



Driven colloidal particles in optical potential energy landscapes

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Abstract

The dynamic behaviour of colloidal particles driven across one-dimensional optical potential energy landscapes is studied. Colloids are driven with a piezo-stage, manipulated with optical tweezers and magnetic fields and imaged using optical microscopy. First, the meta-stable horizontal and vertical states of a colloidal rod in a single optical trap close to a flat wall are explored. A colloidal rod is then driven through a periodic optical potential energy landscape. The equilibrium position of a rod driven below the critical velocity is found to vary substantially from that of a sphere due to the friction coefficient of a rod being highly dependent on its proximity to an optical trap. At higher velocities, a colloidal rod is shown to act similarly to a colloidal sphere, exhibiting dynamic mode locking. Colloidal spheres are then driven across a time-dependent one-dimensional optical potential energy landscape with different modes of dynamic mode locking being observed. The mode locked step width is shown to vary with the oscillation frequency and the coupling strength between the particle and the optical landscape. The particle transport across the time-dependent landscape is also studied by measuring the effective diffusion coefficient which is highly sensitive to the driving velocity and mode locking. Next, chains of interacting colloidal particles are driven through a time-independent optical potential energy landscape. A mismatch between the length scales of the chain and the landscape gives rise to a freely sliding chain in an Aubry-type transition. In this regime a chain exhibits zero static friction despite being subject to a potential energy landscape. Chain motion is inspected for a driven flexible chain that is seen to exhibit breathing modes. Introducing oscillations in the driving force leads to dynamic depinning, which is affected by both the frequency and amplitude of the oscillations. Finally, the stochastic thermodynamics for particles driven across an optical landscape is considered. The work done by a particle in both a time-independent and a time-dependent optical landscape is measured. The optical work in a time-independent landscape is shown to be zero. However, the time-dependent counterpart exhibits a finite amount of work due to the optical landscape. The magnitude of the observed total work is considered in light of the mechanism of particle motion along with analysis of the contributing optical work and driving work.

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

Introduction

Out-of-equilibrium systems are inherent to the natural world, ranging from complex weather systems, which constantly evolve and develop with time, to turbulent flow in a bath tub [1]. Systems can be forced out of equilibrium by an external driving force. This is particularly pertinent in systems with a high level of complexity and with many interactions such as active suspensions [2]. A further understanding of out-of-equilibrium systems is paramount as they can often exist in a state where a small fluctuation can have catastrophic implications, as is seen for avalanches and mudslides [1].

One particular example of out-of-equilibrium systems is that of a moving body close to a surface. In this case, the presence of a surface gives rise to friction and this is exhibited for moving vehicles [3], as well as in solvent flow through nanotubes [4]. Surfaces can vary in roughness, which provides a source of interesting dynamics as it is the cause of friction on both the macroscopic and microscopic scales. Natural examples of both include undulating sand dunes [1] and atomically rough surfaces [5]. Rough surfaces can be random or structured, and their structure vastly affects the resulting friction [6]. Possibly the simplest structured surface is the so-called ‘washboard potential’, which corresponds to a one-dimensional sinusoidal surface [7, 8].

Seemingly simple systems can be driven across rough surfaces to create deceptively complex systems. The driven version of the ‘washboard potential’ is called the ‘tilted washboard potential’ and is a widely studied system [6, 9–13] due to its rich dynamics and applications to condensed matter systems, such as Josephson junctions in superconductors [14]. Many more rough surfaces

have been explored, such as quasi-crystalline surfaces [15, 16] and random surfaces [16–18]. A powerful method of studying the tribology of particles interacting with rough surfaces is with the use of colloidal particles to create observable and easily manipulated systems.

1.1 Colloids

Colloidal systems consist of finite sized particles dispersed in a ‘continuous’ medium, with common examples in nature, including milk and blood as well as many cosmetic products. Colloidal systems are often realised in the form of solid particles dispersed in a liquid. In order to treat the liquid as continuous, the particle size must be on the order of tens of nanometres or greater [19]. A key feature of colloidal particles is that they exhibit Brownian motion due to the thermal motion of the solvent molecules [20]. For this to be observed, the particle size must be on the order of tens of micrometres or less. This sets the colloidal length scale between tens of nanometres to tens of micrometres [19].

The Brownian motion that colloidal particles exhibit is due to constant bombardment from solvent molecules [20]. This causes particles to carry out a ‘random walk’ as they diffuse and for colloidal particles, this motion happens on the timescale of seconds [21]. This random motion allows the particles to explore phase space, much like an atomic or molecular system, making them a powerful model system for atoms and molecules [22]. Indeed, colloidal systems exhibit similar phase behaviour to atomic and molecular systems with colloidal crystal, liquid and gas phases all exhibited [22] as well as more complex phases such as the nematic and smectic phases in colloidal liquid crystals [23]. In colloidal systems, the particle concentration, often characterised by the volume fraction, acts as an ‘inverse temperature’. As such, a colloidal crystal melts to form a colloidal fluid as the volume fraction is lowered [22, 24], corresponding to an increase in temperature in an atomic system.

Experimentally, colloidal particles are readily observable with optical microscopy [25, 26] due to their inherent length scales being in line with the diffraction limit of visible light, ~ 200 nm, and their timescales being on the order of seconds. Colloidal particles can also be designed and synthesised in many different shapes, ranging from rods [27] to polyhedra [28], and dimpled particles for self assembly [29]. Furthermore, particle interactions can be tuned by altering the surface chemistry [26, 30–32]. Additionally, external fields can be used to manip-

ulate colloidal systems and common techniques include the use of magnetic fields [33], electric fields [34,35], gravitational fields [19,31], and light fields [36–38].

1.2 Optical potential energy landscapes

Ashkin first observed light exerting a force on particles in 1970 [39] and this has since been developed into the versatile technique of optical trapping. An optical trap is a tightly focussed laser beam which attracts micrometre sized objects of high refractive index in a background of low refractive index. Due to the similarity in the length scales of colloidal particles and the wavelength of visible light, optical trapping is a particularly powerful technique in the area of colloidal research [40]. It has many applications, from determining the structure and friction of proteins [41–43], to forming micro-machines [38,44–46] and addressing fundamental condensed matter problems such as dynamic mode locking [12,47,48]. Single optical traps have also been used to measure the strength of DNA [40], to measure extremely small forces on particles in a fluid [49], and to probe the impact of impurities in colloidal crystals [50].

