



Dynamics of grain boundaries in two-dimensional colloidal crystals

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Abstract

The dynamics of grain boundaries in two-dimensional colloidal crystals is studied using optical microscopy and holographic optical tweezing. First, grain growth in a polycrystalline monolayer is investigated. The bond-orientational correlation function is found to satisfy scaling features predicted for systems containing random domain walls. The time-evolution of the correlation length indicates abnormal grain growth, which is shown to be due to the preferential coarsening of the large angle grain boundaries. Next, the segregation of impurities to grain boundaries is studied by embedding large spherical impurities in a polycrystalline monolayer of small colloidal spheres. The segregation behaviour is found to be in very good agreement with equilibrium grain boundary segregation, which enables the direct measurement of the free energy of adsorption. Near saturation, the formation of clusters of impurities in the boundary region is found to strongly depend on the size ratio between the impurities and the small particles, due to non-additivity effects and geometrical constraints imposed by the lattice. In order to characterise the geometry of grain boundaries, a new method to extract their geometrical features directly from microscopy images is developed. This method is used to determine the local normal direction, tangent direction and curvature of a grain boundary in a two-dimensional colloidal polycrystalline material. Further insight between the geometry and dynamics of grain boundaries is gained by analysing the shrinking kinetics of circular grain boundaries created using optical vortices. Upon increasing misorientation, these strongly curved boundaries exhibit a geometrically determined transition between pure sliding and shrinkage. In addition, the shrinking rate is found to decrease when increasing the misorientation. Dislocation reactions, which cause the reduction of the grain boundary length, are directly visualised and correlated to the kinetics of shrinkage. Finally, the dynamics of the particles during the migration of circular grain boundaries is analysed. The presence of dynamical heterogeneities is shown to be strongly determined by geometry, especially in the case of coincident site lattice boundaries where coincident particles exhibit no motion during grain boundary migration. The particle displacements involved in the motion of dislocations, which constitute the elementary mechanism of grain boundary migration, are revealed.

Declaration

This thesis is submitted for the degree of Doctor of Philosophy in Physical and Theoretical Chemistry at the University of Oxford. No part of this thesis has been accepted or is currently being submitted for any degree, diploma, certificate or other qualification in this University or elsewhere. This thesis is wholly my own work, except where indicated.

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Chapter 1

General introduction

Metallurgy is one of the earliest industries, with its emergence dating back to 5000 BC based upon evidence of copper smelting activities at that time [1]. Improving the strength of metals by alloying, which has been known since the Bronze age [2], and the subsequent discovery of iron in Antiquity [3], have both been major steps to make longer lasting materials in the ancient times. Nevertheless, the mass production of steel was only established during the Industrial Revolution with the invention of the converter [4]. Nowadays, metals are irreplaceable materials in numerous technological applications due to their toughness, strength, electrical conductivity and stability over a wide range of temperatures [5]. The current issues of metallurgy include making lighter metals to design energy-efficient systems [6], increasing the resistance of metals to extreme external conditions [5] and improving their bio-compatibility for medical applications [5,6]. A more recent challenge is to make metallurgy part of a “circular economy”, where extraction of natural resources and waste are minimised by recycling old products [7]. This implies that new techniques must be developed to de-alloy, de-laminate or de-coat old metallic products at a large scale [7].

Despite the very early mastering of the techniques to produce metals, the fundamental understanding of their properties is based on more recent scientific concepts. Indeed, it was only in the early 19th century that advances in thermodynamics enabled a better understanding of the thermo-chemical aspects of the fabrication process of metals [8]. This led to major technological developments in the mid-19th century such as the Bessemer process [4], which involves blowing air through molten iron to oxidise and remove the impurities it contains. The development

of X-ray diffraction in the early 20th century has been key to gain insight at a smaller scale and highlight the crystalline structure of metals [9]. The direct visualisation of the periodic arrangement of atoms in metals, however, was not achieved until the early 1980s with the use of scanning tunneling microscopy [10]. In this respect, metals may be considered as a particular class of crystalline materials and metallurgy can be seen as a branch of crystallography. Despite this, predicting the properties of alloys from those of their elementary metallic compounds require many other factors to be taken into account beyond geometry, including size ratios, electro-negativity ratios, chemical bonding between the atoms and the presence of defects in the crystalline structure [11].

1.1 Grain boundaries

Perfectly crystalline materials are extremely rare in nature as most materials contain impurities or defects [12,13], which disrupt the crystalline order. Many materials are in fact polycrystalline as they are made of a collection of different crystals called grains [12,13]. Everyday examples of polycrystalline materials include the vast majority of metals, ceramics, rocks and ice. The surface between two adjacent grains is called a grain boundary, and in polycrystalline materials the grain boundaries form a network [12,13]. Importantly, the mechanical properties of polycrystalline materials are not primarily controlled by their precise chemical composition, but by their average grain size [12]. Surprisingly, the strength of polycrystalline materials is usually higher than that of the corresponding pure crystalline material. This is due to the fact that the presence of grain boundaries leads to a resistance against deformation by stopping the propagation of defects in the material, which is known as the Hall-Petch effect [14,15]. However, when the grain size becomes too small, the strength of a material decreases as deformations are enabled by a process termed grain boundary sliding [14,16], which is often referred to as the reverse Hall-Petch effect. As a consequence, controlling the grain size is absolutely central to tuning the mechanical properties of materials in between the two extreme cases corresponding to maximum strength [15] and superplasticity [17].

A grain boundary is different from more common interfaces such as oil/water or liquid/vapour interfaces as it separates two grains of identical chemical compositions and densities. Indeed, the only difference between the two grains is their crystallographic orientation [12,18],

which implies that the geometry and structure of grain boundaries can be understood from a pure crystallographic point of view [18]. In addition, grain boundaries are also dynamic interfaces, which are able to move when subject to forces [12]. This process, termed grain boundary migration, is the main contribution to the phenomenon of grain growth in polycrystalline materials, and is usually spontaneously driven by capillary forces due to the curvature of grain boundaries [12]. It is clear that grain boundary migration is achieved by the rearrangement of atoms at the microscopic level, which is the starting point of many early theories of grain boundary migration [19]. However, testing these models by directly probing the dynamics of atoms during grain boundary motion is extremely difficult due to the small time and length scales involved [20, 21]. Hence, experimental advances in the field of grain boundary dynamics can emerge from studies on model systems, which facilitate the preparation, manipulation and observation of such grain boundaries in real space and time. Usual model polycrystalline systems include bubble rafts [22], dusty plasmas [23], block copolymers [24] and colloidal systems [25].

1.2 Colloidal model systems

Colloids consist of small solid particles with a typical size ranging from 10 nm to 10 μm , dispersed in a liquid solvent [26]. Examples of natural colloids include clays, opals and bacterial suspensions, while paints, India ink and toothpaste are examples of synthetic colloids. Colloidal particles are much larger than the molecules of the solvent but small enough to exhibit Brownian motion, which is the random motion of the colloidal particles induced by their collisions with the thermally agitated solvent molecules [26]. Colloids can be used as convenient model systems for atomic and molecular matter due to their inherent properties. Indeed, assemblies of colloidal particles exhibit analogous phase behaviour to their atomic counterparts [27, 28], as Brownian motion enables them to explore the available phase space, in the same way that thermal agitation does in atomic and molecular systems. Moreover, colloidal particles of various materials and shapes, including rods [29], dumbbells [30] and cubes [31], can be synthesised. Furthermore, their interactions can be tuned via modification of the solvent, the addition of salt or depletant [32], the use of magnetic particles that interact with dipolar forces [33], or patchy particles to create specific and directional interactions [34]. These unique properties enable the study of various aspects of phase behaviour and self-assembly of colloidal model systems, including liquid crystalline phases [35], melting [33], “colloidal molecules” [36] and plastic crystals [37].

When the packing fraction of colloidal spheres is high enough, they crystallise into periodic lattices and a colloidal crystal is formed [27]. As such, the role of the packing fraction in colloidal crystallisation is analogous to the inverse of the temperature in the crystallisation of atomic systems. If crystallisation is forced to happen quickly, different grains are formed together with grain boundaries similar to their atomic equivalent [38,39]. The obtained colloidal polycrystalline material can be used as a model system for the study of grain growth and grain boundary dynamics [38,39]. Moreover, confining the colloidal particles to a monolayer enables two-dimensional colloidal crystals or polycrystalline materials to be obtained. Even though two-dimensional systems can have a very different equilibrium phase behaviour from that of their three dimensional equivalent [40], their use as model polycrystalline systems has many advantages. Most two-dimensional colloidal systems form hexagonal crystals at high packing fractions [38], making them suitable model systems for the study of graphene sheets [41] or two-dimensional boron-nitride [42], inherent to their equivalent crystallographic structures. Moreover, these systems are very suitable for the study of grain boundaries as their geometrical description requires fewer parameters than in three-dimensional systems [12,43].

A particular advantage of studying colloidal solids, be they crystalline or polycrystalline, is that they belong to the class of “soft matter” as their Young modulus is smaller by a factor of about 10^{12} than that of molecular and atomic solids [44]. For this reason, they can be readily manipulated and deformed using small external forces generated using e.g. optical tweezers [45], which opens up the possibility of directly interacting with colloidal grain boundaries [46]. Finally, as the time scales governing colloidal systems are of the order of seconds compared to picoseconds for atoms, the direct observation of particles in a colloidal solid can be performed in real space using simple optical video-microscopy [47]. This offers the unique opportunity to directly probe the dynamics of the colloidal particles during the migration of a colloidal grain boundary.

1.3 Scope of the thesis

In this thesis, the dynamics of grain boundaries in two-dimensional colloidal crystals is studied using optical video-microscopy. Polycrystalline monolayers are prepared by confining the colloidal particles to a monolayer by gravity. Grain boundaries are studied as part of a network in a pure polycrystalline monolayer or with added larger colloidal particles, which act as impurities

interacting with the grain boundaries. In addition, circular grain boundaries in a single crystal are created using holographic optical tweezers and their shrinking and particle dynamics are studied in great detail.

Firstly, the basic concepts and methods used throughout this thesis are presented in chapter 2. In particular, a description of the geometry and structure of grain boundaries in two-dimensional hexagonal lattices is provided together with a brief introduction to the physics of colloidal systems. The experimental details are presented, including the methods of sample preparation, image analysis and optical tweezing.

In chapter 3, grain growth in a colloidal polycrystalline monolayer is addressed. The coarsening process is monitored using the bond-orientational correlation function and the grain boundary structure is quantified by measuring the grain boundary character distribution. The origin of the abnormal growth law is discussed based on the evolution of the grain boundary network during coarsening. The abnormal growth law is derived using scaling arguments and is directly compared to the data.

The segregation of impurities at grain boundaries in a polycrystalline system is studied in chapter 4. Embedding larger colloidal particles in the colloidal polycrystalline monolayer enables the preparation of a model colloidal alloy with interstitial and substitutional impurities, which adsorb at grain boundaries. The adsorption isotherms are measured and compared to the Langmuir-McLean model of equilibrium grain boundary segregation. The differences between the clusters of impurities adsorbed at grain boundaries for both kinds of impurities are discussed in light of non-additivity effects and geometrical constraints imposed by the lattice.

Next, in chapter 5, a method to determine the local geometrical features of grain boundaries directly from microscopy images is presented. In particular, the use of principal component analysis to calculate the tangent plane, normal direction and local curvature of grain boundaries is discussed. The method is first tested on artificially generated grain boundaries and then directly applied to colloidal grain boundaries imaged with optical microscopy.

In chapter 6, the shrinking kinetics of circular grain boundaries is investigated. Such grain boundaries are prepared with optical vortices and spontaneously shrink once the vortex is turned off. The different processes involved in the shrinkage are directly visualised and the dependences of the shrinking rate on initial misorientation and curvature are discussed. The role of the initial

curvature of the grain boundary in the existence of a sliding to shrinking transition is explained. The dislocation reactions which enable the reduction of the grain boundary length are directly visualised and used to elucidate the shrinking mechanism.

Finally, the dynamics of the particles during the shrinkage of circular grain boundaries is studied in chapter 7. The relation between the dynamical heterogeneities and the structure of the grain boundary is discussed, and highlighted for the special case of a coincident site lattice boundary. The particle displacements involved in dislocation motion, which is the elementary mechanism of grain boundary migration, are revealed.

Chapter 2

Theoretical background and experimental methods

ABSTRACT

In this thesis, the dynamics of grain boundaries in polycrystalline monolayers of colloidal particles is investigated. This chapter introduces the basic concepts and experimental methods common to all subsequent chapters. It starts with a description of the geometry and structure of grain boundaries in two-dimensional hexagonal lattices. Next, the physics of colloidal particles and colloidal crystallisation in the case of hard core interactions are introduced. Finally, the preparation of the polycrystalline colloidal model system and the main experimental techniques including video-microscopy and holographic optical trapping are described.

2.1 Grain boundaries in two-dimensional polycrystalline solids

2.1.1 Two-dimensional hexagonal crystals

Perfect crystals are structures exhibiting an infinite repetition of a structural unit made of one or several types of atoms, called the primitive cell [48]. This work deals with two-dimensional (2D) hexagonal crystals with one type of atom for which the primitive cell is defined by the two vectors

$$\begin{aligned}\vec{a}_1 &= a\hat{x}, \\ \vec{a}_2 &= \frac{a}{2}\hat{x} + \frac{a\sqrt{3}}{2}\hat{y},\end{aligned}\tag{2.1}$$

where a is the lattice spacing and $(\hat{x}, \hat{y})$ are the two unit vectors in the x - and y -directions, as sketched in figure 2.1(a). The crystal is then described by a lattice where the position $\vec{r}_i$ of a site i containing an atom can be obtained by

$$\vec{r}_i = n_i\vec{a}_1 + m_i\vec{a}_2,\tag{2.2}$$

where n_i and m_i are integers, termed the crystal coordinates of the site i (see figure 2.1(a)) [48]. The expression of the primitive cell vectors in terms of crystal coordinates is then

$$\begin{aligned}\vec{a}_1 &= (1, 0), \\ \vec{a}_2 &= (0, 1),\end{aligned}\tag{2.3}$$

and $\vec{r}_i = (n_i, m_i)$ in this notation.

The topology of the lattice can be analysed using a Delaunay triangulation, which is illustrated in figure 2.1(b). Such a construction defines the nearest neighbours of a lattice site i as the sites directly connected to i by edges of the triangulation. In a perfect 2D hexagonal lattice, the angle between the bond vectors connecting a site i to each of its six nearest neighbours are multiples of $\pi/3$ as shown in figure 2.1(b). The structure is thus invariant under rotations of $k\pi/3$, where k is an integer, which is referred to as a six-fold symmetry. One can also define the Voronoi tessellation, whose cells are hexagons containing one lattice site each for a perfect

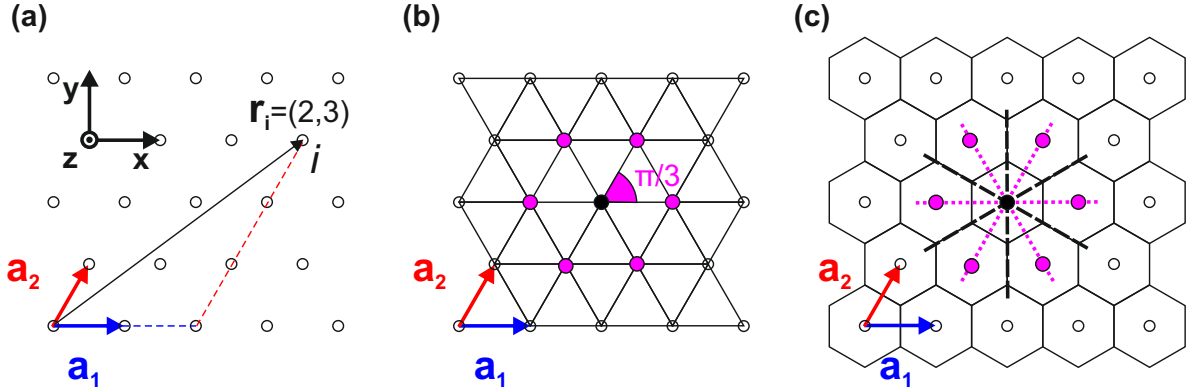


Figure 2.1: (a) Any point $\vec{r}_i$ of a 2D hexagonal lattice can be obtained by integer combinations of the two primitive cell vectors $\vec{a}_1$ and $\vec{a}_2$. (b) Delaunay triangulation of a 2D hexagonal lattice showing that each lattice point (black) has six nearest neighbours (magenta), which form a six-fold symmetric structure. (c) The hexagonal cells of the Voronoi tessellation of the same lattice. The dashed lines correspond to the different axes of reflection symmetry of the structure and make angles with $\vec{a}_1$ that are $0 \bmod \pi/3$ (magenta) or $\pi/6 \bmod \pi/3$ (black).

2D hexagonal lattice, as shown in figure 2.1(c). From the same figure it can also be seen that this lattice features different axes of reflection symmetry with orientations $0 \bmod \pi/3$ or $\pi/6 \bmod \pi/3$.

2.1.2 Dislocations

Most of the time crystals are not perfect as they contain defects that break the periodicity of the lattice. In particular, real crystals contain dislocations, a specific class of defects which, in 2D hexagonal lattices, consist of two neighbouring sites having 5 and 7 nearest neighbours respectively (see figure 2.2(a)) [49,50]. Isolated sites with 5 (7) nearest neighbours are termed positive (negative) disclinations, so that a dislocation can be seen as a pair of opposite disclinations [50]. Dislocations are characterised by a Burgers vector which quantifies the deformation of the lattice [49,50]. Its determination is illustrated in figure 2.2(a) and (b), using the right-hand and finish-start convention (RH/FS) [49,51]. This first consists of drawing a closed circuit counter-clockwise around the dislocation in the distorted lattice as shown in figure 2.2(a). Secondly, one draws the same circuit in the corresponding perfect lattice as in figure 2.2(b). In the latter case, there is a closure failure from the finish to the start of the circuit that corresponds to the Burgers vector $\vec{b}$ as shown in figure 2.2(b). Note that $\vec{b}$ is a pseudo vector as its sign depends on the choice of orientation convention, which can be different from the one used here.

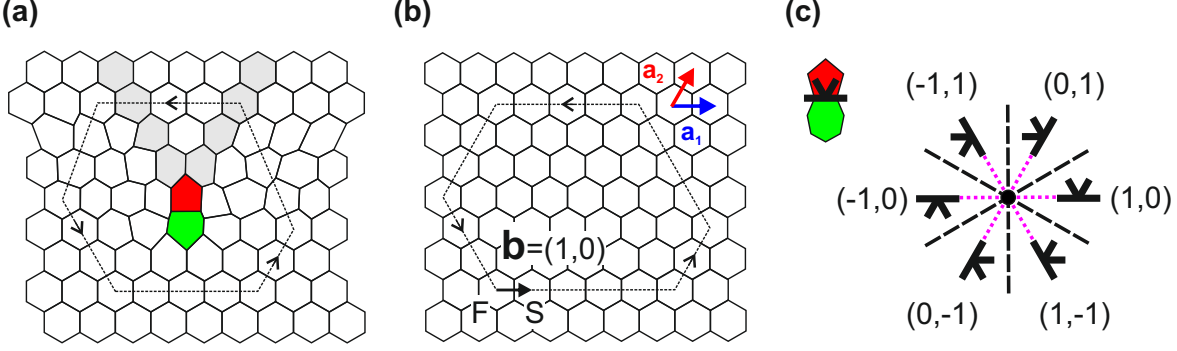


Figure 2.2: (a) A dislocation in a 2D hexagonal crystal consisting of two sites with coordination 5 (red) and 7 (green). It is created by the insertion of two semi-infinite rows of crystal (shaded in grey). The Burgers circuit is drawn counter-clockwise (black dashed line). (b) Closure failure of the Burgers circuit corresponding to (a) in the perfect crystal. The Burgers vector connects the finish (F) to the start (S) of the circuit and corresponds to $\vec{a}_1$ in this case. (c) Notation for the Burgers vector to symbolise the insertion of two semi-infinite rows on the side of the 5-coordinated site (top left and see (a)). The six Burgers vectors of magnitude a with the axes of reflection symmetry of the 2D hexagonal lattice as in figure 2.1(c).

The Burgers vector indicates that a dislocation is a topological defect: it introduces a non-continuous lattice deformation, as it cannot be removed by a simple rearrangement of the sites. Here, this deformation consists of two inserted semi-infinite rows of crystal as highlighted in figure 2.2(a) [52]. In a 2D hexagonal lattice, there are six possible Burgers vectors of magnitude a : $(\pm 1, 0)$, $(0, \pm 1)$, $(\pm 1, \mp 1)$ in crystal coordinates, as illustrated in figure 2.2(c). Burgers vectors of higher magnitudes do exist but are rarely observed in real crystals due to their relatively high energetic cost. In figure 2.2(c) and in the rest of this thesis, the Burgers vector is represented by a large bar parallel to $\vec{b}$ and two small bars symbolising the insertion of the two half rows of crystal on the left hand-side of $\vec{b}$, which corresponds to the side of the 5-coordination site in the dislocation. Note that for every given Burgers vector, there is always a symmetry axis of the crystal parallel to it, and another one perpendicular to it. For instance, $\vec{b} = (1, 0)$ is parallel to the axis of orientation 0 and perpendicular to the axis of orientation $\pi/2$ (see figure 2.2(c)).

As a dislocation introduces deformations in the crystal, it has an associated elastic energy given by

$$E = \frac{b^2 K}{8\pi} \ln \frac{R}{a_c} + E_c, \quad (2.4)$$

where b is the magnitude of the Burgers vector, K the Young modulus, R the system size, a_c

is the radius of the core of the dislocation which is typically several lattice spacings, and E_c is a constant referred to as the core energy [50, 52]. The logarithmic divergence of E with the system size R corresponds to the non-continuous deformation introduced by inserting two half-rows of crystal whose lengths scale as R . From equation (2.4), we see that the elastic energy of one dislocation in a crystal is proportional to b^2 . Hence, most of the dislocations encountered in the following have $\|\vec{b}\| = a$ as larger magnitudes are energetically much more costly. The interaction energy of two dislocations with Burgers vectors $\vec{b}_1$ and $\vec{b}_2$ separated by a bond vector $\vec{r}_{12}$, is [53, 54]

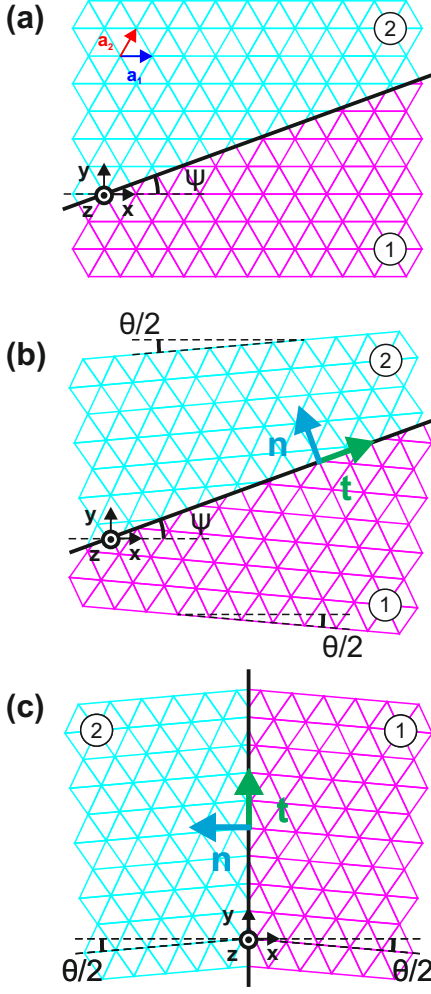
$$E_{12}(\vec{r}_{12}) = -\frac{K}{4\pi} \left[\vec{b}_1 \cdot \vec{b}_2 \ln \frac{r_{12}}{a_c} - \frac{(\vec{b}_1 \cdot \vec{r}_{12})(\vec{b}_2 \cdot \vec{r}_{12})}{r_{12}^2} \right] + E_c(b_1^2 + b_2^2). \quad (2.5)$$

This indicates that if $\vec{b}_1 = \vec{b}_2$, E_{12} is minimum when the Burgers vectors are orthogonal to $\vec{r}_{12}$. Also, when $\vec{b}_1 = -\vec{b}_2$, the dislocations attract each other. Note that in equation (2.5), one should in principle include a term proportional to $\ln R$ as in equation (2.4) for each dislocation. However such a term does not depend on $\vec{r}_{12}$ so it is not written here [53]. Moreover, in the case where $\vec{b}_1 = -\vec{b}_2$, this term exactly vanishes as the total Burgers vector is $\vec{0}$: this situation can thus be obtained from a continuous deformation of a perfect lattice so its energy cannot diverge with $\ln R$ [52].

2.1.3 Geometry of grain boundaries

The vast majority of real materials are not simple crystals containing only dislocations as they can in fact consist of different crystals termed grains. The material is then said to be polycrystalline and the interfaces between the grains are called grain boundaries (GBs). In 2D, a GB is a line characterised by two parameters: the misorientation angle, θ , which is the difference between the orientations of the two grains and the inclination angle, ψ , which corresponds to the direction of the GB [12, 55]. The misorientation θ and the inclination ψ are geometrically defined according to the GB parametrisation illustrated in figure 2.3(a) and (b) [12, 55].

The GB in figure 2.3(b) is called a tilt GB as the axis of rotation, $\hat{z}$, is perpendicular to the boundary normal, $\hat{n}$. The case where $\hat{l}$ is parallel to $\hat{n}$ corresponds to twist GBs, but this only exists in three dimensions (3D) [12]. When the GB line coincides with an axis of symmetry of the lattice (see figure 2.1(c)), the GB is called a symmetrical tilt [12]. This happens for $\psi \equiv 0$



Starting from a perfect reference lattice with $\vec{a}_1 = \hat{x}$ one draws a line, which corresponds to the GB and separates the lattice into two crystals ① and ② in magenta and cyan. The angle between $\hat{x}$ and the GB is the inclination ψ . In this example, $\psi = \pi/9$.

One rotates the lower crystal ① by $\theta/2$ clockwise and the upper crystal ② by $\theta/2$ counter-clockwise, where θ is the misorientation angle, 10° here. The unit vector $\hat{z}$ corresponds to the tilt axis. The boundary unit normal $\hat{n}$ and tangent $\hat{t}$ are such that $(\hat{x}, \hat{n})$ and $(\hat{t}, \hat{n})$ are oriented counter-clockwise. This convention is adopted throughout this work.

An example of symmetrical tilt GB with $\theta = 10^\circ$ and $\psi = \pi/2$, which corresponds to a symmetric direction of the 2D hexagonal lattice.

Figure 2.3: (a)-(b) Parametrisation of a GB in terms of the inclination and misorientation. (c) Illustration of a symmetrical tilt GB.

$\text{mod } \pi/3$ or $\psi \equiv \pi/6 \text{ mod } \pi/3$ and the case $\psi = \pi/2$ is illustrated in figure 2.3(c). Generally, GBs are separated into two classes depending on the value of the misorientation θ . Small angle grain boundaries (SAGBs) refer to GBs with a small misorientation angle, typically $\theta \lesssim 15^\circ$, otherwise they are classed as large angle grain boundaries (LAGBs) when $\theta \gtrsim 15^\circ$. Note that due to the six-fold symmetry, $\theta \in [0; 30^\circ]$.

For specific misorientation angles, a lattice whose sites belong to both neighbouring crystals can be formed and this is named the coincident site lattice (CSL) [18]. A CSL is characterised by a Σ -value, introduced in 1904 by Friedel [56, 57], which is the ratio between the area of the CSL primitive cell and the one of the crystal [18]. In the case of 2D hexagonal lattices, the $\Sigma 7$ CSL for $\theta = 21.8^\circ$ is shown as an example in figure 2.4(a) and (b). All the CSLs for the 2D hexagonal lattice are listed in the table in figure 2.4(c) with the corresponding Σ -values [58].

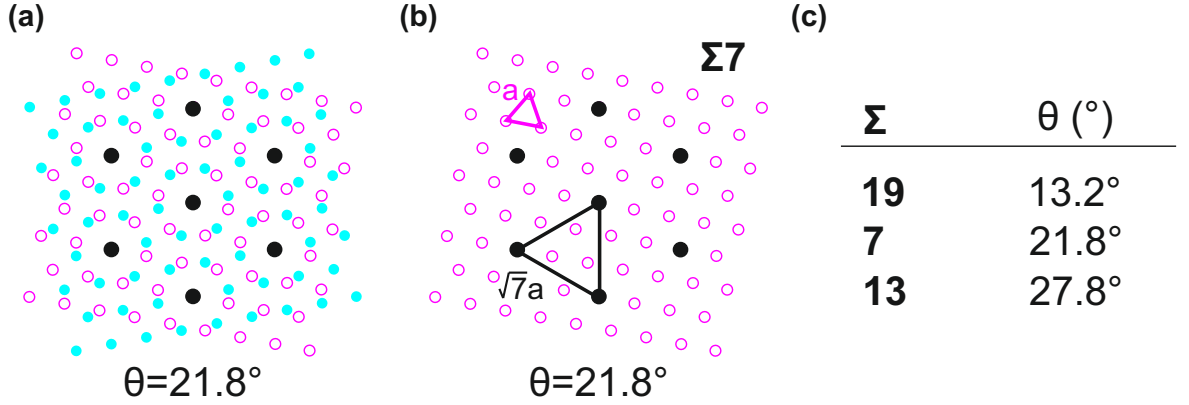


Figure 2.4: (a) Two lattices with misorientation $\theta = 21.8^\circ$ (magenta and cyan) have common sites (black) forming a coincident site lattice (CSL). (b) The area of the primitive lattice cell of the CSL (black triangle) is 7 times larger than the one of the original lattice (magenta triangle) so the Σ -value is 7 in the case of $\theta = 21.8^\circ$. (c) Table with the three CSLs for $\theta \in [0; 30^\circ]$ and their Σ -values.

2.1.4 Dislocation structure of grain boundaries

In 2D, a GB can be modelled by a line of individual dislocations [55]. The dislocation content of a given GB is dictated by a combination of energetic, geometric, and topological constraints. For a given dislocation content, the Frank formula gives a topological constraint by relating the sum of the Burgers vectors of the dislocations along a portion $\vec{r}$ of a GB with tilt axis $\hat{l}$ to its misorientation θ [18, 59, 60]:

$$\sum_i \vec{b}_i = (\vec{r} \times \hat{l})\theta. \quad (2.6)$$

Note that the arrangement of dislocations is not uniquely determined by the Frank formula, which only constrains the sum of the Burgers vectors. Among all the possibilities that satisfy equation (2.6), the most probable is the one with the lowest energy [18]. The following illustrates two configurations of dislocations which are commonly encountered in real polycrystalline materials in the case of 2D hexagonal lattices.

Consider a portion of a GB which contains N identical dislocations of Burgers vector $\vec{b}$. For the situation that $\vec{r} = r\hat{t}$ and $\hat{l} = \hat{z}$, equation (2.6) reduces to

$$N\vec{b} = -r\theta\hat{n}, \quad (2.7)$$

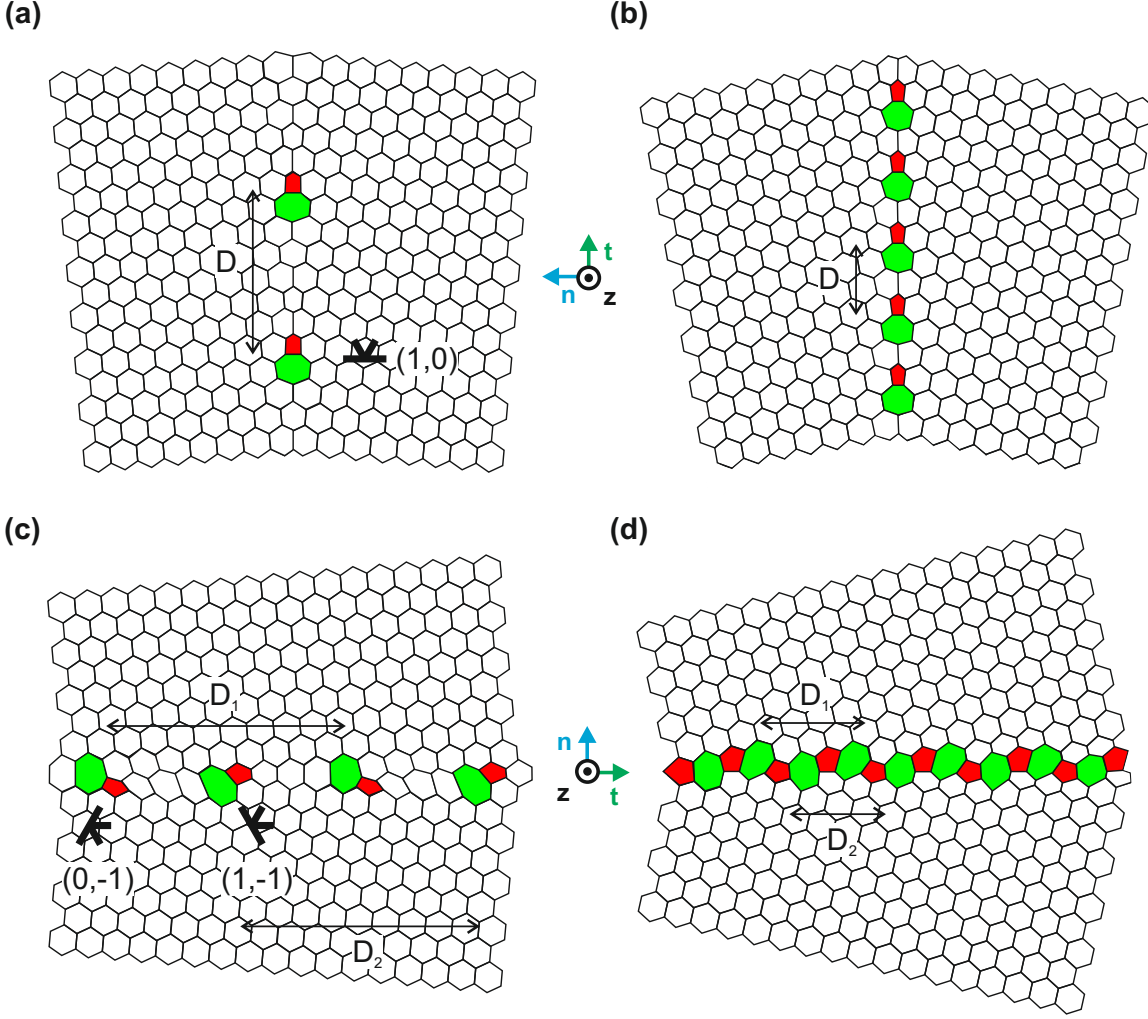


Figure 2.5: (a) Small angle symmetrical tilt GB ($\psi = \pi/2$ and $\theta = 10^\circ$) populated by a single type of dislocations $\vec{b} = (1, 0)$ separated by a large distance D . (b) Large angle symmetrical tilt GB ($\psi = \pi/2$ and $\theta = 20^\circ$). The dislocations are the same as in (a) but they are separated by a smaller distance D . (c) Small angle symmetrical tilt GB ($\psi = 0$ and $\theta = 10^\circ$) populated by two types of dislocations $\vec{b}_1 = (0, -1)$ and $\vec{b}_2 = (1, -1)$ separated by large distances D_1 and D_2 . (d) Large angle symmetrical tilt GB ($\psi = 0$ and $\theta = 25^\circ$) with the same dislocations as in (c). The distances D_1 and D_2 are so small that the GB looks like a continuous wall of dislocations.

which indicates that $\vec{b}$ is perpendicular to the GB and opposite to the normal, within the RH/FS convention and with $(\hat{t}, \hat{n}, \hat{l})$ orientated counter-clockwise. This configuration minimises equation (2.5) as two consecutive dislocations on the GB have $\vec{b}$ perpendicular to their bond vector, which is aligned with $\hat{t}$. In 2D hexagonal lattices, having $\vec{b}$ along $-\hat{n}$ is possible for symmetric tilt GBs with $\psi \equiv \pi/6 \pmod{\pi/3}$ as there exist Burgers vectors orthogonal to these directions (see figure 2.2(c)). For example, in the case of a symmetrical tilt GB with inclination $\psi = \pi/2$, $\hat{n} = -\hat{x}$, so the GB is populated by dislocations of Burgers vector $\vec{b} = (1, 0)$ (see figure 2.5(a)).

Furthermore, by taking the dot product of equation (2.7) with $\hat{n}$, one can get the distance between two consecutive dislocations as a function of the misorientation

$$D(\theta) = \frac{r}{N} = \frac{b}{\theta}, \quad (2.8)$$

where one uses the fact that $\vec{b} \cdot \hat{n} = -b$ with b being the magnitude of $\vec{b}$. Equation (2.8) indicates that the dislocations become closer as the misorientation θ increases. In the SAGB regime, where θ is small, the distance between dislocations is large, so that the GB looks like a line of sparse dislocations. This is shown in figure 2.5(a) where $\theta = 10^\circ$. In the LAGB regime, the distance between dislocations becomes much smaller as illustrated in figure 2.5(b) where $\theta = 20^\circ$. The crossover between the SAGB and LAGB regime is usually considered to be $\theta \simeq 15^\circ$, which corresponds to a point where two consecutive dislocations start having nearest neighbours in common.

In some cases, the Frank formula cannot be satisfied with only one set of dislocations as there can be no Burgers vector perpendicular to the GB line. This happens for example when $\psi = 0$ as can be seen on figure 2.2(c). Considering that the GB contains two sets of dislocations with Burgers vectors $\vec{b}_1$ and $\vec{b}_2$, equation (2.6) becomes

$$N_1 \vec{b}_1 + N_2 \vec{b}_2 = -r\theta \hat{n}. \quad (2.9)$$

The case $N_1 = N_2$ implies that $\vec{b}_1 + \vec{b}_2$ is anti-parallel to $\hat{n}$. To determine $D_i(\theta) = r/N_i$ where $i = 1, 2$, one takes the dot product of equation (2.9) with $\vec{b}_j \times (\vec{b}_1 \times \vec{b}_2)$, where $j \neq i$, leading to [43, 60]

$$\begin{aligned} D_1(\theta) &= -\frac{|\vec{b}_1 \times \vec{b}_2|^2}{\hat{n} \cdot (\vec{b}_2 \times (\vec{b}_1 \times \vec{b}_2))\theta}, \\ D_2(\theta) &= -\frac{|\vec{b}_1 \times \vec{b}_2|^2}{\hat{n} \cdot (\vec{b}_1 \times (\vec{b}_1 \times \vec{b}_2))\theta}. \end{aligned} \quad (2.10)$$

Note that D_1 and D_2 are signed distances, where $D_i(\theta)$ has the sign of $-\vec{b}_i \cdot \hat{t}$, for $i = 1, 2$. The dependence of D_i on the misorientation θ is the same as in the case of one type of dislocation (see equation (2.8)). In particular, if $\vec{b}_1$ is parallel to $\hat{n}$, $D_2 \rightarrow \infty$, which corresponds to the case where there is only one set of dislocations with Burgers vector $\vec{b}_1$.

The case of a GB with inclination $\psi = 0$ is illustrated in figure 2.5(c). As there is no Burgers

vector along the normal $\hat{n} = \vec{e}_y$, two sets of dislocations are needed. Assuming $N_1 = N_2$, one deduces from equation (2.9) that $\vec{b}_1 + \vec{b}_2$ is parallel to $\hat{n}$. A suitable choice is $\vec{b}_1 = (0, -1)$ and $\vec{b}_2 = (1, -1)$, which add up to $-\sqrt{3}\hat{n}$. These two Burgers vectors differ by an angle $\pi/3$, which is energetically favourable (see equation (2.5)). This possible configuration is represented in figure 2.5(c). From equation (2.10), one has $D_{1,2}(\theta) = \pm b\sqrt{3}/\theta$, which indicates that the higher the mismatch, the higher the dislocation density, as in the case of a single dislocation type. Indeed, the dislocations are sparse in the case of a SAGB with $\theta = 10^\circ$ (see figure 2.5(c)). In the case of a LAGB with $\theta = 25^\circ$, consecutive dislocations are in contact and the GB looks like a continuous line of dislocations (see figure 2.5(d)).

Finally, the interfacial free energy of GBs, or simply the GB free energy, originates from the stresses induced by the dislocations. In 1950, Read and Shockley derived the following analytical expression for the GB free energy γ

$$\gamma(\theta, \psi) = \theta(A(\psi) - B(\psi) \ln \theta), \quad (2.11)$$

where A and B depend on ψ [55]. Unlike fluid-fluid interfaces, GBs have an anisotropic interfacial free energy as it depends on both the misorientation θ and the GB inclination ψ . This plays a role in dendritic polycrystalline growth from a melt [61] and GB faceting [62]. Equation (2.11) predicts that γ increases as a function of the misorientation θ , which has been verified experimentally for metals in the SAGB regime [55, 63]. In the LAGB regime, equation (2.11) breaks down as consecutive dislocations are in contact, and γ was found to be independent of θ [55, 63].

2.1.5 Migration of grain boundaries

Grain boundary migration is the motion of a GB in response to an external force. The migration velocity v in the direction normal to the GB can be expressed as

$$v = MP, \quad (2.12)$$

where M is the GB mobility and P the driving pressure [12]. In 2D (3D), P is a force per unit length (area) of a GB and M can be interpreted as the inverse of a friction coefficient per unit length (area) of a GB. As GB migration is a thermally activated process, the temperature

dependence of M is given by an Arrhenius law

$$M = M_0 \exp\left(-\frac{E_{act}}{k_B T}\right), \quad (2.13)$$

where E_{act} is the activation energy, M_0 the pre-exponential factor, k_B the Boltzmann constant and T the temperature [12, 13]. Both equation (2.12) and equation (2.13) have been verified experimentally in metals [13, 64]. Furthermore, the GB mobility is a function of the misorientation and inclination [13], and there is strong evidence from experimental measurements on metals that the mobility increases with the misorientation angle, θ , for SAGBs, and becomes independent of θ in the LAGB regime [13, 65].

