referring to the molecules or poly-molecular particles dispersed in a medium that have at least a particle dimension roughly between 1 μm to 1 nm, or that in a dispersed system discontinuity are found at distances of that order. Some of the distinctive features of Ag, specifically are listed as follows [12, 13, 27, 30]:

1. Metal colloids have defined compositions and the useful amount of particles is $\geq 15\%$ dispersion in size. Colloidal particles contain between 400 and 40,000 metal atoms and their coagulation to the bulk state is restricted by the build-up of charges on their surface with the help of an outer capping agent. These charges potentially arise from the surface of the metal atoms which are either in a pure metal or oxidised metal state, or polymeric ligands attached to the surface of the metal atoms. The charged particles surrounding the colloids in the solution are present in higher concentrations than the bulk of the solvent.
2. In principle, colloids possess the characteristics of optically clear solutions (sols) with spectroscopic properties are related to the size and morphology of the minute particles.
3. Reproducible syntheses have been developed and a wide range of metal colloid sizes are now commercially available.
4. In this work, naphthalene sulfonate-based Ag colloids are not readily isolated as solids

or re-dissolved. However, sulfonate-based colloids have been synthesised in this work which will re-dissolve in organic solvents by changing into alkylamine-based Ag colloids.

Nanoparticles were first called ‘ultra-fine particles’ and they did not have an accepted IUPAC definition. However, the definition given in the UK PAS71 (BSI Standards Publication 2 Nanoparticles- Vocabulary) defines nanoparticle as *a particle having one or more dimensions of the order of 100 nm or less*. The fascinating characteristics of Ag nanoparticles are briefly described as follows [16–19]:

1. Nanoparticles exhibit a unique, well-defined composition and properties which include a wide range of inorganic classes of compounds, such as metals (Ag in this work), oxides, sulphides and *etc.*
2. Nanoparticles can be synthesised to achieve a relatively narrow size range distribution with dispersion less than 15%.
3. The formation of Ag nanoparticles is mainly achieved by the solution method, which is also known as the bottom-up method. In general, some of the nanomaterials are made directly as dry powders *via* the top-down method, which is analogous to the carving of a sculpture which will undergo a change in their condition after storage. In fact, rapid aggregation process occurs due to the solid bridge binding mechanism for a few seconds. The surface dangling bonds of the nanoparticles contribute to their reactivity behaviour. Thus, the wet chemistry method is preferable in order to keep the nanoparticles dispersed and minimise agglomeration since this method retains the nanoparticles in suspension form. This facilitates sufficient inter-particle repulsion forces which will prevent aggregation.
4. Ag and some other nanoparticles can be re-dissolved to form clear solutions in any organic and inorganic solutions.

5. In most cases, Ag and some other nanoparticles demonstrate reproducible electronic and catalytic properties, which are governed by the size of the nanoparticles.

The colour of Ag colloids which is appreciated by the human eyes originates from coherent oscillations of the conduction electrons upon exposure to the oscillating electric field of light which impinges at a specific wavelength. These resonant oscillations are known as localised surface plasmon resonance (LSPR). LSPR contributes to the enhanced light scattering and absorption which are accompanied by a huge local field enhancement close to the surface of the Ag colloids at the resonance condition [31]. LSPR is strongly controlled by the dielectric environment, as well as the composition [32–36], size and morphological dimensions of the Ag nanoparticles. Although considerable effort and investment have been made to synthesise Ag nanoparticles with precise morphologies, the most stable nanoparticles (equilibrium shapes) to date still possess similar optical emissions. Assuming the same volume concentration for all size ranges, the surface plasmon resonance (SPR) for ultra-fine mono-dispersed Ag nanoparticles ($d_m < 6$ nm) results in the absorption of light in the violet portion of the visible spectrum ($\lambda \approx 396$ nm) and the colloid solution is pale yellow and almost colourless [27]. Light within the blue-green portion of the visible spectrum ($\lambda \approx 450$ nm) is reflected, which gives the Ag colloid solution a dense dark yellow colour with a particle size of $d_m \sim 120$ nm. In general, Ag colloids exhibit the same colour over the entire range of larger particle sizes ($d_m \geq 150$ nm) where the cube and tetrahedron structures are dominant. This yields colloids which are either rich dark orange or dark red. The surface charge on the Ag particles becomes neutral whenever the particles agglomerate, forming larger-size of Ag 'colloidal molecules'. The larger mean particle's diameter with the same amount of Ag 'patchy particles' taken results in a similar yellow solution. The breakdown of aggregation level which can be achieved by modifying the surface and function of Ag particle by using polymers, ligands and biological molecules with good donor atoms, for instance, H and N increases the amount of itinerant Ag particles produced [20, 37]. This leads to a significant improvement in their chemical, physical and optical properties. This surface modification and functionalisation of Ag colloids enhances their potential uses in

recent technology which suitable for extensive chemical, biological, engineering and medical applications [22, 27, 35, 36, 38].

Regardless of the shape and symmetry, a key aspect to the proper interpretation of SPR properties of nanoparticles depends primarily on Mie's work in 1908 [10], who was solved and modelled Maxwell's equations in the form of the dielectric function, ϵ for a single spherical particle interacting with the electromagnetic (EM) field. In general, the dielectric function of a metal depends on the wavelength of dipole oscillations of the free electrons and is related to the electronic transitions of the localised and delocalised electrons counterpart in the intra-band and inter-band transitions, respectively [39]. In consequence, the Ag nanoparticles will have the following broad optical features of SPR: (a) a peak position of 450 nm, (b) reduction in the full width at half maximum (FWHM) when the colloid core size is reduced to within a range of diameters from 30 to 4 nm due to the onset of quantum size effects, (c) sharper transitions which indicate the onset of metal-to-insulator transition for particles with diameters ranging from 4 to 1 nm, which correspond to their critical conditions for metallisation, (d) an ultimate decrease in the SPR intensity which attributed to the decrease in the size of the colloid which consistent to the broadening of the bandwidth. Even though the relationship between the SPR properties of Ag and the morphology of nanoparticles has been giving tremendous attention over the years [40], most of the studies typically involve highly non-equilibrium shapes [41–44], which greatly results in dramatic structural variations given by significant contrast in the optical response. Accordingly, the interaction between the ligands and metal atoms usually contribute to the local spectral peak of the SPR excited in the particles and alkyne-functionalized ligands have been shown to bind onto the surface of the Ag atoms as alternatives to thiol-based ligands [45–48]. Besides, the metal core charge is another influential factor in determination of the SPR energy, which results in a shift to higher frequencies of energy with excessive electronic charge and to lower frequencies with electron deficiency [49–51]. In brief, the positions and intensities of the bands are intimately connected to the size, shape and the

local dielectric environment of the nanoparticles which will be discussed further in **Chapter 4**.

Ag nanoparticles are typically synthesised by unsophisticated solution based (bottom-up) method. Solution based method typically involve the reduction of a soluble metal salt using a reducing agent. The presence of a capping agent encases the particles, inhibits aggregation and prevents further growth of the particles in both polar and non-polar solvents [52]. Solution based methods are also governed by the concentration of the chemical reagents used, the reaction temperature, and the amount of surfactant. Solution based synthesis involves an initial reaction in the liquid phase, followed by agglomeration and grain growth. This results in a broad distribution of particle sizes from 1 to 500 nm with a variety of Ag nanoparticle morphologies. However, most of the conventional Ag nanoparticle synthesis methods are rather disadvantageous in the sense that one has little control in tuning the formation or properties of each particle in a precise manner.

The size and morphology-dependent variation in the intrinsic properties of matter, *i.e.* dimensionality, geometry, composition, uniformity and degree of aggregation at the nanoscale, is one of the most enchanting aspects of nanoparticles which need to be understood. The dimensionality of colloids can be broadly categorised in terms of the number of pseudo-infinite axes and it is generally more common to define the dimensionality (n -D) in a precise way upon confinement: (a) zero-dimensional (0-D), (b) one-dimensional (1-D), (c) two-dimensional (2-D) and (d) three-dimensional (3-D). However, based on the geometric arrangement, the nanoparticles can be classified as isotropic and anisotropic nanoparticles. The interesting properties of the various shapes of the Ag nanosystem have offered possibilities in a diverse range of applications. Spherical nanoparticles and clusters are all classified as isotropic nanosystems since they do not have a certain restricted direction of growth and thus, they do not make any difference in the properties in different directions. These nanoparticles are typically classified as 0-D nanosystem. However, 1-D and 2-D Ag

nanoparticles, and particularly 3-D nanosystems demonstrate a specific direction of growth as the electronic motions become confined along specific axes. Thus, these nanoparticles are classified as anisotropic nanoparticles. Anisotropic Ag nanoparticles constitute the entire spectrum of nanostructures such as nanorods, nanowires, nanotubes which are categorised as 1-D nanosystem while triangles, plates and sheets, ribbons or helices, nanobelts and nanocombs categorized as 2-D nanosystems. Anisotropic Ag nanoparticles also include pyramids, stars, flowers, multipods, nanorice, nanocorn, nanoboxes and nanocubes which are categorised as 3-D nanosystem.

Figure 1.2 shows a number of factors which characterise the similarities and differences between Ag colloids, clusters and nanoparticles based on illustrative study by Mingos [27]. Even though this diagram emphasises the differences in the size-related properties between clusters, nanoclusters, nanoparticles and colloids, it does not sufficiently explain the possible range of identical species which exist in every category, such as the effects of dispersity. Studies on atomically precise Ag crystalline molecular clusters are relatively scarce even though several well-defined characterised systems have been investigated in recent years [53–56]. In inhomogeneous (solid) and homogeneous mixture (solution) systems, they generally exhibit equal distributions of identical molecules and may be therefore called 'atomically precise' and 'monodispersed' [57, 58]. Furthermore, in these molecular clusters, the exchange processes at the two site ligands are sufficiently slow such that the solid composition maintained by the solution may undergo intramolecular ligand and skeletal rearrangements on the NMR time scale.

A nanoparticle has two entities: (*a*) a core which in this case, is the Ag metal which governs the properties of Ag nanoparticles and (*b*) a protective thin shell or ligands which can be ionic, polymeric or metallic (Figure 1.2). The protective thin layer ligand provides a strong barrier to inhibit nanoparticle growth and aggregation which is crucial to achieve a number of remarkable applications which exploit the luminescence of the particles. Further

more, the dispersibility of the nanoparticles is adjusted and is determined by the chemical nature of the ligands. It is well-established that the long held view that nanoparticles and clusters of Ag contain a highly symmetric face-centred cubic phase which resembles a thermodynamically stable structure found in bulk Ag, encapsulated by soft ligands bonded to the surface Ag atoms. As the average size of the particles increases and the stabilising ligands become more labile, the relevance of the facile ligands and solvent exchange stability on the Ag particle surface become more significant. Lea's colloid collectively belongs to this category as they have shown a wide range of sizes and shape distributions with different dispersities in solution which is dependent on the Ag atoms as well as the type of solvent and ligands used. The basic concept of colloidal complexity is pictorially illustrated in Figure 1.2.

There is a subtle distinction between nanoparticles and colloids, but one should be clear and specific when defining the properties of this widely articulated 'new' class of quantum particles which are fundamentally different from those of bulk metal although they originate from a similar system. The quantum size particles is considered when the associated de Broglie valence electron of the particles is confined to the same order of the size of a particle atom itself. Nanoparticles having dimensions less than 20 nm fall between the quantum regime of small molecules with discrete electronic energy levels where the size-dependent quantisation effect is observed. The effect of the size of a quantised particle system quite often shows variation in numerous properties. Therefore, it would be of great interest to verifies the influence of size-reduction effect of metal particles to the intriguing problem of the SIMIT.

1.3 Electronic Conductivity of Ag Nanoparticles

1.3.1 Ag

Macroscopic Ag metal has a face-centred cubic (*fcc*) crystal structure with a lattice parameter of 0.4086 nm [59]. A single *s*-electron in the valence band of Ag metal in which the outer shell configuration in the ground state is given by $4d^{10} 5s^1$. The concentration of free electrons in Ag metal is $5.85 \times 10^{28} \text{ m}^{-3}$, which gives the inelastic mean free path for Ag of roughly 145 nm. This makes mesoscopic Ag particles the best electrical conductor (Figure 1.3) that has a Fermi velocity of $1.39 \times 10^6 \text{ cm.s}^{-1}$ and a Fermi energy level, E_F of 5.5 eV at room temperature which participates as the amount of energy given to one electron for

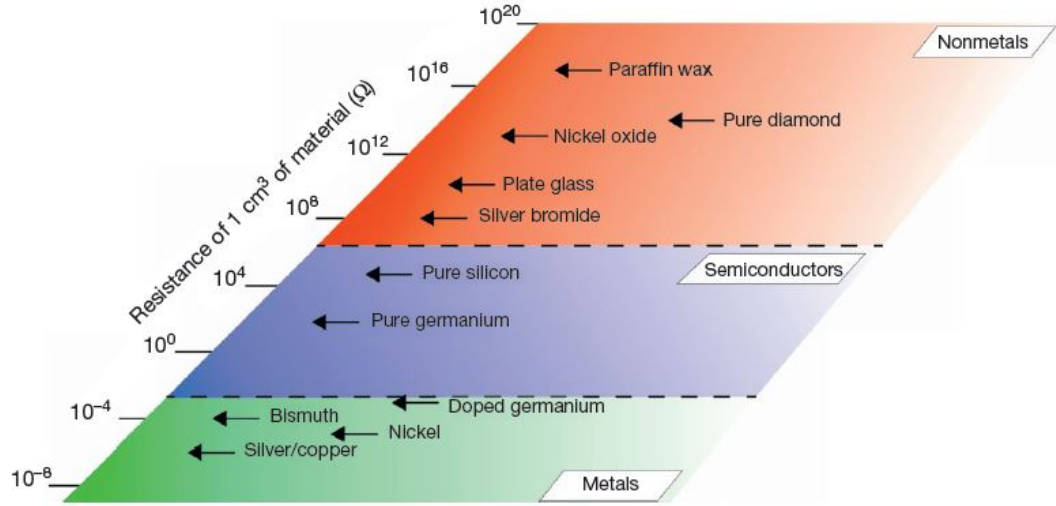


Figure 1.3: Schematic diagram which shows the electrical resistance map of various chemical elements, compounds and materials. Note that the electrical resistance is given only for 1 cm³ of material. The map illustrates a wide range of elements encountered for this fundamental property of substances and their corresponding spread in conductivity at room temperature (*adapted from Edwards et. al. [60]*).

electrical conduction to occur [61]. The electrical conductivity of metallic bulk Ag measured at room temperature is $6.29 \times 10^5 \text{ S.cm}^{-1}$.

1.3.2 Electronic Conductivity

Out of the numerous desirable electrical properties of Ag nanoparticles, the exceptional property that sets mesoscopic Ag *metal* particles apart from microscopic Ag *insulator* particles is its outstanding electrical conductivity property. Most of the mesoscopic Ag particles ($d_m > 100$ nm) will naturally align themselves to form higher aggregates which are held together by *van der Waals* forces within continuum energy level assemblies. Electrostatic forces such as Coulomb force is indeed play a major role in the evolution of nanoparticles in which they are dispersed, and these forces have been shown to have a significant effect on the properties of mesoscopic and microscopic particles in comparison with their macroscopic state [62]. As the size-dependent quantisation effect occurs where the Ag microscopic regime is reached ($d_m \leq 20$ nm), the dynamic change into the standing electronic wave with quantised (discrete) energy level separations are established. A layer of ions typically forms around each Ag particle and previous studies have shown that the dynamics of this charge distribution, which is induced by an external electric field, results in effective and optimally useful dielectric properties [63, 64]. In this work, charged Ag nanoparticle consisting of particles with negative surface charge ions are suspended in hexane solution. Surface charged Ag nanoparticle colloids are implicitly a great asset because they are highly stable and their minute size makes them versatile for a wide range of applications.

The dynamics of the charge distribution within the nanosystem leads to fascinating dielectric properties which occur across a wide range of timescales and are determined by various factors of the system. This study is motivated by the need to investigate the highest conducting pure metallic nanosystem which exhibits losses at microwave frequencies based on SIMIT. Another class of physical system has been proven in this work, and it is found that the dielectric properties of the Ag nanoparticles with almost zero response of the surrounding solvent are significantly different from those of macroscopic Ag. This is likely due to the condition that the charge dynamics within our system in comparison with other literature work [64], with $d_m > 200$ nm, exhibit significant polarisation at microwave

frequencies. By reducing the size of the Ag nanoparticles, the charge dynamics of the system is decelerated and provides huge changes over the dielectric properties of the microscopic Ag particles in the microwave region. In addition, the presence of dielectric heterogeneities in ultra-fine microscopic Ag particles is due to the so-called electrical double layer of stabiliser formed around them has been distinguished in this study with the aid of a microwave cavity resonator. This will be discussed in detail in **Chapter 4**.

1.4 On The SIMIT in Ag Nanoparticles

An ongoing fascination with nanoparticles has led researchers to question how a homogeneous macroscopic metal, having partially filled energy bands can be fundamentally transformed into an insulator and *vice versa*, by merely tuning its physical size [65]. In his 1857 Bakerian Lecture entitled ‘Experimental Relations of Gold (and Other Metals) to Light’, Michael Faraday concluded that “...*the gold is reduced in exceedingly fine particles when becoming diffused, produce a beautiful fluid...the various preparations of gold whether ruby, green, violet or blue...consist of that substance in **a metallic divided state**...*” [3]. Since then, a large number of investigations on gold nanoparticle systems have shown how close Faraday’s conceptions of the problem 160 years ago were to reality. One begins to see how the size and electronic control parameters can be correlated with the actual transition process. These parameters span from the macroscopic bulk state (μm) to microscopic (nm) through the mesoscopic (μm and nm) size regime system (Figure 1.4), where the critical condition of a SIMIT [66] occurs in the middle following the initial idea by Mott on the metal-insulator transition (MIT) [67]. Based on Mott’s work, the term ‘metal’ used throughout this thesis refers to Ag particles whereby the conductivity tends to a finite value for $T = 294\text{ K}$ down to 223 K , whereas the term ‘non-metal’ is used to describe Ag particles for which the conductivity tends to zero at the limit when $T = 294\text{ K}$ down to 223 K .

Over 28 years ago, Edwards proposed a sample criterion (Figure 1.4) to predict the enviable position of metal particles and metal nanoparticles as natural mesoscopic interme-

diaries' between the atomic (quantised state) and bulk (quasi-continuous) regimes. Nimitz was the first who works on the SIMIT in 1888. This issue which originally occupied the thoughts of Professor Sir Nevill Mott, who contributes in the development of the key concepts, models, theories in discussing the fundamental problem of metals *vs.* non-metals in 1986 has been reminiscing in 1996 in his letter to Edwards [68]. In this letter, Professor Sir Nevill Mott notes that “*Dear Peter, I’ve thought a lot about ‘What is a metal?’ and I think one can only answer the question at $T = 0$ K [the absolute zero of temperature]. There a metal conducts, and a non-metal doesn’t.*”. Since then, studies devoted on the prediction of the metallic or insulating behaviour of particles in the condensed state continues [65, 69, 70]. Clearly, the degree of sophistication of the metal-insulator transition issue relies on the answers which one wishes to consider, particularly, the compelling on the change in the electronic properties of mesoscopic Ag particles with respect to changes in their size. Generally, the theoretical basis for size effects on the electronic properties of non-interacting microscopic metal particles is centred on the statistics of the N -fold degeneracy for each electronic energy level. In mesoscopic metal particle system, this degeneracy is removed due to the increase in the inter-atomic electron interaction and the authorised energy states expand into a band. However, in the macroscopic bulk state, the details of this process is out of concerned, rather the crucial role of density of energy state (DOS) takes place. More precisely, the DOS is clarified as the reciprocal of the averaged energy-level spacing over the distribution [70].

Proving the electronic properties to define the direct electronic transition of an isolated finite fragment of metal comprising 10^2 - 10^4 atoms is challenging since the majority of studies are limited by the inadequacy of experimental measurement techniques [71, 72]. Therefore, there is essentially critical need to investigate the electrical properties of Ag particles in the mesoscopic and microscopic size regime since certain metal regimes may either be metallic or insulating, as per due to electron tunneling or transfer between constituent centres [73].

1.4.1 Shedding The Light on The SIMIT

The vital part of this work lies in elucidating the boundary conditions between two limiting electronic regimes, namely localised and itinerant electronic states. Based on the earlier proposal made by Edwards [74], SIMIT is an acceptable prediction for any particle in a condensed state that is originally metallic in the bulk regime as shown in Figure 1.4. The main issue here is to interrogate the change in the overall electronic states of the Ag particle system with the systematic reduction in the Ag size. Based on the Bloch's free electron illustration modified by Edwards (Figure 1.4 (A)), a mesoscopic Ag particle system should be metallic. The dimension of the Ag particles is reduced systematically from the mesoscopic to microscopic states, which is directed by the broadening of the continuum energy levels into a discrete energy band separation as well as the optimum merging at some critical density of metallization [75]. It is expected that the width of ten $4d$ orbitals in the mesoscopic Ag system will split along with a slow increase in both the metal-metal distance (l_{m-m}) and energy gap. These effects become more pronounced as the size of the Ag system is fragmented into an isolated microscopic Ag particle. An important aspect of this work is the spatial confinement of condensed electrons in the Ag system which brings about discretisation of the energy level separation as the atoms coalesce.

Figure 1.4 (B) gives a sense of the intrinsic reduction from bulk-to-atomic that makes it possible for the observation of a SIMIT. In an elemental metal, a sharp distinction exists in nature between metals and insulators for temperatures approaching absolute zero. Their position as intermediaries between the metallic and insulator regimes indicates the involvement of the first-order and continuous transitions which affect the mode of excitation [76] as well as how the inter-particle interactions are replaced by the intra-particles that

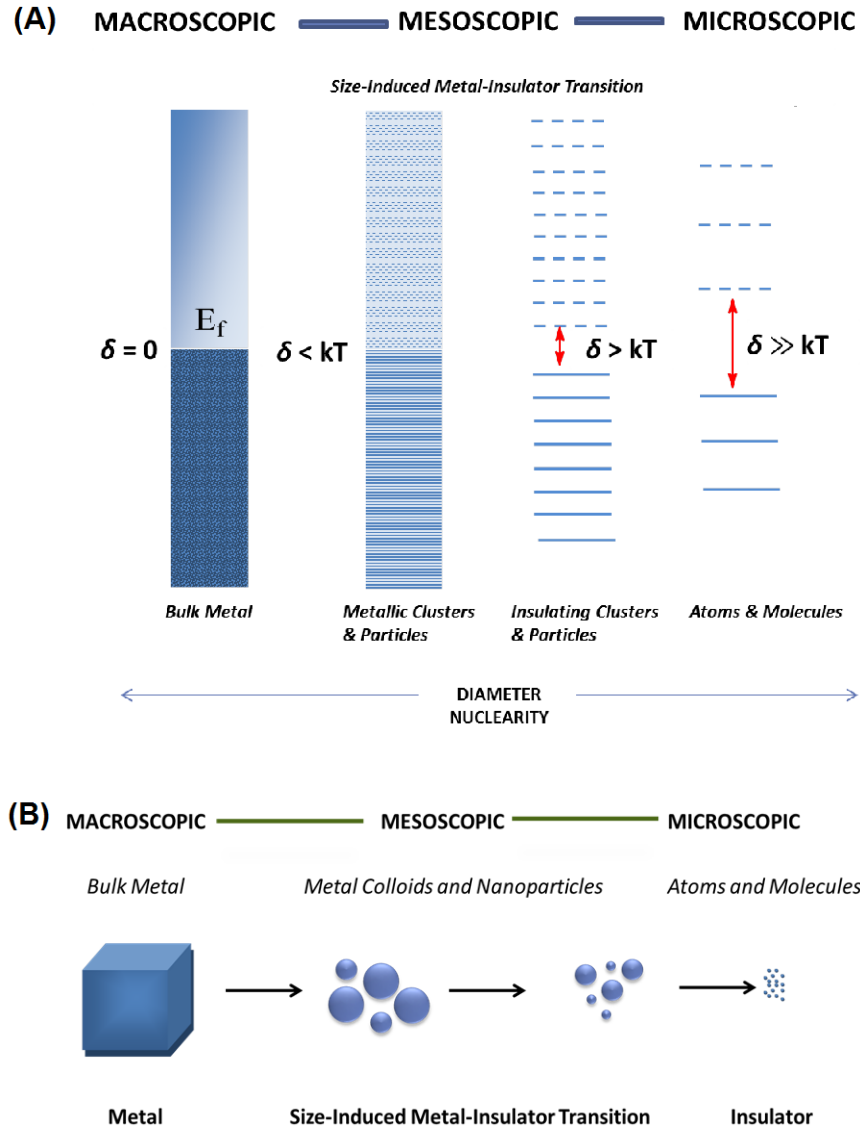


Figure 1.4: Schematic illustration of size-reduction metal-insulator transition from bulk metal (macroscopic) into atomic aggregates (microscopic) through the particulate regime (mesoscopic) with reduction of diameter nuclearity (associated with Fermi Energy, E_F). The electronic energy level separation changes into a discrete energy level separation below the critical density of metallization with an emerging Kubo gap, δ_K arising from the finite particle size (*reproduced from Edwards [74]*). The Kubo gap is describe by $\delta_k = \frac{E_F}{N}$ where E_F is the Fermi energy of bulk metal and N corresponds to the number of atoms in the nanoparticle. It shall be note that the number of valence electrons in metal particles is quantified as a function of n . Therefore, the energy level separation of the particles changes inversely with the N .

confined within the formation of isolated, microscopic cluster states [77]. At present, the

answers to the question '*In what manner and what nuclearity a metallic system behaves as an insulator?*' remain vague. A number of questions' related to the appellation of the onset 'insulator' characteristic in a metallic system suggests that the establishment is not only related to the complete process of electronic wave function in which localisation occurs over the particles, but also the mean free-path which is comparable to the small particle diameters based on the Ioffe-Regel criterion for the MIT. This will be discussed further in **Chapter 4**.

In this regard, the first important point made by Alexander based on the Si:P model system shares the same factor with a continuous transition metal system where the partial delocalisation effect within the mesoscopic regime might induce the extension of the localised electron wave function over several sites in the condensed states [78]. The exchange in energy in the mesoscopic metal particles involves the modifications from inter- to intra-sites as the nuclearity decreases typically in the range of hyperfine energies of Kubo Gap ($\delta_K \sim 10$ meV) in order for distinguishable changes to be noticed [75]. The diminishment of metallic characteristic was envisaged by Edwards later as a criterion for insulator properties within the same metal system as a possibility of the SIMIT [66]. Edwards linked both the issue of SIMIT in single divided particles and the related transition in arrays of particles with ideas and concepts from the mature field of doped semiconductors (Figure 1.5). The key experimental control parameter for instance in a doped semiconductor (*e.g.* Si:P system) that separating the metallic and non-metallic regimes is the mean dopant separation distance, l_{m-m} . In contrast, the corresponding change in the electronic structure of SIMIT within an individual microscopic particle from a gradual reduction in the mean particle diameter, d_m emerging. Here, the critical experimental parameter point in this work would be d_c where such particles in which $d > d_c$ would be metallic, whereas for which $d < d_c$ will response the insulating behaviour at the particular temperature of interest. Therefore, Edwards's contribution illustrates our present purpose in interrogating the importance of the 'quantum' size-induced electronic phase transition from metal to the

insulator specifically in the microscopic metal particle system [74]. This will be a major part of the present investigation.

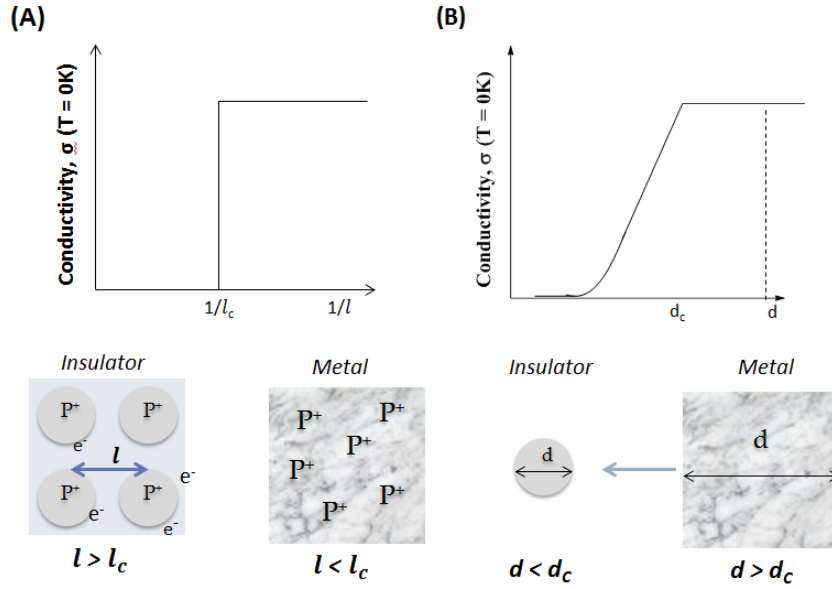


Figure 1.5: Schematic representation of the metal-insulator transition in (A) Si:P (the semiconductor silicon doped with phosphorus) in which l is the average distance between the electrons and (B) a divided metal with d is the mean particle diameter. For Si:P, a first-order transition is expected and both first-order and continuous transitions are expected for *divided metal* (reproduced from Edwards [74]).

1.4.2 Microscopic Ag Particles as Small Metallic Particles

Understanding what comprises metallic or non-metallic behaviour within an isolated metal particle is far from straightforward. The key problem of SIMIT is the division of an isolated grain of metal within the system which originally evolves from the macroscopic solid-state theory. Such a proposal is inappropriate for clusters and particles as noted by Edwards who proposed that the substantial parentage in the atomic or molecular limit for this system contains a small number of metal atoms (~ 2 to ~ 10) [74]. At present, the development of non-metallic properties and SIMIT is measured based on the finite electronic structure of the clusters. This work is focused on comparing the limiting situations of the metal-to-

insulator transition between mesoscopic and microscopic regimes. Studies on a single Ag particle are reviewed and described in detail in the following chapter and includes how the effective volume of particles plays a role in the experimental system.

Recall, that so far the basic concept of SIMIT begins when a macroscopic crystal of bulk Ag metal reduces to the mesoscopic micron scale and finally to the microscopic nanometre scales [60]. In this framework, one can predict that SIMIT will take place since an individual atom can no longer be described as a metal. Parenboom *et al.*, led a discussion on the electronic properties of small metal particles, in which they remarked: ‘*When the number of atoms contained in a grain solid of matter is steadily reduced, it is plausible that in the course of this process a stage is realised when the particle does not behave like a smaller copy of the corresponding bulk solid anymore*’ [79]. This has been verified by a large number of experimental and theoretical studies which have been reviewed extensively by Edwards and Sienko in 1983 [75], Kubo *et al.* in 1984 [73] , Edwards again in 2010 [68].

Following the discovery of the electron by Thomson in 1897, Drude and Lorentz attributed the phenomenon of metallic conductivity to the flow of electrons [68]. Thus, in relation to our present investigation, Ag metal is visualised as a matrix of ions through which itinerant electrons made their way, moving under the influence of an electric field, what they do in gas discharges. Indeed, this is an appropriate point of view since the actual resistivity of a Ag particles was assumed to be caused by collisions between these itinerant electrons and parent ions. The electron gases formed by these free electrons controlled the metallicity of the Ag metal, as assumed by Drude in 1900. Mott proved this idea in 1980 [67] based on the work of Bernal in 1929 [80] where he further extended the discussion by noting that the definition of metals and metallicity was, in essence, a substance which transmits electricity by electron transfer.

In 1970, Feynman *et al.*, remarked that some materials are electrical conductors because

their electrons are free to move whereas others are insulators (non-metals) because their electrons are tightly bonded to the atoms [68]. This focus of this work is to find the answers to Edwards' important question '*Why is it that some substances are metals (conductors), while others are non-metals (non-conductors)?*'. In order to achieve this, the investigation is carried out on a series of Ag particles to determine the onset of metallic behaviour at considerably lower nuclearities in which the size of particles ranges from 1 to 420 nm.

1.4.3 "... a metal conduct and a non-metal doesn't" in Ag Nanoparticles

The electronic system of correlated band theory of the electron is explained briefly in this section along with a brief sketch of the related problem. This system is discussed further, both from theoretical and experimental viewpoints in **Chapter 4**. One of the earliest successful concepts on the quantum theory of solids was demonstrated by Wilson in 1931 [81] which explain the sharp distinction between metals and non-metals in nature. According to the Wilson model, quantum states can be explained by the bands basically, non-metals are elemental materials in which all of the electronic energy bands are either full or empty whereas metals are those in which the bands are only partially full [68]. One can certainly distinguish the electrical properties arising from the characteristics differences in the energy bands of metals and non-metals (insulators), as shown in Figure 1.4 (A).

It is first necessary to assume that all of the quantum states of electrons in an electronic $3d$ band in Ag are fully occupied and thus, the electrons in the band cannot participate in conduction. This assumption is ascribed to the condition where the electrons seems to be 'stuck' because the same number of free electrons are moved from left to right and *vice versa* upon the application of an electric field in the system[68]. Over the entire macroscopic Ag metal, the energy bands which make up the constituent orbital overlap in a way that they are occupied by the available delocalised electrons. Some bands are left only partially occupied to allow the states of Fermi energy, E_F above and below to create an electron-hole pair without suppressing their motion [74]. The application of electric

current gives rise to a spontaneous flow of electric current across the entire crystal and this causes the conducting metallic state. On the other hand, when the bulk Ag metal is reduced to mesoscopic and microscopic sizes (Figure 1.4), the continuum band which contributes towards the electrical properties eventually breaks down [82] and quantised to a discrete energy level separation [83]. The average spacing between the electronic energy levels is approximately $\frac{E_F}{N}$, where N is the total number of atoms in the cluster or particle [82, 83]. The assumption is based on Kubo law where the average energy level separation δ_K , becomes comparable with the ambient thermal energy, kT as the electronic energy levels become discrete rather than continuous. Much of the experimental and theoretical evidence dealing with this situation has been discussed by Edwards *et al.* which is closely related to the SIMIT [65, 66, 68, 74, 75, 77]. Recall, the characteristic parameters of the critical size of Ag particles for the SIMIT is measured as a function of N , and that has a relationship with particle diameter, d . Hence, this vary inversely with the δ_K . Therefore, as we viewed the transition from mesoscopic to microscopic regimes of Ag particle system, it shall be noted that the δ_K change is from smaller to larger value, respectively as indicates in Table 1.1. Clearly, the existance of small particle (< 10 nm) is subject to a significant

Table 1.1: The criterion in distinguishing the states of different metal particles regimes when is viewed from the bulk to atomic regimes (macroscopic, mesoscopic and microscopic). The parameters show that when there is a decrease in the N which is related to the density of states (DOS) near the Fermi level, the value of δ_K increases (*reproduced from Kubo [73]*).

Regime	Particle Diameter, d (nm)	Nuclearity, N	δ_K
Macroscopic	$\geq 10^3$	$\geq 10^{10}$	10^{-6}
Mesoscopic	$10^3 - 10^1$	$10^{16} - 10^4$	$10^{-6} - 1$
Microscopic	$10 - 1$	$10^4 - 10$	$1 - 10^3$

quantum size effects (SIMIT) as indicated by the increasing value of δ_K where the opening of the energy level is significantly larger. At this point, it is important to discuss the fact that this SIMIT is expected to arise in this regime in detail in terms of the dielectric properties. The derivation of the formula for the critical particle size, which the numbers of Table 1.1 are based is given by

$$\begin{aligned}\delta_K &\approx \frac{E_F}{N} \\ &= \frac{E_F}{\frac{3}{4}n} \\ \delta_K &= \frac{4E_F}{3n}\end{aligned}$$

where N is equivalent to the $3/4$ number of valence electrons in the system, n and E_F for Ag is 5.5 eV. For instance, if the particle size of the Ag is 5 nm, the N is $\approx 2.43 \times 10^3$ with $\delta_K = 3$ meV.

This intriguing model of the fundamental differences between metals and non-metals are considered as an electron-electron (Coulomb) repulsive interaction described by Wilson's scheme, whereby the metal systems are non-metals even though they should be metallic conductors [81]. In the 1950s, Mott highlighted that the discreteness of energy levels is symptomatic of the critical role of the electron-electron interactions or correlations which cause them to be insulating when they should be metallic [83–86]. Kubo foreseen significant variation from the behaviour of the mesoscopic metal for $d_m \leq 10$ nm at low temperatures [73, 83]. Kubo was accredited on the development of genuine metallic behaviour which is only conserved in very finely divided metal clusters or particles at finite temperatures when $\delta \approx \frac{E_F}{N} < kT$, where the facile creation of electronic charge carriers by thermal activation [87]. If the particles are not homogeneous in size and shape, the level criteria are given by [74]:

metal

$$\delta_K < kT \tag{1.1}$$

insulator

$$\delta_K > kT \tag{1.2}$$

These conditions define the experimental states for a SIMIT as in a finite metal microscopic where the electrical conductivity in Ag system particularly change by factors of between 10^3 and 10^{10} over these ranges. For a typical *d*-band metal such as Ag which has the $E_F = 5.49$ eV at room temperature ($kT \approx 25$ meV) where the condition presumably is a metallic conduction on the basis of Eq.(1.1), $\delta_K < kT$ with a particle containing more than 300 atoms or a particle diameter of 2.5 nm. With regards to this simple scaling law, as Edwards resembles this as an inevitable conclusion that microscopic Ag particles with the diameter below 2.5 nm would be insulating at room temperature [68]. As dignified by Koutecky & Fantucci [87], one might assume that a one-electron energy gap, δ_K between occupied and unoccupied levels in an isolated cluster or particle.

This condition depends critically on which states are being considered and on the nature of the average Ag system being measured. Appreciating Mott's insight and intuition, Edwards *et al.* reviewed his approach to investigate the problem of interacting or correlated electrons, the so-called Mott metal-insulator transition in two different cases: one at $T = 294$ and the other at $T < 294$ K [68, 88].

1.4.4 Idealised Mott Metal-Insulator Transition

1.4.4.1 The SIMIT at Room Temperature

The physics of Mott's insulators were cultivated by a small number of scientists specialising in metal-insulator transition (MIT) for many years. The model of an isolated metal atom as a perfectly conducting sphere with strongly correlated electrons has achieved great importance in modern condensed matter physics. A metallic Ag system is closely linked with Mott's *Gedanken* experiment which proves that Ag system undergoes SIMIT above its critical point. Ag system is an excellent example to investigate the metal-insulator transition chemically since it can become a non-metallic system when the particles are completely isolated from each other. As the size of Ag reduces to the microscopic size regime, their density also decreases at which each metallic element expands into non-metallic properties with low density. To gain further intuition into the electronic processes in a metallic elemental system, the direct link between Mott's view of metallisation can be seen in terms of the Ioffe-Regel criterion was first reported in 1960 [89] and developed extensively by Mott [85]. The metallic status in disordered metallic systems will fade if the mean free path ξ , of the valence (conductive) electrons is smaller than the mean distance, l , between the constituent atoms or particles, (*i.e.* $\xi \leq l$) which provides carriers of electrical current. Thus, the lower limit of the associated electrical conductivity is now recast for the $T < 294$ K case as the Mott-Ioffe-Regel minimum metallic conductivity and the limiting condition is conceptually taken as $\xi \approx l$, which is the very onset evaluation of SIMIT [68]. Therefore, $\xi \approx l$ indicates the minimum conductivity of the so-called strong-scattering electronic state, which one could anticipate for metallic system at room temperature, where $T < 294$ K. This is described briefly in this section and is discussed further in **Chapter 4**.

1.4.4.2 The SIMIT for $T < 294$ K

Mott has discussed in a series of papers beginning from 1949 [84] on how the monovalent atoms are separated by an inter-atomic distance, ξ where ξ is sufficiently large and the resulting orbital overlapping between the valence electrons is negligibly small and therefore,

it is definitely best described by an atomic wave function. The arrangement of any such atoms is obviously consider as non-conducting at $T < 294$ K, where the electron exchange places occur with surely no net electric current flow. Indeed, Edwards have shown that ‘polar’ ionic states would need to be introduced into the wave function of ground state of the atoms in such a way so as to allow the passage of electric current [68]. In other words, electron conduction within an arrangement of such neutral, non-interacting atoms would require the ionization of an electron from one of the atoms and its subsequent transfer to another (neutral) atom in the assembly. Considering the condition for small separation of the atoms, especially those separations for which ξ is comparable to, or less than the known value for the metallic element, one undoubtedly has metallic character at $T < 294$ K and a free-electron wave function [68].

Mott went further and found that a transition from metallic to atomic-like wave functions occurs as d_m is persistently increased [83, 84]. Edwards suggested that the behaviour of a pure metallic metal SIMIT system including Ag reflects both continuous and discontinues scenarios from a conducting (metallic) $d_m > d_c$, to a non-conducting (atomic), $d_m < d_c$ regime. The qualitative change of SIMIT in the electronic structure of each particle arising from a gradual reduction in the mean diameter d_m , with the critical experimental control parameter is d_c shown in Figure 1.6. It shall be noted that the metal nanoparticles and clusters are considered to be isolated from one another with no possibility of inter-particle electron (quantum) tunneling for the SIMIT. From this point of view, it is presumed that an individual metal particle will remain electrically neutral based on the Kubo criterion for a very fine metallic particle [73].

This aspect is now formally incorporated within the so-called Mott-Hubbard correlation energy $U_{particle}$, which can be viewed as the energy difference between the ionisation energy and the electron affinity $IP_{particle} - EA_{particle}$, of the isolated nanoparticles [65]. Hence, if metal particles are physically well separated or insulated electrically from each other,

the thermal fluctuations by themselves are never adequate to facilitate an individual metal particle to give up or acquire an electron, even though the total number of electrons within each particle may amount to hundreds or thousands. Thus, Mott's intuitive statement clearly shows that when the assemblies of inter-particle distance increases progressively, there will be a sharp transition from the metallic state (having infinite conductivity at $T = 223$ K in this study) to a non-metallic or insulating state in which there is no conduction at the absolute zero of temperature.

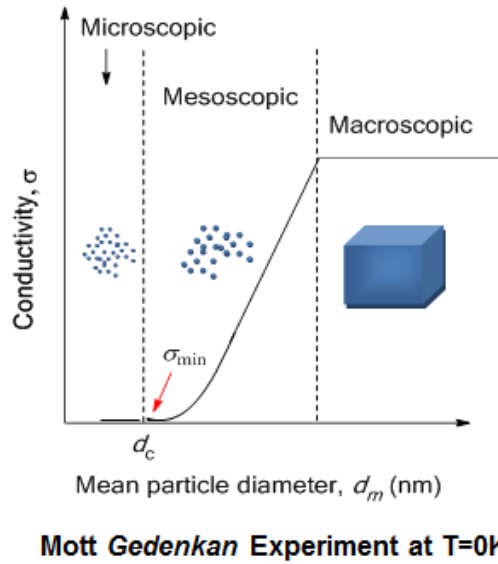


Figure 1.6: Illustration of an idealised Mott metal-insulator transition in an individual polarizable conducting metal atom in the condensed state. The link with Mott's view for the *size-induced metal-insulator transition* (SIMIT) is illustrated by Edwards which leads to a runaway decrease in electronic conductivity from macroscopic to the microscopic size regime, and ultimately, insulation (*reproduced from Edwards [74]*).

Indeed, Mott [85] has shown that at the very transition from a metal to an insulator, there exist a so-called minimum metallic conductivity, σ_{min} . The minimum metallic conductivity conveys the minimum value of the *D.C* and *A.C* electrical conductivity for which the substance can still be justifiably viewed as a metal, prior to the complete localization

of free itinerant electrons as the system moves into the insulator regime. Edwards observed that the SIMIT is influenced by the size of the nanoparticles discussed here and the metal system shows intermediate conductivity values between zero and σ_{min} [68], as estimated by Mott for MIT. This 'zero' parameter appears to be an excellent indicator in explaining the experimental results when $T < 294$ K as most of the dielectric values obtained would be less than zero. Jortner [90] pointed out that the critical size for which the properties of the bulk matter will be reached is dependent on the experimental conditions of the observed system. Hence, the challenge lies in determining whether a complete transformation for SIMIT can be achieved by carrying out the experiments at a considerably higher temperature ($T = 294$ K) and at lower room temperature ($T < 294$ K).

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Chapter 2

Synthesis and Characterisation of Ag Particles

Synthesis of Ag particles and the use of characterisation techniques are reviewed in this chapter. The factors which influence the preparation of size-controlled Ag particles and their surface modifications with the organic functional group to fine-tune the properties of aqueous Ag particles for the application of various microwave tests are discussed in the **first section**. The microwave cavity resonator technique and its theoretical equations, which relate to the adaption of the polarisation and cavity perturbation responses are comprehensively reviewed in the **first part of this second section**. A direct measurement in probing the possibilities of the SIMIT's occurrence at 2.45 GHz takes full advantages in the attempting to solve the electronic properties of the microscopic particle size. Meanwhile, the use of microwave broadband probe technique as a second technique operates at wider frequency range (100 MHz to 10 GHz) compromised the benefit from the first method is further reviewed in the **second part of this section**. Several important mixing laws are employed in order to understand the conductivity behaviour of the particles and their application in modelling both spherical and canonical spheroidal Ag are briefly covered later in the **third part of this section** for better meaningful studies. The basic overview of Ag particle sample preparation and supported instrumentation techniques for size-sorting is

reduced to practice *via* morphological, structural and optical characterisations of Ag-hexane particles is presented in the **third section**.

2.1 Synthesis of Size-Controlled Ag Particles

2.1.1 Solution-Based Chemical Reduction Synthesis

While many Ag particles have been synthesised by various methods, precisely size-selective syntheses and systematic studies in analysing the morphological-control behaviour are rarely performed due to the difficulty in controlling the size, particularly when the mean particle diameter, $d_m \leq 4$ nm. These reasons have motivated us to explore these mesoscopic and microscopic Ag systems in-depth in order to elucidate the size-effect on the conductivity behaviour especially for sub-10-nm Ag particles. For this determination, the Ag particles are initially synthesised in an aqueous medium which is more convenient since water's ability to solubilise DAXAD 19 reducer and Ag precursor is higher comparing to the organic medium. Thereafter, the phase transfer process was accomplished by transferring the aqueous Ag particles produced into hexane medium. Here, a series of homologous amine-stabilised Ag particles dispersed in hexane with different mean diameter (420 to 1 nm) have been studied for a SIMIT.

The synthesis method presented here is experimentally modified to have better control over the diameter size, distribution and morphology. Solution based chemical synthesis is one of the economical and environmentally friendly method that conveniently develop size and shape controllable particles. In this work, nanoparticles are grown from Ag^+ solution which comes from AgNO_3 precursor. The ions are first reduced to Ag^0 atoms by means of reducing agents, which in this case are DAXAD 19 (primary reducer) and polyethylene glycol, PEG (secondary reducer), as illustrated in Figure 2.1. Depending on the availability of the resultant atoms, they can spontaneously grow into several types of small particles which can eventually form larger aggregates. The size and morphology of Ag particles are

most often controlled by varying the reaction temperature [1], or the concentration of the Ag precursor [2] and reducing agent [3].

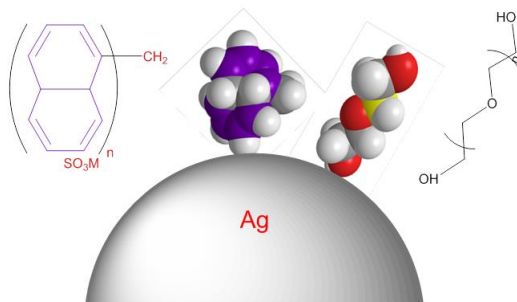


Figure 2.1: Schematic of proposed self-assembly hydrophobic ligand molecule for microscopic Ag particles. Left to right: condensed polynaphthalene sulphonate, Na salt (DAXAD 19) and polyethylene glycol (PEG).

The chemicals used in the preparation of Ag particles were all analytical grade and used without further purification. Silver nitrate (AgNO_3 , 99.9+%, metal basis) and the primary reducing agent which is also act as a stabilising agent of DAXAD 19 (sodium salt of polynaphthalene sulfonate formaldehyde condensate, MW 8,000) was purchased exclusively from GEO Specialty Chemicals, USA [4]. Polyethylene glycol, PEG ($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$), MW 6,000) were purchased from Alfa Aesar (Johnson Matthey Company, Lancashire, UK). PEG was used as the secondary polymeric reductant. Deionised water was used as solvent in all cases.

Table 2.1: Experimental parameters conditions (*i.e.* the molar concentration of AgNO_3 , DAXAD 19, PEG and the reaction temperature) for the preparation of mesoscopic and microscopic Ag particles. Samples 1 through 5 were run accordingly at a reaction temperature of 333K, 353K to 363K.

Chemical Reagents	Concentration (miliMolar)				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
AgNO_3	3.68	7.35	11.04	14.72	18.39
DAXAD 19	10.21	13.32	16.25	20.17	26.62
PEG			9.56		

The Ag particles were synthesised according to the following procedure based on the condition parameters shown in Table 2.1. 6.21 mg of PEG was first diluted in 70 ml of deionised water. The aqueous PEG solution was then stirred and heated to 333K for 30 minutes. Following this, 3.68 mM of AgNO_3 solution was added into the solution while the temperature was kept constant at 333K under magnetic stirring. 10.21 mM of DAXAD 19 solution was then added immediately into the aqueous mixture consisting of AgNO_3 and PEG giving the entire total solution of the reaction to be approximately 80 ml. Once DAXAD 19 solution completely mixed up in the solution, the reaction was left to proceed with constant stirring at 333K for another ~ 2 hours to promote the complete growth of Ag particles. The colour of the solution was observed to change from light yellow to brownish-red and finally into greenish-brown sediment which is interrupted depending upon which particle size is required as shown in **Figure 3.1 (Chapter 3)**. The sediment obtained was then suspended in ethanol and centrifuged at 6,000 r.p.m approximately 15 minutes for several times to remove any impurities present. The sediment was collected and re-dispersed in deionised water for further test. To vary Ag particle sizes, different concentrations of DAXAD 19 were mixed with different concentrations of aqueous solution of AgNO_3 and incubated at different temperatures (333 K, 353 K and 363 K) (Table 2.1).