The field of optical trapping has now greatly developed beyond the use of single traps [41]. In particular, beam steering devices and diffracting optical elements can be utilised to create well defined so-called optical potential energy landscapes, which combine many optical traps to form a potential energy landscape [51–53]. Both random [16,17,54] and periodic [47,55,56] optical potential energy landscapes can be produced, leading to wildly different particle dynamics, from subdiffusion to superdiffusion [6,57]. There are many applications of this, including particle sorting [11] and particle transport [53]. Most recently, this has been used to form a rough substrate over which a two-dimensional colloidal crystal exhibits zero static friction [58]. The introduction of a time dependency in optical landscapes can give rise to further phenomena, including ratchet motion [52] and synchronisation [47,59,60].

1.2.1 Synchronisation

The phenomenon of synchronisation manifests itself in the synchronous flashing of fireflies [61], rhythmic crowd applause [62], and the circadian rhythms of animals [63]. It can even expose weaknesses in macroscopic objects such as the Millennium Bridge in London [64]. It was first observed by Huygens in 1665, who noted that two pendulum clocks, when coupled by a wooden

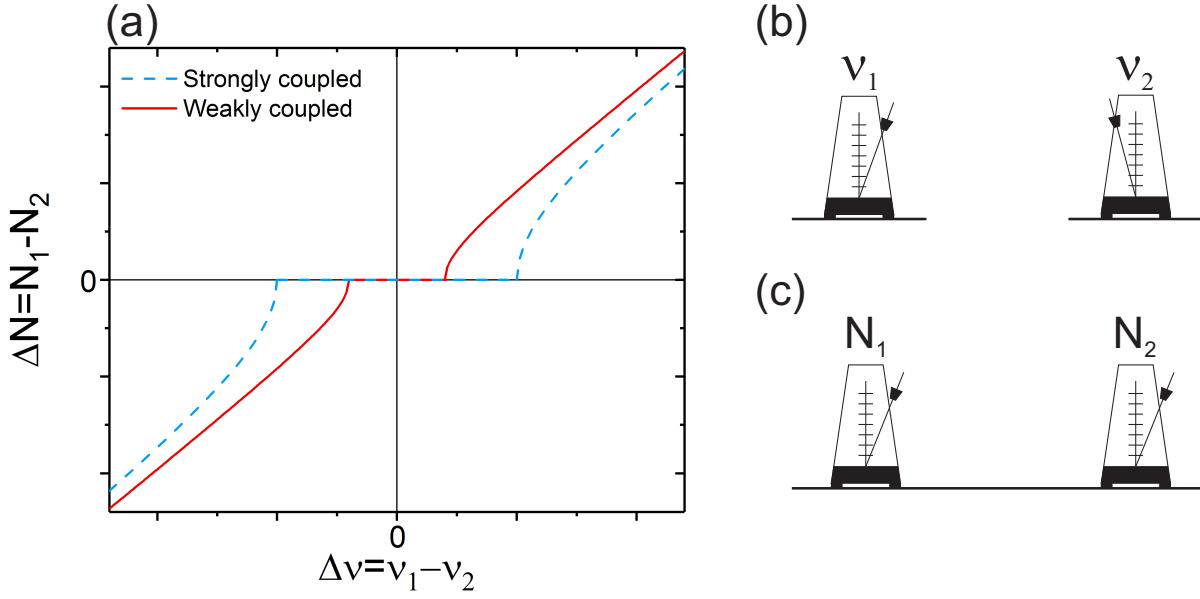


Figure 1.1: (a) A representative plot of how synchronisation affects coupled oscillators. (b) Oscillators are represented here as metronomes where ν_1 and ν_2 are the natural frequencies of the metronomes. (c) When oscillators are coupled, such as by being connected by a table that is able to move slightly, then they can have a different frequency, here shown as N_1 and N_2 .

beam, would synchronise and, even when subject to a perturbation, would reach synchronisation again [65]. This subtle observation has since been greatly studied and is the same phenomena that forms the mechanism behind cardiac pacemakers [66]. Synchronisation has been studied using colloidal systems with both time-dependent optical potential energy landscapes [55,60], and with time-dependent driving forces [47,59] where the static friction shows a strong dependence on the imposed frequency.

In a system with two coupled oscillators, synchronisation may be observed if the frequencies of both oscillators are closely matched. The frequency of these oscillators can be written as ν_1 and ν_2 and the extent to which the oscillators will synchronise is influenced by their coupling, such that synchronisation can be observed over a larger range of $\Delta \nu = \nu_1 - \nu_2$ for strongly coupled oscillators than for those that are weakly coupled [65,67]. This behaviour is shown in figure 1.1 where N_1 and N_2 denote the frequencies of the oscillators when they are coupled, and ΔN is shown to be zero in the case of $\nu_1 \approx \nu_2$. Further to this, more complex cases of synchronisation can be seen in the case of $\nu_1 = n\nu_2$, where n is an integer. This leads to multiple ‘steps’ like the one shown in figure 1.1, but is highly sensitive to the coupling strength and the value of n [47,55,60]. In this thesis, synchronisation is studied for a colloidal rod subject to a time-dependent driving force and for a colloidal sphere driven through a time-dependent optical landscape.

1.2.2 The Aubry transition: zero friction

Although it may seem counter-intuitive, Aubry showed that an inherently rough surface may give rise to a frictionless regime [68]. He predicted that this so-called ‘Aubry transition’ occurs for an infinitely long chain of particles in a washboard potential. This occurs if the relationship between the wavelength of the potential, λ , and the separation between particles, a , is irrational. It is also necessary that the attractive interactions between neighbouring particles are above a critical threshold. If these conditions are satisfied, the system exhibits an infinite number of degenerate ground states which are separated by an infinitesimally small displacement, giving rise to an unpinning chain with zero static friction.

This elusive transition remained largely unexplored until recently, with studies showing an Aubry-type transition, both in one-dimension [69–73], and for a two-dimensional analogue [58, 74, 75]. This static Aubry transition relies on sufficiently strong interactions between neighbouring particles to promote a freely sliding chain. The study of driven colloidal particles in an optical potential energy landscape provides a good model system to experimentally probe phenomena such as synchronisation and the Aubry transition.

1.3 Scope of the thesis

In this thesis, the dynamic behaviour of colloidal particles driven through a one-dimensional optical potential energy landscape is studied. A one-dimensional sinusoidal optical potential energy landscape is used to explore the transport behaviour of colloidal rods and spheres and, in particular, to probe synchronisation phenomena and an Aubry-type transition to zero friction. Finally, the stochastic thermodynamics of a driven colloidal particle in an optical potential energy landscape is addressed.

In Chapter 2 the general theoretical background to the experimental work in this thesis is introduced, with the fundamental length and timescales of colloidal particles being described. The motion of colloidal particles is then characterised with a Langevin equation, where the effects of an external field are accounted for. Next, optical trapping is introduced as a means of manipulating colloidal particles before introducing a description for a one-dimensional optical potential energy landscape. Finally, the key experimental methods and the optical setup are

described.