In the absence of external forces, the only driving force is the capillary pressure due to the mean curvature, κ , of the GB

$$P = \Gamma \kappa. \quad (2.14)$$

Here, Γ is the GB stiffness given by $\Gamma = \gamma + \gamma''$, where γ is the GB free energy and γ'' is its second derivative with respect to the GB inclination ψ [12]. The presence of the term γ'' is a consequence of the anisotropy of the GB free energy as shown by Herring in 1949 [66]. Combining equation (2.12) and equation (2.14) leads to the law of curvature-driven GB migration

$$v = M \Gamma \kappa, \quad (2.15)$$

indicating that GBs migrate until they become flat and stationary. In a polycrystalline material, GBs form a network, which corresponds to a free-energy cost to be minimised. Curvature-driven GB migration is then the main mechanism for spontaneously reducing the total GB length. This is accompanied by an increase of the average grain size, a process called grain growth [12, 13].

2.2 Physics of colloidal systems

2.2.1 Brownian motion

Colloids consist of small solid particles whose typical size ranges from 10 nm to 10 μm , termed colloidal particles, dispersed in a liquid solvent. Due to the thermal agitation, the molecules of the solvent constantly collide with the colloidal particles in all directions. This results in a random walk of the colloidal particles, with no overall displacement. This phenomenon is called Brownian motion as it was first observed by Robert Brown in 1827. The theory of Brownian motion was developed in 1905 by Einstein [67], which, together with the experimental work of Perrin in 1909, provided the definite evidence for the existence of atoms and molecules [68].

The motion of a Brownian particle can be characterised using the mean squared displacement (MSD) $\langle \vec{r}(\tau)^2 \rangle$, where $\vec{r}(\tau)$ is the displacement of the particle within a time lag τ and $\langle . \rangle$ denotes the ensemble average over many realisations of the random walk. The MSD characterises the typical area explored by the particle over a time lag τ . For a free Brownian particle at infinite dilution it is given by

$$\langle \vec{r}(\tau)^2 \rangle = 2dD_0\tau, \quad (2.16)$$

where d is the dimension of space and D_0 is the diffusion coefficient at infinite dilution [67]. As mentioned earlier, there is no average displacement so $\langle \vec{r} \rangle = \vec{0}$. The diffusion coefficient can be expressed in terms of the thermal energy $k_B T$ and the friction coefficient ζ of the particle in the fluid as [67]

$$D_0 = \frac{k_B T}{\zeta}. \quad (2.17)$$

For a colloidal sphere of diameter σ , the friction coefficient is given by the Stokes' formula $\zeta = 3\pi\eta\sigma$, where η is the viscosity of the solvent. This gives the Stokes-Einstein formula [67]

$$D_0 = \frac{k_B T}{3\pi\eta\sigma}, \quad (2.18)$$

which indicates that D_0 decreases when the size of the particle or the viscosity is increased. A

characteristic time scale of diffusion, called the Brownian time, can be defined as

$$t_B = \frac{\sigma^2}{4D_0}, \quad (2.19)$$

which corresponds to the typical time taken by a particle to diffuse over its own area.

The competition between thermal and gravitational energy can be evaluated in terms of the gravitational height, h_g , which is the height by which a particle can be lifted due to a thermal fluctuation of energy $k_B T$. For a colloidal sphere of diameter σ this is

$$h_g = \frac{6k_B T}{\Delta \rho g \pi \sigma^3}, \quad (2.20)$$

where $\Delta \rho$ is the difference in mass density between the particle and the solvent and g is the acceleration due to gravity [26]. If h_g is large, thermal agitation is strong enough to keep the colloidal particles in suspension. Otherwise, the particles tend to sink to the bottom of the sample cell as gravity dominates.

2.2.2 Colloidal interactions

Colloidal particles can be subject to various kinds of inter-particle interactions, depending on many factors including the material they are made of, the nature of the solvent, the amount of salt in solution, specific surface properties and the presence of external fields. The description of interactions is based on a pair potential, U , which is the interaction energy of two particles as a function of their relative position $\vec{r}$. For isotropic interactions, U is only a function of $r = \|\vec{r}\|$.

Colloidal interactions are usually modelled using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory developed the 1940s [69, 70], where the pair potential is the sum of the van der Waals attraction and the electrostatic repulsion [71]

$$U_{DLVO}(r) = U_{vdW}(r) + U_{el}(r). \quad (2.21)$$

The van der Waals attraction corresponds to the sum of all the dispersion interactions between the molecules constituting the colloidal particles. In the case of two colloidal spheres separated

by a distance r , it is given by

$$U_{vdW}(r) = -\frac{A\sigma}{24r}, \quad (2.22)$$

where A is called the Hamaker constant [71]. The repulsion originates from electric charges at the surface of the colloidal particles. In the presence of salt in the solution, counterions accumulate near the surface charges and screen the repulsion, which then decays over a typical length scale l_D , called the Debye length [32, 71]. For two spheres separated by a distance r , the screened electrostatic repulsion is

$$U_{el}(r) = \begin{cases} Z^2 k_B T \lambda_B \left(\frac{\exp(\sigma/l_D)}{1 + \sigma/l_D} \right)^2 \frac{\exp(-r/l_D)}{r}, & \text{if } r > \sigma. \\ +\infty, & \text{otherwise.} \end{cases} \quad (2.23)$$

Here, Z is the number of elementary charges at the surface of the particle and λ_B is the Bjerrum length, the distance at which two elementary charges interact with an energy $k_B T$ [32]. Equation (2.23) has the form of a Yukawa potential with an infinite repulsion at contact to model the non-penetrability of the colloidal particles. The DLVO theory gives a quantitative description of the stability of colloidal dispersion based on the competition between U_{vdW} (equation (2.22)) and U_{el} (equation (2.23)). At high salt concentration, the screening effect is important leading to a small Debye length l_D and a weak repulsion. The van der Waals attraction is then dominant, which can cause the particles to aggregate. By contrast, at low salt concentration, l_D becomes large and the strong repulsion prevents aggregation.

2.2.3 Phase behaviour of colloidal hard spheres

In the case where the van der Waals attraction is weak and the Debye length l_D is small compared to the particle diameter σ , the DVLO potential can be approximated by the hard core potential

$$U_{hard}(r) = \begin{cases} 0, & \text{if } r > \sigma. \\ +\infty, & \text{otherwise.} \end{cases} \quad (2.24)$$

Equation (2.24) indicates that hard spheres are non deformable objects if in contact, and do not interact otherwise. Remarkably, the equilibrium phase behaviour of an assembly of hard

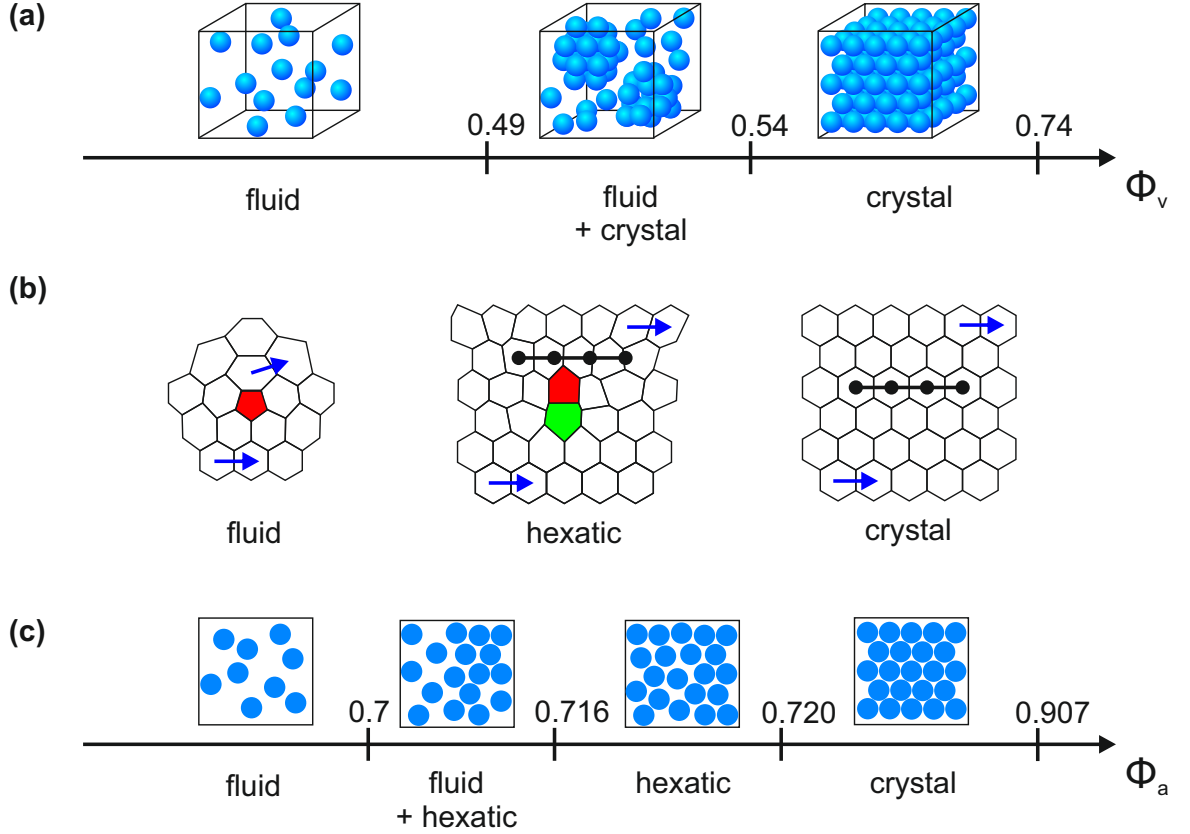


Figure 2.6: (a) Phase behaviour of hard spheres depending on the volume fraction ϕ_v . Hard spheres crystallise via a first order phase transition with a fluid-crystal coexistence. (b) For hard disks, the breaking of crystalline order happens in two steps. Dislocations in the hexatic phase break the translational order of the crystal (black dotted line). Bond-orientational order in the crystal is maintained in the hexatic but broken in the fluid due to isolated disclinations (blue arrows). (c) Phase behaviour of hard disks depending on the area fraction ϕ_a . Melting happens in two steps via a continuous crystal-hexatic transition and a first order hexatic-fluid transition with coexistence [40].

spheres does not depend on the temperature T . In brief, this is because the phase behaviour is determined by the configuration integral comprising the term $\exp(-U_{hard}(r)/k_B T)$, which does not depend on T as it is 1 if $r > \sigma$ and 0 otherwise¹.

In the case of hard spheres in 3D space, the only control parameter is the volume fraction, ϕ_v , defined as the ratio between the volume occupied by the particles and the total volume of the dispersion. In the phase behaviour of hard spheres, the role of the volume fraction ϕ_v is analogous to an inverse temperature. Indeed, at low volume fractions, hard spheres form a

¹The temperature does appear as a pre-factor in the partition function, as a result of the integration over the kinetic degrees of freedom. However this does not determine the equilibrium phase behaviour and T only influences the kinetics of the system.

disordered fluid state², whereas at high volume fractions, they form a crystal [26,27]. The origin of crystallisation of hard spheres is entropy as it is the only contribution to the free energy. The entropy of hard spheres can be split into a configurational part, S_{conf} , and a vibrational part, S_{vib} . Hard spheres crystallise above $\phi_v = 0.49$ (see figure 2.6(a)), as the sum $S_{conf} + S_{vib}$ in the crystal state becomes higher than that of the disordered state (fluid or glass) at the same volume fraction [26]. This is mostly because particles have more space to move around their equilibrium positions in a crystal than in a disordered configuration, where they are caged by their nearest neighbours. This causes a gain in S_{vib} that overcomes the loss in S_{conf} in the crystal phase. Moreover, a disordered state cannot exist above $\phi_v = 0.64$ (random close packing) for geometrical reasons and the crystal becomes the only geometrically acceptable configuration up to $\phi_v = 0.74$, which is the maximum value allowed by geometry (see figure 2.6(a)). This transition was shown to be of the first order, with a coexistence between the fluid and the crystal phase in the region $\phi_v = 0.49 - 0.54$, as illustrated in figure 2.6(a) [27, 72, 73].

The 2D equivalent of hard spheres are hard disks, characterised by their area fraction, ϕ_a . The melting phase behaviour (the reverse of crystallisation) of hard disks is still driven by entropy but turns out to be very different from the 3D case. As shown in figure 2.6(b), the crystalline order is characterised by both bond-orientational order and translational order. The correlation functions $g_T(r)$ and $g_6(r)$ are usually introduced to measure the decay of translational and bond-orientational order as a function of the distance r , respectively [50]. As the crystal phase exhibits long-range bond-orientational order, g_6 is constant in this case. Strictly speaking, long-range translational order does not exist in 2D crystals as thermal fluctuations are strong enough to break it [74, 75]³. Instead there is a quasi long-range translational order with a weak power-law decay of g_T . Unlike the 3D case, melting of hard disks in 2D happens in two steps as both kinds of orders are broken at different values of the area fraction ϕ_a . Firstly, translational order is broken at $\phi_a = 0.720$ by the appearance of dislocations [40, 50, 52], which leave a significant degree of bond-orientational order as shown in figure 2.6(b) and figure 2.6(c). The system ends up in the hexatic phase, which is characterised by short-range translational order and quasi long-range bond-orientational order, corresponding to an exponential decay of g_T and a power law decay of g_6 [40, 50, 52]. Such a transition was found to be continuous in large scale molecular dynamics simulations of hard disks [40]. Secondly, bond-orientational is

²The term ‘fluid’ is preferred in this case as there is no difference between a liquid and a gas for hard core interactions.

³This is known as the Mermin-Wagner theorem, shown in 1966.

Figure 2.7: Characteristics of the colloidal particles used in this work, including diameter (σ), gravitational height (h_g) and Brownian time (t_B).

σ (μm)	h_g (μm)	t_B (s)
2.7	0.08	30
6.1	0.007	350
10.8	0.001	1900

broken at $\phi_a = 0.716$ with the proliferation of isolated disclinations, which break orientational order as shown in figure 2.6(b) [50, 52] and figure 2.6(c). This enables the system to reach the liquid phase below $\phi_a = 0.7$ via a first-order phase transition with a liquid-hexatic coexistence in the interval $\phi_a \in [0.7; 0.716]$, as found in simulations (see figure 2.6(c)) [40]. In the liquid phase, both kinds of order are short ranged with exponentially decaying correlations [40, 50, 52].

2.3 Experimental methods

2.3.1 Colloidal model system

In this work, the colloidal particles are melamine formaldehyde spheres (Microparticles[®]) of diameters $\sigma = 2.7, 6.1$ and $10.8 \mu\text{m}$ (see figure 2.7), with a polydispersity lower than 3%. Their mass density is 1.51 g/cm^3 and their refractive index 1.68. Due to the presence of carboxylic acid groups at their surface, the particles acquire a negative surface charge when dispersed in aqueous solvents, which stabilises the dispersion by electrostatic repulsion against flocculation and attraction to glass walls. Importantly, it has been shown that these colloidal particles behave as hard spheres in these conditions [76].

The colloidal particles are dispersed in a 20/80 $v/v\%$ isopropanol/water mixture. A 1%wt tetramethylammonium hydroxide (TMAH) aqueous solution is added to the isopropanol/water mixture with concentration of 1% in volume, which increases the surface charge of the colloids to prevent any residual sticking to the glass walls. A quartz glass Hellma[®] cell is used as a sample container, with a chamber thickness $200 \mu\text{m}$ and lateral dimensions $9 \times 20 \text{ mm}$, see figure 2.8 (a) and (b). It is cleaned in a 2% aqueous Hellmanex[®] solution at 65° for 2 hours to remove any organic contaminants. The cell is then flushed out successively with deionised water, isopropanol and compressed air until it is completely dry. Finally, the cell is placed in a plasma cleaner for 60s to negatively charge the glass surfaces inside the chamber. The colloidal

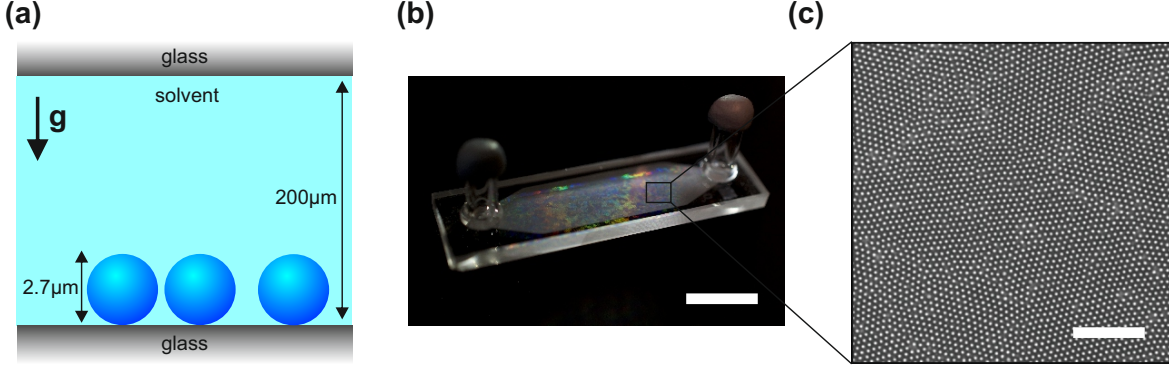


Figure 2.8: (a) Schematic illustration of the sample geometry in the case of a monolayer of colloidal particles of diameter $2.7 \mu\text{m}$ (not to scale). (b) Picture of the sample cell showing the Bragg refraction due to the polycrystalline nature of the monolayer. Scale bar, 1 cm. (c) Microscopy image of the polycrystalline monolayer. Scale bar, $30 \mu\text{m}$.

dispersion is injected into the cell, which is then sealed using Blu-Tack[®]. Note that isopropanol lowers the surface tension of the dispersion, providing a better wetting of glass walls, which makes filling sample cells easier.

The gravitational height, h_g , and the Brownian time, t_B , as defined in equation (2.20) and equation (2.19), are reported in figure 2.7 for each particle size in this solvent. As h_g is very small compared to the diameter in all three cases, the particles sediment quickly (a few minutes) to the bottom of the cell to form a monolayer, as shown in figure 2.8(a). Out of plane fluctuations are so small that the colloids are effectively confined in two dimensions by gravity. The monolayer obtained is characterised by its area fraction

$$\phi_a = \frac{\pi\sigma^2}{4A}N, \quad (2.25)$$

where N is the number of colloidal particles contained in an area A . Moreover, *before* sedimentation occurs, N corresponds to the number of particles contained in a column of colloidal dispersion above an area A , so that

$$N = \frac{6Ah}{\pi\sigma^3}\phi_v, \quad (2.26)$$

where h is the thickness of the cell and ϕ_v is the volume fraction of the colloidal dispersion.

Combining equation (2.25) and equation (2.26) gives

$$\phi_a = \frac{3h}{2\sigma}\phi_v, \quad (2.27)$$

which shows that dense monolayers (ϕ_a high) can be obtained with relatively dilute colloidal dispersions (ϕ_v low) as long as the ratio h/σ is large.

A polycrystalline monolayer is prepared by tuning the volume fraction of the initial dispersion, ϕ_v , such that the area fraction after sedimentation (equation (2.27)) is higher than $\phi_a = 0.72$, above which a crystal is formed. Since sedimentation happens quickly, the in-plane area fraction increases rapidly and crystallites with different local orientations are formed, resulting in a polycrystalline monolayer rather than a single crystal, figure 2.8 (b) and (c). The sample can be left on a flat stage for several days, leaving enough time for grain growth to occur until the desired grain size for a given experiment is reached. The polycrystalline monolayer exhibits Bragg refraction under incident white light due to the presence of the crystalline domains, which can be seen by eye after several days (see figure 2.8(b)).

2.3.2 Video-microscopy

The colloidal polycrystalline monolayer is imaged at single particle resolution using video-microscopy. The sample cell is placed on an inverted optical microscope (Olympus CKX41) and carefully levelled to prevent drift of the colloidal particles. The sample is illuminated with a LED and gray-scale frames are recorded using a Ximea XiQ CMOS camera at various rates ranging from 1/min to 1/s with a $20\times$ or $40\times$ objective, depending on the experiment. In these conditions, the incident light rays near the top of the particle are refracted according to Snell's law and focused towards its centre, as illustrated in figure 2.9(a). This leads to the appearance of a bright spot in the centre of the particle on the image as shown in figure 2.9(b). Conversely, the incident light rays on the edge of the particle have an angle of incidence beyond the critical value and are thus reflected away from the particle (see figure 2.9(a)), which causes the appearance of a dark ring around the centre (see figure 2.9(b)). Note that this effect is amplified by the fact that the focus plane of the objective is near the plane of the centres of the particles. When such particles are close to each other, as shown in figure 2.9(c), the dark rings produce a dark background and their contours cannot be clearly identified due to the drop in light intensity.

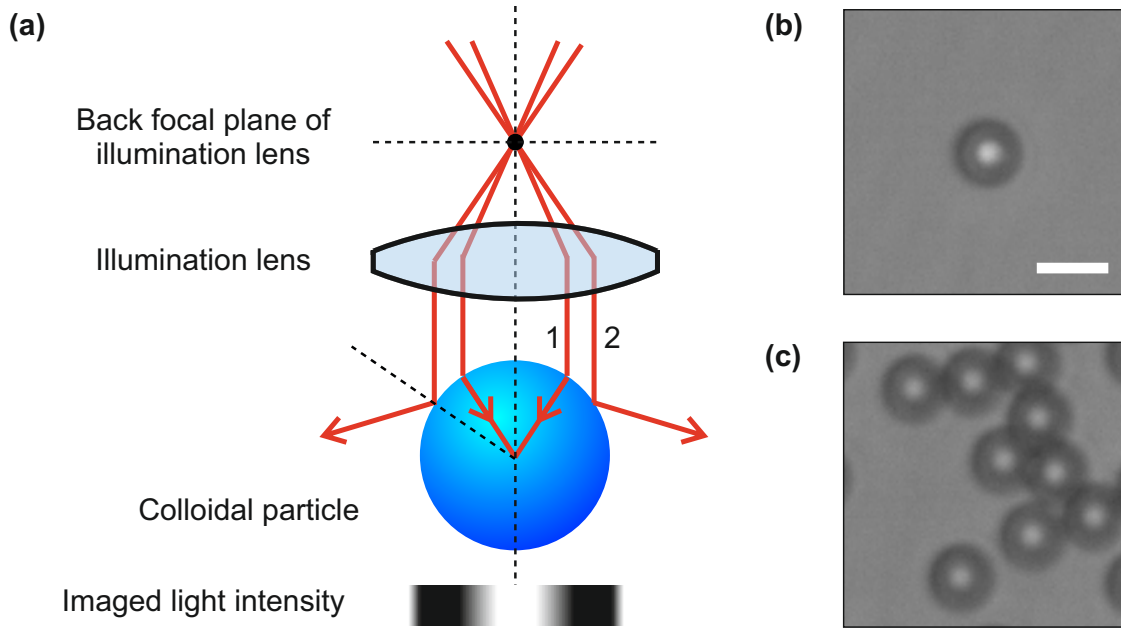


Figure 2.9: (a) Illumination of a colloidal particle of higher refractive index than the surrounding solvent. Incident light rays near the top of the particle are refracted according to Snell's law and focused towards its centre (1), while those on the edge are reflected away from the particle as their incidence is beyond the critical angle (2). The intensity of the light collected in the imaging objective is then higher in the centre and close to zero at the edges of the particle. (b) Optical micrograph of a single colloidal particle under LED light with a $40\times$ objective. A bright spot in the centre of the particle circled by a dark ring can be seen, as a consequence of the interaction with the light (see (a)). Scale bar, $3\text{ }\mu\text{m}$. (c) Assembly of colloidal particles under the same illumination conditions and magnification as (b).

However, the position of the particles can still be unambiguously identified using their bright centres.

Standard image analysis routines [47, 77] are used to detect the particles in the frames and extract their coordinates. Starting from the original image (see figure 2.10(a)), a bandpass filter is applied to retain features lying within a user specified size range (see figure 2.10(b)). The algorithm then looks for local intensity maxima corresponding to particles' positions. The raw data is an array of coordinates x_i and y_i , where i is a particle index, produced for each frame. This is used to determine the Delaunay triangulation and the Voronoi construction of the assembly of colloids (see figure 2.10(c)), which are the starting point to calculate the spatial correlation functions used throughout this thesis. The dynamics of individual particles is studied using a standard particle tracking routine [47, 77] that identifies particles and links their positions in consecutive frames to reconstruct their trajectories (figure 2.10(d)). The raw data consists of an array of coordinates $x_i(t_k)$ and $y_i(t_k)$, where i is the particle identity and t_k

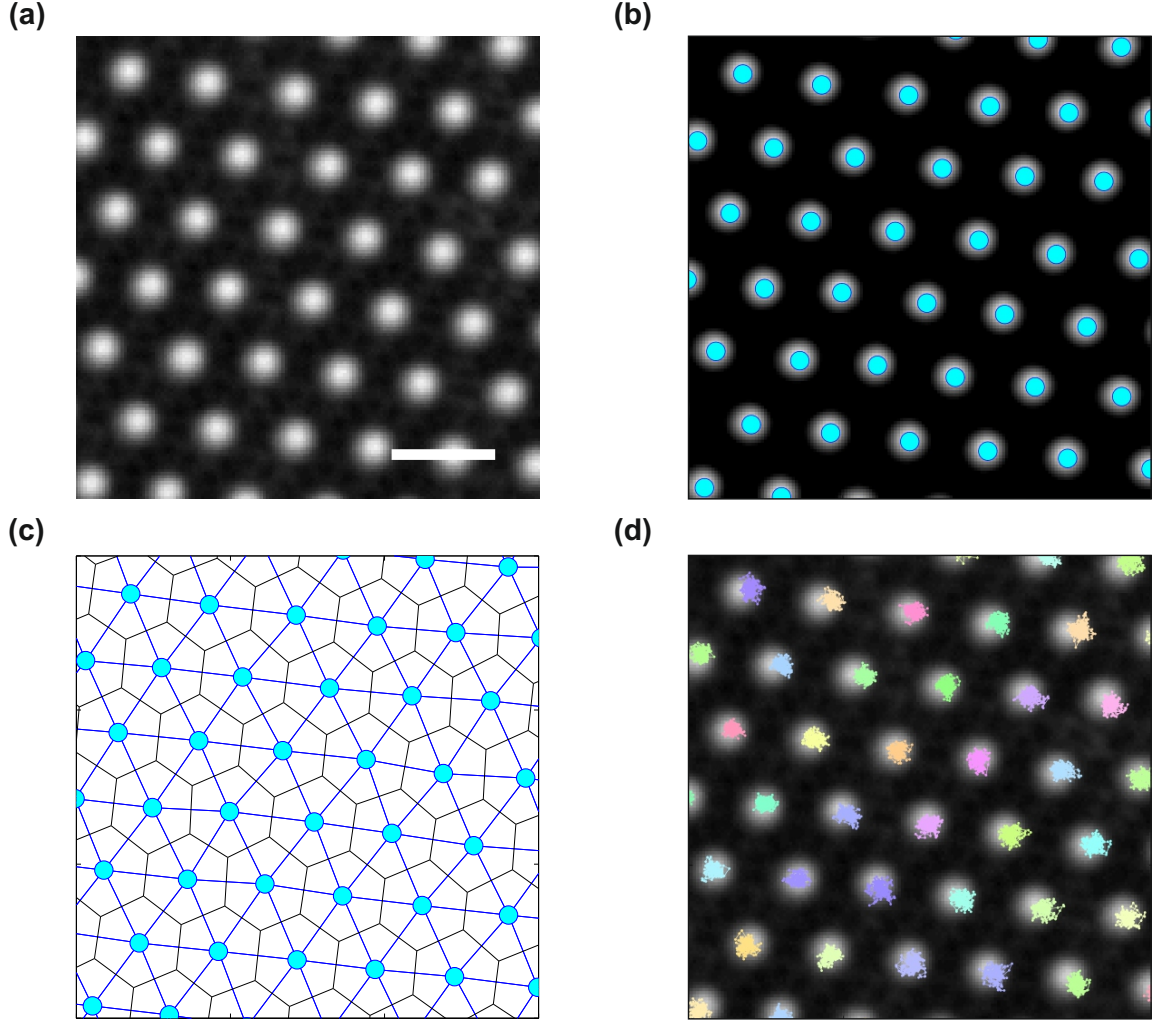


Figure 2.10: (a) Original image of a colloidal crystal. The hard core interaction enables direct contact between neighbours but these cannot be seen due to optical effects as explained in figure 2.9. However the particles can still be identified based on their bright centres. Scale bar, $3\mu\text{m}$. (b) Output of the bandpass filter (background) with features within the size range 1-13 px. The detected particles' positions correspond to the blue dots. (c) Delaunay triangulation (blue mesh) and Voronoi construction (black cells) of the same dataset. (d) Tracks of the particles sampled at 1 frame per second for 100 frames.

the time corresponding to the k -th frame in the sequence. The tracked data is used to compute time-correlation functions in this work.

2.3.3 Optical trapping

In 1970, Ashkin discovered that small dielectric particles can be manipulated using laser light, a technique referred to as optical trapping [78]. To illustrate the principle of optical trapping, we

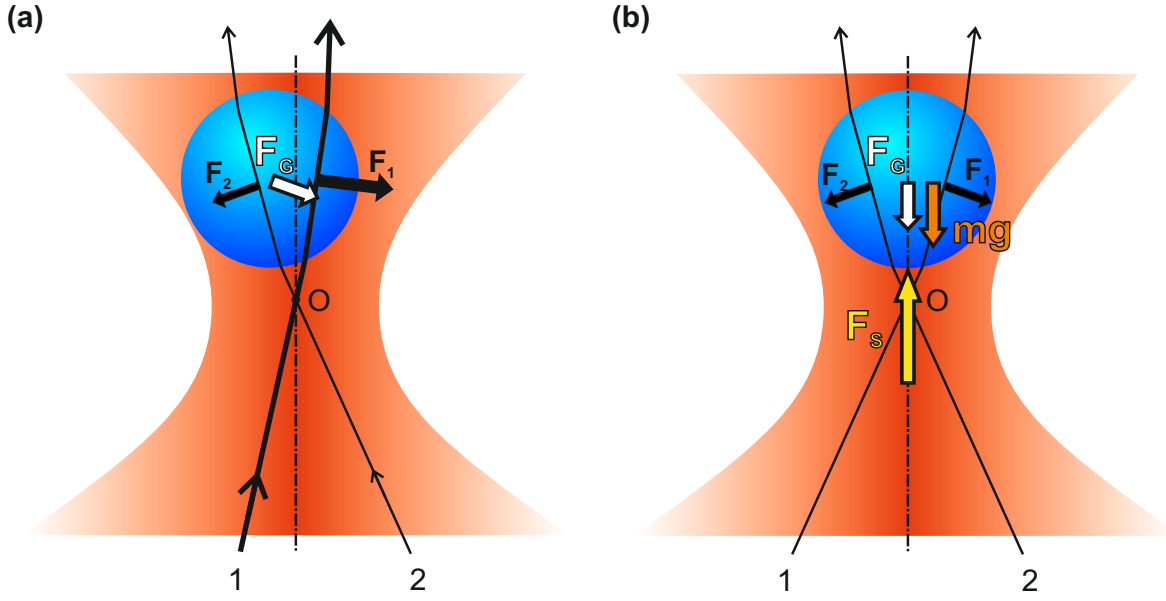


Figure 2.11: (a) The forces $\vec{F}_1$ and $\vec{F}_2$, associated with the refraction of a high (1) and low (2) intensity light rays, add up to the gradient force $\vec{F}_G$ directed towards the beam axis (dashed line). (b) When the scattering force $\vec{F}_S$ balances the weight and the gradient force, the particle is trapped just above the focus point O . Note that this figure is an illustration in which the different effects are exaggerated for clarity.

consider a small dielectric particle whose refractive index is higher than that of the surrounding medium, near the waist of a strongly focussed laser beam. For simplicity of representation, we assume that the size of the particle is larger than the wavelength of the laser light, which is referred to as the ray optics regime [79]. Note that in the experiments described in this thesis, the wavelength of the laser beam is comparable to the size of the particle, which corresponds to the Mie regime [80]. As the physics of the Mie regime is far more complex, the ray optics regime is used here to illustrate the effects of optical trapping [80]. As shown in figure 2.11(a), the particle acts as a lens which refracts the rays of light, causing a momentum transfer, and thus a force in the opposite direction to conserve momentum [79]. When the particle is away from the beam centre, the intensity on the particle's surface is higher on the side of the beam axis due to the intensity gradient. Consequently, the force $\vec{F}_1$ towards the beam centre is then higher than $\vec{F}_2$, the one away from the beam centre, which creates a trapping force $\vec{F}_G = \vec{F}_1 + \vec{F}_2$ towards the center of the beam, called the gradient force [79] (see figure 2.11(a)). A second effect is the radiation pressure of the light hitting the surface of the particle which creates a scattering force $\vec{F}_S$ that pushes the particle in the direction of the beam [78, 79] (see figure 2.11(b)). When the weight of the particle and the gradient force counterbalance the scattering force, the particle

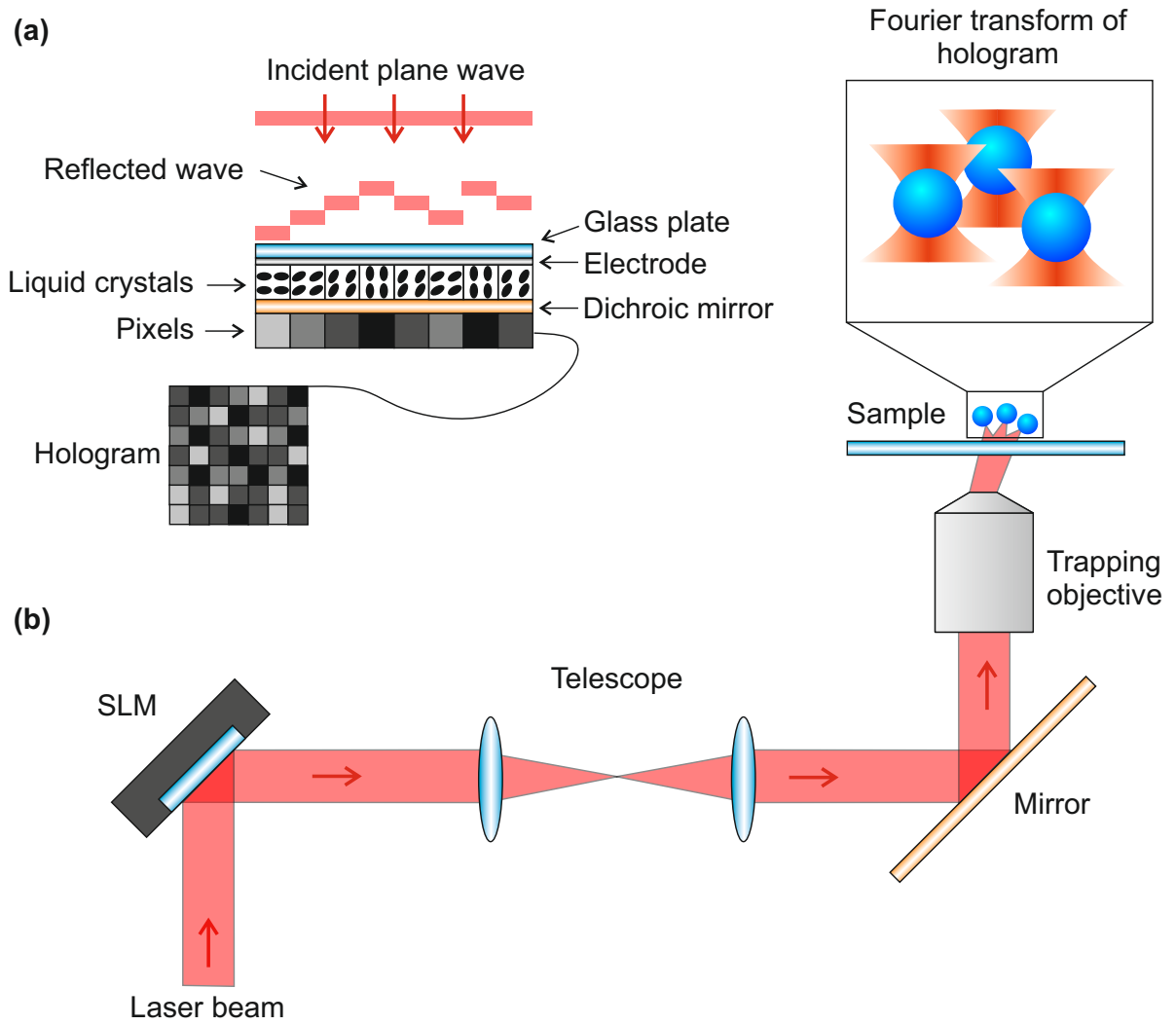


Figure 2.12: (a) Illustration of the principle of a SLM. The hologram is displayed in a liquid crystal device which is illuminated by a plane wave. The phase of the reflected wave depends on the local orientation of the liquid crystal. (b) Overall view of a typical holographic optical trapping stage. After reflection by the SLM the beam is sent to the back aperture of a trapping objective. The latter Fourier transforms the hologram, which creates the trapping pattern.

sits at equilibrium just above the focus point (see figure 2.11(b)). The beam acts as an optical trap which can be moved to manipulate the particle.

Complex optical trapping patterns can be generated using various techniques including acousto-optical-deflectors [81], interference [82], diffraction devices [83] and holographic optical trapping [84]. The latter technique is used in this work and involves shaping a laser beam by reflecting it off a liquid crystal mirror which displays a computer-generated pattern, called the hologram [85,86]. Firstly, as shown in figure 2.12(a), a black and white image corresponding to the hologram is generated with a computer. The hologram is such that its Fourier transform

corresponds to the desired trapping pattern. Secondly, the hologram is displayed onto the spatial light modulator (SLM), which converts the intensity of each pixel into the corresponding orientation of the liquid crystals (see figure 2.12(a)). When the SLM is illuminated with a planar wavefront, the phase of the reflected wavefront is changed according to the local orientation of the liquid crystal for each pixel (see figure 2.12(a)). The image of the shaped wavefront is then sent to the back aperture of the trapping objective via a telescope (see figure 2.12(b)). Finally, the trapping objective Fourier transforms the image of the hologram, which creates an ensemble of traps as illustrated in figure 2.12(b). This technique is very versatile and enables the creation of many different beam shapes like Bessel beams, helical modes and arrays of optical vortices [84].

Acknowledgements

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Chapter 3

Grain growth in colloidal polycrystalline monolayers

ABSTRACT

In this chapter, the grain growth process in a polycrystalline monolayer of colloidal hard spheres is studied. It is found that the bond-orientational correlation function satisfies the dynamic scaling hypothesis and has the general scaling form predicted for systems containing random domain walls. The associated correlation length is a power law in time with an exponent close to $1/3$, indicating the presence of abnormal grain growth. By directly measuring the grain boundary character distribution and monitoring the evolution of the grain boundary network, it is shown that there is a strong annihilation of large angle grain boundaries and that small angle grain boundaries become relatively more present. The origin of abnormal grain growth is shown to be the curvature-driven coarsening of the large angle grain boundaries at a rate which depends on their relative length in the total grain boundary network.

3.1 Introduction

Coarsening phenomena correspond to the competitive growth of ordered domains following a quench from the disordered phase into the ordered phase by quickly varying an external control parameter (e.g. the temperature) [87, 88]. The interfaces between the domains, called domain walls, represent an extra free-energy cost that is minimised by a reduction of the interfacial length, which drives the growth. Coarsening can be observed in a broad range of systems including Ising and Potts models [89], colloid-polymer mixtures [90] and liquid crystals [91, 92].

At late times after the quench, the system enters a scaling regime such that the domain structure is time-invariant when the distances are rescaled by a single time-dependent length, $R(t)$, which behaves as $R(t) \sim t^\alpha$ and corresponds to the typical domain size [88]. In this regime, the correlation function of the order parameter is expected to satisfy $C(r, t) = f(r/R(t))$, which is known as the dynamic scaling hypothesis [87, 88]. The analytical expression of the scaling function f together with the value of the exponent α depend on the dimension of space, the type of order parameter and other conservation laws [87, 88, 93]. The validity of the dynamic scaling hypothesis has been verified in simulations of Ising models, Potts models and experiments on liquid crystals [89, 92]. In all cases the growth exponent was found to be $\alpha = 1/2$, which indicates that the growth is driven by the reduction of the curvature of the interfaces [87, 88].

Grain growth is a particular kind of coarsening process, which is encountered in polycrystalline materials that are composed of adjacent crystalline domains of mismatching orientations, called grains, and separated by domain walls, termed grain boundaries (GBs) [13]. As the mechanical properties of polycrystalline materials are directly related to the size of the constituent crystalline grains [14–16], understanding the underlying grain growth mechanism is key in controlling them. Grain growth has been studied extensively in simulations [94–98] and in experiments on metallic systems [99, 100]. Nevertheless the mechanisms for grain growth are still far from established and it is in fact possible that multiple mechanisms may contribute concurrently [97, 98, 101–103]. It is often assumed that grain growth is purely driven by the curvature of GBs [12, 13, 104], which leads to a growth law of $t^{1/2}$ and is referred to as *normal* grain growth [13, 104]. However, the growth law is often found to be different from $t^{1/2}$, which is referred to as *abnormal* grain growth [13, 105]. The precise mechanism of abnormal grain growth remains unclear as the growth laws usually observed differ from one another depending

on the metal [13, 106]. Variability in the growth exponents was also observed in model systems, such as repulsive colloids [107, 108] and block-copolymer systems [24, 109, 110].

Colloidal polycrystalline monolayers are very convenient model systems to study grain growth since they can be imaged by means of simple optical microscopy at single particle resolution during a significant period of time, which is crucial for probing the coarsening dynamics with sufficient accuracy [25, 47, 108]. Colloidal hard spheres confined to a monolayer crystallise when their area fraction exceeds the value 0.72 [40] and form a hexagonal close-packed crystal. Quenching the system into the crystal phase results in a polycrystalline monolayer, with hexagonal close-packed grains, analogous to polycrystalline graphene sheets [41]. The grains are enclosed by GBs which are characterised by the difference in orientation between the two adjacent crystals, called the misorientation [12], see section 2.1.3. The GBs form a network whose detailed structure can be specified by the relative amount of GBs of each misorientation. This is quantified by the *grain boundary character distribution* (GBCD), which is the central link between the microscopic details and the macroscopic properties of the GB network, such as the average misorientation or average grain size [111, 112]. Hence, the time-evolution of the GBCD is at the heart of the grain growth process.