2.2 Microwave-Assisted Techniques: Measurement of Dielectric Properties

2.2.1 SIMIT and Microwave Methods for Dielectric Characterisation

The system can be considered as an insulating material [5] when the instantaneous size-reduction reaches the metal-insulator phase transition (MIT). In this context, the possibilities of the SIMIT transition can arise from the underlying microscopic pre-quantum mechanical approaches which for instance, can be describes from the Goldhammer-Herzfeld criterion. According to this criterion, the dielectric constant of a substance could diverges from the critical metallisation due to the changes of the particles' density that cause the whole system to become free from the bond of valence electrons [6]. Similar behavioural changes have been viewed by other literature works in term of the magnetic resonance properties by using ESR (Electronic Spin Resonance) which detect what appears to be the onset of de-localisation point for non-metal to metal transition to take place [6]. In particular, ESR measurements are really sensitive to the complete de-localisation of wave function and also to the partial effects that include in the extension of the localised electron wave function. Practically, ESR measurements give variations in the intersite exchange energy, that emerged when the possible SIMIT occurs. This variations can be observed from the measurements that yield the exchange energy to be within the order of magnitude of magnetic Zeeman or hyperfine energies (both generally in the order of 10^{-4} eV) identified in the electron-spin relaxation time. Additionally, the deviation of the electronic structure from that of the bulk has been investigated experimentally on tiny copper particles based on the Nuclear Magnetic Resonance (NMR) results. Such an investigation provides only indirect information on the emerging electronic energy level structure [7]. Even though the precise microscopic origin of the phase transition remains elusive to date, Ag particles still serves as a test bed for correlated-electron MIT dynamics.

The gigahertz (GHz) field pulses are used in this work to provide alternative pathways in

investigating the collective electronic behaviour changes in the size-dependent Ag system due to the structural re-arrangement effect especially within the individual microscopic particle system. Indeed, these current microwave measurements indirectly revealed the excitation behaviour of the electrons across the insulating Kubo gap which results in the changes of the dielectric properties that observed in a nanosecond timescale. Furthermore, these time-resolved GHz measurements have been proved to reveal and correlate several dynamic electronic response initiated by such high microwave fields with other literature studies that could provide an accurate interpretation of the dielectric properties within this frequency range [8, 9]. In this work, microwave-high field techniques is divided into two methods, namely:

1. **Microwave cavity perturbation technique**

2. **Microwave coaxial probe technique**

The microwave perturbation technique is used for measurements of samples with small volumes, *i.e.* volumes that are less than the resonator volume. This technique is chosen because it is suitable for a small scale liquid measurement and the effectiveness of this technique becomes more significant as the microwave E -field is maximum along the axis of the sample's tube [10]. Meanwhile, the microwave coaxial probe technique makes use of the complex reflection coefficient to calculate the complex permittivity. An open-ended coaxial probe has been developed for broad band and non-destructive measurements of permittivity [11–14]. It is found that there is good comparison in the dielectric constant measured using both techniques, which is discussed in detail in **Chapter 4**.

2.2.2 The Microwave Cavity Loss Study of Ag Particles

2.2.2.1 Introduction and Its Brief Historical Review

Metal colloids have been the focus of studies for many years due to its significant distinction properties that has naturally drawn the distinction between their metal and non-metal

characteristics [15–17]. The differences in dynamics charge distributions within these two different systems demonstrate interesting dielectric properties that relate to the inevitable SIMIT although they are composed from the same element which have been introduced in **Chapter 1**. That is, in many instances, the effect of the surface scattering electrons of the electronic energy distribution of metallic particles is of critical importance. Even so, very little attention has been given to examine the electronic properties of this dispersed microscopic metal particles specifically, which should permit more precise observation corresponding to the effect of morphology and atomic structure details. The inducement of our work originates from the need to investigate and understand on how the metallic *versus* non-metallic states occur within the same individual dispersed metal particle, exhibiting either polarisation or perturbation responses at microwave frequencies - such that can be used to understand the emergence of SIMIT. As to date, many attempts have been made to distinguish the occurrence of the *metal-insulator transition* (MIT) *via* potential experimental techniques. Nevertheless, only few have tried to correlates this with SIMIT. It is indeed, the majority of studies are limited by the inadequacy of experimental measurement techniques [18, 19]. Furthermore, techniques used previously such as scanning tunnelling microscopy and NMR have not yet enabled indirect (contactless) conductivity measurement which yields fewer particles destruction that could more or less affect the conductivity reading.

This cavity resonant perturbation technique has for many years been one of the most widely used microwave dielectric measurement techniques [20, 21]. The profound insight of the coherent reactance theorem for a resonator [22] and the method for cavity perturbation measurement were developed in 1946 by Maclean *et al.* [23]. This figure shows a disassembled of a hollow metal cylinder and two identical dielectric samples and also a cover plate of the earlier type of cavity resonator. To measure one sample using this equipment, the sample is placed inside the cylinder and the cover inserted. This followed by the realisation of the approach by Works *et al.* [24] as shown in Figure 2.2. Later, Estin and Bussey

in 1960 [25] further extended and refined the method by noting the correction factors for the presence of sample insertion holes. In this regard, Kobayashi [26] and Krupka [27] provided innovative methods for using this versatile technique later on, even forgoing the requirement to have full resonant structures by using quarter-cut image resonators [28] and half-cut image resonator [29]. These developments have helped microwave perturbation methods become prolific and versatile techniques to be used in many areas of scientific

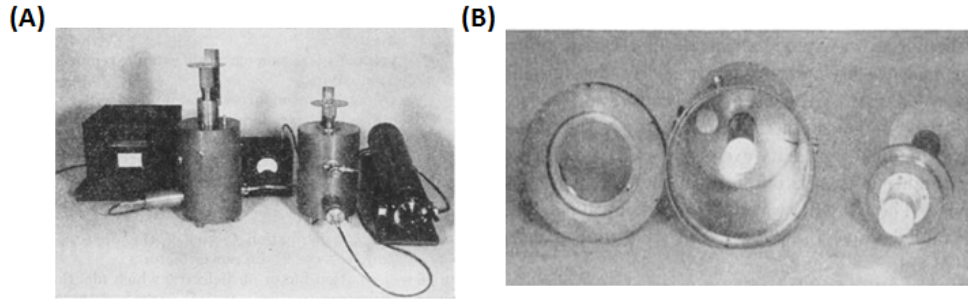


Figure 2.2: (A) The earlier type of cavity resonator setup taken from Works et al., in 1944. (B) The interior view of the cavity resonator. The cavity size is 10 and 6 inches height and diameter, respectively (*reproduced from Works et al., [24]*).

enquiry. Following this, Kent *et al.* [30], in one of their studies set an approach using a split resonant cavity to measure the complex permittivity of dielectric plates. The cylindrical cavity was split half way along the length of the cylinder and dielectric plates were inserted using the transverse electric (TE) of 011 mode. As the method developed, highly complex fringing fields in this configuration were solved rigorously using this specific cavity and it is notoriously difficult. Klein *et al.*, went further and proposed the benchmark in microwave cavity perturbation techniques [31, 32]. They presented details on the principles, experimental scheme and applications of the techniques described and formed the basis for further development in the area of resonant microwave measurements.

The extraction of intrinsic material properties of a sample with this technique has been rigorously reviewed in different theoretical aspects which could be related to size

reduction phenomena. According to Klein *et al.*, several authors have previously studied this problem in a variety of limiting cases. The first study indicated by the review came in 1961 where Champlin and Krongard [33] together with Brodwin and Parsons [34] view that the problem in determining the microwave conductivity and permittivity was solved exactly for macroscopic system of a 1 mm metal sphere placed in the maximum of both the magnetic and electric fields. As Murthy *et al.* reported, Buranov and Schegolev [35] have proved the same in which leads to a closer approximation as Champlin and Krongard's is truly justified. This intimate and all important link between a small particle's properties and its dielectric state was then further investigated by Cohen [36] together with Ong [37] who studied the correlation between prolate spheroid in the electric field which was confined to a small volume near the surface of the sample (skin depth regime). Indeed, Ikeda *et al.*, have simply presented in their review on how small conductive particle ($<100\ \mu\text{m}$) can cause a resonance frequency shift by its minimum sphere's size by using a rectangular cavity [38]. Recent work by Ikeda *et al.*, have presented a complete inspection on the resonance response obtained from rectangular cavity method which shows an equalised sensitivity distribution for micron particles size measurement [39]. As regard to this, we are expanding the possibilities in probing the ultra-fine conducting microscopic metal particles below 10 nm (lower than detection limit from other existing cavity) with an appropriate medium solution which is invisible to microwaves and later verified them.

Hence, microwave cavity resonator indeed provides a robust and versatile method for non-contact and non-destructive measurement on our samples. This method allows samples to be placed directly into the centre of the cavity, where the region of highly uniform electric field is presented in the transverse magnetic (TM) of 010 mode. In this mode, the wall currents traverse no boundaries at the centre of the cavity insertion hole to give further access to the sample under test. Such an insertion hole is highly useful since extensive access of electrical means allows being parallel with sample monitoring during the test. Based on this modern resonant perturbation technique, it is possible to 'isolate' the perturbation

response of the Ag particle sample from the medium where the effective dielectric response is considered to represents mainly the perturbation properties of the inclusion element (Ag nanoparticles) embedded in the medium.

2.2.2.2 Microwave Cavity Resonator: The TM_{010} Cavity

In cylindrical microwave cavity, so-named because it is a resemblance to the cylindrical shape that has the additional 'cup and lid' feature form is really useful from the point of view of accelerating cavities. As a means, this cavity do provides a specific perturbation which greatly aid the benefits for the measurement of spheroidal inclusion sample solution [40]. In general, the resonant modes of a cavity are designed in the standard TM (Transverse Magnetic) or TE (Transverse Electric) modes of electro-magnetic field propagation. In this study, the non-destructive measurement of dielectric properties in monitoring the electrical properties changes on Ag particles is mainly made using the Transverse Magnetic of 010 wave mode, TM_{010} cavity resonator.

In practice, this type of 'cup and lid' cavity used aluminium as a housing frame are bolted together as shown in Figure 2.3 (A). The external coupling structure that is coupled to the cavity by a small wire probe has effect on the cavity performance. The TM_{010} cavity with the radius, r of 4.6 cm and height, d of 4.0 cm has the sample insertion hole axis (Figure 2.3 (B)) [41]. The coupling loop of the cavity is located at the centre of the cavity and created the electric and magnetic fields inside the cavity for this mode (Figure 2.3 (C)). This cylindrical cavity operating in the TM_{010} mode provides a highly uniform electric field distribution along its centre axis with an eigenfrequency of 2.4599 GHz, which is indicated by high field strength (red). Here, the cavity radius r can be relates to the resonant frequency f based on the following equation [41]:

$$f = \frac{ck_\rho}{2\pi}$$

$$= \frac{cp_{01}}{2\pi r}$$

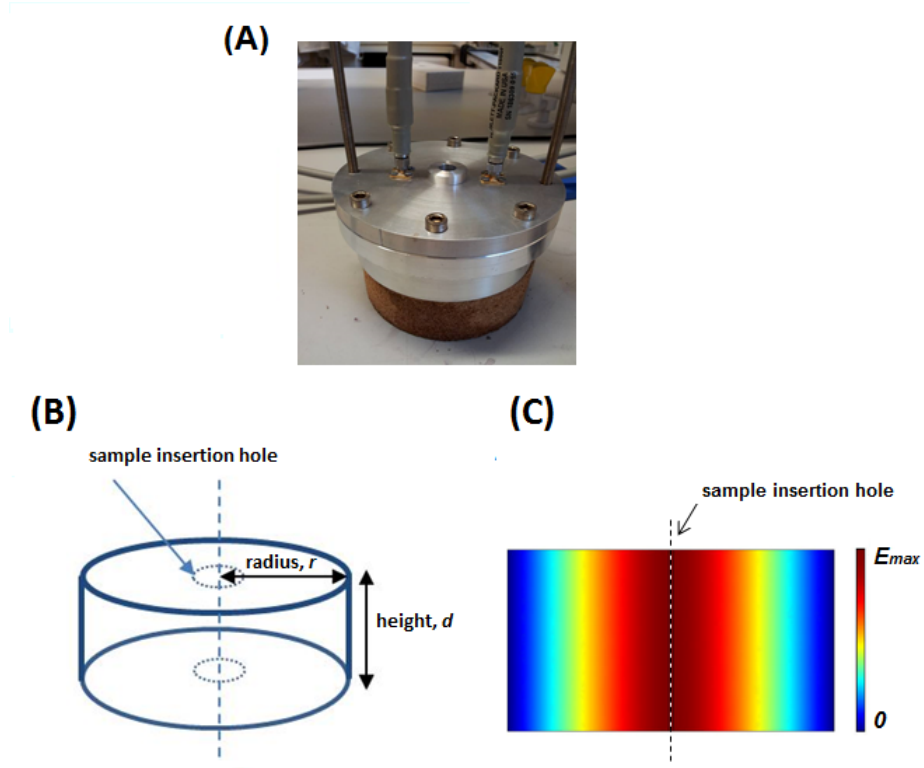


Figure 2.3: A photograph of the laboratory setup of the microwave cavity resonator (A). Schematic of (B) a cylindrical sample inserted axially in the cylindrical cavity resonator and (C) the cross-sectional of normalised TM_{010} electric field distribution with (red) high field strength at the centre hole (*reproduced from Slocombe [41]*).

where $k_\rho = \frac{p_{01}}{r}$ represented the wavenumbers of the frequency in a function of r and first root of the Bessel function of order zero of the first kind $J_0(x)$ with $p_{01} = 2.4048$ with c is the speed of light. Therefore, the f calculated for the cavity presented here is:

$$f = \frac{(3 \times 10^{10} \text{ cm.s}^{-1})(0.52278 \text{ cm}^{-1})}{2 \times 3.142}$$

$$f = 2.495GHz$$

The radial electric field forms a Bessel function of the first kind and a sample can be inserted axially into the point of highest field strength [42]. In particular, for the TM_{010} mode, all field variations occur radially and both electric and magnetic fields are constant along the z -axis in this case.

For the TM_{010} mode, the highly uniform electric field at the centre of the cavity and that within the axial insertion of the sample induced a configuration that may be considered to be in the quasi-static regime. This significantly simplifying the analysis and leading to a more robust experimental arrangement. It should be noted that, the d of the cavity does not influence the transmitted frequency resonance measurement for this mode. However, a longer cavity could create mode degeneracy, which leads to uncertainties in measurements. Clearly, the maximum Q -factor for any of the TM_{0n0} modes occur when the cavity height d , equals the radius r . In fact, the size of the cavity is designed for the frequency interest with the relationship being inverse; higher frequency, smaller cavity.

The exploitation of TM_{010} mode for this type of microwave systems is dominantly due to its usefulness, highly uniform electric field along its central axis and its amenability to precise measurements is higher. Many other modes are possible, some with unique and useful properties for instance, TM_{020} and TM_{210} . However, we only focus on TM_{010} mode in this work. In general, the frequency resonance for the TM_{0n0} modes depend only upon the radius of the cavity. The electric currents associated with these modes all run along the walls of the cavity from the centre of the one-end plate to the centre of the other. This means that in the cavity, currents run parallel to the split and the modes survive even with large diameter of sample's hole. It is clearly proved that, the TM_{0n0} modes remain robust

as it still maintains the high E -field at the centre of the cavity as shown in Figure 2.4 and the higher field uniformity is exhibited by the TM_{010} mode where the magnetic field is null.

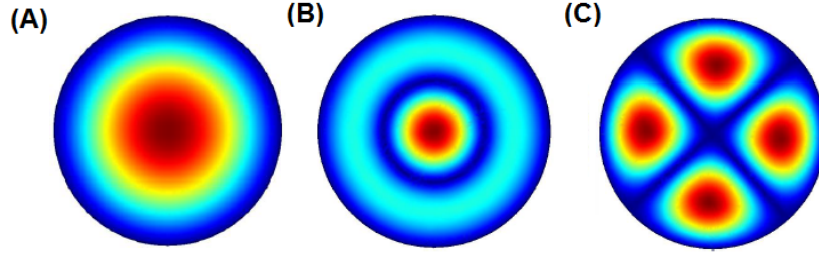


Figure 2.4: E -field distributions in the cross section through cylindrical waveguide displaying high E -field concentration at the centre of cavity. For a cavity with radius of 46 mm, the E -field intensity distribution behaves: (A) TM_{010} , $f = 2.4999$ GHz, (B) TM_{020} , $f = 5.7258$ GHz and (C) TM_{210} , $f = 5.327$ GHz (*reproduced from Slocombe [41]*).

2.2.2.3 The Quality (Q)-Factor

Resonant techniques are most often used for measurement of medium to low loss samples. By reducing the diameter of the inclusion, it is possible to measure low loss samples effectively. A large dynamic range corresponding to high-quality factor is necessary in order to extend the range of the cavity especially with much lower losses sample. In other words, in search for a low losses limit in the cavity, one should account for a high Q -factor cavity. It should be noted that, when a sample is inserted, the observed loaded Q -factor has contributions from other sources of loss including resistive losses in the cavity walls and coupling losses [41]. The various individual factors can combine and read as [41]:

$$\frac{1}{Q_L} = \frac{1}{Q_{\text{resistive}}} + \frac{1}{Q_{\text{coupling}}} + \frac{1}{Q_{\text{sample}}} \quad (2.1)$$

Coupling losses is obtained from a small component of the cavity insertion loss. The

capacitive coupling is attained by using the pin-terminated square SMA launchers that is positioned diametrically opposite to each other on the lid of cavity. By adjusting the pin lengths and measurements of $S_{21} \equiv \text{Forward Transmission Coefficient (gain)}$, the symmetric coupling is attained in the frequency domain using an Agilent E5071B Vector Network Analyser (VNA). On the other hand, the resistive losses which comes from the cavity walls need to be reduced to the minimum value in order to achieve high Q -factor and that means, the cavity walls need to be made from a highly conducting metal [41]. The S_{21} parameter describes the ratio of transmission signal from the input port (port 1) for a transmitted signal incident which is absorbed in this output termination port (port 2). Recall, the dimension d of the cavity is heavily influence the Q -factor of the resonator. However, the height of the cavity insertion hole h , does not compromise the uniformity of the E -field and thus the mode degeneracy is avoided by only limiting the value of d . In this work, the cavity resonator shows that the Q -factor remains high enough (> 6000) to take measurement with less than 3.5% error based upon the measurement results. The data obtained in this work is from real measurement situations. Each transmission trace is made up from 801 frequency spot and each of which associated to the real and imaginary part of S_{21} . The Smith chart methods is used to determine the half-power point that represents the value of the f in order to deduce the Q of the cavity. In determining the Q -factor, the E -field in the cavity is permitted to build up to equilibrium and latter the input power is turn off. This cause the decrement of the exponential power leaving the cavity being measured and fit to determine the cavity's Q -factor.

Recall, the measured Q of the sample is assigned as Q_s - factor in this work and is a 'loaded' value. As we measured the Ag particle sample, the condition of the resonance in the cavity has been changed practically from its ideal condition because of the coupling within the cavity resonator by using a loop. Note that, an ideal cavity resonator is defined here as one without any coupling structure or external circuit of the VNA attached to it, which causes loading of the Q_s -factor. When the Q is loaded, the coupling broadens the

resonant peak and consequently, lowers the Q_s - factor. Thus, the 'unloaded' Q (Q_0 -factor) will be increased slightly when loading effects are accounted for, depending upon how strong the coupling is. Hence, it is important to calculate the 'unloaded' bandwidths of the materials before the data can be used further, since the Q_0 - factor and it's 3 dB bandwidth is independent of coupling and the external circuit [43]. Figure 2.5 indicates a plot of transmitted power of our cavity resonator for non-spherical Ag particles whose overall mean diameter of around $d_m \approx 420$ nm.

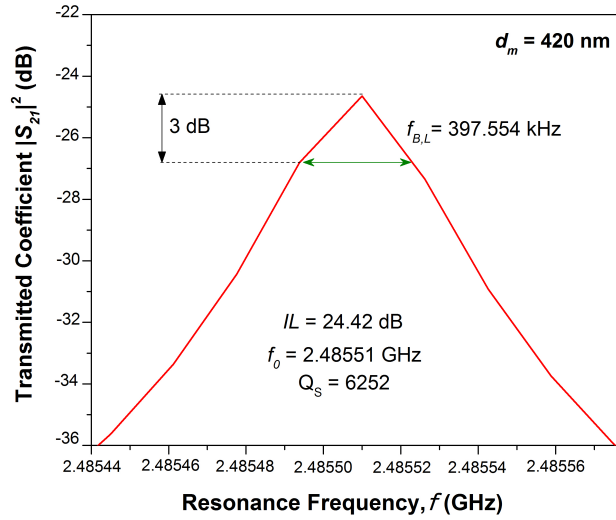


Figure 2.5: A plot of transmitted power obtained from our 'cup and lid' cavity resonator for non-spherical Ag particles whose overall mean diameter of around $d_m \approx 420$ nm.

The measured resonant frequency for this sample is gives as $f_0 = 2.48551$ GHz. The width of the resonance at half power known as loaded 3 dB bandwidth, $f_{B,L}$ is defined in terms of the loaded quality factor by

$$f_{B,L} = \frac{f_0}{Q_s}$$

resulting in the $Q_s = 6252$ as plotted in **Figure 4.1 (Chapter 4)**.

$$Q_s = \frac{2.48551 \times 10^9 Hz}{397.554 \times 10^3 Hz}$$

$$Q_s = 6252$$

Meanwhile, the insertion loss (IL) is accounted to be the peak power (dB) at resonance and evaluating as

$$IL = -10 \log P_0$$

From here, the peak transmitted power, P_0 is calculated which then allowing the calculation of *unloaded 3 dB bandwidth*, $f_{B,0}$ as well as the *unloaded quality factor*, Q_0 .

$$24.42 dB = -10 \log P_0$$

$$P_0 = 10^{-24.42/10}$$

$$P_0 = 3.614 \times 10^{-3}$$

In what follows, the $f_{B,0}$ is considered as

$$f_{B,0} = f_{B,L}(1 - \sqrt{P_0})$$

$$= (397.554 \times 10^3 Hz)(1 - \sqrt{3.614 \times 10^{-3}})$$

$$f_{B,0} = 373.654 kHz$$

with Q_0 to be 6293 as plotted in the **Figure 4.1 (Chapter 4)**.

$$Q_0 = \frac{f_0}{f_B} = \frac{Q_s}{1 - \sqrt{P_0}} = \frac{6252}{1 - \sqrt{3.614 \times 10^{-3}}} = 6263$$

As explained by Slocombe [41], we considered an operating frequency of 2.5 GHz instead of 2.45 GHz as an exact frequency since the dielectric loading of the sample is essentially slightly reduces the frequency. To develop this approach with sufficiently small diameter size of particles, perturbation theory can fulfilled the requirements and therefore can be used to relate the frequency and bandwidth shifts to the permittivity obtained from measurement. With smaller particle size, the analytical approach becomes intractable and the computational modelling of the fields may the only way which permit the calculation of material properties for lower percolation threshold samples, where the distribution of cavity fields and the fields inside the sample itself are considerably different. The discussion made by Li [44], has shown that the sample field distribution of TM₀₁₀ mode within the cavity enabled him to derive the analytical results for a dielectric tube inserted axially into a cylindrical cavity and theoretically suits analytical inversion of resonant measurement for any sample size. Practically, once the particle sample occupying a low proportion of a cavity the resonance will be significantly damped. In this work, both microscopic low-loss resonance (high dielectric losses with lower resistivities) and mesoscopic high loss resonance (high dielectric constant) Ag particles apparently exist simultaneously. The analytic models developed to describe the size-dependent changes in resonance at microwave frequencies will be discussed in following section.

2.2.2.4 The Principles of Microwave Cavity Perturbation Measurement

The generated data is constructed as a measured data in a form of real ε_1 and imaginary ε_2 parts of S_{21} . The real part of the dipole moment relates to polarisation in a sample and the imaginary part relates to losses. In this context, the transmission coefficient, S_{21} voltage of a resonator as a function of frequency which is expressed in logarithmic unit (*i.e.* dB) rather than linear magnitude quantifies the transmission mode parameter of the network analyser used. This complex permittivity relationship is then given as:

$$\varepsilon^* = \varepsilon_1 - j\varepsilon_2 \quad (2.2)$$

where the ε_1 and ε_2 are correspond to the real and imaginary parts of permittivity. According to the perturbation approximation, the variation of complex permittivity ε^* response of materials depends on the shift of resonant frequency Δf and the change in bandwidth Δf_B of the trace. The relative changes in the fractional frequency shift Δf and fractional bandwidth shift Δf_B provide information on the induced dipole moment of the system. The sample response in polarising field can be expressed as [41, 45] :

$$\frac{\Delta f}{f_0} = \frac{-Re(pE_0^*)}{4U}, \frac{\Delta f_B}{f_0} = \frac{-Im(pE_0^*)}{2U} \quad (2.3)$$

$$U = \frac{1}{2}\varepsilon_0 \int_{cav} E^2 dV \quad (2.4)$$

where p is the complex dipole moment created by the inserted sample, E_0 is the cavity electric field and U is the stored energy in the cavity. As shown schematically by the red solid line of the empty cavity resonant curve in the high field of TM₀₁₀ mode in Figure 2.6, the de-tuning of sample resonant curve (blue) is introduced after the insertion of a sample where the frequency trace peak decreases with an increase in a broadening of the bandwidth.

For the case of metal sphere, the response of the dipole moment can be described as [41]:

$$\frac{\Delta f}{f_0} = \frac{3}{2} \frac{V_s}{V_{eff}} \quad (2.5)$$

where V_s is taken as the sample volume and V_{eff} is the effective volume occupied by the cavity field which thus expressed as:

$$V_{eff} = \int_{cav} \frac{E^2}{E_0^2} dV \quad (2.6)$$

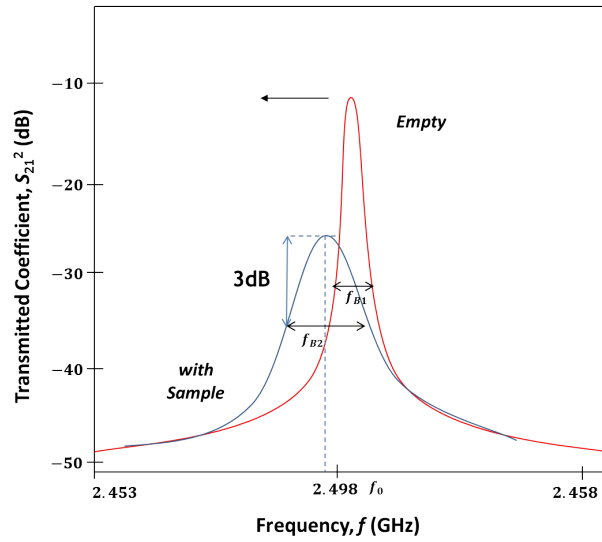


Figure 2.6: Diagram of the resonant curve of the S_{21} transmission coefficient line in the high electric field of TM_{010} mode with f_0 is the resonant frequency and f_{B2-B1} is the broadening of bandwidth referring to half-power (3dB) bandwidth. The red solid line curve shows an empty resonating tube. The blue curve indicates the detuning perturbation response when a sample inserted.

For the TM_{010} cavity mode that is used in this work, V_{eff} give the value of 71.0 cm^3 with the radius of the cavity is 4.6 cm and height is 4.0 cm as obtained below:

$$\frac{V_{eff}}{V_{cavity}} = J_1^2(p_{01}) = 0.267$$

$$\frac{V_{eff}}{265.94 \text{ cm}^3} = 0.267$$

$$V_{eff} = 71.0 \text{ cm}^3$$

where $p_{01} = 2.4048$ represent the first root of the Bessel function of order zero of the first kind $J_0(x)$. The V_s is fixed to the value of $\sim 6.284 \times 10^{-3} \text{ cm}^3$ with the height of the quartz tube (purchased from Glass Workshop, Inorganic Chemistry Laboratory, University of Oxford) is 5 cm and the diameter of inner and outer tube are 0.2 and 0.24 cm, respectively as discussed further in **Chapter 3**. Therefore, the means to directly calculate the shift in frequency for a given volume for the case of metal sphere as expressed in Eq.(2.4) is then able to rationalise the type of the behaviour of the metallic system. One notes that from the sample resonance response in Eq. (2.6), the relationship between the complex permittivity and the shift in either resonant frequency or bandwidth is almost absolutely determined. For cylindrical quartz tube passing completely through the cavity in a non-depolarising configuration, it is shown that the dipole moment is $p = (\epsilon_r - 1)\epsilon_0 E_0 V_s$. One finds that, Eq. (2.4) and (2.6) describe the shift in resonant frequency, f and bandwidth, f_B to be:

$$\frac{\Delta f}{f_0} = -\frac{(\epsilon_1 - 1)}{2} \frac{V_s}{V_{eff}}; \frac{\Delta f_B}{f_0} = \epsilon_2 \frac{V_s}{V_{eff}} \quad (2.7)$$

Here, the SIMIT of particle system is shown by a significant difference in dielectric loss results at operating frequency of 2.50 GHz. This large dielectric loss difference observed is

believed to occur due to the intrinsic size-reduction effect. This effect rose up the structural imperfections within the particles since different size of particles favours different structural effect (different growth direction). This caused the effectivity of E -field penetration is high in microscopic particle size regime. Certainly, this has close relationship with SIMIT. These energy losses are significantly lower in microscopic (low dielectric loss $\approx$ low dissipated energy) than in the mesoscopic (high dielectric loss) size regime. Therefore, the Q -factor is relates to the 'sharpness' of the resonance and that is in conjunction with the condition of the bandwidth. This can be further explained by:

$$Q = \frac{f_0}{f_B} \quad (2.8)$$

Hence, the Q -factor indicates the ratio of the energy stored to the energy dissipated of the system and is given by:

$$Q = 2\pi \frac{E_{stored}}{E_{diss}} \quad (2.9)$$

where E_{stored} is energy stored in the system and E_{diss} is the average energy dissipated in the system over one cycle. For a particle system with negligibly loss (imaginary) permittivity and finite storage (real) permittivity, the disproportionate in Q -factor is observe in **Chapter 4**.

2.2.2.5 The Dielectric Loss and Skin Depth

The resulting dielectric loss can be viewed as an intensity gradient losses much like represented the measured dielectric of the particles. In this work and for all real world dielectric materials studies, a figure of relative permittivity is considered to be complex as expressed previously in Eq. (2.3) [46]:

$$\varepsilon^* = \varepsilon_1 - j\varepsilon_2$$

which represents the real part, ε_1 of ε^* as measuring the electrical energy stored in the dielectric while ε_2 of the imaginary part quantifies the loss or dissipation energy in the medium as heat due to the damping of the vibrating dipole moments [46].

Here, the skin depth is described as a characteristic penetration depth of electric current flows, ϱ (the original symbol is changed to avoid confusion with Kubo gap symbol in this work) through the surface of a conducting material and in this case, within the Ag particles. The distribution of electric current flow density between particles' surfaces is reduces in magnitude to $1/e \approx 37\%$ of its surface value and is then defined as:

$$\varrho = \sqrt{\frac{\rho}{\pi f \mu}} = \sqrt{\frac{2}{\mu_0 \omega \sigma}} \quad (2.10)$$

where $\mu = \mu_0 \mu_r$ is the permeability of the material, ω is the angular frequency ($\omega = 2\pi f$), ρ is the resistivity of operation and σ is the bulk *d.c.* conductivity. Thus, for bulk Ag at room temperature and frequency of 2.45 GHz, the ϱ value is give as $\approx 1.298 \mu\text{m}$ with the $\mu = 1$ and $\rho = 1.63 \times 10^{-8} \Omega\text{m}$.

2.2.2.6 The *D.C* Conductivity Analysis

The Stored and Dissipated Microwave Energy In microwave cavity resonator, the stored and dissipated electrical energy within the metal particles are figured out from direct measurements of the change of resonant frequency and broadening of the resonant bandwidth upon the inserting sample [47]. The results obtained allow extraction of the electronic conductivity of the individual particles from the dielectric measurement. This measurement is not labour-intensive but does consume considerable time. The analysis is crucially rely on the ratio of the electromagnetic skin depth ϱ , to the metal particle diameter d in a function of the angular frequency ω of the incident radiation as given by Eq. (2.11).

The interaction of spherical particles with microwave can be thus classified into two

limiting regimes according to the overall effective magnitude of the mean particle diameter [47]:

(a) *Large particle limit*, $d \gg \varrho$. This electromagnetic fields are limited to the surface of the particle and are then described by classical skin effect theory [48, 49]. The dissipation microwave energy per unit surface area of each particle is proportional to the particle's surface impedance in the cavity, given by $R_s = 1/\sigma\varrho \equiv \sqrt{\mu_0\omega/2\sigma}$, which tends to be zero in the limit of infinite conductivity.

(b) *Small particle limit*, $d \ll \varrho$. This limit is to be contrasted from the other one which, in this case, is the major contributor when considering conducting small particles. The electromagnetic fields now penetrate the sample fully and for small conducting particles placed in a microwave electric field, the dissipation of microwave energy gives rise to the first approximation which is proportional to $\sigma E_{in}^2 V_s$ where E_{in} is the magnitude of the electric field within the particle and V_s is the effective total volume of the particles (exclude the volume of the medium). Therefore, characterising the microwave response in this size regime provides a direct determination of the electrical conductivity of the effective batch of individual particles.

Here, a low conducting spherical particle within the limit of $d \ll \varrho$ is understood as a lossy dielectric material producing a uniform internal E -field, E_{in} within the particle in response to a uniform applied field, E_0 . This quasi-static approximation gives rise to the following relationship between the applied and internal fields [47]:

$$E_{in} = \frac{E_0}{(1 + \frac{1}{3}(\varepsilon_{eff}^* - 1))} \quad (2.11)$$

where the depolarising factor of a small spherical particle is estimated to equal to 1/3. The effective complex permittivity ε^* is expressed as given by Eq. (2.12) where clearly quantifies the stored and dissipated energy related to conductivity when:

$$\varepsilon_{2,eff} = \frac{\sigma_{eff}}{\omega\varepsilon_0} \quad (2.12)$$

The Bandwidth Change of the Resonant The possibility in measuring the change in resonant bandwidth upon the insertion of the sample into the cavity resonator has been realised by other pioneer researchers from the cavity perturbation test. Provided that any resulting perturbation is small (valid if the volume of the particle sample is much less than the volume of the resonator), this reflects that the fractional change in resonant bandwidth, $\frac{\Delta f_B}{f_B}$ is then [50]:

$$\frac{\Delta f_B}{f_B} \approx Q\alpha \frac{|E_{in}|^2}{E_0^2} \varepsilon_2 \approx \frac{Q\alpha\varepsilon_2}{(1 + \frac{1}{3}(\varepsilon_1 - 1))^2 + \frac{1}{9}\varepsilon_2^2} = \frac{9Q\alpha\varepsilon_2}{(2 + \varepsilon_1)^2 + \varepsilon_2^2} \quad (2.13)$$

where Q again is the unloaded quality factor of the resonator and α correspond to the fraction of the total electrical energy stored within the sample. The output of the dielectric conductivity of the particles after loaded through the waveguide can be determined using Eq. (2.14). As addressed by Edwards *et al.*, *two* critical points need to be considered to further examine the nature of the measurement on nanoparticles:

1. *The inevitable particle size distribution*: provided that all of the particles remain in the small particle limit ($d \ll \varrho$), the measured microwave dissipation energy only depend on the *total volume of the particle sample* and not on the details of the size distribution itself. To better visualise the information on total volume of Ag nanoparticles, separate experimental tests were used in **Section 2.3.3** and explained in details in **Chapter 3**.
2. *The influence of local field corrections and the uncertainties*: this includes the nature of the particle, stabiliser and the medium used surrounded the Ag nanoparticles.

Although these corrections can be applied in a rigorous manner as highlighted by Edwards *et al.*, for volume fraction (*i.e.*, well-separated particles) in weakly polar solvents, they can be ignored to a good approximation. Combining the effects of local field corrections and uncertainties associated with grain shapes leads to overall uncertainties of a factor of around 2 when calculating the effective conductivity of mesoscopic and microscopic conducting particles [50] as further discussed in **Section 4.1.1 (Chapter 4)**.

The quasi-static approach of Eq. (2.14) paved the way for the measurement of dielectric conductivity for all range of materials as high as bulk gold which is valid at microwave frequencies ($\sigma = 4.3 \times 10^5 \Omega^{-1} \text{cm}^{-1}$ at room temperature) to even within the small particle limit (which will always be valid at 3 GHz for small Au particles and should be the same for Ag system) [47]. This small (mesoscopic and microscopic) size regime particles is situated either within a suitable high conductivity mesoscopic ($\varepsilon_2 \gg \varepsilon_1$) or low conductivity microscopic ($\varepsilon_2 \ll \varepsilon_1$) limits. For example, at 3 GHz, an isolated individual Au particle will exhibit its full (bulk) microwave conductivity if there is no size-induced suppression of conductivity which is true when the $\varepsilon_2 = \frac{\sigma}{\omega \varepsilon_0} \approx 2.6 \times 10^7 \gg 1$ [47]. Hence, in the present work ***high conductivity in the small particle limit*** can be derived assuming the $\varepsilon_1 \approx 1$, Eq. (2.14) is configured as:

$$\frac{\Delta f_B}{f_B} \approx \frac{9\alpha Q}{\varepsilon_2} \quad (2.14)$$

Edwards *et al.* configured the $\alpha = 0.01$ and $Q \approx 2000$ in their experimental setup. However in our case the α and Q are 0.085 and 8000, respectively. Thus, the fractional change in resonant bandwidth on sample insertion into the cavity resonator is very small in this limit (of the order of 10 parts in a million) would certainly too small to measure with any degree of confidence [50]. Therefore, for ultra-fine *conducting* Ag nanoparticles would then appear almost lossless according to this quasi-static analysis.

Conversely where the conductivity was to be suppressed enormously due to the SIMIT, the *low conductivity in the small particle limit* is then configured as $\varepsilon_2 \ll \varepsilon_1$, and Eq. (2.14) reduces to:

$$\frac{\Delta f_B}{f_B} \approx \alpha Q \varepsilon_2 \quad (2.15)$$

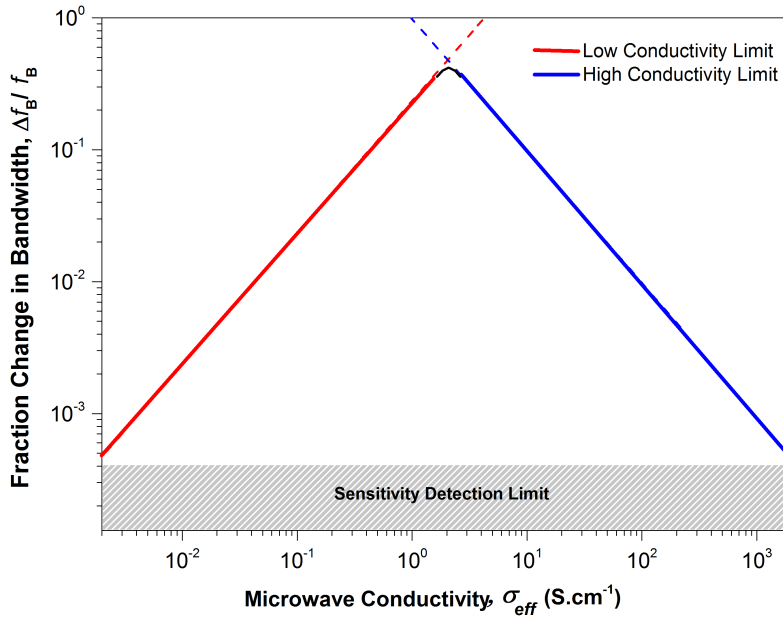


Figure 2.7: A logarithmic plot for both low and high conductivity limits of measured data of Ag particle samples. The data obtained based on Eq. (2.14).

The experimental plot for both conductivity limits of Ag particle system in logarithmic scale based on Eq. (2.14) with sensitivity detection limit of the cavity is shown in Figure 2.7. The variation in the low conductivity limit is in reverse order trend as compared to the particles in a high conductivity limit. The limit sensitivity is calculated to be approximately 1kHz.

This experimental results of the fractional changes in resonant bandwidth as a function of conductivity in these limits of a series of Ag nanoparticles is then further discussed in **Chapter 4**.

Specimen Preparation and Instrumentation Microwave cavity measurements are performed both at and lower room temperatures using an Agilent E5071B network analyser, equipped with an aluminium host cavity resonator. Samples are inserted into the cavity hole in order to perturb the resonant fields and from the transmitted power spectrum, we may infer electrical parameters of the sample. A schematic diagram of the experimental setup is shown in Figure 2.8 for the TM_{010} mode. The Ag particle samples are filled into thin-walled quartz tubes (d_{inner} tube = 2.0 mm, d_{outer} tube = 2.4 mm) and inserted in the cavity axially, through the axial insertion holes at the top lid of the cylindrical cavity. The aluminium cavity (cavity radius, $a = 46$ mm and length, $d = 40$ mm) yields a high quality factor, ($Q > 7000$) which is ensured by excellent electrical connection at the joints to minimise losses caused by currents traversing the scattering boundaries (Figure 2.8) [42].

Each Ag particle solution is filled into the tube to a depth of 50 mm in which 40 mm of the sample will be within the active region of the cavity. This gives a volume of 0.126 cm^3 which is actively exposed to the microwave radiation field. All $|S_{21}|^2$ is measured as a function of frequency for each particle sample using this mode (TM_{010}). The TM_{010} and mode have resonant frequency of 2.498 GHz. The mode is well suited for dielectric property measurements of small Ag particle samples as it has a high and uniform electric field near the cavity axis [42].

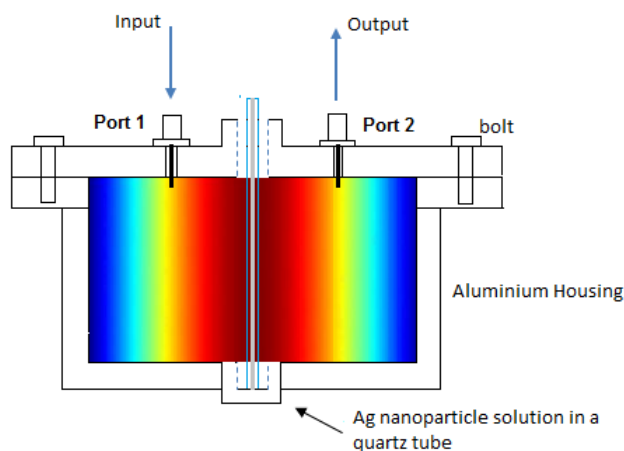


Figure 2.8: Electric field distributions for the TM_{010} mode in the cylindrical cavity. Samples are introduced into the field in small quartz tubes which are placed parallel to the axis of the cylinder. It is assumed that the applied field is uniform for this mode.

Hence, the concentrated electric field is polarised axially, which is parallel to the sample tube (Figure 2.8). This results in minor modifications of the local electric field in the presence of the quartz tube for this mode. It can, therefore, be assumed that the applied electric field is uniform for each mode which discussed further in **Chapter 4**.

2.2.3 The Microwave Broadband Study of Ag Particles

2.2.3.1 Introduction and Abridged Historical Review

One of the earliest recognised successes for the microwave measurement of materials were the broadband method developed by Altschuler in 1955, which were made possible by the inexpensive, rugged and easy to use solid-state microwave sources [51]. In this microwave method, the measurement procedure required shaping the samples into a pellet to place into a suitable waveguide or cavity. Strictly speaking, all the samples needed to be in a powder or solid form, making the study of colloids almost impossible. Nevertheless, Fabry *et al.*, initiated the study of reflection technique produced by a material in front of the waveguide aperture which could be compatible with the special requirements of measuring colloid suspension [52].

Later, an open-ended cavity probe was then first realised using a rectangular waveguide probe by Decreton *et al.*, with the present frequency limitations [53–55]. This approach requires the open-ended cavity probe to be located next to the sample tested or in actual contact with it. In many situations, the practical probe is not to be too large so that the waveguide size operational limitation of frequencies not to be higher than about 8 GHz. Some of the authors evaluated their results on a purely experimental basis by comparing measurement data with similar data obtained with samples of known calibrated properties [56, 57].

In this research, Mott’s MIT can possibly be seen from characterisation of the electrical properties of Ag particles across the mesoscopic and microscopic size ranges. Measuring the conductivity of colloids itself is a challenge. Clearly, the *D.C* measurements of the colloid samples are almost impossible below the percolation threshold since the ‘macroscopic’ current cannot flow through the microscopic samples without complete conduction pathways. However, at microwave frequencies (*A.C* measurements) it is possible to measure the effective complex permittivity that should directly infer the electrical properties of constituent materials of this sample as we did in mesoscopic system. Typically, in a conducting sample, the measured loss can be directly related to the effective dielectric conductivity at the certain frequency measurement. In a recent work by Gregory *et al.*, the onset of *A.C* conduction and the associated low frequency dispersion is adopted using broadband frequency measurement where the maximum concentration of conducting particles under observation approaches and exceeds the percolation threshold [58].

In a conducting nanoparticle solution, a complex relationship observed between the frequency response and the structure of the system as well as the properties of its constituent can explain the SIMIT transition phenomenon. Approaches to modelling the frequency dependent permittivity of mixtures suggest that for a non-conducting spherical particle

(microscopic regime) with outer capping ligand, the frequency of relaxation is proportional to the ratio of particle volume to total volume and the conductivity of the capped ligand as illustrated in Figure 2.9. Models of the frequency response of spheroidal particles indicate that increasing the conductivity of the metallic particle causes an increase in the frequency of maximum dielectric absorption ε_1 which re-normalised due to the skin-depth effect ϱ [59, 60]. The salient point of the case is then further discussed in **Chapter 4**.

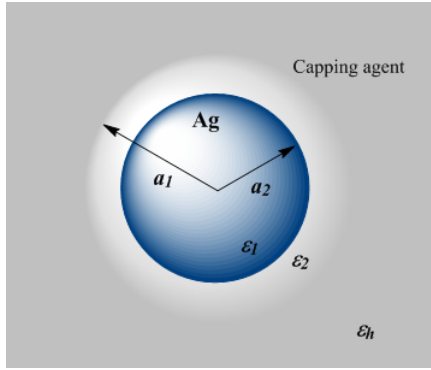


Figure 2.9: Schematic view of spherical microscopic Ag particle coated with monolayer of amine ligand such as octadecylamine (ODA) in this case. Microscopic Ag particles are considered as an inclusion in a hexane matrix with the illustration of the effective medium of Ag itself, ε_1 and capping agent, ε_2 as well as the effective medium of hexane, ε_h .

2.2.3.2 The Principle of Microwave Coaxial Probe

We have discussed how a SIMIT can be observed using the cavity perturbation method, which operates at a fixed resonant frequency (2.5 GHz). Such a SIMIT can also be seen by means of broadband measurements uncovered a rich information and yet fascinating changes corresponding to the situation from large and small separations of the atoms. Broadband reflectance probes operating in a typical frequency range of 0.1 to 10 GHz can be used to yield plots of electrical characteristics for the samples of elemental Ag metal under test. The central paradigm of the coaxial probe over other open-ended electromagnetic sensors is its effectiveness as non-destructive measurement over a broad frequency band, offering the possibility of observing polarisation phenomenon and electrical behaviour across a large

spectral range [41].

The coaxial reflectance probe operates on the basis that the echo signal produced at the end of a coaxial cable is the characteristic of the material terminating it. The fringing electromagnetic fields at the end of the probe interact with the sample, and knowledge of the behaviour of the fields around the aperture lead us to the apparent aperture admittance, Y_L . In Figure 2.10, a finite element model of the coaxial probe used in this study clearly shows that E -field wave distribution radiating from the broadband signal source from the VNA and propagates along the probe end as an open circuit. An open round glass tube is mounted on top of the cell in order to prevent the solution flow and to keep the sample volume constant during the test. The Ag particle solutions of all size used is approximately 5 ml.

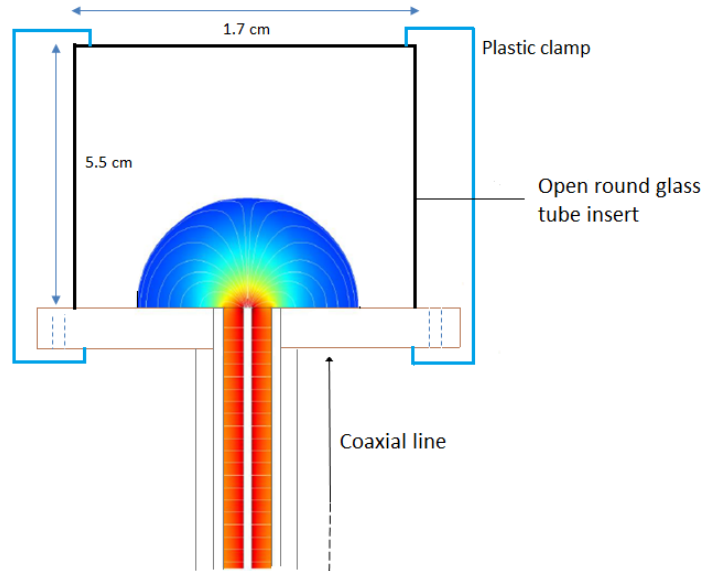


Figure 2.10: Schematic illustration of the asymmetric propagation of the coaxial probe measurement cell including the open round glass tube. The E -field distribution with the presence of Ag particles sample in the middle is simulated using a finite element model. In the real measurement, the Ag sample in the middle is block by the round glass insert ($r_m = 0.85$ cm) to stop solution flow from the centre.

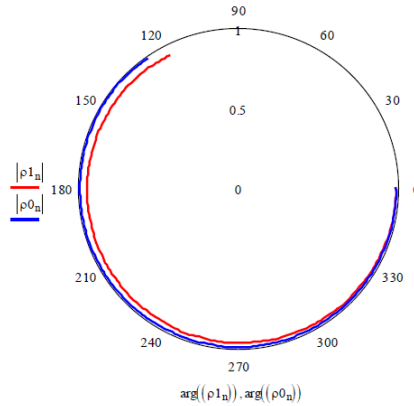


Figure 2.11 shows the example of amplitude of the frequencies for both the air ρ_0 and sample ρ_s terminated probe raw data taken from the VNA for the macroscopic Minattec Gold powder sample from Slocombe's work [41]. The phase plots of θ of the reflection coefficients are based on the S_{11} parameter ($S_{11} \equiv \text{Input Port Transmission Reflection Coefficient}$) operating at the frequency of 300 kHz to 8.5 GHz represent the typical response plot produce during the calibration test. In this work, the same principle is applied here where the S_{11} parameter is used to trace and measure the ratio of transmission signal that reflects from the input port (port 1) for a signal incident in port 1. It is also observed that the losses frequency amplitude of ρ_0 remain higher up to 8.5 GHz with measured magnitude of 1. Once the sample is introduced, the fringing field of the probe, ρ_s clearly exhibits a radial extent of the reflectance associated with a significant phase change and loss (less than magnitude of 1) as compare to the ρ_0 . The calculations performed in a way to determine the permittivity and conductivity from the probe input admittance of the sample is shown in the next **Subsubsection 2.2.3.3**.