The static and dynamic behaviour of a colloidal rod in an optical potential energy landscape is studied in Chapter 3. The stable states of a colloidal rod in a single optical trap close to a flat wall are characterised. A colloidal rod is then placed into a periodic optical potential energy landscape under a constant driving velocity and the equilibrium position of a particle is investigated as it is driven below the critical velocity. Next, the driving velocity is increased to enable the particle to traverse the periodic landscape and the resulting particle velocity is compared to a deterministic expression. Finally, oscillations are introduced to the driving velocity and the arising synchronised motion, known as ‘dynamic mode locking’, is characterised.

In Chapter 4, colloidal particles are driven across a time-dependent one-dimensional optical potential energy landscape. Different modes of dynamic mode locking are observed and are visualised with the use of phase portraits. The effect of the oscillation frequency on the mode locked step width is then addressed and the results are discussed in light of a high frequency theory. Furthermore, the influence on mode locking of increasing the coupling between the particle and the optical landscape is probed. Finally, transport across the time-dependent landscape is studied by measuring the effective diffusion coefficient of a mobile particle which is highly sensitive to the driving velocity and mode locking.

Chapter 5 studies chains of interacting colloidal particles as they are driven through a time-independent optical potential energy landscape. In particular, we establish how a mismatch between the length scales of the chain and the landscape gives rise to a freely sliding chain, where a chain exhibits zero static friction despite being subject to a potential energy landscape. The influence of the chain stiffness on chain motion is studied and the resulting breathing modes are characterised. Oscillations are then introduced in the driving force, leading to the observation of dynamic depinning of a colloidal chain. Finally we explore the influence of the oscillation frequency and the driving velocity on chain motion.

In Chapter 6, the stochastic thermodynamics of colloidal particles driven across one-dimensional optical landscapes is considered. Initially, a time-independent optical landscape is studied and the stochastic work due to the optical landscape is extracted from a particle trajectory. The optical work is then combined with the work due to an external driving velocity and the overall work distributions are studied. A particle is subsequently studied as it is driven through a time-dependent optical landscape at a driving velocity corresponding to mode locked

motion. Finally, the magnitude of the total work is considered in light of the mechanism of particle motion with an analysis of both the optical work and the driving work.

Chapter 2

Theoretical background and experimental methods

ABSTRACT

In this thesis, the dynamics of colloidal particles driven across one-dimensional optical potential energy landscapes are studied. This chapter first lays out the theoretical background before the experimental system is described. Initially, colloidal particles and their interactions are discussed. The Langevin equation is then used to describe particle motion in the presence of an external force. Optical trapping is introduced followed by considerations of the force this exerts on a colloidal particle and a description of the expression for the optical potential energy landscape used in this thesis. Finally the experimental system is described, including details of the colloidal model system, the optical setup, and the software used for controlling the experiments and image processing.

2.1 Colloidal particles

Colloidal particles have a wide range of uses due to their inherent length and timescales. They are characterised as particles that have at least one dimension on a length scale between several nanometres and micrometres [19]. These particles are then dispersed in a ‘continuous’ medium, often a liquid, where the colloidal particles are much larger than solvent molecules. Particles of this size can be readily observed using relatively cheap and simple techniques such as brightfield microscopy (for particles larger than ~ 200 nm) and confocal microscopy.

Colloidal particle motion can be quantified with the use of the mean squared displacement (MSD). Defining the trajectory of a particle as $x(t)$, the MSD is given by

$$\langle x(\Delta t)^2 \rangle = \langle [x(t + \Delta t) - x(t)]^2 \rangle = 2D\Delta t, \quad (2.1)$$

where Δt is the lag time and D the diffusion coefficient. Note that in the limit of infinite dilution, $\text{MSD} = 2dD_0\Delta t$, where d is the dimensionality and D_0 is the diffusion coefficient at infinite dilution. Using equation 2.1, a typical colloidal timescale can be defined, which is known as the Brownian time, τ_B , and is the time taken for a particle to diffuse over its own radius, a . In two dimensions, this is given by

$$\tau_B = \frac{a^2}{4D_0} = \frac{\zeta a^2}{4k_B T}, \quad (2.2)$$

where $\zeta = k_B T / D_0$ is the friction coefficient, T the temperature and k_B Boltzmann’s constant. For typical values used in this thesis of $a \approx 1.5 \mu\text{m}$ and $\zeta \approx 10^{-7} \text{ kg s}^{-1}$, the resulting Brownian time is ~ 15 s at room temperature. This timescale is readily accessible, allowing particles to be probed in real time.

If a colloidal particle has a higher mass density than that of the solvent it is dispersed in, then the effect of gravity relative to thermal energy, $k_B T$, can be characterised by the gravitational height [19]:

$$l_g = \frac{k_B T}{\frac{4}{3}\pi a^3 \Delta \rho g}. \quad (2.3)$$

Here, $\Delta \rho = \rho_{\text{particle}} - \rho_{\text{solvent}}$ is the mass density difference between the colloidal particle and

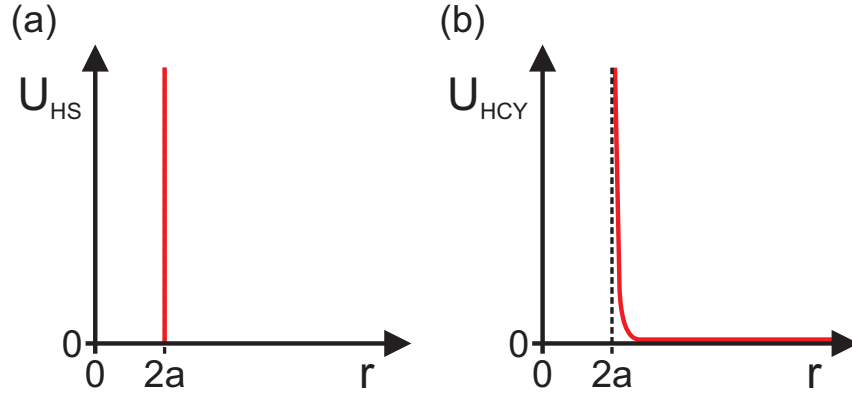


Figure 2.1: Schematic of (a) the hard sphere potential and (b) the hard core Yukawa potential. Both potentials have an excluded volume region for $r < 2a$.

the solvent and g is the acceleration due to gravity. The gravitational height is the distance that a particle can move against gravity due to thermal motion. This means that if $l_g \gg a$, the effect of gravity can be ignored and particles will sediment very slowly. In contrast, if $l_g \ll a$, the particles are confined to the base of the sample cell by gravity. This is a commonly used and simple method for creating a quasi-two-dimensional colloidal system [31, 76].