In this chapter, grain growth in a polycrystalline monolayer of colloidal hard spheres is investigated. Bond-orientational ordering satisfies dynamic scaling with a good agreement between the experimental bond-orientational correlation function and the general scaling form predicted for systems containing random domain walls. Nevertheless, the bond-orientational correlation length is found to satisfy a power-law with an exponent close to $1/3$, suggesting the presence of abnormal grain growth. By directly measuring the GBCD, it is shown that there is a preferential annihilation of GBs with a high misorientation, while the proportion of GBs with a low misorientation increases. The data suggest that the origin of abnormal grain growth lies in the fact that the rate of coarsening of GBs with a high misorientation depends on their relative length in the total GB network. Finally, the GBs with a small misorientation are found to have little impact on the decay of the bond-orientational order.

3.2 Theory

3.2.1 Normal grain growth

The migration velocity v of a GB is usually related to the GB mobility M and the driving force P per unit length of a GB (in 2D) by the Herring relation [12, 66]

$$v = MP, \quad (3.1)$$

where M can be seen as the inverse of a friction coefficient per unit length of a GB. In the case where the curvature of the GB is the only driving force, one has $P = \Gamma\kappa$, with κ the local curvature (in 2D) and Γ the GB stiffness [12, 66]. The GB stiffness represents the interfacial free-energetic cost of GBs, in energy per unit length. Rewriting the Herring relation for the case of curvature-driven GB migration yields

$$v = M\Gamma\kappa, \quad (3.2)$$

which is equivalent to the Allen-Cahn equation for curvature-driven domain wall migration [87, 104]. The product $M\Gamma$, called the reduced mobility in the following [113], has the dimension of an area divided by a time. It corresponds to the migration rate as it is the typical area spanned by a migrating GB per unit time.

In a polycrystalline material, where GBs form a network, the time dependence of the average grain size, $R(t)$, can be obtained from equation (3.2). Assuming that $v \sim dR/dt$ and $\kappa \sim 1/R$, one obtains

$$\frac{dR}{dt} \sim \frac{M\Gamma}{R}, \quad (3.3)$$

which can be integrated to give

$$R(t) \sim t^{1/2}. \quad (3.4)$$

Equation (3.4) is known as the growth law of the Allen-Cahn universality class [87, 88, 104] or *normal* grain growth [13].

3.2.2 Abnormal grain growth

In most polycrystalline materials, however, normal grain growth is not observed as the grain size increases with an exponent different from $1/2$, which is commonly referred to as *abnormal* grain growth [13]. Indeed, as GBs are solid-solid interfaces, both their mobility M and their stiffness Γ depend on the misorientation θ between the two crystals [12, 13], see section 2.1.5. This dependence can be described by various models, which essentially predict that M , Γ and $M\Gamma$ all increase with θ and plateau at high values of θ [13]. Though this does not modify the local dynamics, as described by equation (3.2), it does imply that GBs with different misorientations coarsen at different rates, i.e. that the growth law depends on the detailed structure of the GB network. The latter can be described by the so-called *grain boundary character distribution* (GBCD), denoted $p(\theta, t)$, which measures the length of GBs with a given misorientation θ at time t , $l(\theta, t)$, divided by the total length of the GB network in the system [111]

$$p(\theta, t) = \frac{l(\theta, t)}{\int_I l(\theta, t) d\theta}. \quad (3.5)$$

Here, I denotes the interval of the possible values of θ . The GBCD is the fundamental quantity that relates the details of the microstructure to average quantities describing the GB network [111, 112, 114, 115]. For example, from the misorientation-dependent reduced mobility of each boundary $M(\theta)\Gamma(\theta)$, one can find its time dependent average in the system as [115]

$$\langle M\Gamma \rangle = \int_I M(\theta)\Gamma(\theta)p(\theta, t)d\theta, \quad (3.6)$$

which thus depends on the detailed structure of the GB network via $p(\theta, t)$.

Analogous to normal grain growth described by equation (3.3), in the case where the grain size $R(t)$ is the only relevant length scale in the growth process, one can expect that at late times a scaling regime is reached where the grain size evolves according to [114, 115]

$$\frac{dR}{dt} \sim \frac{\langle M\Gamma \rangle}{R}. \quad (3.7)$$

As $\langle M\Gamma \rangle$ is a function of time, one expects deviations from the law of normal grain growth, i.e. $R(t)$ does not scale like $t^{1/2}$. Note that if the GBCD does not depend on time, $\langle M\Gamma \rangle$ is constant and integration of equation (3.7) leads back to the law of normal grain growth, equation (3.4).

3.3 Methods

3.3.1 Sample preparation

Colloidal polycrystalline monolayers are prepared as described in section 2.3.1, using $2.7\text{ }\mu\text{m}$ diameter melamine formaldehyde colloidal spheres. Imaging is performed by video-microscopy described in section 2.3.2 and an example of a local view of the polycrystalline monolayer is given in figure 3.1(a). Using a $20\times$ objective, images containing $\sim 4 \times 10^4$ particles are recorded at frame rate $1/\text{min}$ for 16h from the time of filling the cell, defined as $t = 0$, and 5 equivalent runs are performed to improve statistics. The particle coordinates are extracted in each frame and the Delaunay triangulation of the dataset is determined as explained in section 2.3.2. Time is expressed in units of the Brownian time, $t_B = \sigma^2/(4D_0) = 28\text{s}$, where D_0 the experimentally determined diffusion coefficient at infinite dilution.

3.3.2 Bond-orientational order analysis

The local bond-orientational order parameter $\psi_6(\vec{r}_j, t)$ is used to quantify the local crystalline order of a particle j located at $\vec{r}_j$ and is defined as [50]

$$\psi_6(\vec{r}_j, t) = \frac{1}{N_j(t)} \sum_{k=1}^{N_j(t)} e^{i6\Delta\theta_{jk}(t)}, \quad (3.8)$$

where $\Delta\theta_{jk}$ is the angle between the x -direction and the bond vector connecting the particle j to one of its N_j nearest neighbours k in the Delaunay triangulation (see figure 3.1(b)). The local orientation of the particle j is then given by

$$\theta_6(\vec{r}_j, t) = \frac{1}{6} \arg(\psi_6(\vec{r}_j, t)), \quad (3.9)$$

and varies from 0 to 60° due to the hexagonal symmetry of the 2D hexagonal close-packed crystal, see figure 3.1(b). A plot of the θ_6 field for a local view of the sample is shown in figure 3.1(c) as an example.

The decay of the bond-orientational order as a function of the distance is measured in terms of the bond-orientational correlation function, $g_6(r, t)$, which requires a specific computation

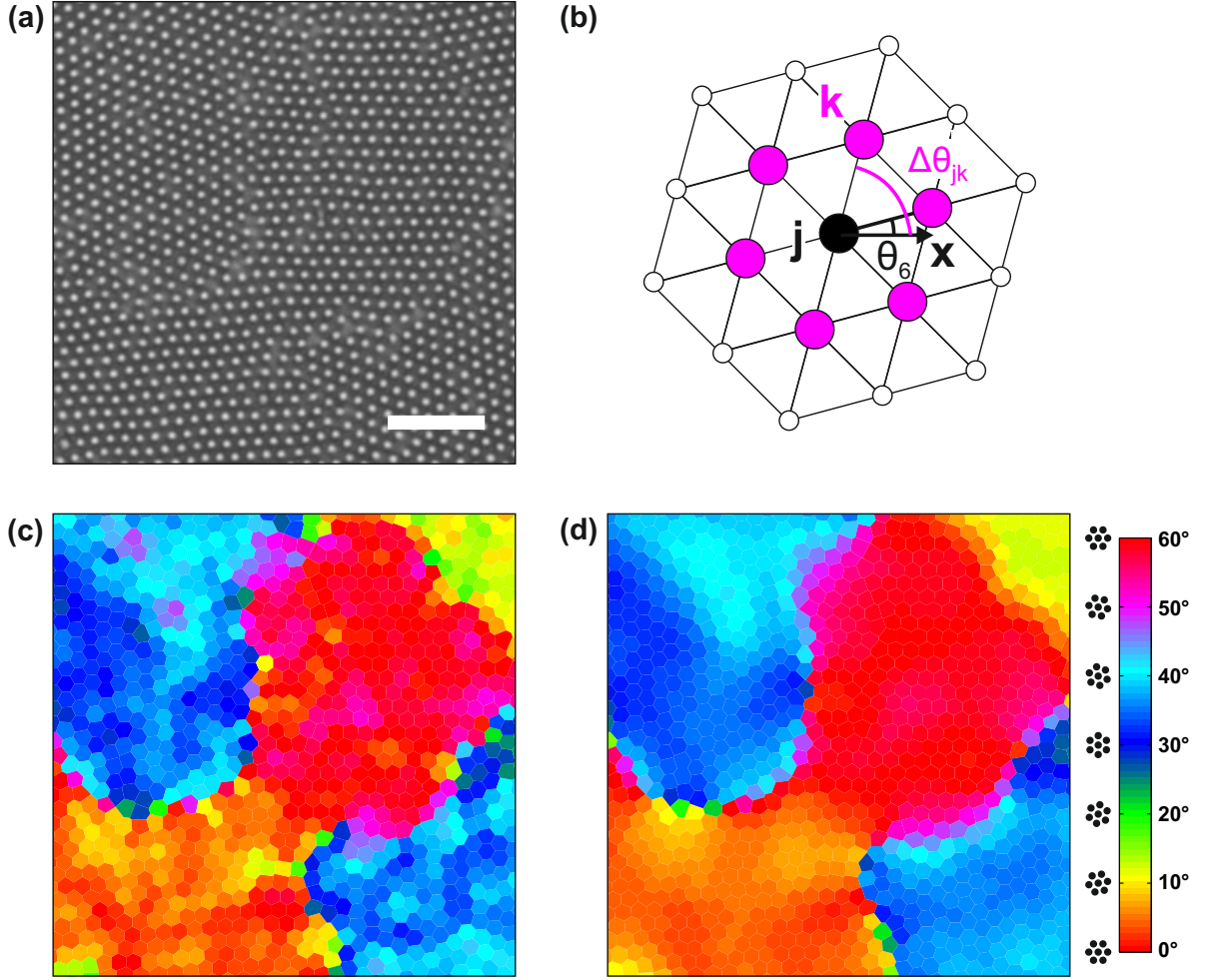


Figure 3.1: (a) Microscopy image of a small area of the colloidal polycrystalline monolayer. Scale bar, 20 μm . (b) A particle j (black disk) with k , one of its 6 nearest neighbours in the hexagonal lattice (magenta disks). The angle between the bond $j - k$ and the x -direction is denoted $\Delta\theta_{jk}$ and is used for the computation of ψ_6 and the local orientation θ_6 (see text). The smoothing of the ψ_6 field requires the particles in the second shell of nearest neighbours (white disks). (c) Voronoi tessellation where each cell is coloured according to the value of θ_6 as indicated by the colourbar. (d) Smoothed orientation field $\tilde{\theta}_6$.

procedure in the case of a polycrystalline sample due to the presence of grain boundaries. First, the field ψ_6 is smoothed by replacing $\psi_6(\vec{r}_i, t)$ with its average over the particles constituting the first two coordination shells of the particle i (see figure 3.1(b)). The smoothed field is denoted $\tilde{\psi}_6(\vec{r}_i, t)$ and the smoothed local orientation field is defined by $\tilde{\theta}_6 = \arg(\tilde{\psi}_6)/6$, see figure 3.1(d) for an illustration. This operation prevents the correlation function from sharply dropping at small distances due to noise in the ψ_6 field [92]. The field $\tilde{\psi}_6$ is then normalised according to $\hat{\psi}_6 = \tilde{\psi}_6/|\tilde{\psi}_6|$, which enables a more accurate probing of the correlations at short distances [93].

Eventually, the bond-orientational correlation function $g_6(r, t)$ is computed as

$$g_6(r, t) = \text{Re} \left(\left\langle \hat{\psi}_6^*(\vec{r} + \vec{r}_0, t) \hat{\psi}_6(\vec{r}_0, t) \right\rangle \right), \quad (3.10)$$

where $\langle . \rangle$ denotes the average over all the pairs of particles separated by a distance r . Within this definition, $g_6(r, t)$ is simply the average cosine of $6(\tilde{\theta}_6(\vec{r} + \vec{r}_0, t) - \tilde{\theta}_6(\vec{r}_0, t))$ and thus only probes the spatial correlations in the argument of the bond-orientational order parameter at different times.

3.3.3 Detection of grain boundaries

To extract the GBs and their misorientation θ , the grains are first detected using a procedure similar to the one used by Dillmann et al. [108]. An example for a small part of the system is shown in figure 3.2(a). The set of crystal-like particles is defined as those particles for which $|\tilde{\psi}_6|$ is greater than 0.7. If a crystal-like particle has at least 3 crystal-like neighbours whose $\tilde{\theta}_6$ differ by less than 0.75° , then these particles belong to the same grain. A grain containing less than 19 particles is discounted as this corresponds to the size of a cluster formed by a particle and its two shells of nearest neighbours¹. The output is shown in figure 3.2(b) where the particles of each grain have been coloured according to the average $\tilde{\theta}_6$ of the particles within that grain.

Next, the GBs are determined by constructing the Delaunay triangulation of the crystal-like particles *only*, as shown in figure 3.2(c). From this, the triangulation edges connecting the particles belonging to two neighbouring grains are detected and form the *GB connectors*, such as $k - i$ or $k - j$ in the inset figure 3.2(c). The triangulation edges which form the envelope of the grains are detected as well and called the *grain edges*, such as $i - j$ in the inset of figure 3.2(c). The two GB connectors $k - i$ and $k - j$ are *consecutive* as they are linked by only one grain edge, $i - j$ (see the inset of figure 3.2(c)). Note that in this case, i, j and k form the vertices of a triangle of the Delaunay triangulation. Linking the centres of two consecutive GB connectors gives a *GB segment*, as seen in the inset of figure 3.2(c). It is clear from figure 3.2(c) that the GB segments determined by such a method provide a reasonably good representation of the GBs in the system.

To compute the misorientation of GBs, one starts by defining the misorientation of a GB

¹This criterion actually matches the cut-off for the smoothing of the ψ_6 -field.

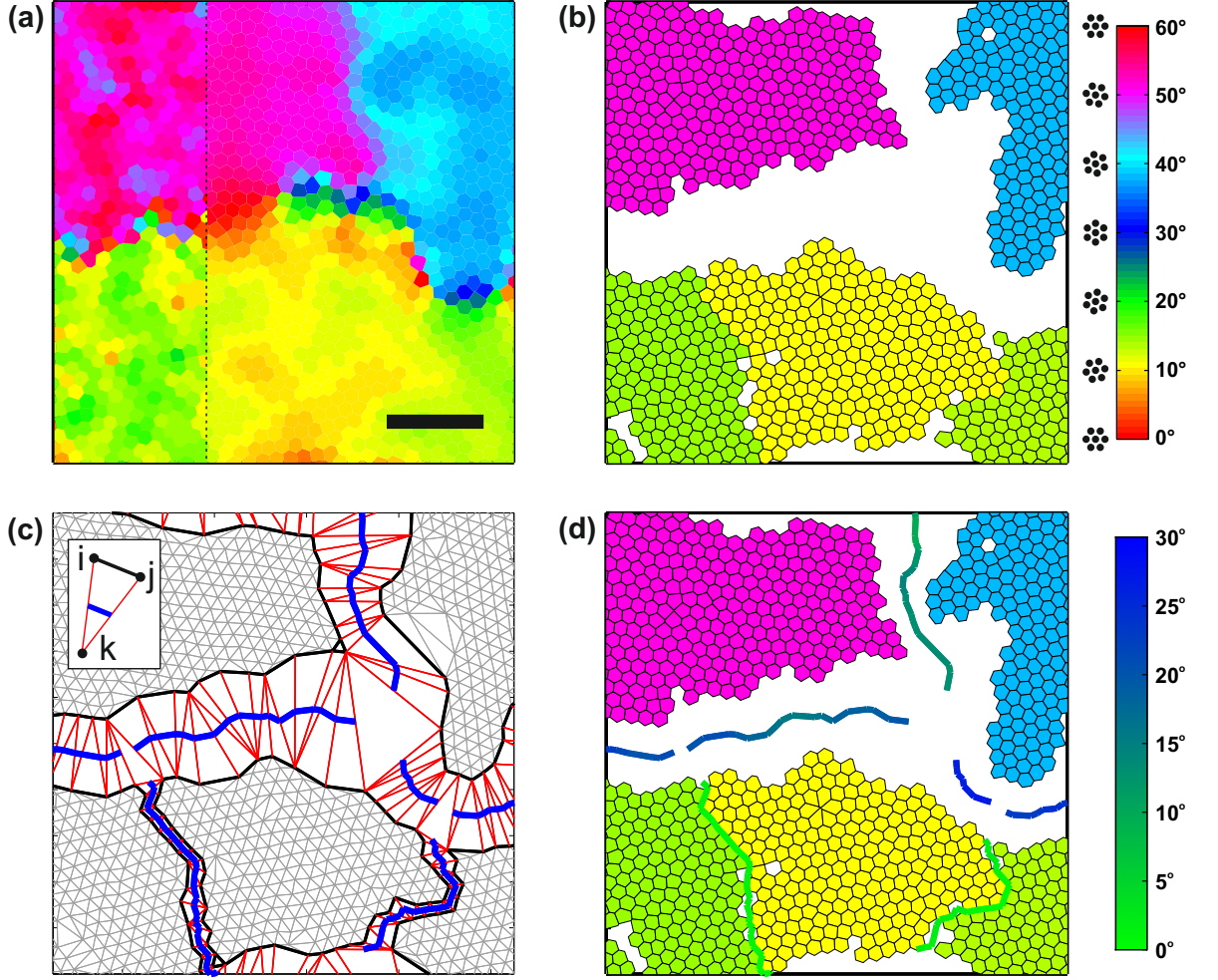


Figure 3.2: (a) Local view of the smoothed orientation map $\tilde{\theta}_6$. The inset on the left of the snapshot shows the raw orientation map θ_6 before smoothing. Scale bar, 20 μm . (b) The output of the grain detection algorithm adapted from Dillmann et al. [108]. Each grain is coloured according to the average $\tilde{\theta}_6$ of the particles within it. (c) Delaunay triangulation of the crystal-like particles. The GB connectors are coloured in red, the grain edges in black, and the GB segments in blue. The inset shows the construction of a GB segment involving three particles i , j and k (see text). (d) The output of the grain detection together with the GB segments coloured according to their misorientation as indicated by the colourbar.

connector as

$$\theta_{ik} = \min(|\tilde{\theta}_{6,i} - \tilde{\theta}_{6,k}|, 60^\circ - |\tilde{\theta}_{6,i} - \tilde{\theta}_{6,k}|) \in [0, 30^\circ], \quad (3.11)$$

where $\tilde{\theta}_{6,i}$ is the smoothed orientation at the site i . Note that the expression of θ_{ik} respects the symmetry $\theta \rightarrow 60^\circ - \theta$ of hexagonal closed-packed crystals. The misorientation θ_{kij} associated to a GB segment involving the two consecutive GB connectors $k-i$ and $k-j$ is then calculated

via

$$\theta_{kij} = \min \left(\left| \frac{\theta_{ki} + \theta_{kj}}{2} \right|, 60^\circ - \left| \frac{\theta_{ki} + \theta_{kj}}{2} \right| \right), \quad (3.12)$$

which lies in the range $0 - 30^\circ$ as well. The GB segments, coloured according to their misorientation, are plotted in figure 3.2(d) to directly visualise the local misorientation of the GBs. One can see that the algorithm is able to detect most GBs present in the snapshot, including two GBs with a small misorientation $\simeq 5^\circ$.

Finally, the GBCD is determined from the length l of each GB segment. The lengths of the GB segments with a misorientation in the interval $[\theta; \theta + \delta\theta]$ are added together and this sum is denoted $l(\theta, t)$. Dividing $l(\theta, t)$ by the total length of GB segments yields the value of the GBCD, $p(\theta, t)$, according to equation (3.5). The value of $\delta\theta$ is set to 0.75° in this chapter.

3.4 Results and discussion

3.4.1 Bond-orientational ordering

Figure 3.3(a)-(c) show representative microscopy images of a small area of the colloidal polycrystalline monolayer at different times, indicating an evident increase of the average grain size. The smoothed orientation fields corresponding to the exact same times are shown in figure 3.3(d)-(f) for the whole field of view, where the colour of a grain corresponds to the local orientation of the crystallite. Consistent with the microscopy images in figure 3.3(a)-(c), the average grain size clearly increases and the total grain boundary length decreases over time, indicating that significant grain growth takes place within the time scale of the experiments.

Figure 3.4(a) shows the bond-orientational correlation function g_6 , defined by equation (3.10), as a function of r for different times. The range of the bond-orientational correlations clearly increases with time indicating strong ordering, consistent with the images and orientation fields in figures 3.3(a)-(c) and 3.3(d)-(f). A bond-orientational correlation length R_6 is defined by $g_6(R_6, t) = 0.5$ and is determined for all times [89, 92]. The time-dependence of R_6 is shown in figure 3.4(b) and is fitted by $R_6 \sim (t - t_6)^{\alpha_6}$ following [91], where t_6 is the time at which coarsening starts. The fit gives $t_6 = 5t_B$ and a growth exponent $\alpha_6 = 0.35 \pm 0.02$, which is lower

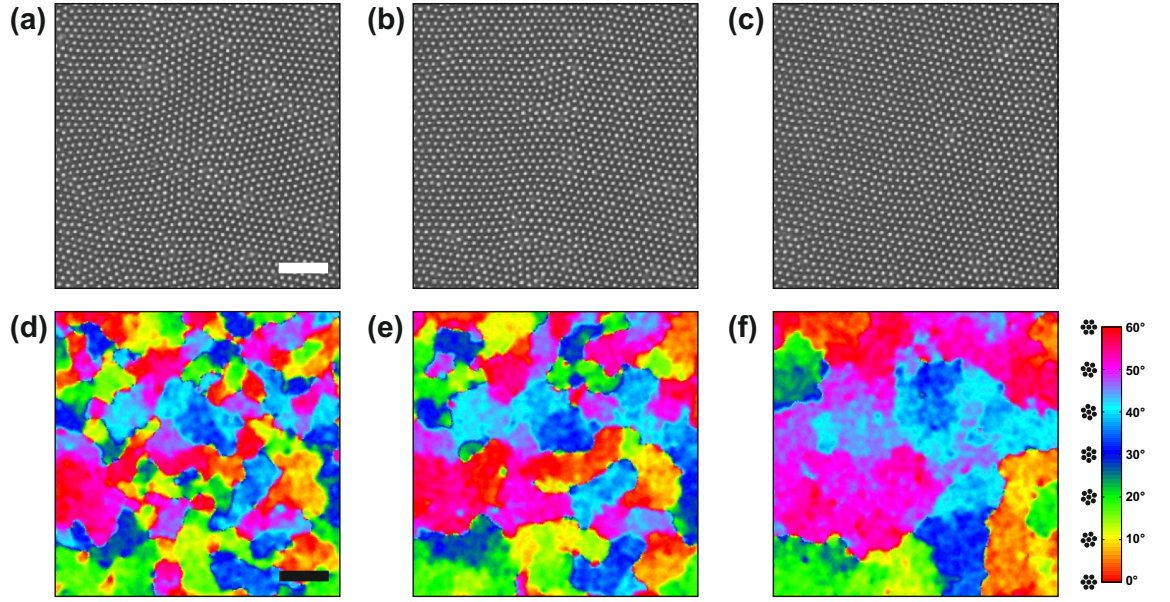


Figure 3.3: (a)-(c) Microscopy images of the colloidal polycrystalline monolayer at different times during grain growth: $32 t_B$ (a), $100 t_B$ (b) and $1000 t_B$ (c). Scale bar, $20 \mu\text{m}$. (d)-(f) The corresponding smoothed orientation fields (full field of view) at the same times. Scale bar, $100 \mu\text{m}$.

than the exponent expected for normal grain growth, $\alpha = 1/2$, as in equation (3.4) [87, 89, 92].

Plotting g_6 as a function of the rescaled distance r/R_6 shows an excellent collapse of the data (figure 3.4(c)), indicating that the dynamic scaling hypothesis [87, 88] is satisfied by g_6 and that the growth length R_6 is the only relevant length scale in the bond-orientational ordering process [87, 88]. Note that redefining R_6 by changing the constant in the right-hand side of $g_6(R_6, t) = 0.5$ does not affect these results as the new growth length is then proportional to the former one as a consequence of dynamic scaling.

The scaling form of g_6 is compared to Ohta-Jasnow-Kawasaki (OJK) theory, which states that the correlation function for a growth process driven by the motion of random domain walls after a quench into the ordered phase is given by [116, 117]

$$C_{OJK}(x) = \frac{2}{\pi} \arcsin \left(e^{-x^2/2} \right), \quad (3.13)$$

where $x = r/R(t)$ is the distance in units of a time dependent growth length $R(t)$. As R_6 is the only relevant length scale here, equation (3.13) is directly tested by plotting g_6 as a function of $x = r/R_6(t)$ in figure 3.4(c). The excellent agreement between $g_6(r/R_6)$ and C_{OJK}

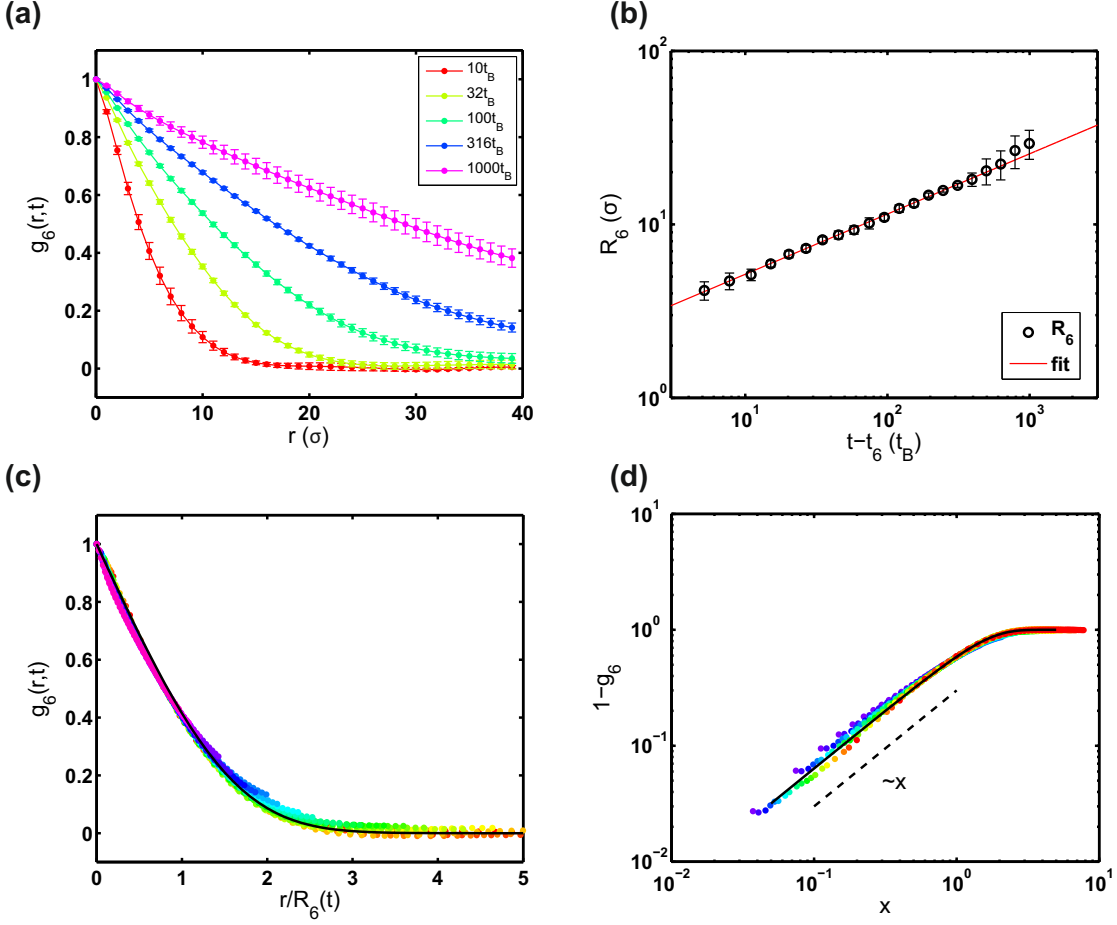


Figure 3.4: (a) The bond-orientational correlation function $g_6(r, t)$ as defined by equation (3.10) for different times. (b) Time-evolution of the orientational correlation length R_6 . The red solid line is the result of the fit to $R_6 \sim (t - t_6)^{\alpha_6}$. All error bars correspond to the standard deviation of the different experimental runs. (c) The correlation function g_6 as a function of the distance rescaled by the correlation length R_6 . The solid black line is the correlation function given by OJK theory, see equation (3.13). (d) A log-log plot of $1 - g_6$ as a function of the rescaled distance $x = r/R_6(t)$, which scales as x (black dashed line) following the prediction from Porod's law, see equation (3.14).

in figure 3.4(c) shows that GBs act as random domain walls in this system. At short distances or late times, which is equivalent to small values of x , the correlation function behaves as $C_{OJK}(x) \simeq 1 - 2x/\pi$ [93, 117]. This leads to a linear decay of the correlations

$$g_6(r, t) \simeq 1 - \frac{2}{\pi} \frac{r}{R_6(t)}, \quad (3.14)$$

which is the real-space counterpart of the well-known Porod's law [87, 93, 117]. This feature can be directly tested by plotting $1 - g_6$ in terms of $x = r/R_6(t)$, as shown in figure 3.4(d). The data exhibits a very clear linear behaviour as $x \rightarrow 0$, which is in excellent agreement with Porod's

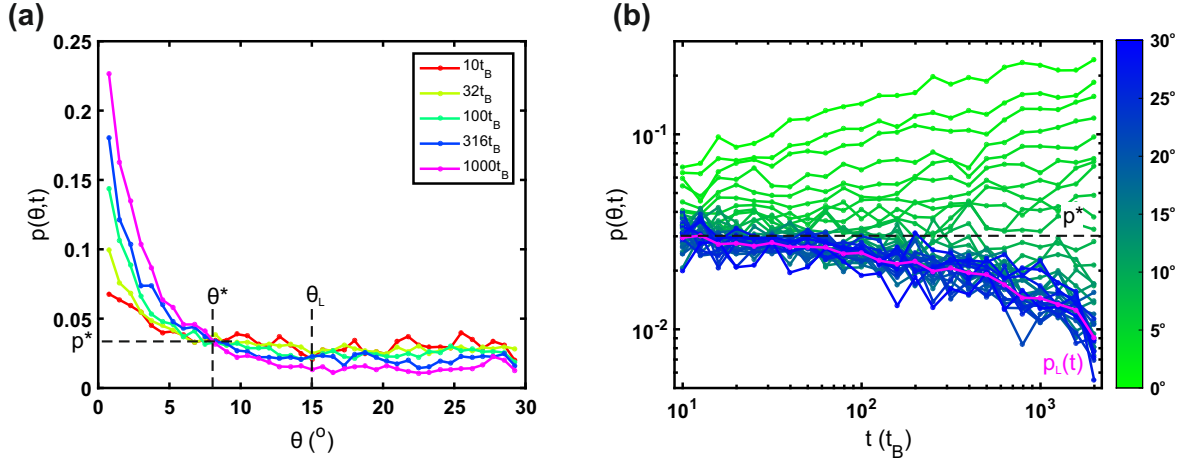


Figure 3.5: (a) Grain boundary character distribution (GBCD), $p(\theta, t)$, as a function of the misorientation, θ , for different times during coarsening. The LAGB regime is defined as GBs with misorientations above θ_L . The value θ^* is a crossover point in the SAGB regime corresponding to the value p^* of the GBCD. (b) GBCD as a function of time for different misorientations, where each curve is coloured according to the misorientation as indicated by the colourbar. The time dependence of the GBCD is strongly angle dependent below θ_L , with a transition from increasing to decreasing at the crossover value θ^* , where the GBCD equals p^* . Above θ_L , the GBCD curves decay in the same fashion, which corresponds to an average master curve denoted $p_L(t)$ (magenta line).

law. Note that both the OJK scaling form and Porod's law were found to be valid in coarsening systems containing random domain walls such as Potts models [89] and liquid crystals [91, 92]. Finally, the OJK form in equation (3.13) is noticeably different from the expressions of g_6 in each of the equilibrium phases of hard disks in 2D space, namely liquid, hexatic and crystal, for which g_6 is respectively a decaying exponential, a power law and a constant [33, 40, 50].

3.4.2 Grain boundary character distribution

The fact that the growth exponent, $\alpha_6 \simeq 0.35$, is different from $1/2$ suggests the presence of abnormal grain growth in this system, which points towards a misorientation dependence of the reduced mobility, $M(\theta)\Gamma(\theta)$, as can be seen from equation (3.6) and equation (3.7).

In order to check whether the kinetics of GBs depend on their misorientation, the relative length of GBs with a given misorientation θ is monitored by computing the GBCD, $p(\theta, t)$, as explained in section 3.3.3. The GBCD as a function of the misorientation θ is shown in figure 3.5(a), for different times during coarsening. Additionally, the GBCD is plotted as a function of time for different values of the misorientation in figure 3.5(b). Clearly from figure 3.5(a), the

GBCD is a decaying function of θ with a plateau at high θ , typically above a value $\theta_L \simeq 15^\circ$. The height of the plateau decreases as a function of time, which is clear from the time-decay of the GBCD curves for $\theta \geq \theta_L \simeq 15^\circ$ in figure 3.5(b). Strikingly, one can see from figure 3.5(b) that for misorientations above $\theta_L \simeq 15^\circ$, the GBCD becomes independent of the misorientation, so that

$$p(\theta, t) = p_L(t) \quad \text{for} \quad \theta \geq \theta_L. \quad (3.15)$$

Experimentally, $p_L(t)$ can be determined by averaging the GBCD over the interval $[\theta_L, 30^\circ]$, as shown by the magenta line in figure 3.5(b). One concludes that GBs with a misorientation greater than $\theta_L \simeq 15^\circ$ have the same kinetics, as it is governed by $p_L(t)$, which does not depend on θ . In the following, GBs with a misorientation $\theta \in [\theta_L; 30^\circ]$, where $\theta_L = 15^\circ$, are referred to as *large angle grain boundaries* (LAGBs). Otherwise they are termed *small angle grain boundaries* (SAGBs).

Interestingly, the kinetics of SAGBs strongly contrast with that of LAGBs. Indeed, the combined inspection of figure 3.5(a) and figure 3.5(b) reveals that for misorientations below θ_L , the GBCD can increase or decrease depending on whether θ is smaller or larger than a crossover value θ^* . From the data in figure 3.5(a), one can estimate the location of the crossover to be $\theta^* \simeq 8.5^\circ$, which corresponds to a *constant* value of the GBCD, $p^* \simeq 0.03$, as can be seen from figure 3.5(b). This shows that unlike LAGBs, the kinetics of SAGBs strongly depends on the value of their misorientation.

3.4.3 Kinetics of the grain boundary network

To clarify the contributions of LAGBs and SAGBs to the coarsening kinetics, the GB network is directly visualised in figure 3.6(a)-(c), which shows snapshots of the GBs coloured according to the magnitude of their local misorientation θ for the whole field of view. These snapshots indicate a significant annihilation of LAGBs, leaving large areas containing mainly SAGBs, which enclose smaller grains. This can be quantified by monitoring the evolution of the total

lengths of GBs, SAGBs and LAGBs defined by

$$\Lambda_k = \int_k l(\theta, t) d\theta, \quad \text{with } k \text{ corresponding to } \begin{cases} I = [0; 30^\circ] & \text{for GBs} \\ S = [0; \theta_L[& \text{for SAGBs} \\ L = [\theta_L; 30^\circ] & \text{for LAGBs,} \end{cases} \quad (3.16)$$

and such that $\Lambda_I = \Lambda_S + \Lambda_L$. The time-evolution of the Λ_k 's is shown in figure 3.7(a). While Λ_I decreases slightly over time, there is a significant annihilation of LAGBs as indicated by the strong decrease of Λ_L , consistent with the behaviour of the GBCD in figure 3.5(a) and (b). This is in clear contrast with the very weak increase of Λ_S indicating that overall, the SAGBs become relatively more present in the system.

In light of the snapshots in figure 3.6(a)-(c) and the differences in the kinetics between SAGBs and LAGBs visible in figure 3.7(a), the network of GBs can be seen as having two components: the LAGBs, which are in the minority, and the SAGBs. Based on this, one defines two typical length scales

$$R_S = \frac{A}{\Lambda_S}, \quad (3.17a)$$

$$R_L = \frac{A}{\Lambda_L}, \quad (3.17b)$$

where A is the area of the field of view. Within this definition, R_S (R_L) corresponds to the average distance from one SAGB (LAGB) to the other. It is important to note that R_S and R_L are different from the grain size, $R_I = A/\Lambda_I$, which is the mean distance from one GB to another, regardless of their types.

In order to derive the growth laws corresponding to R_S and R_L , it is reasonable to assume that the kinetics of SAGBs and LAGBs are driven by the curvature of the GBs of their own type. Consequently, the kinetics can be described by two equations analogous to equation (3.7) corresponding to each network as

$$\frac{dR_S}{dt} = \frac{\langle M\Gamma \rangle_S}{R_S} \quad (3.18a)$$

$$\frac{dR_L}{dt} = \frac{\langle M\Gamma \rangle_L}{R_L}. \quad (3.18b)$$

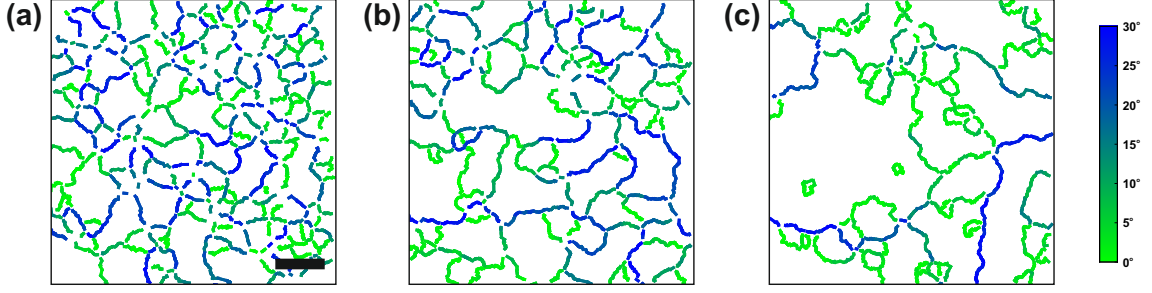


Figure 3.6: (a)-(c) View of the GBs coloured according to the value of their misorientation at the exact same times as in figures 3.3(a)-(c) and (d)-(f). This provides a direct way to visualise the SAGBs and LAGBs during coarsening. Scale bar, 100 μm .

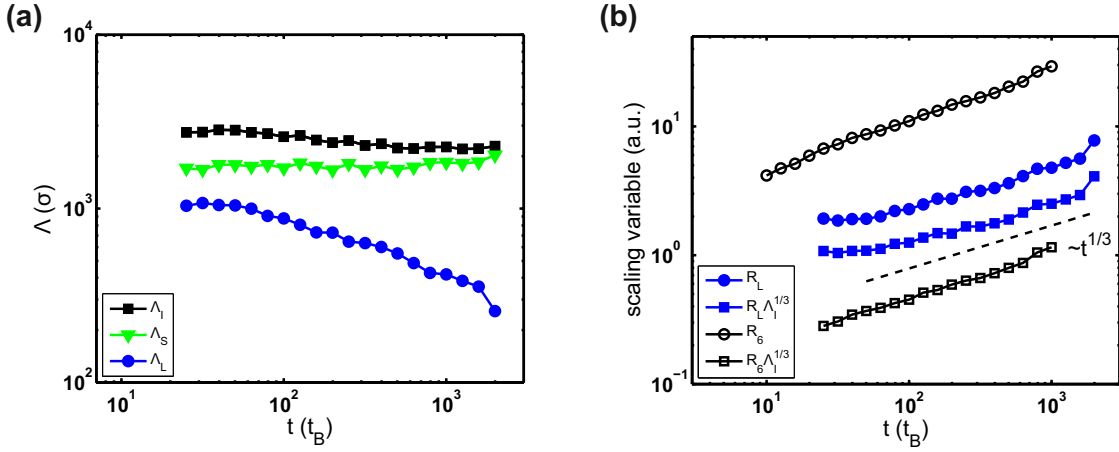


Figure 3.7: (a) Time-evolution of the total lengths of GBs, SAGBs and LAGBs, namely Λ_I , Λ_S and Λ_L in units of particle diameters. (b) Time-evolution of the length scale R_L , obtained from A/Λ_L where A is the area of the field of view. The quantity $R_L \Lambda_I^{1/3}$ behaves as $t^{1/3}$ (black dashed line) at long times. The bond-orientational correlation length, R_6 , exhibits the same scaling properties as R_L .