2.2.3.3 The A.C. Conductivity from Admittance Characteristics

The calculations of the dielectric permittivity of measured data require considerable computational techniques since the raw data obtained from the VNA is in the form of reflection values. To understand the polarisability enhancement effect of a small microscopic Ag particles, the initial reflection coefficient of a sample is described by [41]:

$$\rho_s = \frac{Z_s - Z_0}{Z_s + Z_0} \quad (2.16)$$

where Z_s is the impedance of the Ag particle sample and Z_0 is the characteristics impedance of the source (50Ω). Recall, when considering the associated phase of reflection when the sample is introduced, Eq. (2.16) is rewritten in terms of the present of the sample admittance, Y_s and becomes:

$$\rho_s = \frac{1 - Z_0 Y_s}{1 + Z_0 Y_s} e^{j\theta} \quad (2.17)$$

The phase information involved in this reflection coefficient measurement is in a frequency dependent range. However, additional phase change component due to the electrical length of the probe itself indicated by $e^{j\theta}$ is also need to compromised. Therefore, in order to account the difference in electrical length, the $e^{j\theta}$ terms is eliminated by dividing ρ_s with a reference measurement ρ_{air} that has the same phase change since the VNA calibrated only the plane of the port, and this becomes:

$$\frac{\rho_s}{\rho_{air}} = \frac{1 - Z_0 Y_s}{1 + Z_0 Y_s} \frac{1 + Z_0 Y_0}{1 - Z_0 Y_0} \quad (2.18)$$

At this point, the presented aperture admittance information need to follow by a model that can directly relates to the Ag particle properties. In fact, it is easy to extract the aperture admittance of Y_s if the aperture admittance of the air terminated probe Y_0 is known. From a practical point of view, it means that the Y_0 need to be determine first. Clearly, the aperture admittance of the air is readily well-documented. According to Slocombe [41], criterion of Eq. (2.19) give further indication of the theory breakdown for aperture admittance model used in this study yielding:

$$Y_s = jA\omega\varepsilon + jB\omega^3\varepsilon^2 + C\omega^4\varepsilon^{5/2} + O(\omega^5\varepsilon^3) \quad (2.19)$$

where the coefficients of A , B and C are governed by the geometry of the aperture. However, it is found that the subsequent terms in the series are with the assumption that the aperture of the probe is electrically small and radiation is trivial. In this case, Y_s is reduces to:

$$Y_s = jA\omega\varepsilon \quad (2.20)$$

The coefficient A can now be determined experimentally or analytically for the geometry of the probe in use. The value of A was calculated by measuring dielectric of known permittivity, yielding a result of $8.2 \pm 0.5 \times 10^{-15} \Omega^{-1} \text{s}$. Therefore, this may be predicted as quantifying the fringing field that propagates into the Ag particle sample from the end of the probe. The Y_s is defined as the inverse of the characteristic impedance, Z_s , that is:

$$Y_s \equiv \frac{1}{Z_s}$$

From here, the dielectric permittivity of the Ag particle sample is obtained. It shall be noted that, a calibration measurement necessary to be taken for each set of measurement, and the working measurement take seconds to complete. Provided that by simply removes the sample from the probe and exposing it to the air later, the inversion is then automatically completed. In addition, the measurement is fully depend on the surface condition at the probe tip. Thus, it is essential to ensure the surface of the probe especially the tip area is cleaned after each measurement on dielectric liquid where a constant contact between the probe and Ag particle sample need to be established. By using a simple clamping setup, the reflectometry coaxial probe is also useful for characterising liquids, with no issues caused by poor contact between the probe and the sample. The clamping setup help to prevent any possibilities of glass tube movement making the control of the flow rig's condition better.

Conventionally, the aperture broadband probe can be calibrated using *Through-Reflected-Line* (TRL) calibration kit or *Short-Short-Load* (SSL) procedures [62, 63]. However, in this case, the so-called *Open-Short-Load* (OSL) routine has been used in all liquid measure-

ments. This OSL routine is beneficial since it does not involve complicated kit connection to the aperture probe but yet is still very robust. Nevertheless, the accuracy of this OSL calibration is prominently affected by the performance of the waveguide and the accuracy of the values of calibration procedures from user's requirement. The combination of transmission line, S_{11} with the OSL routine is used for fixed-waveguide in this system and can perfectly detect the error due to the systematic noise caused mainly by the discontinuities in the electromagnetic field at the open-end of the probe. Therefore, the inverse procedures involved the use of rigorous integral admittance can predict the SIMIT possibility of ϵ^* of Ag nanoparticle that can be compared with **Microwave Perturbation Cavity** results which have been discussed in the previous section.

Specimen Preparation and Instrumentation Coaxial probe measurements are performed at room temperature using an Agilent E5071B network analyser, equipped with novel miniaturised coaxial probe based on an Anritsu K-connector (here K102F). Each of Ag particles solution is dropped on the surface of the aperture within the round glass tube mounted on top of the cell until the aperture is fully covered by the solution (approximately 5 ml). It shall be noted that, since hexane evaporates very easily into the air, it should have a reasonably large Ag solution on top of the aperture in order to minimise the uncertainty in the measurement. The K-connector used in here has an inherent bandwidth from *d.c.* up to 40 GHz, making the whole broadband range of 200 MHz up to 8.5 GHz accessible. An *Open-Short-Load* (OSL) calibration routine is necessary for this open-ended waveguide system due to the stray of the capacitance across the aperture waveguide must be taken into account. The OSL calibration routine determine two different measurement (reference and sample) of equivalent offset short circuit from the aperture, which for a certain frequency yields the same measured reflection phase as the phase of the shorting material at the aperture [64, 65]. For this measurement, the OSL calibration routine is repeated for each frequency point.

A schematic of the open-ended coaxial probe is shown in Figure 2.9. The probe's inner

and outer radii are $r_{inner} = 141.82 \mu\text{m}$ and $r_{outer} = 758.37 \mu\text{m}$, respectively. Hence, the aperture remains electrically small as the wavelength is much than $r_{outer} - r_{inner}$ over the full range of measurement frequencies (up to 8.5 GHz). Ag colloid samples are placed directly on the coaxial aperture. Measurements of the voltage reflection coefficient $S_{11} \equiv$ (Input Reflection Coefficient), were taken in the range of 100 MHz to 8.5 GHz using an Agilent ENA 5071B Vector Network Analyser (VNA). Measurements are normalised against the reflectance of the probe without the sample. The complex permittivity of the sample can be determined by using the simple inversion process based on a capacitive aperture admittance model which is discussed further in **Chapter 4**.

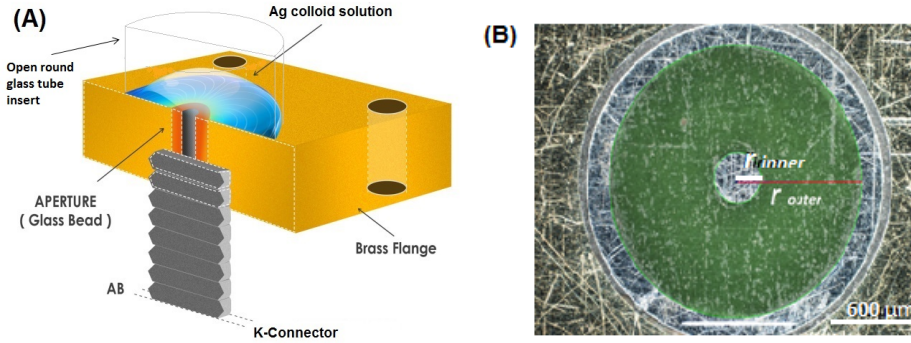


Figure 2.12: Schematic illustration of the open-ended coaxial excitation probe with the (A) side view with E -field distribution at the AB plane and (B) close-up front view dimension of the probe.

2.2.4 Effective Permittivity of Mixture: Numerical Validation Approach

2.2.4.1 Basic Principle of the Effective Medium

In hindsight, it is essential to provide some resolution to the dilemma in understanding the classification of *metal versus non-metal* dielectric properties of small conducting metal particles. The interest lies in to provide a nearly exact electromagnetic description analysis of SIMIT based on the dielectric structural complexity changes of Ag particles in which seems to be a strenuous task. Nonetheless, to the best of our knowledge predictive mixing

models are capable in performing the approximate state of SIMIT in any system. Hence, the essential part of this section reclines in precisely idealising and explaining the size changes effect based on simplest microstructure models that should yields an approximate dielectric mixing rule properties close to the real boundary between these two limiting regimes; itinerant-electronic (mesoscopic) and localised (microscopic) states.

In principle, it is always possible to use dielectric mixing models to transform all the complex effective permittivity, ε_{eff}^* of the constituent into specific complex permittivity mixing rule by using its fractional volume information and possibly other parameters that could characterise the SIMIT from its metallic to non-metallic states of the mixture. In this context, the mixture of Ag particles (consist of mesoscopic and microscopic regimes) is considered as a discrete system. This means that the random homogenous Ag particle inclusions from both regimes are embedded in homogeneous hexane medium and should exhibit a continuous permittivity function. In other words, the randomness of the Ag inclusions in the medium was limited to the plane where the geometry or morphology would not vary. Obviously, when taken SIMIT (reduced dimension) into consideration, the concept of *effective* permittivity which implies the mixture responds to electromagnetic excitation now is no longer constant as in bulk (macroscopic) permittivity.

This intimate and important link to the homogenisation *below* mesoscopic media is certainly crucial as the electromagnetic waves of higher frequency can only view more accurately '*real space*' medium which associated with its '*atomistic*' details. Therefore, for particle size less than 5 nm, the uncertainty in the measurement within long wavelength limit is higher and often derived using static or quasi-static arguments. In fact, the primary concerns are the size of the microscopic Ag particle in the mixture and the spatial correlation length of their permittivity function is considerably smaller with respect to the wavelength. In particular, the validity of the ε_{eff}^* modelling is generalised to include the first-order scattering effects of the complex particle geometries of Ag particle inclusions.

The mesoscopic Ag elements in the condensed state shows a polarising effect which entails its dielectric losses and purposely contribute to the energy radiating from the imaginary electric dipole of the ε_{eff}^* . For microscopic Ag inclusions that exposed to an electromagnetic field, it is predicted that their polarisation is almost the same with a static excitation. In contrast for mesoscopic Ag inclusions, they tend to fully perturb the field to the lowest order of an electric dipole which is further underlined in next section in terms of polarisation behaviour.

2.2.4.2 Polarisability of Ag Particles

Adopting a model of an isolated spherical inclusion as a perfectly conducting sphere embedded in a background medium shown that the produced polarisability of an inclusion is classified as a measure to its overall effective response to an incident E -field that is explained in terms of a dipole moment given by

$$\bar{p}_m = \alpha \bar{E}_m \quad (2.21)$$

where polarisability of the inclusion, α ($Asm^2.V^{-1}$) is a relation between the dipole moment, $\bar{p}_m$ (Asm) of the atomic inclusion polarised by the applied electric field, $\bar{E}_0$ ($V.m^{-1}$). Hence, the polarisability of sphere inclusion is consider to be proportional to the internal field within the inclusion (consider as a total particles' volume) and the dielectric contrast between the inclusion and the host phase. In the current context, the two-component mixture is often referred as a *phase* and the environment phase termed as *host* with the inclusion phase know as a *guest*. Since the E -field, $\bar{E}_h$ uniformly propagates within the sphere as well as the static external field, $\bar{E}_m$ ($V.m^{-1}$), the parallel $\bar{E}_m$ is then expressed as:

$$\bar{E}_m = \frac{3\varepsilon_h}{\varepsilon_s + 2\varepsilon_h} \bar{E}_h \quad (2.22)$$

The polarisability can be re-written:

$$\alpha = V(\varepsilon_s - \varepsilon_h) \frac{3\varepsilon_h}{\varepsilon_s + 2\varepsilon_h} \quad (2.23)$$

where the permittivity of the inclusion and its environment are denoted by ε_s and ε_h with the V is the volume of the sphere, respectively. For dielectric system given the permittivity of the *inclusion* phase is ε_s which is said to occupy a fraction of the total volume f the dielectric background ε_h in which the sphere resides is set to have a volume fraction of occupying host to be $1 - f$ as illustrated in Figure 2.13 [41].

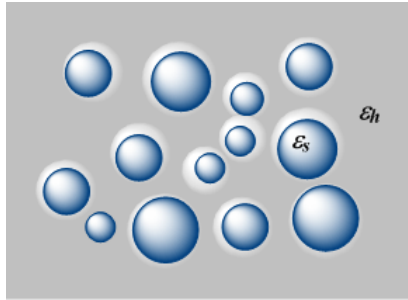


Figure 2.13: Schematic of a two-component mixture with dielectric spherical inclusions distribution, ε_s occupy in a homogeneous dielectric host background, ε_h .

In the so-called quasi-static limit of infinite wavelength approximation, the effective electromagnetic characteristics of the mixture can be thoroughly described by two independent quantities; a single effective permittivity and a single effective permeability to the entirety of the mixture. However, the interest of this work practically is in its effective permittivity of the homogeneous mixing Ag properties as its own entirety with the infinite

wavelength approximation should suffice.

2.2.4.3 Clausius-Mossoti (CM) Mixing Formula

To simulate the proof of SIMIT, observing the polarisability of a single sphere that relates to the effective permittivity of the components are useful in predicting and understanding the complex dielectric behaviour for both mesoscopic and microscopic Ag particles mixture. In principle, from the ε_{eff} point of view, the physical understanding of how the mesoscopic and microscopic components of resonance media interact with the E -field can be calculated as a function of a sphere's density number. The ε_{eff} of this mixture can be considered *via* the constitutive relation of the volume-averaged electric field, $\bar{E}_h$ and electric flux density, $\bar{D}$ ($As.m^{-2}$):

$$\bar{D} = \varepsilon_{eff} \bar{E}_h = \varepsilon_{eff} \bar{E}_h + \bar{P} \quad (2.24)$$

where the average polarisation density, $\bar{P}$ ($As.m^{-2}$) is equivalent to the dipole moment density in the mixture:

$$\bar{P} = np_{mix} \quad (2.25)$$

and here, n (m^{-3}) is the number density of dipole moments which are all assumed to be of equal strength.

The Clausius-Mossoti (CM) formula gives predictions of the polarisability of each particle as a dipole and sets out the particles in a background of averaged polarisation densities. CM formula would be an improvement of the Maxwell-Garnett (MG) formula, in which the MG formula might ignore its *guests* in the host medium which will be discussed later. Concerning that CM method describes the ε_{eff} of a particle as a function of the polaris-

ability, it is indeed contains an explicit detail of the individual particles polarisation. The dipole moment of the mixture, p_{mix}^- is proportional to the internal field within the particle, its volume and the dielectric contrast between the permittivity:

$$\bar{p}_{mix} = \int (\varepsilon_s - \varepsilon_h) E_s dV \quad (2.26)$$

With the E_s , it can be write:

$$p_{mix}^- = (\varepsilon_s - \varepsilon_h) \frac{3\varepsilon_h}{(\varepsilon_s + 2\varepsilon_h)} E_h V = 4\pi a^3 \varepsilon_h \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + 2\varepsilon_h} E_h \quad (2.27)$$

and so the polarisability produced is re-write:

$$\alpha = V(\varepsilon_s - \varepsilon_h) \frac{3\varepsilon_h}{\varepsilon_s + 2\varepsilon_h} \quad (2.28)$$

Taking Eq. (2.28) into consideration, the $\bar{p}_{mix}$ is define as the dipole moment of a single Ag particle in the mixture and is different from the previous calculated dipole moment in Eq.(2.26). The intrinsic local field around the particle, E_L must change although the polarisability remains constant and is expressed by:

$$\bar{p}_{mix} = \alpha E_L \quad (2.29)$$

Combining the Eq. (2.29) and (2.30),

$$\bar{P} = n\alpha E_L \quad (2.30)$$

The convergences of the particle response based on the classical description are that the external electric field is consider to produce a uniform internal field where less inclusion particle is placed. However, in dense mixture system, the external field is observes to distorted due to the polarisation of the particle and that results in a high local field. In other words, the surrounding polarization increases the local field effect of the mixture. Thus, the contribution of the local field due to the polarisation of one inclusion (often called as the *Lorentzian* field) is governed by the geometry and size of the inclusion. Therefore, for a sphere inclusion this leads to:

$$E_L = E_h + \frac{1}{3\varepsilon_h} \bar{P} \quad (2.31)$$

where the 1/3 coefficient corresponds to the depolarisation factor of the sphere. Considering Eq. (2.31) in Eq.(2.32) gives the average polarisation and re-write:

$$E_L = \frac{E_h}{1 - \frac{n\alpha}{3\varepsilon_h}} \quad (2.32)$$

By substituting Eq.(2.33) into the Eq.(2.25), the Clausius-Mossotti mixing formula (also deserve to be label as *Lorrenz-Lorenz* formula) leads to:

$$\varepsilon_{eff} = \varepsilon_h + \frac{n\alpha}{1 - \frac{n\alpha}{3\varepsilon_h}} \quad (2.33)$$

The equation can often be seen in the form of:

$$\frac{\varepsilon_{eff} - \varepsilon_h}{\varepsilon_{eff} + 2\varepsilon_h} = \frac{n\alpha}{3\varepsilon_h} \quad (2.34)$$

As the n is reduced, for relatively low concentration and dilute mixture approximation gives by:

$$\varepsilon_{eff} \approx \varepsilon_h + n\alpha \quad (2.35)$$

In reality, the polarisabilities and scattered densities are not always those most convenient to use. Rather it is friendlier to play with the permittivity of the components of the mixtures. In this study, it is then adjusted by combining CM formula with the polarisability expression in Eq. (2.35) can be expressed as:

$$\frac{\varepsilon_{eff} - \varepsilon_h}{\varepsilon_{eff} + 2\varepsilon_h} = \varphi \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + 2\varepsilon_h} \quad (2.36)$$

where $\varphi = nV$ is corresponds to the volume fraction of the inclusions in the mixture. This also known as *Rayleigh mixing formula*. This formula provides that only the volume fraction and the permittivity been addressed in the mixing rule, their spherical size need not be the same if only all of them are small compared to the wavelength.

2.2.4.4 Maxwell-Garnett (MG) Mixing Formula

As we have explained before, the focus attention in this study is limit to the 0-D mixtures. The mixture consists of two dielectric components, of which one is treated as host and the other as an inclusion phase. Now, the averaged fields can now be considered as the sum of averaged fields in the respective phases weighted by the volume fraction as [41]:

$$\bar{D} = \varepsilon_{eff} \bar{E}_h \quad (2.37)$$

with

$$\bar{D} = \varphi \varepsilon_s E_h + (1 - \varphi) \varepsilon_h E_h \quad (2.38)$$

and

$$\bar{E} = \varphi E_h + (1 - \varphi) E_h \quad (2.39)$$

Considering the ε_{eff} in general is obtains from:

$$\varepsilon_{eff} = \frac{\varphi \varepsilon_s \left(\frac{E_s}{E_h} \right) + \varepsilon_h (1 - \varphi)}{\varphi \left(\frac{E_s}{E_h} \right) + (1 - \varphi)} \quad (2.40)$$

It is convenient to view this Eq.(2.41) as a relationship between the internal and external E -field for particles in the mixture. Considering the case of a single dielectric sphere placed in the host of dielectric medium which subjected to a uniform polarising field, E_0 as indicates in Figure 2.14, the applied uniform field is distorted by the presence of the inhomogeneity. Thus, the field accumulating within the sphere produce a uniform depolarising field and is in opposite direction to E_0 . With the component of the electric field of the particle and its host denoted by E_s and E_h respectively, it can be recast by:

$$\left(\frac{E_s}{E_h} \right) = \frac{3\varepsilon_h}{(\varepsilon_s + 2\varepsilon_h)} \quad (2.41)$$

Thus, the prediction of the effective permittivity for the whole mixture, ε_{eff} according to

the Maxwell Garnett mixing rule reads as [66]:

$$\varepsilon_{eff} = \varepsilon_h + 3\varphi\varepsilon_h \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + 2\varepsilon_h - \varphi(\varepsilon_s - \varepsilon_h)} \quad (2.42)$$

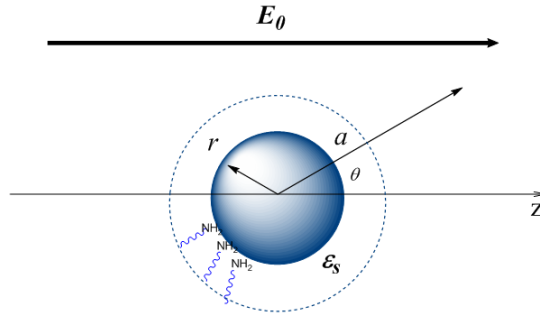


Figure 2.14: Schematic of dielectric sphere of a radius r under the applied external field E_0 act along the z -axis with the intrinsic permittivity ε_s with the host matrix permittivity ε_h .

Here, the permittivity of canonical spheroid ε_s is located randomly in a homogeneous host ε_h with $\varphi = nV$ being the fraction of a volume ratio of the embedded small particulate inclusion is $0 \leq \varphi \leq 1$ of the final mixture. The analysis of the MG formula shown above is off basis importance when studying mixing formulas of this type and serves to expose the limitations of the approach. Therefore, it is known that for a dominant dipole contribution where the particle size is so large that do not meet the quasi-static condition, it is reasonable to assume that the MG theory is rather in doubt for larger size particle.

2.2.4.5 Bruggeman Mixing Formula

In respect to a view where the inclusion was no longer treated as a perturbed constituent in host material, Bruggeman come up with a more accurate formula where different constituent (different geometry and size) were assumed to be embedded within the host [67].

It shall be noted that the approximation of effective permittivity of canonical spheroids of mixing particles colloids have recently been shown to provide an inexact result. In the analysis of arbitrary morphology media, the dominant problem which we have to deal is how to correctly take into the account the interaction between constituents. Certainly, the observation of the sparse mixture shows that the interaction effect is almost negligible in microscopic colloids and the dominant estimation contribution is by the inclusions present with the average polarization, $\bar{P}$ as provided in the derivation of the MG formula previously. However, in a dense or larger mesoscopic inclusion mixture where the interaction between particles is dominant, this condition may no longer be valid.

The symmetric Bruggeman mixing rule also known as Bottcher formula [68] is very often encountered in anisotropic material modelling studies. To explore this connection quantitatively, the basic Bruggeman formula is given by:

$$(1 - \varphi) \frac{\varepsilon_h - \varepsilon_{eff}}{\varepsilon_h + \varepsilon_{eff}} + \varphi \frac{\varepsilon_s - \varepsilon_{eff}}{\varepsilon_s + \varepsilon_{eff}} \quad (2.43)$$

Assymmetric Bruggemen mixing rule:

$$\frac{\varepsilon_s - \varepsilon_{eff}}{\varepsilon_s - \varepsilon_h} = (1 - \varphi) \left(\frac{\varepsilon_{eff}}{\varepsilon_h} \right)^{\frac{1}{3}} \quad (2.44)$$

where ε_{eff} is the effective dielectric constant of medium and $1 - \varphi$ is the volume fraction occupying the inclusion which depends on the shape and size of the inclusion which discussed further in **Chapter 4**.

2.2.4.6 Critical Analysis of Numerical Validation Approach

Among these three effective medium approximations present here, the best practical criterion to use to predict the SIMIT size of Ag particle dielectric samples is MG mixing formula. The effective medium theory like MG explain the dielectric properties of an individual polarisable particles in a transparent solution medium. The MG approach is complete in the sense that the percolation, that is, the conductive path through the particle sample is exclude even at larger particle size. This is an important factor that needs to be addressed in the prediction of electronic properties especially for mesoscopic Ag particle size that usually tends to aggregate even at lower particles volume. In this work, the φ is less than 0.1, and the results of percolation give less prominent to MG's formula medium for both mesoscopic and microscopic particle regimes. Since the morphology of the Ag particles in the dielectric matrix is independent of the nature of the dielectric, the calculation by MG's approximation is close to the results obtained from the cavity perturbation technique. The calculations for CM and Bruggeman indicated that the percolation and microstructure are crucial that yield different results for Ag particle inclusions, which cannot be explained within the context of the MG's theory. The comparison for these three models for Ag particle inclusions ($f = 0.008$) in hexane solution is discussed further in **Chapter 4**.

2.3 Basic Instrumental Characterisation Techniques

2.3.1 Size and Morphological Characterisations of Mesoscopic and Microscopic Ag Particles

It is important to note that, before any dielectric measurements are taken, it is necessary to anchor the qualitative analysis of the Ag particles produced. At this point, any troubleshooting on the quality of synthesis control issue can be easily monitored based on the morphological results.

2.3.1.1 Transmission Electron Microscopy (TEM)

Transmission Electron Microscope (TEM) becomes the main cutting-edge instrument in resolving individual columns of particle atoms in mesoscopic and microscopic crystalline materials. In this work, JEOL JEM-3000F 300 kV field emission gun (FEG) transmission electron microscope (TEM) was used to study the quantitative morphological *in-situ* SIMIT experiment.

Specimen Preparation and Instrumentation A JEOL JEM-3000F 300 kV field emission gun (FEG) transmission electron microscope (TEM) was used in the Department of Materials, University of Oxford. The microscope is in ultrahigh resolution configuration and demonstrates a resolution better than 0.17 nm, a probe size of below 0.3 nm and an energy resolution better than 0.7 eV. The sample can be tilted approximately at $\pm 25^\circ$. All the as-synthesized Ag nanoparticle samples were re-dispersed in ethanol. The specimen was then prepared by placing the Ag nanoparticles in dispersion drops on a continuous carbon-coated copper grid. The ethanol solvent was left to evaporate in order to ensure that the Ag nanoparticles are fixed on the surface of the grid. The specimen was placed into its corresponding specimen column which was tilted and rotated under different viewing conditions during the analysis. The quantitative experiment analysis was facilitated by Gatan Imaging Filter (GIF) 2000TM which is equipped with a 2k x 2k CCD camera. An additional 1k x 1k CCD camera which is located before GIF is used for acquisition of high-resolution electron microscope (HRTEM) images. Both image acquisition and external microscope alignment and control are performed using the Digital MicrographTM scripting language and software. In this work, bright field TEM images were taken for all Ag nanoparticles samples in order to confirm their shape and size distribution. This is discussed further in **Chapter 3**.

2.3.1.2 Ultra Violet-Visible Spectroscopy (UV-Vis)

Apart from TEM, the influence of size and shape-tunable properties of surrounding media on surface plasmon absorption of Ag particles related to SIMIT was studied. This instrument is used to characterise the kinetic formation and final stability which facilitates the SIMIT of our Ag nanoparticle samples. The optical properties of mesoscopic and microscopic Ag nanoparticles are the consequence of the electromagnetic field induced collective oscillation of the conduction band electrons known surface plasmon [69]. These resonances are indeed a small particle effect, since they are absent in the individual atoms as well as in the bulk [70, 71]. Existence of plasmon modes rise strong absorption in UV-Vis spectral range ($\lambda = 300 - 800$ nm) where the number, shape and position of plasmon absorption bands in the absorption spectrum of metal nanoparticles are determined by particles size, shape, dielectric constant, composition and dielectric constant of the surrounding medium [71]. However, the size dependence of the surface plasmon absorption rather complicated unlike semiconductor nanoparticles which will be discussed further in **Chapter 3**. In this work, UV-Visible spectroscopy is utilised to review the size reduction dependence related to SIMIT of the optical absorption spectra of Ag particles in colloidal solution.

Fundamental Principles of the Instrument Typically, a beam of light from a visible and UV light source (coloured red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn splits into two equal intensity beams by a half-mirrored device, as shown in Figure 2.15. One beam, the

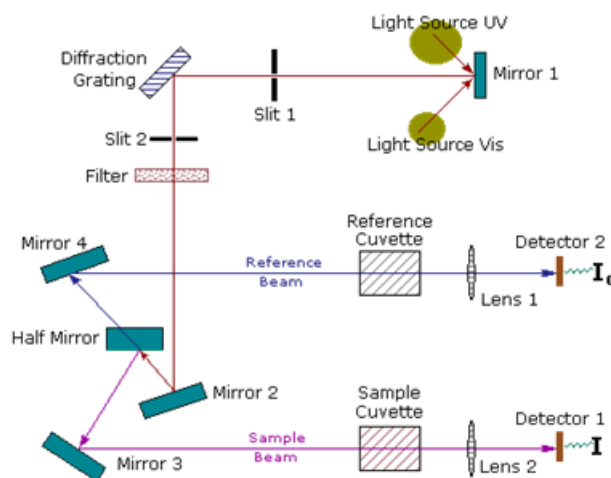


Figure 2.15: A full diagram of the components of a typical spectrometer (*adapted from www.msu.edu*).

sample beam (coloured magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The reference beam (coloured blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and then compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0 . The intensity of the sample beam is defined as I . Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The tunability of the plasmon band for spherical (microscopic) metal nanoparticles is small since its frequency is independent on the size as long as diameter is much smaller than the wavelength. The size effect on the surface plasmon absorption of mesoscopic and microscopic Ag particles with diameters varying from 1 nm and 500 nm.

Furthermore, the concept of full width at half maximum (FWHM) of the corresponding peaks describes the dispersity for both microscopic and mesoscopic Ag particles. Typically, a large FWHM value is corresponded to peak broadening which define a polydispersity

nanoparticle system. Further decrease in Ag particle size to microscopic regime will yield significant peak narrowing with a decrease in FWHM is discussed further in **Chapter 3**.

Specimen Preparation and Instrumentation 10 ml of the as-synthesized Ag-hexane solution was diluted in the hexane solution for this measurement. 3.5 ml of the sample solution was used to fill the quartz cell. In order to get an accurate measurement, it is important to ensure that there are no air bubbles formed inside the cell. The cell was wiped carefully before placing it into the spectrometer. The *n*-hexane solution was used as a reference solution throughout the measurement. The light absorption of Ag-hexane samples was measured using Perkin Elmer Lambda 750S spectrometer. The absorption spectra of the samples were observed within a spectra range of 300 to 800 nm with the data collection interval of 1.0 nm and a scan speed of and 600 nm/min using tungsten lamp as a radiation source.

2.3.2 Metallicity Characterisations of Ag Particles

As far as the electrical properties are concerned, it is necessary to shed some light on the structural properties apart from the morphological and volumetric characteristics of Ag particles. In practice, structural characterisation is a secondary technique used to compare the analysis of polycrystalline mesoscopic with ultra-fine microscopic Ag particles.

2.3.2.1 Powder X-Ray Diffraction (PXRD)

In this work, powder X-ray diffraction (PXRD) was used to identify the phases present and determine a given Ag nanoparticles' unit cell dimension which provides information of the absolute fractional coordinates of the constituent atoms in Ag. From this point, it is possible to obtain information of materials which will assist the understanding of the structural behaviour (crystallographic, crystallite size and favourable orientation) in Ag nanoparticles. PXRD is also commonly used to identify an unknown substance, by differentiating the XRD profile data with a database conserved by the International Centre for Diffraction Data.

Fundamental Principles of the Instrument In brief, electron beams are emitted from a heated tungsten element in a vacuum tube accelerated through 40 kV which are then impacted on a copper target with sufficient energy. This causes the ejection of an electron from a copper in a typical X-rays laboratory instrument. The interaction between the X-rays with the substance's atoms is considered as a secondary point sources which can re-radiate the X-rays in all directions. The constructive and destructive interference phenomenon of diffraction can occur if the atoms exist in a periodic array which is simply described by Bragg's Law. The diffracted beam of X-rays is regarded as reflecting plane which can be defined in terms of a set of integers (hkl) known as Miller indices which are the reciprocals of the fractional intercepts of the interest plane with the crystal axes. The Bragg plane for cubic crystal with d_{hkl} distance between the adjacent planes is represented by the following equation:

$$d_{hkl} = a \frac{1}{\sqrt{h^2 + k^2 + l^2}} \quad (2.45)$$

For an X-ray of a specific wavelength, λ and angle of incident, θ with respect to a Bragg plane (not normal to the plane), the scattered waves from diverse ions lying in a single Bragg plane will be coherent if the angle of reflection equals to the angle of incidence as shown in Figure 4.5. The path difference between two reflected beams is equal to $2d \sin\theta$ which must be equal to an integer number of wavelength, $n\lambda$ [72].

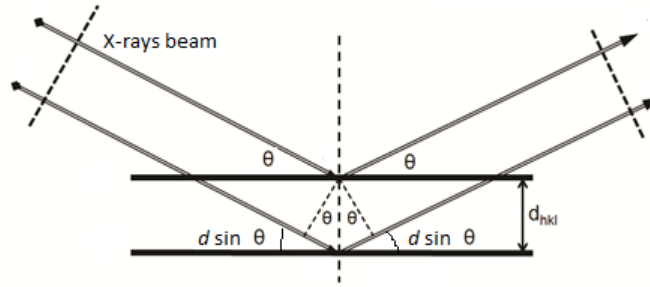


Figure 2.16: Illustration of Bragg's diffraction showing the constructive interference of a front wave of parallel X-ray beam.

The effect of the finite crystalline size of Ag nanoparticles can be observed by the broadening of peaks in an X-ray diffraction pattern. The crystallite size of the Ag nanoparticles is estimated using Scherrer equation. It shall be noted that this 'crystallite size' refers to the size of a zone of coherent scattering which is slightly different from the whole set of crystallite size of the samples and definitely not synonymous with the 'particle size'. The approximate average crystallite size, L , is obtained from the half-width of the diffracted beam in the form of:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2.46)$$

where K is a constant related to the crystallite shape ($2 (\ln \frac{\pi}{2})^2 = 0.9503$), normally taken as 0.9, λ is the X-radiation wavelength in nanometre (nm), β is the peak width of the diffraction peak profile at half maximum height resulting from small average crystallite size in radians and θ is half of the diffraction angle. However, with the instrument used in the present study, it is impossible to reliably predict the average crystallite size of particles smaller than 100 nm due to various factors that can contribute to the narrowing and

broadening width of diffraction peak [73].

Specimen Preparation and Instrumentation A glass substrate of 1×1 cm was washed with double distilled water and ethanol and left to dry for a few minutes. A few drops of silver-hexane sample were drop cast on the surface of the glass slide. The crystalline phases of the Ag particle samples were identified using Powder X-Ray Diffraction (XRD) on PANalytical X'Pert PRO diffractometer instrument (Inorganic Chemistry Laboratory, University of Oxford) in Bragg-brentano geometry with monochromated Cu $K\alpha_1$ ($\lambda = 0.15418$ nm) radiation. The voltage of the anode was operated at a line focus of 45 kV and the emission current was set as 40 mA throughout the measurements. The diffraction profiles were measured within an angle range of 10° to 90° with a scan rate of 0.03°s^{-1} and a step size of 0.008° . The slit width between the source and monochromator crystal was set at 0.02 mm. This slit defines the programmed incident beam operated to ensure that the whole sample was irradiated with X-rays throughout the scan.

In this work, we only consider particle size observed under TEM which is accurately illustrates the real mean particle diameter that we're looking for. Thus, PXRD used to only quantifies the phases and structural presents based on the lattice plane of the constituent atoms in Ag.

2.3.2.2 X-Ray Photoelectron Spectroscopy (XPS)

In this work, quantitative measurements for surface elemental composition and the chemical and electronic states of the Ag nanoparticles elements were ruled out by X-ray photoelectron spectroscopy (XPS). In general, XPS is obtained as a plot of the number of detected electrons by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy of the electrons emitted from the top 1 to 10 nm of the material being analysed. It is indeed a surface-sensitive technique when applied to dry Ag nanoparticles. The XPS X-ray penetrates a substantial distance into the sample ($\sim\mu\text{m}$). This excitation technique imparts no surface sensitivity at the required atomic scale. For instance, when

electrons of a given energy E_0 , are emitted from atoms in a solid at various depths d , below a flat surface, only those electrons which reach the surface and at the same time leaving the solid will have their initial energy (E_0) detected.

In XPS tests, only these photoelectrons possessing characteristic emission energies and contributing to the peaks are considered for subsequent analysis. Photoelectrons which have lost some energy and contribute to the background of the spectrum rather than a specific peak are not considered. The process by which the electron can lose energy as it travels through the solid is known as 'inelastic scattering' as illustrated in Figure 2.14 (A). Each inelastic scattering justifies a reduction in the electron energy and a change in the direction of travel. Therefore, the surface sensitivity must arise from the emission and detection of the photo-emitted electrons. The necessity of chemical state information obtained with XPS is more focused on the oxidation states of the chemical elements bonding.

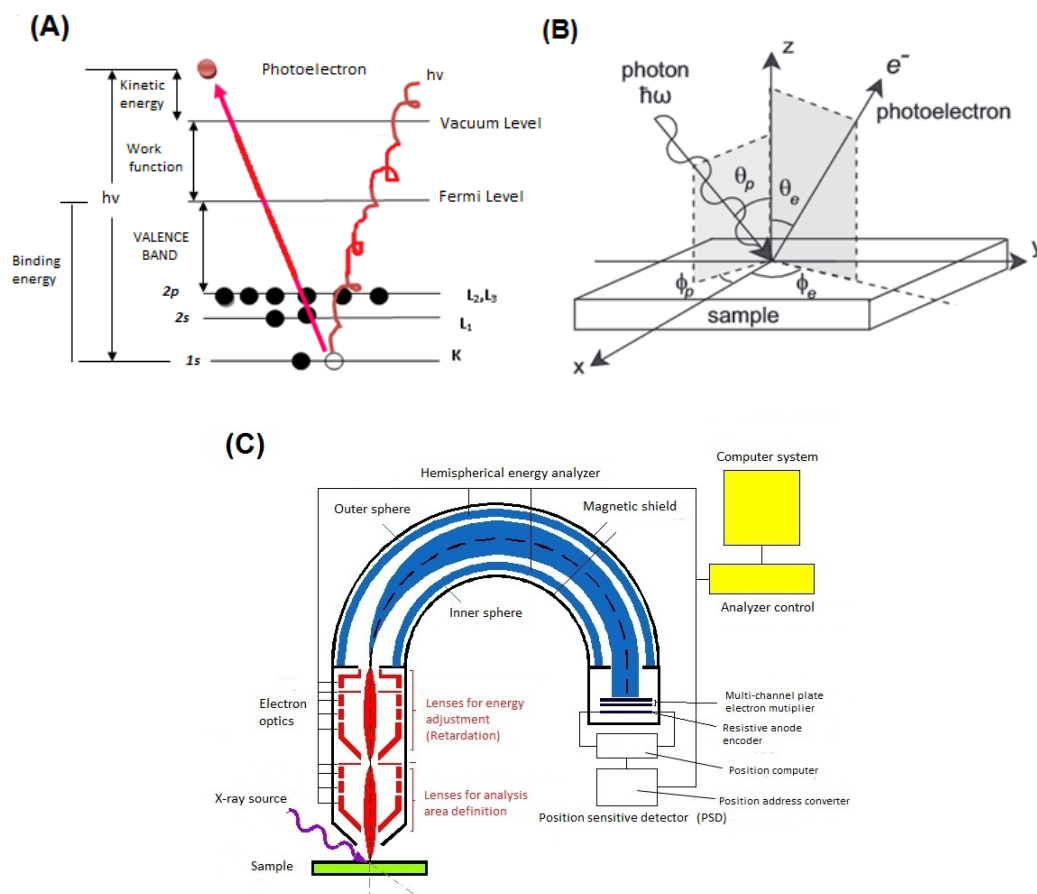


Figure 2.17: Schematic representation of XPS (A) emission process for a typical model atom where the incident beam consists of monoenergetic X-rays whereby the corresponding emitted beam is made up of electrons and energy balance within the framework of a single particle. A photon of energy $h\nu$ is illustrated as in (B) impinges on a solid surface and after absorption of the photon an electron is ejected in a given direction (θ_e, ϕ_e) with respect to the reference system inside the XPS instrumentation (C) (*reproduced from www.casa.xps.com and www.ph.tum.de*).

Fundamental Principles of the Instrument XPS signal works based on Einstein's theory of the photoelectric effect as illustrated in Figure 4.6 (B). The energy of a photon of all types of electromagnetic radiation is expressed by the basic Einstein relation, $E = h\nu$, where h is the Planck constant ($6.62 \times 10^{-34} \text{ J.s}$) and ν is the frequency (Hz) of the radiation. When a solid surface is radiated with soft X-ray photon, an incident photon of energy, $h\nu$ can be absorbed by an electron with binding energy, E_b below the vacuum level (Figure 4.6 (B)). As a result, the photoelectron is ejected into the vacuum with kinetic energy

expressed as:

$$E_{kin} = h\nu - E_b \quad (2.47)$$

For a typical solid surface sample, the E_b is conventionally measured with respect to the Fermi level rather than the vacuum level (Figure 2.14 (C)) and the relationship is written as:

$$E_{kin} = h\nu - E_b - \phi_\omega \quad (2.48)$$

where ϕ_ω is the work function of the material and represents the minimum energy required to remove an electron from the solid, it can be seen as an energy barrier that electrons need to overcome in order to escape from the surface into the vacuum [74].

The binding energy can be regarded as the energy difference between the initial and final states after the photoelectrons have left the atom. Since there is variety of possible final ion states from each type of atom, the corresponding variety of kinetic energies of the emitted electron is also varies. It shall be noted that, each element has a unique set of binding energies and therefore, XPS can be used to identify and determine the type and concentration of an element on the surface of the Ag sample. Variations in the elemental binding energies in terms of chemical shifting particularly arise from the differences in the chemical potential and polarisability of the Ag particles sample which will be discussed further in **Chapter 3**.

The exact binding energy of electrons is not only dependent upon the level from which photoemission occurs but also on the formal oxidation state of the atom and the local

chemical and physical environment. In other words, the analysis of chemical shift of a peak's position is indeed can be correlates with the change in binding energy due to a change in its chemical bonding. It shall be noted that core binding energies are determined by the electrostatic effect between the core level and nucleus which can also reduce by the electrostatic shielding of the nuclear charge from all other electrons in the atoms. The removal or addition of electronic charge as a result of changes in bonding will alter the shielding, in which the withdrawal of valence electron will lead to an increase in binding energy whereas the addition of valence electrons will cause a decrease in binding energy. In this work, the initial-state effect showed the most prominent consideration analysis for the XPS as it can explain literally the influences of the binding energy of the atomic orbital before the photoemission process occur which generally cause the chemical state shifts and inhomogeneous matrix broadening. The threefold importance of this binding observation explain both:

1. *Chemical state shifts* which occur between the different chemical states of an atom depend on the type of bond it produces; *i.e.*, metallic, covalent or ionic. Dispersive or hydrogen bonding also plays a role, as well as the hybridisation in a covalently bonded system. All these factors affect the partial charge on the atom. However, the differentiation of chemical state information is not that straightforward for all elements.
2. *Inhomogeneous matrix broadening* arises because not all atoms are in exactly equivalent bonding configurations in a material. The B_e of an orbital will differ from an atom due to localised differences either in the composition or structure surrounding each atom.

Specimen Preparation and Instrumentation The same specimen prepared for PXRD were used for XPS measurements. In order to examine the pure chemical components of the silver particle samples, high resolution X-ray photoelectron spectra measurement were performed on a Thermo Scientific $K\alpha$ instrument in the UK's National ESPRC XPS User's

Service (NEXUS) hosted by nanoLab nearby the centre of Newcastle-upon-Tyne at University of New Castle, UK. The samples were placed in an ultrahigh vacuum environment exposed to a low-energy, monochromatic X-ray beam. The incident X-rays eject core-level and valence electrons from sample atoms.

The instrument uses micro focus monochromated Al $K\alpha$ radiation source which is operated under 1486.6 eV X-ray energy at voltage power of 12 kV at 400 x 800 microns default spot size for large area spectroscopy. The analyser provides 200 eV pass energy with high default resolution regions of 40 eV for a 10 scan survey with default high resolution regions of 10 scans within 10 m.s dwell time. The spectra were charged corrected by shifting the $C1s$ peak to 284.5 eV which is regularly used to calibrate the spectrometer based on the adventitious surface carbon. The core level of $O1s$, $Ag3d$ and the narrow scan across valence band were identified individually by applying Shirley background to the substrate and inelastic background of each signal. The curves were fit and discussed further in **Chapter 3**.

2.3.3 Volumetric Characterisation of Mesoscopic and Microscopic Ag Particles

In studying SIMIT and the size depletion of Ag nanoparticles volumetric data are always come forward when investigate the effective conductivity of dispersed Ag nanoparticle system for dielectric measurement especially when using microwave cavity resonator technique. Thus, the evaluation of the total particle volume is carried out using Nanoparticle Tracking Analysis (NPTA) Nanosight LM10 instrument.

2.3.3.1 Nanosight LM10

Despite being a powerful and accessible instrument, the TEM technique has a major drawback in determining the amount of individual particles collected in a certain amount of liquid. In this work, each volume of Ag-hexane nanoparticles injected into a quartz tube

must be constant over the entire range of mesoscopic to microscopic sizes. It is common that the small amount of mesoscopic particles can impede an accurate determination of the particle volume. Nanoparticle Tracking Analysis (NPTA) is as one of the innovative systems for sizing particles from about 1 to 1,000 nm in which the lower detection limit is dependent on the refractive index of the nanoparticles.

Fundamental Principles of the Instrument This technique integrates laser light scattering microscopy with a charge-coupled device (CCD) which permits the visualisation and recording of liquid-based nanoparticles on a laser illuminated microscopy technique. This technique enable a sufficient number of particles to be analysed within an acceptable time period (*e.g.*, < 60 seconds) from which a statistically meaningful and that consistent particle size distribution profile can be achieved. The ideal sample should accommodate between 10^7 and 10^9 particles/ml which is often required to achieve this limit.

In general, a finely focused 635 nm laser beam is passed through a prism-edged optical flat. The beam reflects at the interface between the optical flat and the liquid layer above it (Figure 4.8 (A)). The beam compresses to a low profile due to refraction within the intense illumination region. The nanoparticles suspended in a liquid above the flat glass can be easily visualised *via* a long working distance, which is a microscope objective with magnification of $\times 20$ (Figure 4.8 (B)). A CCD camera mounted on a C mount operating at 30 frames per second is used to capture a video field of view approximately $100 \times 80 \mu\text{m}$ [75]. The particles in the scattering volume are observed to be moving rapidly under the Brownian motion.

This capability can be advantageous for small amounts of liquid nanoparticle characterisation since each particle can be visualised and analysed simultaneously but separately. The NPTA software has the ability to identify and track individual nanoparticles moving under Brownian motion which is associated to the movement of a particle size according to the equation derived from Stokes-Einstein [75]:

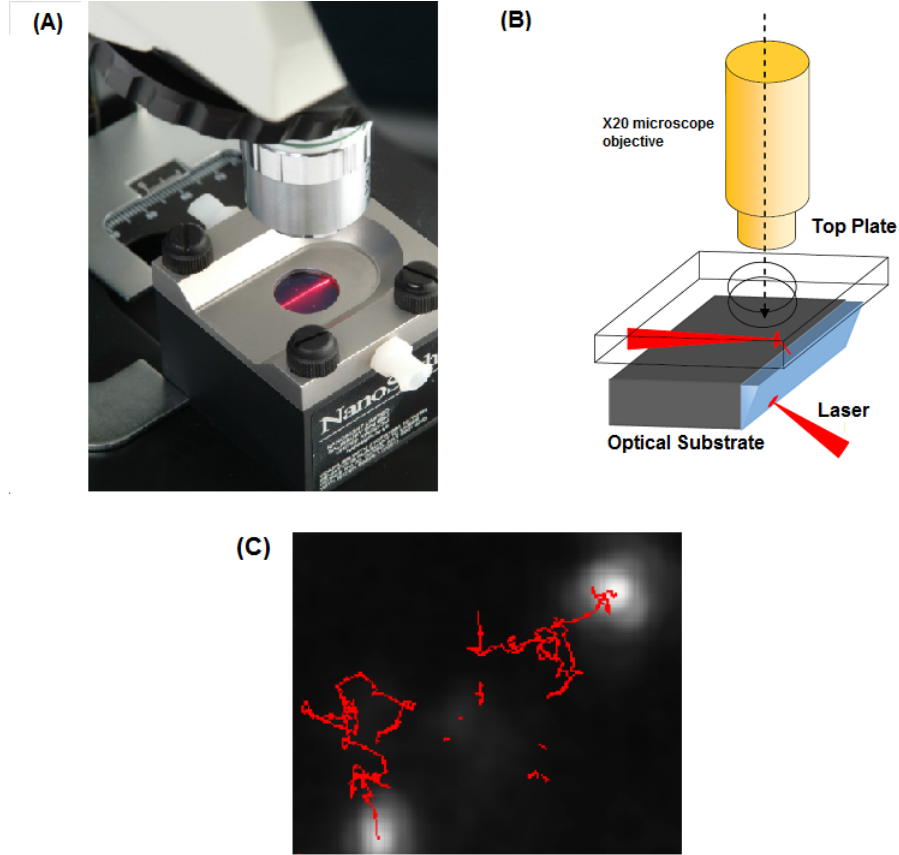


Figure 2.18: Nanoparticle Tracking Analysis (NPTA) (A) based on a laser illuminated microscopic technique where the Brownian motion of nanoparticles is analysed in a real time by a CCD camera with (B) 635 nm laser beam passed through prism-edge optical substrate. (C) The refractive index of which refracts at the interface between the flat and a liquid layer placed above it (*reproduced from* Nanosight [76]).

$$\overline{(x, y)^2} = \frac{2k_B T}{3r_n \pi \eta} \quad (2.49)$$

where $\overline{(x, y)^2}$ is the mean squared speed of a particle and k_B is the Boltzmann constant at

temperature T , in a viscous medium η , with a hydrodynamic radius of r_n . The NPTA programme identifies and tracks the centre of each nanoparticle simultaneously on a frame-by-frame basis throughout the length of the video (typically 900 frames in 30 seconds). Figure 4.8 (C) shows an example of an enlarged image of two such particles and the trajectory they have taken over several frames, as recorded by the NPTA image analysis programme. The ability of NTA to simultaneously measure particles volume based on the nanoparticle size and scattering intensity allows heterogeneous nanoparticles measurement to be resolved and more importantly, the volumetric particles can be estimated directly based on the particle concentration profile. The nanoparticle size distribution profile obtained by the NPTA is relatively a direct number/frequency distribution [75].

Specimen Preparation and Instrumentation The total volume of dispersed Ag nanoparticles is a critical factor for microwave loss measurements and is highly sensitive to the differences in the total particle volume as the measurement is known as volumetric basis [77]. The NPTA enables visualisation of each sample and provides an approximate total particle volume based on the recorded particle counts. The Ag-hexane solution was diluted based on the concentration needed for the NPTA measurements. The amount of each solution used in this experiment was kept constant at approximately 1.5 ml in each injection measured under NPTA.

The NPTA measurements were carried out using Nanosight LM10 (Nanosight Ltd, London, UK) equipped with a chamber with a 640 nm laser and a Viton fluoroelastomer O-ring. Particle samples were prepared by diluting the stock suspension of Ag nanoparticles to desired amount of concentration in hexane. The samples were injected into the sample chamber using a sterile syringe (EMD Millipore Millex, Fisher Scientific, UK) until the liquid covers the whole glass plate and reaches the tip of the nozzle. All measurements were performed at room temperature. NTA 2.0 Build 127 software was used to record and analyse the data. The samples were measured for 40 seconds with manual shutter and gain adjustments. The 'single shutter and gain mode' was used to capture the mono-dispersed

and poly-dispersed mesoscopic and microscopic Ag nanoparticles at this time point. Data was output as the concentration distribution of particles of different diameters.