2.1.1 Hard sphere interactions

The simplest repulsive interaction potential is the hard sphere potential (see figure 2.1a) defined as

$$U_{HS}(r) = \begin{cases} \infty, & r < 2a \\ 0, & r \geq 2a. \end{cases} \quad (2.4)$$

As such, the free energy of hard spheres is solely reliant on entropy [31], and the simplicity of this model makes it particularly versatile. Particles with more complex interactions are often treated as hard spheres with an introduced perturbation [77]. One such perturbation leads to the hard core Yukawa potential (see figure 2.1b) where an additional electrostatic term governs the interactions at $r \geq 2a$ [78]:

$$U_{HCY}(r) = \begin{cases} \infty, & r < 2a \\ k_B T Z^2 \lambda_B \left(\frac{\exp(2a\kappa)}{1+2a\kappa} \right)^2 \frac{\exp(-\kappa r)}{r}, & r \geq 2a. \end{cases} \quad (2.5)$$

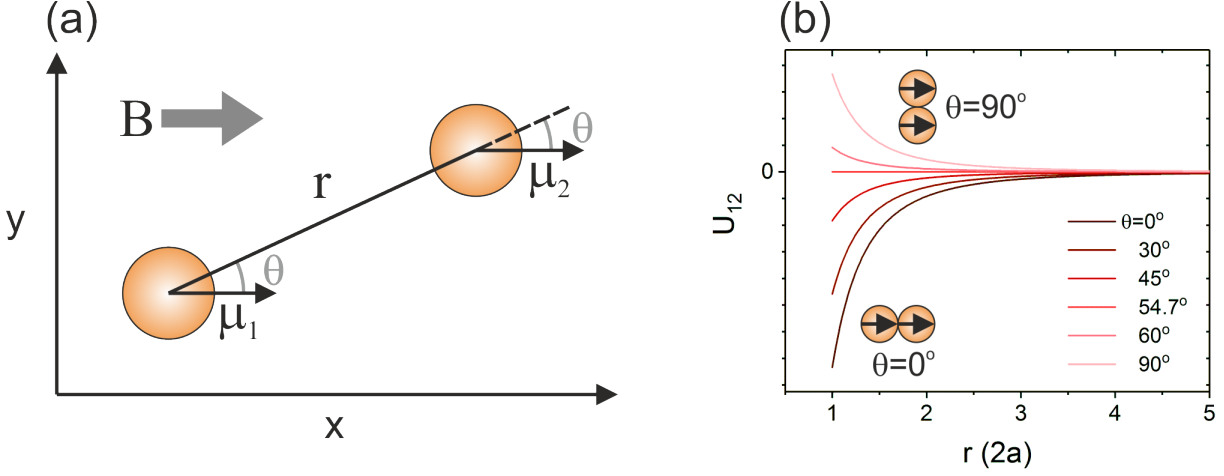


Figure 2.2: (a) Two superparamagnetic particles have associated dipoles, μ_1 and μ_2 , that align with the external magnetic field, $\mathbf{B}$, and are separated by $\mathbf{r}$ with a relative angle, θ . (b) The interaction potential between two superparamagnetic particles at different relative angles and distances. Here the magnetic field strength, B is fixed.

Here the additional term introduces a repulsion with Z , the effective charge number, λ_B , the Bjerrum length, and κ^{-1} , the Debye length. This system can be emulated experimentally using charged surface groups. In the limit $\kappa^{-1} \ll 2a$ the repulsive interactions are very short-ranged and an effective hard sphere system is obtained [31].

2.1.2 Magnetic interactions

In this thesis, superparamagnetic particles are used, allowing for tunable interactions. These particles are made of non-magnetic cross-linked polystyrene doped with magnetic nanoparticles. In the absence of a magnetic field, these magnetic sub-domains rapidly reach thermal equilibrium, hence random orientations, and the colloidal particles have no overall magnetic moment. However, when the colloidal particles are subject to an external magnetic field, the sub-domains align with this field such that the particles obtain an overall magnetic moment [79].

Two magnetic moments, $\mu_{1,2}$, have an interaction strength that depends on their distance and orientation in the following manner [79]:

$$U_{12} = \frac{\mu_0}{4\pi r^3} \left(\mu_1 \cdot \mu_2 - \frac{3}{r^2} (\mu_1 \cdot \mathbf{r}) (\mu_2 \cdot \mathbf{r}) \right), \quad (2.6)$$

where μ_0 is the permeability of free space, $\mathbf{r}$ is the vector between μ_1 and μ_2 as depicted in figure 2.2a and r is the magnitude of $\mathbf{r}$. In the case of superparamagnetic colloidal particles,

each particle has an equivalent induced dipole moment leading to $\boldsymbol{\mu}_1 = \boldsymbol{\mu}_2 = \boldsymbol{\mu}$. This means that equation 2.6 can be written as

$$U_{12} = \frac{\mu_0}{4\pi r^3} (\mu^2 - 3\mu^2 \cos^2 \theta) = \frac{\mu_0 \mu^2}{4\pi r^3} (1 - 3 \cos^2 \theta), \quad (2.7)$$

where μ is the magnitude of $\boldsymbol{\mu}$, and θ is the angle between the magnetic field and $\mathbf{r}$, as is shown in figure 2.2a. The magnetic moment of each colloidal particle can be expressed in scalar form as

$$\mu = \chi B, \quad (2.8)$$

where χ is the magnetic susceptibility, and B is the magnetic field strength. Equations 2.7 and 2.8 combine to give the following expression for the interaction between two superparamagnetic particles

$$U_{12} = \frac{\mu_0 \chi^2 B^2}{4\pi r^3} (1 - 3 \cos^2 \theta). \quad (2.9)$$

This expression is shown in figure 2.2b for a fixed magnetic field at different angles and can lead to attractive or repulsive interactions. At the ‘magic angle’ of $\theta = 54.7^\circ$, the magnetic interactions are zero at all separations. In this thesis, the experimental geometry is quasi-one-dimensional and as such $\theta = 0^\circ$, which leads to attractive dipolar interactions between particles.

The magnetic interactions are usually characterised using a dimensionless magnetic interaction parameter, Γ , which quantifies the magnetic interaction strength at contact, in comparison to thermal energy. This is calculated by assuming two colloidal particles are in contact, $r = 2a$, and the angle between their connecting vector and the magnetic field is $\theta = 0^\circ$:

$$\Gamma \equiv -\frac{U_{12}(r = 2a, \theta = 0^\circ)}{k_B T} = \frac{\mu_0 \chi^2 B^2}{16\pi k_B T a^3}. \quad (2.10)$$

In this thesis, typical experimental values of $\chi = 7 \times 10^{-12} \text{ A m}^2 \text{ T}^{-1}$ [59], $a = 1.5 \mu\text{m}$ and $B = 1 \text{ mT}$ result in a magnetic interaction parameter of $\Gamma \approx 80$ corresponding to attractive energies much stronger than thermal energy.