Here, $\langle M\Gamma \rangle_S$ and $\langle M\Gamma \rangle_L$ are two time-dependent reduced-mobilities defined by

$$\langle M\Gamma \rangle_S = \int_S M(\theta) \Gamma(\theta) p(\theta, t) d\theta \quad (3.19a)$$

$$\langle M\Gamma \rangle_L = \int_L M(\theta) \Gamma(\theta) p(\theta, t) d\theta \quad (3.19b)$$

and such that

$$\langle M\Gamma \rangle_I = \langle M\Gamma \rangle_S + \langle M\Gamma \rangle_L, \quad (3.20)$$

where $\langle M\Gamma \rangle_I$ is the total reduced mobility. Note that all $\langle M\Gamma \rangle_k$'s with $k = I, S, L$, represent

coarsening rates, which depend on the configuration of the GB network via $p(\theta, t)$. From the experimental data in figure 3.6, it is clear that Λ_S hardly changes at all so $dR_S/dt \simeq 0$, and therefore one focuses on the case of LAGBs described by equation (3.18b). Using successively the definition of $\langle M\Gamma \rangle_L$ in equation (3.19b) and the property of the GBCD for LAGBs as given by equation (3.15), one obtains

$$\begin{aligned} \langle M\Gamma \rangle_L &= \int_L M(\theta)\Gamma(\theta)p(\theta, t)d\theta \\ &= \int_L M(\theta)\Gamma(\theta)p_L(t)d\theta \\ &= p_L(t) \int_L M(\theta)\Gamma(\theta)d\theta \\ &\sim p_L(t), \end{aligned} \tag{3.21}$$

as the remaining integral over θ is time-independent. Note that, importantly, the last equation means that the behaviour of the GBCD for LAGBs, p_L , is directly proportional to the average reduced mobility of LAGBs, $\langle M\Gamma \rangle_L$. As p_L decreases during coarsening (see figure 3.5(b)), one can deduce that $\langle M\Gamma \rangle_L$ decreases as well, *without a priori knowledge* of $M(\theta)\Gamma(\theta)$. Finally, one can derive the time-dependence of R_L by combining its definition, $R_L \sim 1/\Lambda_L$, with equation (3.16). This gives

$$R_L \sim \left(\int_L l(\theta, t)d\theta \right)^{-1}, \tag{3.22}$$

which can be rewritten using successively equation (3.5), equation (3.15) and equation (3.16) as

$$\begin{aligned} R_L &\sim \left(\int_L p(\theta, t) \int_I l(\theta', t)d\theta'd\theta \right)^{-1} \\ &\sim \left(\int_L p_L(t)\Lambda_I(t)d\theta \right)^{-1} \\ &\sim (p_L(t)\Lambda_I(t))^{-1}, \end{aligned} \tag{3.23}$$

since the integrand does not depend on θ in the second-last line of equation (3.23). Combining equation (3.21) and equation (3.23) yields $\langle M\Gamma \rangle_L \sim 1/(R_L\Lambda_I)$, which can be inserted into equation (3.18b) to give

$$\frac{dR_L}{dt} \sim \frac{1}{\Lambda_I R_L^2}. \tag{3.24}$$

Assuming that R_L can be described by a power law in the regime probed here, one has $dR_L/dt \sim R_L/t$ and a simple rearrangement of equation (3.24) finally leads to

$$R_L \Lambda_I^{1/3} \sim t^{1/3}. \quad (3.25)$$

The growth law corresponding to equation (3.25) is directly tested on the experimental data in figure 3.7(b). One can see that the quantity $R_L \Lambda_I^{1/3}$ is parallel to the $\sim t^{1/3}$ curve at long times, indicating that equation (3.25) is satisfied. This means that equation (3.18b) is valid to describe the kinetics of the LAGB network, which is driven by the curvature of LAGBs only, but with a time-dependent reduced mobility, $\langle MT \rangle_L$, that depends on the fraction of LAGBs in the system at a given time. The same scaling is also valid for the quantity $R_6 \Lambda_I^{1/3}$, which means that R_L and R_6 correspond to the same length scale (see figure 3.7(b)). This indicates that the bond-orientational ordering process is equivalent to the coarsening of the LAGB network, suggesting that the bond-orientation correlation function g_6 is quite insensitive to the presence of SAGBs. Note that R_L and R_6 follow power laws close to $\sim t^{1/3}$ (see figure 3.7(b)), indicating that these quantities dominate Λ_I , which decreases very weakly. In fact, the small decrease of Λ_I implies that R_L and R_6 grow a bit faster than $t^{1/3}$, consistent with the data.

3.5 Conclusions

In summary, we have shown that grain growth in a colloidal polycrystalline monolayer of hard spheres is characterised by a strong bond-orientational ordering, which has general scaling features of systems with random domain walls. However, it exhibits abnormal grain growth as the correlation length grows with an exponent lower than 1/2. By monitoring the kinetics of the grain boundaries as a function of their misorientation, it has been shown that there is a preferential annihilation of large angle grain boundaries and that the relative amount of small angle grain boundaries increases. The experimental growth law associated to the network of large angle grain boundaries is consistent with kinetics driven by their own curvature, but with a time-dependent reduced mobility, which depends on their relative length with respect to the whole network of grain boundaries. Finally, the bond-orientational ordering process was shown to be equivalent to the coarsening of the large angle grain boundary network, which dominates the decay of the correlations.

Acknowledgements

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Chapter 4

Equilibrium grain boundary segregation of impurities

ABSTRACT

In this chapter, the segregation of impurities to grain boundaries in colloidal polycrystalline monolayers is investigated using video-microscopy. A model colloidal alloy is prepared by embedding large spherical impurities in a polycrystalline monolayer of small colloidal hard spheres, which enables the grain growth to be stopped at a finite grain size. The partitioning of impurities between the grains and the grain boundaries is found to be in very good agreement with the Langmuir-McLean adsorption model for equilibrium grain boundary segregation, which enables the direct measurement of the free energy of adsorption for two types of impurities. Furthermore, the spatial distribution of impurities at grain boundaries near saturation is characterised and is found to strongly depend on the size ratio between the impurities and the small particles. This is due to the fact that the relative importance of clustering and mixing due to non-additivity is determined by geometrical constraints imposed by the lattice.

4.1 Introduction

The process of alloying, i.e. the incorporation of solute atoms of one or several other elements in a metal, can dramatically change the properties of a material [13]. For example, solute atoms, or impurities, can interact with grain boundaries (GBs) via impurity drag [12, 118] or Zener pinning [12, 119, 120], which stops the grain growth process at a given average grain size [13, 121, 122]. Controlling the grain size turns out to be key in tuning the mechanical properties of a material due to the Hall-Petch effect, which predicts that the strength of a material sensitively depends on the grain size [14–16].

In a polycrystalline alloy, impurities tend to be adsorbed at GBs, as they offer more free volume than the grains, a phenomenon known as GB segregation [43, 123]. This is similar to the adsorption of a gas onto a solid surface, with the impurity concentration in the bulk crystal being analogous to the pressure of the gas [123–125]. At equilibrium, the surface coverage as a function of the pressure in the gas phase is given by the Langmuir adsorption model, in the ideal case where there is no interactions between adsorbed atoms [126, 127]. An analogous adsorption model for GBs has been proposed by McLean [123] and good agreement with experimental data was found for different alloys [128, 129]. Nevertheless, different behaviours can be observed depending on e.g. the solute-solvent interactions, the solute-solvent size misfit and the lattice structure [43, 125].

Colloidal polycrystalline systems with embedded impurities have already been proven to be good model systems to directly visualise GB segregation using brightfield or confocal microscopy [39, 107, 130]. Grain size control [107, 131, 132] together with the dynamics of segregation during crystallisation have been investigated in detail using such systems [133, 134]. Also from a more fundamental point of view, monolayers of colloidal spheres with added impurities are very interesting to study as they provide a simple realisation of a non-additive binary system [135, 136], which can exhibit a very rich phase behaviour caused by the clustering of the impurity particles due to depletion effects [135–138].

In this chapter, GB segregation in a polycrystalline monolayer of hard spheres with added impurities of larger size is studied using video-microscopy. Two types of impurities are studied with different size misfits and degrees of non-additivity. Very good agreement with the

Langmuir-McLean adsorption model is found, which enables the direct measurement of the free energy of adsorption for both types of impurities used in this colloidal system. In addition, the spatial distribution of impurities close to saturation is studied, highlighting different relative contributions of clustering and mixing due to non-additivity. These differences are shown to be due to geometrical constraints imposed by the lattice.

4.2 Theory

In this section, the McLean model to describe adsorption of impurities at GBs is presented together with the derivation of an adsorption isotherm, mainly following [123] and [124].

We consider a lattice of N undistorted sites containing P impurities, corresponding to the impurities in the bulk crystal. The GBs are modelled by n distorted sites, with p “adsorbed” impurities distributed among them. The free energy costs corresponding to an impurity occupying an undistorted or distorted lattice site are denoted E and e , respectively. The configurational entropy of the system is $S = k_B \ln \Omega$, where k_B is the Boltzmann constant and Ω is the number of configurations given by

$$\Omega = \Omega_{bulk} \Omega_{GB} = \frac{N! n!}{P! (N - P)! p! (n - p)!}.$$

The free energy $F = E - TS$ is then found as

$$F = PE + pe - k_B T \ln \left(\frac{N! n!}{P! (N - P)! p! (n - p)!} \right). \quad (4.1)$$

As the total number of impurities $Z = P + p$ is constant, we can rewrite the free energy as a function of p only and the equilibrium configuration is obtained by solving $\partial F / \partial p = 0$:

$$\begin{aligned} 0 &= \frac{\partial}{\partial p} \left[(Z - p)E + pe - k_B T \ln \left(\frac{N! n!}{(Z - p)! (N - Z + p)! p! (n - p)!} \right) \right] \\ &= -E + e - k_B T \ln \left(\frac{(Z - p)(n - p)}{p(N - Z + p)} \right). \end{aligned} \quad (4.2)$$

Here, the Stirling formula, $\ln N! \approx N \ln N - N$ for large N , has been used as a simplification.

Rearranging the last line of equation (4.2) leads to

$$\frac{p(N - Z + p)}{(Z - p)(n - p)} = \exp\left(\frac{E - e}{k_B T}\right), \quad (4.3)$$

and using $P = Z - p$ again, this equation becomes

$$\frac{p}{n - p} = \frac{P}{N - P} \exp\left(\frac{e_a}{k_B T}\right), \quad (4.4)$$

where $e_a = E - e$ is the adsorption energy of an impurity at a GB.

Next, we introduce the number concentration of impurities in the bulk crystal, $X_b = P/N$, and note that saturation does not necessarily correspond to a full coverage of the distorted sites. We can account for this by considering a number $n_{tot} \geq n$ of distorted sites, out of which n can be occupied at most. The fraction of impurities at GBs is then $X_{gb} = p/n_{tot}$ with a saturation value $X_{gb}^{sat} = n/n_{tot}$. Taking this into account, equation (4.4) becomes

$$\frac{X_{gb}}{X_{gb}^{sat} - X_{gb}} = \frac{X_b}{1 - X_b} \exp\left(\frac{e_a}{k_B T}\right). \quad (4.5)$$

Defining the equilibrium constant as $K = \exp(e_a/k_B T)$ and considering the dilute limit $X_b \ll 1$ for which $X_b/(1 - X_b) \simeq X_b$ to the lowest order, equation (4.5) simplifies to

$$\frac{X_{gb}}{X_{gb}^{sat}} = \frac{K X_b}{1 + K X_b}. \quad (4.6)$$

Equation (4.6) is analogous to the Langmuir adsorption isotherm [126, 127]. This relation indicates that X_{gb} increases linearly with X_b in the limit of small X_b as the denominator is close to unity. At high X_b , X_{gb} reaches a constant equal to the saturation level X_{gb}^{sat} .

4.3 Methods

4.3.1 Preparation of “colloidal alloys”

The experimental system consists of polycrystalline monolayers with added larger colloidal particles, termed impurities. The particles of the crystalline matrix are melamine formaldehyde spheres of diameter $\sigma_s = 2.7 \mu\text{m}$, as introduced in section 2.3.1. The impurity particles are also

melamine formaldehyde spheres, with diameters $\sigma_i = 6.1 \mu\text{m}$ and $10.8 \mu\text{m}$. In the following, the size ratio between the impurity and the matrix particles is denoted by $\lambda = \sigma_i/\sigma_s$.

Impurity-doped polycrystalline monolayers are prepared using the same method as described in section 2.3.1, with different concentrations of impurities. The sample cell is placed on a levelled microscope stage and the polycrystalline monolayer is left to coarsen until grain growth has stopped due to the presence of impurities. All the samples are prepared 24h before data acquisition as this corresponds to the coarsening time of the samples with the lowest concentration of impurities. Images of the polycrystalline structures are recorded as described in section 2.3.2 using a $20\times$ objective. As the area of the sample cell is much bigger than the area of interest, images containing $\sim 4 \times 10^4$ particles are taken at different locations within the monolayer to improve statistics for a given concentration of impurities. This was found to be necessary as the fluctuations in the number of impurities per frame can be significant, especially when their concentration is small.

4.3.2 Composition variables

The confinement of the matrix and impurity particles into a monolayer leads to non-additivity as the effective impurity size in the plane of the small particles, which is the observation plane, can be significantly different from the actual impurity size, see figure 4.1(a). Using elementary geometry, the effective in-plane impurity size, σ'_i in figure 4.1(a), is found as

$$\sigma'_i = \sigma_s \left(2\sqrt{\frac{\sigma_i}{\sigma_s}} - 1 \right), \quad (4.7)$$

which is used to define the effective in-plane size ratio as $\lambda' = \sigma'_i/\sigma_s$. The non-additivity is quantified by the non-additivity parameter, Δ , defined by [137,138]

$$\frac{\sigma_s + \sigma'_i}{2} = \frac{\sigma_s + \sigma_i}{2}(1 + \Delta), \quad (4.8)$$

which can be expressed in terms of the size ratios as

$$\Delta = \frac{\lambda' - \lambda}{\lambda + 1}. \quad (4.9)$$

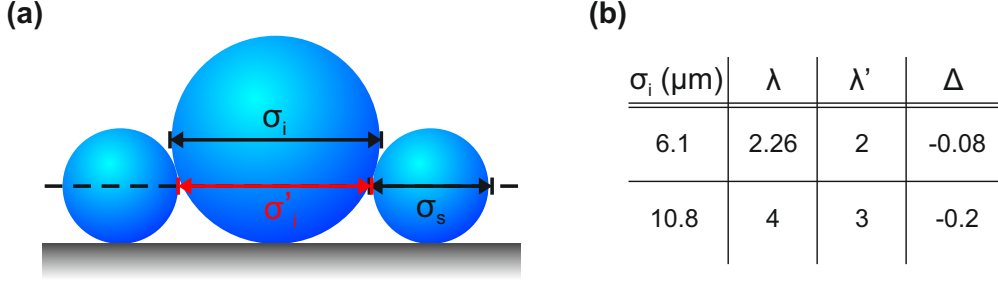


Figure 4.1: Schematic view of close-packed hard spheres of two different sizes arranged in a monolayer. The diameters of the small and large particles are denoted σ_s and σ_i respectively. The effective diameter in the plane of the small particles (dashed line) is denoted σ'_i . (b) Characteristics of the two types of impurity particles: diameter σ_i , real and in-plane size ratios λ and λ' , together with the non-additivity parameter Δ .

The characteristic geometrical quantities of the two types of impurities are given in figure 4.1(b), showing that Δ is negative and that the in-plane size ratios are integers in both cases.

The area fractions within the plane of observation are defined by

$$\phi_s = \frac{\pi \sigma_s^2 N_s}{4A} \quad \text{and} \quad \phi_i = \frac{\pi \sigma_i'^2 N_i}{4A}, \quad (4.10)$$

where N_s and N_i are the number of particles of each kind present within a given area of interest A . The total area fraction is then given by $\phi_s + \phi_i$, which is a good approximation as long as the number of contacts between impurities is relatively small [76]. Following [76], the composition of the sample is defined by

$$Q = \frac{\phi_i}{\phi_s + \phi_i} = \frac{\lambda'^2 N_i}{N_s + \lambda'^2 N_i}, \quad (4.11)$$

whose value varies between 0 and 1, corresponding to the cases where no and only impurities are present, respectively. Similarly, composition variables for impurities in the bulk and in the GB are defined as

$$Q_b = \frac{\phi_i^b}{\phi_s^b + \phi_i^b} = \frac{\lambda'^2 N_i^b}{N_s^b + \lambda'^2 N_i^b}, \quad (4.12a)$$

$$Q_{gb} = \frac{\phi_i^{gb}}{\phi_s^{gb} + \phi_i^{gb}} = \frac{\lambda'^2 N_i^{gb}}{N_s^{gb} + \lambda'^2 N_i^{gb}}. \quad (4.12b)$$

Here, ϕ_i^b (ϕ_i^{gb}) is the area fraction of impurities in the bulk (GBs) and N_i^b (N_i^{gb}) is the number

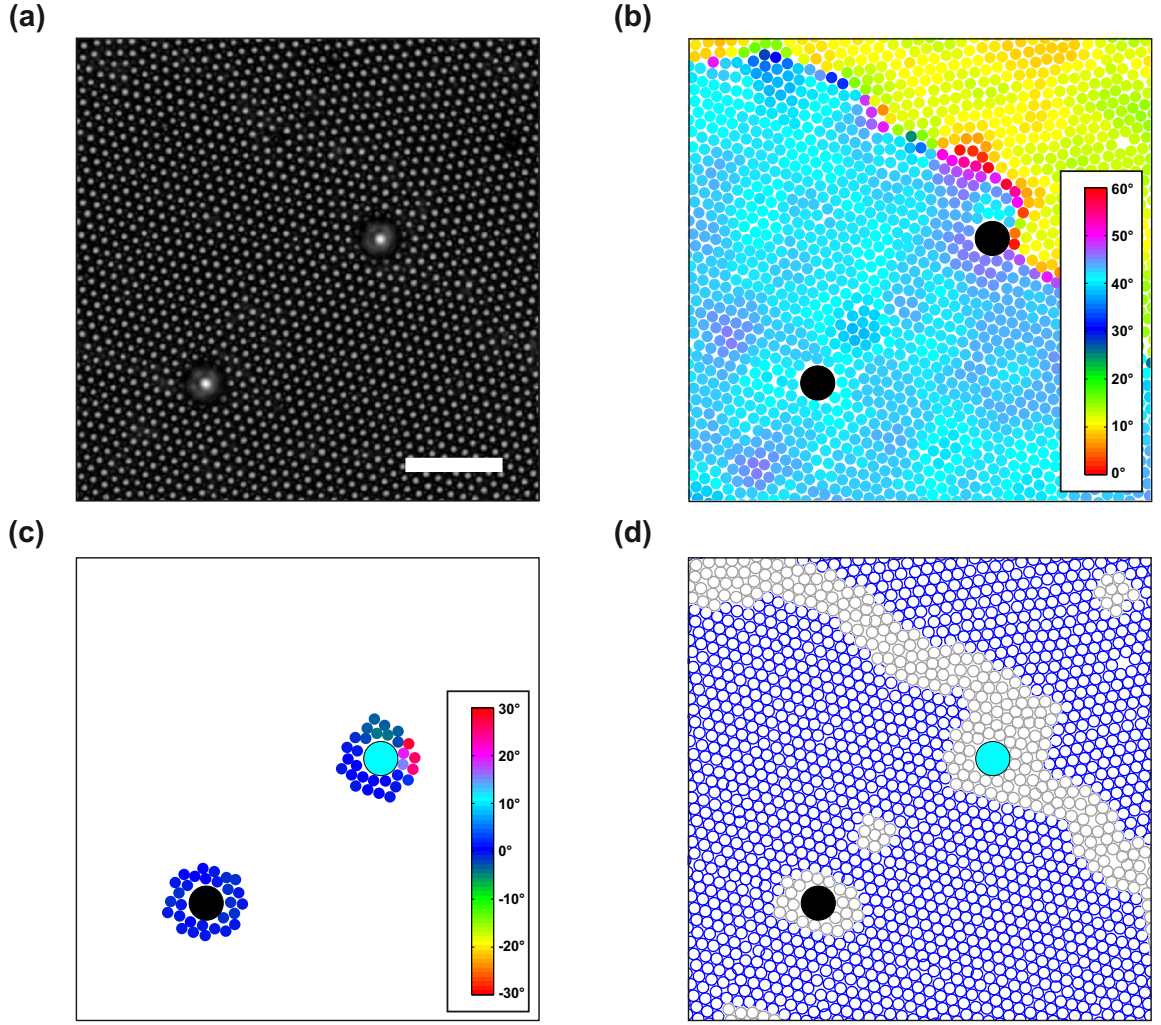


Figure 4.2: (a) Image of a small area of a colloidal polycrystalline monolayer containing impurities of size ratio $\lambda' = 3$. Scale bar, $30\mu\text{m}$. (b) Output of the particle detection where impurities are black disks and matrix particles are coloured according to their orientation θ_6 , indicated by the colourbar. (c) Impurities with their two shells of nearest neighbours, coloured according to the value of their orientation relative to the mean, θ_6^0 (see text), as indicated by the colourbar. The impurity successfully detected as belonging to the grain boundary is coloured in cyan. (d) Crystal and GB matrix particles coloured in blue and grey respectively with the two discriminated impurities.

of impurities in the bulk (GBs). The same notation applies to small particles. Note that both Q_b and Q_{gb} vary between 0 and 1.

4.3.3 Detection of adsorbed impurities

Standard image analysis routines are used to obtain the coordinates of the particles in each frame (see section 2.3.2), and the impurity particles are discriminated from the small ones based

on their size and brightness, see figure 4.2(a). For all particles, the smoothed bond-orientational field, $\tilde{\psi}_6$, is calculated together with the smoothed orientation for each particle, $\tilde{\theta}_6$, as described in section 3.3.2. In the following they are denoted by ψ_6 and θ_6 for simplicity. An example of output of the image analysis is shown in figure 4.2(b) for $\lambda' = 3$, where two impurities can be seen, one in a grain and the other in a GB.

To determine whether impurities are located in grains or adsorbed at GBs, a procedure is developed based on the local orientation around impurities, as it is uniform if they lie in a grain and strongly varies if they are located at a GB. Firstly, for every impurity, the two shells of nearest neighbours are selected, a set denoted S_2 (see figure 4.2(c)). Next, for each particle $j \in S_2$, the orientation relative to the mean is defined as

$$\theta_6^0(\vec{r}_j) = \frac{1}{6} \arg \left(\frac{\psi_6(\vec{r}_j)}{\langle \psi_6(\vec{r}_k) \rangle_{k \in S_2}} \right), \quad (4.13)$$

where $\langle . \rangle$ denotes the average over S_2 and the argument is taken in the interval $]-\pi/6; \pi/6]$. By definition, θ_6^0 is always distributed around 0, which avoids having the discontinuity between 0 and $\pi/3$ present in the θ_6 -field due to the 6-fold symmetry. The neighbours of impurity particles adsorbed at GBs typically have large values of θ_6^0 , while neighbours of bulk impurities have θ_6^0 close to 0, as can be seen from figure 4.2(c). Finally, an impurity is considered as adsorbed in a GB if at least 3 particles in its neighbourhood S_2 have $|\theta_6^0| > 3^\circ$. The value of this cut-off was chosen by trial and error on representative snapshots, and figure 4.2(d) shows that the impurity adsorbed in the GB is successfully discriminated by the algorithm. When performed on a whole snapshot, this analysis enables the direct measurement of the number of impurities in the bulk, N_i^b , and in the GBs, N_i^{gb} .

To discriminate the matrix particles belonging to crystalline grains and the GBs, the following criterion is applied: a matrix particle j is considered to be in a GB if $|\psi_6(\vec{r}_j)| < 0.7$, otherwise, it belongs to a crystalline grain. Note that this criterion is consistent with the one used in chapter 3 for GB detection. Figure 4.2(d) shows the crystalline matrix particles in blue and the GB ones in grey. The latter correspond well to the GBs, but also include distorted layers around bulk impurities. The numbers of matrix particles in the bulk crystal and in the GBs, N_s^b and N_s^{gb} , together with N_i^b and N_i^{gb} , are used to determine the composition of the bulk and the GBs, Q_b and Q_{gb} , according to equations (4.12a) and (4.12b).

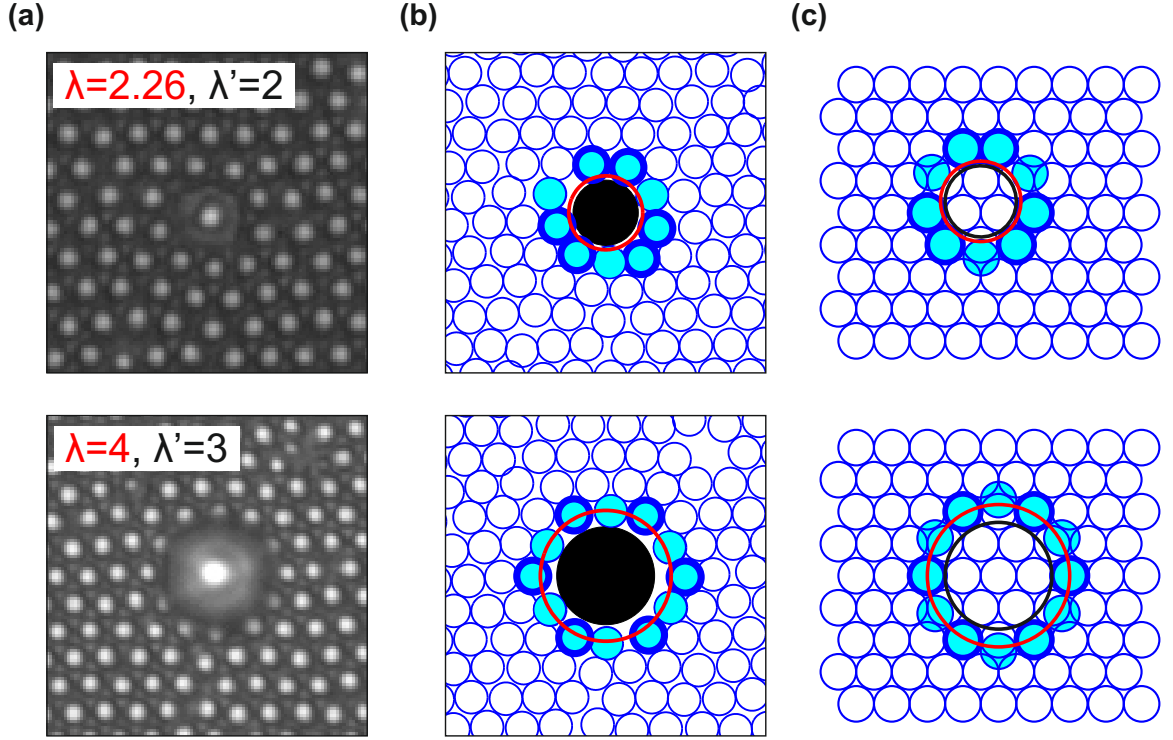


Figure 4.3: (a) Microscopy images of isolated impurities of each size embedded in the crystal. (b) Corresponding reconstructions of the images where each particle is represented by a disk with the relevant hard sphere diameter. Matrix particles are in blue with diameter σ_s , and the impurities are represented by a black disk of diameter σ'_i and a red circle of diameter σ_i . The first shell of nearest neighbours is coloured in cyan, and the thick circles highlight particles in coincidence with the crystal. (c) Equivalent geometric constructions on an ideal lattice with the same colour code, showing that the center of mass of an impurity with $\lambda' = 2$ occupies an interstitial site, while it occupies a crystal site for an impurity with $\lambda' = 3$.

4.4 Results and discussion

4.4.1 Characterisation of impurities

Figure 4.3(a) shows microscopy images of isolated impurities embedded in the bulk crystal for both size ratios. The corresponding computer reconstructions of these two snapshots are shown in figure 4.3(b), where each particle is represented by a disk with the relevant hard core diameter. For the matrix particles (blue) this is σ_s , while for the impurity particles two disks of diameters σ_i (red) and σ'_i (black) are used. The nearest neighbours (cyan) are arranged in a ring around the impurities which is partly distorted compared to the bulk crystal structure that is recovered at longer distances [130, 139].

Interestingly none of the impurities introduce any dislocations in the lattice as Burgers circuits drawn around them form closed loops. This suggests that they can fit within the lattice, presumably with their centre coinciding with a lattice or an interstitial site. This was rationalised by overlaying a disk of diameter σ'_i on a perfect hexagonal lattice and looking to maximise the number of nearest neighbours that coincide with bulk lattice sites (thick circles in figure 4.3(b) and (c)). The best matching situations are shown in figure 4.3(c), where the impurity is located at an interstitial site¹ in the case $\lambda' = 2$, and at a lattice site in the case $\lambda' = 3$. In fact, these plots show that impurities with $\lambda' = 2$ behave as interstitial impurities, while impurities with $\lambda' = 3$ behave as substitutional impurities. This terminology is used in the remainder of this chapter.

4.4.2 Grain boundary segregation and adsorption isotherms

Figure 4.4 shows partial views of polycrystalline structures with a stationary grain size for three values of the bulk composition, $Q_b = 10^{-3}$, 10^{-2} and 10^{-1} . The impurities are coloured in black if embedded in a grain and in cyan if adsorbed at a GB. Most impurities clearly populate the GBs, which indicates that GB segregation is occurring in the system. The grain size is observed to decrease with increasing Q_b , confirming that the addition of impurities is a way to control the grain size, consistent with [132,139]. Notably, for $Q_b = 10^{-3}$, only a few impurity particles adsorbed at GBs are already sufficient to stop grain growth, for both size ratios. Next, for $Q_b = 10^{-2}$, significantly more impurities are located at the GBs compared to the number of impurities in the grains, clearly indicating further GB segregation, while the sample remains polycrystalline. Finally, in the case $Q_b = 10^{-1}$, the GBs are loaded with many impurities and the polycrystalline nature is preserved. Note, however, that some areas of the sample look quite disordered, especially for $Q_b = 10^{-1}$ and $\lambda' = 2$. This is consistent with recent studies on colloidal microgels, which have shown that high impurity concentrations can lead to vitrification of the sample [140]. Overall, the tendency of impurities to segregate at GBs can be explained by the fact that the strain energy is much lower in the case of an impurity located at a GB than in the case of an impurity embedded in the bulk crystal [43].

Next, the GB segregation is quantified by determining the adsorption isotherms, i.e. plot-

¹In metallurgy, interstitial impurities are usually smaller than the atoms in the crystal, which contrasts with the present case.

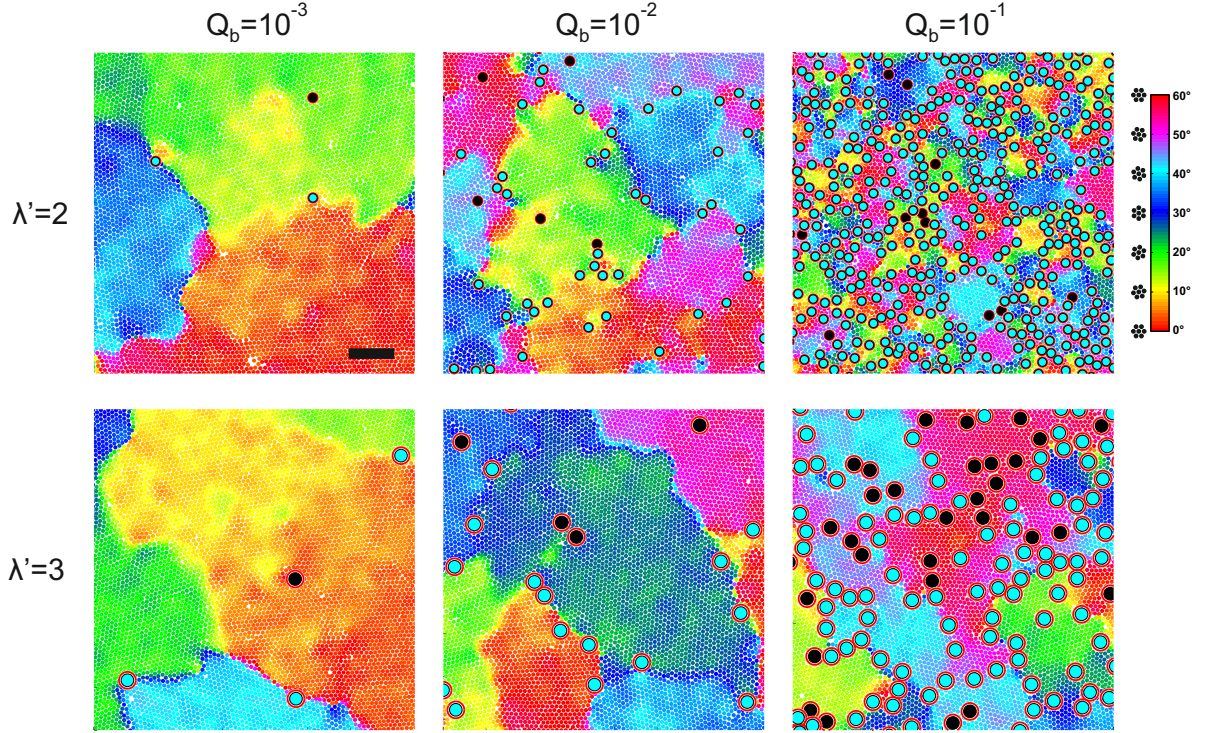


Figure 4.4: Partial views of the polycrystalline monolayer for the two types of impurities (in-plane size ratio λ') at three different bulk impurity compositions Q_b . The small particles are coloured according to their local orientation (see colourbar) while the impurities are shown in black if in a grain and in cyan if adsorbed at a GB. The red circles correspond to the actual dimensions of the impurities. Scale bar, $30\mu\text{m}$.

ting Q_{gb} as a function of Q_b , as shown in figure 4.5(a) and (b) for impurities with $\lambda' = 2$ and 3, respectively. In both cases, the data covers the dilute regime where Q_{gb} increases linearly up to $Q_b \sim 10^{-2}$, and a more concentrated regime which approaches saturation around $Q_b \sim 10^{-1}$, where the curves flatten. The solid lines correspond to fits to the Langmuir-McLean isotherm (see equation (4.6)) for each size ratio, but now rewritten in terms of composition variables

$$Q_{gb} = Q_{gb}^{sat} \frac{KQ_b}{1 + KQ_b}, \quad (4.14)$$

where the GB composition at saturation, Q_{gb}^{sat} , and the equilibrium constant, K , are the fitting parameters. As can be seen from figure 4.5(a) and (b), the Langmuir-McLean model describes the experimental data very well, indicating that equilibrium between the impurity content of the GBs and the grains has been reached.

The saturation levels for the two size ratios are very similar as the fits give $Q_{gb}^{sat} = 0.40 \pm 0.07$

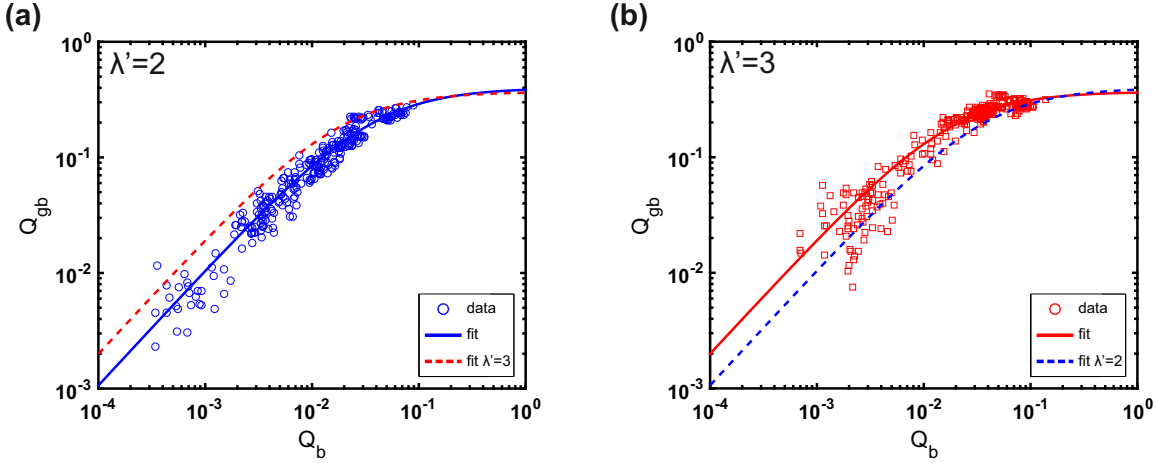


Figure 4.5: (a) Variation of the GB composition Q_{gb} as a function of the bulk composition Q_b for impurities with in-plane size ratio $\lambda' = 2$. (b) Same data in the case $\lambda' = 3$. The solid lines are fits to the Langmuir-McLean theory and the dashed lines correspond to the fitted curve for the other size ratio on each graph to allow for direct comparison.

for $\lambda' = 2$ and 0.37 ± 0.07 for $\lambda' = 3$. Interestingly, these values are significantly below unity, indicating that saturation does not correspond to a GB fully covered by impurities. In fact, the majority of the distorted sites constituting the GBs are still vacant as Q_{gb}^{sat} is well below 0.5. Studies of GB segregation in metals also report partial coverage in most cases [43, 124, 125].

Importantly, the free energy of adsorption is also directly determined from the isotherm via $e_a/k_B T = \ln(K)$. The obtained adsorption free energies are $e_a/k_B T = 3.29 \pm 0.12$ for $\lambda' = 2$ and 4.00 ± 0.11 for $\lambda' = 3$. Thus the large impurities have a larger adsorption free energy than the small impurities, leading to a higher coverage of the GBs at equal Q_b (see figure 4.5). Still, the values of Q_{gb}^{sat} and e_a are quite similar between the two size ratios, suggesting that the interstitial or substitutional character of the impurities has little impact on their adsorption behaviour. Interestingly, the adsorption free energy has an entropic origin as there are only hard core interactions in this system. The value of the adsorption free energy is only a few $k_B T$ in both cases, indicating that adsorption at GBs is reversible. This corroborates that the observed GB segregation corresponds to equilibrium segregation, as already suggested by the agreement with the Langmuir-McLean model.

4.4.3 Distribution of impurities at grain boundaries

Pair correlation function

The spatial distribution of impurities in the GBs close to saturation is analysed for both size ratios, i.e. for interstitial ($\lambda' = 2$) and substitutional impurities ($\lambda' = 3$). To this end, the pair correlation function, $g(r)$, of the impurities located at GBs *only* is computed according to

$$g(r) = \frac{\pi \sigma_i'^2}{4 N_i^{gb} \phi_i^{gb}} \left\langle \sum_{j=1}^{N_i^{gb}} \sum_{k \neq j} \delta(\vec{r} - \vec{r}_j + \vec{r}_k) \right\rangle, \quad (4.15)$$

for samples having Q_{gb} close to the saturation level. Figure 4.6(a) shows the $g(r)$ of interstitial impurities ($\lambda' = 2$) for $Q_{gb} = 0.24 \pm 0.02$, and the same quantity is shown in figure 4.6(b) for substitutional impurities ($\lambda' = 3$) at $Q_{gb} = 0.30 \pm 0.03$. Note that, in all of the following, the distance r is expressed in units of σ_s , which corresponds to the lattice spacing at close packing.

For interstitial impurities ($\lambda' = 2$), the first peak (I) is located at $r_I \simeq 2.3$, which is very close to $\lambda = 2.26$, indicating direct contact between impurities. For substitutional impurities ($\lambda' = 3$), the value $r_I \simeq 4$ fits with $\lambda = 4$, which is also consistent with direct contact between impurities. The second and third peaks (II and III) are located at integer values of r , indicating that the distance between the impurities is commensurate with the lattice spacing at small distances. At larger distances, the amplitude of the peaks decreases drastically indicating a loss of order. Strikingly, for interstitial impurities ($\lambda' = 2$), the second peak at $r_{II} \simeq 3$ is as high as the first peak. This is in strong contrast with substitutional impurities ($\lambda' = 3$), where the height of the second peak at $r_{II} \simeq 5$ is about a third of that of the first peak. The second peak is incompatible with direct contact, as r_{II} is not a multiple of λ , and hence corresponds to mixing with the matrix particles.