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Chapter 3

Properties of Ag Particles : Results

Probing a quantum phase transition that signifying the natural transformation of conductive mesoscopic to insulating microscopic of individual dispersed Ag particles is the focal point of experimental interest in this study. This chapter presents results of the auxiliary techniques which provide the basic morphological properties of mesoscopic and microscopic Ag particles at room temperature. The **first section** of this chapter reports the synthesis results of Ag particles with a combined theoretical and experimental study on the growth mechanism of microscopic and mesoscopic Ag particles. The **following section** discussed the morphological property highlights the fundamental variation of features in mesoscopic and microscopic Ag assemblies that should relate to their metal and non-metal behaviour and the SIMIT that will be discussed in **Chapter 4**.

3.1 Synthesis of Ag Particles

The formation of Ag particles with various sizes ranging from ultra-fine microscopic particles to mesoscopic aggregates indicates that this is a size-selective synthesis where the final product obtained is related to the changes of two important experiment parameters; (i) the concentration of chemical reactant and (ii) reaction of temperature.

3.1.1 Effects of Concentration Parameter

This work reported a success in synthesising various sizes of Ag particles which satisfying the particle size range where the onset of probable SIMIT salvation in a metallic system would occurs. For the first time, Ag particles with tunable sizes ranging from 420 to 1 nm were successfully prepared. It is important to note that, systematic details in mechanistic study on the formation of such particles need to be understood thoroughly before any SIMIT analyses resume. By comparing the formation mechanisms of such structures will lead us to the preliminary details on the control factor that governed the size-dependent dielectric behaviour of the particles. It is known that smaller spherical mesoscopic and microscopic particles ($d_m < 100$ nm) can be successfully obtained where the precursor will have greater solubility in the medium which depends upon several factors [1–3]. One of the factors that directly relates to the alterations of the structure and morphology of the particles during the synthesis is the concentration of a reactive components with respect to the entire total electrolytic concentration of the medium.

The size of Ag particles can be systematically controlled by varying the concentrations of reducing agent (DAXAD 19) and precursor (AgNO_3) [4–6]. For instance, in the present work, a decrease in the reductant to precursor concentration results in fast formation of a large number of nuclei, which leads to minute and mono-dispersed microscopic Ag formation. During the growth of the nuclei, the particles are hindered from intensive coalescence due to less accumulation energy exist in bridging the particles to be in contact to each other. Increasing the amount of DAXAD 19 minimises the chances of the particles to interact with the surrounding that cause a substantial decrease in its surface free energy. Low energy free surface will results in a decrease in physical interaction of the particles with the surrounding thereby lowering the overall surface chemical reactivity. This process will accelerates the formation of the additional particles and leads to an increase of the growth rate (more clusters are formed). Therefore, an increase in the DAXAD 19 reducer and Ag precursor leads to a faster formation of a smaller number of nuclei, and results in larger

aggregates with considerable morphological heterogeneity such as prism and other truncated shapes [1]. It was observed that in **Section 3.1.4**, with increasing the concentration of DAXAD 19 from 6.21 mM to 13.32 mM, 16.25 mM, 20.17 mM and 26.62 mM (Figure 3.1), the Ag particles mean sizes were increased from 1 ± 0.9 nm to 5 ± 0.6 nm, 42 ± 0.7 nm, 152 ± 3.4 nm and 276 ± 3.5 nm, respectively.

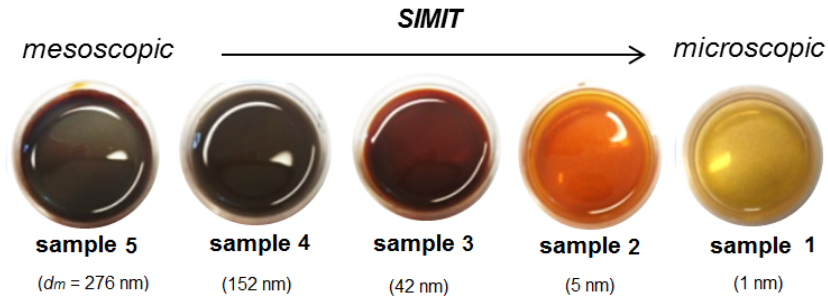


Figure 3.1: A distinctive colour change of the mesoscopic and microscopic Ag hydrosol in the presence of DAXAD 19 as a reducing agent and stabiliser at 353 K. Sample 5 to 1 with decreasing molar concentration of DAXAD 19 and AgNO_3 based on the values shown in **Table 2.1**. The corresponding mean particle diameter shows that various size can be achieved by varying the concentration of the reducer and Ag precursor.

Larger mesoscopic Ag particles in the range of 200 to 300 nm are normally achieved by further increasing the concentration of DAXAD 19 and AgNO_3 precursor used. For instance, platelet-like Ag aggregates (276 ± 3.5 nm) with smaller constituent particle size of ≤ 50 nm (**Figure 3.5 (I)**) is formed by doubling the amount of DAXAD 19 and Ag precursor added during the synthesis as discussed further in the mechanism section of **3.2.1**. Ideally, reducing the size of mesoscopic Ag particles to microscopic crystallite Ag can further increase both its surface-to-volume ratio and the mean particle-particle distance l_{m-m} , and therefore boosting its non-metallic character over its conventional metallic counterparts that should reflect its SIMIT probability.

3.1.2 Effects of Temperature Parameter

Another advantage of this synthesis technique is the ability to synthesise size-controlled Ag particles by adjusting the reaction temperature from 333 K to 363 K. In this work, it is apparent that mesoscopic particles as large as 420 nm are produced at the highest reaction temperature which in this case is 363 K. The formation of larger Ag platelet-like particles can be enhanced by mainly increasing the reaction temperature apart from increasing the concentration of DAXAD 19 and Ag precursor. Considering Mirkin's description [7–9] on the bimodal growth of anisotropic Ag particles, the observed growth process of mesoscopic Ag flakes occurs through an edge-selective particle fusion mechanism, with several small anisotropic Ag particles coming together in step-wise fusion to form a larger particles. On this basis, the formation of mesoscopic Ag plates occurs only after small mesoscopic Ag particles have accumulated under an appropriate heating process (353 K and 363 K). Basically, the higher the reaction temperature, the faster the growth rate of the particles. This indicates that high-temperature reaction greatly influenced the intensive reaction capability of components due to the intense number of high energy collisions. The result therefore, clearly demonstrates that the growth of larger platelet-like mesoscopic Ag (> 150 nm) can be easily formed in a rich-heated environment as the coalescence reaction rate is superior and higher where the nuclei is almost 100% change to particles.

3.1.3 Ligand Exchange Approach

The main reason for us not to synthesise Ag particles in organic solvent is due to the limited range of sizes that can be produced from the reaction medium [10]. It is known that the surfaces of the aqueous Ag particles are covered by hydrophilic ligand molecules which prevent the aggregation of the particle cores. The bonds between the surface of the Ag particles and charged naphthalene sulfonate group of ligands are balanced by higher electrostatic repulsion. Hence, the charged ligands lead to the isolation of particles especially at smaller particle sizes. This holds until attractive forces (*e.g.* van der Waals forces) are sufficient to allow the particles to agglomerate [11]. The strongly charged sulfonic ligand

molecules are found to highly stabilise the particulate Ag system and usually, Ag particles stabilised by the naphthalene sulphonate ligand are stable for up to 3 years.

Since microwave dielectric properties can be distracted by a dipole moment of water molecules, Ag particles have to be transferred to non-aqueous solution in order to ensure the chemical compatibility with our particular microwave dielectric measurement. In the present work, colloidal Ag particles have been synthesised in water medium beforehand, which may lead to the deterioration in the appropriate *quality-factor* (Q-factor). Therefore, a phase transfer protocol is necessary so that the microwave measurements can be executed for this non-aqueous hexane solution. It is noteworthy that, phase transfer approach is frequently strenuous to reproduce depending upon its ligand composition [2, 12–14]. In this study, the naphthalene sulfonate molecules stabilising the colloidal Ag particles in water phase are replaced by aliphatic octadecylamine (ODA) molecules. The amine group is presumed to attach to the surface of the Ag particles, replacing the sulfonate ligand molecules, resulting in hydrophobic character that is preferable for microwave measurement [11].

3.1.3.1 One-Step Phase Transfer Approach

As previously mentioned, colloidal Ag particles have been synthesised beforehand as described in **Section 2.1.1**. For this phase transfer experiment, 10 ml of as-synthesised aqueous Ag particles solution is placed in a clean glass vial. 10 ml of a 3.71 mM solution of ODA (97%, Sigma Aldrich, UK) in hexane was added to produce immiscible layers of colourless organic solution on top of the yellow-coloured Ag nanohydrosol. Brisk shaking of the vial leads to the transfer of the Ag particles into hexane. This can be observed by the yellow colour of the hexane solution, which corresponds to the loss of yellow colour in the Ag-water solution. The swift exchange can be qualitatively understood as the test occurs impromptu and does not require the addition of acid, which is a necessary ingredient in the alkanethiol-coupled phase transfer procedure. In a successful experiment, all Ag particles are transferred into the hexane solution when it is left standing overnight. The

solutions are then separated by centrifuging the Ag-hexane solution for 15 minutes at 6,000 r.p.m, and then re-dispersing them in the same volume of hexane solution. It was observed that the Ag particles do retained their particle size distribution as initially observed in Ag hydrosol samples (Figure 3.2). These amine-protected mesoscopic and microscopic Ag particles can be easily re-dissolved in other common organic solvents such as toluene, benzene and dichloromethane based on the required application.

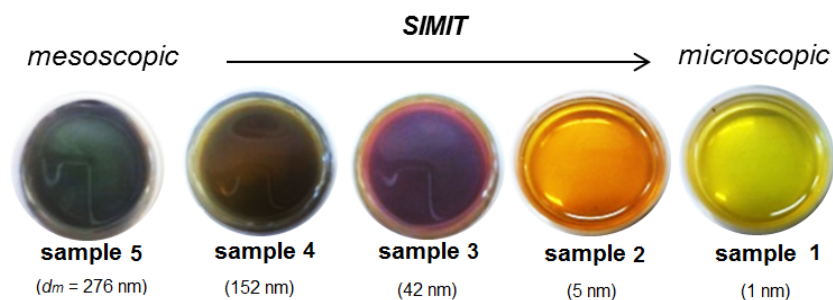


Figure 3.2: A distinctive colour change of the mesoscopic and microscopic Ag organosol in the presence of ODA as a stabiliser at 353 K. The corresponding mean particle diameter shows that the particle size does not varied after phase transfer process.

In general, the dielectric properties of this highly-hydrophobic chain of ODA-Ag particles (positively charged) is quite lower which is similar to saturated hydrocarbon chain [15] as compared to a metal system. It shall be noted that the alkylamine do not form a compact ligand on particle surface as there is no cross-linking head groups to occur as found in alkylsilane [15]. In the microscopic regime, the volume fraction of ligand might occupy considerably higher volume than some of the smaller particles in the solution. If we considers microscopic Ag particles of 4 nm size in diameter, the passivated ligand might occupy $\approx 50\%$ of the volume fraction. Thus, the effect of ligand is greatly increase as the particle size get smaller causing the contribution of the dielectric properties measured become significant. This assumption suggests that it is significantly more difficult to develop free-ligand measurement for smaller particles (< 4 nm). Therefore, the results presented

here on smaller particle size (< 4 nm), mobile charges of ODA are assumed to be dominant in the observed contribution of the dielectric properties. The dielectric constant of a dense solution of ODA is $\epsilon = 2$ [15] and will not as high as other ionic mobility materials in water solution. Clearly the volume of the ODA-Ag particles is considerably lower in this dispersed solution and the effect is not significant. In addition, the ODA-Ag particles are nearly as stable as their thiol-capped counterparts as proven by Kumar *et al.*, (Figure 3.3) even though amine has been recorded to form only weakly bound and chemically unstable monolayers on higher aggregates Ag mesoscopic particles surfaces [11, 16]. The particle size distribution of Ag particles produced from this phase transfer protocol should have poly-dispersities as low as 6.9 % which means the probabilities of changing the size and morphology of the original aqueous Ag particles is less [17, 18].

3.1.4 The Growth Mechanism

Solution chemical synthesis allows exceptional control over the size, structure and morphology of the resulting Ag particles. The emergence of ultra-fine microscopic Ag particles with a well-defined morphology serves as a starting point for their growth into poly-dispersed mesoscopic particles. Here, a series of Ag particle samples were successfully synthesised in Ag/DAXAD 19/water system, and then changed into the Ag/ODA/hexane system *via* phase transfer process as discussed previously in **Section 3.1.3**. This solution-based synthesis produced both mono- and poly-disperse Ag particle samples covering the mesoscopic and microscopic size regimes, which will allow further direct identification of their electronic energy states as localised or itinerant under ambient conditions in **Chapter 4**. It is useful to view all the observed particle size changes here based on two commonly accepted mechanisms for metal nanoparticle formation which is the reverse of the direction one would traverse a metal-insulator transition:

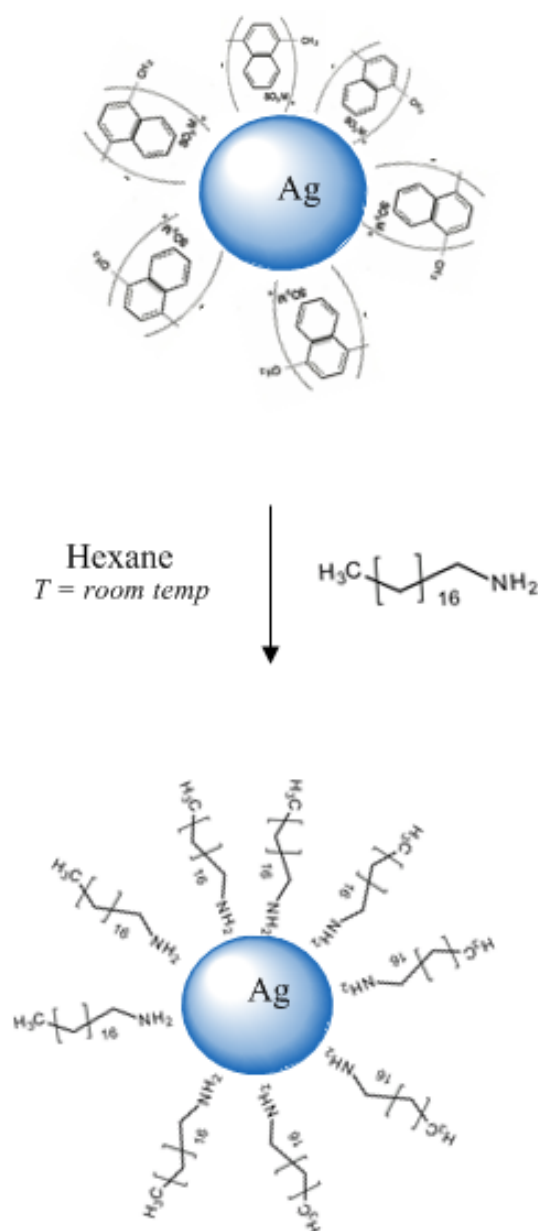


Figure 3.3: Example scheme for the phase transfer reaction between sulfonate-protected to organoamine functional Ag nanoparticles.

1. The classical LaMer growth mechanism, which includes burst nucleation from super-saturated AgNO_3 solution with subsequent slow uniform growth achieved *via* diffusion

processes [19, 20] and,

2. The grain coarsening mechanism, in which the dissolution of small Ag particles provides a nutrient supply for the growth of larger mesoscopic Ag particles [21, 22].

In general, metal atom nominally couple into dimers, fewer trimers and so forth where the coagulation growth would stop depending on their critical coagulation concentration and temperature conditions. The system is discretely going into particles population stability through particles aggregation which mostly yields a broader particle size distribution. In this study, atomic metal is refers to the starting (primary) particles where the interplay of spatial correlations between primary particles and the isothermal dynamic arrangement of the polymeric matrix (reducer and stabiliser) in the early stage of particle growth formation usually take place in the ultra-fine Ag particles (microscopic regime) giving to a narrow distribution of particle size [23]. This continuous growth behaviour in mesoscopic regime compensates for the atomic depletion with aggregation take place, giving a broad size distribution centred at small sizes. This situation favours inhomogeneous size and geometry of particles [24]. Reflecting the viewpoint of Matijevic *et al.*, if the thermal stability and concentration factors are further altered, the ultra-fine Ag particles which are sufficiently sparse in a solution can periodically transform to final particles (mesoscopic) by an independent evolution process [23, 25].

The formation of monodisperse ($d_m < 25$ nm) and poly-disperse ($d_m > 25$ nm) Ag particles from a two-stage growth process is schematically illustrated in Figure 3.4 for the synthesis parameters tabulated in **Table 2.1 (Chapter 2)**. The first stage is considered to be nucleation and growth of the primary microscopic Ag as deduced in Figure 3.4 (A to B) with the average particle diameter is less than 10 nm. The construction of ultra-fine Ag particles takes place by the consecutive addition of individual atoms Ag to form a simple tetrahedral unit (Figure 3.4 (C)). This specific mechanism yields that small numbers of atomic tetrahedra give results to the sequence of poly-tetrahedral growth and this conse-

quently favoured *fcc* particle arrangements under the LaMer growth mechanism ($10 < d_m < 25$ nm) as shown in Figure 3.4 (A) to (C) [26]. The second stage corresponds

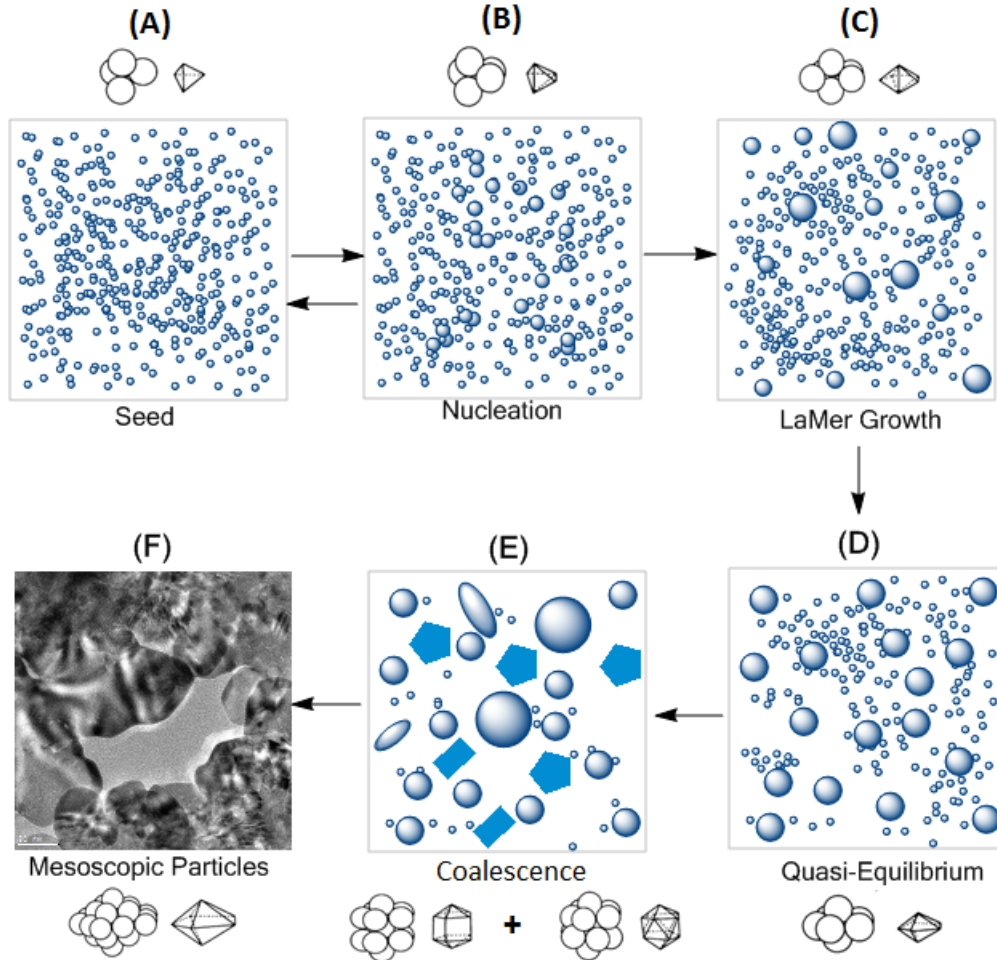


Figure 3.4: Proposed model for the growth of microscopic and mesoscopic Ag particles by the diffusion growth mechanism in aqueous systems. The black illustration scheme of spherical particles shows the construction of particle lattice. Successive addition of individual atoms to (A) a tetrahedral cluster leads to (B) the growth of trigonal bipyramids and (C) a capped trigonal bipyramid in LaMer growth. At this stage, simple decahedra or pentagonal bipyramids form during the quasi-equilibrium process. Further coalescence and coarsening of metallic particles (D and E) lead to the development of decahedra or icosahedra (F) with further aggregation into the complex decahedra (*modified from Duff et al., [26]*).

to the formation of secondary mesoscopic particles ($d_m > 25$ nm) through the coalescence or aggregation of the primary mesoscopic particles as schematically shown in Figure 3.4 (D to F). This stage is also known as size-selection and 'laze' stage process and commonly contributes to the growth variation in Ag particles morphologies. This situation eventually leads to decahedra (Figure 3.4 (D)) and icosahedra (Figure 3.4 (E)) particles with pentagonal symmetry which then progress to an infinite stable lattice of mesoscopic Ag particles with the addition of atoms in the normal metallic Ag packing ($d_m > 100$ nm). In most standard condition of metallic element growths, this coalescence process is results from major changes in the structural development parameters (temperature and concentration) (Figure 3.4 (F)) as already discussed in **Sections 3.1.1** and **3.1.2**.

3.2 Size and Morphological Changes of Ag Particles

In general, the understanding mechanisms of particle nucleation and their subsequent growth is a critical stage in grasping the intrinsic physiochemical properties of the metal nanoparticle system. Previous works have shown that the distinctions between metallic and non-metallic Ag become even more pronounced as the particle goes to the ultra-fine size regime (microscopic) in which the behaviour of its bulk properties starts to diminish [27–30]. Therefore, the actual transition point between the metallic and non-metallic regimes is basically determined by their combined particle size and morphology factors.

In solution-based syntheses, the controlled growth of Ag particles requires specific experimental parameters [28, 31–33]. Recall that so far, among the experimental parameters, synthesis temperature and concentration ratio of reducing agent to Ag precursor have been considered of great importance in this work [28, 31, 34–36]. Here, we systematically studied the effect of these parameters, particularly, on the size and shape of Ag particles. We systematically visualise indirectly the possibility of SIMIT based on their sizes and morphological effects by studying the growth and nucleation of ultra-fine microscopic Ag initially formed in aqueous solution, and then transferred into our preferred microwave suspension

medium, *n*-hexane (C_6H_{14}). As for current situation, hexane is considered to be the best medium to use for the microwave permittivity measurements and is used throughout this study. Since solution chemical synthesis is a bottom-up synthesis technique, the discussion in this sub-section reflects the sequence of morphology from ultra-fine particulate Ag to Ag flake aggregates, which is the reverse of the direction one would traverse a metal-insulator transition.

3.2.1 Observation on the Size and Shape of Ag Particles

3.2.1.1 Transmission Electron Microscopy (TEM)

To tailor the particle size and shape of mesoscopic and microscopic Ag particles, the aqueous phase synthesis parameters such as the ratio of DAXAD 19 (reducing agent and stabiliser) to $AgNO_3$ (precursor) and reaction temperatures were varied according to the conditions summarised in **Table 2.1 (Chapter 2)**. Seeing that solution-based synthesis method can greatly well-defined the size-distribution of Ag particles in aqueous phase, the original condition of the as-prepared particles in H_2O medium can be preserved even after the transfer process into hexane.

Figure 3.5 presents typical TEM images of selected Ag-hexane after the phase-transfer process for different concentrations of DAXAD 19 / $AgNO_3$: 11.04/16.25 mM at 363 K (Figure 3.5 (A1)), 18.39/26.62 mM at 333 K (Figure 3.5 (B1)) and 18.39/26.62 mM at 363 K (Figure 3.5 (C1)). In contemplation to determine the particle size distribution of Ag, the calculation of d_m was made based on the particles counted taken at least 8 different spots for individual Ag sample. At low concentrations of DAXAD 19 reducer to Ag precursor and high reaction temperature (363 K), spherical Ag particles of ~ 26 nm in diameter with unimodal size distribution were made as shown in Figure 3.5 (A3). It is clearly shown that these particles exist as multiply-twinned particles (MTPs) with a decahedral shape which is formed by small selection segment of the (111) and (200) orientations of lattice atoms [37]. Here, the mono-dispersed particle size distribution is weighted towards smaller diameter

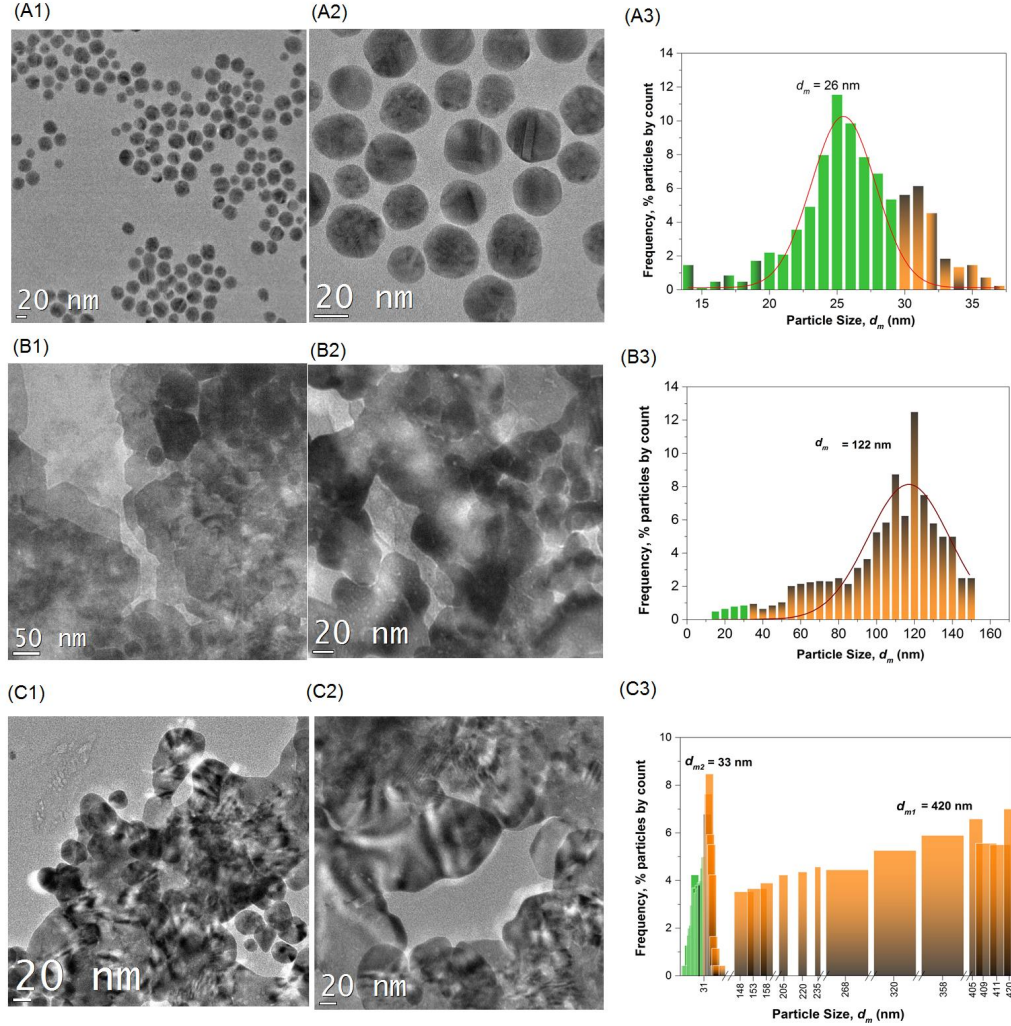


Figure 3.5: Representative TEM images of Ag particle systems indicates by their mean particle diameters before (A1 to C1) and after the phase transfer process (A2 to C2) with $d_m \approx 26$ nm, 124 nm and 420 nm and its corresponding particle size distribution (A3 to C3) synthesized at 363, 333 and 363 K with different amount of chemical reactants concentrations. It should be noted that for (C3) where $d_m \approx 420$ nm, the distributions can only be presented for smaller particles as the larger Ag particles covers most of the field of view. The distributions are coloured to emphasize (green) the presence of $d_m < 30$ nm, which correlate to the normal metallic growth commences with greater number of icosahedral multiply twinned-particles (MTPs) in Ag.

which certainly undergo diffusion-controlled processes [38, 39]. Even after the vigorous

shaking of the biphasic mixture (Ag-H₂O/ODA-hexane), the particle size distribution remains the same for all representative samples (Figure 3.5 (A3 to C3)). The excellent chemical and thermal stability of these particles is attributed to the small particle separation of the crystallisation and grain growth processes [39]. Hence, the particles should possess superior chemical homogeneity and stability at some point during the growth process. The d_m increases up to ~ 122 nm as the concentration of Ag precursor and DAXAD 19 is increased at 333 K (Figure 3.5 (B1 and B2)). In this reaction, anisotropic crystal growth of aggregated particles as large as ~ 150 nm occurs while very few particles with particle size < 30 nm remain. This presumably is the major factor responsible for the change of electronic properties when larger Ag aggregates are present in the system. Thus, the synthesised Ag particles are characterised by relatively a broader poly-dispersed size distribution (Figure 3.5 (B3)). The particle growth process is then further maximised in the sense of size and geometry by increasing the concentration of Ag precursor and DAXAD 19 at 363 K. This is the highest temperature the reactions can proceed as the boiling point of water is relatively low (373 K). The particle growth was significant as reflected by the appearance of continuous Ag nanoflakes covering the whole TEM field of view (Figure 3.5 (C1 and C2)). However, this sample which is representative of larger mesoscopic aggregates has a very tight size distribution when considering only the coarse-grained Ag nanostructures.

The Ag nanoflakes in the sample possess a broad, bimodal size distribution (Figure 3.6 (C3)). Thus, in this case the particle size distribution includes both measured smaller mesoscopic particles which certainly remain as minor contributes particle size element compare to the larger ones. Here, the diffusion-limited growth governs the narrowing of size distribution as discussed by the theoretical work on larger mesoscopic particle systems [40]. This experimental observation on the irreversible higher mesoscopic Ag particles in particular, conclude that a coarsening mechanism is active with clearly broader formation of larger particle size distribution as discussed previously causes from a very slow and almost

insignificant subsequent cluster growth.

To examine the size-controlled effect of Ag particles synthesised over the particle size range of 1 - 420 nm, a representative periodic size growth of Ag nanoparticles with more subtle random structures are shown in Figure 3.6. To unambiguously distinguish a size-triggered Ag particles in a sense which expected to be metallic or non-metallic, we focused on the size depletion from ultra-fine individual microscopic Ag particles to continuous Ag mesoscopic flakes particles (Figure 3.6 (A) to (L)), respectively. The comparison of TEM micrographs here clearly indicates that, larger particles have sharper interfaces while smaller particles are separated by distinct inter-particle regions. Therefore, the atomic crystallites (Figure 3.6 (A)) forming the primary (microscopic) of Ag particles (Figure 3.6 (B)) indicates that the microscopic grains in this regime are in isolated state and is believed to be separated by thin inter-granular regions of an amorphous phase containing Ag and oxygen on the surface of the Ag particles. The grains are also separated by empty insulating regions which in reality, act as potential barriers blocking the inter-particles interaction. Furthermore, from the perspective of electrical transport, these particles can be considered as ensembles of metallic microscopic grains embedded in a poorly conducting disorder particle matrix. Figure 3.6 (C) clearly demonstrates that these primary mesoscopic particles have a highly spatial mono-dispersed distribution, which resulted from the presence of ODA capping ligand on their surfaces. The particles are completely crystallised and the dispersion does not lead to a complete conduction percolation path indicated by the empty separation region, l_{m-m} between the nanoparticles.

Later, the secondary (mesoscopic) (Figure 3.6 (D to L)) particles undergo re-structuring and re-arrangements of their structures, resulting in more compact and denser particles that yields heterogeneous Ag nanostructure preferences [23, 25]. The 'chosen' morphology of mesoscopic Ag particles is firmly driven by a combination of the energy supply and the

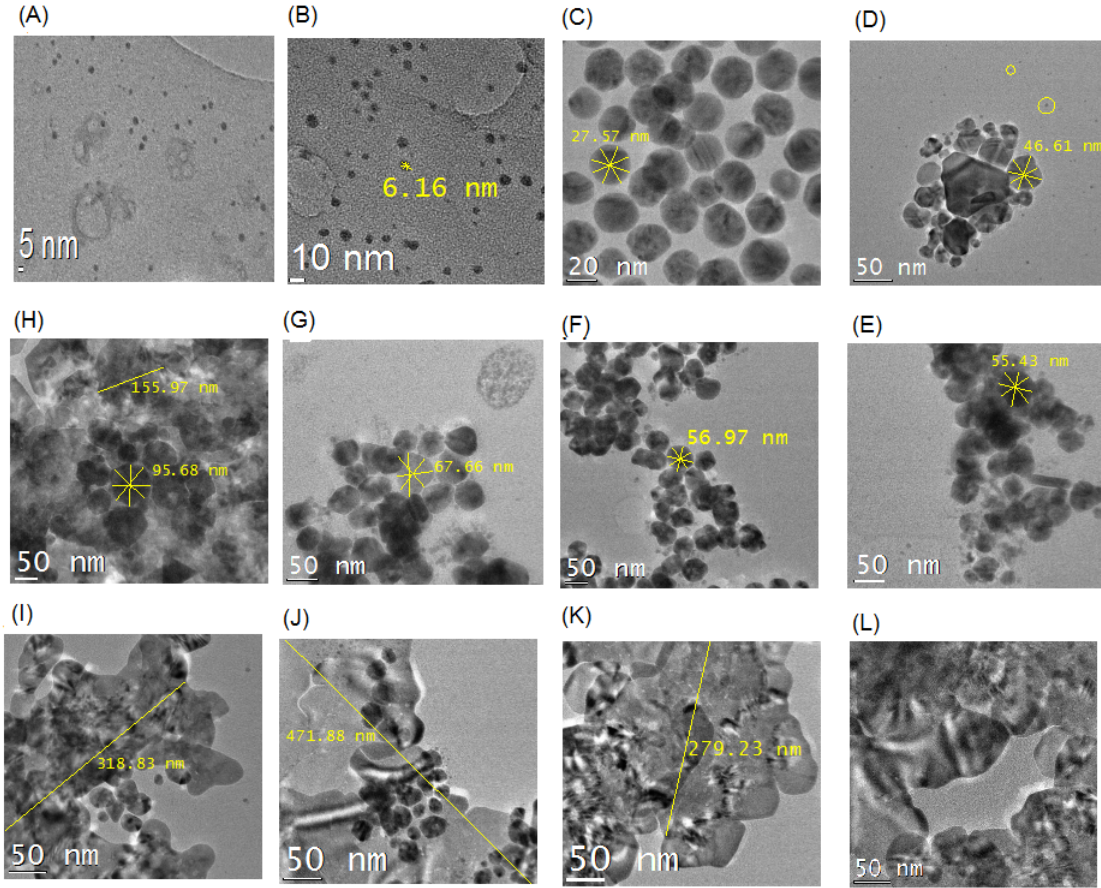


Figure 3.6: *Ex-situ* bright-field TEM micrograph of Ag particle samples suspended in hexane with mean particle diameter, d_m (A) $\sim 2 \pm 0.7$ nm, (B) $\sim 14 \pm 0.5$ nm, (C) $\sim 26 \pm 1.3$ nm, (D) $\sim 51 \pm 0.5$ nm, (E) $\sim 60 \pm 1.5$ nm, (F) $\sim 69 \pm 2.2$ nm, (G) $\sim 89 \pm 2.5$ nm, (H) $\sim 130 \pm 2.7$ nm, (I) $\sim 276 \pm 3.5$ nm, (J) $\sim 350 \pm 4.6$ nm, (K) $\sim 395 \pm 4.8$ nm and (L) $\sim 420 \pm 4.3$ nm, respectively. It shall be note that the micrographs here represent only one spot from 10 different spots measured for the particle size distribution calculation for each sample.

flux of reactants upon the formation of nuclei [41]. Perfect thermodynamic growth takes place when there is an ample supply of energy and a low density of reactants that often results in the genesis of spherical structures *via* uniform growth of all crystal faces [41]. The particles with orientation that produce strong Bragg reflections falling into the angular selection range of the objective aperture in TEM which exhibit bright interface grains contrast, indicating that the particles are single crystal (Figure 3.6 (D to L)). Part of the

particles' grain showed bright contrast and the other parts are darker which indicates MTP structure and their distribution among the particles. Formation of the particles with a broad, poly-disperse size distribution is clearly not a diffusion-controlled growth process. Rather a process route may be better viewed as *particle evolution* mechanism leading to size-growth metallisation.

Figures 3.6 (I to L) show that mesoscopic Ag particles displays high resolution image details revealing good crystallinity with sharper interfaces of the grain. Hence, Ag particles with $d_m > 100$ nm, should behave essentially like semi-bulk metals as the particles consist of closely packed grains that have strong inter-granular coupling, reflected from Goldhammer-Herzfeld criterion which will be discussed in detail in **Chapter 4**.

3.2.1.2 Powder X-Ray Diffractometer (PXRD)

To further confirm the presence of mesoscopic and microscopic Ag particles, the samples were measured by using powder X-ray diffraction (PXRD). All of the XRD spectra have similarities with those previously reported in other existing literatures on Ag particles [42–44]. Figure 3.7 shows representative patterns for mesoscopic and microscopic Ag particles for $2\theta(^{\circ})$ ranging from 30° to 90° . The entire Ag peak shows to the particle size depletion of periodic arrangement from mesoscopic Ag aggregates to ultra-fine microscopic Ag particles. All of the peaks were indicated using the face centred-cubic (*fcc*) Ag structure (JCPDS Card No. 04-0783) and correspond to reflections of the (111), (200), (220), (311) and (222) lattice planes. The pattern of the crystallite size changes are not in agreement with the previous TEM observations as evidenced in Figure 3.7. The evaluation of crystallite size turns out to be quite impossible due to the inevitable process of aggregation of the particles during the drying process. Therefore, it is not really meaningful to take the crystallite size calculated through Scherrer formula in this case. In addition, the changes in the peak broadening is not significant in the results which should be observed in this spectrum. It is well recognised that the peak broadening is primarily due to the miniaturisation process and attendant

defect due to the concentration and low crystallinity of ultra-fine Ag particles as shown in Figure 3.7 (A) to (C).

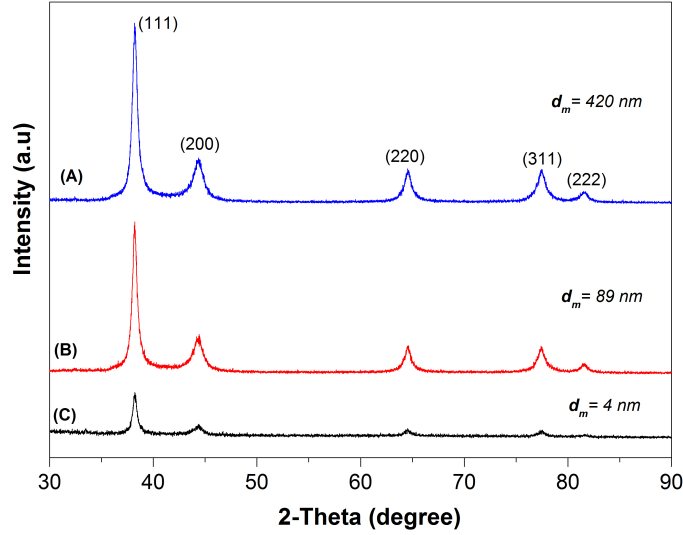


Figure 3.7: Powder X-Ray Diffraction (PXRD) data for two different regimes of Ag particles collected at 333 K for (A and B) larger mesoscopic Ag particles (~ 420 and ~ 89 nm) and (C) microscopic Ag particles (~ 4 nm). The particle diameters are taken from the TEM measurement.

To elaborate further, the integrated intensity of the profiles is indirectly related to the volume (*i.e.* number of atoms) of the coherently scattering domain. Hence, large crystals give sharper and more intense peaks compared to smaller crystals. Figure 3.7 (A) to (C) shows that the XRD data from mesoscopic down to microscopic Ag particles gradually becomes more noisy, indicating a decreasing signal of strong crystallite dispersity factor (note that no smoothing has been applied to these data). Basically, the lines of mesoscopic Ag particles should be markedly narrower than the lines of ultra-fine Ag microscopic particles where the broadening of microscopic Ag particles are significantly wider than the lines of the mesoscopic ones.

3.2.1.3 UV-Visible Spectroscopy (UV-Vis)

It is important to note that the noble metals (such as Ag) show strong responses to visible light, which arise from the collective oscillation of conduction electrons present in the material [45]. The so-called localised surface plasmon resonance (LSPR) due to the excitation of particles depends on their particle size, the poly-dispersity of the particles and the presence of ligand adsorbed on the surface of the particles [45]. The LSPR can be considered as a free carrier absorption which is enhanced by the electric force field perturbing the free motion of electrons at the frequency of plasmon mode. In other words, the damping of plasma oscillations is related to the correlation forces perturbing the conducting electron. In this case, the correlated force field perturbs into small microscopic metal particles is considered a surface force since the force is only exerted at the surface of the particle. This surface force determines the mean free path of the particles. On the other hand, for mesoscopic metal particles that mimic the bulk metal state, the force field that gives rise to the scattering of conduction electrons is due to the phonons or lattice defects [46]. Therefore, the LSPR response modes in ultra-fine Ag particles are not the same as in larger mesoscopic Ag aggregates.

As illustrated in Figure 3.8, the strong and broad LSPR peaks in these UV-Vis spectra of various Ag particles with sizes ranging from ~ 1 to ~ 420 nm are located between 410 to 430 nm. For the effect of ultra-fine microscopic Ag particles on the LSPR absorption, Kreibig has pointed out two main aspects considered here that relates to the size-reduction of the metal nanoparticles. The first one is Kawabata-Kubo effect [46] and the second is

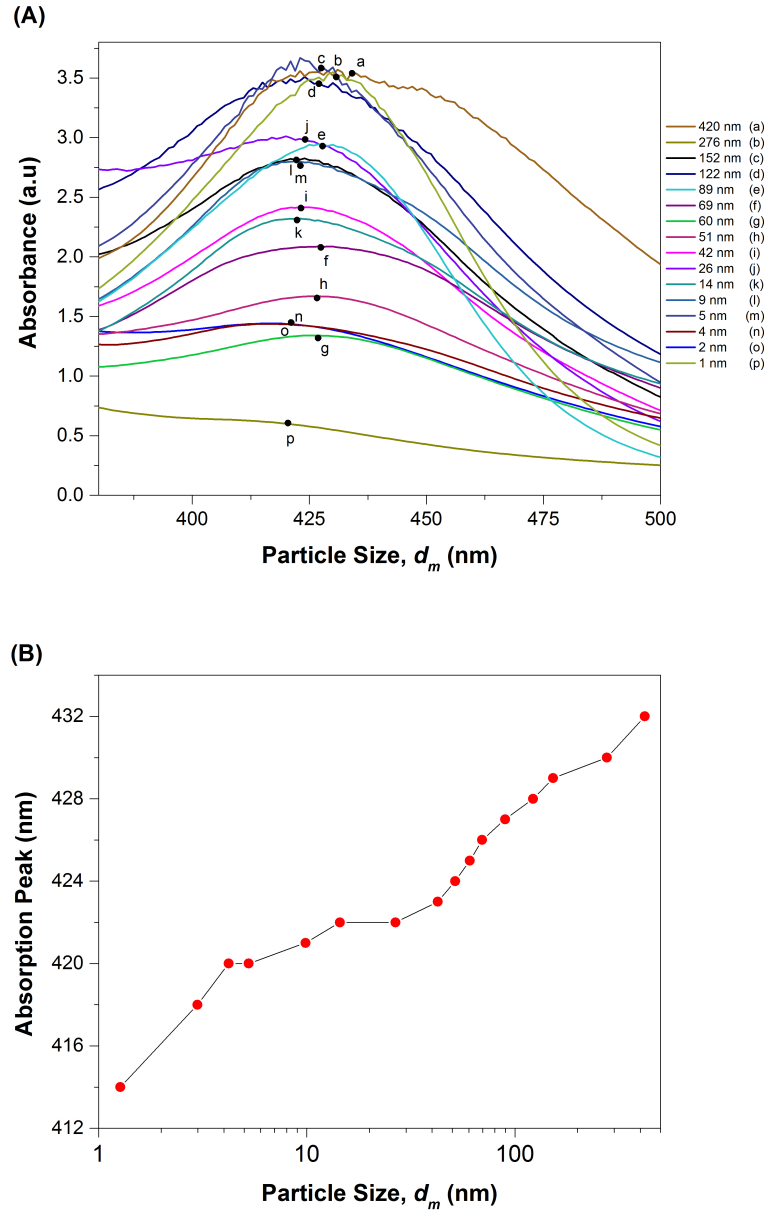


Figure 3.8: Variation of (A) local surface plasmon resonance (LSPR) coupling of UV-Visible absorption between Ag particles prepared using various reactant ratios based on **Table 2.1 (Chapter 2)** at temperatures of 333 K, 353 K and 363 K with the black dotted and alphabet labels show the peak and corresponding LSPR absorption of the particles. (B) Variation of the wavelength peak values as a function of Ag particle size, d_m . It is observed that the peaks have a pronounced blueshift for smaller Ag particles.

the scattering path effect. According to the first plasmon mode effect, Kawabata-Kubo

effect is referred to the formation of atomic Ag nanoparticles ($d_m \leq 10$ nm) where the absorption plot should be broadened and damped that could even disappear due to weak of energy transfer from the plasmon to single-electron excitations between quantised levels. In this case, Figure 3.8 (A) shows that the ultra-fine Ag particles were more prone to aggregation, which leads to insignificant absorption and almost peakless spectra in accordance with the quantum size theories. Within this microscopic regime ($d_m \leq 10$ nm), the relative mean particle diameter is decreased with increasing the effective surface layer of Ag nanoparticles giving a blue-shifted trend in comparison with other mesoscopic sizes. This also explains the phenomenon observed by Sobczak-Kupeic *et. al*, [36], where a blue shift is due to the decrease of Ag nanoparticles nuclearity that comes into play when the d_m becomes comparable to the mean free path of electrons as in the Ag bulk metal. For the microscopic Ag particles where the d_m is so small that the quantised energy levels of conduction electrons are discrete, lattice imperfections will no more play the role of scatterers but only affect the wave functions and energy levels of each quantised state.

The second effect takes into account is the scattering of conduction electron at the mesoscopic particle surface. Larger mesoscopic Ag particles are assumed to have the same LSPR response from the scattering contribution of phonons as that of the bulk Ag [47]. As shown in the Figure 3.8 (A), the increase in peak area of the band indicates a decrease in inter-particle spacing, which results from the particle aggregation process. At this stage, the formation of larger nanoparticles primarily results from the *van der Waals* force with very weak columbic repulsion between the particles. It shall be noted that the increase in the maximum absorbance is due to the particle density which strongly depends on the amount of Ag nanoparticles in the solution [48]. The red shift in the peaks of the mesoscopic particles implies that the particles are growing larger. Thus, the broadening of the LSPR spectrum with intense peak characteristics showed that the distribution of mesoscopic Ag particles becomes wider.

The corresponding LSPR peak value recorded for this series of particle size (420 - 1 nm), are in accord with the principal of nucleation growth by the greater coarsening mechanism as highlighted in a previous section (Figure 3.4 (F)). The analyses of the LSPR shift were found to be in a satisfactory agreement with the interaction contribution of d_m to the applied external electric field. Figure 3.8 (B) shows the peak position is red shift if viewing from the reverse of the direction for metal-insulator transition and blue shift if *vice versa*. For larger mesoscopic Ag particles, the peak wavelength is about 432 nm and the smallest particle has the absorption peak at 414 nm. A red shift in the maximum absorption is explained by the presence of multipole interactions among the high density of Ag MTPs in an external electric field. Hence, it is found that Kawabata-Kubo and free path effects both have a major effect on these samples. We have therefore used the size-dependent dielectric permittivity, taking into account the conduction electron scattering at the surface of Ag particles in a microwave field which gives rise to their electrical conductivity as discussed further in **Chapter 4**.

LSPR absorption can also explain the main interest of our work on the structure of the Ag particles. In principle, the heterogeneity shape of Ag particles could be a dominant effect in the broadening mechanism of the resonance. This consideration leads to the result that the broadening of LSPR increases proportionally to the associate changes in sizes and shapes of the particles. The symmetry (bisector corner) of Ag particles controlled the ways that they are polarised by the collective oscillations of their conduction electrons. The number of these ways correlates to the symmetry of the LSPR resonance. Typically, for ultra-fine Ag particles with the most symmetric shapes with less particles density such as spheres would have just one peak that could almost disappear since an individual small spherical particle could be weakly polarised only in a dipole mode (Figure 3.9 (1)). If surface charges are polarised according to the edge of symmetry as depicted in Figure

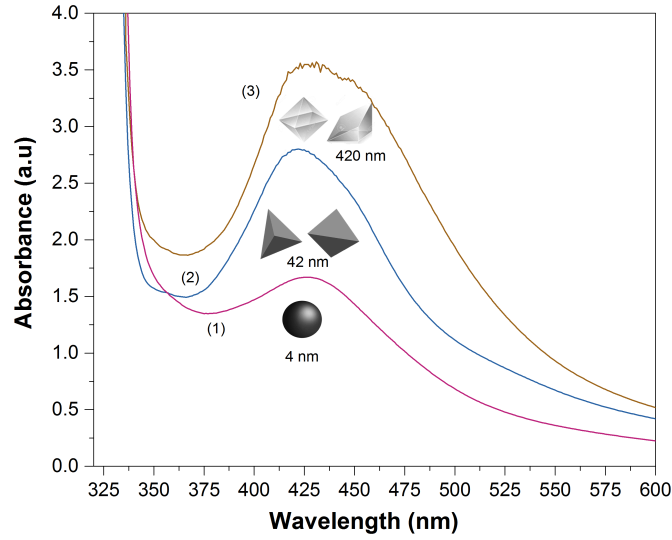


Figure 3.9: Variation of LSPR absorption characteristics for different Ag particle shapes: (1) spheres (~ 4 nm), (2) tetrahedra (~ 42 nm) and (3) octahedra (~ 420 nm).

3.9 (2), the total dipole moment will increase according to the number of bisector corner giving a broader and more intense peak of the plasmonic resonance. The total dipole moment will continuously increase as the accumulation of the electrons in bisector corners is doubled. Therefore, the number of plasmon peaks will increase which increases the intensity of absorption spectra (Figure 3.9 (3)).