2.1.3 The Langevin equation

Newton's second law of motion states that $\Sigma \mathbf{F} = m\mathbf{a}$ and this can be used as a basis to describe the motion of a colloidal particle of mass m , where $\mathbf{a} = d^2\mathbf{r}/dt^2$. Due to the one-dimensional nature of experiments in this thesis, scalar notation can be used, such that $\mathbf{r} = x\hat{\mathbf{r}}$, where $\hat{\mathbf{r}}$ is a unit vector pointing along the direction of motion. The forces that act on a colloidal particle can be broken up into three terms as in the following equation:

$$F(x, t) = F_{ext}(x, t) - \zeta \frac{dx}{dt} + \xi(t). \quad (2.11)$$

Here F_{ext} is a force due to an external perturbation, such as gravity or a driving force. The second term, where ζ is the friction coefficient, is negative as it expresses the drag felt by a particle moving through a solvent. This force always acts in the opposite direction to the velocity. The final term, $\xi(t)$, describes the instantaneous force felt by a particle due to Brownian noise and has a Gaussian distribution centred at zero, $\langle \xi(t) \rangle = 0$. Its correlation function takes the form:

$$\langle \xi(t)\xi(t') \rangle = 2\zeta k_B T \delta(t - t'), \quad (2.12)$$

where $\langle \dots \rangle$ represents an average over time. According to Newton's second law, the resulting equation of motion thus becomes

$$m \frac{d^2x}{dt^2} = F_{ext}(x, t) - \zeta \frac{dx}{dt} + \xi(t). \quad (2.13)$$

With the inclusion of Brownian noise, this equation is called the Langevin equation [80].

The relative importance of stochastic (Brownian) and deterministic (externally imposed) forces can be quantified using the Péclet number which is defined as

$$\text{Pe} = \frac{av}{D_0} = \frac{av\zeta}{k_B T}, \quad (2.14)$$

where v the particle velocity and in the limit of high Péclet number, diffusion can be ignored. In this thesis, typical values of $a \approx 1.5 \mu\text{m}$, $v \approx 2 \mu\text{m s}^{-1}$ and $\zeta \approx 1 \times 10^{-7} \text{ kg s}^{-1}$ lead to $\text{Pe} = 75 \gg 1$, signifying that the effects of diffusion are negligible.

In classical mechanics, inertia plays an important role, but in colloidal dispersions this is

often not the case. The Reynolds number can be used to quantify the effect of inertia and is given by

$$\text{Re} = \frac{\text{Inertial forces}}{\text{Viscous forces}} = \frac{\rho a^3 \frac{v}{t}}{\eta \frac{a^2}{t}} = \frac{\rho a v}{\eta}, \quad (2.15)$$

where ρ is the solvent mass density, t time, and η the fluid viscosity. For typical values used in this thesis of $\rho = 10^3 \text{ kg m}^{-3}$, $a = 1.5 \mu\text{m}$, $v = 10 \mu\text{m s}^{-1}$ and $\eta = 1 \times 10^{-3} \text{ N s m}^{-2}$, the result is a Reynolds number of $\text{Re} \approx 10^{-6}$. In this regime where $\text{Re} \ll 1$, viscous forces are dominant and any inertia is immediately ($\sim 50 \text{ ns}$ [81]) dissipated by the surrounding fluid. In this limit, inertia and thereby the acceleration term can be ignored and equation 2.13 is reduced to the Langevin equation in the overdamped limit:

$$\zeta \frac{dx}{dt} = F_{ext}(x, t) + \xi(t). \quad (2.16)$$

The external forces, F_{ext} , may take many forms and in this thesis the system is driven, either with a constant or a modulated driving force, F_{drive} . In addition, the particle is placed in an optical potential energy landscape that also exerts a force on the particle, F_{opt} . The Langevin equation thus takes the form:

$$\zeta \frac{dx}{dt} = F_{drive}(x, t) + F_{opt}(x, t) + \xi(t). \quad (2.17)$$

The drag force felt by a spherical object moving through a bulk viscous fluid can be calculated using Stokes' law as [82]

$$\zeta = 6\pi\eta a. \quad (2.18)$$

However, this does not correspond to the experimental geometry used in this work. Here particles are close to a wall that influences the drag force as they move through the solvent. It is found that a particle moving close to a wall has an increased level of drag, reducing its ability to move and diffuse. This perturbed diffusion coefficient can be expressed as [83]

$$\frac{D(z)}{D_0(z = \infty)} = \frac{6\pi\eta a}{\zeta(z)} = 1 - \frac{9}{16} \left(\frac{a}{a+z} \right) + \frac{1}{8} \left(\frac{a}{a+z} \right)^3 - \frac{45}{256} \left(\frac{a}{a+z} \right)^4 - \frac{1}{16} \left(\frac{a}{a+z} \right)^5, \quad (2.19)$$

where z is the distance between the particle and the wall and $D(z)$ refers to motion parallel to

the wall. For a system where z is small, this results in a much larger friction coefficient and thus a much reduced diffusion coefficient.

2.1.4 Optical trapping

A tightly focused laser beam can be used to exert a force on a particle [39]. If this is carefully controlled then a particle with a higher refractive index than its surrounding medium can be confined within this so-called optical trap. An exact description of an optically trapped particle can be obtained by solving Maxwell's equations, but often an approximation is used to allow a more insightful description [49]. To this end, we will consider a particle that is either much larger than the wavelength of the light, $a \gg \lambda$, or much smaller than the wavelength, $a \ll \lambda$.

First, considering the regime where $a \gg \lambda$, the particle is treated as a spherical lens and ray optics can be used as shown in figure 2.3. Laser light can be refracted by a colloidal particle, causing the light to change direction. Due to the Gaussian nature of the beam, the particle will be subject to a force restoring it to the trap focus if a particle is axially off centre as shown in figure 2.3a. This is because laser light has an inherent momentum which changes as the light passes through the solvent-particle interface. This change in momentum is compensated for by an equal and opposite change of momentum by the particle. If a particle fluctuates such that it moves above or below the trap focus, as shown in figure 2.3b, then the change in momentum of the light results in a force on the particle directed towards the trap focus. Some light will not be refracted, and will simply be scattered by the solvent-particle interface. This leads to scattering forces that act in the direction of laser beam propagation, shown in figure 2.3c. At equilibrium, trapping (gradient) forces and scattering forces are balanced and the particle is considered to be trapped.