Importantly, the number and magnitude of the peaks in the $g(r)$ for both size ratios are very different from the case of a dilute 2D fluid of hard spheres at the same area fraction [76]. This indicates that the distribution of impurities is structurally very different from that of a 2D fluid of the impurities alone. This very likely originates from depletion forces caused by the small particles in the GBs [137, 138], which leads to clustering of impurities as expected for systems with negative non-additivity parameters [135, 136]. Note that clustering is facilitated by the fact

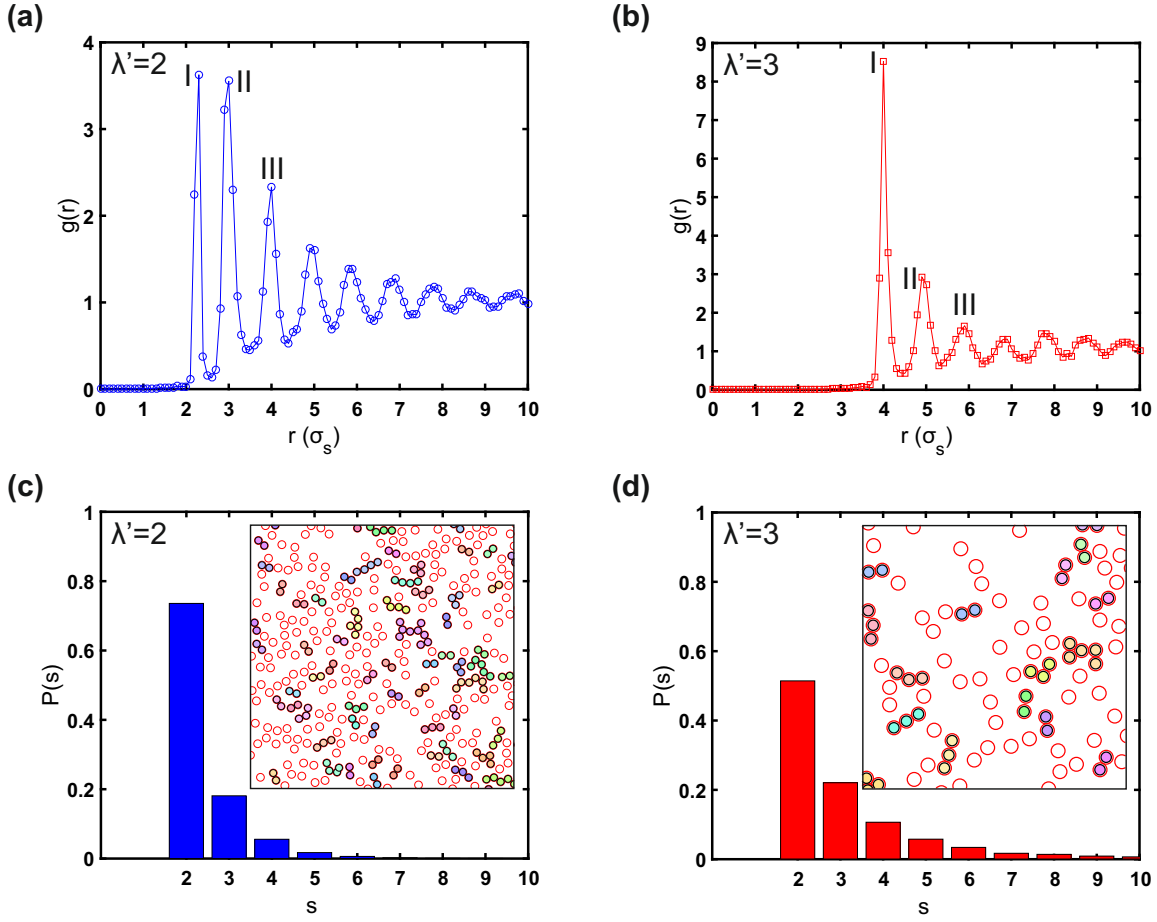


Figure 4.6: (a) Average pair correlation function of the impurities adsorbed at GBs in the case $\lambda' = 2$ for samples of composition $Q_{gb} = 0.24 \pm 0.02$. The first three peaks (I, II and III) are described in the text. (b) The same quantity for the case $\lambda' = 3$ with $Q_{gb} = 0.30 \pm 0.03$. (c) Size distribution of the clusters of GB impurities for $\lambda' = 2$, dominated by the presence of dimers. The data is the same as in (a). The inset shows a representative partial view of the clusters (colours) together with isolated impurities (circles). (d) Same as in (c) for $\lambda' = 3$. The decay of the distribution is much smoother indicating the presence of larger clusters at the expense of dimers.

that the impurities are mobile and thus free to rearrange in the grain boundaries. A competition between clustering and mixing is expected due to the non-additivity in the system [135, 136], where clustering contributes to peaks in the $g(r)$ located at multiples of λ , and mixing contributes to peaks at non-multiple values of λ . Here, however, the relative importance of clustering and mixing seems to strongly depend on the size ratio as suggested by the clear qualitative differences in the $g(r)$ for both types of impurities. This points towards the importance of geometry in determining the distribution of impurities.

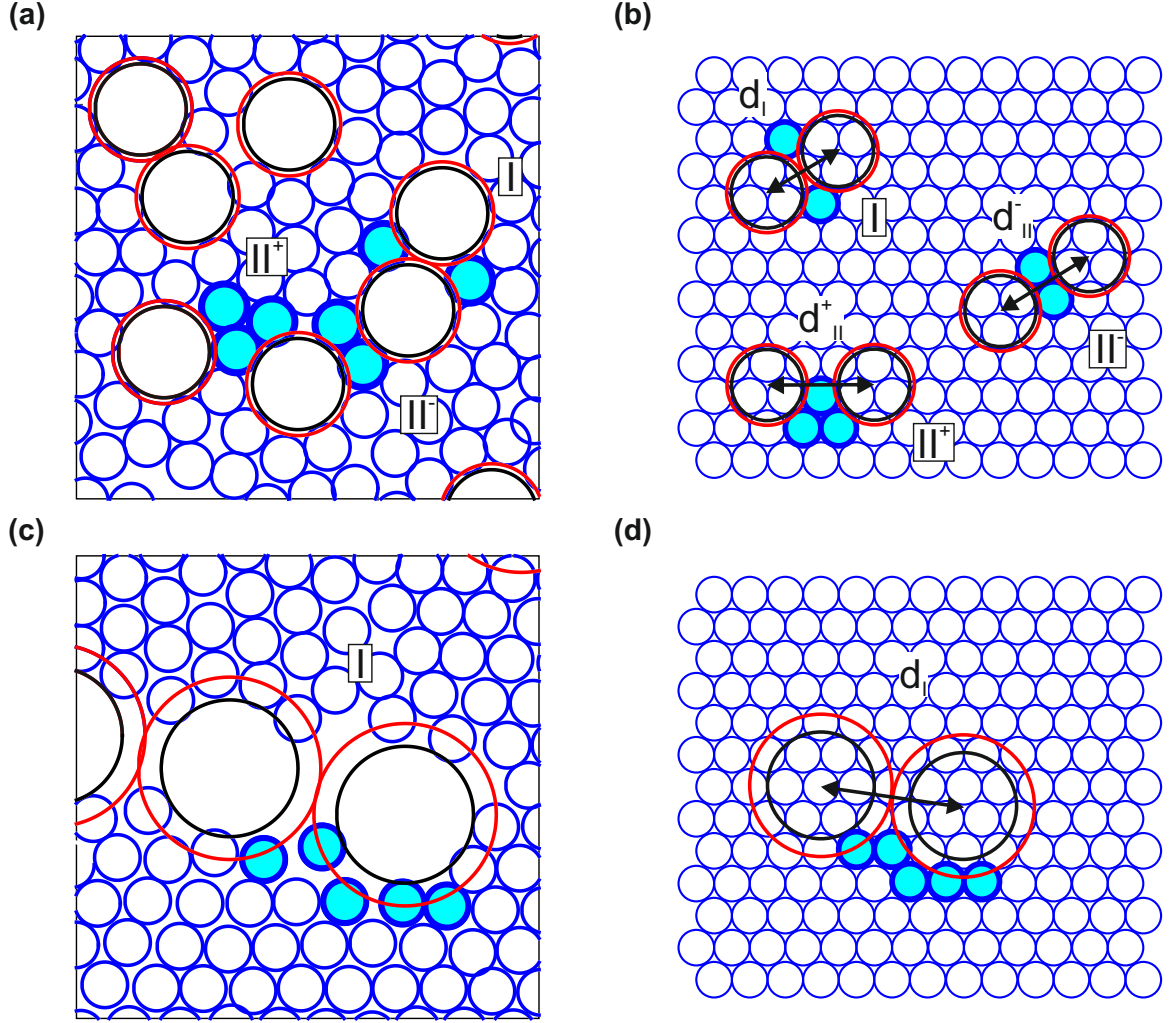


Figure 4.7: (a) Computer reconstruction of a local view of impurities segregated at a GB in the case $\lambda' = 2$. The three types of configurations contributing to the values of $g(r)$, I, II⁻ and II⁺ are illustrated. (b) The same three configurations but now on a perfect lattice. The particles in coincidence with the lattice are highlighted in cyan and thick circles. This enables geometrically calculating the values of the distances in between impurities, d_I , d_{II}^- and d_{II}^+ . (c) and (d) Same representation for a possible configuration in the case $\lambda' = 3$.

Cluster formation

To gain more understanding about the role of depletion and clustering in the system, which contribute to the first peak of $g(r)$, an analysis of the clusters formed by the impurities is performed. Two impurities are considered to be in the same cluster if their centre-to-centre distance is less than $(r_I + r_{II})/2$. The size distributions of the clusters, $P(s)$, as a function of the size, s , are presented in figure 4.6(c) and (d) for the two types of impurities, respectively. The insets show the output of the cluster analysis for the images in figure 4.4 at $Q_b = 10^{-1}$. In the case

of interstitial impurities ($\lambda' = 2$), the formation of dimers ($s = 2$) is clearly preferred over the formation of clusters of size $s \geq 3$, as inferred from the sharp drop in the probability $P(s)$ above $s = 2$ (figure 4.6(c)). In contrast, the decay of $P(s)$ is much smoother for substitutional impurities ($\lambda' = 3$), which indicates that larger clusters are more frequent in this case (figure 4.6(d)). In the following, simple geometric arguments are given to rationalise the prevalence of dimers for interstitial impurities compared to substitutional impurities.

In the case of interstitial impurities ($\lambda' = 2$) the first peak of $g(r)$ (I) corresponds to configuration I in figure 4.7(a): the two impurities form a dimer with two small particles on either side. One can see that such a configuration consists of four close-packed particles and for this reason, it is reasonable to expect that their positions can be mapped onto a perfect hexagonal closed-packed lattice. Indeed, it turns out that an equivalent configuration exists on a perfect lattice, with two impurities at interstitial sites and the two side particles in coincidence with crystal sites (see figure 4.7(b)). Note that the location of the two impurities are consistent with their interstitial nature. Using simple geometry, the distance in between the two impurities is found to be $d_I = 4/\sqrt{3} \simeq 2.31$, which is in very good agreement with the experimental location of the first peak, $r_I \simeq 2.3$.

The second peak in $g(r)$ (II) actually consists of a shoulder at $r_{II}^- = 2.9$ and a maximum at $r_{II}^+ = 3$, which correspond to two configurations with no direct contact between impurities. The first configuration, denoted II^- in figure 4.7(a), has a dimer of small particles in between the two impurities. Again, mapping this configuration onto a perfect lattice with the dimer in coincidence with two lattice sites and the two impurities located at interstitial sites leads to an ideal distance of $d_{II}^- = 10/\sqrt{12} \simeq 2.9$, which is in perfect agreement with the observed r_{II}^- . The second configuration, II^+ , corresponds to two impurities sitting at interstitials situated on the same row of lattice sites with a triplet of small particles on one side, separated by a distance $d_{II}^+ = 3$ (see figure 4.7(a) and (b)). Again, this agrees very well with the observed value for r_{II}^+ .

Importantly, these three configurations (I, II^- and II^+) compete against each other, as their associated values of $g(r)$ are comparable. Configuration I contributes to clustering, as it corresponds to direct contact. However, it is important to note that the geometry of the lattice does not allow such contacts to be repeated, which thus represents the first source of inhibition for the formation of clusters larger than $s = 2$. The second source is the fact that II^- and II^+ break direct contact between the interstitial impurities, not allowing further aggregation.

These two sources have a clear geometric origin and explain why dimers are relatively more frequent. Both sources of inhibition for the formation of clusters larger than $s = 2$ can be seen as a form of geometric frustration due to the interplay between depletion, non-additivity and lattice geometry. This is remarkable as Δ is the smallest in the case of interstitial impurities ($\lambda' = 2$).

In the case of substitutional impurities ($\lambda' = 3$) the very high first peak in the $g(r)$ at $r_1 \simeq 4$ corresponds to direct contact as it is equal to λ . As the impurities are substitutional, the expected configuration is two impurities located at two crystal sites on the same crystal row separated by a distance $r = 4$. Remarkably, many other configurations like the one presented in figure 4.7(c) are also found, where one impurity sits on a crystal site and the other impurity sits at an interstitial site right below the crystal row. Note that in this case, the ideal lattice used for the mapping has a clear physical interpretation as it corresponds to one of the grains adjacent to the GB (see figure 4.7(c) and (d)). The distance between the two impurities in this case is $d_I = \sqrt{49/3} \simeq 4.04$, which is consistent with a contribution to the first peak, involved in aggregation. Crucially, these configurations enable impurities to cluster into longer strings, in contrast with the interstitial impurities. It is also interesting to note that impurities can change from being substitutional to interstitial due to interactions with others.

4.5 Conclusions

To summarise, it has been found that colloidal alloys provide very interesting model systems to systematically study the effects of size misfit and non-additivity on grain boundary segregation. For the two types of impurities studied here, the adsorption isotherms agree very well with the Langmuir-McLean model of equilibrium grain boundary segregation and the measured free energy of adsorption is small enough to allow for reversible adsorption. Detailed insight has been obtained into the configuration of impurities close to saturation of the GBs. The relative balance between clustering and mixing due to non-additivity is found to strongly depend on the size ratio between the impurity and the matrix particles. This is due to geometrical constraints imposed by the lattice, which prevent the formation of clusters larger than two impurities for the smallest size ratio, while for the largest size ratio, the lattice geometry allows the formation of larger clusters of impurities.

Acknowledgements

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Chapter 5

Determining the geometry of grain boundaries from microscopy

ABSTRACT

This chapter describes a new method to determine the local normal direction, tangent plane and curvature of grain boundaries from microscopy images using point sampled surface analysis techniques. The algorithm is used to study the boundary of a shrinking grain in a two-dimensional colloidal polycrystalline material. The method can be generalised to three dimensions, which makes it applicable to the wide range of interfaces encountered in soft matter physics.

5.1 Introduction

The origin of grain growth can be traced back to the motion of curved grain boundaries (GBs) along their normal directions in order to reduce their local curvature [12, 19]. The local normal velocity v of a migrating GB is then given by the Herring relation (equation (2.15)) [12, 141]

$$v = M\Gamma\kappa, \tag{5.1}$$

where M is the mobility of the grain boundary, Γ the GB stiffness and κ the local curvature. While M and Γ can be directly obtained from the capillary fluctuations of flat GBs [38, 113, 142, 143], directly testing the Herring relation requires detailed knowledge of the local geometrical features of the GB, and in particular its local curvature.

Experimentally, GBs in atomic systems are typically studied using high-resolution electron microscopy techniques [20, 21, 144]. Though they provide detailed insight into the structural properties of GBs, directly accessing the interface dynamics, including curvature driven migration, is generally problematic due to the short time and length scales [20]. Colloidal model systems have been proven very useful in microscopy based single-particle level studies of GBs [25, 38, 130, 145–150]. However, at this scale, GBs have a width of a few particle diameters and exhibit deformations due to thermal fluctuations [38, 113, 142, 143, 145, 151]. The particles belonging to the GB thus form a noisy discrete cloud of points from which the local geometrical features of the embedded idealised continuous GB may be extracted.

Detecting and extracting the geometrical characteristics of an interface of unknown shape can be done using various techniques, depending on the dimension and topology of the interface and the spatial resolution of the data. Interfaces can be detected using the variations of the intensity on raw images [152], snake algorithms [153], lattice based methods [154], the level set method [155] or particle-based criteria [38, 145, 156–158]. Specific geometrical features, such as the normal and tangent planes or the curvature of fluid-fluid interfaces, are usually determined using lattice based methods [154, 155] although they are more adapted to simulations where the interface evolves via imposed rules. In experiments, where interfaces are sampled by a discrete cloud of points, the local curvature can be extracted using circular [153] or parabolic fits [159] to the data points, though this only gives reliable results as long as the noise level is low.

The noisy nature of fluctuating colloidal GBs therefore makes determining their local geometrical features from microscopy images cumbersome and clearly, a robust analysis method is required for this purpose. This chapter presents a relatively simple method to fully quantify the local geometrical features of GBs sampled by discrete points obtained from microscopy images. The method is first outlined for one-dimensional (1D) interfaces in 2D systems. It is then tested on artificially generated and experimental GBs in 2D colloidal crystals. Finally, the extension of the method to 3D systems is also described in appendix A, which broadens its relevance to the wide range of interfaces encountered in the physics of soft matter.

5.2 Geometrical analysis of point sampled interfaces

We consider a cloud of points in 2D space which samples a 1D interface L , whose parametrisation is unknown (see figure 5.1(a)). The purpose is to recover the local geometrical features of L from the discrete cloud of points. We first describe how to determine the local normal and tangent directions to L using standard principal component analysis (PCA) [160–162]. Then two methods are proposed to compute the local curvature along the interface.

5.2.1 Local normal and tangent directions

For a given point P in the cloud sampling the 1D interface, we define the neighbourhood of P as being the set Ω_P containing the m points located within a distance r_c from P (see figure 5.1(a)). We define the m -dimensional vectors $\mathbf{x} = (x_1, \dots, x_m)$ and $\mathbf{y} = (y_1, \dots, y_m)$, where (x_i, y_i) are the coordinates of a point i belonging to Ω_P . Note that in the following, the notation $\mathbf{x}$ refers to m -dimensional vectors while the notation $\vec{u}$ refers to vectors in the 2D plane. The covariance matrix C_P of the coordinates of the points within the neighbourhood of P is defined by [160–162]

$$C_P = \begin{bmatrix} \text{Cov}(\mathbf{x}, \mathbf{x}) & \text{Cov}(\mathbf{x}, \mathbf{y}) \\ \text{Cov}(\mathbf{y}, \mathbf{x}) & \text{Cov}(\mathbf{y}, \mathbf{y}) \end{bmatrix}, \quad (5.2)$$

where

$$\text{Cov}(\mathbf{x}, \mathbf{y}) = 1/m \sum_{i=1}^m (x_i - \bar{x})(y_i - \bar{y}) \quad (5.3)$$

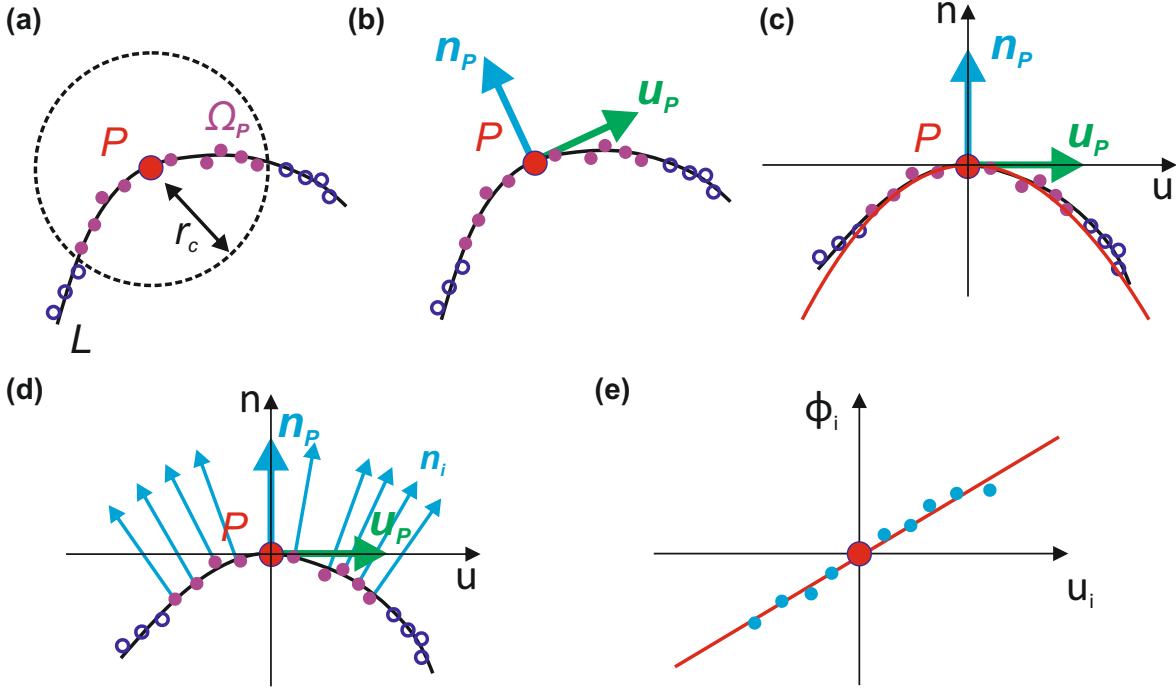


Figure 5.1: (a) Local view of a 1D interface L sampled by a cloud of points. The neighbourhood of a point P is the set of points Ω_P within a distance r_c from P . (b) The tangent and normal unit vectors, $\vec{u}_P$ and $\vec{n}_P$ at P . (c) The osculating parabola $n = 1/2 a u^2$ (red line) in the local tangent frame $(\vec{u}_P, \vec{n}_P)$ of P . The local curvature is given by a which is negative here. (d) The variation of the normal vectors $\vec{n}_i$ within Ω_P . (e) The variation of $\phi_i = \vec{n}_i \cdot \vec{u}_P$, as a function of u_i , the coordinate along $\vec{u}_P$. The gradient of the line is $-\kappa_P$.

is the covariance of the two vectors $\mathbf{x}$ and $\mathbf{y}$, with $\bar{x} = 1/m \sum_{i=1}^m x_i$. Because the covariance matrix is symmetric, it has two orthogonal eigenvectors. In particular, any covariance matrix is positive semi-definite, which implies that it has positive eigenvalues. The normalised eigenvector associated with the lowest eigenvalue of C_P is the normal vector to the interface at P , $\vec{n}_P$, while the other normalised eigenvector corresponds to the tangent vector at P , $\vec{u}_P$ [160–162]. By performing this operation for all the points P in the cloud, one can obtain all the corresponding normal and tangent vectors along the 1D interface.

As the normal vector at P can be oriented in two different directions, it is necessary to enforce a consistent orientation along L so that for two neighbouring points P and Q , $\vec{n}_P \cdot \vec{n}_Q \geq 0$ [162, 163]. In simple cases, this can be achieved by forcing the normals to point towards a common observation point located at $\vec{v}_0$, far away from the interface [163]. Equivalently, this implies that every point P with position $\vec{r}_P$ and normal vector $\vec{n}_P$ has to satisfy:

$$\vec{n}_P \cdot (\vec{v}_0 - \vec{r}_P) > 0. \quad (5.4)$$

If a common observation point cannot be defined, more sophisticated methods based on graph theory can be used [162]. Finally, the condition $\det(\vec{u}_P, \vec{n}_P) = 1$ fixes the direction of the tangent vector $\vec{u}_P$ as shown in figure 5.1(b).

5.2.2 Local curvature

Next, the local curvature κ_P at every point P in the cloud sampling the 1D interface L is determined using two different methods which will be compared in the following. The first one is based on the osculating parabola (OP) of the points in Ω_P . First, the reference frame is changed to the local tangent frame $(\vec{u}_P, \vec{n}_P)$ centred at P : the new coordinates of the points in Ω_P are now denoted $\mathbf{u} = (u_1, \dots, u_m)$ and $\mathbf{n} = (n_1, \dots, n_m)$. In the local frame, the coordinates of P are $(u, n) = (0, 0)$ and the interface L is locally described by the equation $n = f(u)$ where f is a function such that $f(0) = f'(0) = 0$ (see figure 5.1(c)) [164]. Here, f' is the derivative of f with respect to u . As a result, to the lowest order in u , f reads

$$f(u) = \frac{1}{2}f''(0)u^2 + \mathcal{O}(u^3), \quad (5.5)$$

and the osculating parabola to L is given by $n = \frac{1}{2}f''(0)u^2$. The local curvature at P is thus $\kappa_P = f''(0)$ [164]. Hence, fitting a function of the form $n = \frac{1}{2}au^2$ to the points $(\mathbf{u}, \mathbf{n})$ yields the local curvature as $\kappa_P \simeq a$, see figure 5.1(c).

The second method to determine the local curvature κ_P is based on the variation of the normal direction along the interface within Ω_P . Though similar methods have been used in surface feature detection, they are computationally expensive [165] or give dimensionless curvature indicators [160, 166]. Here, a normal variation (NV) method that is fairly easy to implement and fast to apply to large data sets is introduced. In the local tangent frame, we introduce the map ϕ , which tracks the variation of the normal $\vec{n}(u)$ along the tangent direction at P , $\vec{u}_P$ (see figure 5.1(d)):

$$\phi : u \mapsto \phi(u) = \vec{n}(u) \cdot \vec{u}_P. \quad (5.6)$$

If L is locally flat, then ϕ is zero as $\vec{n}$ is perpendicular to $\vec{u}_P$. If L is positively (negatively) curved, ϕ decreases (increases) with u as illustrated in figure 5.1(e). As ϕ vanishes at P , i.e.

$u = 0$, its expression to the lowest order in u is given by

$$\phi(u) = \phi'(0)u + \mathcal{O}(u^2). \quad (5.7)$$

Importantly, the map ϕ can be related to the local curvature as follows. The curvature κ_P of L at a point P of curvilinear abscissa s_P is defined by

$$\kappa_P = \left. \frac{d\theta(s)}{ds} \right|_{s=s_P}, \quad (5.8)$$

where $\theta(s)$ is the angle between the tangent to the curve $\vec{u}(s)$ at a point of curvilinear abscissa s and the x -axis. In the tangent frame $(\vec{u}_P, \vec{n}_P)$ associated to P , the map ϕ satisfies $\phi(s_P) = 0$. Close to P , one has $\theta(s) = \theta(s_P) + \delta\theta$ and $\phi(s) = \phi(s_P) + \delta\phi$ to first order. As $\phi(s_P) = 0$, one merely has $\phi(s) = \delta\phi$. Moreover, by definition of ϕ (equation (5.6)), $\delta\phi = -\sin(\delta\theta) \simeq -\delta\theta$ to the lowest order. This implies that $d\phi/ds = -d\theta/ds$ and because $ds \simeq du$ to the lowest order, one eventually has

$$\kappa_P = - \left. \frac{d\phi(u)}{du} \right|_{u=0} = -\phi'(0). \quad (5.9)$$

Combining equations (5.7) and (5.9) leads to

$$\phi(u) = -\kappa_P u + \mathcal{O}(u^2), \quad (5.10)$$

so that fitting a function of the form $\phi = \alpha u$ to the points $(\mathbf{u}, \phi)$, where $\phi = (\phi_1, \dots, \phi_m)$ with $\phi_i = \vec{n}_i \cdot \vec{u}_P$, directly leads to the local curvature via $\kappa_P \simeq -\alpha$. An example for $\kappa_P < 0$ is shown in figure 5.1(e).

The method to find the local normal and tangent directions and both methods to determine the local curvature can be straightforwardly extended to surfaces of any dimensions. The details for two-dimensional surfaces in 3D space can be found in appendix A.

5.3 Validating the method on artificial grain boundaries

5.3.1 Generating the artificial grain boundary

First, the method is validated by applying it to an artificial grain boundary of known curvature. Two overlaying hexagonal lattices of orientations $\theta_1 = 15^\circ$ and $\theta_2 = 40^\circ$ are generated. A curve $y = -A \sin(2\pi x/\lambda)$ is plotted on top of the two hexagonal lattices and the sites of the lattice of orientation θ_1 (θ_2) located below (above) the curve form the grain G_1 (G_2). During this process, all the overlapping particles are removed. As a result, a grain boundary between G_1 and G_2 has been generated, with analytically known shape and, hence, local curvature (see figure 5.2(a)). The parameters A and λ are set to $A = 12\sigma$ and $\lambda = 20\sigma$, where σ is the lattice spacing.

To generate the cloud of points that sample the grain boundary, one first selects the lattice sites belonging to the edges of G_1 and G_2 enclosing the grain boundary (see the red and blue stars in figure 5.2(a)). To ensure that the cloud of points samples the grain boundary, which is located in between the edge sites of G_1 and G_2 , interpolating sites half way in between consecutive edge sites are generated (see the magenta dots in the inset of figure 5.2(a)). Hence, the final cloud of points sampling the grain boundary consists of the edge and the interpolated sites.

As real grain boundaries exhibit thermal noise, the corresponding cloud of points can be quite wide. To assess the effect of noise on the analysis method, the cloud of points sampling the artificial grain boundary is smoothed by replacing every point P in the cloud by the centre of mass of all the points situated within a cut-off radius r_0 from P [161].

5.3.2 Geometrical features of the artificial grain boundary

First, the cloud of points is smoothed using a cut-off radius of $r_0 = 2.5\sigma$ and then the normal and tangent directions of the artificial grain boundary are computed using PCA with a neighbourhood cut-off radius of $r_c = 2.5\sigma$ (see section 5.2.1). The common observation point is positioned far up in the top half-plane, in order to ensure that the normal is consistently orientated along the grain boundary. Next, the local curvature is determined using both the OP and the NV methods (see section 5.2.2). Figure 5.2(b) shows the smoothed cloud of points, which are coloured according to the local curvature determined using the NV method, and the normal

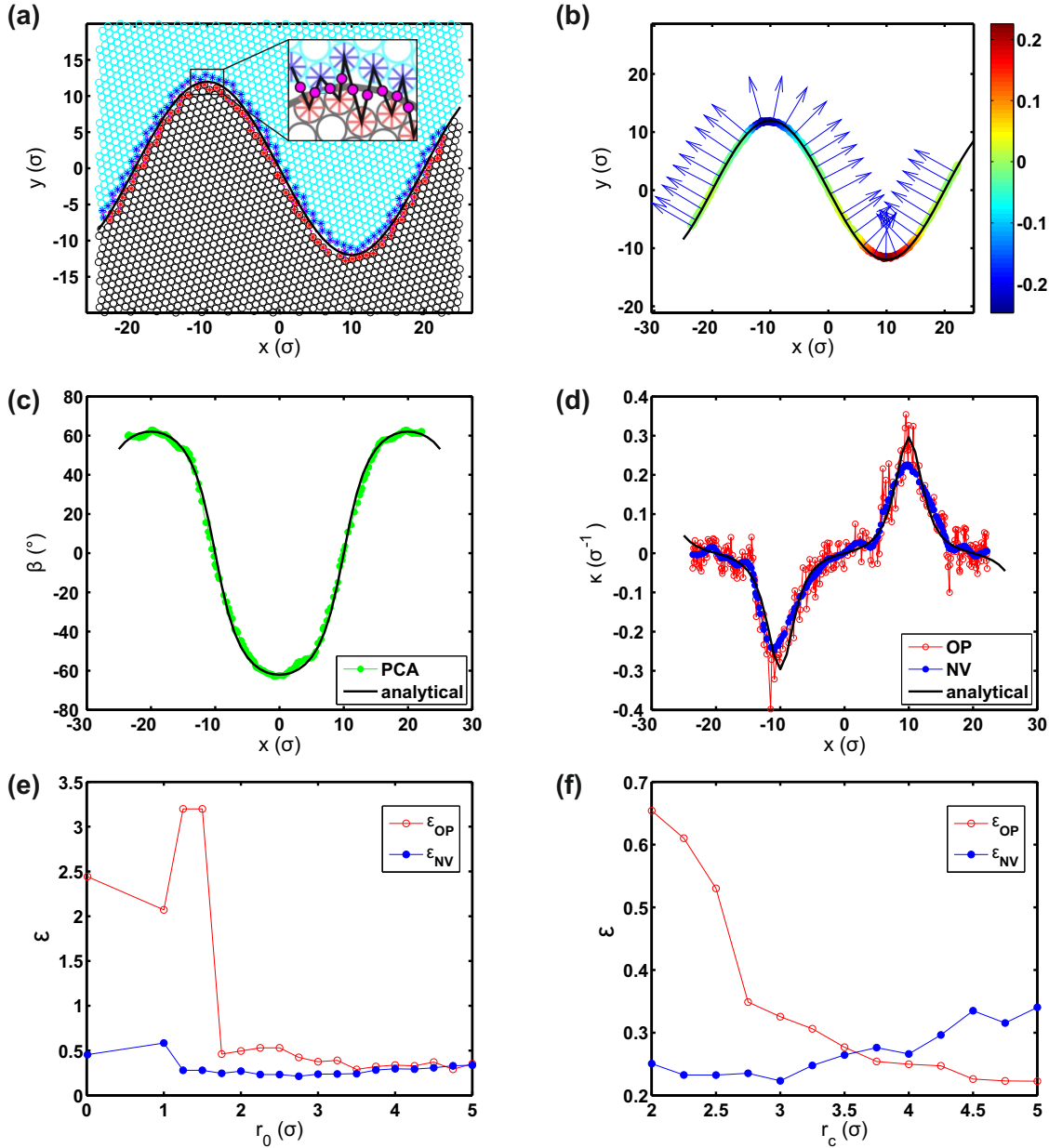


Figure 5.2: (a) Two perfect hexagonal grains separated by an artificial grain boundary of a known shape (black line). The sites constituting the edges of each grains are marked by red and blue stars. The magenta dots correspond to the interpolated sites sampling the grain boundary. The inset illustrates the generation of the interpolating sites in between consecutive edge sites. (b) The smoothed cloud of points ($r_0 = 2.5\sigma$) sampling the grain boundary. The points are coloured according to their local curvature in units of σ^{-1} (colourbar). The arrows are the normal vectors computed using PCA. (c) Comparison between the orientation of the tangent found using the PCA, β , and its analytical value. (d) The local curvature determined using the OP and NV methods together with the analytical local curvature. (e) The relative error ϵ (equation (5.11)) as a function of r_0 for fixed $r_c = 2.5\sigma$. (f) The relative error ϵ (equation (5.11)) as a function of r_c for fixed $r_0 = 2.5\sigma$.

vectors. The smoothed cloud of points shows a good consistency with the exact shape of the artificial grain boundary. The angle β between the tangent direction and the x -axis is plotted in figure 5.2(c) and also shows excellent agreement with the value derived from the analytical interface profile, confirming the accuracy of the PCA with the chosen parameters.

Figure 5.2(d) is a plot of the local curvature computed using the two different methods together with the analytical local curvature. Both methods show good agreement with the analytical curvature, though the OP method is more noisy and the NV method tends to underestimate large curvatures at these cut-offs. For each method, the result depends on the choice of r_0 , the cut-off radius for smoothing the cloud of points sampling the grain boundary (section 5.3.1), and r_c , the cut-off radius for defining the neighbourhood of a point P (section 5.2.1). This is quantified by computing the relative error in the curvature via

$$\epsilon = \sqrt{\frac{\langle (\kappa - \kappa_0)^2 \rangle}{\langle \kappa_0^2 \rangle}}, \quad (5.11)$$

where κ is the local curvature obtained using either of the two methods and κ_0 is the analytical local curvature. In figure 5.2(e) ϵ is plotted for both methods as a function of r_0 for a fixed $r_c = 2.5\sigma$. The OP method shows relatively large errors for small r_0 , which corresponds to noisy interfaces. In contrast, the NV method is not affected by the noise level of the interface and the error is relatively independent of r_0 . Figure 5.2(f) shows the error as a function of r_c for a fixed $r_0 = 2.5\sigma$. For small r_c the error in the OP method is relatively large, but rapidly decreases for increasing r_c . In contrast, the NV method shows the opposite trend as ϵ increases with r_c .

The result of the OP method is sensitive to the noise of the interface because it probes the second order variation of the interface, which becomes more accurate when the cloud of points sampling the interface is smoother, which corresponds to a large r_0 (figure 5.2(e)). Similarly, when r_0 is fixed, the method becomes more accurate when r_c increases (figure 5.2(f)), as more points are taken into account. Notice however that the values of r_0 and r_c should not be larger than the typical size of geometrical features to be detected. As the NV method performs a linear analysis on the output of the PCA, which overall corresponds to two successive linear analyses, it is more robust at small cut-off distances and therefore relatively accurate for noisy interfaces (figure 5.2(e)), but underestimates large curvatures, which causes the error to increase with r_c for fixed r_0 (figure 5.2(f)).

5.4 Application to grain boundaries in colloidal systems

5.4.1 Experimental details

Next, the method is applied to real grain boundaries in a colloidal polycrystalline monolayer. The sample is prepared according to the method in section 2.3.1 using melamine formaldehyde particles of diameter $2.7\text{ }\mu\text{m}$, and the system is imaged using video-microscopy as described in section 2.3.2. A picture of a grain that will be used as an example for the analysis is shown in figure 5.3(a). Note that this grain is not stable and shrinks over time to eventually disappear. The coordinates of the particles are obtained using standard image analysis techniques as explained in section 2.3.2.

To identify the central grain in figure 5.3(a) the smoothed local orientation for each particle j , denoted $\tilde{\theta}_6(\vec{r}_j, t)$, is determined as explained in section 3.3.2 (equation (3.9)). Smoothing reduces the noise in the bond-orientational field near grain boundaries and enables a better determination of the contour of the grains. In the following, $\tilde{\theta}_6$ is merely called the “orientation” and is denoted θ_6 for simplicity. A plot of the local orientation is shown in figure 5.3(b) and clearly shows the central grain with an orientation $\theta_6^1 \simeq 40^\circ$ surrounded by four other grains, two of orientation $\theta_6^2 \simeq 12^\circ$ and two of orientation $\theta_6^3 \simeq 20^\circ$. This is confirmed by the histogram of orientations which has three peaks centred at these values (see figure 5.3(c)). The particles having an orientation larger than 30° are selected to identify the central grain (see figure 5.3(b)).

The particles corresponding to the GB are detected by selecting the particles at the edge of the central grains, as well as those at the edges of the surrounding grains. Using these positions, a cloud of points sampling the interface can be generated (see figure 5.3(b)). As the grain is approximately circular, the cartesian coordinates are converted into the polar coordinates (ρ, ϕ) with respect to the centre of mass of the grain O (see figure 5.4(a)). As described in section 5.3.1, interpolating sites are then generated in between consecutive edge sites along ϕ to ensure that the cloud of points samples the grain boundary (see inset of figure 5.3(b)).

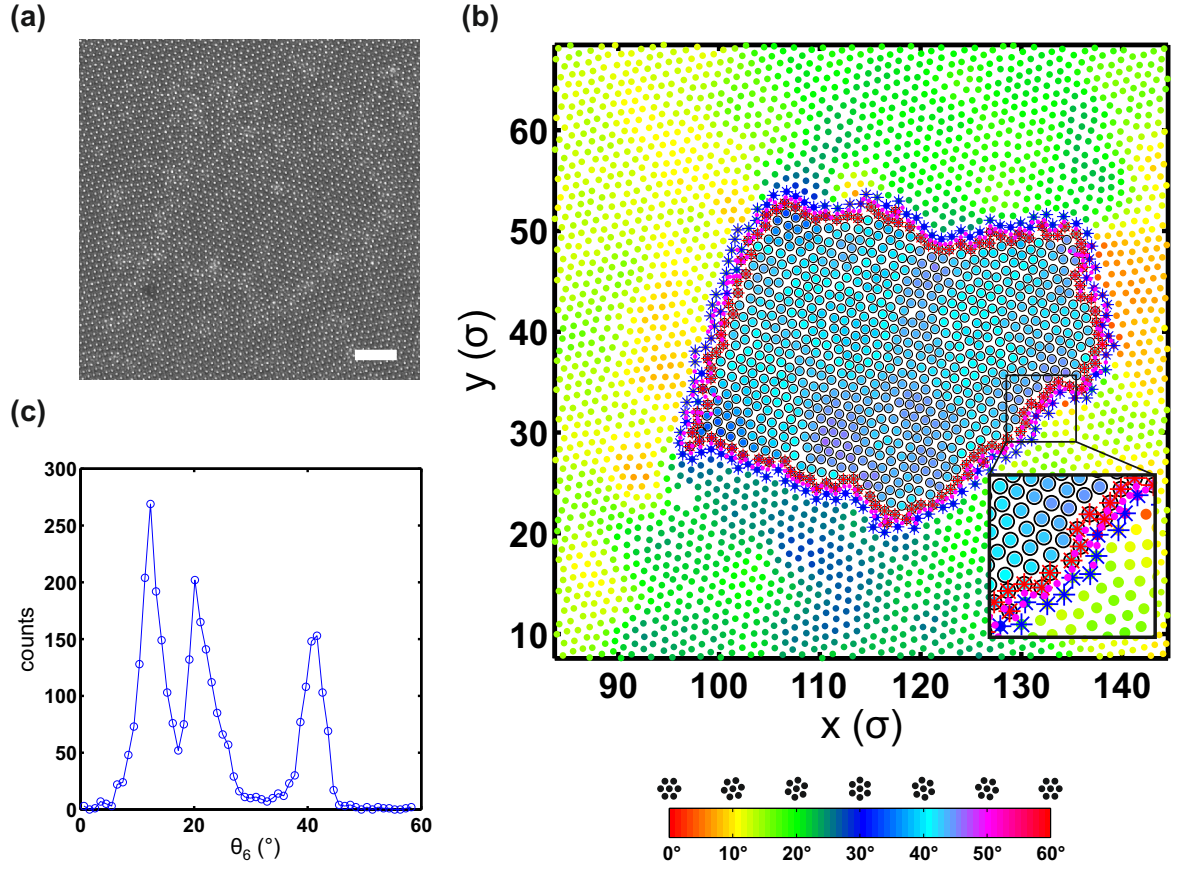


Figure 5.3: (a) Microscopy image of a grain in a colloidal polycrystalline monolayer. Scale bar, 20 μm . (b) Local orientation of the particles in panel (a) as defined by the colourbar. The central grain has an orientation $\simeq 40^\circ$ and its particles are circled in black. The particles constituting the edges of the central grain are marked by red stars and the ones at the edges of the surrounding grains are marked by blue stars. The interpolated sites are marked by the magenta dots (see inset). (c) Histogram of the orientations of the particles in panel (b).