The geometries of the Ag particles have also been clearly analysed by the direct differences of the full width of half maximum (FWHM) of the Ag samples (Figure 3.10 (A) and (B)). The FWHM of the observed peaks for smallest ultra-fine microscopic Ag particles greatly decreases to about ~ 3 nm as comparing with that of the largest mesoscopic particles of about ~ 118 nm (Figure 3.10 (B)). One can accept that this is due to the mono-dispersity of the homogeneous particles geometry took place in microscopic regime as indicated in the plot of FWHM as a function of d_m . Therefore, decreasing the size of Ag particles does indeed lead to pronounced changes of its geometry as well as its structure. Hence, the change in the sizes and structures of Ag particles typically leads to the change

of their properties.

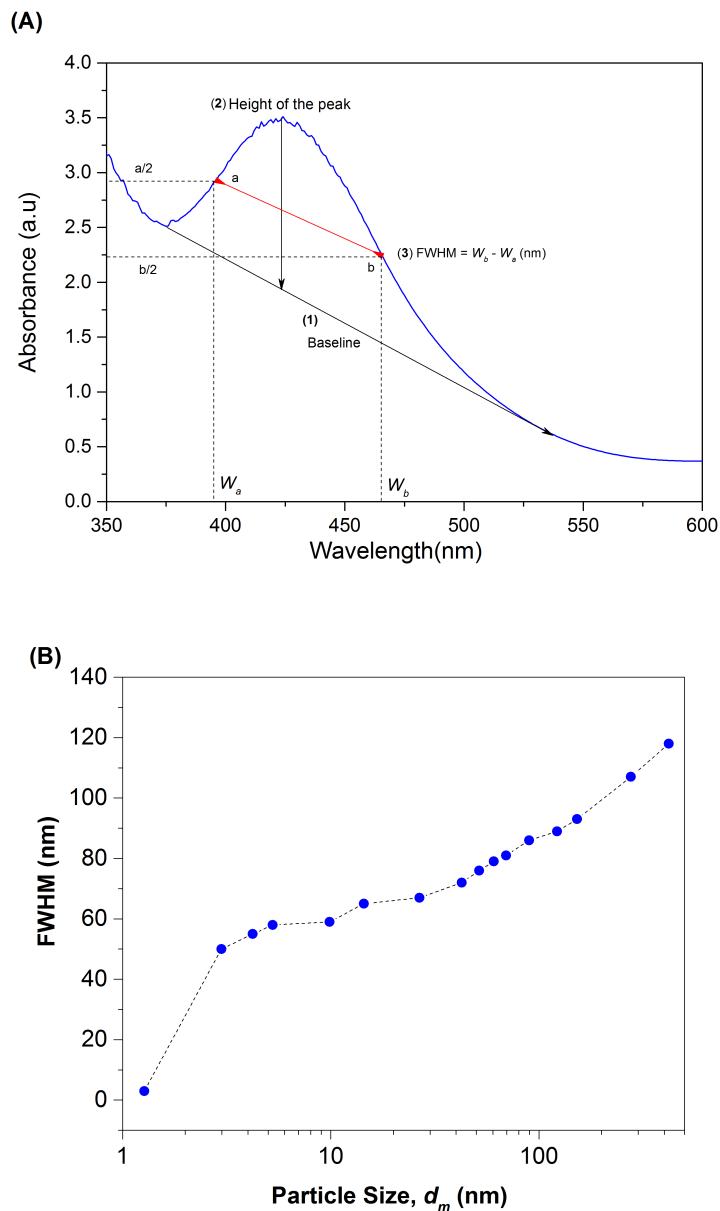


Figure 3.10: The full width at half maximum (FWHM) of Ag particle samples. (A) The FWHM of UV-Vis spectra was manually calculated by these three simple steps: (1) to (3), and then be compared to a value obtained directly from the spectrometer. (B) Variation of LSPR absorption of FWHM dependency upon the particle size of Ag, d_m . The plot shows that the decrease in particle size results in a decrease in the calculated FWHM of plasmon resonance.

3.2.1.4 X-Ray Photoelectron Spectroscopy (XPS)

It appears that an obvious indicator here is the critical influence of size-dependent behaviour, which is for sure significantly affected by the combined effect of the amount of surface particles and atomic parts in these samples. Since binding energy (BE) is also affected by d_m , this significantly complicates the interpretation of X-Ray Photoelectron Spectroscopy (XPS) results for these samples. There are some previous experimental situations similar to this study, which dealt specifically with small microscopic Ag particles [49, 50]. This can give valuable insights for us to understand the changes in the chemical environment either corresponding to the size-dependent SIMIT or changes in the oxidation state in ultra-fine individual Ag nanoparticles.

Almost certainly, the very first attempts to explain the occurrence of Ag metallic *vs.* non-metallic behaviour are based on a positive core level shifting of the $3d_{5/2}$ peak as an overall final state which often found in condensed metallic phase [34, 51]. Clearly as shown in Figure 3.11, for microscopic Ag particles ($d_m \leq 10$ nm), the positive core level shifting corresponds to the final state of the photoemission process where the less conductive system is presumably less efficiently screened. This has led to a more realistic picture of the transition region to smaller microscopic particle size and more often explained in terms of the final state effect of the shortage electron on any one atom. Thus, as the d_m is reduced to microscopic size regime one can explain the results based on the inefficient positive hole screening of the final state of the photoemission process due to the less conductive particles presence that is responsible in triggering a positive core level shift of the system. Assigning the dynamic change of positive Ag $3d_{5/2}$ core level shifts to insufficient conductance of ultra-fine Ag nanoparticles with a corresponding shift start from 367.72 to 368.02 eV should imply that with decreasing d_m can affect the core level shifts as shown in Figure 3.11 (A) and (B). Specifically for mesoscopic and microscopic Ag particles of ~ 420 and ~ 1 nm, core level shifts of $+0.03$ and $+0.34$ eV can be observed with respect to the $3d_{5/2}$ level of Ag bulk crystal (Figure 3.11 (C)), respectively.

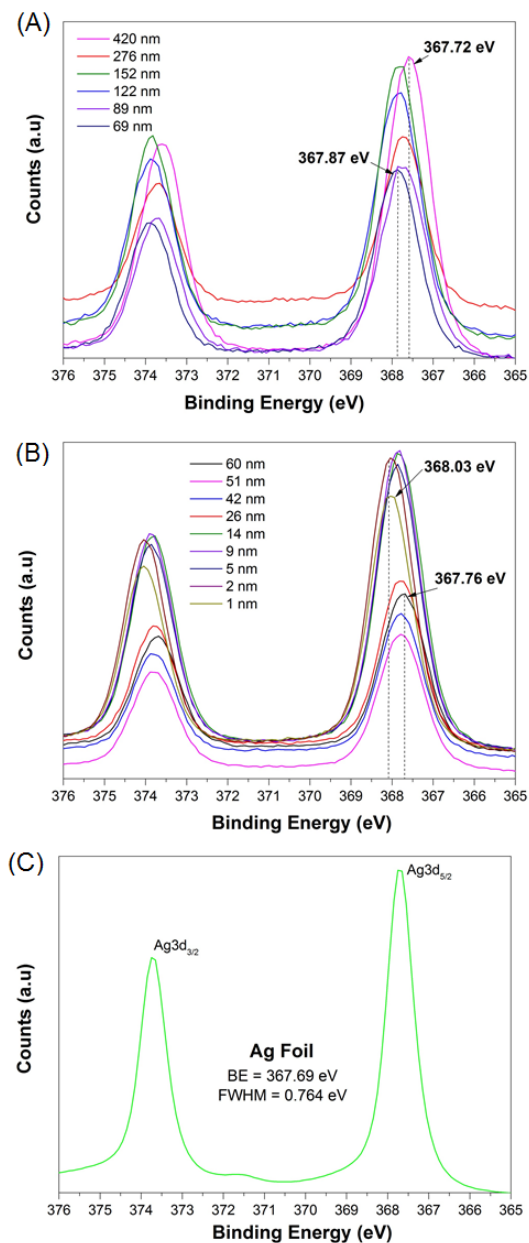


Figure 3.11: Ag_{3d} electron region of the X-ray photoelectron spectrum of some mesoscopic (A) and microscopic (B) Ag particles and the corresponding spectrum of a bulk Ag in a form of Ag foil as a reference (C). A shift to a higher binding energy from 367.72 to 368.03 eV shows that the properties of Ag particle samples are almost resembles the pure bulk Ag as a reduction of the particle size takes place.

Vijayakrishnan *et. al*, have pointed out that the observed positive spectral shifts cannot be accounted for final-state effects alone but should generally interpreted in combination with initial-state effects as well [52]. The initial-state effect leads to the positive chemical shifts due to changes in valence band positions where the depletion of valence band electron is significant when the size of mesoscopic Ag particles gradually reduced to microscopic size. This factor consequently contributes to dramatic core level shifting. Another important point to notes is that the direct consequence of initial-state effect which arises from the formation of such a discrete energy level structure may also result from the increased in the lattice strain in microscopic Ag particles system. This could preliminary manifest the size-reduction of the SIMIT of Ag particles based on the decrease in the core-hole screening effect. Thus, it is reasonable to anticipate that ultra-fine Ag nanoparticles show a corresponding spectral shift to higher BE . The ΔBE shifting of small microscopic Ag particles have been observed previously to be around 0.5-2.0 eV compared to the core levels of the high nuclearity macroscopic Ag crystal [34, 51–54]. Specifically for mesoscopic and microscopic Ag particles d_m , of ~ 420 , ~ 276 , ~ 152 , ~ 122 , ~ 89 , ~ 69 , ~ 60 , ~ 51 , ~ 42 , ~ 26 , ~ 14 , ~ 9 , ~ 5 , ~ 4 and ~ 1 nm, core level shifts of $+0.03$, $+0.03$, $+0.04$, $+0.1$, $+0.1$, $+0.1$, $+0.1$, $+0.13$, $+0.14$, $+0.17$, $+0.17$, $+0.18$, $+0.18$, $+0.19$, and $+0.34$ eV can be observed with respect to the $3d_{5/2}$ level of Ag bulk crystal (Figure 3.11 (C)), respectively. Obviously, the apparent binding energy of $Ag3d_{5/2}$ electron for both mesoscopic and microscopic energy were higher than the value in bulk Ag (Figure 3.11 (C)).

The BE values as a function of particle size d_m is shown in Figure 3.12. The $Ag3d_{5/2}$ level of microscopic system is only shifted by -0.17 eV as the diameter of particle increases from ~ 1 nm to ~ 9 nm. This serves to increase the effective probability to the presence of uncoordinated atoms considering that the $Ag3d_{5/2}$ core level shifts due to the major contribution of initial-state effect is significant when the $d_m < 10$ nm. Further increase of the particle size to lower mesoscopic particle ~ 42 nm results in additional shifts to lower BE by 0.2 eV. In this work, for Ag particle systems, the core level BE 's prove to almost

converged near to the bulk values when the size of Ag particle exceeds the particle diameter of ~ 122 nm. This effect agrees well with the previous work made by Radnik *et al.*, where the core level shifts are sensitive to the structure and morphology of the particle [55]. It is suggested that the mesoscopic Ag particles have more irregular shapes compared to the microscopic Ag particles, giving higher densities of uncoordinated atoms on the surface of the particles. For mesoscopic Ag particles ($d_m > 10$ nm), the observations on the core level shifts as compared to the core level BE of Ag bulk indicated that the core level shifts may quite sensitive to the particle shape apart from the size effect [55]. The existence of uncoordinated atoms can change the electronic structure of the Ag particles. The transition of the SIMIT that will be addressed in **Chapter 4** could be suggested occur due to this core level shifts as a function of particle size as presented in this section. However, considering that the $Ag3d_{5/2}$ level shifts related to the initial electronic structure of the Ag nanoparticles in the addition to the final state effect alone cannot completely rationalise the SIMIT. Therefore, the initial state effects prove to be explained by combinations of quantum size effect, the presence of uncoordinated atoms and perhaps also the increased in lattice strain in smaller Ag particles.

In the present context, the reduction of particle size should necessarily lead to broadening of the $Ag3d_{5/2}$ signal (Figure 3.12). The broadening of the $Ag3d_{5/2}$ core level FWHM for microscopic particles can be explicitly attributed to time-energy broadening of the hole state due to the presence of different particle sizes [56]. This reflects the fact that, the electronic properties of the ultra-fine Ag nanoparticles are significantly different from those of the corresponding mesoscopic Ag particles, in accord with the principle of the size-dependent alteration of electronic structure, which give rise to localization of electronic wave functions in the microscopic regime (< 10 nm). It is worth to mentioned that based on the plot in Figure 3.12, there is a discontinuity in either BE and FWHM values for Ag particles between ~ 4 nm to ~ 2 nm as shown by the turquoise gap. From this, we can deduce that the intrinsic properties of this size range are subtly influenced by differences

not only in size but also in particle geometry.

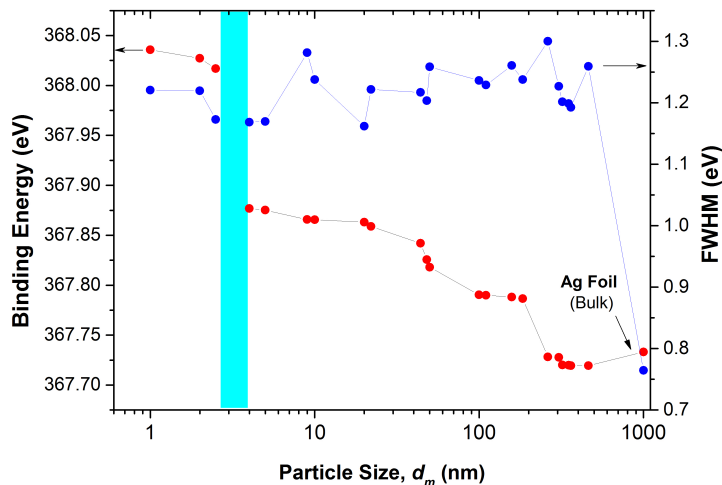


Figure 3.12: Variation of binding energy values, BE and the broadening of the $Ag3d_{5/2}$ signal (FWHM) as a function of particle size, d_m . The critical size dictated at ~ 10 nm shows discontinuity as clearly indicates between the ~ 2 nm and ~ 4 nm particles as shown by the turquoise colour gap. The shifts in the BE of particles relative to the measured bulk Ag foil are also included for comparison. The sizes of the particles were determined by transmission electron microscopy (TEM). One should take into account that the FWHM effect could more or less explicitly expressed the size changes in Ag particle samples.

3.3 Proving the Chemical Status of Ag Particles

3.3.1 Observation on The Chemical State

3.3.1.1 XPS

Perhaps some doubts may arise in accepting that our Ag particles are fully pure particles without a significant presence of silver oxide or other highly oxidised silver states. This argument gains more importance as we discuss the chemical states of ultra-fine Ag nanoparticles. A common laboratory technique for the quantitative and qualitative analyses of the oxidation states of Ag particles is performed by X-Ray photoelectron spectroscopy (XPS) in this case. In practice, it is hard to use XPS to correctly identify the oxidation state

since the experimental binding energy (BE) in a solid may vary a lot from compound to compound with changes in the environment. However, XPS is still one of the most reliable and acceptable techniques to analyse the existence of oxide element that mostly observed at the interface between the Ag metallic core and a possibly oxidised Ag surface layer[57]. Based on several published works [58–60] and the NIST XPS database [61], the reported BE values of the three different Ag chemical states of Ag, AgO and Ag₂O are within 0.6, 0.9 and 0.8 eV interval, respectively. Precisely, assigning spectral features is thus not a straightforward analysis. This conclusively has been no proved to be responsibly fixed to a certain value. Thus, the range of BE values for Ag $3d_{5/2}$ taken from other literature works [57–59, 61] are:

- from 367.9 to 368.4 eV for Ag⁰;
- from 367.6 to 368.5 eV for Ag₂O; and
- from 367.3 to 368.1 eV for AgO.

In addition to this difficulty, it is almost impossible to analyse smaller metallic particles, where a positive charge develops as the sample is irradiated with X-rays. Neutralising this charge with a flood gun or correcting the shift always demands a reference and frequently it is a strenuous task to find an appropriate one [62]. Despite years of intensive efforts, there is now a wealth of experimental evidence which shows that the chemistry of the silver-oxygen system is not well understood, as the system can be continuously varied with the handling conditions (*i.e.*, the BE of an oxide does not uniquely determine the composition) [63, 64].

Thinking back to the pure Ag system previously discussed, the peaks for mesoscopic Ag⁰ from $d_m \sim 420$ to ~ 42 nm centred from 367.72 to 367.86 eV are reasonably close to the bulk Ag $3d$ peak which is sufficient to show that the XPS core level shifts can be influenced by the particle size and shape. Here, the Ag $3d_{5/2}$ core level shift with increasing oxidation for both mesoscopic and microscopic Ag particles is illustrated in Figure 3.13. To achieve varying degrees of Ag oxidation, all the Ag particle samples discussed in **Section**

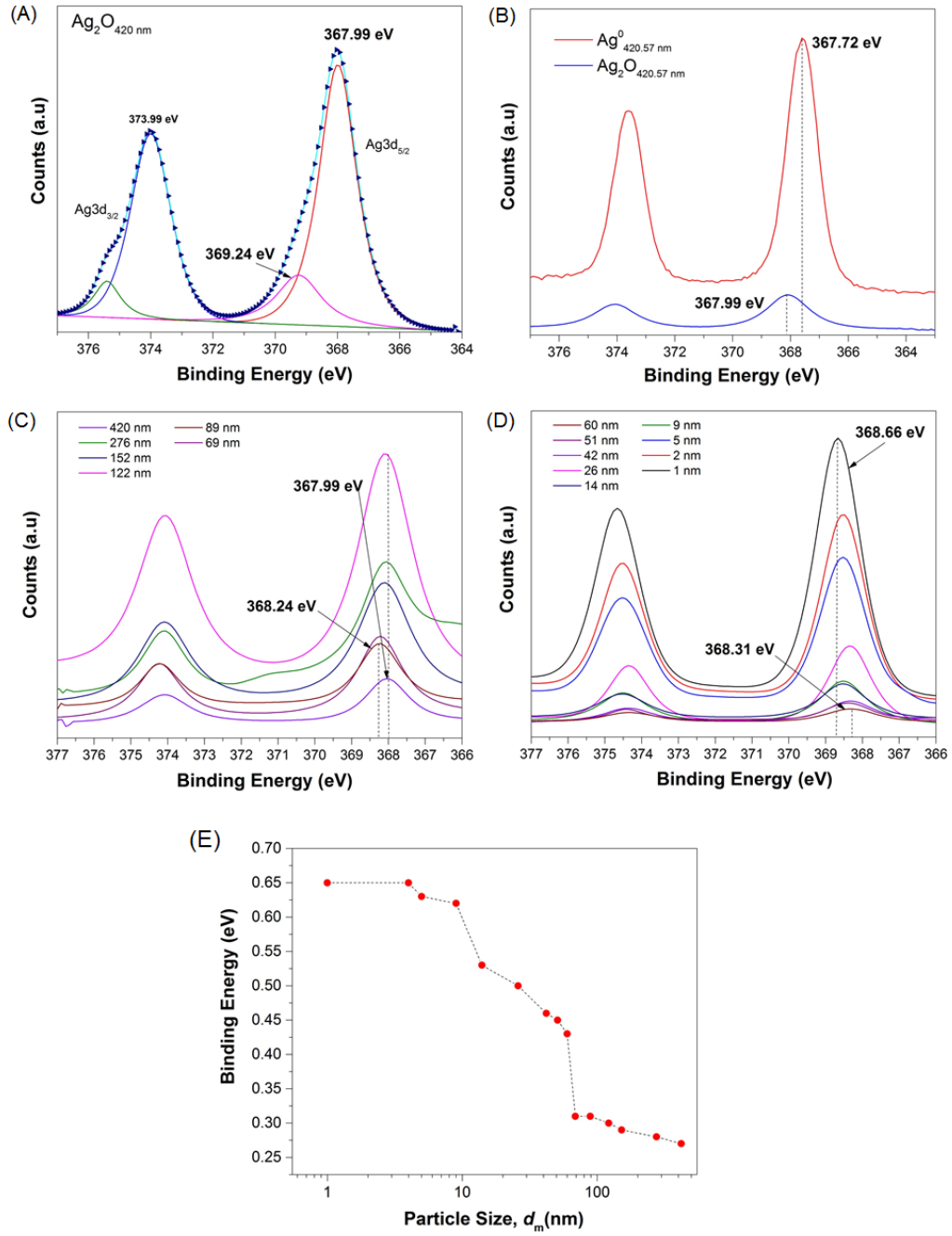


Figure 3.13: High resolution X-ray photoelectron spectrum (XPS) collection of (A) Ag3d spectra fitted with two components of higher aggregates oxidised Ag with (B) comparison of spectra for Ag₂O and pure Ag⁰ for $d_m \approx 420$ nm. The data of the oxidised Ag3d_{5/2} for both (C) mesoscopic and (D) microscopic particle domains with BE values of both summarised in (E).

3.2.1.4 were placed under oxygen flux at a reaction temperature of 424 K for 24 hours. These conditions should sufficiently oxidise the starting Ag nanoparticles, resulting in a partially oxidised phase of both Ag^0 particle and oxidised Ag as shown in Figure 3.13 (A). It is clear that the 420 nm particle peaks represent oxidised Ag as the sole oxidised phase considering the mildly oxidative conditions occurred at 424 K. For instance, the $\text{Ag}3d_{5/2}$ spectrum is fitted with two peaks; one fixed to the parameters for Ag^0 and the other centred at 369.23 eV with higher $\text{FWHM} = 1.67$ is clearly visible (Figure 3.13 (A)). The metallic contribution is relatively low ($\sim 19\%$) with respect to that of oxidised Ag state, showing the very low amount of remaining metallic Ag present. One can see that 81% of the system here corresponds to the oxidised Ag states and yields completely different characteristics as compared to the Ag^0 . The position of the $\text{Ag}3d_{5/2}$ peak is well agreed with previous assignments of Ag (I) in Ag_2O [65]. The presence of Ag_2O as the dominant oxidised phase of Ag is sensible in accounting the mild oxidative states of the system. This also indicates that the Ag particles will not easily oxidise in the presence of molecular O_2 at room temperature [66]. The central idea is that the BE characteristics of pure Ag^0 and oxidised Ag of similar size have different final and initial state effects as shown in Figure 3.13 (B). With the oxide present, the Ag samples showed a significant decrease in both the $C1s$ peak and the Ag $3d$ peak intensities, indicating that the characteristics of oxidised Ag state would have relatively significant difference from the pure ones. Concomitantly, the $\text{Ag}3d_{5/2}$ level shifts to higher BE with oxidation. The previous statements can also be recast in terms of oxidation state where the charge transfer of the additional screening of the holes state in Ag surrounded by oxide is due to the atomic relaxation, or the reduced final state charging effect that leads the system to undergo the changes. Specifically for mesoscopic and microscopic oxidised Ag particles d_m of ~ 420 , ~ 276 , ~ 152 , ~ 122 , ~ 89 , ~ 69 , ~ 60 , ~ 51 , ~ 42 , ~ 26 , ~ 14 , ~ 9 , ~ 5 , ~ 4 and ~ 1 nm, core level shifts of $+0.27$, $+0.28$, $+0.29$, $+0.30$, $+0.31$, $+0.31$, $+0.43$, $+0.45$, $+0.46$, $+0.50$, $+0.53$, $+0.62$, $+0.63$, $+0.65$, and $+0.65$ eV can be observed with respect to the $3d_{5/2}$ level of pure Ag particle system from Figure 3.13 (C and D) are summarised as shown in Figure 3.13 (E). These

confirmed that higher oxidation rates occur from the huge shifting of the *BE* peak from 368.03 to 368.66 eV as the oxidised Ag particle size is reduced from ~ 420 to ~ 1 nm.

To obtain more information on the oxidised-Ag states, the corresponding *O1s* core level spectrum is observed to consist of one single main component of lattice oxygen at a high *BE* of 531.70 to 532.30 eV which can be related to the metal-OH bonds of Ag particles as shown in Figure 3.14 (A and B) [67, 68]. For ultra-fine Ag nanoparticles ($d_m \leq 4$ nm), the oxygen component is shifted towards a higher *BE* that is usually assigned to absorbed oxygen and O-C=O bonds [68, 69]. The same kind of analysis fitting is applied to the *O1s* signal using the same FWHM and a lines shapes as for $\text{Ag}3d_{5/2}$. The oxidised Ag particle peak intensity are increased from d_m of ~ 420 , ~ 276 , ~ 152 , ~ 122 , ~ 89 , ~ 69 , ~ 60 , ~ 51 , ~ 42 , ~ 26 , ~ 14 , ~ 9 , ~ 5 , ~ 4 to ~ 1 nm with *BE* contributions at 531.93, 532.13, 532.21, 532.25, 532.36, 532.48, 532.69, 532.70, 532.76, 532.79, 532.84, 532.87, 533.10, 533.11 and 533.20 eV indicating that Ag-OH bonds might contribute to the spectra as the Ag particle sizes decreases as shown in Figure 3.14 (E). The *O1s* spectrum of Ag_2O samples is shown in Figure 3.14 (C). The peak at 530.79 eV with a FWHM is 1.43 eV of again consistent with Ag_2O [65] and a higher *BE* contribution at 531.92 eV is clearly noticed. It is now apparent that the presence of a huge contribution of the oxygen bonded to Ag mesoscopic metal within this range is mainly due to the lattice oxygen present in oxidised Ag (Ag_2O). Therefore, these observations show that oxidised Ag nanoparticles shows different properties as compared to our pure Ag $3d$ metallic mesoscopic and microscopic samples. Considering the chemistry of pure Ag samples, these results can be the basis for differentiating Ag and its oxidised species. The experimental spectrum of pure Ag^0 and oxidised Ag samples in this work do not match well showing that the Ag samples used for the study of the SIMIT are substantially non-oxidised.

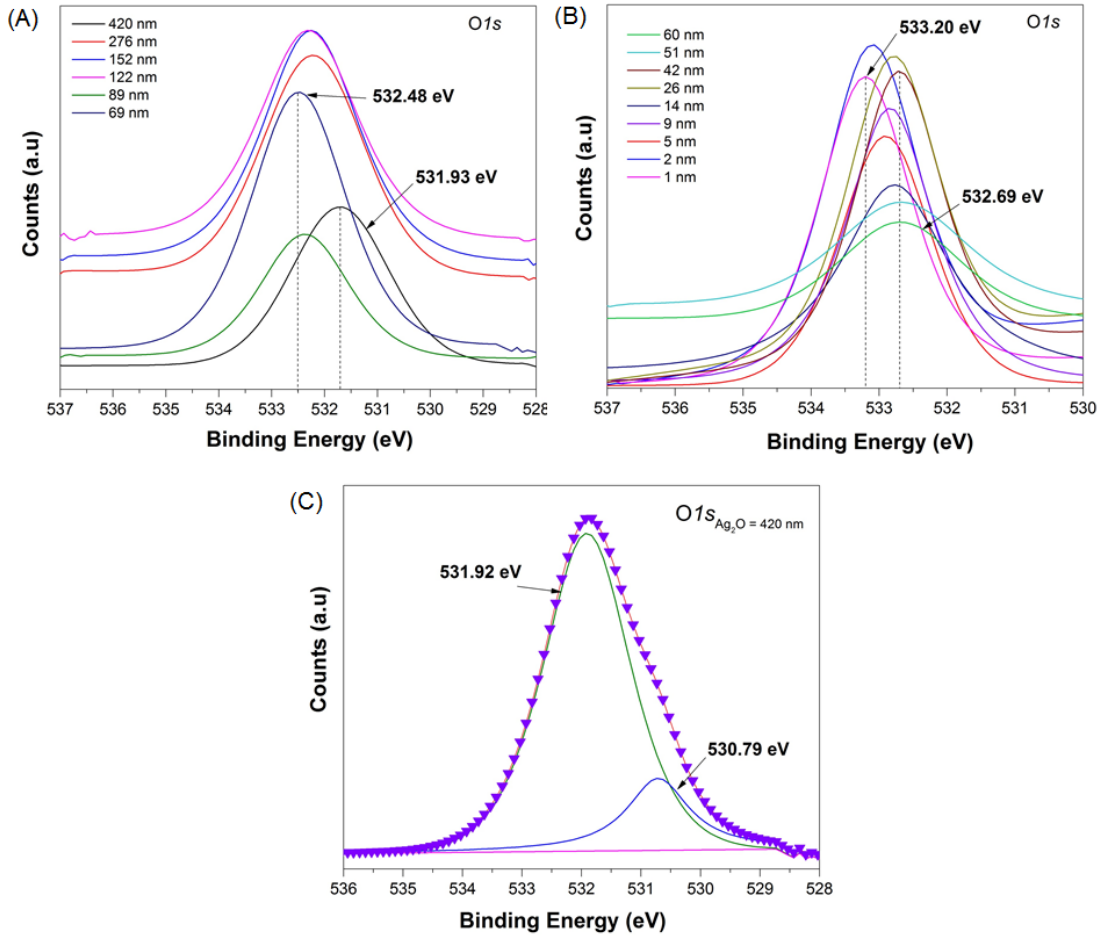


Figure 3.14: O 1s electron region of the XPS spectrum for both (A) mesoscopic and (B) microscopic Ag particles samples after oxidation at 424 K for 24 h. The original samples were pure Ag^0 used throughout the experiment previously. The corresponding corrected component fitted peak for the $d_m \approx 89.68$ nm sample (C) is shown as thin solid lines with the peak sum is shown as symbolised line.

3.3.1.2 PXRD

As seen in Figure 3.15, the structures of Ag particles seem to change from crystalline to partially crystalline as the size change from the mesoscopic to the microscopic regime. To verify the Ag nanocrystal structure changes for both regimes, Rietveld refinements on the PXRD data were done, using the space group of $Fm\bar{3}m$. Figure 3.15 represents the differences of representatives PXRD profile after a final cycle of refinement for ~ 89 and ~ 4 nm Ag particle samples, representing two different size regimes. Both ~ 89 nm and ~ 4 nm

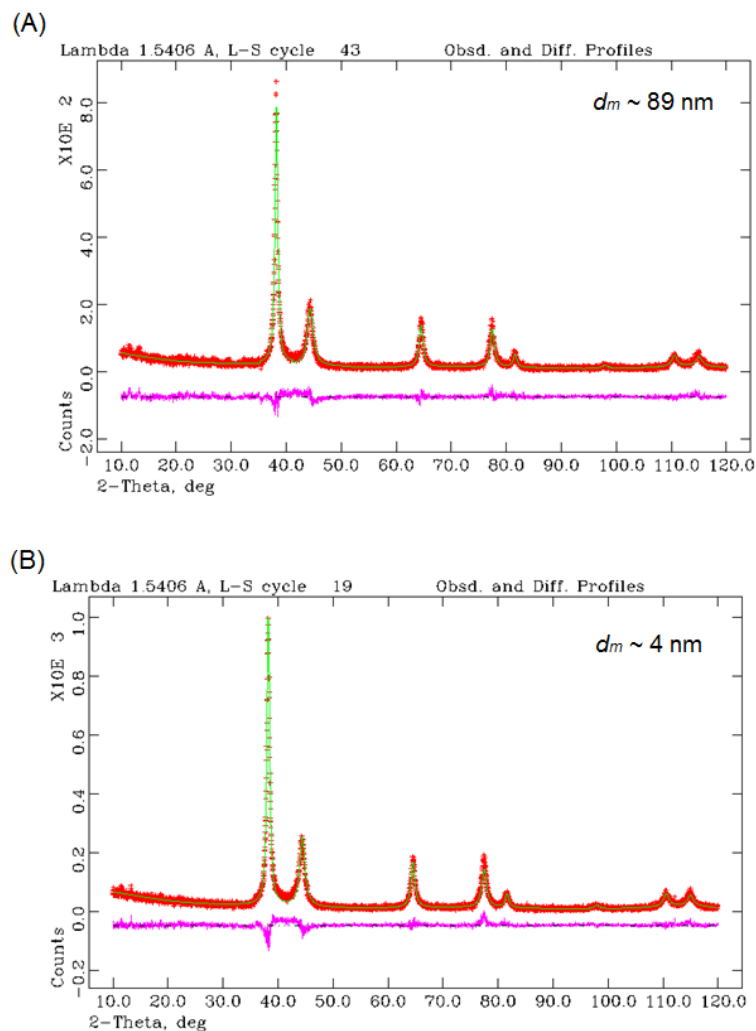


Figure 3.15: The two patterns of particulate size of ~ 89 nm (B) and ~ 4 nm (C) were fitted using the pure phase of Ag bulk as a reference. The green line (in B and C) indicates the calculated fit with the insignificant difference between the calculated and observed pattern given in a pink line below. The peak match is significant as enclosed by the blue tick overlapping with the pink line.

calculated Ag profiles (Figure 3.15 (A) and (B)) depict that they are perfectly matched with the reference profile of pure phase of Ag bulk, which is well supported by the values of $\chi^2 = 1.98$ and 2.05 , respectively. It shall be noted that the aim of the profile fitting process is to minimise χ^2 function [70]. An χ^2 value between 1 and 2 is considered excellent. In our case, the obtained χ^2 values should also affect from the factor of the Ag particles surrounding such as the type of the capping agent present. The higher the value, more interference present due to the interference in the crystallinity. We believe that the smaller the Ag particle size is, the more an amorphous layer of capping agent or oxidation will be present.

One can distinguish from the plot that the intensity ratio of (111) to (200) corresponding profile planes give 4.5 and 0.3 for ~ 89 and ~ 4 nm Ag samples, respectively. The intensity ratio value for the ~ 89 nm Ag sample is slightly higher than the standard value '4'. This implies that the mesoscopic Ag particles are abundant in the (111) orientation plane. This value also indicates that the microscopic Ag particles are still in (111) orientation but sharing another phase with another element. Thus, diffraction intensity of (111) lattice plane should be greatly enhanced compare to the other planes.

3.3.2 Observation on The Crystallinity

3.3.2.1 High Resolution Transmission Electron Microscopy (HRTEM)

In the present context, the aggregation of Ag particles could be facilitated by changes in the chemical environment of the Ag solution. For instance, decrease in the ionic strength (due to the decrease in the concentration of reagents and reactant temperatures) facilitates an increase of electrostatic barriers (electrostatic forces), which promotes particle separation. This particle's isolation led to the increase in the number of Ag nuclei and also contributed to the change in the structure of individual microscopic Ag. Thus, it is useful to investigate the common structure of microscopic particles mostly surrounded by partially crystalline and amorphous microscopic Ag particles. As shown in Figure 3.16 (A1),

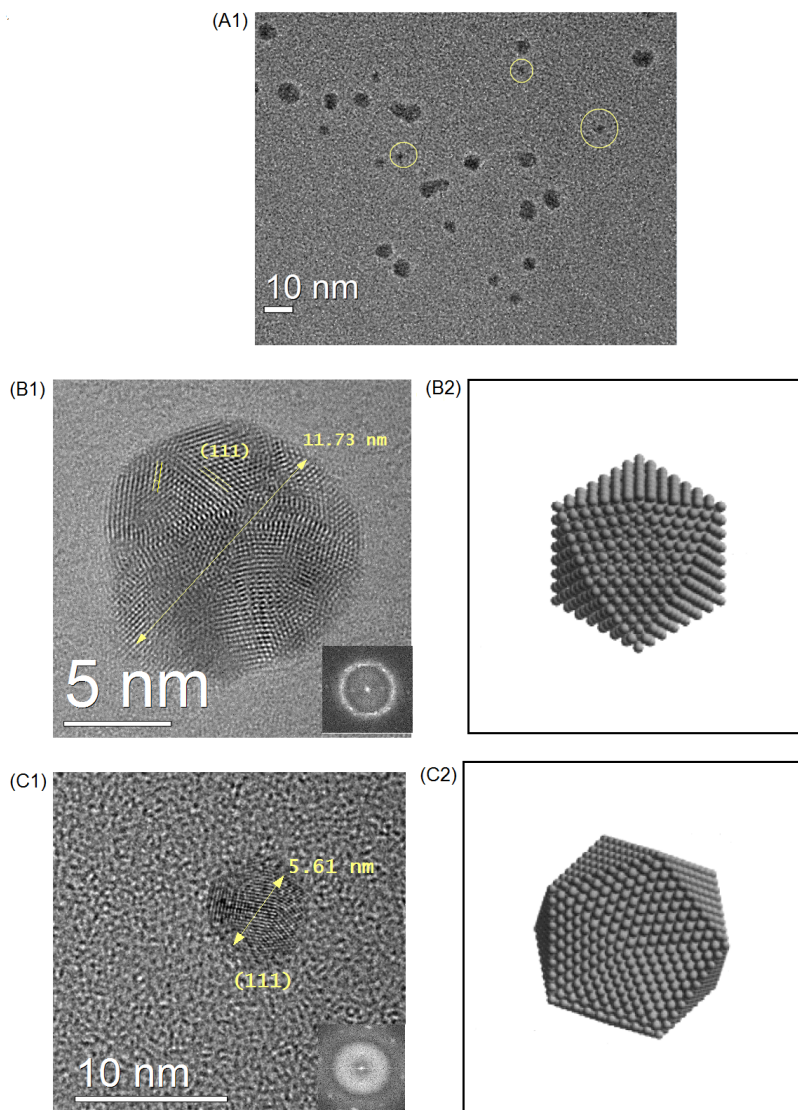


Figure 3.16: HRTEM images of microscopic Ag particles ($d_m \approx 5$ nm) prepared at the lowest reaction temperature (333 K) with 1.8 concentration ratio of DAXAD 19 to Ag precursor. (A1) The presence of several amorphous microscopic Ag is marked by the yellow circles pointing to the availability of small individual particles before coalescence. (B1 and C1) HRTEM images show microscopic Ag particles with average particle diameter of ~ 13 nm and the other with d_m of about ~ 7 nm; the reduced Fast Fourier Transform (FFT) are shown as insets in the bottom right of micrographs (B2 and C2). The electron diffraction pattern of pattern showing both exist as partially crystalline and amorphous regions.

microscopic Ag particles (≤ 3 nm) were dominantly observed to be scattered across most of the region marked by the yellow circles. Generally speaking, a large number of ultra-fine Ag nanoparticles were observed, thus it is difficult to classify this particulate Ag according to its structure due to unfavourable observation conditions, as well as the irregular atomic arrangements present. The larger particles observed in this sample had particle diameters of ~ 15 nm. This indicates that the LaMer growth ripening had increased the mean size of Ag particles (initially $d_m \leq 5$ nm) and narrowed the particle size distribution.

HRTEM micrographs of these partially crystalline and amorphous microscopic Ag with $d_m \approx 13$ and 6 nm are shown in Figure 3.16 (B1) and (C1) which confirm that all the particles were still icosahedrons after the LaMer growth occurred. The TEM images in Figure 3.16 (B1) and (C1) show the (111) orientation reflection for both smaller particles of ~ 13 and ~ 6 nm, respectively. From the lattice distance (0.19 nm) measured using Fast Fourier Transform (FFT) shown as an inset in the bottom right of the micrographs, fitted well to the simulation of the reciprocal lattice section at corresponding reflection. The FFT featured diffuse ring from the amorphous part and rings comprised of discrete reflections for typical microscopic particles part (Figure 3.16 (B1)). This FFT could be more or less shows their partial crystalline nature. One needs to be aware that the diffuse ring could also result from the amorphous background of the image. One can see uniform contrast from the amorphous part and alterations of contrast in the microscopic Ag particles part yielding from similar orientation of the grain size (111) in the range of few nanometers from the inset. This indicates that in microscopic particles regime, neither crystallisation of the amorphous nor grain growth of microscopic Ag particles has taken place as we have stopped the reaction before this stage. The segregation of constituents in microscopic particles should therefore be visible when analysing the FFT of the smaller microscopic particles (Figure 3.16 (C1)). Contrast changes are weak within the amorphous part, indicating the presence of an abundance of ultra-fine microscopic Ag particles ($d_m \leq 3$ nm) with similar composition to the crystallite ones.

From HRTEM images of individual microscopic Ag particles with $d_m \approx 13$ and 7 nm, the particles show almost no distortions from multiply twinned icosahedral shapes viewed along the 5-fold and 3-fold symmetry axis, respectively (Figure 3.16 (B2 and C2)). These are actually two typical views of icosahedra existing in this microscopic regime [23, 25, 26]. The dominance of Ag microscopic icosahedral particles is common in this regime since icosahedral MTPs are thermodynamically unstable based on its internal strain considerations and can be easily oxidised [71] which could also manifest as a higher interfacial electrical resistance.

3.4 Controlling the Total Volume of Ag Nanoparticles

3.4.1 Nanosight Particle Tracking Analysis (NPTA)

The effective total volume of Ag particles in the solution must be known for microwave loss measurements since the measurement is volumetric and thus highly sensitive to the differences in total sample volume [72]. Here, the NPTA enables the visualisation of the amount of Ag particles present in each of the Ag samples and provides an approximate total volume based on the recorded submicron particle counts.

In general, the 'effective' total volume of particles can be calculated from the total number of tracked particles and the sample concentration values as shown in Figure 3.17. Basically the NPTA technique identifies and tracks individual particles based on its attribution to the characteristic function of Brownian motion [73]. This observation is further confirmed by the tracked videos which reveal that, as we move up to mesoscopic size regime, the amount of mesoscopic Ag aggregates is reduced in order to balance the V_s . It is considered that different total particle population within mesoscopic systems leads to different electronic properties, as the effect of polarisation phenomenon would be far higher in a denser aggregate population. Thereby, a distinctive difference exists in the total number of particles for larger mesoscopic size population (0.06×10^6 particles/ml) in comparison to

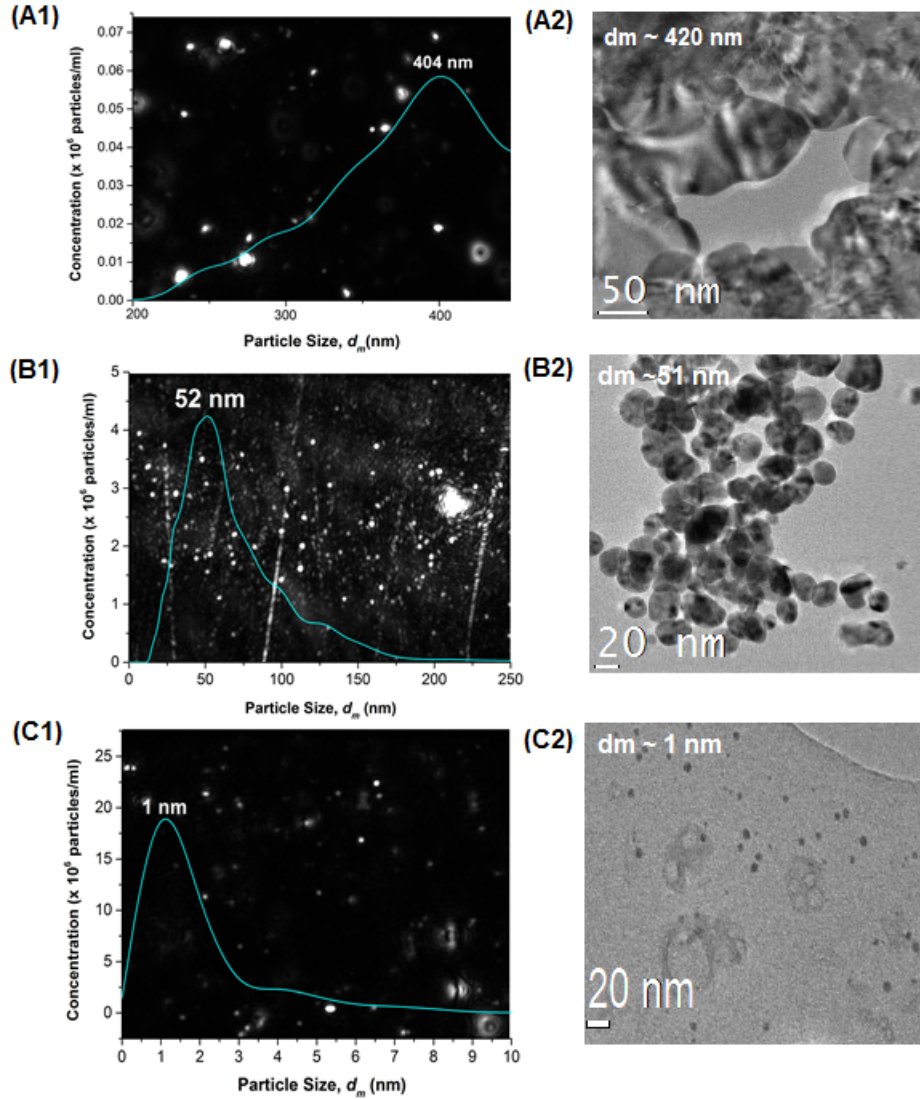


Figure 3.17: The total volume evaluation based on nanosight particle tracking analysis (NPTA) for various Ag particle sizes. NPTA measurements were slightly different from previous TEM (A2 to C2) observations for Ag sample size of d_m (A1) ~ 420 , (B1) ~ 51 and (C1) ~ 1 nm Ag particles with their corresponding NPTA video frames background. The total particle volume of each sample is fixed at $\sim 6.284 \times 10^{-3} \text{ cm}^3$ per 0.3 ml of solution by altering the total amount of Ag particles detected in each Ag particle solutions.

ultra-fine Ag microscopic sample of ~ 1 nm size (18×10^6 particles/ml). It shall be noted that, the local field corrections and uncertainty effects associated with the morphology of

the grain structures contributes to the overall uncertainty of the system which is assumed to be uniformly distributed to about 2.5% utmost based on the series of volumes measured at $\sim 75\%$ confidence level.

In this work, the total particle volume of each sample can not precisely controlled as the size of the Ag particles is broadly varied especially for mesoscopic samples where smaller particle size could also exist. Thus, the volume calculated here is based on the 'effective' total of individual Ag nanoparticles that the NPTA identified and tracked moving under Brownian motion depends on the movement of particle size. Figure 3.17 (A1 to C1) shows the size distribution of the particles as measured by the NPTA software (d_m vs. concentration) and its corresponding background video frames for three 0.2 ml Ag particle samples of d_m (A1) ~ 420 , (B1) ~ 51 and (C1) ~ 1 nm. Using this information, the total volume of each sample was kept constant at a value of $V_s \approx 6.284 \times 10^{-3} \pm 0.0015$ cm³ for each 0.2 ml sample studied using microwaves.

3.4.1.1 The Total Effective Sample Volume, V_s Dependency

Since microwave cavity perturbation measurement crucially depends on the effective total volume of the Ag particle samples that could give variation in the bandwidth change value, it is crucial to prove that the V_s chosen here is still in the acceptable range for the whole size range of Ag particles. This can ultimately determine the direction and strength of the V_s value in its random distribution system. Figure 3.18 shows representative results for mean bandwidth change, Δf_B as a function of the total effective volume, V_s for mesoscopic (~ 60 nm) and microscopic (~ 5 nm) Ag samples. This to confirm that Δf_B parameter is directly proportional to V_s and that Δf_B is a function of σ_{eff} , as expected which is taken during dielectric properties measurement of the Ag nanoparticles. Here, we found that the Δf_B of small spherical microscopic Ag particles of each total volume are treated dependently to increase with increasing V_s as shown in Figure 3.18 (A). The V_s of ~ 5 nm Ag particle samples in Figure 3.18 (A) were randomly chosen and each of the V_s is rolled

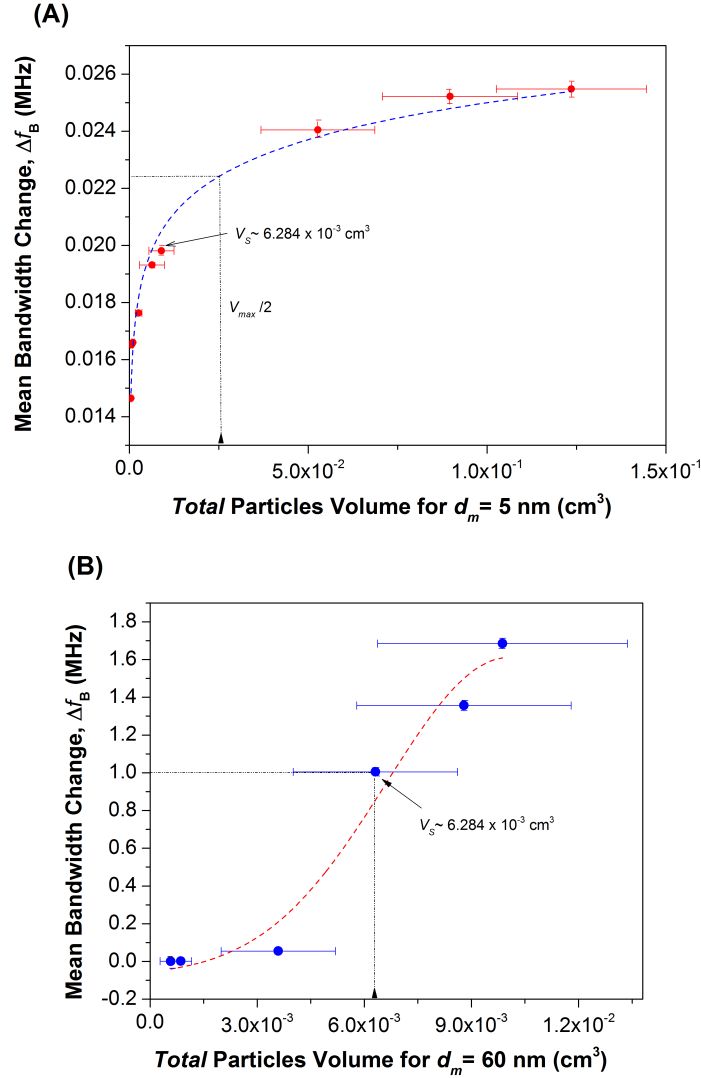


Figure 3.18: Change in resonant bandwidth for (A) Ag sample ($d_m \approx 5$ nm) and (B) $d_m \approx 60$ nm measured from microwave cavity resonator as a function of total particle volume measured by NPTA for eight and six different sample concentrations, respectively. The maximum volume value, V_{max} ($V_s \approx 6.284 \times 10^{-3} \pm 0.0015 \text{ cm}^3 < V_{max}$) represents the maximum volume constant is taken as the fixed total effective particles volume for the rest of conductivity microwave measurements discussed in **Chapter 4**. The dotted blue line (A) and (B) red line are non-linear curves. The error bars of the experimental data points represent the standard deviation for each different total volume determined from NPTA measurement of three different concentrations for each concentrations of the particles.

for 3 times which results in a non-linear fits along the calculated mean function of Δf_B . From these randomisations, the observing gradient change shows that the probability of having any V_s within this linear range (up to $\frac{V_{max}}{2}$) yields similar results behaviour. Since all V_s values for spherical microscopic regime exhibit similar behaviour across this range, all the Δf_B should also exhibits a similar trend of increasing values. *The Δf_B increases with increasing Ag particles volume, asymptotically approaching its maximum estimation of V_{max} .* Therefore, it is clear that the chosen V_s value ($V_s \approx 6.284 \times 10^{-3} \pm 0.0015 \text{ cm}^3$) projected the validity range of the quantitative extraction of V_s as specified in this work.