To gain insight into the effect of particle size and refractive index, it is useful to consider the Rayleigh regime ($a \ll \lambda$), where the particle is treated as an induced point dipole that interacts with the electric field. The light exerts a force on the particle as it is absorbed and randomly re-emitted. This is known as the scattering force and is described as [84]

$$F_{scat} = \frac{158\pi^5 a^6 n I_0}{3\lambda^4 c} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2, \quad (2.20)$$

where n is the refractive index of the surrounding medium, I_0 is the intensity of the light, c is

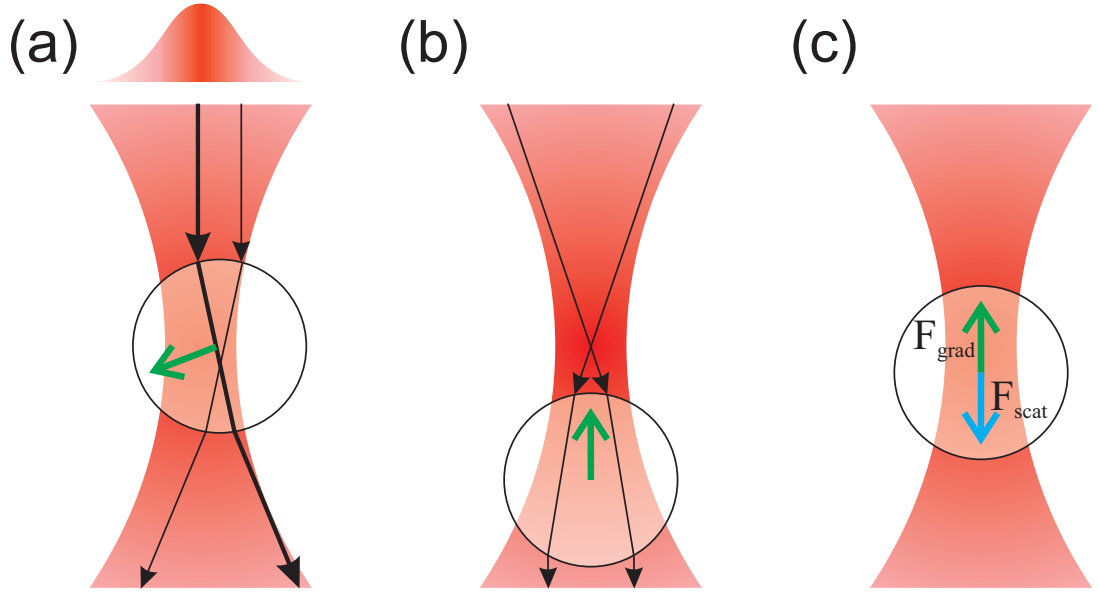


Figure 2.3: Ray optics schematic of a spherical colloidal particle confined in an optical trap. The laser source is shown from above with a Gaussian intensity. (a) The colloidal particle is axially off-centre but experiences a net force (green arrow) that pulls it towards the trap focus. (b) The colloidal particle is below the focus but has a force (green arrow) that will restore it towards the focus of the trap. (c) In the absence of any other external forces, a colloidal particle is in equilibrium when the gradient force (green arrow) and scattering force (blue arrow) are equal and opposite.

the speed of light, and m is the ratio of the refractive indices of the particle and the surrounding medium. This force always results in the particle being pushed away from the light source. Additionally the gradient force experienced by the particle due to the inhomogeneity of the electromagnetic field must be considered. This force is given by [84]

$$F_{\text{grad}} = \frac{2\pi a^3 n \nabla I_0}{c} \left(\frac{m^2 - 1}{m^2 + 2} \right), \quad (2.21)$$

where ∇I_0 is the gradient of the light field. This force acts towards the region of highest light intensity so causes a particle to be drawn to the focus of a laser beam. An important note is that the scattering force has a much greater size dependence than the gradient force ($F_{\text{scat}} \propto a^6$ cf. $F_{\text{grad}} \propto a^3$), meaning that as a particle increases in size, the scattering forces will begin to dominate and large particles will become unstable in an optical trap.

The potential that a particle trapped in a single Gaussian optical trap experiences is given by [11, 51, 52]

$$U_{\text{opt}}(x) = -V_0 \exp \left[-\frac{k(x - x_0)^2}{2V_0} \right], \quad (2.22)$$

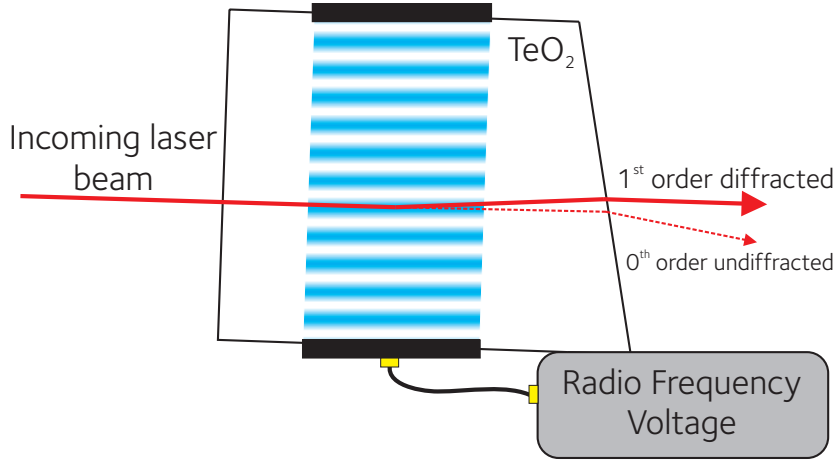


Figure 2.4: Diagram of an acousto-optic deflector with an incoming laser beam entering from the left. A standing wave is created within the crystal and by varying the applied voltage, the extent to which the first order beam is diffracted can be controlled.

where x is the displacement, x_0 is the position of the trap, and k is the trap stiffness. V_0 is the depth of the trap and is typically $\sim 10\text{--}100\ k_B T$. If its displacement from the trap centre is small, then a particle confined to an optical trap can be approximated as being attached to a Hookean spring which corresponds to a harmonic optical potential [40, 41, 85]:

$$U_{opt}(x) = \frac{kx^2}{2} - V_0. \quad (2.23)$$

This assumption breaks down at large displacements from the centre of an optical trap where the optical force drops to zero, which is clearly inconsistent with equation 2.23.

Acousto-optic deflectors

There are many common techniques to steer a laser beam and create multiple traps including the use of a spatial light modulator (SLM), interference methods, and acousto-optic deflectors (AODs) [86]. Here the principles of AODs are discussed as this technique is used throughout this thesis. A standing wave is created within the TeO₂ crystal contained inside each AOD, generating a diffraction grating, resulting in the ability to diffract incoming light. The 0th order beam passes through without being diffracted, but the 1st order beam is diffracted, as shown in figure 2.4, and can be directed into subsequent optics. By tuning the applied radio frequency and changing the wavelength of the standing wave, the 1st order beam can be steered.