5.4.2 Geometrical features of colloidal grain boundaries

First, the cloud of points is smoothed with a cut-off radius $r_0 = 2.5\sigma$ (see section 5.3.1) and then the normal and tangent directions of the colloidal grain boundary are computed using PCA with a neighbourhood cut-off radius of $r_c = 2.5\sigma$ (see section 5.2.1). The common observation point is positioned at O so that all the normals are oriented consistently. Next, the local curvature is determined using the OP and the NV methods (see section 5.2.2). Figure 5.4(b) shows the smoothed cloud of points, which is coloured according to the local curvature determined using the NV method, together with the normal vectors. The local curvature obtained by both methods is shown as a function of the polar angle ϕ in figure 5.4(c). Both methods give consistent local curvatures, showing that one can successfully determine the local curvature of

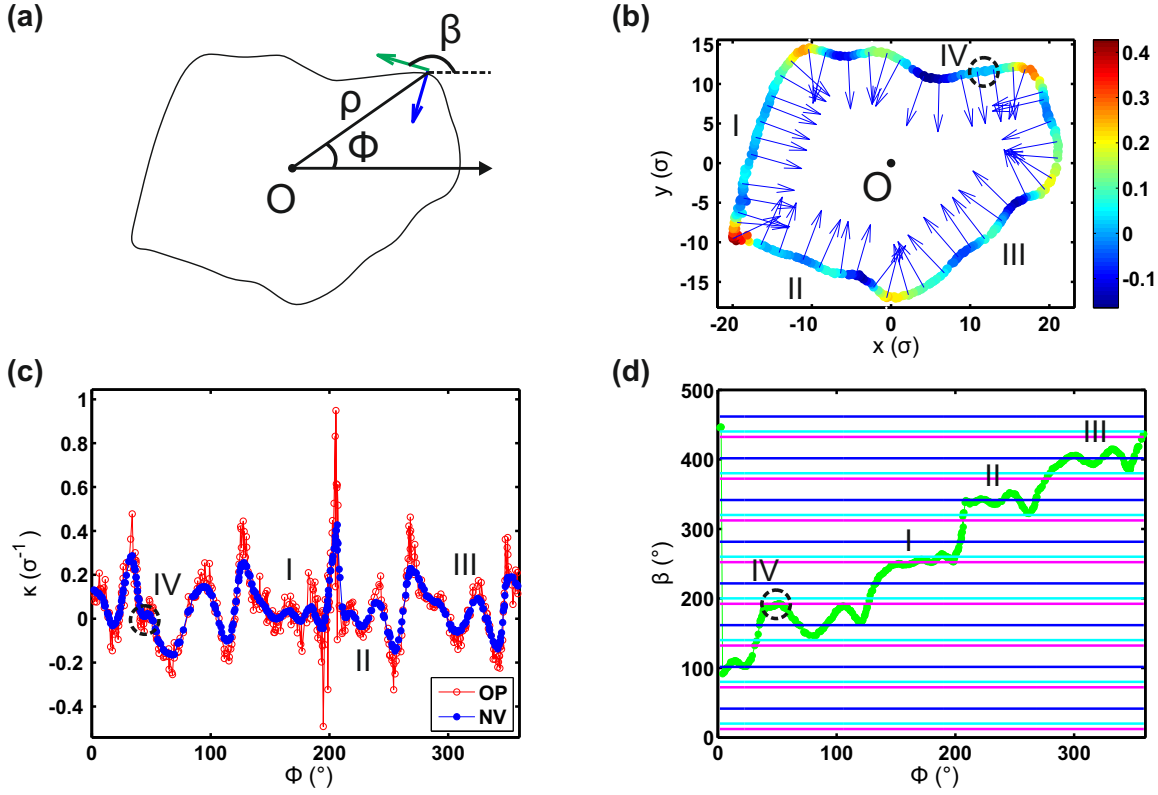


Figure 5.4: (a) Polar coordinates (ρ, ϕ) used to study the geometry of the grain. The origin O corresponds to the centre of the grain. The normal and the tangent directions to the boundary correspond to the blue and green arrows. The angle in between the x direction and the tangent is denoted β . (b) The smoothed cloud of points coloured according to the local curvature determined using the NV method in units of σ^{-1} (colourbar) with several normal vectors (blue arrows). The origin O is also shown. (c) Curvature of the grain boundary determined using the OP and the NV methods. (d) Orientation of the boundary as a function of the polar angle ϕ . The horizontal lines represent the 6-fold symmetric directions of the inner grain, $\omega_{1,k}$ (blue), and the two outer grains, $\omega_{2,k}$ and $\omega_{3,k}$ (magenta and cyan) as defined in the main text. The numbers I, II and III correspond to relatively flat edges of the grain respectively oriented along the crystal directions of an outer grain ($\omega_{2,4}$) and of the inner grain ($\omega_{1,5}$ and $\omega_{1,6}$). The number IV corresponds to an inflection point (dashed circle) where the boundary is also oriented along a crystal direction of an outer grain ($\omega_{2,3}$).

grain boundaries from microscopy images. As was also shown for the artificial grain boundary (figure 5.2(d)), the result of the OP method is quite noisy and the output of the NV method is much smoother, yet large local curvatures may be underestimated. Interestingly, comparing figure 5.3(b), figure 5.4(b) and (c) reveals that the points of high local curvatures correspond to triple junctions between the central grain and two neighbouring grains. The grain boundary is relatively flat in between the triple junctions, as indicated by the numbers I, II and III in figure 5.4(b). Also, there is a noticeable point of inflection indicated by number IV.

Figure 5.4(d) is a plot of the tangent direction of the grain boundary β as a function of the polar angle ϕ . Also shown are the horizontal lines corresponding to the 6-fold symmetric lattice directions of the inner and outer grains, $\omega_{i,k} = \theta_6^i + k\pi/3$ where θ_6^i is the orientation of the grain corresponding to the peaks observed in figure 5.3(c) and k is an integer. Interestingly, the orientation of each flat part of the grain boundary – as indicated by I, II and III – is locked to the crystal direction of a grain adjacent to it and indeed corresponds to nearly zero curvatures in figure 5.4(c). This is also observed for the inflection point – indicated by IV – in figure 5.4(b)-(d). While the equilibrium shape of a grain can be determined using the Wulff construction [18], very little is known about the shape of out of equilibrium grains. In this context, the methods presented here are useful techniques to obtain new results about out of equilibrium grain boundaries studied at the single particle level.

5.5 Conclusions

It has been shown that the analysis of point sampled lines is a powerful tool to determine the local geometrical features of grain boundaries from microscopy data at the single particle level. A method to obtain local curvatures from a discrete cloud of points sampling grain boundaries has been presented. Principal component analysis gives the normal and tangent directions while the local curvature can be determined using a local parabolic fit or variations of the normal. The procedure has been validated using artificially generated grain boundaries, showing that the local parabolic fit is more affected by noise, while the normal variation method tends to underestimate large curvatures. The method has been applied to grain boundaries in 2D colloidal systems and it was found that the flat grain boundaries of a shrinking grain are aligned with one of the crystal directions of the surrounding grains. This is also true for the direction of the boundary at inflection points. As this method can be generalised to surfaces in 3D space, it may fruitfully be applied to many of the interfaces encountered in soft matter science.

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Chapter 6

Shrinking kinetics of circular grain boundaries

ABSTRACT

In this chapter, the shrinking kinetics of circular grain boundaries in colloidal crystalline monolayers is studied. Circular grain boundaries with controlled initial curvature and misorientation are created using an optical vortex. The spontaneous shrinkage of the circular grain obtained is monitored after the optical vortex is turned off. The area of the circular grain is found to decay linearly in time, and the shrinking rate is found to decrease upon increasing initial misorientation and upon increasing initial radius of the grain. At low misorientations, a transition between pure sliding and shrinkage is observed, which has a clear geometrical origin and is shown to be specific to highly curved grain boundaries. Shrinkage is achieved by different processes including grain rotation by grain boundary sliding and coupled migration. The reduction of the grain boundary length is enabled by dislocation reactions, which are directly visualised and linked to the observed shrinking kinetics.

6.1 Introduction

It is well accepted that grain growth is driven by the migration and annihilation of grain boundaries (GBs). The migration of GBs is generally driven by their curvature [167, 168], though other mechanisms such as grain rotation or coupling between migration and rotation are reported, and their relative contributions are unclear [102]. The reduction of the GB area is achieved by dislocations reactions, which enable the annihilation of the dislocations that constitute the GB [103, 169]. Experimental observations of these processes exist [170], but the link to GB migration remains elusive as direct observation at the atomic level is cumbersome.

Circular GBs have attracted a lot of interest in the field of grain boundary migration as their curvature provides a spontaneous driving force for migration. In the absence of other processes, the area enclosed by the GB decreases at a constant rate, which is termed the reduced mobility [141, 171, 172]. The reduced mobility is a kinetic coefficient that depends on the misorientation between the inner circular grain and the outer crystal. Nevertheless, this dependence is far from established as simulations have both reported an increase [103] and a decrease [97] of the reduced mobility upon increasing the misorientation. Circular grains are furthermore convenient as they enable dislocation reactions to be studied, due to the fact that dislocations are forced to annihilate until a single crystal is left. This has been investigated fairly recently using simulations [60, 103], though to date no experimental data are available, as circular shapes are either extremely rare in real materials or impossible to prepare.

As colloidal crystals are inherently soft [44], they offer a unique model system as they can be readily manipulated with external fields. Indeed, optical tweezing has been used to generate dislocations and GBs [46] or induce local melting [45] in a colloidal crystal. More specifically, holographic optical tweezers can be used to create circular GBs with a high level of control and reproducibility [46]. Due to their typically high curvature, the shrinkage of such circular grains should be fast enough so that the time scale of GB migration and dislocation reactions become similar. Simple video-microscopy can then be used to achieve direct and simultaneous imaging of the migration process and the reactions between the dislocations.

In this chapter, the shrinking kinetics of circular GBs in colloidal polycrystalline monolayers is studied. The circular GBs are created using optical vortices generated by holographic optical

trapping. By subsequently turning off the laser beam, the grain is allowed to shrink and this process is monitored at single particle resolution using video-microscopy. The reduced GB mobility is found to decrease with the initial misorientation of the grain and to increase with its initial curvature. Interestingly, these highly curved GBs exhibit a transition between pure sliding and shrinking at a misorientation that corresponds to the stability limit of dislocations in circular GBs. It is shown that grain shrinkage is the result of many processes, including grain rotation by GB sliding and coupled migration. The dislocation reactions involved in the reduction of the GB length are directly visualised and linked to the observed shrinkage.

6.2 Theory

We consider a circular grain of radius R_G embedded in another crystal. The circular GB that separates the two grains is characterised by a misorientation θ and a stiffness Γ . The minimisation of the interfacial free energy cost leads to a spontaneous shrinkage of the grain until a single crystal is left. Complete shrinkage can be achieved by curvature-driven migration of the GB and/or grain rotation. In the following, the three main mechanisms for grain shrinkage and rotation are introduced [102, 103]. For the sake of clarity, they are treated independently here, while in practice they can contribute simultaneously to grain shrinkage.

6.2.1 Curvature-driven shrinkage

In the case of pure curvature-driven shrinkage, the normal velocity of the GB, v_n , is proportional to its curvature, κ , according to

$$v_n = M_n \Gamma \kappa, \quad (6.1)$$

where M_n is the mobility corresponding to normal motion and Γ is the GB stiffness [66, 102]. For a circular grain of radius R_G in 2D, $v_n = -dR_G/dt$ and $\kappa = 1/R_G$ so that

$$\frac{dR_G}{dt} = -\frac{M_n \Gamma}{R_G}, \quad (6.2)$$

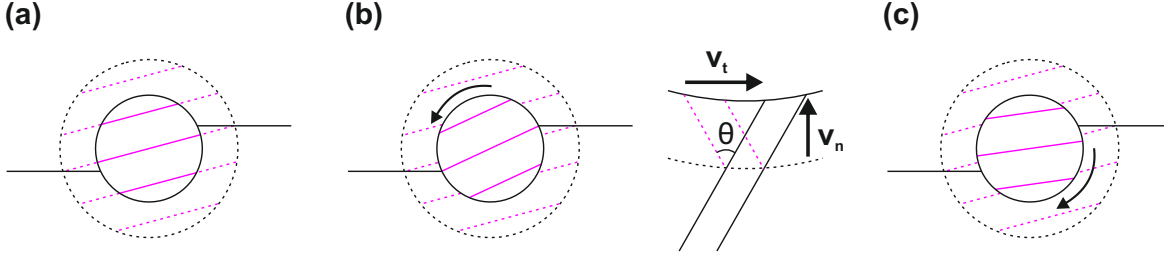


Figure 6.1: (a) Circular grain before (dashed circle) and after (solid circle) curvature-driven shrinkage. The black solid lines represent rows of the outer crystal after shrinkage. The magenta lines illustrate the orientation of the circular grain before (dashed lines) and after shrinkage (solid lines). No grain rotation happens in this case. (b) Illustration of coupled GB migration, where the continuity of crystal rows is ensured by grain rotation towards higher angles (black arrow). The tangential velocity v_t and the normal velocity v_n are related by $v_t = 2 \tan(\theta/2)v_n$, where θ is the misorientation. (c) Illustration of GB sliding where grain rotation happens towards lower angles (black arrow).

where both M_n and Γ depend on the misorientation θ [102, 103]. Assuming that there is no grain rotation, i.e. $d\theta/dt = 0$, M_n and Γ are constant and the integration of equation (6.2) gives the parabolic law of grain shrinkage

$$R_G^2(t) = R_G^2(0) - 2M^*t. \quad (6.3)$$

Here, $M^* = M_n\Gamma$ is the reduced mobility [141]. Note that in this case, the grain area $A_G = \pi R_G^2$ decreases with a constant rate given by [171]

$$\frac{dA_G}{dt} = -2\pi M^*. \quad (6.4)$$

This indicates that the reduced mobility is proportional to the shrinking rate of the grain area and can be measured directly by monitoring the time-evolution of R_G or A_G . An illustration of pure curvature-driven grain shrinkage is shown in figure 6.1(a).

6.2.2 Coupled grain boundary migration

In coupled GB migration, the continuity of the crystal rows is maintained between the central grain and the outer crystal. This purely geometrical constraint implies that the tangential

velocity is proportional to the normal velocity

$$v_t = \beta v_n, \quad (6.5)$$

where β is the coupling factor, which depends on the misorientation θ [102]. As can be seen from figure 6.1(b), the requirement for the continuity of crystal rows yields

$$\tan\left(\frac{\theta}{2}\right) = \frac{v_t}{2v_n}, \quad (6.6)$$

which leads to the expression for the coupling factor: $\beta = 2 \tan(\theta/2)$ [102]. As for a circular grain $v_n = -dR_G/dt$ and $v_t = R_G d\theta/dt$, equation (6.5) can be rewritten as

$$R_G \frac{d\theta}{dt} = -2 \tan\left(\frac{\theta}{2}\right) \frac{dR_G}{dt}. \quad (6.7)$$

Integration of equation (6.7) results in

$$R_G(t) \sin\left(\frac{\theta(t)}{2}\right) = R_G(0) \sin\left(\frac{\theta(0)}{2}\right), \quad (6.8)$$

where $t = 0$ corresponds to the beginning of coupled migration. Equation (6.8) means that the quantity $R_G(t) \sin(\theta(t)/2)$ is conserved during coupled migration. Hence, as $R_G(t)$ decreases, the grain *always* rotates towards *higher* misorientations (see figure 6.1(b)). It has been reported that the parabolic law of shrinkage (equation (6.3)) should hold during coupled GB migration, but with a reduced mobility M^* different from $M_n \Gamma$ [102, 103].

6.2.3 Grain boundary sliding

Grain rotation without the requirement for continuity of crystal rows is called GB sliding [102, 103], see figure 6.1(c). In this case the tangential velocity is given by

$$v_t = -M_t \frac{\Gamma'}{R_G}, \quad (6.9)$$

where $\Gamma' = d\Gamma/d\theta$ and M_t is the mobility associated with tangential motion [102, 103]. As for a circular grain $v_t = R_G d\theta/dt$, one has

$$\frac{d\theta}{dt} = -M_t \frac{\Gamma'}{R_G^2}, \quad (6.10)$$

which indicates that the grain rotates towards a minimum of Γ . At low θ , one expects $\Gamma' > 0$ so that the rotation occurs towards lower angles [103], which clearly differs from coupled GB migration (see figure 6.1(c)).

6.3 Methods

6.3.1 Creation of circular grains

Colloidal polycrystalline monolayers are prepared as described in section 2.3.1 using melamine formaldehyde particles of diameter $2.7\mu\text{m}$ and left to coarsen for at least 24h to obtain very large grains. The sample cell is placed in a holographic optical trapping setup, which is illustrated in figure 6.2(a). Details about the main elements of the setup can be found in section 2.3.3. In short, a 1064 nm laser beam is reflected off a spatial light modulator (SLM) and sent into the back aperture of a $50\times$ trapping objective, located above the sample. The sample is illuminated by a broadband light source via the trapping objective, and imaging is realised by a $40\times$ objective located below the sample stage and a Ximea XiQ CMOS camera (1280×1024 pixels).

The SLM is used to generate a Laguerre-Gaussian (LG) beam [84, 173], whose hologram is illustrated in figure 6.2(a). The LG beam has a helical wavefront and its intensity profile in the trapping plane consists of a central principal ring surrounded by higher-order fringes with decreasing intensity [173], as shown in figure 6.2(b). A single particle trapped in the primary ring will orbit inside it as the helical wavefront transmits angular momentum [84, 173]. As such, a LG beam is referred to as an optical vortex.

Applying an optical vortex on a 2D colloidal crystal results in the rotation of the portion of crystal within the vortex, thereby creating a circular grain. In addition, a defocused Gaussian beam centred in the optical vortex is superimposed to the LG beam to ensure that the grain stays intact during the rotation (see figure 6.2(c)). Figure 6.2(d) illustrates the experimental protocol

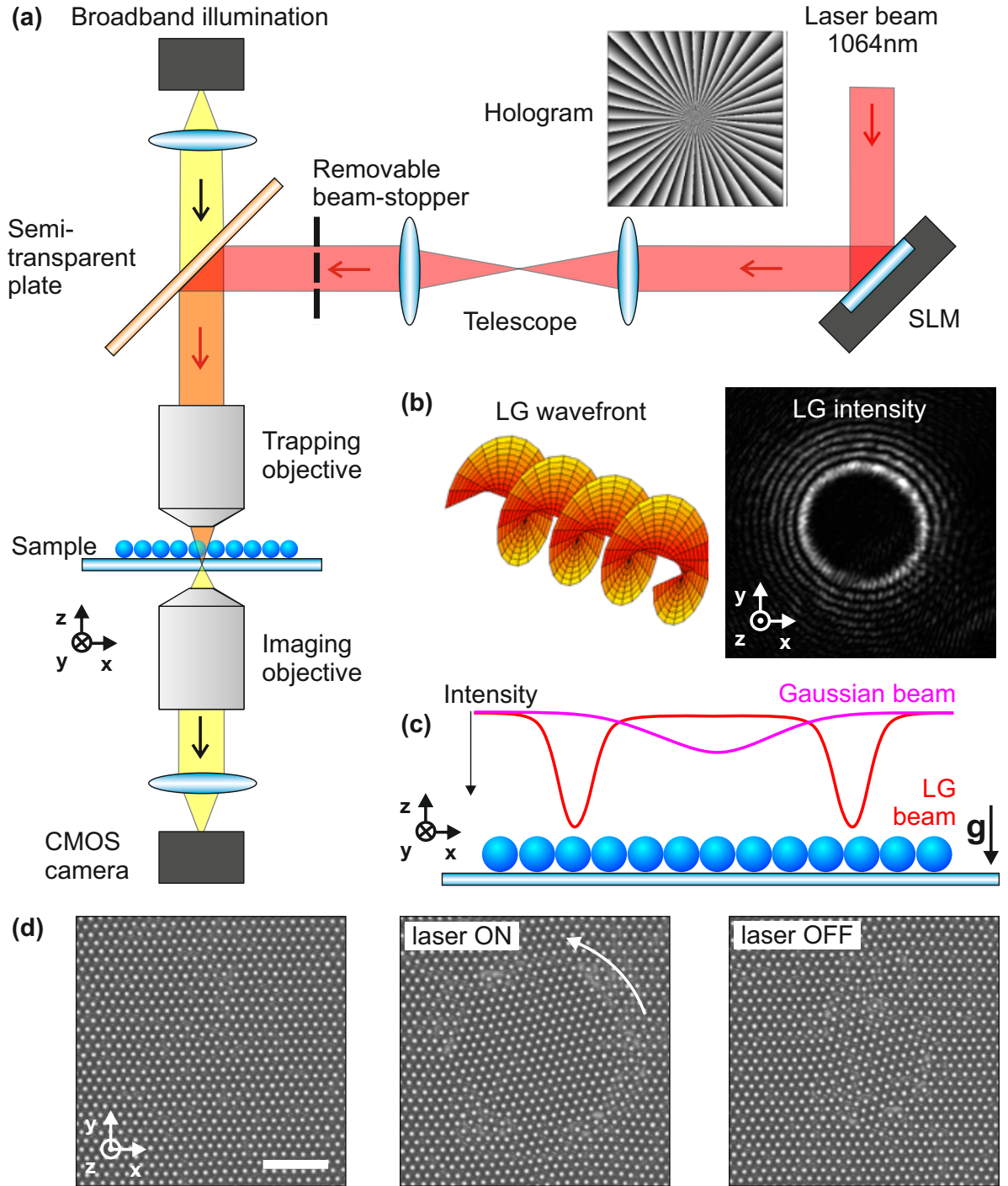


Figure 6.2: (a) Schematic view of the holographic optical trapping setup and the hologram to generate the LG beam. (b) Schematic of the wavefront and image of the intensity profile of a LG beam. The helical wavefront enables particles to orbit along the central ring of intensity. (c) Schematic cross-section of the trapping beams. A LG beam is applied from the top (red) together with a Gaussian beam (magenta) to ensure that the rotated crystal stays intact. (d) The beam shown in (c) is applied to a single crystal (left), which results in the creation of a grain by rotating the structure counter-clockwise (centre). The beam is subsequently blocked and the grain spontaneously shrinks (right). Scale bar, 20 μm .

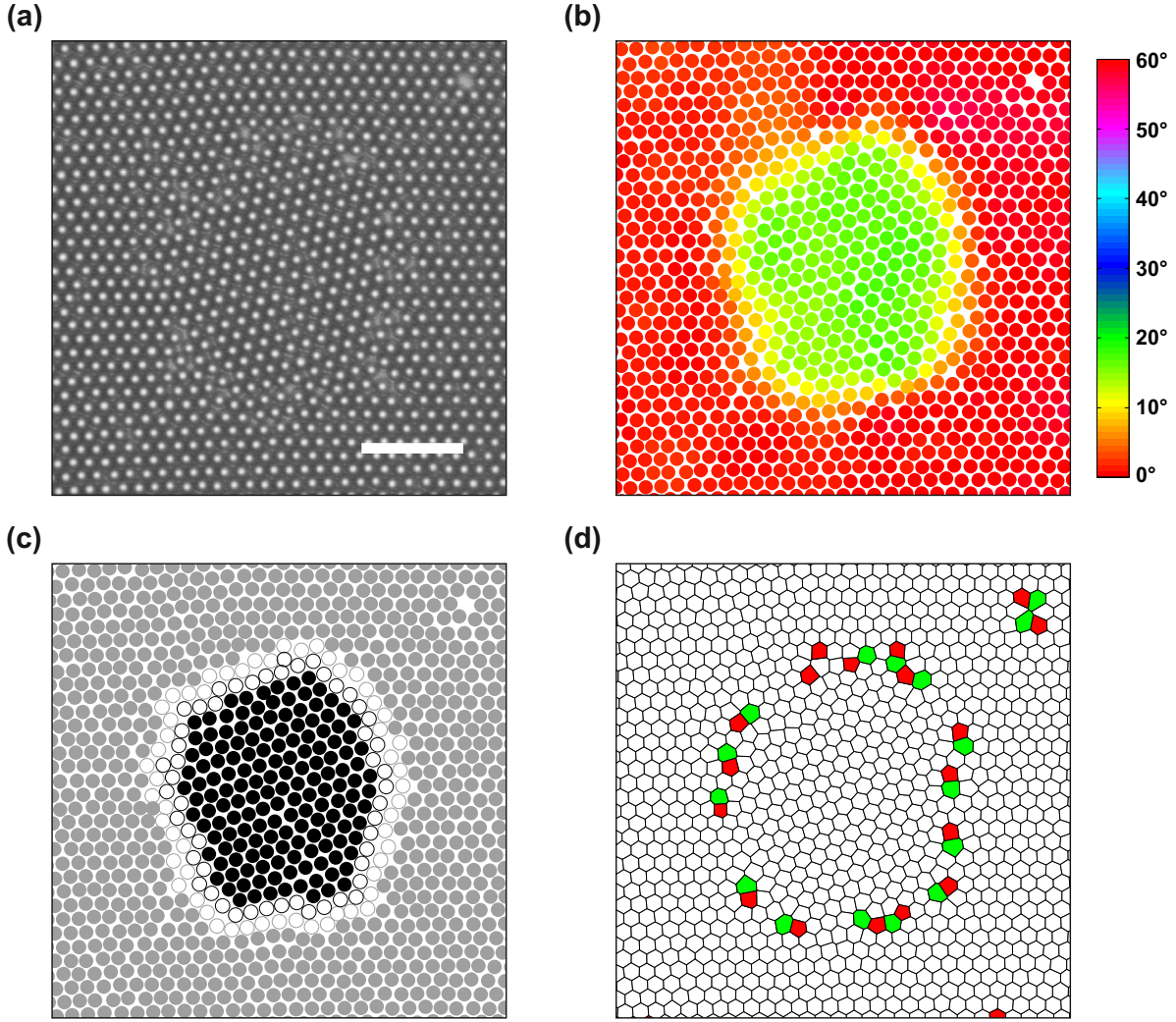


Figure 6.3: (a) Microscopy image of a circular grain created with an optical vortex. Scale bar, $20\ \mu\text{m}$. (b) The corresponding orientation map. The misorientation is $\theta = 16^\circ$ in this case. (c) Discrimination between particles belonging to the central grain (solid black) and its edge (black circles), the outer crystal (solid grey) and its edge (grey circles). Both edges constitute the GB. (d) Dislocations along the circular GB, where the 5 (7) coordinated particles are coloured in red (green).

used in this chapter. Starting from a single crystal within the field of view, the optical vortex is applied and a circular part of the crystal starts to rotate. When the desired misorientation is reached, the beam is blocked to stop the rotation. The grain is then free from external forces and starts shrinking. This whole shrinkage is monitored by recording images at 1 frame/s for different initial misorientations ranging from 0° to 30° . The radii of the created grains lie within the approximate range $8\sigma - 11\sigma$, where σ is the particle diameter. The speed of rotation is about $0.3^\circ/\text{s}$ in these experiments, which is low enough for the grain to stay intact during rotation.

6.3.2 Data analysis

From the microscopy images (see figure 6.3(a)), the positions of the particles are detected using the methods introduced in section 2.3.2. Subsequently, the smoothed bond-orientational field and the orientation $\tilde{\theta}_6$ are determined for each particle as described in section 3.3.2 (see figure 6.3(b)). In the following, the smoothed orientation is denoted θ_6 and is called the “orientation” for simplicity. The distribution of the local orientation θ_6 is bimodal, corresponding to the orientations of the inner grain and the outer crystal. This enables the discrimination of the particles belonging to the central circular grain and to the outer crystal, together with the particles at their edges, which constitute the GB (see figure 6.3(c)). Finally, the 5- and 7-coordinated particles are detected, which enables the dislocations along the circular GB to be directly visualised using a Voronoi tessellation, as shown in figure 6.3(d).

The shrinking kinetics of the grain are studied by monitoring the time-evolution of the radius of the grain in units of σ as given by

$$R_G = \sqrt{\frac{N_G}{\pi}}, \quad (6.11)$$

where N_G is the number of particles belonging to the grain and the inner GB edge. The misorientation θ between the inner circular grain and the outer crystal is also monitored and is defined by

$$\theta = \min(|\theta_6^{in} - \theta_6^{out}|, 60^\circ - |\theta_6^{in} - \theta_6^{out}|), \quad (6.12)$$

where θ_6^{in} and θ_6^{out} are the average orientations of the particles in the central grain and the outer crystal, respectively. Note that the GB particles are not included due to the noise in θ_6 near the GB. Finally, the shrinkage is also studied in terms of the time-evolution of the number of dislocations on the grain perimeter, N_D .

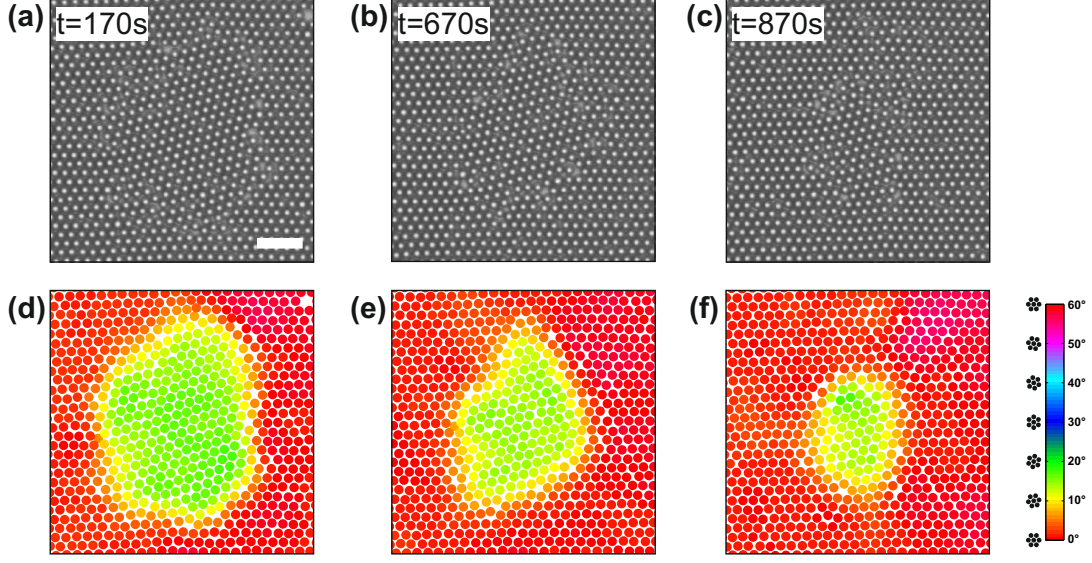


Figure 6.4: (a)-(c) Microscopy images of a shrinking grain with misorientation $\theta = 16.4^\circ$ and initial radius $R_G(0) = 10.3\sigma$ at different times after the laser beam has been blocked. Scale bar, $12\text{ }\mu\text{m}$. (d)-(f) Orientation maps corresponding to the same times as in (a)-(c).

6.4 Results and discussion

6.4.1 Shrinking kinetics

Figure 6.4 shows microscopy images and the corresponding orientation maps of an initially circular grain with $\theta = 16.4^\circ$ and $R_G(0) = 10.3\sigma$ at three different times after the laser beam is turned off, i.e. when shrinking starts. It can be seen that the grain spontaneously shrinks, while maintaining a roughly circular shape, until a single crystal is left (not shown here). The shrinking kinetics are quantified by monitoring the time-evolution of the radius, R_G , for circular grains with similar initial radii, $R_G(0)$, but different initial misorientations, $\theta(0)$, with the outer crystal. The results for $R_G(0) = 10.8 \pm 0.5\sigma$ and misorientations $\theta \in [9^\circ, 28^\circ]$ are shown in figure 6.5(a). In all cases, $R_G(t)$ decreases monotonically before it sharply drops to zero, indicating the end of shrinkage at a time t_f . Also, it is clearly observed that the higher the misorientation, the longer the shrinkage takes for these equally sized circular grains. Plotting the misorientation θ as a function of time for the exact same grains (see figure 6.5(b)) shows that the misorientation is not strictly constant, but both increases and decreases during shrinkage. This indicates the occurrence of multiple mechanisms for grain shrinkage, including curvature-driven migration,

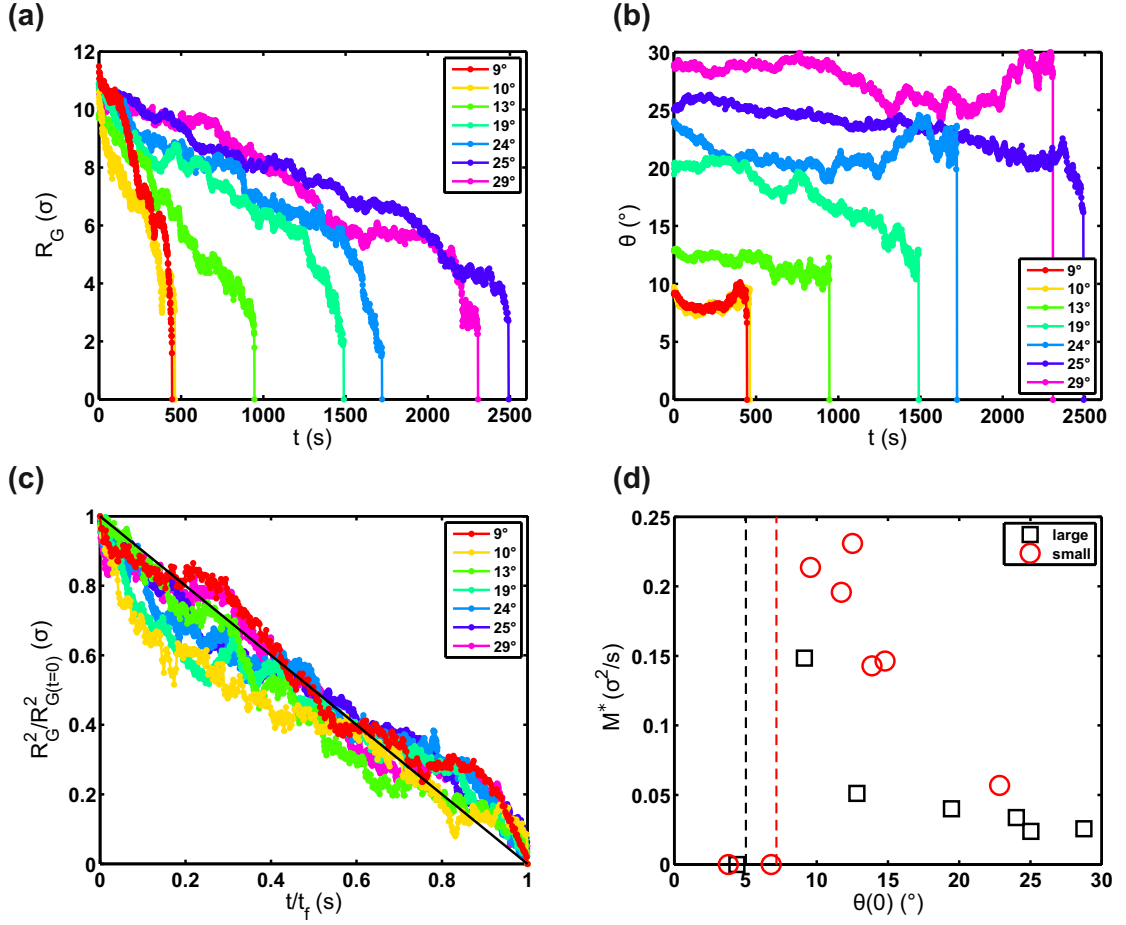


Figure 6.5: (a) Time-evolution of the radius of the circular grain for different initial misorientations with the outer crystal and similar initial radii $R_G(0) = 10.8 \pm 0.5\sigma$. (b) Time-evolution of the misorientation for the same data as in (a). (c) Direct test of the parabolic shrinkage scaling (black solid line, see text) where t_f is the time for complete shrinkage. (d) Decrease of the reduced mobility M^* as a function of the initial misorientation θ_0 for large grains (black squares, $R_G(0) = 10.8 \pm 0.5\sigma$) and small grains (red circles, $R_G(0) = 8.4 \pm 0.8\sigma$). For large and small grains, pure sliding with $M^* = 0$ is observed below $\theta(0) \simeq 5^\circ$ and 7° respectively, as indicated by the vertical dashed lines.

coupled GB migration and GB sliding.

Next, the parabolic law of grain shrinkage (equation (6.3)), is directly tested on the data by re-writing it as

$$\frac{R_G^2(t)}{R_G^2(0)} = 1 - \frac{t}{t_f}, \quad (6.13)$$

where $t_f = R_G^2(0)/(2M^*)$ is the time corresponding to the end of shrinkage. Subsequently plotting $R_G^2/R_G^2(0)$ as a function of t/t_f in figure 6.5(c) shows good agreement with the scal-

ing predicted by equation (6.13) for all considered misorientations. Note that this does not necessarily imply that shrinkage is purely curvature-driven as other mechanisms can also lead to a parabolic law [102, 103]. Instead it means that shrinkage can be characterised by a *single* kinetic coefficient, the reduced mobility M^* . In particular, it means that the area of these grains decreases at constant rate $2\pi M^*$ according to equation (6.4).

The variation of the reduced mobility, M^* , as a function of the initial misorientation, $\theta(0)$, is shown in figure 6.5(d). The values of M^* are directly obtained from $M^* = R_G^2(0)/(2t_f)$ and are first reported for grains with $R_G(0) = 10.8 \pm 0.5\sigma$ (black squares), referred to as “large grains”. The reduced mobility *decreases* upon increasing initial misorientation, indicating that circular small angle GBs (SAGBs) shrink faster than circular large angle GBs (LAGBs), consistent with figure 6.5(a). Interestingly, for the grain with $\theta(0) \simeq 4.5^\circ$, no shrinkage is observed, instead, the grain rotates towards *lower* angles until it merges with the outer crystal. This corresponds to pure GB sliding, where $M^* = 0$ as there is no migration of the GB.

To investigate the role of the initial grain size, or equivalently the curvature, the same analysis was repeated on a second set of grains with a smaller initial radius, $R_G(0) = 8.4 \pm 0.8\sigma$ (red circles), termed “small” grains. Pure GB sliding is observed as well, but now below $\theta(0) \simeq 7^\circ$, which is a slightly higher misorientation than for large grains. Above this angle, the reduced mobility M^* again *decreases* upon increasing θ . For small grains, M^* is generally higher than that of large grains with the same misorientation. This shows that the reduced mobility is a decreasing function of the initial grain size, i.e. that it increases when the initial curvature is increased. For example, a curved GB with $R_G(0) \simeq 10.8\sigma$ at $\theta(0) = 19^\circ$ has a reduced mobility of $M^*(19^\circ) \simeq 0.05 \sigma^2/s$, which corresponds to $M^*(19^\circ) \simeq 3.6 \times 10^{-13} m^2/s$. This is indeed significantly higher than the reduced mobility of a flat symmetric tilt GB with misorientation $\theta = 20^\circ$, which was found to be $M_{flat}^*(20^\circ) = 1.3 \times 10^{-13} m^2/s$ in the exact same colloidal system [38].

Both the decay of the reduced mobility with increasing misorientation and its dependence on the initial radius of the grain are remarkable effects. Particularly notable is the *decrease* of M^* with increasing θ , as it is the opposite of the behaviour commonly observed in atomistic simulations of circular grains [103]. Nevertheless, phase field simulations that take into account energy dissipation in the central grain due to lattice rotation are consistent with both effects observed here [97]. When dissipation in the grain dominates the dissipation at the GB and

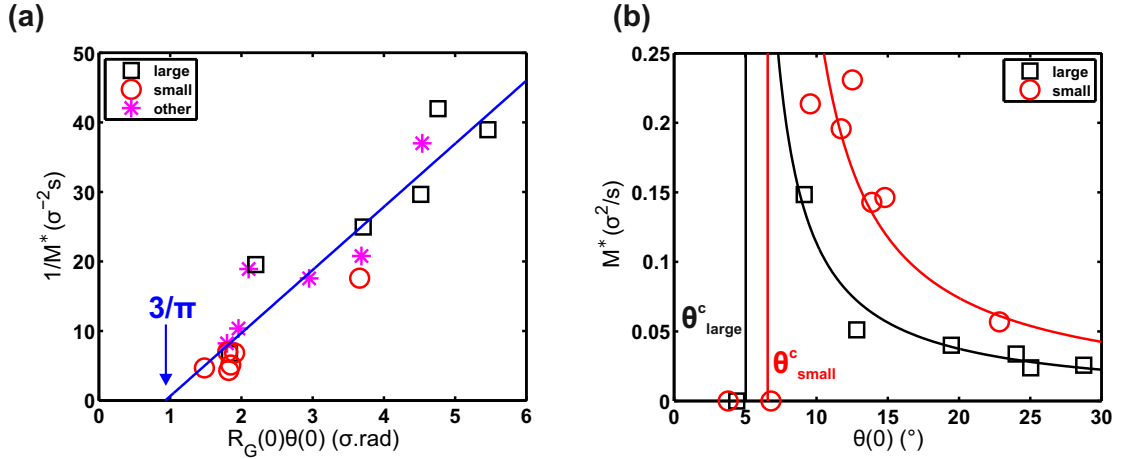


Figure 6.6: (a) Linear behaviour of $1/M^*$ as a function of the product $R_G(0)\theta(0)$. The line crosses the x -axis at a critical value $[R_G\theta]^c = 3/\pi$ below which pure GB sliding takes place. (b) Reduced mobility M^* as a function of initial misorientation $\theta(0)$ for large and small grains together with the theoretical curves. The thresholds θ_{large}^c and θ_{small}^c corresponding to the sliding-shrinking transition agree very well with the data.

during coupled GB migration, M^* is predicted to obey

$$\frac{1}{M^*} = A(R_G(0)\theta(0) + B), \quad (6.14)$$

where A and B are two positive constants [97]. This relation is directly tested on the experimental data by plotting $1/M^*$ as a function of $R_G(0)\theta(0)$ in figure 6.6(a). The data points comprise both large and small grains, together with other grains that do not fall into either of these two classes. Good agreement with equation (6.14) is found, even though coupled GB migration does not happen in most cases here. This suggests that equation (6.14) is possibly more general or that dissipation in the grain dominates shrinkage in the present case.

6.4.2 Sliding-shrinking transition

Interestingly and in contrast with equation (6.14), a linear fit of the collapsed data in figure 6.6(a) gives a negative y -intercept. This implies that

$$M^* = \frac{1}{A(R_G(0)\theta(0) - [R_G\theta]^c)}, \quad (6.15)$$

where $[R_G\theta]^c \simeq 0.93$ is the value of the x -intercept¹ obtained from the fit in figure 6.6(a). Figure 6.6(b) shows the variation of M^* as a function of the initial misorientation for large and small grains again, but now together with the fits according to equation (6.15), where the experimental values for $R_G(0)$ have been used. The fits show excellent agreement and, strikingly, the vertical asymptotes exactly correspond to the transitions between pure sliding and shrinking, which are located at

$$\theta^c = \frac{[R_G\theta]^c}{R_G(0)}. \quad (6.16)$$

For the large and small grains, this gives $\theta_{large}^c = 4.9^\circ$ and $\theta_{small}^c = 6.4^\circ$, which are in remarkably good agreement with the experimental data points. This strongly suggests that the lower bound for $R_G(0)\theta(0)$, namely $[R_G\theta]^c$, is the critical value corresponding to the sliding-shrinking transition.