Figure 3.18 (B) shows Δf_B as a function of V_s for larger Ag aggregates ($d_m \approx 60 \text{ nm}$). A cubic polynomial trend best describes the relative role of the V_s , which is sensitive to the structure and morphology of the higher aggregate particles. The inflection point in V_s at $V_s \approx 6.284 \times 10^{-3} \pm 0.0015 \text{ cm}^3$ represent the $\sim 70\%$ confidence interval of the calculated mean Δf_B . It is further emphasised that for V_s ranging from 10^{-3} to 10^{-2} , particularly in this $d_m \approx 60 \text{ nm}$ system, there is a limit where the change in complex dielectric permittivity properties ϵ_{eff}^* would have an accuracy of $> 2\%$ which should be done at the volume range of 10^{-3} [25]. This can prove the control ambient experiment that we present to quantitatively specified the value of the V_s we run throughout the experiment.

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Chapter 4

Dielectric Response of Ag Particles : Results

The application of microwave electric field (E -field) has been identified as one of the potential techniques to probe the quantum SIMIT phenomenon since the microwave E -field can interrogate the electronic states of particles directly in terms of dielectric constant, ε . However, probing the Mott metal-insulator transition by microwave E -field typically requires robust and high E -field cavity methods. This chapter is focused on the analyses of the discrete energy band state changes from mesoscopic to microscopic size regimes that represent the size-dependent behaviour of the system. The probability on the existence of SIMIT in Ag particles based on the results of $D.C$ and $A.C$ measurements at $T = 294$ K is described in the **first section**. This is followed by a discussion on the observation of the SIMIT describes by the $A.C$ conductivity results for $T < 294$ K in the **second section**. Some of the well-established modelling theories that can be used to interpret the SIMIT are presented in the **final section** of this chapter.

4.1 The Dielectric Response of SIMIT at $T = 294$ K

4.1.1 Cavity Perturbation Dielectric Properties

In this work, microwave perturbation technique enables one to probe the unique phenomenon of quantum confinement effect of the SIMIT in Ag particle systems. Both mesoscopic and microscopic Ag particles are considered to serve as additives in the measurement which will augment the microwave absorption characteristics and allows one to effectively estimate the conductivity from the dielectric properties of the systems. In particular, a robust current electromagnetic cavity resonator used in this study is suitable for probing the dielectric properties especially for ultra-fine microscopic size due to its strong squeezing of the microwave E -field and is a modification version to the earlier design of microwave copper hairpin resonator reported by Edwards *et. al.* in 2002 [1]. The optimisation of the cavity resonator for dielectric measurement could give more reliable and better analytical results of the samples especially when dealing with dispersed particle system at room temperature ($T = 294$ K). The objective of this section is to achieve reliable results at 2.498 GHz using TM₀₁₀ mode followed by the analyses of frequency dependence of dielectric stored (ϵ_1) and dissipated (ϵ_2) energy characteristics of the particles for the observation of the SIMIT.

4.1.1.1 The Effect on The Quality (Q)-Factor

The 'cup and lid' type of microwave cavity resonator here is one of the cavities that can be used to determine the electromagnetic properties of metal nanoparticle sample. This method describes a simple and yet, an extremely sensitive assay to measure small volume of solutions. This sensitivity is crucially depends on the quality factor (Q) of cavity. Higher Q -value demonstrates higher accuracy of the measurement. This indicates by a narrower bandwidth of the transmission coefficient scan of cavity resonator. Hence, it is first necessary to study the effect on the Q -value when the cavity is filled with Ag particle samples. This is done to ensure that the sensitivity of the cavity resonator is still high during the

measurements. In practice, the introduction of a sample within the cavity hole is essentially have effect in lowering the overall Q -factor of the system. Using the measured results of TM_{010} mode for various sizes of Ag samples, the change of Q -factor is calculated based on the series of unloaded Q_0 and loaded Q_s sample insertion values as shown in Figure 4.1.

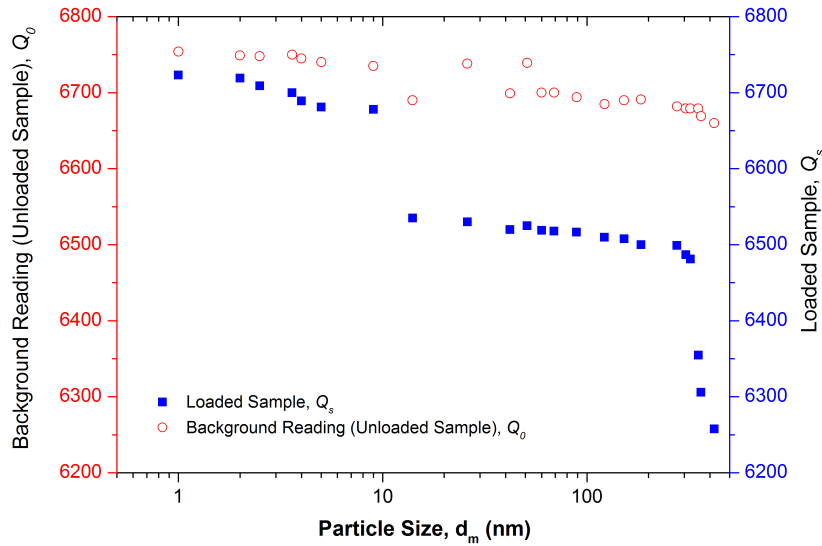


Figure 4.1: Variation of Q -factor for loaded Q_s and unloaded (background reading) Q_0 samples for a series of Ag particle samples under TM_{010} mode. The Q -factor remains remarkably high and is higher than 6200. This suggests that the measurements are considerably reliable in which there is an efficient coupling build up within the cavity during the test.

The Q -value remains remarkably high since the measured values are still above 6000 for all the units of measurement carried out consecutively at 294 K. The Q -factor is proved to be higher than 6000 where it is consider that almost all of the power is reflected from the cavity. This is attributed to the suppression and minimisation of the electromagnetic wave as well as energy losses that are caused by the penetration of electromagnetic field into Ag metal particle samples. In particular, the cavity resonator is weakly coupled as it appears that the holes size in the lid and bottom cup of the cavity are small enough to prevent

electromagnetic disturbance too much. The Q_s is still considerably high which is better for the purpose of this application since it suggests that accurate test can be reproduced for the whole series of measurements to a precision better than 0.1% as compared to the previous version of cavity resonators (hairpin resonator type) [1]. These results reflect the reliability and robustness of this cavity which can isolate both environmental and aging effects (stabilisation) that usually influenced the sensitivity of the oscillation power growth (resonance frequency) within the cavity. The measurement is also highly repeatable for a given cavity configuration at low temperatures ($T < 294$ K) as can be seen in **Section 4.2**.

4.1.1.2 Electric Dipole Absorption : Probing The Size-Dependent Electronic Conductivity

In microscopic regime, the power absorption of each small Ag particles is strongly governed by their morphological shape. Based on the conventional assumption described that, for microscopic particles are all of spherical shape in nature. It is clear that this assumption of 'particle morphology picture' is not valid for mesoscopic Ag particles as it is essentially contrary to the experimental evidence given in **Chapter 3** which shows the presence of that array of complex Ag MTP structures with bi-sector corner in this system. This is one of the effects of decreasing particle size that carry the dominant differences of mesoscopic and microscopic particles accordingly. Thus, the success of this microwave criterion shows the importance of the *total Ag particles volume* (morphology dependency) rather than the size distribution itself. The basic idea of this approach is, therefore, to keep the volume of the particles constant at a value of $V_s \approx 6.284 \times 10^{-3} \pm 0.0015 \text{ cm}^3$ for each 0.3 ml sample under examination. Furthermore, Ag particles in this system are well-dispersed with a low volume filling fraction given that $\varphi \leq 0.01$ within hexane host medium. This implies that the technique is intrinsically measuring the individual particles present in the solution where the differences of resulting dielectric properties are dependently induced by the particle element as the deciding factor. Clearly, this is the highlight of this non-invasive

microwave technique; that directly yields the dielectric properties of the inclusion element (Ag particles) and the outcome of the measurement is considered in form of 'effective' complex permittivity as a whole. On this sense, there is no need to apply a local field correction since the systems have been measured in a highly non-polar medium.

This cavity is one of the laboratory equipments that can highlights and observes the changes of the dielectric properties from electronic state itinerancy (when the energy gain becomes sufficient to overcome the site (single-particle) charging energy) to localisation across the range of Ag particle sizes. Figure 4.2 shows the changes of the transmitted resonance trace of $|S_{21}|^2$ (dB) as a function of resonance frequency (GHz) f , measured at approximately 294 K. The $|S_{21}|^2$ of hexane and the empty quartz tube shown in Figure 4.2 (A) have the characteristic peaks of $f_0 = 2.49825$ and 2.5829 GHz, respectively. Hence, the difference in the resonance response would be expected to arise only from the inclusion (Ag particles) in the solution as reported by Chen *et al.* [2]. The difference in complex frequency between hexane and Ag-filled tubes yields the 'effective' complex dielectric properties of the Ag particles. This validates our preference in choosing hexane as a medium for its remarkably low microwave absorption characteristic that does not affect dielectric measurements of the particles. We do not need to use the 'effective' medium theory to estimate the intrinsic permittivity in this context, rather we take 'effective' values for the particles which will certainly be lower than the intrinsic values due to the depolarisation of the small particles.

The changes in the resonant frequency and bandwidth are sensitively monitored *via* VNA where the echo response of the microwave pulse is generated from various signal responses of the particles, depending on the nature of the particle size. Interestingly, the resonant response traces show almost identical results with no significant trend changes on the broadening of the bandwidth for different particle diameters. However, this insignificant variability of the dielectric spectrum is commonly found when the measurements are

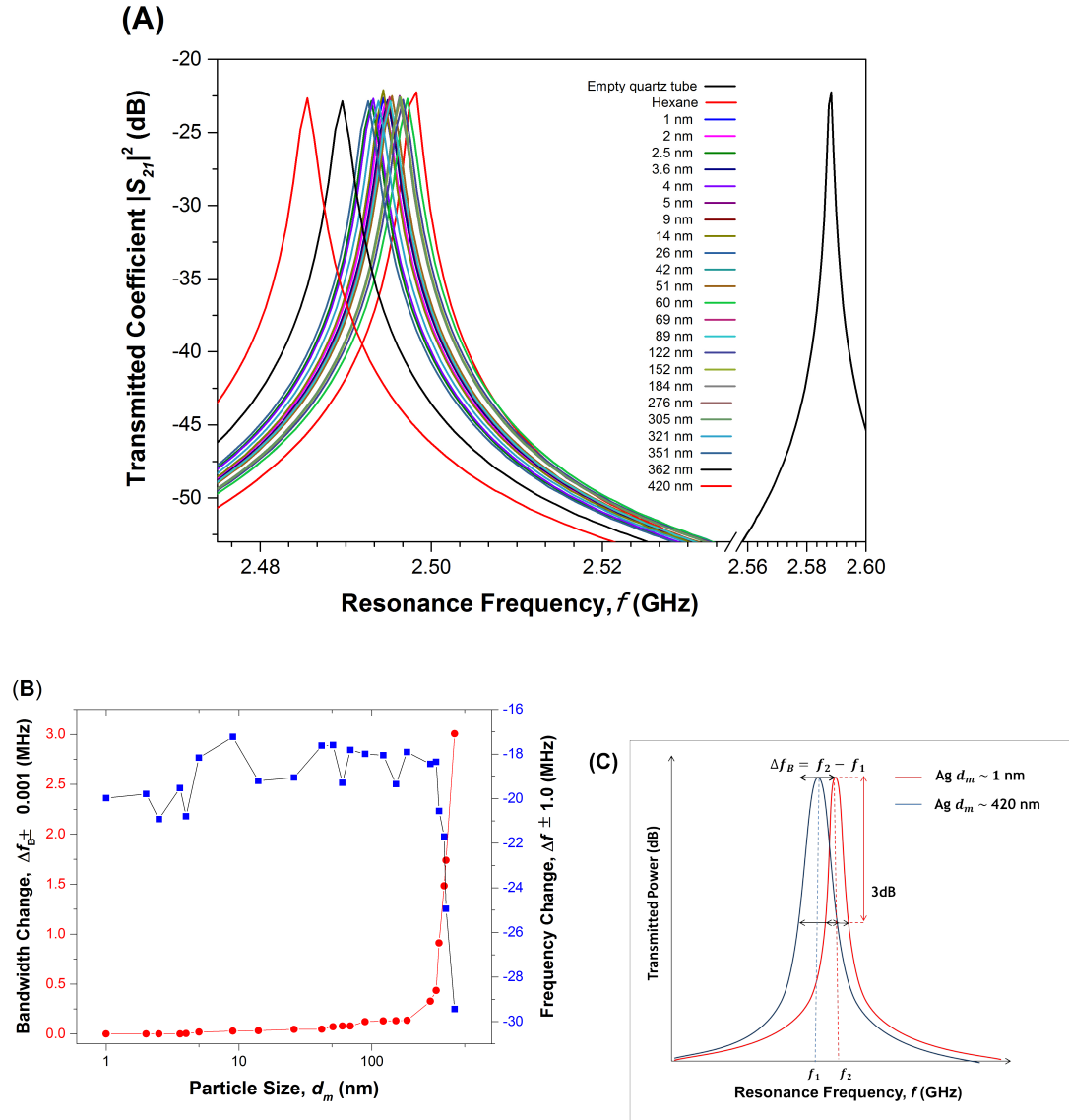


Figure 4.2: (A) Transmission characteristics of suspended single isolated Ag particle samples within a size range of 1 to 420 nm in terms of transmitted resonance intensities with the f separated by at least 10 MHz. The empty quartz and hexane filled tube results are provided as reference. The resonance frequency decreases with an increase in particle size. It shall be noted that the volume of each particle size system is equal to each other. (B) Traces value of frequency and broadening of bandwidth of the transmission coefficient scans for a selected calibration of all Ag particle samples at a frequency of 2.450 GHz which shifts to ~ 2.499 GHz in the TM_{010} mode. The recorded values showed that the calculated errors for both Δf and Δf_B are 1 MHz and 1 kHz, respectively. (C) Schematic illustration of the transmitted power responses of the TM_{010} mode for solution sample of different particle size. The difference in frequency shifting between the two Ag samples is slightly observed and only minor changes occur in the broadening of the bandwidth.

carried out in a solution medium with a high dispersity of the inclusion in the solution. Provided that an equal volume of Ag particles is used for all size range in the measurements, there will be no substantial difference between the transmitted resonance response which in turn, should facilitates the difference in dielectric properties. This typically result in less intense and slight broadened transmitted resonance response for higher aggregates of mesoscopic particles. Since it is anticipated that the microscopic Ag particles will dominant in these samples, it can be seen that there is a slight decrease in the broadening of resonance from -22.1 to -22.6 dB (Figure 4.2 (A)). The differences in the change of bandwidth and shift of frequency give the calculated value of errors of 1 MHz and 1 kHz, respectively, between microscopic and mesoscopic Ag systems as the size and morphological properties of the particles vary (Figure 4.2 (B)). Additional information can be gleaned from the shift to lower resonant frequency (2.498 to 2.485 GHz) with the maximum Δf_B is almost 13 MHz upon the insertion of the Ag particle sample since all the particles develop changes in electric dipole moment which is much prominent in this system. This can be explained in terms of the Coulumbic force of the particle's charge. The transmitted resonance frequency depends on the strength of Coulumbic force between the separated charges. Meanwhile, the strength of Coulumbic force and hence the charge separation distance depends on the size of the particles in the system. Therefore, a change in resonance frequency is represented by the contribution from the change of the particle size.

All of the transmitted resonance traces of the samples show slight changes in intensities and broadening of bandwidths, which indicates such well-intrinsic inter-particle separation dispersion that contributed to the similarities in the response for the real and imaginary parts of the dielectric properties. As we go back to the original idea, the particles are widely separated from each other that essentially makes them remain dispersed to enable a reasonable determination of dielectric changes regardless of their size. Therefore, it is worth to mentioned here that a slight broadening of the resonance bandwidth ($d > 184$ nm)

is due to the limited collisions between the particles and cavity wall which is reasonable to produce identical results for each sample especially when the V_s is constant. Recall, the equal particle volume filling factor φ plays an important role to determine quantitatively the size-dependence electronic structure of Ag colloids. Nevertheless, the intense local E -field enhancement on larger particle's surface ($184 \text{ nm} < d < 420 \text{ nm}$) particularly within bisector corner areas gives additional broadening response of the bandwidth (up to 13 MHz). As for size-dependent dielectric properties, the detuning from lower ($\sim 420 \text{ nm}$) to higher resonant frequency samples ($\sim 1 \text{ nm}$) is entirely due to the enhancement in the perturbation of the electromagnetic activity. In other words, an increase in resonant frequency is related to the decrease in stored energy of the perturbed cavity.

Therefore, the basic ideas here are - the induced dipole moment of dispersed Ag nanoparticle in the polarising field does cause slight changes to the fractional frequency and also exhibits minor resonance changes in broadening of the bandwidth. This information is further illustrates in Figure 4.2 (C). This transpires that the measurement of cavity has limitations. Having in mind that one of these limitations is that there are almost 40 times fewer particles that contribute to the dielectric response in the solution compared to the powder sample measurements reported in other literature studies[3, 4]. This suggests two important points here. First, the contributions of dispersed Ag particles in the transmitted resonance response is substantially less on this basis alone. Second, taking the consideration of the presence of individual particle characteristics across the samples suggests that the particle-particle interaction (l_{m-m}) will always be discontinuous, and therefore, it may well prove the impossibilities to observe a significant changes as found in solid sample. Both of these effects can be understood as the consequences of the assembly of isolated single Ag particles and also to the quantum confinement effect. This results in the absence of neighbouring particles and, thus the Ag particle samples possess very low conductivity over the distance, l_{m-m} of $\sim 185 \text{ nm}$ [5]. Therefore, the following approximations are necessary in analysing the preliminary changes of the effective metallic or insulating dielectric char-

acteristics for both mesoscopic and microscopic Ag particles, especially for this dispersed solution system:

1. A shift of resonance frequency to a higher frequency value (from mesoscopic to microscopic Ag particle regimes) corresponds to an increase in the real part of the dielectric response, $\varepsilon_{1,eff}$ of the sample.
2. A decrease in bandwidth value (from mesoscopic to microscopic Ag particle regimes) corresponds to a decrease in the imaginary part of the dielectric response, $\varepsilon_{2,eff}$ that is related to the particle structure (morphology and size) and inter-particle spacing, l_{m-m} changes.

The effective complex permittivity is given by:

$$\varepsilon_{eff}^* \approx \frac{-i\sigma_{eff}}{\omega\varepsilon_0} \quad (4.1)$$

where σ_{eff} is the effective microwave electrical conductivity of Ag, ω is the angular frequency and ε_0 is the permittivity of free space. The effective permittivity of metallic conductivity is theoretically constitution of $\varepsilon_{eff}^* \approx \varepsilon_{1,eff} - \frac{i\sigma_{eff}}{\omega\varepsilon_0}$ where ε_{eff}^* represents the overall conductivity of the elemental Ag and is assumed to be $\varepsilon_{eff}^* \approx 1 - \frac{i\sigma_{eff}}{\omega\varepsilon_0}$ over a wide range of particle diameter at fixed V_s [1, 6, 7]. On the experimental front, the particle conductivity is given by:

$$\sigma_{eff} \approx \omega\varepsilon_0\varepsilon_{2,eff} \quad (4.2)$$

where $\varepsilon_{2,eff}$ is used in calculating the microwave conductivity of the SIMIT's possibility. The important feature of SIMIT analysis is determined by the validity of their polarising mechanism which has been confirmed by experimental values of $\varepsilon_{2,eff}$. This effect shows that the decrease in the $\varepsilon_{2,eff}$ is due to the size-reduction that gives rise to the E_0 perturbation effect. For $d_m > 10$ nm, the $\varepsilon_{2,eff}$ of the system begins to screen out the E_0 which

is significantly enhanced at $d_m \geq 100$ nm. More importantly, the dissipation property is dependent on d_m , which means that the contribution of E_0 screening of a single ~ 420 nm mesoscopic Ag particle is 5 orders of magnitude higher than that of a particle of ~ 1 nm for an equal overall V_s . In mesoscopic regime (metallic), it is clear that the dissipated energy E_0 is dominant for all particle sizes. A combination of small grains yields larger particles which are highly conductive. Therefore, mesoscopic Ag particles will have high values of $\varepsilon_{2,eff}$ where the effect of grain boundaries are now gradually increase while the grains' effect becomes less significant as it is less conductive now and posses smaller values of $\varepsilon_{2,eff}$ accordingly.

Figure 4.3 shows the diminishment of calculated σ_{eff} values for a series of Ag particle samples having the following d_m : $\sim 420, \sim 362, \sim 351, \sim 321, \sim 305, \sim 276, \sim 276, \sim 184, \sim 152, \sim 122, \sim 89, \sim 69, \sim 60, \sim 51, \sim 42, \sim 26, \sim 14 \sim 9$ and ~ 5 nm where inter-particle interaction is considered to be negligible with the error value of 1 kHz in Δf_B . The solution samples are carefully sonicated before measurements are taken for the entire range of sizes at room temperature (approximately at $T = 294$ K). Here, the attenuation of σ_{eff} due to screening loss is dependent to the surface dispersity of particles ($\frac{d}{\rho} \ll 1$) and so, directly linear to $\varepsilon_{2,eff}\omega\varepsilon_0$. Therefore, any error in their extracted values of σ_{eff} is defined directly to the relative values of $\varepsilon_{2,eff}$. The estimate calculated value for $\sigma_{eff,min}$ is also indicated in Figure 4.3. At a particle size range of $25 < d_m \leq 420$ nm, the σ_{eff} gradually decreases by 2 orders of magnitude where the σ_{eff} is already high as much as $221.751 \text{ S.cm}^{-1}$ at $d_m \approx 420$

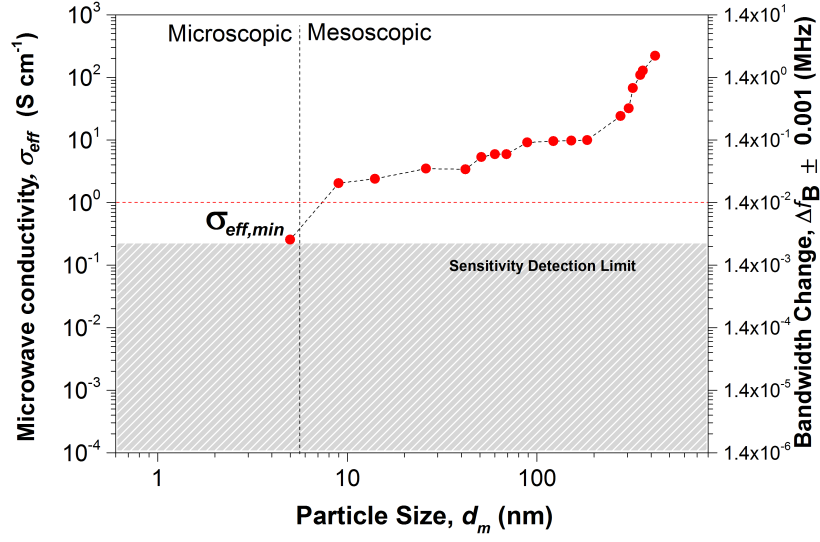


Figure 4.3: A logarithmic relationship of microwave conductivity obtained from microwave cavity resonator measurements for equal V_s as a function of various Ag particle mean diameter d_m by electric field at TM_{010} mode. There is a minimum effective conductivity $\sigma_{eff,min}$ which solely set based on the minimum absorption value of the $\varepsilon_{2,eff}$ (via $\sigma_{eff} \approx \varepsilon_{2,eff}\omega\varepsilon_0$) that can be accepted within a state of confidence limit with the calculated error of 1 kHz. Here, the σ_{eff} is the outcome of the measured bandwidth Δf_B is observed during the measurement.

nm for such a total volume. Here, the Ag particles samples are considered to retain their minimum metallic characteristics when the sample is dominated by higher microscopic particles ($5 \leq d_m \leq 25$ nm; $1.460 \leq \sigma_{eff} \leq 3.402$ S.cm⁻¹). Theoretically, in large particle limit, $d \gg \rho$ (macroscopic metal system), the $\varepsilon_{1,eff}$ is usually equal to the permittivity of the space and the $\varepsilon_{2,eff}$ is consider zero. Thus, for macroscopic Ag system (≥ 1000 nm), the σ_{eff} is caused totally from the collisions of electrons and the polarisation contribution is negligible [7]. However, in this small particle limit ($d \ll \rho$) the perturbation is gradually enhanced and the power of polarisation is dropped once this limit is reached. Therefore, decreasing the particle size from mesoscopic ($d_m = 420$ nm) to microscopic regime ($d \leq 10$ nm) will further increase the E_0 perturbation contribution on the surface of particles. The electrons on the particle surface tend to be partially polarised and perturbed at the same time when the E_0 is applied, $E_i = 3E_0/(\varepsilon_{eff}^* + 2)$ within the particle. In fact, when $d_m < \rho$,

it is expected that the electric dipole absorption will dominate the microscopic regime, since the E_0 is fully screened within this sparse particle solution.

It shall be noted that, the validity of the results below 5 nm has been crucially raised and the lack of criteria in deciding the validity of data fail since the measurements falls below the cavity's sensitivity limit. The lowest Δf_B that can reliably measured in these experiments is around 5 kHz as shown by the horizontal line at Δf_B of 5×10^{-3} MHz. This strongly indicates that there is no results can be plotted below this line as they are of values below the resolution limit of the cavity. For this microscopic regime ($d_m < 5$ nm), it is concluded that the SIMIT can not be fulfilled due to these reasons. All that can be observed is the σ_{eff} is steadily decreases as the d_m reduces. The results showed here is a continuous process, having only one sample with conductivity lies below the $\sigma_{eff,min}$. This system yields the minimum metallic conductivity at $d_m \sim 5$ nm when σ_{eff} is about ~ 0.255 S.cm⁻¹. In this case, it is no way to determine the distinction between metal and non-metals for this system. Hence, it can be deduced that the values of σ_{eff} that are less than 1 S.cm⁻¹ represent an opaque region, in which the conductivity is invalid. The experimental observation indicates here shows that the size-reduction effect leads to modification of dielectric permittivity of Ag particle systems that directly change their microwave conductivity values. As mentioned in **Subsubsection 2.2.2.8 (Chapter 2)**, the σ_{eff} values in *low conductivity in the small particle limit* are based on the changes in $\varepsilon_{2,eff}$ property (**Eq. 2.15**). Therefore, the σ_{eff} is directly dependent upon their bandwidth change, Δf_B as plotted along the secondary axis in Figure 4.3 (A)). The Δf_B results exhibit a difference of 2.956 MHz where the values drop significantly from 3.006 MHz to 11.5 Hz for ~ 420 and ~ 5 nm samples, respectively. The experimental results for both Δf_B and σ_{eff} have the same form which fully dependent on the prescription of the V_s . That means, both values will change if the V_s of sample changes.

Based on experimental evidence given, this type of cavity measured Δf_B accurately to

at least 5 part in 10^3 . This enables the determination of the σ_{eff} of individual particles for just above 5×10^{-3} MHz. As discussed earlier, the changes of Δf_B gives firmer consistency within *low conductivity in the small particle limit* as indicate by the calculated fractional change in the bandwidth $\Delta f_B/f_B$ plot using **Eq. 2.15 (Chapter 2)** as shown in Figure 4.4. It is evident that, both mesoscopic and microscopic Ag particles dominates within this limit where $\sigma_{eff} > 0.255 \text{ S.cm}^{-1}$ for $d_m > 5 \text{ nm}$. The $\Delta f_B/f_B$ ratio decreases linearly with a reduction in d_m down to a particle diameter of $\sim 5 \text{ nm}$. This implies that both mesoscopic ($\varepsilon_{2,eff} \gg \varepsilon_{1,eff}$) and microscopic ($\varepsilon_{2,eff} \ll \varepsilon_{1,eff}$) Ag particles possess low conductivity at the small particle limit ($\varepsilon_{2,eff} \gg \varepsilon_{1,eff}$). The values are subjected to an experimental error of $\pm 2 \%$ due to the large uncertainties in the volume fractions which propagate in the overall experimental uncertainty when extracting the representative values of $\Delta f_B/f_B$.

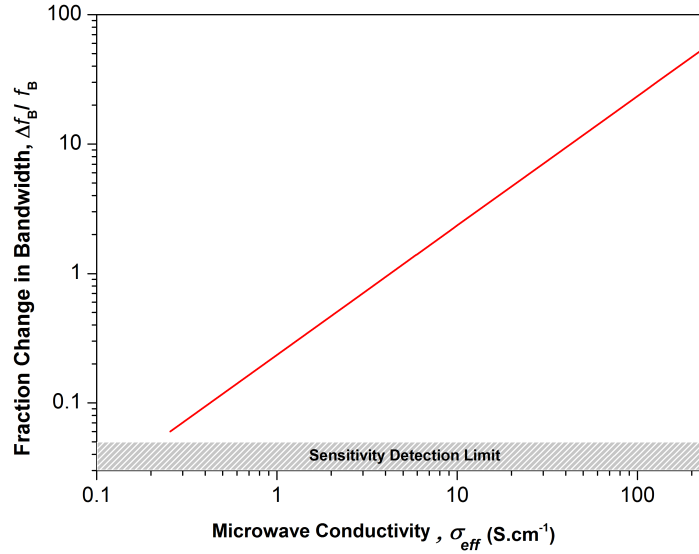


Figure 4.4: The variation in the calculated experimental fractional change in bandwidth, $\Delta f_B/f_B$ as a function of microwave conductivity (S.cm^{-1}) in logarithmic scale using TM_{010} mode at 294 K. Given that most of the bandwidth contribution lies in the low conductivity in the small particle limit, $\frac{\Delta f_B}{f_B} \approx \alpha Q \varepsilon_{2,eff}$ with sensitivity detection limit of the resonator shown in the plot.

4.1.2 Kubo Gap Characteristics

The development of the insulating phase with decreasing particle size is a captivating area to explore [8]. For metal particles, the opening of a gap with decreasing diameter, d_m has been predicted extensively based on the Kubo effect (quantum-size effect, QSE). Looking at the behavior of QSE as a function of d_m , it can be seen that the experimental data usually show the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap, which is much smaller than that predicted by the QSE. Such a difference is expected since the SIMIT of the Ag system occurs at small microscopic particle sizes. For instance, the individual Ag nanoparticles having a particle size of ~ 3 nm that are fragmented to roughly 1000 Ag atoms, would have a Kubo gap, δ_K of ~ 5 -10 meV [9]. In this case, the optical band gap of the ~ 4 nm Ag nanoparticles correlates well with the theoretical result, in which the band gap value is ~ 2.65 meV. Therefore, QSE is evaluated based on the following formula:

$$\delta_K = \frac{4E_f}{3n} \quad (4.3)$$

The formula above shows the relationship between the number of atoms in the particles, n and correlates directly to the radius of the particles, r [10, 11]. It can be seen from Table 4.1 that as the system deepens into the microscopic size regime, the theoretical value of δ_K decreases from the metallic phase, *i.e.* 5.09×10^{-8} meV ($d_m \approx 420$ nm) towards the non-metallic phase with a value larger than 0.38 meV (≤ 10 nm) across the possible SIMIT. The theoretical value of δ_K is 3.12 meV, for a particle size of ~ 4 nm, in which the onset of the insulating phase occurs, based on the microwave cavity measurements. However, the theoretical value of δ_K for the ~ 4 nm Ag nanoparticles should be metallic at $T = 294$ K where the $kT \approx 25$ meV. It shall be highlighted here that there will be a slight difference between the experimental and theoretical values since the experimental data takes into account the local field corrections associated with the solvent and stabilizers surrounding the Ag nanoparticles [8]. The δ_K in small microscopic Ag particles is comparable to kT at

$T < 294$ K, and thus, the systems exhibit non-metallic behaviour. This is proven by the microwave cavity measurements at lower room temperatures as shown in **Section 4.1.2**. Nevertheless, the values of the δ_K indicate the increase in the spacing between intra-band energy levels with a decrease in particle size, whereby the atomic s/p to d orbitals transform from a continuous broadened energy band and forms a discrete energy level separation.

Table 4.1: The theoretical Kubo Gap, δ_K calculated based on the Kubo gap equation, $\delta_K = \frac{4E_f}{3n}$ of six microscopic size particles carried out in this experiment.

Particle Size, d_m (nm)	Conductivity, σ_{eff} (S.cm ⁻¹)	Number of Atoms, n	Kubo Gap, δ_K (meV)
420	221.75	143,866,774	5.09×10^{-8}
10	2.21	19,418	0.38
9	2.04	14,155	0.52
5	1.46	2,427	3.12
4	0.26	1,242	5.93
2	7.88×10^{-3}	155	47.21
1	8.52×10^{-4}	19	377.60

4.1.3 Open-Ended Coaxial Probe and The SIMIT

The open-ended coaxial probe is particularly one of the transmission line techniques developed for the measurement of the electric properties of liquid samples. The determination of the dielectric permittivity made from this measurement is indeed more delicate and depends crucially on the contact between the liquid sample and the surface of the aperture probe. This technique includes in retrieving the complex permittivity of a sample from the measurement by relating it to the admittance properties, Y_s of the aperture surface and as a result, the measured reflection coefficient, ρ_s is obtained. The admittance properties of Ag particle sample, $Y_s(f, \epsilon)$ is a function of complex relative permittivity ϵ determined over a

whole frequency range f of interest. Noteworthy, this section is focused on the evaluation of the admittance data by comparing the sample aperture admittance, Y_s with corresponding air-terminated aperture admittance, $Y_{s,air}$ data. The sets of frequency dependent permittivity values for both $\varepsilon_{1,eff}$ and $\varepsilon_{2,eff}$ are then extracted from the analysis of Y data as discussed earlier in **Chapter 2 (Eq. 2.19)** :

$$\frac{\rho}{\rho_{air}} = \frac{1-Z_0 Y_s}{1+Z_0 Y_s} \cdot \frac{1+Z_0 Y_{s,air}}{1-Z_0 Y_{s,air}}$$

The electrochemical performance for both mesoscopic and microscopic Ag particles are shown in Figure 4.5 by the appearance of semicircular arcs over a wide frequency range of 0 - 800 kΩ in a form of complex impedance spectrum (Z' vs. Z'') in the Nyquist plots. To isolate the effect of the size-reduction from mesoscopic (Figure 4.5 (A and B)) to microscopic (Figure 4.5 (C)) states, it is first necessary to look at the dielectric relaxation trend in the frequency domain. It shall be noted that, the intercept of the semicircle on the Z' at high frequency region represents the bulk (grain boundary) resistance R_{gb} of higher aggregates of mesoscopic Ag. The diameter of the semicircle is analogous to the charge-transfer resistance R_{ct} and the grain resistance R_g . Hence, the appearance of a full semicircle data suggests the presence of both bulk (inter-granular) R_{gb} as well as individual (intra-granular), R_g+R_{ct} of the particles. The curvature at low frequencies is referring to the resistive-capacitance (RC) of the system which indicates gradual transition from 'particle stacking-domination' (mesoscopic) to 'particle diffusion-domination' (microscopic) responses over the RC frequency, ω_{RC} . The intercept of semicircles found at the lower frequency region is a direct measurement of R_{ct} caused by the discrete energy level of small Ag particles which associated by the reaction of active electron within the surface of the grains. The RC element ideally creates a semicircle towards high frequencies with its summit at ω_{RC} with the value should be less than 10 kΩ. Therefore, larger mesoscopic Ag particles exhibit smaller value of R_{ct} due to the higher transfer rate of electrons *via* inter-granular interaction [7, 12]. Full semicircle of experimental data is observed within mesoscopic regime ($d_m > 122$ nm) indicates major contribution of R_{gb} effect within the

particles. Interestingly, only mesoscopic particles' data exhibit some depression degree at the Z' axis that is caused by the distribution of relaxation time. The depression of experimental semicircle's data is thus provide further evidence for polarisation system and contributes to a distribution of relaxation times. This behaviour in mesoscopic system can be linked to several factors, including grain boundary and atomic defect distribution.

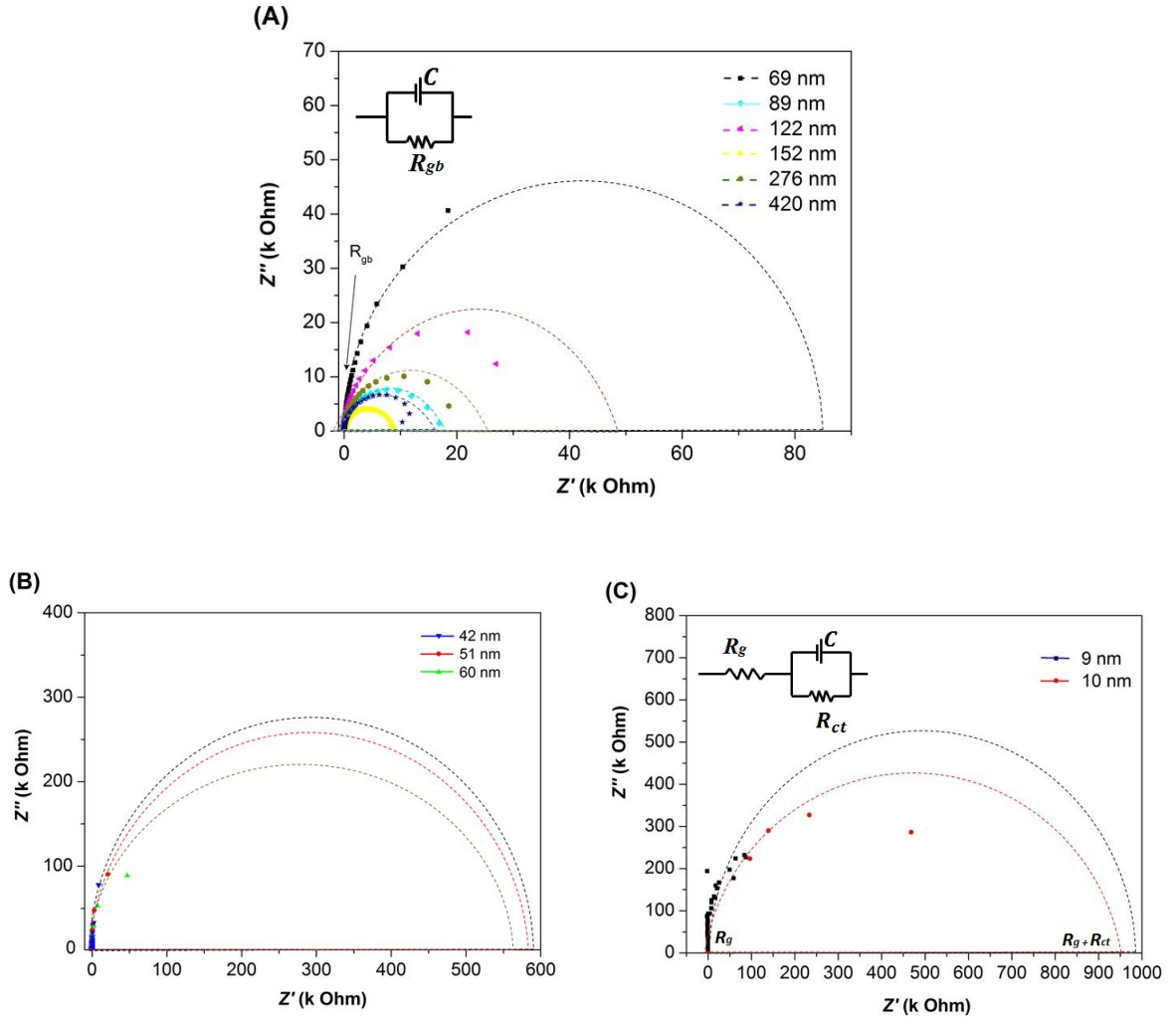


Figure 4.5: Nyquist spectrum, Z' vs. Z'' of (A and B) mesoscopic and (C) larger microscopic Ag particle domains using $|S_{11}|^2$ transmission signal line with grain boundary, grain and charge transfer resistance, R_{gb} , R_g and R_{ct} criteria, respectively. The abrupt curves obtained from smaller Ag microscopic samples are not shown here since the irrelevant percentage measurement for smaller microscopic Ag particles is high when $d_m < 9$ nm. Insets show in (A and C) are the proposed equivalent electrical circuit of the systems.

A distribution of relaxation times and the capacitance, C indicates more accurately behaviour of the grain boundary and its interior grain conditions as well as the electrode processes [7]. It is clear that the R_{gb} value increases with decrease in the d_m and yet it changed into R_g . This shows the typical positive resistivity characteristics that is usually

found in a material that has a conductivity between that of an insulator. Smaller mesoscopic and microscopic Ag particles ($d_m \leq 60$ nm) appear to be absent from the second arc of experimental data (Figure 4.5 (B and C)). Therefore, the solid lines of the graph indicate the fitting to the semicircular response to distinguishing the difference in the R_{ct} values of each spectrum. It is also observed that with the decrease in d_m , the diameter of semicircle increases and most of the data disappeared representing an enlargement in the overall resistivity. The presence of a single arc with a substantial increase in its amplitude confirms the depolarisation mechanism that correspond to the electron isolation effect arising in the intra-granular boundary as the d_m decreases. Since the abrupt plots appear most when $d_m < 9$ nm, the assessment of the results is not considered due to the irrelevant data obtained. Such result is rather expected, since it is assumed that the first charge capacity is weakly redistributed by microscopic Ag particles. Thus, for particles with $d_m < 9$ nm possess to have low first charge capacity due to high R_{ct} caused by the reduction of d_m . Due to these effects, the C for both systems is therefore calculated based on this relation:

$$C = \frac{1}{\omega_{RC}R} \quad (4.4)$$

where ω_{RC} is the angular frequency at the maxima of the semicircle that is equal to $2\pi f_{RC}$. Table 4.2 shows the variation of C calculated from the Nyquist plots (using R_g and R_{gb} values) at different d_m .

Table 4.2: Grain boundary(R_{gb}), grain (R_g) and capacitance(C) of mesoscopic and microscopic Ag particles data taken from Nyquist plot.

Particle Size, d_m (nm)	Resistance, R (Ω)	Capacitance, C (nF)
420	9123.7	3.81×10^{-5}
276	15 756.5	2.299×10^{-5}
152	18 921.3	2.015×10^{-5}
89	48 927.6	8.997×10^{-4}
42	558 132.4	2.232×10^{-4}
10	950 932.6	2.804×10^{-3}
9	958 474.3	2.468×10^{-3}

Figure 4.6 shows the imaginary part of impedance Z'' with the corresponding f at different d_m . The peak position of Z'' determines the relaxation time and the space charge of the particles based on the equation derived from Debye expression, *i.e.*, Cole-Cole expression [6, 13] $\tau_0 = \frac{1}{\omega_0} = \frac{1}{2\pi f}$, where τ_0 and ω_0 represents the relaxation time and the characteristics angular frequency, respectively. The Z''_{peak} gradually shift to lower frequency with the decrease in d_m in which represents a relaxation loss behaviour as the particles changed to microscopic regime. On the other hand, another factor to be considered is the significant broadening of the peaks with increasing d_m indicates the existence of electrical processes within the larger particle size with distribution of relaxation time. These conditions may contribute from the presence of delocalised electron within microscopic particles and defect sites on mesoscopic particle surface structures. The observations on mesoscopic particles made here regarding the distribution of relaxation time due to the effect of particle surface defect, is accountable for electrical conduction by electrons hopping across the available localised sites in the particles. The intensity of the peaks shown to increase with the decrease in f and d_m . It shall be noted that, the mesoscopic particles' peak merge in the high frequency domain. These behaviours suggest the presence of space charge polarisation within microscopic particles (lower frequencies) and disappearance within mesoscopic

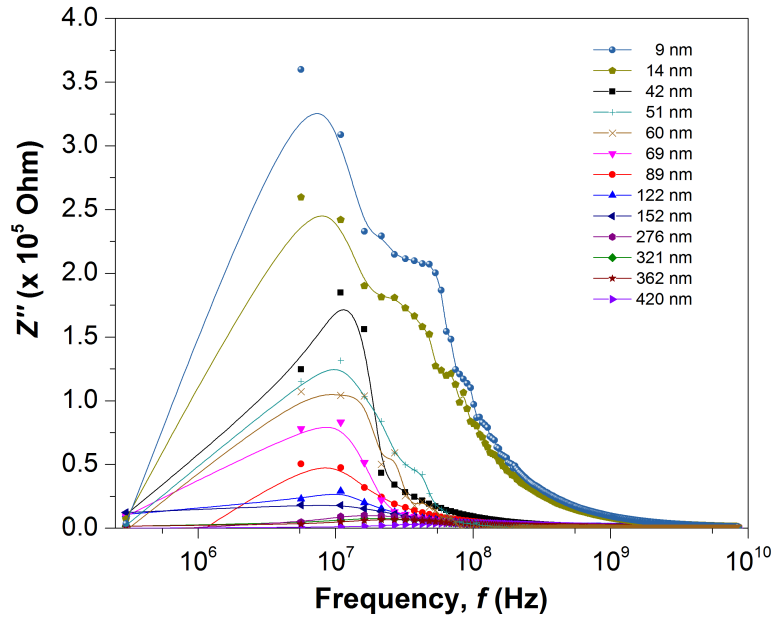


Figure 4.6: The imaginary part of impedance, Z'' as a function of frequency at various particle diameter d_m . The extent screening for $d_m < 9$ are too weak and hence they are intrinsically doubt to be considered.

particles (higher frequencies). The fast rising trend of the peaks where the fragments of the particles is assumed to be more than 60% of the volume fraction ($d_m \leq 14$ nm) is caused by the depolarisation mechanism associated with the de-localised conduction of electrons (detainment of space charge) as the effect of the intra-granular resistance becomes prominent [14]. The detainment of space charge is the result of the increase in barrier properties at lower frequencies of microscopic Ag particle grains [15] and become one of the responsible factor for the reduction of the electrical conduction at higher frequencies within mesoscopic particles regime. This illustrates the Mott-Hubbard correlation energy [16] where the charge fluctuations within the microscopic Ag atom is eventually suppressed and gradually indicates the opening of insulating phase system.

The related frequency dependence of dielectric constants, $\varepsilon_{1,eff}$ at various d_m is shown in Figure 4.7. It is observed that the $\varepsilon_{1,eff}$ gradually increase as the d_m is decreased. The emergence of these flat lines for larger mesoscopic particles ($51 \leq d_m \leq 420$) at higher frequency region indicates lower absorption energy with a value close to zero ($2.0 < \varepsilon_{1,eff} < 3.5$) due to the existence of heterogeneous geometry. On the other note, the trace of hexane solution shows a quite low $\varepsilon_{1,eff}$ at a value of 1.75 which is not unreasonably high. The $\varepsilon_{1,eff}$ of microscopic particles are literally accumulated at relatively low frequency showing a relaxation of polarisability originated from the limited mobility of permanent dipoles [17, 18]. Therefore, as the f increased, the dipoles of the particles will no longer be able to rotate fully and only progress with half cycle of reorientation. Hence, the oscillation start to lag under the E_0 and the $\varepsilon_{1,eff}$ reaches a limit value at high frequencies [17]. The large differences in the magnitude of $\varepsilon_{1,eff}$ to the particle size range of $42 \leq d_m \leq 1$ is caused by the intrinsic size effect of Ag particles. One can easily see the monotonous increase in $\varepsilon_{1,eff}$ at high frequencies on these curves as well as a distinguish step-like of half peak plot dispersion. The electrons within the particles is trapped by the transport through the material under E_0 which is known as space charges [17]. In the present context, the increase in the $\varepsilon_{1,eff}$ with decrease in d_m is due to the decay of the space charges accumulation that leads to high dielectric constant and significant frequency dispersion. These space charges disfigure the E_0 distribution and this uneven distribution is one of the main causes for the electric breakdown of linked particles and become more pronounced as the l_{m-m} increases. Therefore, a lower mesoscopic regime ($d_m \leq 42$ nm), describes the space charge decay distribution during de-polarisation in the Ag samples which develops at a frequency of ~ 1 GHz than that of the microscopic Ag clusters, $d_m < 10$ nm at 9 GHz. It shall be noted that, the space charge distribution in this case is associated with the conventional picture of the increase of one-electron energy gap δ that works as a key indicator in dictating the magnitude of the electrical conductivity within a particle. Itinerant electrons that are spatially localised because of the stringent disorder constraints in the lattice are essentially one of the reasons for this occurrence. Although the disorder in the lattice does not lead

by itself, it substantially facilitates the formation of this behaviour. Therefore, the increase in $\varepsilon_{1,eff}$ can be caused by the disorder which weakens the Coulomb interactions between the electrons that depart to another unit cell and leave behind the vacancy.

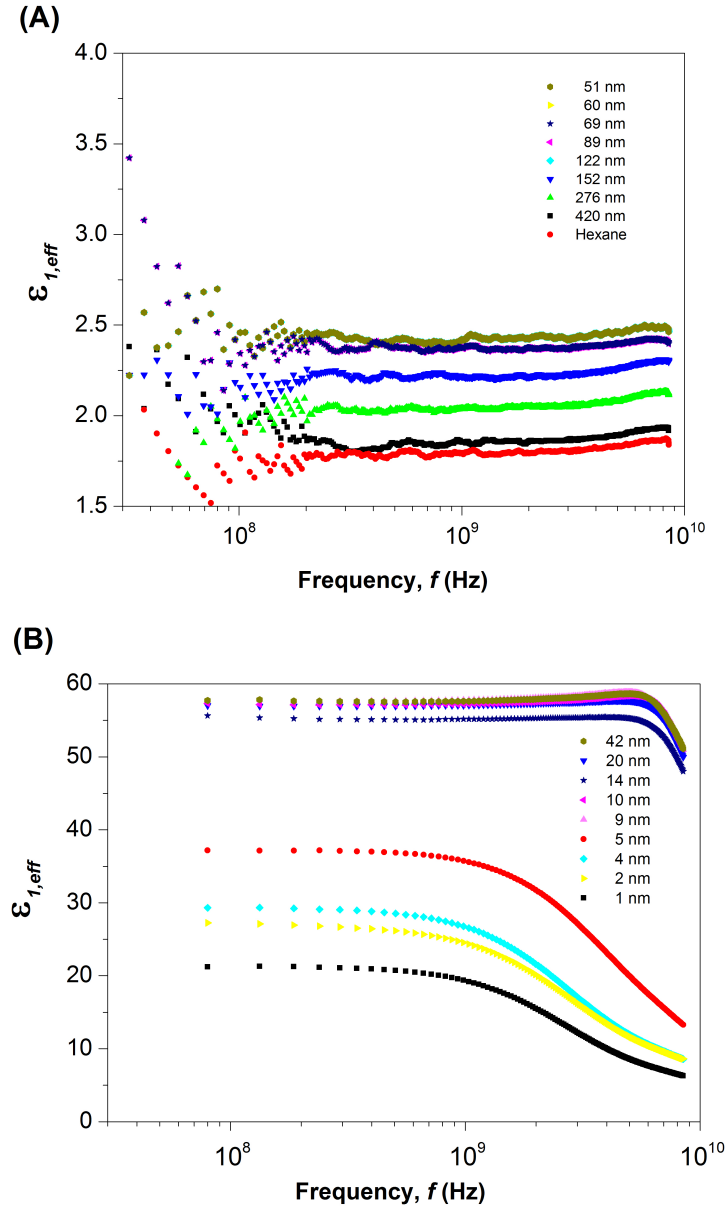


Figure 4.7: The plots of dielectric constants $\epsilon_{1,eff}$ as a function of log frequency f at various particle size range obtained from the admittance analysis, $Y_{s,eff}$. (A) Shows the change in permittivity $\epsilon_{1,eff}$ of mesoscopic and (B) microscopic Ag particles solution samples gives rise to the dielectric constant value of the particles. The high values are due to the presence of the Ag particles with the only trace showing hexane solution is quite low at a value of $\epsilon_{1,eff} = 1.75$.