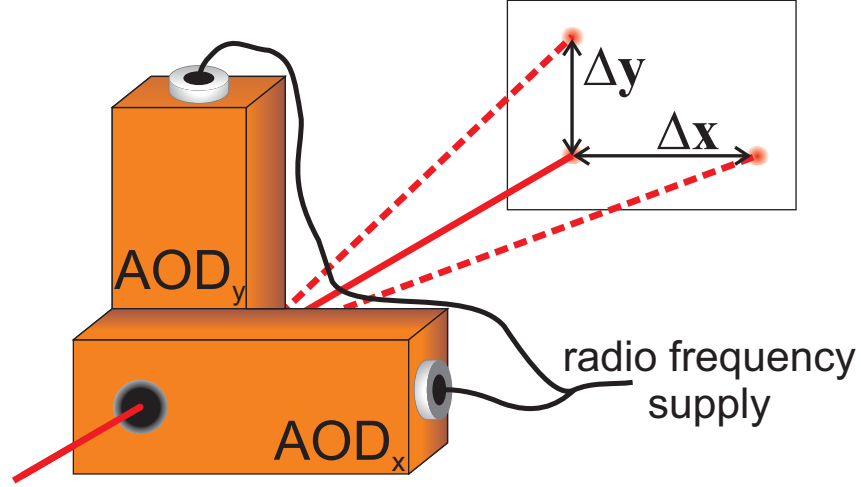


Figure 2.5: Schematic of AOD setup with an incoming laser beam entering from the bottom left. The beam passes through two AODs; one controlling the x axis and the other controlling the y axis. Combined, these are used to translate the laser beam in two dimensions.

A single AOD only allows control in one direction so two perpendicular AODs give full control of the laser focus in the two-dimensional sample plane, as displayed in figure 2.5. While AODs can only instantaneously create one trap, they can move this single trap at very high speeds, enabling a time sharing technique to create hundreds of traps. This is done by rapidly changing the AOD frequencies at a rate of up to 100 kHz, which is much faster than the timescale of colloidal motion ($\tau_B \approx 15$ s, see section 2.1). This results in a colloidal particle simultaneously experiencing the effect of all formed optical traps but with an effective intensity, $I_0 < \frac{I_{tot}}{n_{traps}}$, where I_{tot} is the total intensity from a single, permanent trap, and n_{traps} is the number of optical traps. This inequality is due to the fact that the AODs take a small but finite amount of time to move between subsequent time-shared optical traps.

Optical potential energy landscapes

A single optical trap is the simplest optical potential energy landscape (optical landscape), but these can take many forms. In this thesis, the central optical landscape considered is formed by creating a line of optical traps with regular spacing, λ . The total potential corresponding to this optical landscape can be found by summing over the potential for all the individual traps expressed in equation 2.22 [51]. Assuming an infinitely long line of traps,

$$U_{opt}(x) = \sum_{i=-\infty}^{\infty} -V_0 \exp \left[-\frac{k(x - i\lambda)^2}{2V_0} \right]. \quad (2.24)$$

We can employ the identity, $F_{opt}(x) = -dU_{opt}/dx$ to obtain the force due to the one-dimensional periodic optical landscape

$$F_{opt}(x) = -k \sum_{i=-\infty}^{\infty} (x - i\lambda) \exp \left[-\frac{k(x - i\lambda)^2}{2V_0} \right]. \quad (2.25)$$

It has been shown that closely spaced optical traps form a sinusoidal optical landscape [87] which can be seen as follows. Due to its periodic nature, the optical landscape can be written as a Fourier series with the form

$$U_{opt}(x) = \frac{1}{2}a_0 + \sum_{m=1}^{\infty} \left[a_m \cos \left(\frac{2\pi mx}{\lambda} \right) + b_m \sin \left(\frac{2\pi mx}{\lambda} \right) \right]. \quad (2.26)$$

The first Fourier coefficient, a_m , is calculated to give [59]

$$a_m = \frac{2}{\lambda} \int_{-\lambda/2}^{\lambda/2} U_{opt}(x) \cos \left(\frac{2\pi mx}{\lambda} \right) dx = -\frac{\sqrt{8\pi}V_0^{3/2}}{\lambda k^{1/2}} \exp \left(-\frac{2\pi^2 m^2 V_0}{\lambda^2 k} \right). \quad (2.27)$$

The second Fourier coefficient,

$$b_m = \frac{2}{\lambda} \int_{-\lambda/2}^{\lambda/2} U_{opt}(x) \sin \left(\frac{2\pi mx}{\lambda} \right) dx = 0, \quad (2.28)$$

by definition because it is an odd function and is being integrated symmetrically around zero. Combining the expressions for a_m and b_m with equation 2.26 along with the fact that $a_0 = a_{m=0}$, we reach

$$U_{opt}(x) = -\frac{\sqrt{8\pi}V_0^{3/2}}{\lambda k^{1/2}} \left[\frac{1}{2} + \sum_{m=1}^{\infty} \exp \left(-\frac{2\pi^2 m^2 V_0}{\lambda^2 k} \right) \cos \left(\frac{2\pi mx}{\lambda} \right) \right]. \quad (2.29)$$

For the typical parameters used in this thesis, λ is small compared to $\sqrt{m^2 V_0/k}$ when $m > 1$ which means that we can ignore the terms $m > 1$, leading to

$$U_{opt}(x) \approx -\frac{\sqrt{8\pi}V_0^{3/2}}{\lambda k^{1/2}} \left[\frac{1}{2} + \exp \left(-\frac{2\pi^2 V_0}{\lambda^2 k} \right) \cos \left(\frac{2\pi x}{\lambda} \right) \right]. \quad (2.30)$$

This in turn, gives

$$F_{opt}(x) = -\frac{2(2\pi V_0)^{3/2}}{\lambda^2 k^{1/2}} \exp \left(-\frac{2\pi^2 V_0}{\lambda^2 k} \right) \sin \left(\frac{2\pi x}{\lambda} \right). \quad (2.31)$$

Table 2.1: Properties associated with the colloidal rods used in this thesis [88].

Parameter	Symbol	Rod
Length	L	3-4 μm
Width	W	$\sim 500\text{ nm}$
Material	-	Silica
Density	ρ	$2.2 \times 10^3\text{ kg m}^{-3}$
Surface functionality	-	SiO_2
Gravitational height	l_g	0.5-2 μm

As such, the force due to the one-dimensional optical landscape for small trap spacings is indeed shown to have a sinusoidal nature and this expression for F_{opt} is used throughout this thesis.