To understand the origin of this lower bound for $R_G(0)\theta(0)$ in the shrinkage regime, consider a grain with initial radius $R_G(0)$ and misorientation $\theta(0)$. As shown in appendix B, the minimal number of dislocations along a circular GB is 6. As they are equally spaced on the grain perimeter, the dislocation spacing is $D_6 = \pi R_G(0)\sigma/3$ along the circular GB². In addition, the dislocation spacing is related to the misorientation via $D = b/\theta(0)$ (equation (2.8))³. Consequently, the condition for the 6 dislocations to fit on the circular GB is $D_6 \geq D$. Taking the magnitude of the Burgers vector to be $b = \sigma$, this condition can be rewritten as

$$R_G(0)\theta(0) \geq \frac{3}{\pi}, \quad (6.17)$$

which yields a critical value of

$$[R_G\theta]^c = \frac{3}{\pi} \simeq 0.96. \quad (6.18)$$

This is in excellent agreement with the experimental value of 0.93, as can also be seen from the x -intercept in figure 6.6(a). This critical value thus corresponds to the transition between pure GB sliding for $R_G(0)\theta(0) < 3/\pi$ and GB shrinkage for $R_G(0)\theta(0) \geq 3/\pi$. In the case $R_G(0)\theta(0) < 3/\pi$, the 6 dislocations are not stable and the grain rotates towards lower angles by

¹Note that here, the y -intercept is negative, but the x -intercept is positive.

²Note that the actual radius is $R_G(0)\sigma$ as R_G is dimensionless.

³Here, the dislocation spacing is assumed to be the same as for a flat GB.

pure GB sliding, until it merges with the outer crystal. If $R_G(0)\theta(0) \geq 3/\pi$, the 6 dislocations are stable and shrinkage happens with a reduced mobility given by equation (6.15). Note that at a given starting radius $R_G(0)$, the critical misorientation is given by

$$\theta^c = \frac{3}{\pi R_G(0)}, \quad (6.19)$$

which is a decreasing function of the initial grain size, $R_G(0)$, which is again consistent with the data. Thus the sliding-shrinking transition is an effect that occurs for small grains, when the dislocation spacing and the grain radius are comparable. It is interesting to note that this transition has never been observed in simulations as the grains are usually too large, nor in experiments, where these length scales are not accessible in atomic systems. Finally, this transition is *solely* determined by geometrical constraints, which depend on the type of lattice but not on the details of the system.

6.4.3 Kinetics and dislocation density

In order to gain more insight into the mechanisms of grain shrinkage, the evolution of the density of dislocations at the GB during shrinkage is probed for both SAGBs and LAGBs.

Small angle grain boundaries

Figure 6.7(a) shows the time-evolution of the radius, R_G , the number of dislocation along the GB, N_D , and the misorientation, θ , for a small grain enclosed by a SAGB with $R_G(0) = 8.9\sigma$ and $\theta(0) = 9.6^\circ$. While the grain keeps shrinking, the number of dislocations, N_D , exhibits two types of behaviour: it decreases for $t < 40s$ and $t > 130s$, but is constant between $t = 40s$ and $130s$. Importantly, this period of conservation of the number of dislocations corresponds to grain rotation towards *larger* misorientations as is evident from figure 6.7(a). This somewhat counter-intuitive behaviour can be explained by considering the definition of N_D ,

$$N_D = \frac{2\pi R_G}{D(\theta)}, \quad (6.20)$$

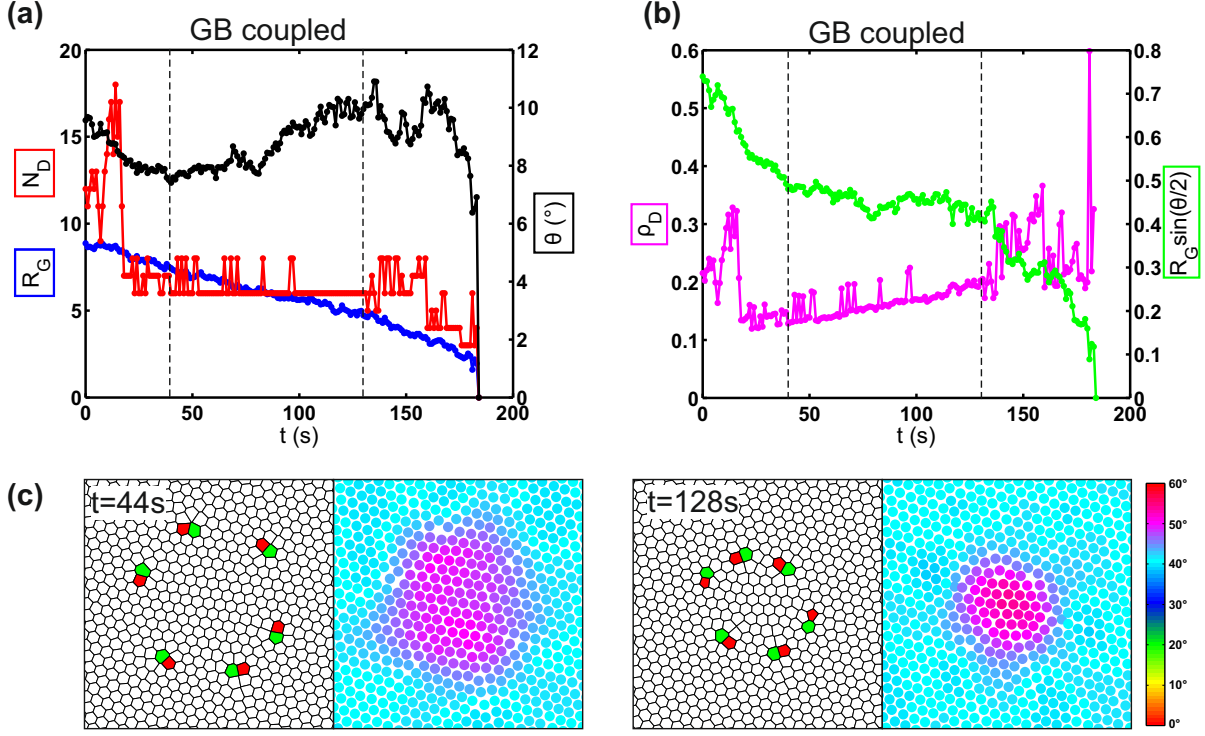


Figure 6.7: (a) Time-evolution of the radius of the grain (R_G), the number of dislocations along the GB (N_D) and the misorientation with the outer crystal (θ). The initial radius and misorientation are $R_G = 8.9\sigma$ and $\theta(0) = 9.6^\circ$. (b) Time-evolution of the dislocation density ρ_D and $R_G \sin(\theta/2)$. (c) Voronoi tessellations showing the dislocations at the circular GB together with the orientation maps at the beginning and at the end of coupled migration.

where $D(\theta)$ is the dislocation spacing, which can be approximated by its value for a flat GB, $D(\theta) = b/\theta$, with b the Burgers vector (equation (2.8)), resulting in

$$N_D = \frac{2\pi R_G \theta}{b}. \quad (6.21)$$

When N_D is conserved, combining equation (6.20) and equation (6.21) implies that

$$R_G(t)\theta(t) = C, \quad (6.22)$$

where C is a constant. Equation (6.22) indicates that when $R_G(t)$ decreases in time, $\theta(t)$ has to increase because of the conservation of the number of dislocations, as indeed observed in figure 6.7(a). Note that equation (6.22) is nothing but equation (6.8) in the limit of small misorientations for which $\sin(\theta/2) \simeq \theta/2$. This confirms that the period of time over which the number of dislocations is conserved corresponds to coupled GB migration. Indeed, the quantity $R_G \sin(\theta/2)$ is constant during this period, highlighting the occurrence of coupled migration (see

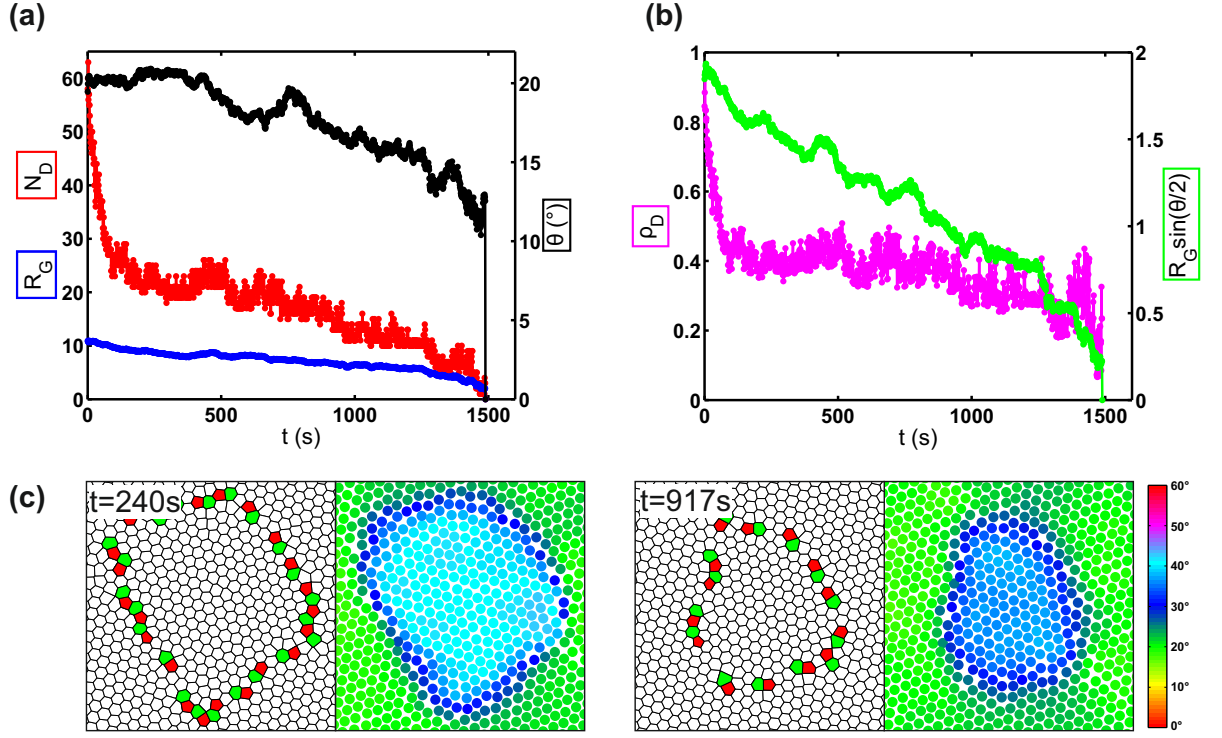


Figure 6.8: (a) Time-evolution of the radius of the grain (R_G), the number of dislocations along the GB (N_D) and the misorientation with the outer crystal (θ). The initial radius and misorientation are $R_G = 10.9\sigma$ and $\theta(0) = 19.5^\circ$. (b) Time-evolution of the dislocation density ρ_D and $R_G \sin(\theta/2)$. (c) Voronoi tessellations showing the dislocations at the circular GB together with orientation maps at two different times during shrinkage.

figure 6.7(b)). Coupled GB migration therefore leads to an increase of the dislocation density, $\rho_D = N_D/(2\pi R_G)$ (see figure 6.7(b)), corresponding to the dislocations getting closer to each other as θ becomes larger (see figure 6.7(c)).

Large angle grain boundaries

The case of a grain enclosed by a LAGB is illustrated in figure 6.8(a), where $R_G(0) = 10.9\sigma$ and $\theta(0) = 19.5^\circ$. Both the radius of the grain, R_G , and the number of dislocations, N_D , decrease without exhibiting any plateau, in strong contrast with the SAGB case. Indeed, the fact that the quantity $R_G \sin(\theta/2)$ keeps decreasing (see figure 6.8(b)) confirms the absence of coupled migration. However, the misorientation θ decreases monotonically, which suggests the presence of GB sliding throughout shrinkage.

Comparing figure 6.8(b) with figure 6.7(b) shows that the density of dislocations, ρ_D , is much higher for LAGBs than for SAGBs. This is also obvious by directly comparing the

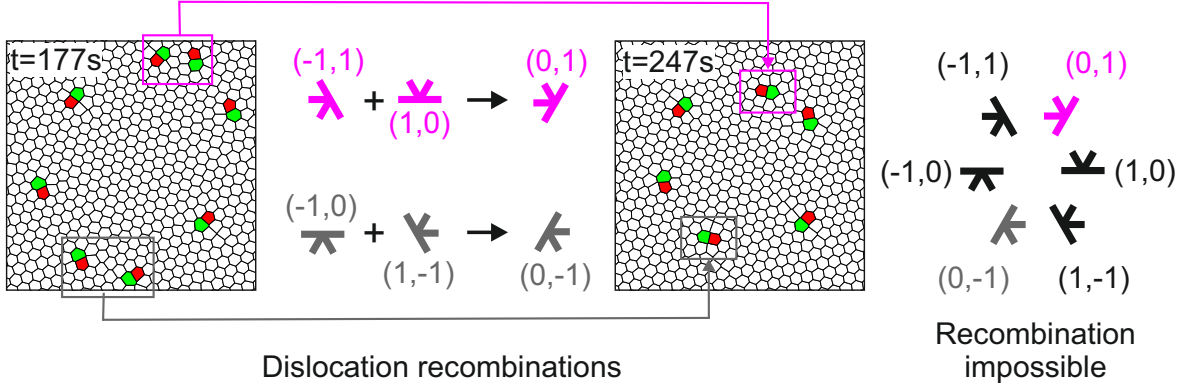


Figure 6.9: Reduction of the number of dislocations along the circular GB from 8 to 6 enabled by two dislocation recombinations. Once in the configuration with 6 dislocations, no recombination is possible. The notation for Burgers vectors is the same as in figure 2.2.

distribution of dislocations in figure 6.8(c) (LAGBs) and figure 6.7(c) (SAGBs). Importantly, ρ_D is roughly constant during most of the shrinkage of LAGBs, indicating that the main mechanism to reduce the grain size is the annihilation of dislocations.

6.4.4 Dislocation reactions

The complete shrinkage of a grain must be accompanied by the annihilation of dislocations, which is achieved by so-called dislocation reactions [103, 169]. In this section, the dislocation reactions leading to the complete shrinkage of a large grain with a low misorientation are directly visualised and classified into different elementary processes. In the case discussed here, $R_G(0) = 10.8\sigma$ and $\theta(0) = 9^\circ$, which is a small enough misorientation to have well separated dislocations and facilitate the direct observation of their reactions during shrinkage.

Dislocation recombination

At the early stages of shrinkage, the GB consists of 8 dislocations that are relatively far apart, see figure 6.9 (left). The dislocations with opposite Burgers are diametrically opposed, which makes any direct annihilation impossible. Instead, the recombination of neighbouring dislocations takes place [174]: two dislocations of Burgers vectors $\vec{b}_1$ and $\vec{b}_2$ are converted into a dislocation with

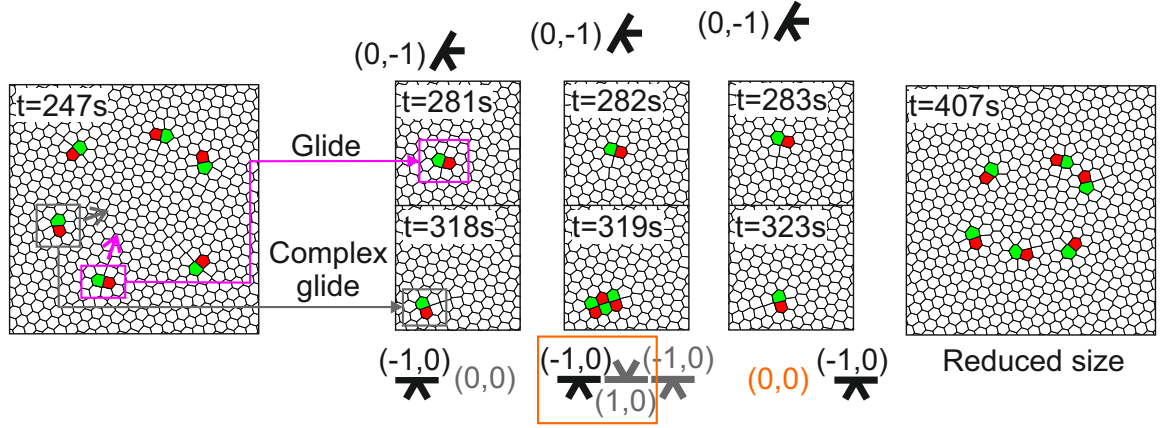


Figure 6.10: Reduction of the grain size at constant number of dislocations by dislocation glide, as indicated by the arrows (left). Complex glide is realised by creation of a dislocation pair (bottom row, middle).

Burgers vector $\vec{b}_3$ such that

$$\vec{b}_1 + \vec{b}_2 = \vec{b}_3, \quad (6.23a)$$

$$b_1^2 + b_2^2 \geq b_3^2. \quad (6.23b)$$

The first condition, equation (6.23a), is the conservation of the total Burgers vector before and after recombination. The second condition, equation (6.23b), corresponds to the requirement of lowering the elastic energy after recombination⁴. Figure 6.9 shows that two recombinations between neighbouring dislocations enables the number of dislocations to be reduced from 8 to 6, thereby reducing the GB length. However, further recombinations are impossible in the configuration with 6 dislocations as adding the Burgers vectors of two neighbouring dislocations would violate equation (6.23b).

Dislocation glide

The next stage of grain shrinkage involves a reduction of the grain perimeter at constant number of dislocations. As established in the previous section, this stage corresponds to coupled GB migration, which leads to grain rotation towards higher angles. At the level of single dislocations, coupled GB migration is achieved via dislocation glide, which is the motion of a dislocation along

⁴Note that a rigorous balance of the elastic energy must include the interactions between all pairs of dislocations on the GB, not only the contributions of single dislocations. Nevertheless, the condition can be taken as a rule of thumb to evaluate the possibility of a recombination.

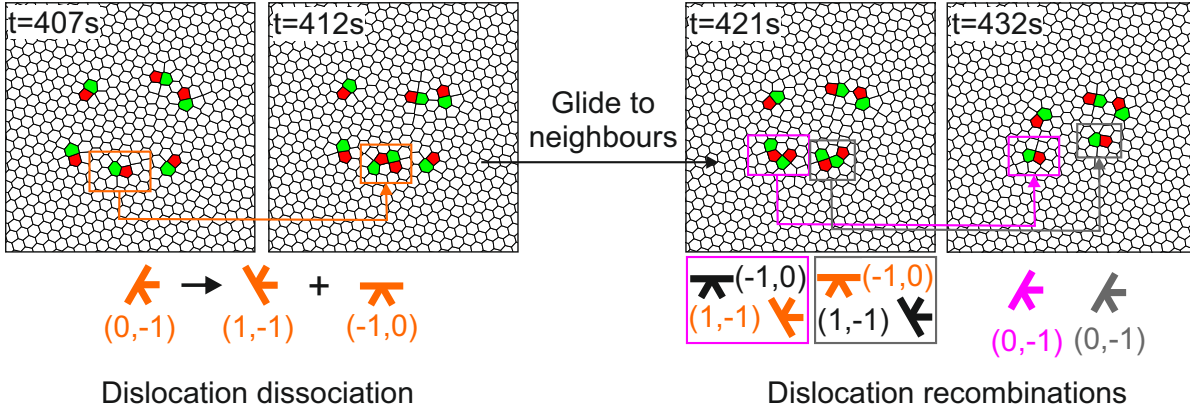


Figure 6.11: Dislocation dissociation process followed by glide towards the nearest neighbours. Two subsequent dislocations recombinations enable the number of dislocations to be reduced to 5.

its Burgers vector, in the same or the opposite direction. In the present case, the Burgers vectors of all 6 dislocations point radially outwards from the grain, which means that glide anti-parallel to the Burgers vectors leads to shrinkage without dislocation reactions (see figure 6.10). Note that glide can be accompanied by the creation and annihilation of pairs of dislocations with opposite Burgers vectors, as illustrated in figure 6.10, which is referred to as complex glide [41] and is responsible for the fluctuations in N_D during coupled migration in (see figure 6.7(a)).

Dislocation dissociation

Further shrinkage is achieved by dislocation dissociation [174], which involves the splitting of a dislocation of Burgers vector $\vec{b}_1$ into two dislocations of Burgers vectors $\vec{b}_2$ and $\vec{b}_3$ such that

$$\vec{b}_1 = \vec{b}_2 + \vec{b}_3, \quad (6.24a)$$

$$b_2^2 + b_3^2 - b_1^2 \text{ minimised}, \quad (6.24b)$$

where the second term represents the increase in elastic energy⁵. As $\vec{b}_1$ has magnitude 1 in most cases, the condition given by equation (6.24b) is satisfied when $\vec{b}_2$ and $\vec{b}_3$ also have magnitude 1. Figure 6.11 shows that the dissociation of one of the 6 dislocations leads to the creation of two dislocations, which can each glide towards their respective nearest neighbours. The resulting two pairs of dislocations can then recombine as their Burgers vectors are compatible

⁵As for the recombination, this expression is just an estimate of the energy difference.

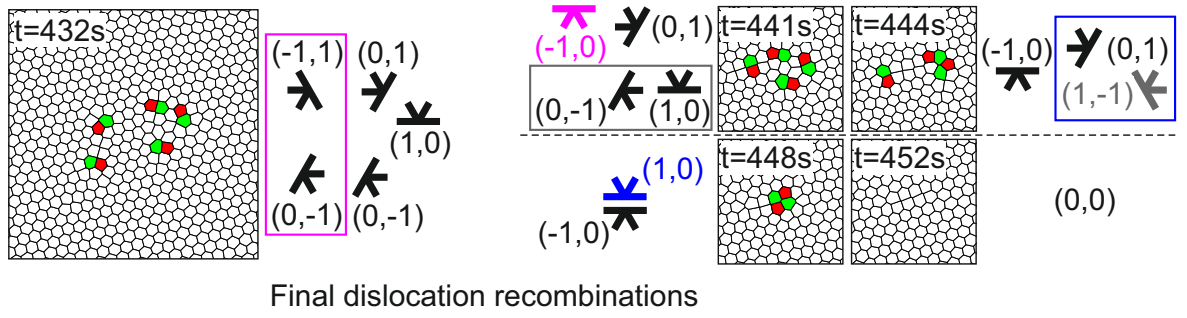


Figure 6.12: Dislocation recombinations leading to complete shrinkage of the grain with no free dislocations left as imposed by the conservation of the total Burgers vector to $\vec{0}$.

with equation (6.23b). This enables the number of dislocations to be reduced to 5, thereby further shrinking the circular GB (see figure 6.11).

Final recombinations

Complete shrinkage is finally achieved by successive dislocation recombinations as illustrated in figure 6.12. The final state is the perfect crystal with no free dislocations as the total Burgers vector is conserved and equals $\vec{0}$ throughout the whole process.

6.5 Conclusions

In summary, it has been shown that circular GBs in colloidal crystals exhibit very rich spontaneous shrinking kinetics, which includes curvature-driven shrinking, GB sliding and GB coupled motion. The kinetics are well characterised by a single kinetic coefficient, the reduced mobility, which depends both on the initial misorientation and size of the grain enclosed by the GB. It has been shown that highly curved circular GBs exhibit a sliding-shrinking transition, which is fully determined by geometrical constraints. Finally, the dislocations reactions underlying the kinetics of shrinkage have been directly visualised.

Acknowledgements

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Chapter 7

Particle dynamics during grain boundary migration

ABSTRACT

In this chapter, the dynamics of particles during the migration of circular grain boundaries in colloidal crystals is investigated. Circular grain boundaries are prepared using holographic optical tweezers and start shrinking as soon as the tweezers are turned off. The dynamics of the particles swept by the migrating grain boundary are very heterogeneous, with some particles exhibiting significant motion and others hardly moving at all during grain boundary migration. In the specific case of coincident site lattice boundaries, the particles located at coincident sites remain at these sites during the whole process and their local orientation is changed by a simple rotation of their nearest neighbours. The motion of dislocations and their reactions, which enable the migration of the grain boundary, are found to be the main source of dynamical heterogeneities. In particular, the dynamics of particles during the glide of dislocations is revealed.

7.1 Introduction

Many direct observations confirm that grain boundaries (GBs) can migrate over distances large enough to induce major structural changes in polycrystalline materials [99, 100]. Remarkably, these distances are well above the width of GBs [168], which typically equals several atomic diameters in most metals [12], enabling the conversion of one of the two adjacent grains into the other. It is clear that at the microscopic level, GB motion originates from the displacements and rearrangements of atoms [19, 175, 176]. The migration of GBs can also be considered from a topological point of view, where the motion and reactions of dislocations enable the reduction of the GB area [60, 103]. However, the precise mechanisms of GB migration at the atomic level and their relation to the dislocation reactions remain unclear, mainly because the direct observation of the dynamics of atoms over such short time scales is difficult with current microscopy techniques [20, 21].

Molecular dynamics simulations have been a very useful tool to probe the dynamics of atoms at GBs [177, 178]. Studies of flat fluctuating GBs have revealed similarities with the dynamics of glass-forming liquids [151], marked by dynamical heterogeneities and collective string-like motion [179–182]. Also, in the case of migration of flat GBs subjected to a driving pressure, chain-like motion of atoms, both parallel and perpendicular to the GB plane has been found [183, 184]. An alternative approach that does not require any external drive is the study of the particle dynamics during spontaneous curvature-driven GB migration [185], which has recently given some insight into the link between particle dynamics and dislocation reactions during GB migration [174].

One route to experimentally study the mechanisms of GB migration is to use colloidal model systems. Indeed, the migration time scale of colloidal GBs is slow enough to allow for direct monitoring using simple video-microscopy [47]. While studies of flat fluctuating colloidal GBs have reported particles dynamics akin to that of supercooled liquids [145, 150], experimental studies of the particle dynamics during GB migration are still lacking. In the previous chapter, holographic optical tweezers were used to create circular GBs in colloidal crystals [46]. As these circular GBs undergo spontaneous curvature-driven migration until complete annihilation, they are ideal for the study of both the particle dynamics and dislocation motion during GB migration.

In this chapter, the dynamics of particles during the migration of circular GBs in colloidal crystals is studied using video-microscopy. Circular GBs are prepared using holographic optical tweezers and start shrinking once the optical tweezers are turned off. The trajectories of the particles are then monitored until shrinkage is complete. The dynamics of the particle swept by the GB are characterised by strong dynamical heterogeneities indicating a wide variation in the magnitude of the displacements. In the specific case of coincident site lattice (CSL) boundaries, the particles located at the sites of the CSL remain there during the whole process. Interestingly, their crystal orientation changes without motion due to a simple rotation of their nearest neighbours. Finally, it is shown that the particle dynamics corresponding to the glide of dislocations is the main origin of the dynamical heterogeneities.

7.2 Methods

7.2.1 Experiments

The experimental methods are the same as in chapter 6 and their description can be found in section 6.3.1. The data is analysed as described in section 6.3.2, and additionally, the trajectories of the particles are reconstructed using standard particle tracking algorithms [77], see section 2.3.2. In the following, the trajectory of a particle i is represented by a time dependent vector $\vec{r}_i(t)$.

7.2.2 Time-correlation functions

The dynamics of the particles during shrinkage of the circular grain is characterised using different time-correlation functions. Firstly, the self part of the van Hove correlation function in 2D is defined as [186]

$$G_s(\vec{r}, \tau) = \left\langle \frac{1}{N} \sum_{i=1}^N \delta^{(2)}(\vec{r} - (\vec{r}_i(t_0 + \tau) - \vec{r}_i(t_0))) \right\rangle, \quad (7.1)$$

where $\delta^{(2)}$ is the two-dimensional Dirac distribution, N is the number of particles, τ is the time lag and the average $\langle . \rangle$ runs over different initial times t_0 . The values of $G_s(\vec{r}, \tau)$ represent the

distribution of particle displacements during a time lag τ . The n^{th} moment of G_s is defined by

$$\langle \vec{r}^n(\tau) \rangle = \int \vec{r}^n G_s(\vec{r}, \tau) d^2 \vec{r}, \quad (7.2)$$

where n is an integer. The second moment of G_s , corresponding to $n = 2$ in equation (7.2), gives the mean square-displacement (MSD):

$$\langle \vec{r}^2(\tau) \rangle = \frac{1}{N} \sum_{i=1}^N \left\langle (\vec{r}_i(t_0 + \tau) - \vec{r}_i(t_0))^2 \right\rangle, \quad (7.3)$$

which is a measure of the typical area explored by a particle during a time lag τ .

Within the Gaussian approximation, the self part of the van Hove function is given by a Gaussian distribution [186],

$$G_s^0(r, \tau) = \frac{1}{\pi \langle \vec{r}^2(\tau) \rangle} \exp \left(-\frac{r^2}{\langle \vec{r}^2(\tau) \rangle} \right), \quad (7.4)$$

with the normalisation condition $\int_0^{+\infty} 2\pi r G_s^0(r, \tau) dr = 1$. Note that G_s^0 is isotropic as it depends only on $r^2 = \|\vec{r}\|^2$, see equation (7.4). The deviation of an experimental G_s from the Gaussian expression in equation (7.4), where $\langle \vec{r}^2(\tau) \rangle$ is taken to be the experimental MSD, can be quantified by the 2D non-Gaussian parameter [180, 187], $\alpha_2(\tau)$, as

$$\alpha_2(\tau) = \frac{\langle \vec{r}^4(\tau) \rangle}{2 \langle \vec{r}^2(\tau) \rangle^2} - 1, \quad (7.5)$$

which is zero if G_s is Gaussian [188].

In analogy to the displacements in space, the changes in the local orientation of the particles are analysed by introducing the self orientational correlation function, $\Theta_s(\theta, \tau)$, defined as

$$\Theta_s(\theta, \tau) = \left\langle \frac{1}{N} \sum_{i=1}^N \delta(\theta - (\theta_{6,i}(t_0 + \tau) - \theta_{6,i}(t_0))) \right\rangle. \quad (7.6)$$

Here, $\theta_{6,i}(t)$ is the local orientation of the particle i in the interval $]-\pi/6; \pi/6]$ at time t , as defined in section 3.3.2. The values of $\Theta_s(\theta, \tau)$ represent the distribution of local orientation changes within a time lag τ .

7.3 Results and discussion

7.3.1 Dynamical heterogeneities during grain boundary migration

The dynamics of the particles swept by the GB during the shrinkage of the grain is first characterised by directly visualising their trajectories. Figure 7.1(a) shows the trajectories of the particles from the start of shrinkage ($t = 0$) to three different times, for a circular grain of initial radius $R_G(0) = 10.8\sigma$ and misorientation $\theta(0) = 9^\circ$. At early times ($t = 300s$), the GB has already migrated significantly as can be seen from the two boundary positions at $t = 0$ and $t = 300s$ (see figure 7.1(a), left). Among the particles initially in the inner grain, the ones that have been swept by the GB exhibit motion, while the others are still located at their original crystal sites. At intermediate times ($t = 500s$, figure 7.1(a), centre), shrinkage has just completed, which implies that all the particles have been swept by the GB. Among those, some have moved significantly while others have hardly moved at all, indicating a wide range of displacements. At late times ($t = 700s$, figure 7.1(a), right), the overall trajectories are not significantly different from those at intermediate times, as particles have been confined to their new crystal sites between $t = 500s$ and $700s$. A closer inspection of the trajectories of three selected particles, initially located in the central grain, reveals that at early times, the particles have only been moving around their initial crystal sites as they have not been swept by the GB (see figure 7.1(b), left). At intermediate times, they leave their crystal site and hop towards their new crystal site due to the passage of the GB (see figure 7.1(b), centre). At late times, they are located in and confined to a crystal site corresponding to the new grain (see figure 7.1(b), right).

The dynamics of the particles is quantified by computing the MSD and the non-Gaussian parameter, α_2 , whose time-evolutions are shown in figure 7.2(a) and (b), respectively. For comparison, the same quantities are shown for particles in a crystal. While the MSD of the crystal particles reaches a plateau at long times¹ and their α_2 is close to zero at all times, the MSD of the particles swept by the circular GB exhibit a crossover between a subdiffusive regime at intermediate times and a diffusive regime at long times (see figure 7.2(a)). In addition, their

¹Notice that strictly speaking, due to the absence of long-range translational order in 2D, the MSD does not reach a constant value at large time. Modified expressions of the MSD can be used to account for this effect, but this is beyond the scope of this work.

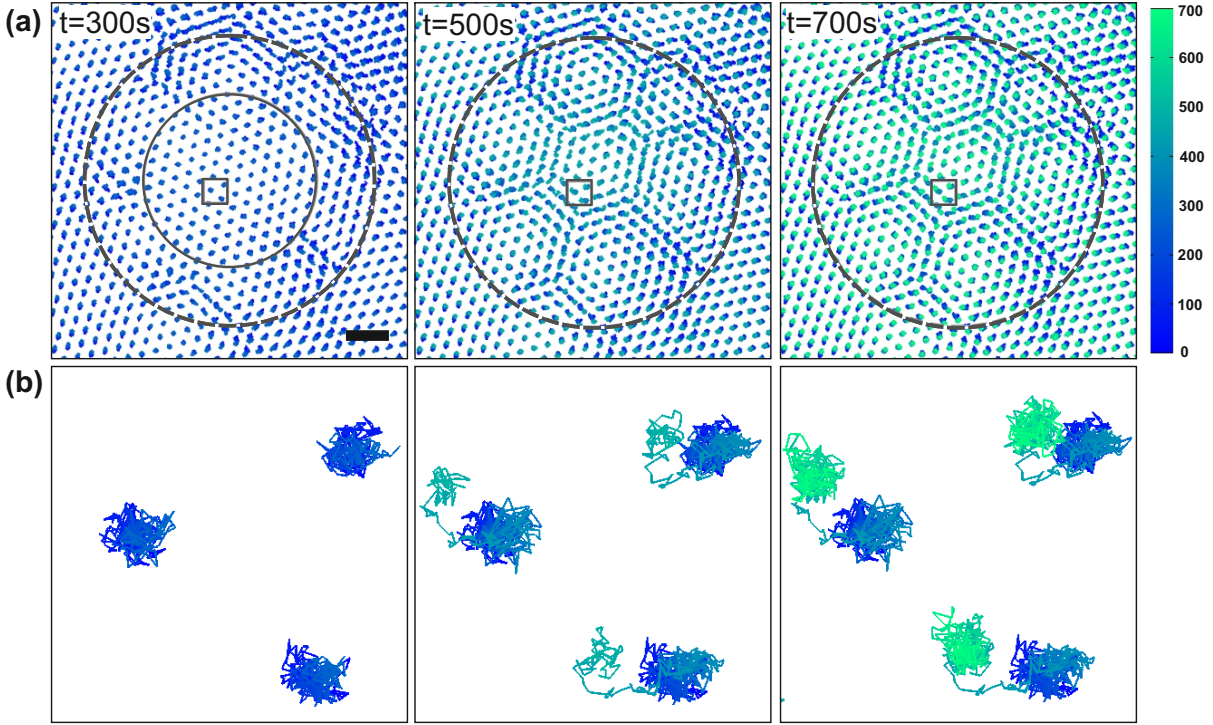


Figure 7.1: (a) Trajectories of the particles coloured according to the elapsed time in seconds (see colourbar) for three different times. The grey dashed line corresponds to the position of the GB at $t = 0$. The grey solid line (left) corresponds to the current position of the GB which has completely shrunk by $t = 500s$. Scale bar, $10\mu m$. (b) Local view of the trajectories of three particles initially within the inner circular grain (see grey rectangle in (a)) at the same times, clearly showing the jumps from sites of the former to the new grain.

α_2 exhibits a significant peak at a time lag $\tau^* \simeq 120 s$ (see figure 7.2(b)), which is consistent with the crossover in the MSD.

Further insight into the particle dynamics is gained by plotting G_s and Θ_s for different time lags, τ , as shown in figure 7.2(c) and (d), respectively. The insets show the same quantities for the crystal particles at the same time lags for comparison. In the case of the pure crystal, the behaviour of G_s is clearly Gaussian and does not change at long times. This indicates that the crystal particles are confined to their crystal sites, consistent with the plateau in the MSD (figure 7.2(a)) and the very small and constant α_2 (figure 7.2(b)). However, in the case of the particles swept by the GB, G_s loses its Gaussian character by developing a tail for $\tau \geq 20s$. This tail corresponds to particle displacements beyond their crystal sites, consistent with the hopping seen in figure 7.1(b) and the increase in α_2 (figure 7.2(b)). These are signatures of the presence of dynamical heterogeneities, which are commonly encountered in supercooled liquids [179–182], concentrated liquids at equilibrium [187, 189] and crystals [190]. Similarly, the Θ_s for the GB

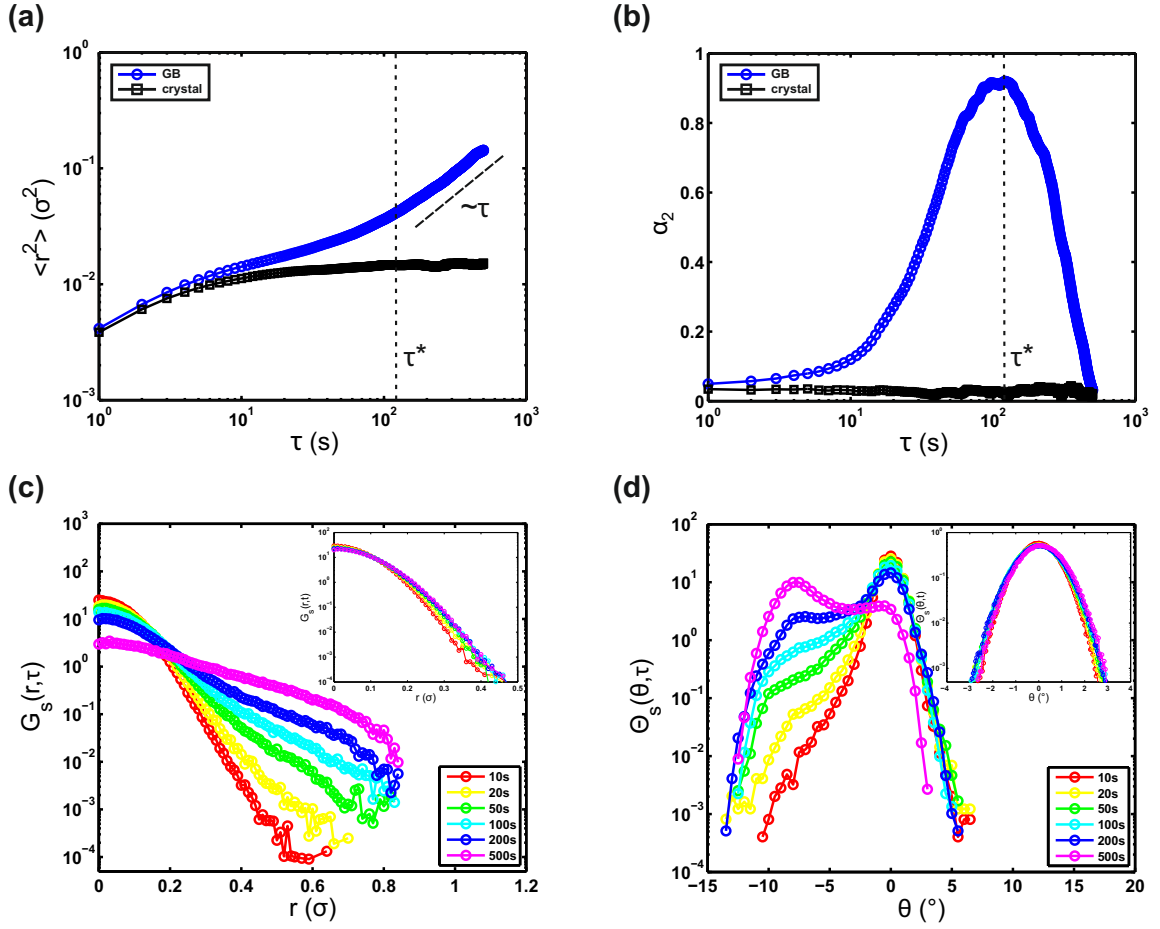


Figure 7.2: (a) Time-evolution of the mean square-displacement of particles swept by the GB (blue dots) and crystal particles (black squares). The mean square-displacement is in units of σ^2 , where σ is the particle diameter. The crossover time to the diffusive regime ($\langle r^2 \rangle \sim \tau$) is τ^* . (b) Time-evolution of the non-Gaussian parameter, α_2 , which peaks at τ^* . (c) Self part of the van Hove correlation function, $G_s(r, \tau)$, as a function of the distance r in units of the particle diameter, σ , for different time lags. The inset shows the same quantity for crystal particles. (d) Self orientational correlation function $\Theta_s(\theta, \tau)$ as a function of the orientation change, θ , for the same particles at the same time lags.

particles also clearly develops a tail for $\tau \geq 20$ s, which grows into a peak at $\theta \simeq -9^\circ$ at long times, indicating that their local orientation changes due to the migration of the GB. Consistently, $\theta \simeq -9^\circ$ is the opposite of the initial misorientation of the GB, and by $t \simeq 500$ s, the majority of the particles have changed orientation, i.e. have changed grain. Conversely, Θ_s remains Gaussian at all times for the crystal particles as their orientation fluctuates around a fixed value. Note that the corresponding behaviours of G_s and Θ_s indicate that the hopping of the particles between their former and their new crystal sites occurs simultaneously with the crossing of the GB on average.