The variation of the dielectric properties is further manifested from the observation of its dielectric loss $\epsilon_{2,eff}$ in a log function of frequency, f at various d_m as shown in Figure

4.8. As indicated in Figure 4.8 (A), one can see that at the end of the scans, the plots are left with a prominent characteristic of mesoscopic Ag peaks which emerge at higher amplitude of extended frequency above 10 GHz ($122 \leq d_m \leq 420$ nm). The peak frequency signifies the emergence of unique electronic properties in microscopic Ag particles based on the weak screening effect related to their electrical conduction [19]. This suggests that full peak could form above this frequency ($> 10^{10}$ Hz) and depict much more prominent $\varepsilon_{2,eff}$ values for larger mesoscopic Ag particles. The high value of $\varepsilon_{2,eff}$ at larger d_m and the huge reduction of $\varepsilon_{2,eff}$ with decrease in f down to 10^9 Hz indicate the effect of electrical conduction reduction with increase in space charge decay. This suggests the reduction in dielectric relaxation caused by the influence of the internal particle size effect. The fast reduction of $\varepsilon_{2,eff}$ values to low frequencies region indicates by an abrupt data (Figure 4.8 (B) is due to the de-polarisation mechanism of weak screening effect related to the perturbation enhancement process [19]. The effects of weak polarisation of electrons yields the finite probability of a *ground state configuration* where one valence electron is localised on the same surface site of Ag. This indicates that the discreteness of electronic energy levels could suppresses the space charge polarisation within small nanoparticles which gives awful scattering of the data [20, 21].

Hence, the effect of dielectric function in respect with the influence of the internal size effect explained in the form of the frequency dependence $A.C$ electrical conductivity is shown in Figure 4.9 based on the following relationship:

$$\sigma_{AC} = \frac{Y_L}{2\pi} \ln \frac{r_{outer}}{r_{inner}} \quad (4.5)$$

as discussed in **Subsubsection 2.2.2.3 (Chapter 2)**. This proves that the frequency dependent conductivity plots show three different regions that includes plateau at lower

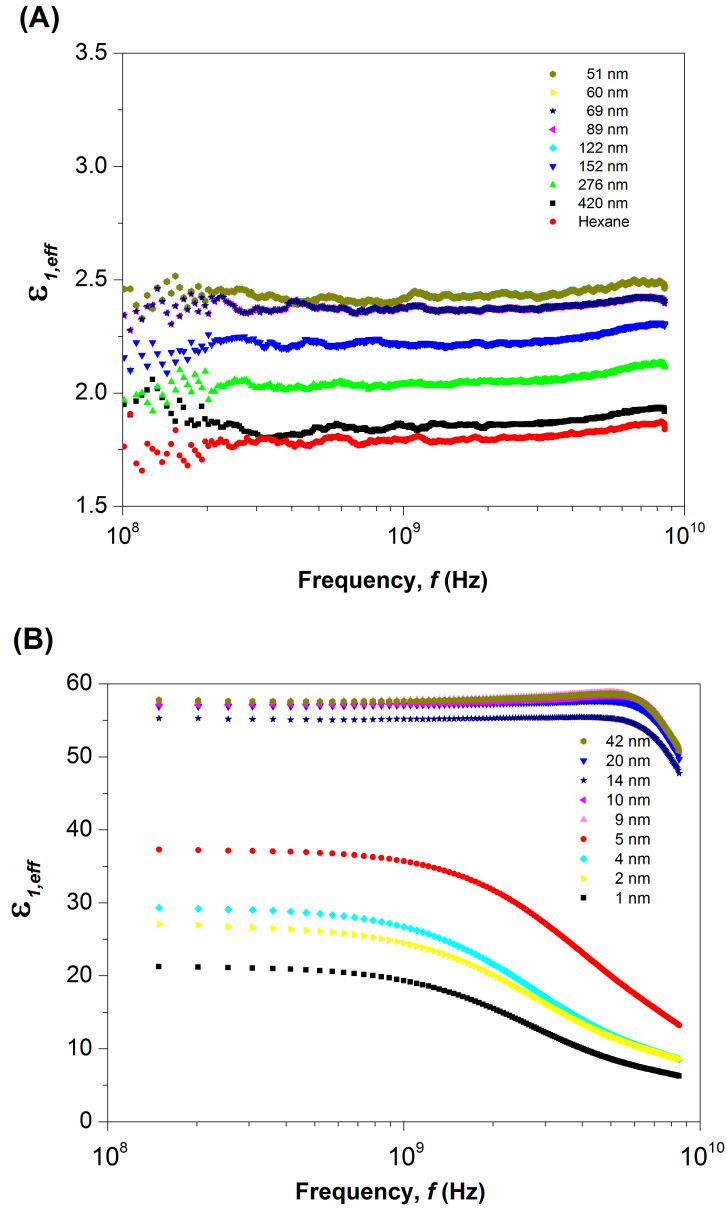


Figure 4.8: The imaginary part, $\epsilon_{2,eff}$ as a function of log frequency f for both (A) mesoscopic and (B) microscopic Ag particle domains obtained from the admittance measurements, $Y_{s,eff}$. The energy loss, $\epsilon_{2,eff}$ decreases with a decrease in particle size.

frequency, an intermediate conductivity dispersion and plateau at high frequencies (Figure 4.9 (A)). The result indicates that the σ_{AC} decreases with decreasing d_m . The variation

of σ_{AC} in the low frequency region originated from the polarisation effects of grains [22]. The accumulation of space charge take place at very low frequencies, hence the σ_{AC} drop occurs within mesoscopic regime. In the intermediate frequency region, the σ_{AC} patterns is found to be frequency-dependent and equivalent to σ_{DC} in high frequency region as the conductivity increases with f . It can be seen that the dispersion data appears to be a smooth increase with increasing f for all mesoscopic Ag samples with the most pronounced dispersive behaviour above 5×10^8 Hz and a high frequency plateau above 1×10^9 Hz. The appearance of conductivity tail ($f \approx 5 \times 10^8$ Hz) suggests the polarisation effect due to the co-effect of grains and grain boundaries [2, 23, 24]. The σ_{AC} at higher frequencies which also known as hopping frequency is very sensitive to any changes on the scattering of the electrons from the surface of the particles. Within this frequencies, the σ_{AC} gradually increases due to the delocalisation of electrons and thus, the particles shows the relaxation polarisability properties. The large abrupt data of σ_{AC} in microscopic samples is due to the fact that the leakage path of the disordered lattice cannot be evaluated with precision (Figure 4.9 (B)). This condition is attributed to the increase in the E -field of re-stored energies that results in the anomalous dispersion which is the characteristic of various non-conducting materials responds [25]. This condition can be attributed to an increase of the electrical resistance and capacitive phase between the particles as the number of inter-granular electron hopping diminishes as the d_m is reduced.

The plateau region at high frequency region of 2.50 GHz is a correspondence frequency independent conductivity known as $D.C$ conductivity that we are looking for where the transport of delocalised electrons under the E_0 is higher in this region. The size dependent of σ_{DC} for Ag particle samples is shown in the Figure 4.10. From Table 4.3, the gradient increases as the proportion of capacitive phase increases, just as in this RC network interpretation. Indeed, when the size is less than ~ 14 nm, in which the capacitive phase (finite

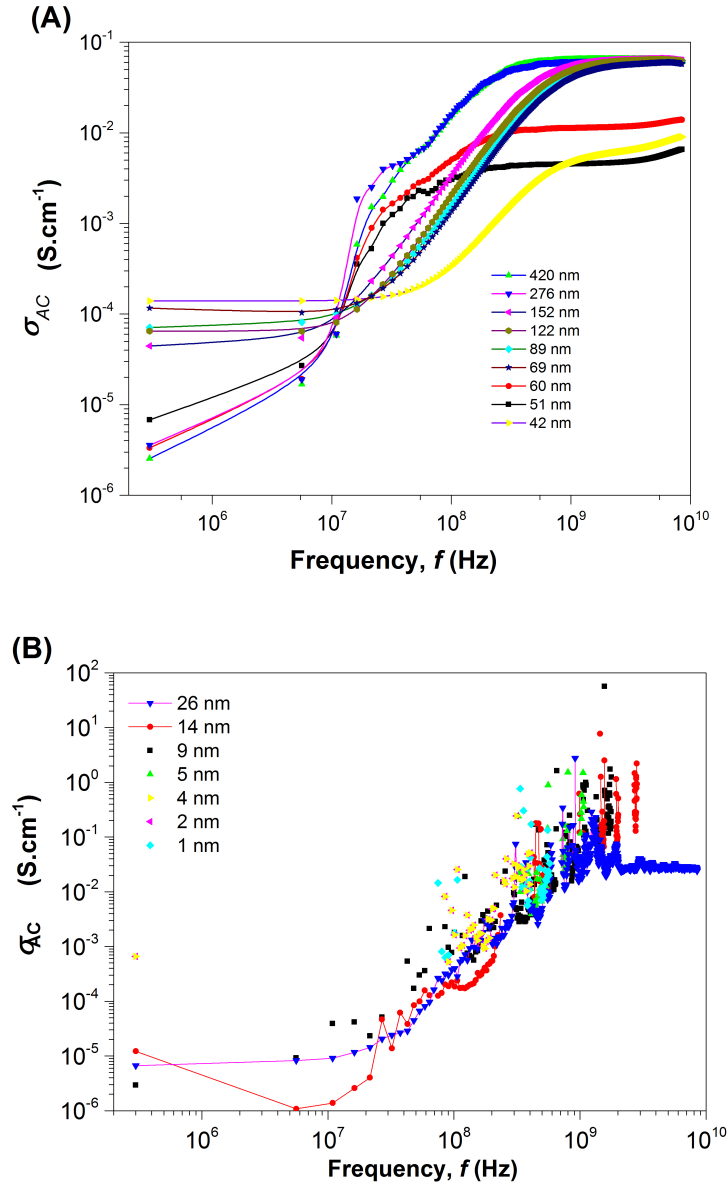


Figure 4.9: The effective *a.c* conductivity as a function of $\log f$ at various d_m of (A) mesoscopic and (B) microscopic Ag particles regimes. The f indicates $\omega/2\pi$ in cycles per second. It can be observed that the σ_{AC} values in the microscopic Ag domain is almost negligible due to the poor scattering of the data. The poor scattering is attributed to the leakage path owing to the generation of the depletion region and particle lattice breakdown.

individual elemental Ag) increases the gradient to 0.952 within the estimation - the role of the conductive particle is almost absent. The de-polarisation here deviates from the

predicted behaviour of the power law, even though the emergent behaviour of decreasing conductivity is present. In this regard, the application of anomalous power law is only valid for Ag systems with the d_m is above 14 nm.

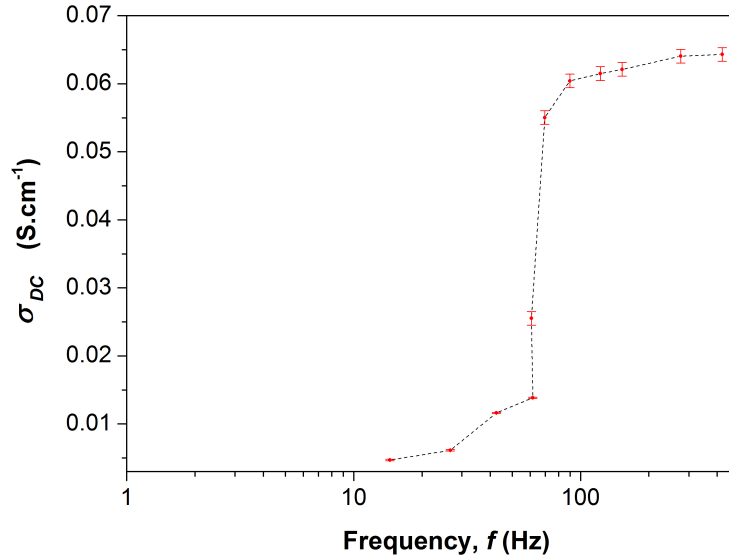


Figure 4.10: The size-dependence of *D.C* conductivity for both mesoscopic and microscopic Ag particle systems at 2.50 GHz. It shall be noted that the data are unacceptable for particles smaller than 14 nm.

Table 4.3: Gradient in the anomalous power law dispersion region of $\sigma_{2,eff}$ for different mean particle sizes, d_m as the Ag particle-particle distance is increased and transits suddenly into the non-metallic state.

d_m (nm)	89	69	60	51	42	26	14
Gradient	0.648	0.659	0.662	0.928	0.939	0.948	0.952

4.1.4 Critical Summary

The dielectric permittivity of Ag particles depends on the internal size effect. Needless to say, the dielectric permittivity of macroscopic (bulk) Ag prove to be changed as the

internal size effect is include as the d_m becomes smaller than the electron mean path of the macroscopic ones. As we compared the calculations data of the internal size effect between cavity perturbation and broadband techniques, different values of results obtained depending on the equipment used and their calculations. The increase and decrease of the real and imaginary part of permittivity of Ag particles as the size-reduction effect take place is true. Hence, from the results we can say that the structure defects that is gradually developed as the d_m decreases contribute to the shallow level of electrons in the system. These defects enhance the trapping electron processes which make the electrons easily roaming around and act as conducting electrons under the E_0 . In other words, the size-reduction effect leads to the decrement in conductivity that results from a decrease in electron scattering rate on the particle surface and thus, decrease in $\varepsilon_{2,eff}$. This can be further explained by the dispersive behaviour of van der Waals forces. The thermal fluctuations between the mesoscopic particles induces the dipole moment in a close neighbouring particles. The minimisation energy results from this interaction increase the attraction of van der Waals forces. The two dipoles have a tendency to attract each other with a strong force since they possess the same resonance frequency. As the d_m decreases, the larger absorption cross sections form. The size-reduction effect broadens the absorption band within microscopic particles size and contributes to the absorption of E_0 . The absorption energy of the microscopic particles becomes stronger and therefore the dissipated energy becomes weaker.

4.1.5 Generalised Model Equations for Dielectric Mixtures from an Open-Ended Coaxial Probe Technique

4.1.5.1 Overview

Self-organisation of mesoscopic particles that mimic the bulk properties of a metal formed from the continuous interactions of microscopic particles is indeed unique in condensed matter physics. The ultra-fine Ag nanoparticles from the microscopic domain in their ground state condition (low nuclearity phase) having a much broader class of discrete molecular

eigenstates (localised electrons) exhibit a continuous decrease in electrical conduction which should be within a size range near the SIMIT. This work demonstrates that a continuous decrease in conductivity results from the effect of size-dependent particle systems at 294 K. In the so-called 'quasi-static limit', the effective electromagnetic characteristics of mixtures involves Ag particles inclusion and hexane as a medium facilitated the correspondence of a single 'effective' electrical property that represents the entirety of the system for both regimes.

The driving transport of this metal-insulator transition can be defined from the interpretation of the changes in the charge distribution that leads to the variation of measured dielectric properties of Ag inclusions under the application of E -field torque, $\vec{E}_0$. This is illustrated in Figure 4.11 where the alignment of the Ag inclusions with $\vec{E}_0$ is imperfect.

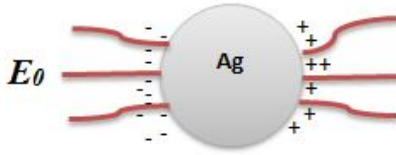


Figure 4.11: Schematic illustration of charge re-distribution resulting from the applied field, $\vec{E}_0$. An electric field causes the Ag mesoscale particles' positive and negative charges to separate slightly, making the particle effectively polar.

Here, when Ag inclusion is placed in the $\vec{E}_0$, the field pushes the positive charges in Ag atoms in the direction of the field whereas the negative charges are pushed in the opposite direction. In principle, this causes re-distribution of the charge on the surface of the Ag particles - the so-called *induced* dipoles. With either mesoscopic domain or microscopic domain behaviour particle, the re-distribution of charge caused by E_0 leads to the formation of a charge layer on the surface of each dielectric Ag atoms. These charge layers are known as the surface charge effect which also contribute to the changeover of the electronic levels

from quasi-continuous to discrete energy level separation that yield the effective microwave conductivity σ_{eff} .

The electron charges are not free to move in smaller metallic particles - rather, the charges act as electron surface charges and makes the particles produced restricted charge re-distribution. However, in mesoscopic metallic particles, which are found in metallic macroscopic conductor, each charge will be bound to a particle. In fact, they can be generally interpreted as bound charge where the re-distribution of the charge is known as polarisation process. The metallic particle usually stays polarised in this state. In this section, the different mixing rules are presented and fitted to the simulated re-normalised effective dielectric permittivity results. Surely, such behaviour is related to the internal size-reduction effect caused by the conduction of the surface electrons of the nanoparticles. The accuracy and relevance to the impending polarisation catastrophe of the fits are examined thoroughly and the results shown in this section are corresponds to the fact that the reduction of conductivity is model-dependent behaviour. Therefore, the SIMIT's point can not be predicted accurately from these models. Hence, the decrease in the model conductivity data reveals only the size-reduction effect of the particles.

4.1.5.2 The Clausius-Mossotti (CM) Polarisability

The frequency dependency of CM describes the measured difference of the experimental dielectric data of our samples consist of the ellipsoidal mesoscopic and spheroidal microscopic of Ag particle inclusions. The CM mixing rule considers that the whole set of inclusions are spherical shaped regardless the heterogeneity of each particle's morphology in the samples. The approximation value of the induced E_0 having φ constant (same value) is characterised by the permittivity of the matrix ε_h and sample ε_s . The frequency-dependent behaviour resides in the CM polarisability is given by **Eq. (2.37 in Chapter 2)** as:

$$\frac{\varepsilon_{eff} - \varepsilon_h}{\varepsilon_{eff} + 2\varepsilon_h} = f \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + 2\varepsilon_h} \quad (4.6)$$

Thus, the onset of electron localisation is then expanded by splitting the real, $\varepsilon_{1,K}$ and imaginary, $\varepsilon_{2,K}$ components of CM factor and this gives [26]:

$$\varepsilon_{K1,eff}(\omega) = \frac{\varepsilon_{s1}^2 + \varepsilon_{s2}^2 + \varepsilon_{s1} \cdot \varepsilon_{h1} - 2\varepsilon_{h1}^2 + \varepsilon_{h2}(\varepsilon_{s2} - 2\varepsilon_{s2})}{\varepsilon_{s1}^2 + \varepsilon_{s2}^2 + 4\varepsilon_{s1}\varepsilon_{h1} + 4\varepsilon_{h1}^2 + 4\varepsilon_{h2}(\varepsilon_{s2} + \varepsilon_{h2})} \quad (4.7)$$

$$\varepsilon_{K2,eff}(\omega) = \frac{3\varepsilon_{s2}\varepsilon_{h1} - 3\varepsilon_{s1}\varepsilon_{h2}}{\varepsilon_{s1}^2 + \varepsilon_{s2}^2 + 4\varepsilon_{s1}\varepsilon_{h1} + 4\varepsilon_{h1}^2 + 4\varepsilon_{h2}(\varepsilon_{s2} + \varepsilon_{h2})} \quad (4.8)$$

This relation is one of the effective means to investigate the changes of electrical conductivity behaviour of the size-induced Ag particles. Figure 4.12 shows the CM relation as a function of frequency, retrieving the dielectric permittivity at various d_m in hexane medium. This time, the real permittivity of Ag inclusions $\varepsilon_{K1,eff}$ (Figure 4.12 (A)) determines the polarisability behaviour for both mesoscopic and microscopic Ag particles. The real part $\varepsilon_{K1,eff}$ of CM factor exhibits both positive and negative regions due to the strong polarisation and perturbation forces centred at the collective surface grains, the so-called 'homogeneous' Ag inclusion distribution in the matrix that relates to the limitation of the electron mean free path [27]. The partial penetration of the field through the mesoscopic particles is described by higher value of $\varepsilon_{K1,eff}$. The size of microscopic particles is just off the mean free path, l that results in the loses of the phase coherence of the wave function which gives lower $\varepsilon_{K1,eff}$ of the CM factor. It is obvious that the free electron charges in

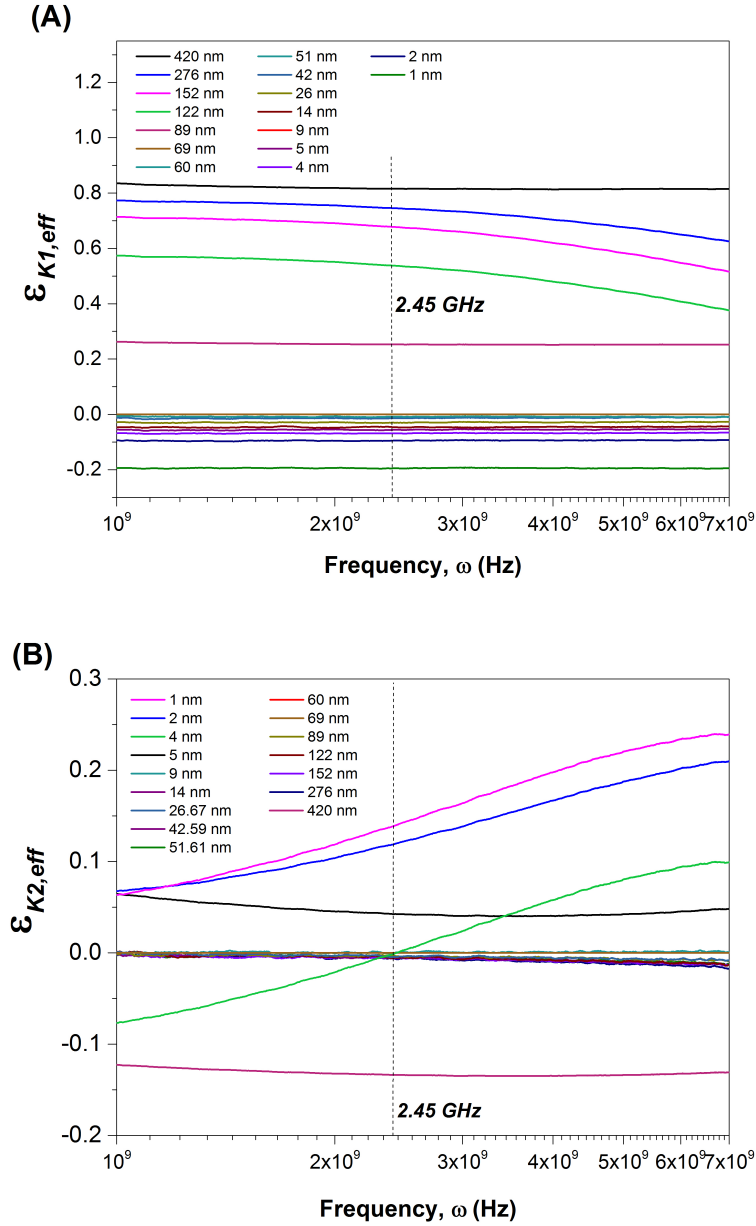


Figure 4.12: The real $\epsilon_{K1,eff}$ and imaginary $\epsilon_{K2,eff}$ parts of the Clausius-Mossotti factor as a function of frequency ω for a series of Ag particle size.

a conductive mesoscopic Ag particle will exactly cancel out the E_0 in the system. However, the charges in microscopic Ag particles responds to the E_0 in such a way as to partially cancel the E_0 . This takes into the account that the 'decay' of free electron charge at the surface in response to the $A.C$ contributes to the imaginary part of the CM factor $\epsilon_{K2,eff}$.

Since the decay of the charge is totally off for a conducting particles in the system, the $\varepsilon_{K2,eff}$ vanishes as the $\varepsilon_{K1,eff}$ of the CM function approaches a positive value ($d_m > 10$ nm). The decay begins to dominate the system ($d_m < 10$ nm), where $\varepsilon_{K1,eff}$ is negative and $\varepsilon_{K2,eff}$ is positive at all locations.

Certainly, the transitions from mesoscopic to microscopic Ag samples indicates a sharp crossover from 1.6 ($\sigma_s > \sigma_h$) to -1.6 at 2.45 GHz when the $\omega < 10$ GHz as shown in Figure 4.13 (A). It shall be noted that dispersed Ag particles are typically stabilised electrostatically which results in the formation of interfacial layer of charge on the surface of the particles. The ligand layer will also contributes in the total particle's permittivity especially for microscopic particles where the volume of the ligands is dominant, which decreases the $\varepsilon_{K1,eff}$ values of the CM factor. However, the values of $\varepsilon_{K1,eff}$ remain close to +1 at this frequency even after accounting for these effects. Furthermore, it is well-known that mesoscopic metallic particles (particularly, Au and Ag nanoparticles), have a constant positive response to the E_0 since these particles are always polarisable than the hexane medium at low frequencies (< 10 GHz) [26].

It is worth to note that $\sigma_{K1,eff}$ defines the ratio of measured current to the effective surface electric field of the whole system. The effective conductivity represents the depolarisation factor of the constituent grains present. For a single inclusion in the matrix, the effective conductivity of Ag particles is generally described as a sum of two components; the bulk conductivity of inclusion $\sigma_{s,bulk}$ and a general surface conductance which is given by [28–30]:

$$\sigma_{K1,eff} = \sigma_{s,bulk} + \frac{2K_{s1}}{r} \quad (4.9)$$

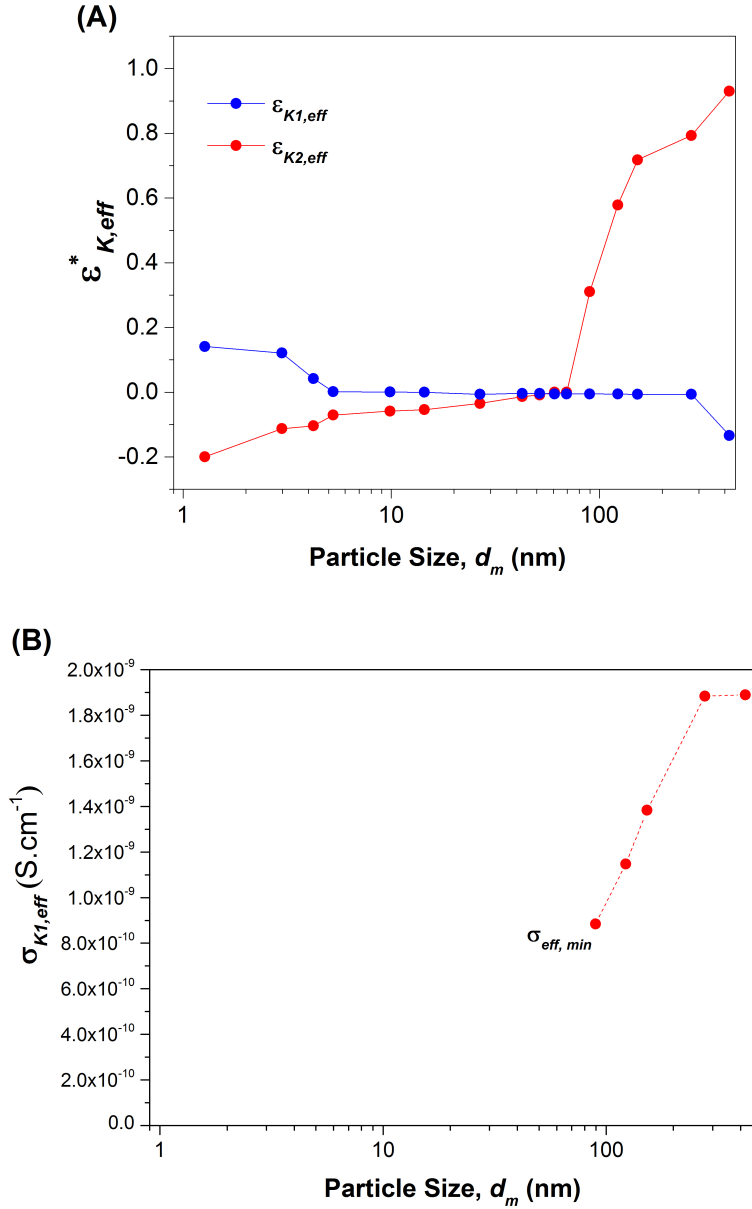


Figure 4.13: Plots showing the variation in the real part of the Clausius-Mossotti (CM) factor $\epsilon_{K1,eff}$ (A) and its calculated effective conductivity $\sigma_{K1,eff}$ and the estimate of $\sigma_{eff,min}$ is also indicated (B) as a function of the particle diameter, d_m .

For microscopic Ag particles, the bulk conductivity is negligible, and the σ_{eff} of the particle is governed by the surface conductance. As it can be seen from Eq. (4.9), that for our Ag particle samples, the small changes in surface conductance (as the d_m is reduced to the microscopic regime) gives rise to major changes in the E_0 distribution where the perturbation

of E_0 inside the system is dominant. The surface conductivity of the Ag particle system caused two separate charge electron behaviours. The first behaviour is the increase in the energy of the E_0 of mesoscopic particles where the electric moment of the bisector corner of the particles is orientated along the E_0 , which caused strong distortion of the lines of E_0 . This makes the electrons polarise faster along the surface. It can be observed that the second behaviour of mesoscopic Ag nanoparticle ($d_m \geq 89$ nm) leads to the electronic polarisability, where the surface capacitance induced from bisector corners of the particles contribute in the total conductivity. The total conductivity becomes less pronounced as observed in smaller mesoscopic Ag particles when $d_m < 89$ nm [28, 31]. It can be seen from Figure 4.13 (B) that the small changes in $\varepsilon_{K1,eff}$ associated with surface conductance for smaller mesoscopic and microscopic Ag particles gives rise to large changes in the $\sigma_{K1,eff}$ behaviour. This effect makes sense as the surface functionalities of mesoscopic Ag particles will be different from those of minute ones as the value of $\sigma_{K1,eff}$ is 1.18×10^{-9} and 8.85×10^{-10} S.cm $^{-1}$ when the d_m is ~ 420 and ~ 89 nm, respectively.

This should be sufficient to describe the depletion of the electronic conductivity of microscopic Ag particles from that of high-nuclearity mesoscopic Ag since the microscopic particle domain produces only a very thin stream of particles where the diffusion amount of the particle related to the particle collision is below the limit and the perturbation of the E_0 dominates in this regime (Figure 4.13 (B)). This strongly supports the idea that the metallic (mesoscopic) and insulating (microscopic) extremes are composed of the same element!

4.1.5.3 A Parallel Derivation to the Maxwell-Garnett (MG) Formula

The MG formula is widely used to describe the effective permittivity properties of a two-phase mixture, in particular those containing the inclusion of canonical geometries (spheroidal or ellipsoidal). In this study, the MG formula is applicable since the dielectric-conducting inclusion mixture is below the percolation threshold. Thus, the MG formula for

randomly oriented and spatially distributed Ag particles inclusion in a hexane host matrix is define by:

$$\varepsilon_{eff} = \varepsilon_h + 3f\varepsilon_h \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + 2\varepsilon_h - f(\varepsilon_s - \varepsilon_h)} \quad (4.10)$$

In reality it is impossible to separate ellipsoidal from spheroidal particles and *vice versa*, and therefore, a reasonable approximation is taken when dealing with Ag particle samples consists of heterogeneous particle's morphology. It shall be highlighted that the concentration of the Ag particles is lower than the percolation threshold, whereby the diameter of larger mesoscopic Ag particles is generally much smaller than the skin depth at the frequency range of interest 10^9 - 10^{10} Hz. The MG conductivity of Ag particles at microwave frequencies is varies and essentially depends on the frequency, which is given by the following relationship:

$$\sigma_{MG,eff}(\omega) = \sigma_{1,eff}(\omega) + j\sigma_{2,eff}(\omega) \quad (4.11)$$

where $\sigma_{1,eff}$ is deduced from $\varepsilon_{2,eff}$. The $\sigma_{2,eff}$ contributes to the $\varepsilon_{1,eff}$ supposing that the dielectric regions are surrounded by the 'effective medium'. Eq. (4.11) was then solved numerically in order to obtain the effective dielectric constant over the whole range of d_m . The calculated parts of the dielectric constant (Figure 4.14 (A) and (B)) show the importance of $\varepsilon_{1,eff}$ in determining the $\sigma_{MG,eff}$ when renormalised conductivity that includes the skin depth effect take place [32].

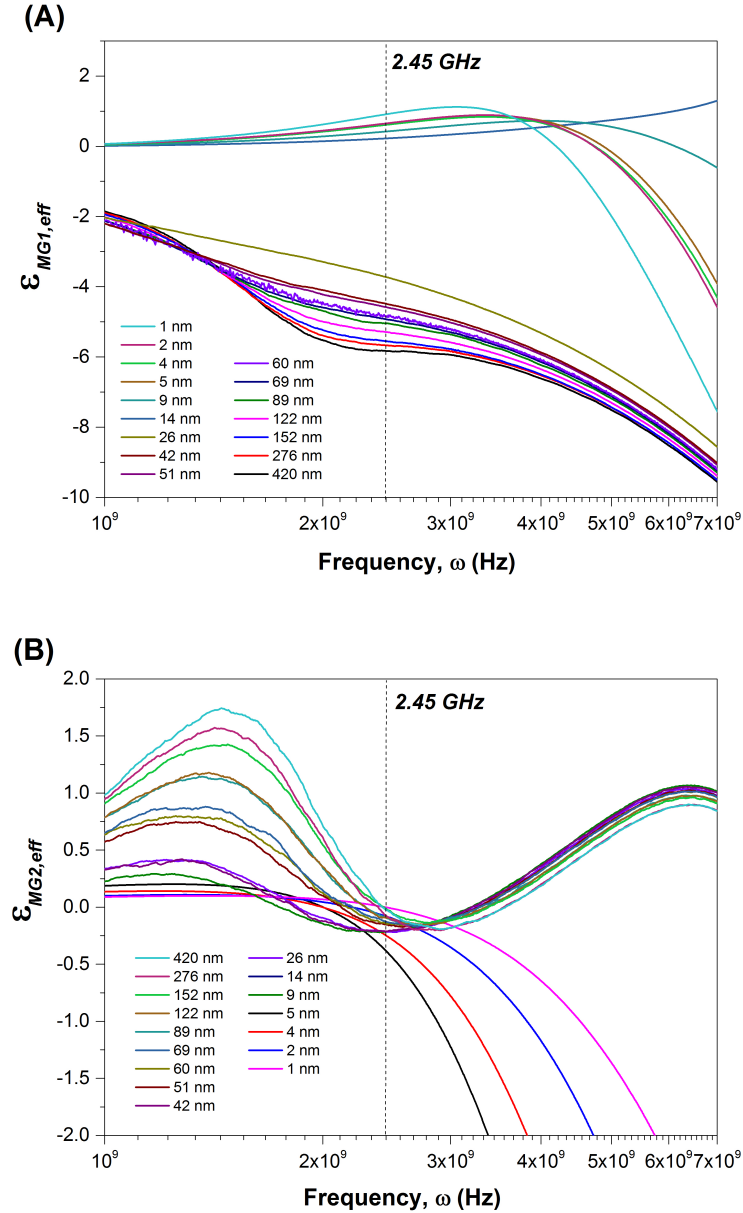


Figure 4.14: The real (A) $\epsilon_{1,eff}$ and imaginary (B) $\epsilon_{2,eff}$ parts of the Maxwell-Garnett (MG) formula for both Ag mesoscopic and microscopic regimes show a variation in the dielectric permittivity with frequency-dependency across the transition size where $f = 0.19$. Due to the large dielectric contrast between the finite insulating particles and higher aggregates metallic domain in Ag, the MG conductivity across the SIMIT is manifested directly from its $\epsilon_{1,eff}$. It is shown that as the Ag particle size decreases and becomes comparable to the mean free path of electrons in Ag, the $\epsilon_{1,eff}$ decreases substantially since surface and grain boundaries become imperceptible.

In this context, it is assumed that the Ag particles for all d_m is in a spherical shape that has

no bisector corners, that suggests a concrete reason for the local environment of dielectric region to be spread equally. The wider peak in $\varepsilon_{1,eff}$ becomes noticeable as $d_m \sim 122$ nm and shifts far away from the percolation threshold when the frequency ω increases as indicated by the decay of the peak. For $\omega \geq 3.4 \times 10^9$ Hz, the effective dielectric constant has a relaxation dispersion in the entire range of d_m while the relaxation time somewhat decreases with increasing d_m . The Ag particles may possess the tendency to get close to each other which results in capacitive coupling. This causes $\varepsilon_{1,eff}$ to increase which typically observed in the solution consists of a periodic array of spheres [33–35]. This means that there are two assumptions involved in the standard effective medium theory: (a) the metal grains as well as dielectric are embedded in the same homogeneous effective medium which will be determined on an ongoing basis and (b) the metal grains all have the same shape [36]. It is clear that the assumptions made calls for the symmetrised MG approximation.

Here, we believed that the complex dielectric constant $\varepsilon_{MG,eff}^*$ achieved is sufficiently far below the percolation threshold (diluted conductive solution) where the effect is not associated with the formation of long range connectivity of metallic particles which usually appraised in the percolation threshold theory [37, 38] as depicts in Figure 4.15 (A). It can be seen that the measurement results of $\varepsilon_{1,eff}$ is always positive while the imaginary part $\varepsilon_{2,eff}$ is negative due to the renormalisation of the skin depth effect. The negative value of $\varepsilon_{2,eff}$ characterises the insulating state as the medium has no more conducting-like element. It appears that the behaviour of $\varepsilon_{2,eff}$ is not considered in detail since only the $\varepsilon_{1,eff}$ takes on huge different values over a wide frequency range ω in the estimation of the $\sigma_{MG,eff}$. The MG theory is not capable of modelling the $\varepsilon_{2,eff}$ since it produces unrealistic values (below zero limit). The changes in $\sigma_{1,eff}$ and $\sigma_{2,eff}$ as the d_m is decreases reveal that these two conductivities contribute independently to each permittivity independently since their effects are separated as the frequency moves through the mesoscopic to microscopic regimes as illustrated in Figure 4.15 (B). It shall be noted that the validity of the experimental correlation with this size-dependent plot is confirmed by taking the quasi-static particle

approximation, assuming that the spherical particles is much smaller than the wavelength. The quasi-particle effects are accountable for a renormalisation of the dissipated energy function of $\varepsilon_{2,eff}$ ($\frac{1}{\varepsilon_{2,eff}}$) [38, 39] The previous statement where the dielectric conductivity of Ag particles can be recast in terms of MG relationship associated with the Drude model is now replaced by [40]:

$$\sigma_{2,eff} = \left(1 - \varepsilon_{1,eff} - \frac{\omega_p^2}{\omega^2 + \gamma^2} \right) \cdot \varepsilon_0 \omega \quad (4.12)$$

$$\sigma_{1,eff} = \left(\varepsilon_{2,eff} - \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)} \right) \cdot \varepsilon_0 \omega \quad (4.13)$$

where ω_p is the angular plasma frequency of the free electrons and γ is the angular relaxation frequency. These equations are also applicable in calculating the dielectric conductivity for the Bruggeman model which is discussed in the next subsection. The electron of the parent site slowly becomes insufficiently screened by the electron cloud where the binding energy of the itinerant electrons is increased. This is equivalent to the polarisation or dielectric catastrophe at the critical particle size when $\sigma_{2,eff}$ is reduced from 1.03×10^{-3} to $1.68 \times 10^{-4} \text{S.cm}^{-1}$. The dielectric conductivity enhancement at mesoscopic Ag particles is attributed to the decay of the electron charges due to the size and geometrical effects of the less packed constituents in the microscopic regime [39–42]. The σ_{eff} from the mesoscopic particle side originates from the enhancement of the capacitive coupling between the Ag aggregates that are closely packed together. Therefore, the possible origin of this convergence is that the capacitive coupling between the particles appears as a benefactor to the conduction current that passes in the medium, reconstructing the phase. Since the out of phase conduction is reached as the size is reduced, the capacitive coupling become less

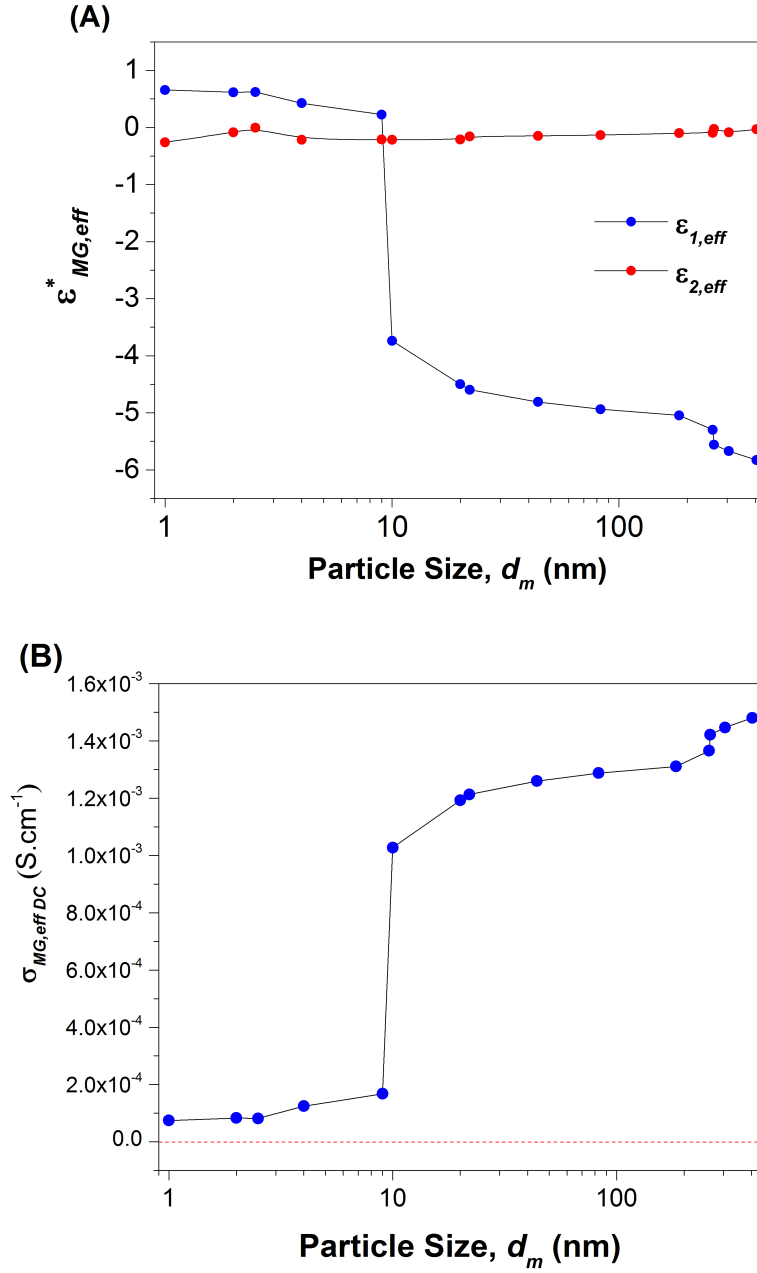


Figure 4.15: Calculated MG data for Ag nanoparticles at 294 K. The real $\epsilon_{1,eff}$ and imaginary $\epsilon_{2,eff}$ parts (A) show variation in the dielectric permittivity with frequency ω screening in both metallic and insulating-like states. (B) The imaginary $\sigma_{2,eff}$ parts of MG at DC conductivity as a function of d_m at 2.50 GHz.

effective and the particles begin to have bound localised states. It is evident that these

data can be used to illustrate the basic physico-chemical properties underlying the reduction of conductivity when the intrinsic size-reduction effect taken explicitly into account. Nevertheless, the Mott-Edwards SIMIT idea can not be determine accurately from here. However, the quantitative comparison between experimental data of dielectric functions with the models thus produce constraints on the size-reduction effect in Ag particle systems.

4.1.5.4 The Bruggeman Factor

Bruggeman improved the results of Clausius-Mossotti and Maxwell-Garnett formulae by essentially iterating the polarisation of the sphere and the matrix until the average net polarisation vanishes. This is known as consistent field calculation [43]. Bruggeman's idea is advantageous over previous formulae since the model does not have any preference towards the embedded particle or medium. In other words, the Bruggeman model treats both the inclusion and medium equally [22, 44]. Figure 4.16 (A) shows the Bruggeman dielectric functions for both mesoscopic and microscopic Ag particles. The model has been shown to work well with mesoscopic Ag particle aggregates based on **Eq. (2.45 in Chapter 2)**. The values of $\varepsilon_{BG1,eff}$ become negative above 51 nm, demonstrating the anticipated metallic behaviour of higher mesoscopic Ag particle aggregates. The value of $\varepsilon_{BG1,eff}$ increases strongly when $d_m < 51$ nm, indicating very weak metallic behaviour. It can be observed that all the $\varepsilon_{BG1,eff}$ as a function of ω have a similar pattern, characterise by the flat plot pattern. The flat plot of $\varepsilon_{BG1,eff}$ shows a little frequency dependence which nearly have no difference across the frequencies. The $\varepsilon_{BG2,eff}$ drops consistently across the particle size range. It shall be noted that Bruggeman not only consider the connectedness of individual particles but also the presence of other component in the solution *e.g.* ODA ligand. In other words, Bruggeman characterise the microstructure, distribution and interconnectivity for entire components within the sample. The presence of the ligand significantly effect both $\varepsilon_{BG1,eff}$ and $\varepsilon_{BG2,eff}$ that the values are much higher than those for CM and MG formulae.

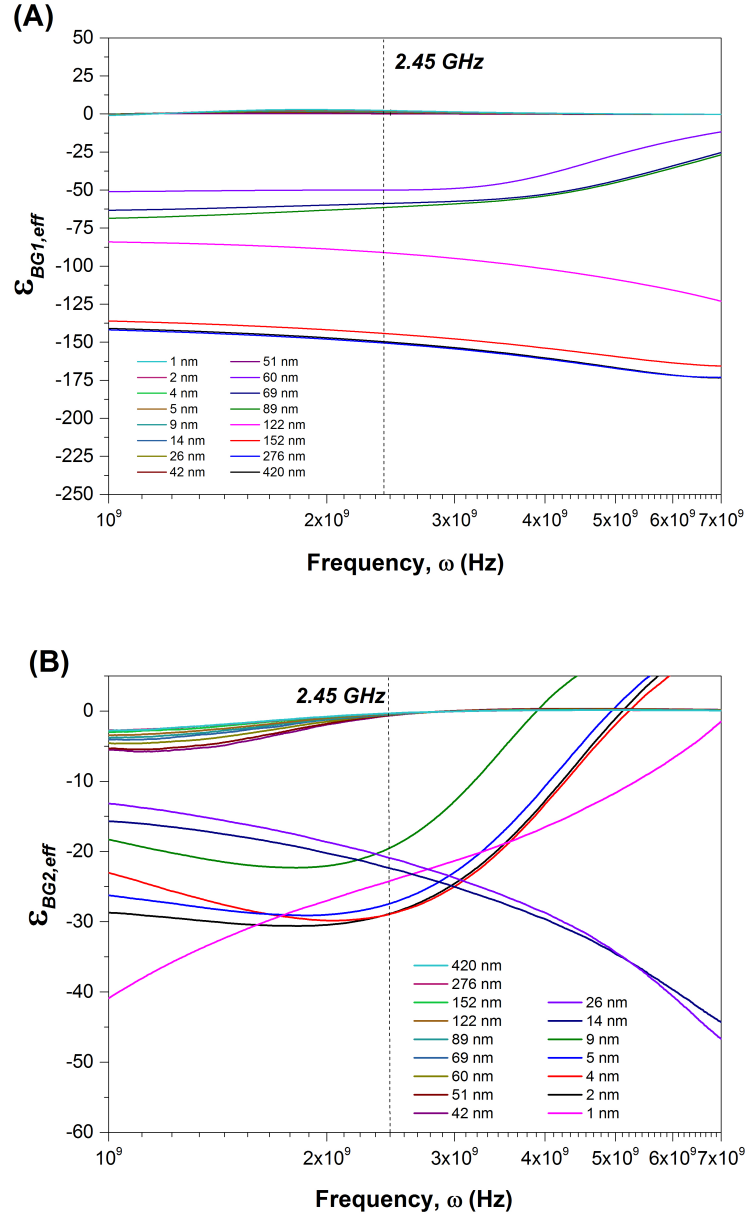


Figure 4.16: The permittivity plots of (A) $\epsilon_{BG1,eff}$ and (B) $\epsilon_{BG2,eff}$ for both mesoscopic and microscopic Ag particles. The dotted line indicates a frequency of 2.50 GHz indicating the point of transition for both domains.

Therefore, the dielectric functions of the samples are summarised in Figure 4.17 (A). The

effective dielectric constant obtained using the Bruggeman effective medium approximation is $1.04 - j\ 21.01$, $1.21 - j\ 22.47$, $1.32 - j\ 19.34$ and $1.61 - j\ 24.09$ for d_m of ~ 26 , ~ 14 , ~ 9 and ~ 5 nm, respectively. The variance for both permittivity plots is a measure of the total amount of microwave dielectric polarization corresponding to the amount of dielectric contrast in the medium, which is dependent upon the d_m . The equivalent conductivity of the inclusion particles based on Bruggeman's effective permittivity is shown in Figure 4.17 (B). The lower the $\varepsilon_{BG1,eff}$, the greater the $\sigma_{eff,DC}$. Even though the reduction in particle size is a primary factor, the decrease in the absolute value of the conductivity suggests that the increased in the interfacial charge surface layer effect (counting the contribution of ligand) results in lower solution conductivities. This is very likely to be found in a solution where the l_{m-m} of the particles assembly is relatively high due to the present of ligand as it also produces gradients in both permittivity and conductivity for the whole system. These gradients can anticipate with the electric field to produce either polarisation or perturbation conditions of the system. This comparison indicates that this Bruggeman model predicts different conductivity behaviour compared to the CM and MG formulae. However, the interpretations of the dielectric conductivity behaviours are the same for these three models.