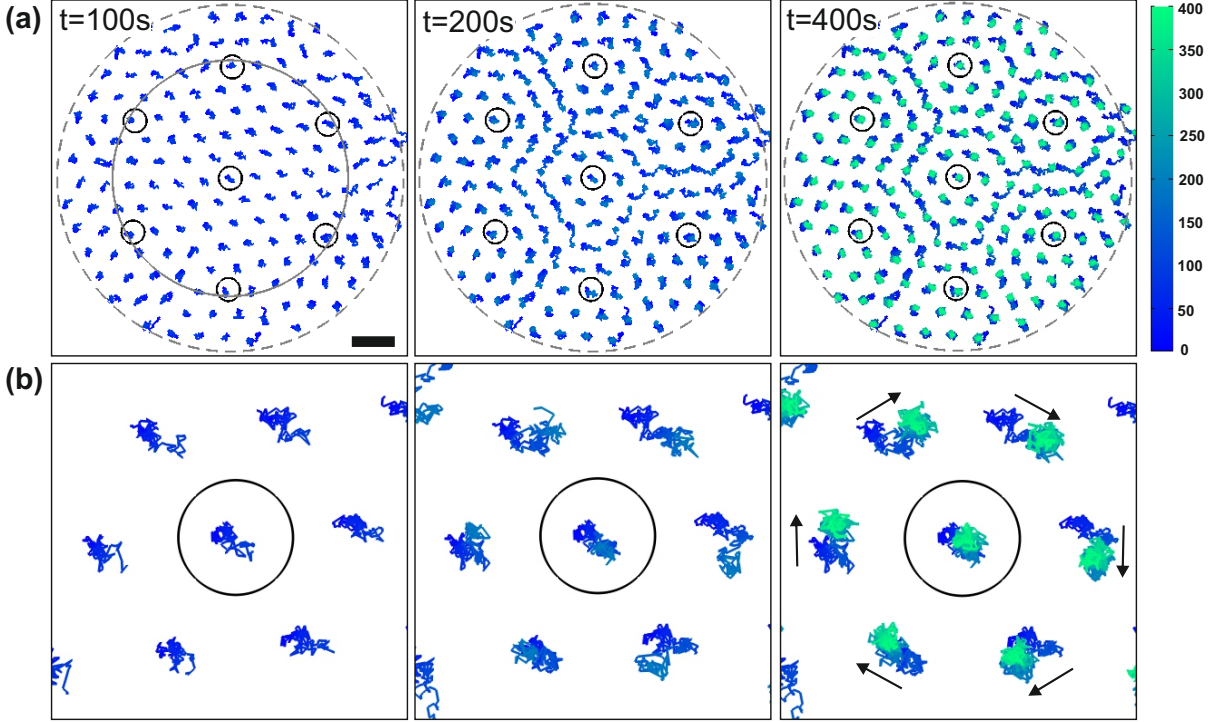


Figure 7.3: (a) Trajectories in the case of a $\Sigma 19$ GB at different times together with the sites of the CSL (black circles) located within the initial circular grain. The colourbar indicates the elapsed time in seconds. The grey dashed line corresponds to the position of the GB at $t = 0$. The grey solid line is the current position of the GB, which has shrunk by $t = 200s$. Scale bar, $5 \mu m$. (b) Local view of the trajectories of the particles around a site of the CSL. While the particle located at the CSL site stays in there, the others rotate around it as illustrated by the arrows, thereby changing its local orientation without overall displacement.

7.3.2 Case of coincident site lattice boundaries

In order to elucidate the origin of the heterogeneities in the particle displacements, an equivalent study is performed for the special case of a coincident site lattice (CSL) boundary. In this case, a lattice of sites belonging to both grains is formed as explained in section 2.1.3 and illustrated in figure 2.4. Such CSL boundaries correspond to specific values of the misorientation and are characterised by a Σ -value, as shown in figure 2.4(c). Here, a circular grain with initial misorientation $\theta(0) = 13.4^\circ$ and radius $R_G(0) = 6.8\sigma$ is created, which is very close to the $\Sigma 19$ boundary at $\theta^{CSL} = 13.2^\circ$. Figure 7.3(a) shows the trajectories for different times together with the sites of the CSL within the region of the initial circular grain. Strikingly, the particles initially located at sites of the CSL remain there during the whole process of shrinkage. This is confirmed by zooming in on one of these particles, which indeed does not leave the CSL site despite being swept by the GB (see figure 7.3(b)). Importantly, the particles located next to

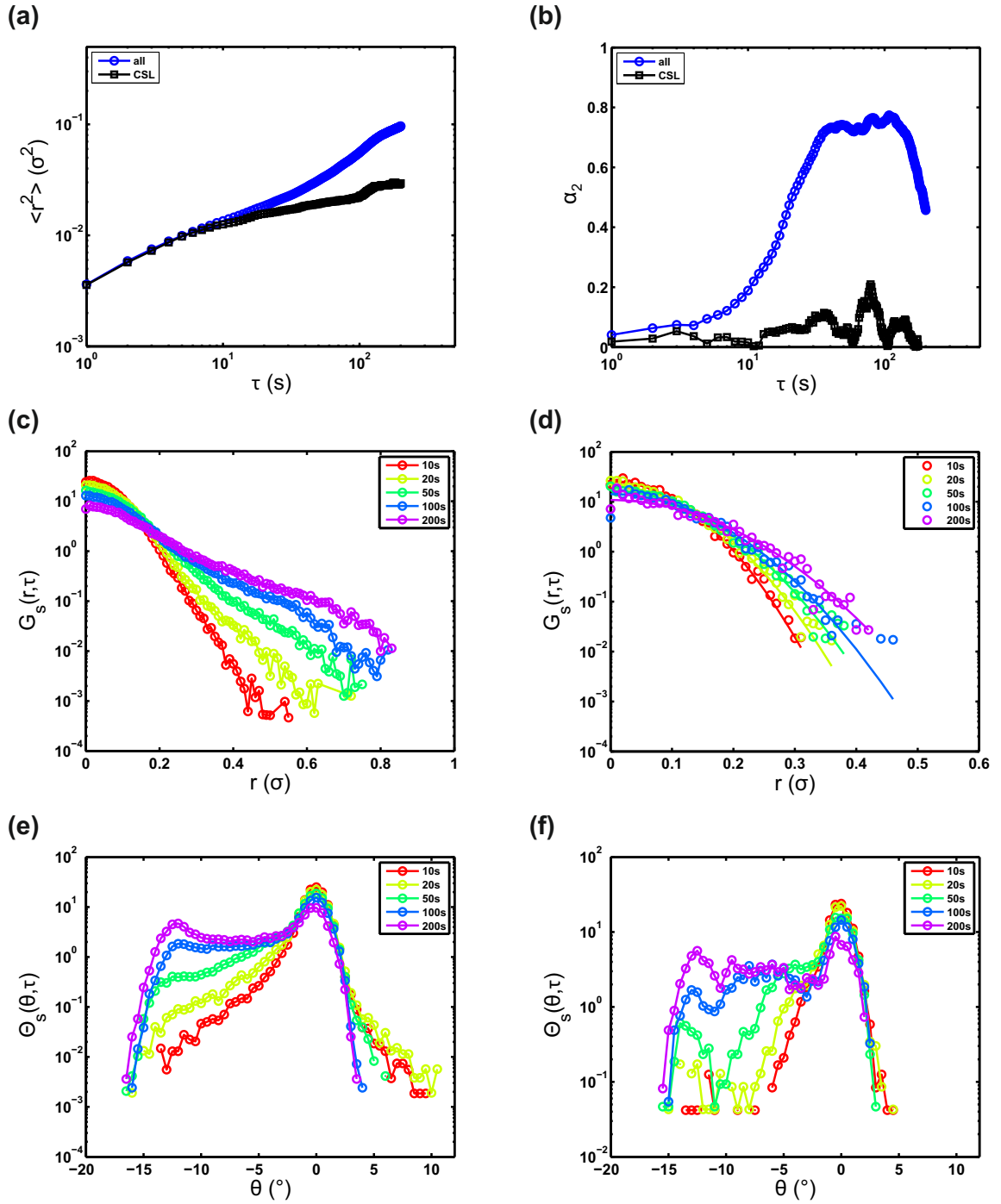


Figure 7.4: (a) Time-evolution of the mean square-displacement of all the particles swept by the GB (blue dots) and CSL particles (black squares). (b) Time-evolution of the non-Gaussian parameter for the same sets of particles. (c) Self part of the van Hove correlation function, $G_s(r, \tau)$, for all the particles swept by the GB, as a function of the distance r in units of the particle diameter, σ , for different time lags. (d) Same quantity for the CSL particles only. The lines correspond to the Gaussian approximation (equation (7.4)), with $\langle r^2 \rangle$ taken to be the MSD of CSL particles only. (e) Self orientational correlation function, $\Theta_s(\theta, \tau)$, for all the particles swept by the GB, as a function of the orientation change, θ , for different time lags. (f) Same quantity for the CSL particles.

the CSL site all rotate around it, thereby changing the local crystal orientation of the particle at the CSL site, which thus changes grain *without moving* (see figure 7.3(b)).

This unique dynamics distinguishes CSL particles from the others, whose trajectories are similar to the ones observed in figure 7.1(a). This is highlighted by the fact that the MSD of the CSL particles is significantly lower than that of all the particles swept by the GB (see figure 7.4(a)). Also, the α_2 of the CSL particles remains very close to zero and does not exhibit a clear peak (see figure 7.4(b)). In fact, the dynamics of the CSL particles are very similar to those of the crystal particles in figure 7.2(a) and (b). This is further confirmed by the Gaussian nature of G_s in figure 7.4(d), as opposed to the tail visible in the G_s of all the particles swept by the GB in figure 7.4(c). Indeed, applying the Gaussian approximation (equation (7.4)), with $\langle r^2 \rangle$ taken to be the MSD of the CSL particles only, shows excellent agreement with the G_s data for the CSL particles (see figure 7.4(d)). The plots of Θ_s for all the particles and the CSL particles only are shown in figure 7.4(e) and (f), respectively. Remarkably, there is no difference in the reorientation dynamics of the CSL particles and that of all the particles swept by the GB, implying that the difference between the two only lies in the particle displacements.

These results show that there is a clear link between the structure and the dynamical heterogeneities in the case of a CSL boundary. Indeed, the particles located at CSL sites remain at their sites during GB migration while the other particles exhibit very heterogeneous dynamics. Even though CSL boundaries are specific GBs, they give a possible explanation for the origin of dynamical heterogeneities in the case of a general GB, as the latter can always be locally approximated by the nearest CSL. In other words, the particles located near the sites of this approximate CSL will only exhibit very small displacements in contrast to the particles further away from them, which leads to dynamical heterogeneities during GB migration.

7.3.3 Link between particle, dislocation and grain boundary dynamics

The migration of GBs can also be considered from a topological point of view by examining the changes in the configuration of dislocations. To establish the link between the dislocation motion, the particle dynamics and the migration of the GB, a stack of the positions of the 5- and 7-fold disclinations constituting the dislocations (see section 2.1.2) is shown in figure 7.5(a), for the period of time corresponding to complete shrinkage. Note that this is shown for the same

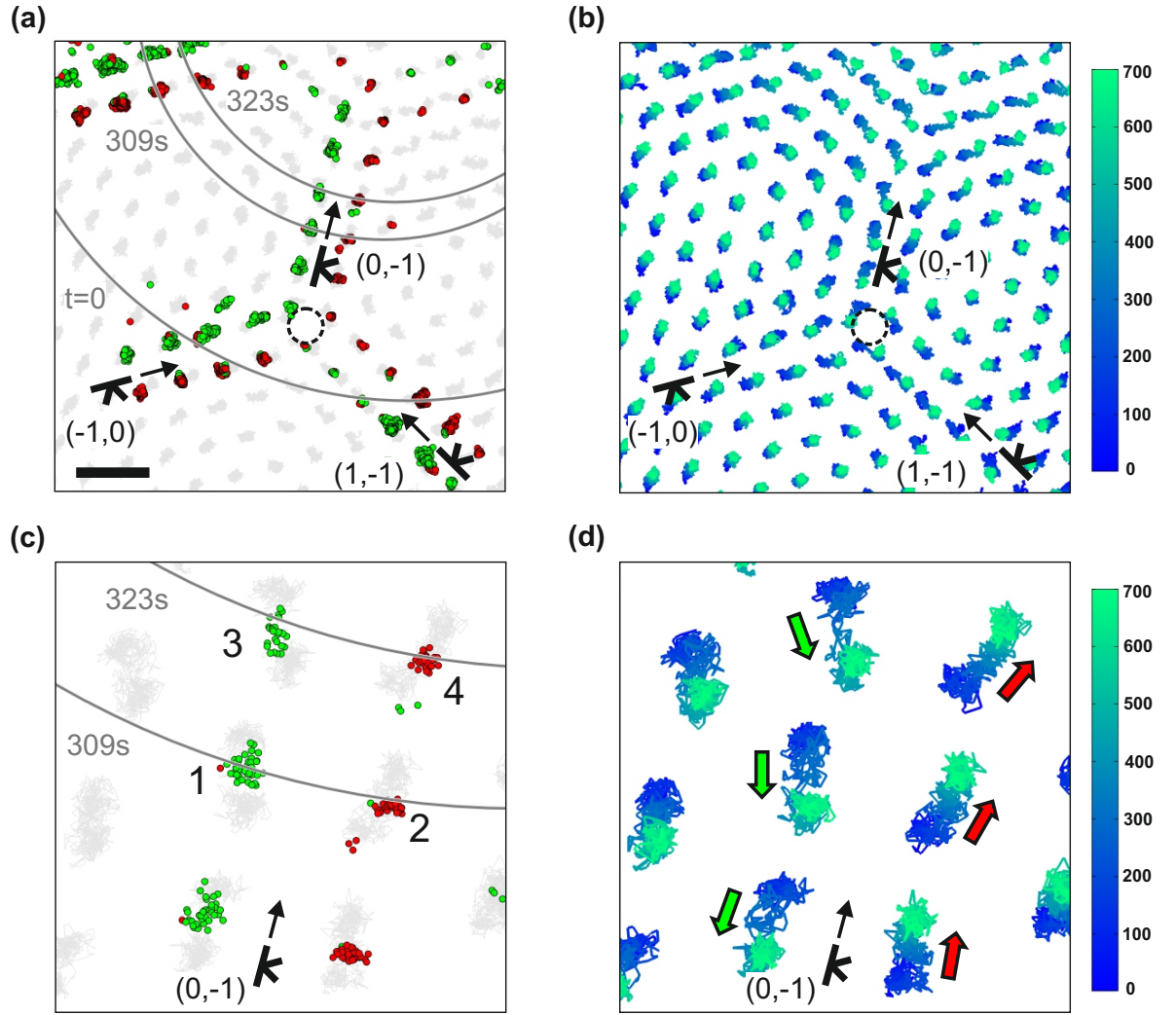


Figure 7.5: (a) Stack of the positions of the 5- and 7-fold disclinations (red and green dots) showing the traces of the dislocations during shrinkage, together with the trajectories of the particles (light grey). The black arrows correspond to the direction of motion of the three dislocations and the dashed circle corresponds to the location of a dislocation recombination. The position of the GB is represented at three different times (grey curves). Scale bar, 5 μm . (b) Corresponding trajectories of the particles coloured according to the elapsed time as indicated by the colourbar. (c) Local view of the glide of the $(0,-1)$ dislocation in (a). (d) Corresponding trajectories with the red and green arrows indicating the displacements of particles located at the 5- and 7-fold disclinations forming the dislocation.

grain as in figure 7.1(a). To visualise the migration of the GB, its position is illustrated at three different times in figure 7.5(a) as well. The particle trajectories during the same period of time are shown in figure 7.5(b). Clearly, the path taken by the dislocations in figure 7.5(a) corresponds to those particles exhibiting the largest displacements in figure 7.5(b). Importantly, this implies that dynamical heterogeneities originate from the motion of dislocations. Interestingly, two dislocations with Burgers vectors $(-1,0)$ and $(1,-1)$ are observed to glide and recombine into a

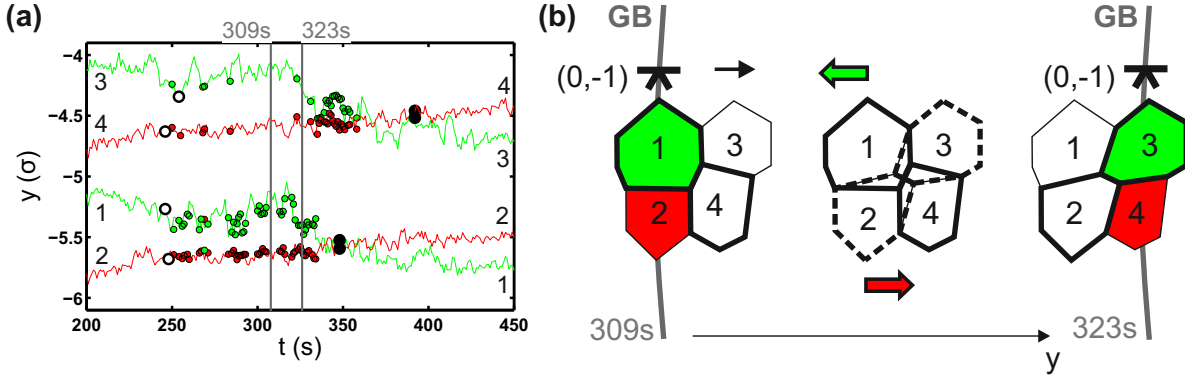


Figure 7.6: (a) Evolution of the y coordinates of four particles, labelled 1-4, involved in the dislocation glide in figure 7.5(c) and (d). Entry in (exit of) the GB is symbolised by a white (black) dot. Red (green) dots correspond to when the particle has coordination 5 (7). The grey lines mark the two times reported in figure 7.5(c). (b) Illustration of the changes in the Voronoi tessellation during the glide of a dislocation involving the four particles. The position of the GB is illustrated by the gray lines.

third one, with Burgers vector $(0, -1)$, at a vertex indicated by the dashed circle in figure 7.5(a) and (b). As can be seen from figure 7.5(a), these glide and recombination events enable the GB to migrate between $t = 0s$ and $t = 309s$. As the Burgers vector of the $(0, -1)$ dislocation is perpendicular to the GB, the further migration of the GB between $t = 309s$ and $t = 323s$ is directly driven by the glide of this dislocation. Indeed, the GB moves significantly during this process, as illustrated in figure 7.5(c). Strikingly, figure 7.5(d) reveals that the glide of the dislocation is achieved by the particles corresponding to the 5-fold disclination moving in the direction *of* the glide, and the particles corresponding to the 7-fold disclination moving in the direction *opposite* the glide (see figure 7.5(c) and (d)).

To understand how such particle displacements lead to dislocation glide and eventually to GB migration, the y -coordinate² of the 4 particles involved in the glide during the time interval $[309s; 323s]$ is plotted as a function of time in figure 7.6(a). On this graph, the time of entry of a particle in the GB is marked by a white dot, and the time of exit from the GB is marked by a black dot. In addition, the red dots indicate when the particle has coordination 5 and the green dots indicate when the particle has coordination 7. The dislocation initially consists of particles 1 and 2, with particles 1 and 4 being nearest neighbours (see figure 7.6(b)). When the 7-fold particle, 1, moves in the *negative* y -direction, the 5-fold particle, 2, moves in the *positive* y -direction (figure 7.6(a) and (b)). As a consequence, the particle 3 and 2, become closer and

²The y -coordinate is chosen here as it happens to roughly correspond to the direction of the glide.

end up being nearest neighbours (figure 7.6(a) and (b)). This topological change³ leads to the motion of the dislocation in the *positive y*-direction, which now consists of particles 3 and 4 (see figure 7.6(b)). Noticeably, this process enables the GB to move with the dislocation since the pair 1-2 exits the GB before the pair 3-4 does, as shown in figure 7.6(a) and (b).

The above shows how small changes in the topology of the lattice lead to the motion of dislocations in a given direction, and eventually to the migration of the GB. Further migration can require dislocation reactions, though the migration mechanism in between such events is expected to be the same. While these observations are facilitated by the fact that the present GB has a low dislocation density, these principles should remain valid for large angle grain boundaries even if their dislocation density is much higher.

7.4 Conclusions

It has been shown that the dynamics of single particles during the migration of circular GBs is marked by dynamic heterogeneities which correspond to particles hopping from crystal sites of the former grain to those of the new grain. In the particular case of a CSL boundary, the particles initially present at sites of the CSL do not leave these sites during the migration of the GB and even exhibit crystal-like dynamics. The local reorientation of the CSL particles without motion is simply achieved by the rotation of the nearest neighbours around the CSL site. Finally, an explicit link has been made between the dynamics of the particles and the motion of dislocations by revealing the particles' displacements during the glide of dislocations, which underlies GB migration.

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³This can be seen as a rotation by 90° of the bond linking particles 1 and 4, called a Stone-Wales transformation, usually mentioned as causing the appearance of dislocation pairs in pure crystals [41].

Conclusions

In this thesis, the dynamics of grain boundaries in two-dimensional (2D) colloidal crystals is studied. Grain boundaries as geometrical objects are well understood within the framework of crystallography [18] but their behaviour as dynamic entities remains unclear. Indeed, grain boundaries can migrate when subjected to a force, be it an external stress or their own curvature [12]. The phenomenon of grain boundary migration implies changes at the atomic level, which are cumbersome to observe experimentally [20, 21]. Here, this difficulty is overcome by studying the dynamics of grain boundaries in colloidal crystals, which are good model systems for real materials [38, 39]. The slow Brownian dynamics and the relatively large size of colloidal particles facilitate the direct monitoring of grain boundary dynamics using simple optical video-microscopy [47]. Moreover, the inherent softness of colloidal crystals enables the direct manipulation of grain boundaries using optical tweezing [46].

The choice of a colloidal model system is always a compromise between experimental constraints, simplicity of use and cost. In the present work, the colloidal system consists of $2.7\mu\text{m}$ diameter melamine formaldehyde spheres in an aqueous solvent, as introduced in chapter 2. Due to their relatively large size and mass density, these particles form a monolayer by sedimentation, which can be easily observed using optical microscopy. In addition, this system is equivalent to a 2D fluid of hard spheres [76], which is the simplest possible interaction and has been previously used in the group to study grain boundaries [38, 145]. Moreover, the hexagonal close-packed crystal structure formed by hard spheres provides a simple lattice, which greatly simplifies the geometry of the observed grain boundaries. Despite the fact that such a model system could be considered as a “toy model” compared to the complexity and variety of grain boundaries found in real materials, it does provide valuable general insights on the dynamics of grain boundaries. Finally, the high refractive index mismatch between the particles and the solvent makes them

particularly suitable for optical trapping experiments, as high forces are required to deform a 2D crystal of colloidal hard spheres.

In chapter 3, the dynamics of grain boundaries in a colloidal polycrystalline monolayer is studied. The grain boundaries form a network, which spontaneously coarsens to reduce the overall length of the grain boundaries, leading to grain growth [12]. The precise coarsening mechanism and its scaling features were elucidated using a combination of video-microscopy, image analysis and theory. In particular, this was done by both analysing the bond-orientational order and measuring the relative length of grain boundaries of a given misorientation. This was challenging because of the difficulty in defining the grains and getting a robust measurement of the misorientation angle due to noise in the data. In addition, the detection of small angle grain boundaries is cumbersome as they can have an arbitrarily low misorientation, while, in practice, the algorithm requires a low angle cut-off. Overall, the algorithm convincingly showed the preferential annihilation of large angle grain boundaries via curvature-driven coarsening with a time dependent rate. Using simple scaling arguments, it was shown how this behaviour leads to the observable time dependence of the bond-orientational correlation length. The behaviour of small angle grain boundaries depends strongly on their misorientation as their relative amount can increase or decrease. This behaviour could in principle be clarified by studying the coarsening at later times, though experimentally these time scales are not reachable as the correlation length becomes comparable to the size of the field of view.

To stop grain growth in the polycrystalline monolayer, impurities in the form of larger colloidal particles were added and their partitioning to the grain boundaries was studied in chapter 4. The quantitative study of the adsorption behaviour required developing a robust algorithm to discriminate between the impurities within the grains and those in the grain boundaries. This was complicated by the fact that the structure close to the impurities is disordered irrespective of whether they are in the grains or in the grain boundaries. Another challenge that had to be overcome was the difficulty in defining the relevant number concentrations as used in common adsorption models. For this reason, the adsorption was studied in terms of composition variables. The adsorption behaviour was confirmed to be consistent with the equilibrium adsorption isotherm given by Langmuir-McLean theory [123,124] and the free energy of adsorption was measured to be a few times $k_B T$, consistent with reversible adsorption. Depending on their size ratio with the host particles, impurities can act as substitutional or interstitial impurities,

analogous to the case of real alloys [43]. When adsorbed at grain boundaries, impurities can form clusters whose size distribution is strongly affected by geometrical constraints imposed by the size ratio and the crystal lattice.

Chapter 5 presents a method to determine the geometrical features of grain boundaries directly from microscopy images. Defining quantities such as the tangent and normal directions or the curvature is difficult in the case of grain boundaries inherent to their noisy nature. This problem was overcome by adapting techniques from geometrical analysis of noisy clouds of points, commonly used in surface reconstruction problems [160–162, 165]. The initial goal was to relate the local curvature to the velocity of a grain boundary. However, measuring the velocity turned out to be very challenging as the length of a grain boundary varies while it is moving. The presence of noise further complicates measuring the overall displacement from instantaneous microscopy snapshots. However, this method was found to be particularly fruitful to directly measure the local inclination of a grain boundary, a degree of freedom that is rarely directly measured.

The structural complexity of networks of grain boundaries makes it difficult to study the kinetics, dislocation reactions and single particle dynamics during grain boundary migration. Experiments involving a single grain boundary with a controlled misorientation and curvature proved to be a much better approach. This was achieved by creating a circular grain boundary using optical vortices [84]. Once the laser beam is turned off, these grain boundaries spontaneously shrink due to capillary forces. The design of this experiment required several months of developing the correct experimental geometry, which included redesigning the microscope stage and the optical pathway for the delivery of the laser beam into the sample. In addition, it was cumbersome to establish the correct experimental protocol for first making a defect-free 2D crystal and then creating a well-defined circular grain boundary in it. Once the experiment was fully established, the creation of circular grains was very robust, reproducible and could be performed on demand.

In chapter 6, a detailed study of the shrinking kinetics is performed together with a study of the dislocation reactions that enable complete shrinkage. A key non-trivial step in quantifying these kinetics was to measure the rate of shrinking, termed the reduced mobility, and directly link it to the product of the initial misorientation and radius of the grain, consistent with previous theoretical work [97]. However, this theory does not predict the existence of the geometrically

determined shrinking to sliding transition that was observed in this work, so further theoretical work is required in the future. The elementary dislocation reactions that lead to full shrinkage of the grain were directly visualised, which provided key insights into the microscopic details of grain boundary dynamics.

In chapter 7, the dynamics of single particles swept by the grain boundary during its migration were found to be very heterogeneous due to some particles hopping out of their crystal site and others hardly moving at all. In the case of coincident site boundaries [18], the particles occupying the coincident sites remain there despite being swept by the migrating grain boundary, directly linking the structure to the observed particle dynamics. The origin of the largest displacements was found to be due to the motion and reaction of dislocations by direct visualisation. Finally, establishing the link between particle, dislocation and grain boundary motion required the simultaneous, and therefore challenging, consideration of the particle trajectories, the time dependence of the coordination number and the period that the particles were resident in the grain boundary.

Based on the experiments and results presented in this thesis, several suggestions for future investigations can be made. In particular, the use of optical trapping as a way to design experiments with controlled grain boundary geometries on demand is unique and hugely promising. Examples of future experiments include the preparation of bi-crystals, tri-crystals, triple junctions and the manipulation of impurities at grain boundaries. This would for instance enable systematic studies on the dynamics of triple junctions [191] and the direct deformation of grain boundaries using the Zener pinning effect [13]. In addition, the design of colloidal mixtures in which the impurity-particle interactions differ from the particle-particle ones, could be a promising route to systematically study impurity segregation and its impact on the (micro)mechanical properties of alloys. Finally, extending the experiments described here to three-dimensional colloidal systems would be very worthwhile. Such a route is still seriously challenging as this requires the design of new colloidal model systems together with a combination of optical tweezing and confocal microscopy [192]. It would be very valuable to test to what extent the physics described in this thesis holds in three-dimensional colloidal polycrystalline materials, which would be a step closer to many real materials.

Appendix

A Geometrical features of grain boundaries in 3D using point cloud analysis

The method to find the local normal and tangent directions and both methods to determine the local curvature of one-dimensional grain boundaries in 2D materials, described in chapter 5, can be straightforwardly extended to surfaces of any dimensions. In this appendix, the case of two-dimensional surfaces in 3D space is detailed.

We consider a cloud of points which samples a surface S embedded in 3D space. The coordinates of the points belonging to the neighbourhood Ω_P of a point P of the cloud are contained in the vectors $\mathbf{x} = (x_1, \dots, x_n)$, $\mathbf{y} = (y_1, \dots, y_n)$ and $\mathbf{z} = (z_1, \dots, z_n)$. The covariance matrix then reads [160–162]:

$$C_P = \begin{bmatrix} \text{Cov}(\mathbf{x}, \mathbf{x}) & \text{Cov}(\mathbf{x}, \mathbf{y}) & \text{Cov}(\mathbf{x}, \mathbf{z}) \\ \text{Cov}(\mathbf{y}, \mathbf{x}) & \text{Cov}(\mathbf{y}, \mathbf{y}) & \text{Cov}(\mathbf{y}, \mathbf{z}) \\ \text{Cov}(\mathbf{z}, \mathbf{x}) & \text{Cov}(\mathbf{z}, \mathbf{y}) & \text{Cov}(\mathbf{z}, \mathbf{z}) \end{bmatrix}. \quad (\text{A.1})$$

As for the 2D case, the normalised eigenvector associated to the lowest eigenvalue of C_P is the normal vector $\vec{n}_P$ at P . The two other normalised eigenvectors form an orthonormal basis of the tangent plane [160–162] and are denoted $\vec{u}_P$ and $\vec{v}_P$ in the following. A consistent orientation of the normal vectors can be obtained using the same method as in the 2D case. The directions of $\vec{u}_P$ and $\vec{v}_P$ are fixed such that the condition $(\vec{u}_P \times \vec{v}_P) \cdot \vec{n}_P > 0$ is satisfied.

The OP method generalises as follows: in the local tangent frame $(\vec{u}_P, \vec{v}_P, \vec{n}_P)$ where the coordinates of P are $(u, v, n) = (0, 0, 0)$, the surface S is locally described by the equation

$n = f(u, v)$ where f is a function such that $f(0, 0) = \partial_u f(0, 0) = \partial_v f(0, 0) = 0$. Its expression to the lowest order is then given by [164]

$$f(u, v) = \frac{1}{2}(u, v)^T H_P (u, v), \quad (\text{A.2})$$

where H_P is the Hessian matrix of f at P defined by

$$H_P = \begin{bmatrix} \partial_{uu}f & \partial_v \partial_u f \\ \partial_u \partial_v f & \partial_{vv}f \end{bmatrix}. \quad (\text{A.3})$$

Fitting a form $n = 1/2(au^2 + bv^2 + 2cuv)$ to the data points $(\mathbf{u}, \mathbf{v}, \mathbf{n})$ enables us to estimate the Hessian matrix of f as

$$H_P \simeq \begin{bmatrix} a & c \\ c & b \end{bmatrix}, \quad (\text{A.4})$$

whose eigenvalues are estimates of κ_1 and κ_2 [164].

In the case of the NV method, the map ϕ which tracks the variations of the normal $\vec{n}(u, v)$ along the tangent plane at P , generalises as follows:

$$\phi : \begin{bmatrix} u \\ v \end{bmatrix} \mapsto \begin{bmatrix} \phi_u(u, v) \\ \phi_v(u, v) \end{bmatrix} = \begin{bmatrix} \vec{n}(u, v) \cdot \vec{u}_P \\ \vec{n}(u, v) \cdot \vec{v}_P \end{bmatrix}. \quad (\text{A.5})$$

The expression of ϕ to the lowest order is given by

$$\phi(u, v) = J_P \begin{bmatrix} u \\ v \end{bmatrix}, \quad (\text{A.6})$$

where J_P is the Jacobian matrix of ϕ :

$$J_P = \begin{bmatrix} \partial_u \phi_u & \partial_v \phi_u \\ \partial_u \phi_v & \partial_v \phi_v \end{bmatrix}. \quad (\text{A.7})$$

This quantity is equivalent to the curvature tensor at P [165]. Fits of $\phi_u = \alpha u + \beta v$ and $\phi_v = \gamma u + \delta v$ to the data points $(\mathbf{u}, \mathbf{v}, \phi_u)$ and $(\mathbf{u}, \mathbf{v}, \phi_v)$ yield an estimate of the curvature

tensor as

$$J_P \simeq \begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix}, \quad (\text{A.8})$$

whose eigenvalues are estimates of $-\kappa_1$ and $-\kappa_2$ [165].

B Inclination and dislocation distribution for a circular grain boundary

As a curved grain boundary (GB) does not have a constant inclination, the distribution of dislocations is strongly related to the shape of the GB. In this appendix, the local inclination and the distribution of dislocations are determined for a circular GB, as studied in chapter 6 and chapter 7. From the geometrical parametrisation of a circular GB in figure B.1(a), it can be inferred that the local inclination of the GB, ψ , is given by

$$\psi = \beta - \frac{\theta}{2} - \alpha, \quad (\text{B.1})$$

where β is the orientation of the tangent direction, α the orientation of the outer grain and θ is the misorientation of the GB. As seen in section 2.1.3, the two types of symmetrical tilt GBs correspond to $\psi \equiv 0$ and $\psi \equiv \pi/6 \pmod{\pi/3}$, due to the 6-fold symmetry. To identify the portions of the circular GB that correspond to either of the two types of symmetrical tilt GB, a “reduced” inclination is defined as

$$\bar{\psi} = \min(\psi \pmod{\pi/3}, \pi/3 - (\psi \pmod{\pi/3})), \quad (\text{B.2})$$

which varies between 0 and $\pi/6$. Importantly, $\bar{\psi}$ equals 0 or $\pi/6$ for symmetrical tilt GBs. In the case of a perfectly circular GB, this quantity can be determined analytically since the orientation of the tangent direction is given by $\beta = \phi + \pi/2$, where ϕ is the polar angle (see figure B.1(a)). The values of ϕ corresponding to symmetrical tilt GB portions can then be found by solving $\bar{\psi}(\phi) = 0$ and $\bar{\psi}(\phi) = \pi/6$. As illustrated in figure B.1(b), this gives six locations where the GB is equivalent to a symmetrical tilt with $\bar{\psi} = 0$ (black triangles) and six others with $\bar{\psi} = \pi/6$ (black squares). The key consequence of this result is that the *minimum* number of

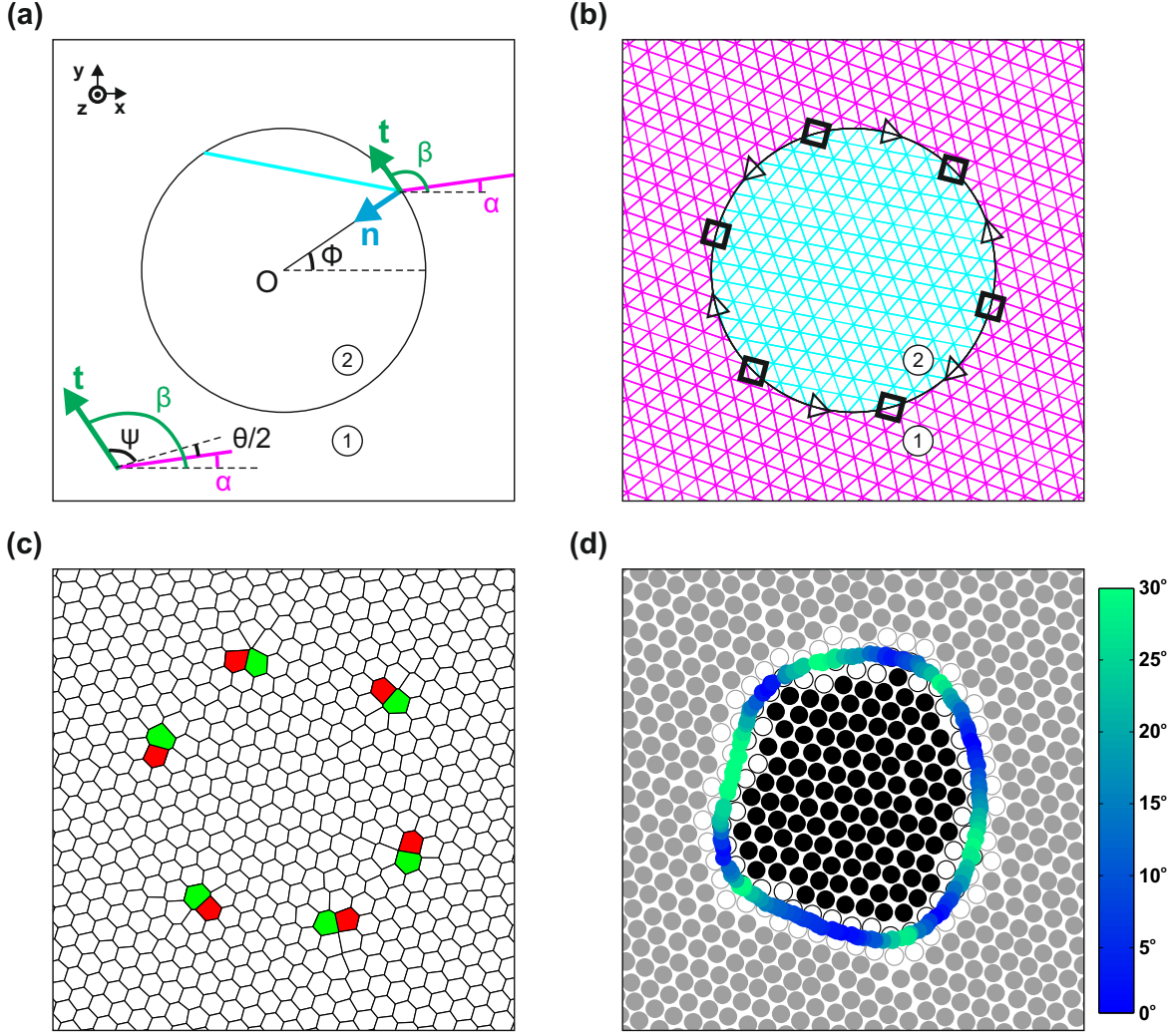


Figure B.1: (a) Parametrisation of a circular GB between the outer grain ① and the inner grain ②. The orientation of ① (②) corresponds to the magenta (cyan) line. The orientation of ① is denoted α and the orientation mismatch between the two crystals is θ . The position on the GB is given by the polar angle ϕ , and the tangent (normal) direction is denoted $\hat{t}$ ($\hat{n}$). The inclination of the GB, ψ , is defined as sketched at the bottom left corner, following section 2.1.3 and figure 2.3. (b) Artificial circular GB with the analytical positions of the symmetric tilt GB portions with reduced inclination $\bar{\psi} = 0$ ($\bar{\psi} = \pi/6$) represented by black triangles (squares). (c) Dislocation configuration consisting of 6 dislocations whose locations coincide with symmetrical tilt GB portions with $\bar{\psi} = \pi/6$, see (b). (d) GB coloured according to the local reduced inclination, $\bar{\psi}$, as indicated on the colourbar, in degrees.

dislocations that a *circular* GB can contain is 6. Indeed, the only symmetrical tilt portions that can be populated by only one type of dislocation each are the ones with $\bar{\psi} = \pi/6$, or equivalently $\psi = \pi/6 + k\pi/3$ with $k = 0, \dots, 5$ (see section 2.1.4 and figure 2.5), which gives 6 dislocations on the whole GB, assuming that there is one dislocation per portion. Note that the other type of symmetrical tilt ($\bar{\psi} = 0$) would contribute with *at least* two dislocations per portion (see

section 2.1.4 and figure 2.5) which would lead to an overall number of dislocations higher than 6 for the whole GB.

This 6-dislocation configuration is indeed commonly observed for circular GBs with low initial misorientations in chapter 6 and chapter 7. An example corresponding to $R_G(0) = 8.9\sigma$ and $\theta(0) = 9.6^\circ$ is given in figure B.1(c), where the location of the six dislocations are in perfect agreement with the predicted symmetrical tilt portions with $\bar{\psi} = \pi/6$ (see figure B.1(b)). One can actually directly measure the reduced inclination of the GB, using equation (B.2) and measuring the direction of the tangent, β , with the method detailed in section 5.2.1. The output is plotted in figure B.1(d), where the GB is coloured according to the value of the local reduced inclination, $\bar{\psi}$. The GB portions where $\bar{\psi} = \pi/6$ correspond very well to the locations of the 6 dislocations and to the predictions in figure B.1(b).

In summary, the fact that the reduced inclination $\bar{\psi}$ equals $\pi/6$ six times around a circular GB implies that the minimum number of dislocations in the GB is six, each of them populating a portion of symmetrical tilt GB, where $\bar{\psi} = \pi/6$. For low misorientations, this configuration exists and plays a role in the onset of the sliding to shrinking transition as described in section 6.4.2. If the misorientation is higher or the grain diameter is larger, more dislocations than 6 are required to maintain the dislocation density imposed by the misorientation (see equation (2.8)) and facets with consecutive dislocations having equal Burgers vectors will be formed. Note that even in the case where the GB may not remain circular in shape, the method for the computation of $\bar{\psi}$ using principal component analysis can still be performed to probe the link between shape and dislocation configuration.

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List of publications

To date the following publications based upon work in this thesis have been submitted or are in preparation:

François A. Lavergne, Dirk G. A. L. Aarts and Roel P. A. Dullens, *Abnormal grain growth in colloidal polycrystalline monolayers*, In preparation, (Chapter 3)

François A. Lavergne, Samuel Diana, Dirk G. A. L. Aarts and Roel P. A. Dullens, *Equilibrium grain boundary segregation of impurities in colloidal polycrystalline monolayers*, In preparation, (Chapter 4)

François A. Lavergne, Dirk G. A. L. Aarts and Roel P. A. Dullens, *Determining local geometrical features of grain boundaries from microscopy*, J. Phys. Condens. Matter **27**, 194117 (2015) (Chapter 5)

François A. Lavergne, Arran Curran, Dirk G. A. L. Aarts and Roel P. A. Dullens, *Shrinking kinetics and dislocation reactions in circular grain boundaries*, In preparation, (Chapter 6)

François A. Lavergne, Arran Curran, Dirk G. A. L. Aarts and Roel P. A. Dullens, *Particle dynamics during the migration of circular grain boundaries*, In preparation, (Chapter 7)

Other publications:

Aletta A. Verhoeff, François A. Lavergne, Denis Bartolo, Dirk G. A. L. Aarts and Roel P. A. Dullens, *Optical trapping of interfaces at ultra-low interfacial tension*, Soft Matter **11**, 3100-3104 (2015)

Colin P. Reynolds, Kira E. Klop, François A. Lavergne, Sarah M. Morrow, Dirk G. A. L. Aarts and Roel P. A. Dullens, *Deterministic aggregation kinetics of superparamagnetic colloidal particles*, J. Chem. Phys. **143**, 214903 (2015)

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