Critical Summary In summary, the method involved in the effective medium approach in evaluating the conductivity across Ag particle size range leads to different value of minimum conductivity, $\sigma_{eff,min}$. The former is the CM theory, followed by Bruggeman and the latter is the MG formula. At this point, the formulae used depend to some extent on the condition and the intrinsic behaviour of Ag particles we are modelling. Nevertheless, the concept remain the same as presented here include: (i) the volume fraction of the Ag particle inclusions is significantly smaller than the percolation threshold; (ii) the σ_{eff} of the Ag particles mainly depends on the effective dielectric function, $\varepsilon_{eff}(\omega)$ and (iii) Ag particles exhibit frequency dependence due to the intrinsic size effect where the mean free path of particle's electrons smaller than the characteristic size of the particles

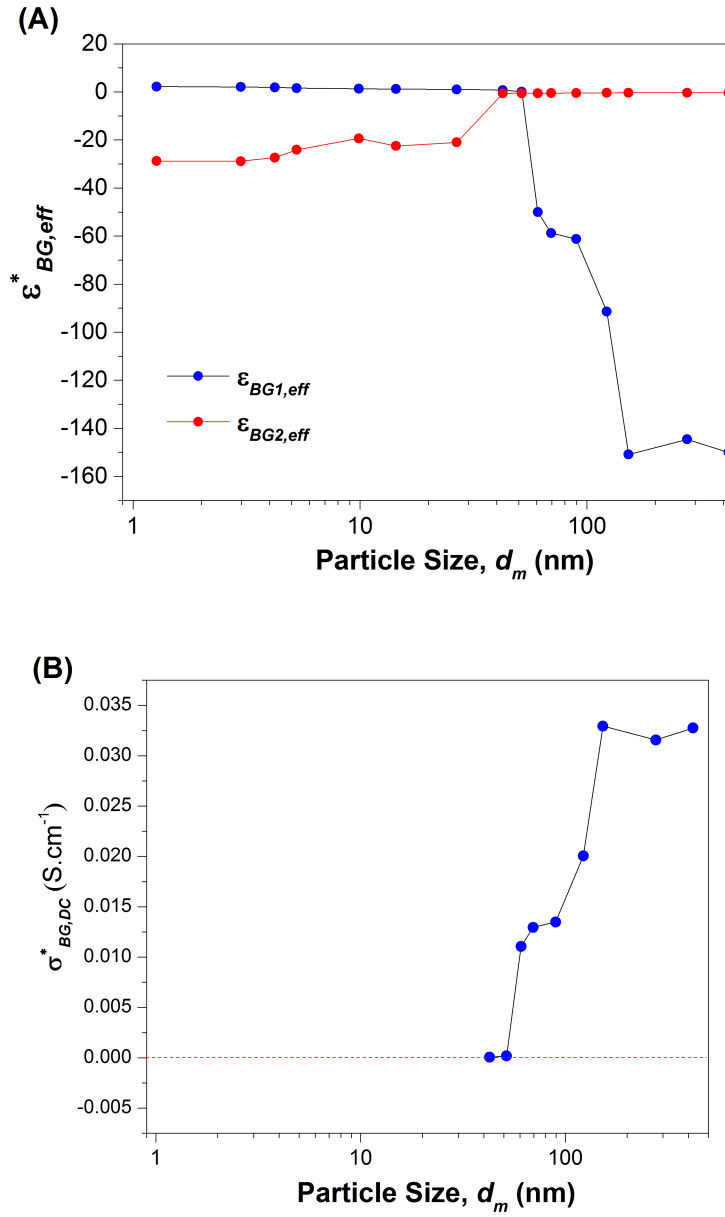


Figure 4.17: The measured (A) complex permittivity and corresponding (B) effective DC conductivity plots as a function of d_m at 2.50 GHz using Bruggeman formula for both mesoscopic and microscopic Ag particles.

itself (quasi-static limit) and substantially reduced the observed electrical conductivity of the particles. We have described that MG approximation is the closest one to treat

differences in the $\varepsilon_{eff}(\omega)$ for mesoscopic and microscopic Ag colloidal in an isotropic hexane host. The advantages of MG's formulation as previously discussed involve: (i) the phase mixture including the anisotropic particles (spheroidal and ellipsoidal); (ii) literally account the role of ligands surrounded the metal particles and (ii) the formula is simplest and provides fairly description for dispersed phase. The model leads to a microscopic dielectric behaviour as the d_m decrease which qualitatively agrees with the *A.C* experimental results and accounts for the dependence of ε_{eff} on the *D.C* electrical conductivity. Specifically, the ε_{eff} is negative over the mesoscopic particle size range, while the microscopic particle size range exhibit positive values, which results from de-localised and localised electron charge, respectively, within the particles.

4.1.6 Overall Discussion

To summarise this section, these experimental evidences provide a set of data for which the two techniques of effective dielectric approach can be potentially employed in identifying the probabilities of SIMIT's answers. As we refer back to SIMIT discussion, it shall be noted that the possibility to examine a complete transition behaviour (from metal to insulator regimes) using this laboratory equipments show to have their distinct benefits and limitations. At this point, the application of microwave cavity perturbation and coaxial probe techniques still have the constraints to some extent in evaluating the dielectric property especially in measuring the microscopic particle sample. The lowest σ_{eff} at $d_m \approx 5$ nm reveal significant differences from the one obtained at 420 nm signifying distinct overall limiting electric perturbation factor. The σ_{eff} are reduced by 2 orders-of-magnitude as they reached microscopic size regime which is nowhere near such value of 7 to 8 orders-of-magnitude attained relative to the value measured from macroscopic (bulk) Ag metal. The mesoscopic Ag particles are highly polarised when placed in a microwave *E*-field as they automatically screen out the E_0 within the particles ($\varepsilon_{2,eff} \gg \varepsilon_{1,eff}$). High field develops at the surface mesoscopic particles at sufficiently high electric field strength, which increases the dielectric dissipated energy, $\varepsilon_{2,eff}$. This results in higher σ_{eff} given for a

similar particle's volume fraction across the particle size range. Certainly, the value is not as pronounced as that for bulk Ag. The electric dipole absorption confound significantly ($\varepsilon_{2,eff} \ll \varepsilon_{1,eff}$) and minimised the dissipation energy within low nuclearity cluster of microscopic particles (~ 10 and ~ 5 nm). A weak suppression of σ_{eff} from ~ 10 to ~ 5 nm anticipates the characteristics of non-metallic behaviour which suddenly disappearing below 5 nm. Theoretically, the microscopic Ag particles constitute small subgrain boundaries with the superposition of twin planes induces additional scattering of conduction electrons that reduces the conductivity values by a factor of 10 to 100. This meaningful changes firmly proposed that there is quantitative correlation between the size-dependent property and σ_{eff} of particles. On the basis of these data, it is conclude that for microwave cavity resonator technique, the critical size for the minimum conductivity to achieved is at around 5 nm at room temperature as it is impossible to perform the dielectric measurement due to the sensitivity limit of the cavity itself.

The second observation was done by utilising microwave coaxial broadband technique. The charge transport mechanism of the colloidal solution is reported as a parallel RC circuit across the wide range of d_m . The RC circuit increases with increasing in l_{m-m} . The observation confirms that the strongest *D.C* electrical conductivity $\sigma_{DC,eff}$ of mesoscopic Ag particles at 2.50 GHz arises from the dominant contribution of inter-hopping mechanism of electron through the fragmented particle boundaries. Microscopic Ag particles refute the *A.C* conductivity with the abrupt change in the dielectric profile revealing the quantum confinement effect due to the presence of large space charge accumulation (intra-hopping electron fluctuation) within the energy barrier. The crystal structure and its symmetry have broken down where the low coordinated surface atoms of microscopic Ag particles influenced the observed size-dependent behaviour of the system. The role of SIMIT in our system is not clear. We did not observed such SIMIT from the samples due to the disappearance of reflectance spectrum. An alternative explanation is that the $\sigma_{DC,eff}$ plot is consistent with the reduction of metallic conductivity routes. Nevertheless, we have

demonstrated that the $\sigma_{DC,eff}$ changes shows the remarkable size effect from this technique with the lowest size below 14 nm. The effective medium approximation employed here are treated as a separate systems for both spheroidal and ellipsoidal inclusions. The CM, MG and Bruggeman formulas are certainly not the only three effective medium theories. They are consider as the most common theories employed depending on the parameters and the properties that we would expect. In this case, the theories are based on the experimental results obtained from the microwave coaxial broadband technique. The specification of volume fraction control the exact theories of the formulas. MG is the best approximation where the discrepancies from the experimental results is the lowest, whereby the CM is the worst. Nonetheless, Bruggeman is the most sophisticated and certainly qualitatively accurate for the effort in justification of the critical percolation threshold of the particles.

These two techniques and the procedures of effective dielectric approaches illustrate the reduction of dielectric conductivity due to the size-reduction effect of Ag particles at room temperature. As discussed in **Section 4.1**, the non-metallic ground state at this temperature is not the lowest energy state of the particles since the effect associated with electrons' exchange is still observed at this temperature. The latter section described the analysis of dielectric conductivity at lower room temperatures ($T < 294$ K), as we shall see the hopping of the electron from one site to another is almost impossible since the orbitals of the electrons are non de-generated at microscopic sizes. In the last section, we shall complete this chapter based on the summary of the main result and then analyse the cases concerning the pre-quantum theories.

4.2 Dielectric Response and the SIMIT for $T < 293$ K

4.2.1 Cavity Perturbation Dielectric Properties

It is worth noting that the definition of original Mott's insulator transition occurs at $T = 0$ K. Mott and Edwards [1, 45] reported that dispersed mesoscopic metallic particle

system with a half metallic character of bulk metal at room temperature becomes fairly non-metallic at 0 K. Hence, it is essential to determine the effective microwave conductivity of the size-dependence Ag particle systems at lowest temperature as possible which is all pervasive subject when dealing with SIMIT. Nevertheless as noted in **Section 4.1**, the development of SIMIT in this systems is not possible due to the limitations of sensitivity and specificity of the equipment. However, the unusual dielectric ground state at the lowest particle size of ~ 5 nm is still acceptable and valid. To compensate for this, the microwave cavity resonator was immersed in liquid nitrogen at 77 K, where all parts of the cavity holes are closely tight in order to prevent the leaking of liquid nitrogen as well as the E -field leakage from the cavity body. It shall be noted that, the temperature of the sample is slightly higher than the temperature of the cavity. The temperature is measured directly at the outside of the quartz tube and not on the outer side of cavity resonator body. The temperature difference between the sample and cavity is sufficiently large therefore, the lowest temperature achieved is 223 K for this setup. The automatic alteration of its frequency resonant occur over a small frequency range, thus, the extraction of the sample properties is similar with the one at room temperature as the cooling do not disturb the electromagnetic field in the cavity. We only interested in the changes of the dielectric properties of Ag samples at only one particular frequency, *e.g.* 2.50 GHz and the results show that the f remains the same and thus the conductivity calculation's procedure still the same as the one we calculated at room temperature. Furthermore, the sample size is rather small which can be heated up quickly and homogeneously where the reliability and stability of the measurement is acceptable. Meanwhile, the homogeneous cooling maintain the temperature of the sample at reasonable time. All the measurements taken are sufficiently quick such that the measurements can be completed before the temperature of the samples changed.

Figure 4.18 shows the transmitted resonance response plot for the sets of Ag particles with $d_m \sim 420$ nm (A), ~ 60 nm (B) and ~ 5 nm (C) measured at temperatures of 287,

273, 271, 263, 259, 253, 244, 241, 233, 228, 225 and 223 K. The decrease in d_m leads to a

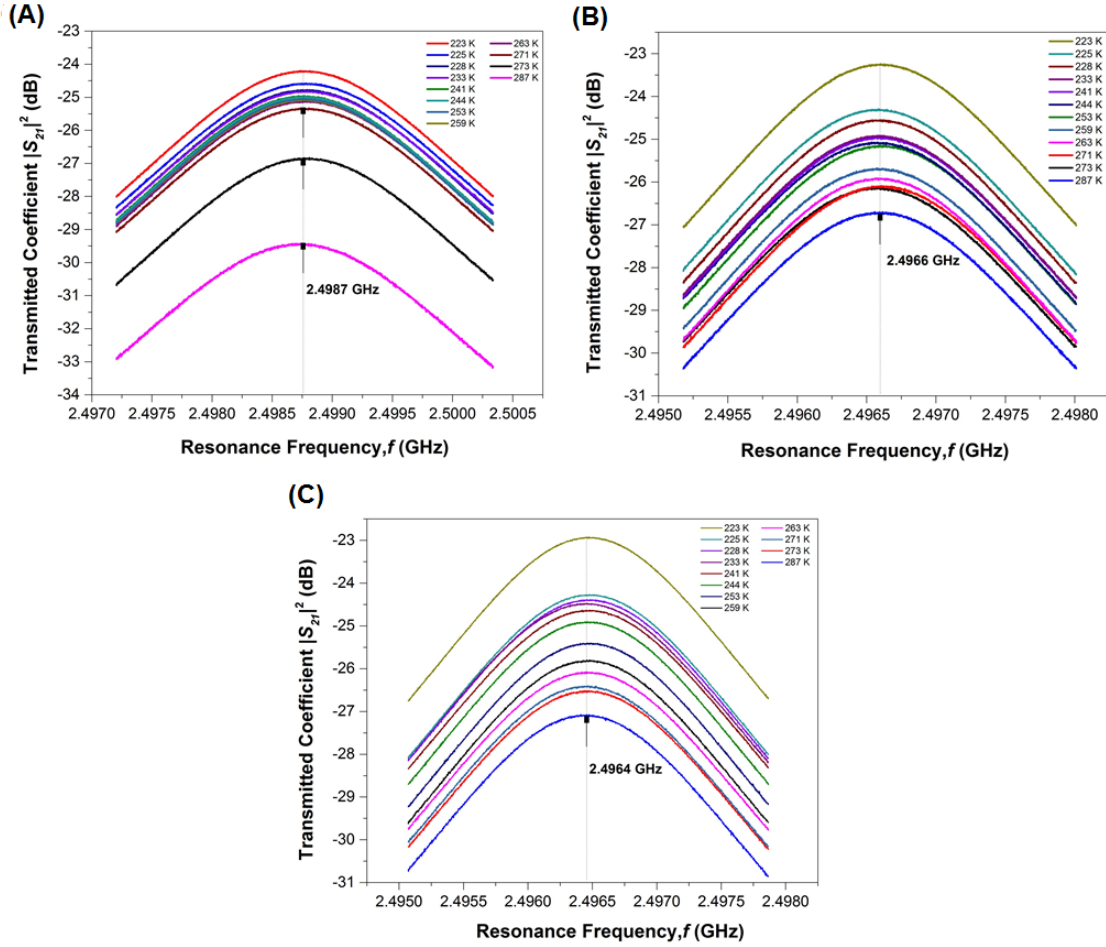


Figure 4.18: Microwave cavity perturbation traces of TM_{010} mode for Ag particles suspended in solution of different particle sizes: (A) ~ 420 nm, (B) ~ 60 nm and (C) ~ 5 nm which continuously measured at temperature of 287, 273, 271, 263, 259, 253, 244, 241, 233, 228, 225 and 223 K. The shift in resonance frequency to a lower frequency (A to C) corresponds to an increase in the $\epsilon_{1,eff}$ of the complex permittivity, whereby the difference in frequencies among the samples is small.

shift of the transmission coefficients to lower frequencies from 2.4987 to 2.4966 and 2.4964 GHz for $d_m \sim 420$, ~ 60 and ~ 5 nm, respectively. The results have shown that the homogeneous heating is possible, in the case of dipole rotation still exist indicates by the shifting of the f . The transmission behaviour for all set of d_m is shown to have a reliable value of

Q -factor at each temperature. This indicates by the exact resonance frequency value where the fluctuations of Q -factor levels do agree against each other. Static resonance frequency help us to accurately determine the values of permittivity. It can be seen that the transmitted coefficient curve reaches a minimum (-30.6 dB) when $d_m \sim 420$ nm at highest cooling temperature (287 K) (Figure 4.18 (A)). Meanwhile, the relative Δf_B for ~ 420 to ~ 5 nm at 287 K (Figure 4.18 (A) to (C)) is approximately 0.6501 to 4.27×10^{-2} with an increase in transmitted power loss from -29.4 to -28.1 dB, respectively. If there is a decrease in Δf_B , there will be an increase in the dielectric conductivity of the particles.

The temperature dependence of the bandwidth change Δf_B of representative particle size are summarised in Figure 4.19 (A). It is interesting to note that the minimum valid data of Δf_B from a quasi-linear in- T dependence plot for the particles with $d_m \sim 420, \sim 60$ and ~ 5 nm are at temperature of 223, 225 and 259 K, respectively. The corresponding values obtained below these temperatures can not be real as they are below the sensitivity limit of the cavity. As clearly seen from the plot, as the d_m decreases with T , the Δf_B is also decrease, indicating that the cooling condition facilitates the destruction mechanism of polarisation. This contributes to the localisation of electrons given that the current flow from the electron hopping becomes almost impossible. At this point, these findings agree well with the consideration that, weak coupling progressively built up between the particle grains towards lower temperatures and that, tends to alter the initial metallicity state of metal particles. The Δf_B are controlled by the local quantum physics, that is, the sensitivity of the grains arrangement where the electron tunneling conductance through fragmented particles under the E_0 is expected to change and appeared to be more tedious upon cooling to low temperature. The electron hopping length is the same as in room temperature system and thus, the electron hopping should still occur at these low temperatures. The electrons organised themselves and gradually freeze out onto localised state results in the decrement of $\varepsilon_{2,eff}$ as shown in Figure 4.19 (B). Since the σ_{eff} shows linear changes with the change

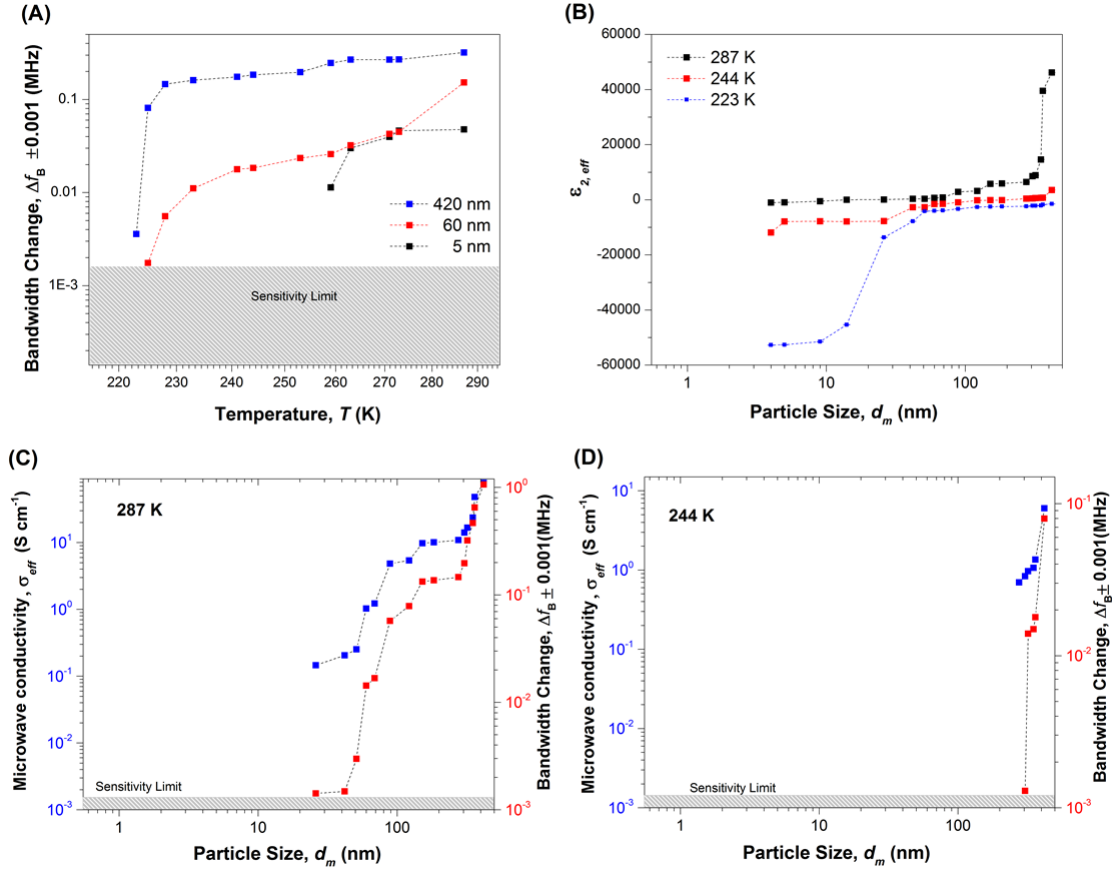


Figure 4.19: The temperature T dependent of the bandwidth change Δf_B for three sample sizes (A) as discussed in the text. The effective dielectric permittivity function of (B) imaginary part $\varepsilon_{2,eff}$ is shown as a function of particle size d_m measured at 2.50 GHz at temperatures of 287, 244 and 223 K. The microwave conductivity σ_{eff} as a function of d_m at $T = 287$ K (C) and 244 K with the correspondance Δf_B of each system. It shall be noted that for $T = 223$ K, all the values are below the sensitivity limit. No valid data can be accounted for this temperature. The error values reflect the repeatability of the measurements.

in $\varepsilon_{2,eff}$, the corresponding σ_{eff} clearly reveals that the particle system progressively gets into the localisation state as the d_m is reduced (Figure 4.19 (C and D)). In Figure 4.19 (C) and (D), the conductivity is plotted as $\log \sigma_{eff}$ versus d_m . The minimum σ_{eff} for 287 and 244 K are shown to take place at 26 nm and 276 nm, respectively where the anomalies are suppressed and the d_m range of zero conductivity expanded. Various anomalies controlled

in the physical properties of the dielectric factor that change with temperatures includes the dipole moment, particles structure and electrons hopping. The anomalies in the dielectric properties becomes more pronounced at 223 K where a drastic drop to zero conductivity occurs. It is apparent that there are no positive conductivity values for both mesoscopic and microscopic Ag particles at 223 K, indicating that there is a continuous depletion of conductivity during the cooling even at 420 nm, since electric current flow can not induced the electron's hopping between the sites. This implies that the minimum σ_{eff} for the observation of SIMIT for these systems can not be real as these anomalies is masked by rapid decrease in the electric dipole in the temperature range above 0 K of Mott's transition temperature. Thus, the data taken on the representative samples confirm that the SIMIT is not producable with good reliability from this measurement at low temperatures. We can only confirm that the $\sigma_{min,eff}$ of size-dependent Ag nanoparticles at 287 K is 26 nm and becomes considerably increase to 276 nm at 224 K before suddenly dissappearing above the d_m range (> 420 nm). Nevertheless, these results are meaningful in a view that a strong quantitative relationship is gleaned between the d_m and T . The fragmentation of the particle's structure and the existance of surface coordinated atoms give rise to the observed size-dependent behaviour of electrical conductivity of individual Ag particles, which becomes significant at low temperatures.

Critical Summary To this end, it is necessary to further scrutinise the quantitative relationship between the size-reduction effect and temperature of Ag particle systems. Theoretically, SIMIT that follows Mott's MIT should be observed at lowest temperature (0 K) with valid data down to 10 nm. However, in our case the sign of SIMIT is not clear as the data below certain particle size can not be real. The observations confirm that the expected changes at temperatures of 287 and 244 K show no σ_{eff} below particle size of 26 and 276 nm, respectively. Interestingly, the σ_{eff} completely absent at the lowest temperature of 223 K from this setup indicating that the dipole moment changed and the electrons are no more de-localised between the sites. The main contribution factor that feature the fundamental role of this condition especially at low temperature system is the significance discreteness

of the electronic energy levels due to the electronic quantum effect at low temperatures. The electronic transfer is already weaker as the low coordinated atoms is increased which gives a drastic change in the symmetry. This condition becomes more pronounced below room temperature phase as the whole particles undergoing a freezing of electron's hopping. Up to this point, we can deduce three pre-liminary statements based on the these results: (i) the anomalies observed below 26 and 276 nm at 287 and 244 K, respectively could be due to the combination effect of increasing in fragmented particles (size-reduction effect) and the low temperature conditions, (ii) space charge accumulation corresponding to a significant suppression of charge fluctuations becomes more pronounced with the help of freezing temperatures and (iii) the dielectric conductivity is completely absent at the lowest temperature of the experiment (223 K) indicating that no polarisation is released from all d_m , indicating that the particle size for $\sigma_{min,eff}$ would be greater than 420 nm.

4.3 Overall Discussion

4.3.1 The SIMIT at Room Temperature

In this study, we report the observation of the particle size-reduction effect on microwave conductivity in one of the conductive metallic element in periodic table, that is Ag. The measurements of the perturbation microwave response based on the dielectric permittivity was observed by using microwave cavity resonator studied at 2.45 GHz. The σ_{eff} result reveals that the size-dependent effect shows to drop as much as two orders of magnitude within the particle size range of ~ 420 nm down to ~ 5 nm at room temperature. By combining the data taken from all samples, the trace of SIMIT is concluded to be impossible *via* this method as the detection is nearly reach the sensitivity limit of the cavity resonator. Thereby, the lowest size effect that can be exploited above the detection sensitivity limit is ~ 5 nm with the σ_{eff} decreases to 0.25 S.cm^{-1} based on the d_m versus σ_{eff} plot. The decrement in the σ_{eff} value from 221.75 to 0.25 S.cm^{-1} from mesoscopic to microscopic Ag particles (420 to 5 nm) are valid for metal particle systems that exhibit a similar size

effect in the dielectric response, for instance, gold particles. This firmly suggested that there is quantitative relationship between the d_m and electronic conductivity. Meanwhile, the reduction of σ_{eff} from coaxial probe technique led us to the conclusion that as the d_m decrease, the larger absorption cross sections form. The size-reduction effect broadens the absorption band within microscopic Ag particles and contributes to the absorption of E_0 . The decrease in the σ_{eff} from 0.064 to 0.0047 S.cm⁻¹ for 420 to 14 nm was observed, respectively. The procedures involved in the effective permittivity approximations in evaluating the conductivity lead to different $\sigma_{min,eff}$ of Ag system that we are modelling as long as the d_m smaller than the wavelength of light. Nevertheless, the procedures involved remain the same. At this point, it is important to note that, the reduction to a lower state of conductivity is accompanied by the results of electron localisation due to the complex interplay between the increase in the discrete energy level separation and dipole moment of particles. The size-reduction effect in Ag particles is mainly related to the distribution of small microscopic Ag particles consist of large numbers of low coordinated atoms at the surface. This contributes to a significant broken particles' symmetry that caused an increase in the internal lattice strain where the wave functions becomes discrete and the electrons are now completely localised. In other words, an intense conductivity evidently occurs at d_m at which the particles can no longer disperse completely in the system ($d_m > d_{c,m}$) when they can touch and 'glued' to each other despite some degree of disorder as the electrons are distorted sideways (accumulation of electrons at bisector corner). It is readily be seen from both techniques that the σ_{eff} from a fractured particles' network form inevitably broken conductivity bridge that gives a sudden decrease in σ_{eff} .

The quantum size-effect is governed by the electron's behaviour where they exhibit different types of electron movements at the surface of particles either in mesoscopic or microscopic regimes. The itinerant effect in mesoscopic Ag particles originates from the fact that the motion of the electrons moving at these surfaces is perfectly reversed and polarisation occurs as shown in Figure 4.20. The surface electrons of mesoscopic Ag particle

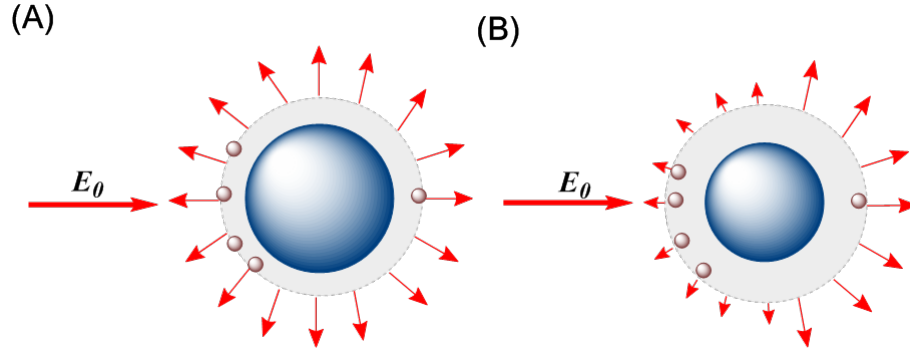


Figure 4.20: Polarisation of electron on the Ag particle surface. (A) Electrons (brown) on a surface of mesoscopic Ag are scattered off the Ag in all directions with equal polarised probability. (B) For small microscopic Ag insulator that has a metallic rather than an insulating surface, the electrons are preferentially scattered at a small distance and have zero probability of being polarised in the direction of E -field, E_0 (*reproduced from Roushan et. al.[46]*).

are scattered off in all directions as waves rather than as particles at an atomic distance [47]. Nonetheless, mesoscopic Ag particles possess to have semi-metals property since their microwave conductivity values are quite low compared to bulk state of Ag. Semi-metals possess to have properties similar and in the midpoint between metals and nonmetals. This semi-metallic state particle still retains the original strong spin polarisation of bulk Ag based on its dielectric response to the E_0 . The changes in the surface properties is linearly dependent with the presence of low-coordinated atoms that becomes more significant in microscopic regime. Interestingly, microscopic Ag particles retain half of the semi-metal property of mesoscopic particles and tends to mimic non-metals property. Unlike in a genuine insulator system, microscopic Ag particles have no real band gap in the electronic energy state, rather the density of metallic electrons diminishes as the size-reduction effect take place with less accumulation of electrons at a point of bisector corner. The fragmented coordinated atoms gradually alter the electronic energy wave function of the particles and amplify the effects of electron perturbation mechanism under the E_0 , which is often found

to be trapped or localised even when they continue to diffuse [47]. To some extent, the diffusion of the electrons that characterise the metal's conductivity appear to be degraded. Thus, the localisation effect is clearly develop as observed in this system, however, to claim the SIMIT's occurrence within the size range exploited here is far from valid.

With regards to the electronic energy wave function, the Fermi energy level E_f of metal, indicates the essential maximum energy in terms of 'wave number space' for an electron to occupied at 0 K. The elementary distinction between metal and non-metal relies on how the electrons behave as they are moving near to the E_f . Therefore, this unique condition disengages the occupied from unoccupied electron energy levels that can describes the actual conditions of how the metal behave at this temperature. For a metallic state, the E_f lies in the middle of a band, whereas the E_f in non-metallic lies in a gap between the electronic states. This can actually explain the reason why mesoscopic Ag particles possess high conductivity whereas microscopic particles do not. In the real environment, mesoscopic Ag particles still be able to mimic their bulk Ag properties version, as they always contain electrons in unfilled levels above the energy gap. This means that, mesoscopic Ag particles still have free Fermi surface from which electrons can be raised to allow and occupy the conduction band. In comparison to the ones in bulk Ag state, the conductance produced is transported by comparatively more free electrons than the E_0 . These electrons accelerated into higher unfilled energy state as such the overlapping band gap is gradually changed into discrete energy level separation and that the conduction is limited to these few electron wave function. The simplified consideration here is that the reduction of σ_{eff} for microscopic particles has been corrected when the particle size becomes comparable with mean free path of electrons which in turn reveal the size-dependence of dielectric responses. .

As the conductivities gradually vanish at ~ 5 and ~ 14 nm (**Sections 4.1.1 and 4.2.1**), the polarisation disintegration induced by E_0 occurs due to the decreasing of the E_1 passing over the particles. As a consequence of this electronic motion, the kinetic energy of

electrons gradually losing its dominance in the interaction between the electrons. For quasi-static particles, the energy eigenstates are now controlled by the grain boundaries which increases with the atom-atom distance and continues until the particles is well separated. Obviously, Mott's MIT through size-reduction control strongly governs the central idea of the observation and provides useful descriptions of these electronic states although the exploited size range of the particles is limited due to the sensitivity limitation of the cavity. In fact, Mott's insulator states of individual metal particles are once classified by Edwards [1] as the atomic counterpart in the Mott-Hubbard correlation energy and also know as charge transfer insulators, $U_{particle}$ where metal inter-particle interactions are generally assumed to remain electrically neutral. The interaction is considered in term of the effective field approximation. The average effect of the electron repulsion can be seen as the d_m is reduced. To bring an electron from one site to another that already occupied with electron needs a finite excitation energy which is known as Mott Hubbard energy gap where the average field theory does not forecast the value gap of the DOS at Fermi level. As shown

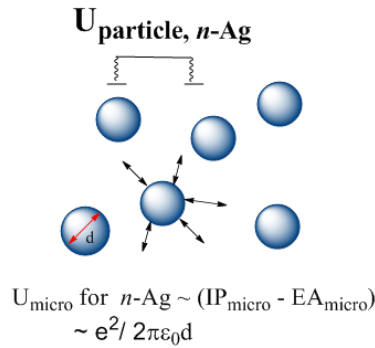


Figure 4.21: Illustration of the Mott-Hubbard correlation energy, $U_{particle}$ corresponding to the 'charging energy' of individual microscopic Ag particles for the *size-induced metal-insulator transition* (SIMIT).

in Figure 4.21, for individual microscopic Ag particle charging energy, $U_{particle}$ can be viewed as the difference between the ionisation energy and the electron affinity ($IP_{particle} -$

$EA_{particle} \approx \frac{e^2}{2\pi\epsilon_0 d_m}$) of the isolated Ag particle. In mesoscopic particles, the Columbic attraction between oppositely charged particles should serve to reduce the charging energy $U_{particle}$, when there is significant inter-particle contact presence [48]. Therefore, when Ag particles are physically well-separated from each other, thermal fluctuations by themselves are never adequate to enable the individual Ag particles to lose or gain the electron although the total number of electrons within each particle is more than thousands [48]. The decrease in the charge fluctuations of small particles is large enough to induce the system to the Mott-Hubbard insulator state and expected to occurs when the particle size is below 5 nm whereby $U_{particle} \geq 2.224 \times 10^{-19}$ eV calculated from the data. In particular, the exact d_m of potential Mott-Hubbard insulator state can not be determined correctly. Surface modification of microscopic Ag particles could led the overall system to have partial crystalline as well partial amorphous surface (ligand) and tends into the formation of metal oxide that may also enable the particles to locally achieve the level of 'insulating' within the system.

The decrease in σ_{eff} can be discussed further in association with Goldhammer-Herzfeld and Mott criterions where the understanding of electronic mode role is taken into account for the precise control of the electron-electron interaction. The decrease of σ_{eff} takes place when the columbic potential of an electron-hole pair $V(r)$ within the particle becomes insufficiently screened *via* itinerant conduction electrons and thus, a localised state follows [48–50]. Here, the eletron-hole pair is defined as $V(r) = \frac{-e^2}{\epsilon l_{m-m}}$ where ϵ is the effective dielectric constant of the system and l_{m-m} is the mean distance between the particles. As proved by dielectric permittivity results discussed previously in **Section 5.3**, the reduction in Ag particle size leads to a decrease in Ag elemental density. Clearly, the larger particles would have greater polarisation with higher elemental density where there is an intense probability of interactions between the particles and this leads to higher measured microwave conductivity value. As the 'conducting spheres' is no longer overlap to each other and the total electrons within the particle itself is reduced, the system forbidding the electrons to freely roam over the entire site of particles. According to this criterion,

non-metallic transition is inevitable when the dielectric constant which relates to the l_{m-m} of the Ag particles rises below the critical diameter d_c of the system due to the decrease in the electron-electron repulsion. Therefore, we predict that, there is no SIMIT above 5 nm in this study.

The decrease in σ_{eff} can be related to the deviations where the large fragments of atoms in a particle are part of the surface and defined as $F_s(N) = 4N^{-1/3}$. This idealised equation indicates that the number of atoms exist per particle will considerably decrease when the d_c is decreased and their surface fraction increase accordingly. For instance, ~ 20 nm size-particle possess to has a value of more than 10% of the atoms on the surface. Hence, the overall electronic properties of mesoscopic particles is entirely different from the individual microscopic particles. Within individual microscopic particles, the electrical conduction breaks down as the mean free path of the electrons, ξ approaches the inter-atomic distance of the particles, l_{m-m} and this process known as Ioffe-Regel criterion. Ioffe-Regel predicted that there should be a metal-insulator transition when the criterion of $k_F\xi \approx 1$ is fulfilled, in which the Fermi wave vector is defined as $k_F = (3\pi^2 n_{particle})^{1/3}$. Here, n is the charge density of the particles and mean free path of electrons $\xi = \frac{\hbar k_F \sigma}{n_{particle} e^2}$ [51] . According to this criterion, for $k_F\xi \gg 1$, the system is metallic whereas for $k_F\xi \ll 1$, the phase is insulating. The mesoscopic Ag particles in this study will attain truly metallic status since ξ of the conductive electrons exceed the l_{m-m} between the particles [48]. The minimum metallic conductivity (Mott-Ioffe-Regel criterion) is taken as the limiting situation when $\xi \approx l_{m-m}$, which expected to be observed below 5 nm where they exhibit no conductivity from both measurements.

This definition of non-metallicity is therefore not as simple as it seems. It applies all the circumstances related to the electron-electron interaction correspondence to the size-dependence of particle's properties. The measurements of quasi- $D.C$ conductivity at GHz frequencies definitely circumvent the difficulties that potentially arise when dealing with

metal colloids. The outcome of the experiments especially for particle size below 5 nm would be remains an open question.

4.3.2 The SIMIT for $T < 294$ K

As we have noted, the described discrete energy level separation depends critically on the value of inter-atomic distance, l_{m-m} . If l_{m-m} is sufficiently large, each valence electron is now described by the atomic wave function. Clearly, the arrangement of the Ag atoms in this case is intuitively corresponds to the non-conducting particles assembly when the cooling temperature is achieved. As presented in **Section 4.1.2**, all of Ag particle systems become non-conducting when $T = 223$ K (the lowest temperature in this study) is reached. It shall be noted that, hexane solvent is used as the suspension medium in this work, any ground state wave function behaviour observed comes from the Ag nanoparticles themselves. Edwards *et al.*, suggested that the electrons of the particle can definitely move from one site to another within the particle, however the net electric current flow E_i would surely not be possible in this condition [48]. There is little chance that the E_0 to go through the Ag sample if all of the particles are 'crystallised'. However, if a 'polar' ionic medium is used instead, this would have obviously enabled the passage of electric current, but this is not the case in this work. This means that, electron conduction does not cause polarisation within the assembly of the non-interacting particles at this low temperature.

The Mott-Hubbard correlation energy, $U_{particle}$ that occurs at $T = 294$ K has been discussed in the previous section, and this aspect can also be highlighted in the cooling state for the isolated Ag particles. The Coulomb interactions between Ag particles play a dominant role in the polarisation mechanism in the system. The upper and lower Hubbard bands indicate that for large values of l_{m-m} in this work, the Coulomb interactions have been split into the electronic bands and so that an electron's energy can either rest in a full band or an empty one [8, 48, 49]. Therefore, if the Ag particles are separated such that l_{m-m} is comparable to or less than 185 nm, as discussed by Gaidarzhy *et al.* [5], the

Ag particles will surely have metallic characteristics at $T = 223$ K. However, it is found that the l_{m-m} is less than 185 nm as proven by the transmitted resonance response plots, as discussed in **Sections 5.1.1.2** and **5.2**. This gives a continuous changes for conductive (mesoscopic) to zero conductive (microscopic) Ag particle regimes. If the l_{m-m} is more than 185 nm, the electrons are completely not free to move at this temperature within this regime. In other words, the role of Coulomb gap was believed to control the electron localisation in low-temperature system [18]. Obviously, the lower temperature dependence is expected for the 'freeze' of the hop-over of electrons as the density of localisation electron states near the E_F is finite and constant in mesoscopic particle regime. As the temperature of sample cools down, the electron in the wave function freeze and thus immediately destroy metallicity leading to the zero conductivity.

The Ioffe-Regel criterion is also applies at low temperatures that leads to the temperature dependence of mean free path of electron ξ . This is of course relevant to the case of our Ag particles since the hallmark of the conductivity reduction criterion is strongly dependent on the temperature of the system when $n \geq n_c$ [52]. Since the conductivity of mesoscopic particles decreases with decreasing temperature for system when $n \geq n_c$, the corresponding $\xi(T)$ also decreases with decreasing temperature accordingly. Furthermore, the Fermi vector of $k_F \propto n^{1/2}$ is completely temperature independent by definition. This holds well that $n_c(T)$ increases with decreasing temperature where non-metallic could be observed even in high nuclearity of mesoscopic Ag particle systems. The situation leads to a conclusion that the Ag particles conductivity is changed monotonically with a function of temperature which eventually decreases with decreasing temperature for $T \leq T_F$.

According to the Mott's prediction at absolute zero of temperature $T = 0$ K, as the inter-particle distance continuously increased, there will be a sharp transition from a metallic to non-metallic states in which at some point there is no conduction at all would occur [50]. Nevertheless, this is not the case observed in this system as the lowest temperature

is only down to 223 K. The sensitivity limitation of the cavity as well as the volume fraction of Ag particles used in this study are probably too small to allow the observation for complete electron localisation. These pronounced limitation makes it difficult to judge the metallicity of microscopic and even half of the mesoscopic Ag samples at low temperatures. The amount of Ag particles contributing to the dielectric response was forty times less than that measured in powder form. The total number of Ag nanoparticles present is not the same in suspension form. It is believed that the particle electrons at such a low total particle volume might 'crystallise' and become localised once in the medium. Nonetheless, the quantisation of continuum electronic energy level of macroscopic Ag caused by the microscopic size of the Ag does lead to the discrete energy level distribution. The morphological changes to spherical symmetry of microscopic Ag does impose a DOS with significant energy level bunching. Hence, the real metal is therefore proved to have continuous reduction of σ_{eff} and having zero conductivity occurred through the alterations in particle size [50] and temperature of the system. It seems that the reduction of the Ag nanoparticle size does not only play the authorised role in the size-dependent behaviour of metal particles. Perhaps the most important facet of this work is the realisation that the observed electronic change is a consequence of the behaviour of the electrons at the particles surface, which is a related function of the particle size. In such a case for SIMIT, one can deduce that the SIMIT should occur below the sensitivity detection limit of the cavity. Therefore, it is beneficial to propose an enhancement of the cavity sensitivity limit which at least to below 1×10^{-4} MHz. These findings call for a more detailed experimental study to unveil the consequences of the SIMIT.

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Chapter 5

Conclusions and Future Work

5.1 Conclusions

The principal aim of this thesis is to investigate the size-dependent dielectric conductivity of mesoscopic and microscopic Ag particles by using both microwave cavity resonator and microwave coaxial probe techniques. As the particle size decreases towards the microscopic size regime where the size of the particles is smaller than the electron mean free path in macroscopic Ag metal, it is proved that the conductivities depend on the size of the particles. This thesis therefore has fulfilled these two main objectives:

1. Emphasising the application of microwave E -field as one of the non-destructive techniques to identify the decrease in the effective microwave conductivity σ_{eff} as the size of Ag particles decreases.
2. Emphasising that the particle size plays the vital key role in the transition from high to lowest conductive states of Ag particles. The size-dependent effect is related to the internal size effect triggered by the increment of scattering of conduction electrons existing on the surface of microscopic particles.

Despite of these, there are some limitations of convergences within the works, that is surprisingly emerged when the methods are used. The highlighted problems identified further from the objectives include:

1. The so-called *size induced metal-insulator transition* (SIMIT) over the Mott's insulator transition theory can not be fulfilled based on their dielectric response due to the sensitivity limitation of the cavity and broadband measurements.
2. For sub-5 nm Ag particles that are well ligated within the microscopic structure and assumed to contribute decisively to the E -field response cannot be determined due to the lack of techniques available.

The consequences imply that conductivity is bound to be size-dependent where the reduction in σ_{eff} of Ag particles can be defined as a function of particle size. From this work, the definition of metallicity for Ag particles can be confusing at some point. Therefore, the lowest metallic conductivity that can be detected above sensitivity limit of the setups at room temperature are set for 5 and 14 nm of Ag particles for cavity resonator and coaxial probe techniques, respectively. At low temperatures (287, 244 and 223 K), such particle sizes are not metallic nor will conduct.

These are comprehensively discussed in **Chapter 4** where all the mesoscopic and microscopic Ag particles are believed to exist as pure metallic Ag (Ag^0) with a solid core structure. For cavity resonator technique, the dielectric response set out the differences between mesoscopic and microscopic Ag particle behaviours based upon the frequency shift (Δf) and bandwidth change (Δf_B) in the resonant cavity upon sample insertion. There are two major implications of this technique can be made: (i) no longer unperturbed reference measurement has to be taken before the sample is inserted in order to invert the measurement and (ii), the shift in frequency at this mode is mainly due to the influence of environment conditions rather than due to the properties of the Ag samples themselves. In this case, we can see that there is shifting in frequency at $T = 294$ K from 2.498 to 2.484 GHz. Meanwhile, when the measurements carried out at the temperature range of $223 \text{ K} < T < 294 \text{ K}$, we found changes in the frequency mode shifted from 2.498 to 2.466 GHz. Using this fact, we can account that the major changes of dielectric properties are particularly due to the changes in ambient temperature in a combination with the particle

size-reduction effect and not due to any external effects. Both of these facts are successfully demonstrated experimentally in this chapter. The σ_{eff} was believed to have a continuous conductivity decrement that should follow the trend of Mott's *Gedanken* graph but not entirely draws the important distinction between metal and insulators for all the temperature measurements especially at $T = 294$ K and $T = 223$ K. The conducting Ag particles are all behave like an insulator as the temperature is reduced down to 223 K. The onset of metallisation also increase as the temperature system decreases. We predicted that the onset of zero conductivity could occur when the mean particle diameter, $d_m < 5$ and > 420 nm at 294 and 223 K, respectively. This adds further evidence that the variation of the onset of zero conductivity is broad and crucially depends on the temperature condition of the size-dependent Ag particle system.

From coaxial broadband measurement (100 MHz - 10 GHz), we observed that the imaginary permittivity ($\varepsilon_{2,eff}$) plays an important role in giving the *D.C.* conductivity of the Ag SIMIT system at 2.50 GHz. The theoretical formulae of Clausius-Mossotti (CM), Maxwell-Garnett (GM) and Bruggeman calculations based on experimental results employed in this work yield convincing arguments for the existence of decrement in dielectric conductivity in the size-dependent Ag particle system. The calculations validate the experimental behaviour observed in these samples. The results confirm that high frequency measurements are invariant through the percolation threshold above the relaxation frequency. The results of CM show that the surface functionality of mesoscopic Ag particles will be different from those of microscopic ones as the value of K_{s1} of ~ 420 nm is 1.18×10^{-9} down to 8.85×10^{-10} S.cm $^{-1}$ when the size is ~ 89 nm. Among the dielectric permittivity approach, MG result provides almost an excellent agreement with Mott's *Gedanken* experiment trend. The electron of the parent site based on MG's calculation slowly becomes insufficiently screened by the electron cloud where the binding energy of the itinerant electron increased. This is equivalent to the polarisation or dielectric catastrophe at the critical particle size when $\sigma_{2,eff}$ is reduced from 1.03×10^{-3} to 1.68×10^{-4} S.cm $^{-1}$. Meanwhile, the Bruggeman results

show that less dense medium (smaller Ag particle size) has higher Bruggeman dielectric constant than denser medium due to the re-normalisation of conductivity caused by the skin-effect. We have reviewed the Mott's insight for delving the experimental results by emphasising the related theory of Mott-Hubbard correlation energy, Goldhammer-Herzfeld and Ioffe-Regel criteria in the third section of **Chapter 4**. These pre-quantum theories are briefly explained in this chapter which described the conditions of metal and non-metal particles emphasising the pivotal role of microscopic particle properties in dictating the conductive and non-conductive status of Ag particles both at $T = 294$ K and $T < 294$ K.

As we reviewed the discussions in **Chapter 3**, the prepared mesoscopic and microscopic Ag particles exhibit exciting particle growth mechanisms where the surface being coated by DAXAD 19 in water medium and transferred to the hexane medium which coated with octadecylamine (ODA) by the interphase transporter. The high frequency measurements in this work require the transfer of Ag particles from a water (polar) medium to a hexane (non-polar) environment in order to maximise the benefits offered by hexane solvent based on microwave processing considerations. The size and morphology of Ag particles were found to be particularly sensitive to the variation of parameters during the synthesis. Significant effort has been put in the exploration of the origin of size and morphological changes of the particles by using the TEM, HRTEM, PXRD, UV-Vis and XPS techniques. The size-dependent electronic properties can be understood further based on the experimental study of the size and structure of amine-protected Ag particles. A straightforward synthesis of large amount of Ag particles with controllable range of sizes promises to make this solution synthesis technique to be very useful for further research and experimental developments. After the discussion of synthesis of Ag particles is presented, the emphasising of the nature of ODA ligands in stabilising the Ag particles is proved to be very susceptible to oxidation which is important where all electrical properties measurements carried out in this work are coming from Ag^0 system. The Ag particles are proved to be inert and have long term stability even after the phase transfer process for both mesoscopic and larger microscopic

size regimes except for ultra-fine microscopic Ag particles with $d_m < 5$ nm. It is known that this range of microscopic Ag particles will simply produce silver oxide on the particle surface when exposed to the heat in open air. Therefore, we proved that Ag particles of this tiny size are semi-stable and partially crystalline that has been overshadowed by the excess amount of amorphous ODA ligand. A comparison between pure metallic Ag particles and Ag oxides is made based on the qualitative and quantitative analysis of elements presents in both systems by means of XPS analysis.

Overall, all the discussions involved lead to the conclusion that a precise determination where SIMIT take place is impossible from these measurements as the sensitivity limitations are too high. The SIMIT transition can be uniquely defined at definite size below the sensitivity limit of the setups. We do observe a gradual increment in the splitting of the energy wave function (DOS) at E_F with significant variations raised upon not only by the influence of the microscopic grains but also authorise by the electron-electron interaction. These should shed new light on the directions for further improvements in understanding the behaviour of pure individual metallic systems in the characterisation techniques as well as in the implementation of device system when SIMIT is reached.

5.2 Future Works

The future directions of this work can be as follows:

1. It is instructive to improvise the cavity resonator that would enable lowering the sample temperature even further and make the cold temperature measurement system setup more effective, powerful and easy to handle.
2. Most work has so far concentrated on electrical properties of Ag system. An important future direction is therefore should be the measurement of magnetic properties through the possible application of TE_{0n0} modes. The measurements of the permittivities have already indicated the Mott's size-induced metal-insulator transition of

Ag particles. The magnetic properties of Ag particles will undoubtedly yield the same important clues about the values of permeabilities and the physics' of Mott's SIMIT transition.

3. If Ag system does gain permittivity changes when SIMIT is reached, other transition metals commonly used in electronic device applications including Cu and Au from periodic table should also be considered for the measurements. If SIMIT's dielectric properties of these metals are fulfilled by these techniques, we may envision the periodic electron behaviour changes of the elements at both room and low temperature measurements.
4. Providing proof of Mott *Gedanken* graph from several complementary techniques should also benefit for SIMIT analysis. The method of combining complementary techniques with our current work should sufficiently show the reliability of our microwave measurements. These complementary techniques should thus rule out the physics of SIMIT as the 'consistent' is totally nailed down for these established instruments.