2.2 Experimental methods

2.2.1 Colloidal model system

In this thesis, two different types of colloidal particles are used: rods (Chapter 3) and spheres (Chapters 3 to 6). In this section, their physical and chemical properties are outlined.

Colloidal rods

The colloidal rods used in this thesis are made of silica. They are synthesised initially in a bullet shape [89] before successive silica shells are added [88]. This maintains a consistent refractive index throughout the particle whilst transforming the bullet shaped rods, shown in figure 2.6a, into larger, more symmetrical, capsule-like rods, as displayed in figure 2.6b. This process of adding shells is particularly important, as the rods must be suitably large to image using optical microscopy, which is only possible if all dimensions of the rod are larger than $\sim 200\text{ nm}$. The mass density of the colloidal rods is $2.2 \times 10^3\text{ kg m}^{-3}$ and they are dispersed in water, which has a mass density of $1 \times 10^3\text{ kg m}^{-3}$. From this we can estimate that for an average particle with length $L \approx 3\text{ }\mu\text{m}$, and width $W \approx 0.5\text{ }\mu\text{m}$, the gravitational height (equation 2.3) is $l_g \approx 0.5\text{ }\mu\text{m}$. This ensures that the rods will sediment to the bottom of the sample cell. Note, however that l_g is very sensitive to the size of the particle, $l_g \propto L^{-1}W^{-2}$. This means that a particularly long or

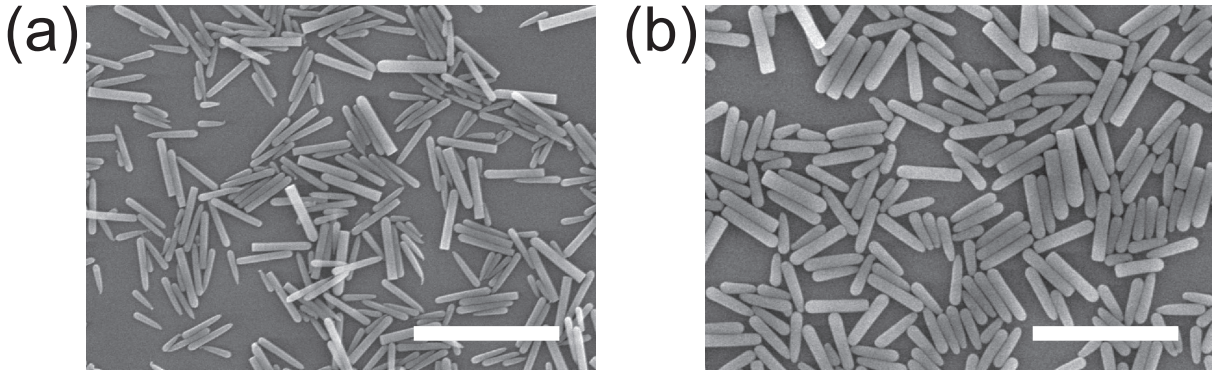


Figure 2.6: SEM images of (a) bullet shaped rods from initial synthesis, and (b) more capsule-like rods achieved after 3 successive shell growths. Scale bars in both images represent 5 μm .

wide rod, will be confined by gravity with its long axis parallel to the substrate. However, for a smaller rod, the gravitational height is larger and when reaching the point where $l_g \approx L/2$, the thermal energy of the system is sufficient to force the particle into an upright orientation. The rods have a high level of polydispersity, which is known to affect phase behaviour in the bulk [90]. However, at the single particle level used in our experiments, this is not relevant as rods are only used if their dimensions are suitable for imaging and optical manipulation. The surface of these silica rods has an inherent negative charge, which prevents them from aggregating. A summary of the characteristics of the colloidal rods used is given in table 2.1.

Colloidal spheres

The colloidal spheres used are Dynabeads M-270 Carboxylic Acid (Invitrogen), which have a diameter of 3 μm when dispersed in 20% EtOH(aq). These are commercially available cross-linked polystyrene particles doped with evenly distributed iron oxide magnetic nano-particles. Due to the iron oxide nano-particles, the particles exhibit superparamagnetic behaviour (see section 2.1.2). This means that in the absence of a magnetic field, each magnetic core randomly orients as a result of thermal energy, and the particles have no net dipole. However, as they are introduced into an external magnetic field, the magnetic moments align with the external field, giving the particle a field dependent magnetic moment. The gravitational height of these colloidal spheres is $l_g = 50 \text{ nm}$, which is less than 2% of the particle diameter. This means that a colloidal sphere is confined against the sample wall, forming a quasi-two-dimensional system as described in section 2.1. The colloidal particles have surface functionality of COOH, resulting in short range repulsive forces due to a build up of negative charge at the surface which prevents

Table 2.2: Properties associated with the colloidal spheres used in this thesis [59].

Parameter	Symbol	Sphere
Radius	a	1.5 μm
Material	-	86% Polystyrene 14% Iron oxide (by mass)
Density	ρ	$1.6 \times 10^3 \text{ kg m}^{-3}$
Surface functionality	-	COOH
Friction coefficient	ζ	$9.19 \times 10^{-8} \text{ kg s}^{-1}$
Brownian time	τ_B	15 s
Gravitational height	l_g	50 nm
Magnetic susceptibility	χ	$6.7 \times 10^{-12} \text{ A m}^2 \text{ T}^{-1}$

particles from aggregating. A summary of the characteristics of colloidal spheres studied in this thesis is shown in table 2.2.

2.2.2 Sample cells

We use commercially available quartz glass cells (Hellma) as sample containers (see figure 2.7 inset). These cells have an internal cavity size of $\sim 90 \mu\text{L}$. The cell has a flat base, an internal depth of $200 \mu\text{m}$, a width of 9 mm and a length of 20 mm . Sample cells are cleaned between experiments initially by flushing through water, then 20% EtOH(aq), and finally EtOH(l). They are then immersed in a 2% Hellmanex solution at 50°C for one hour before being flushed with EtOH(l) and dried in air. Subsequently, they are exposed to an oxygen plasma to remove any organic material that may still be adhered to the substrate surface. The plasma treatment leaves the surface hydrophilic, allowing the aqueous dispersion to be inserted into the cell easily with a reduced chance of introducing air bubbles. After the colloidal dispersion has been inserted into the cell, both apertures are sealed with Blu Tack to minimise solvent evaporation and introduction of dust to the sample.

2.2.3 Experimental setup

The optical setup used is custom built and combines an inverted brightfield microscope with a laser tweezing setup and a piezo-electric sample stage. This setup is built upon an optical table (Newport RS-4000) that is damped using passive pneumatic legs (Newport PL-2000) to minimise the effect of external vibrations. A schematic of the optical system used is shown in figure 2.7.

Optical trapping setup

A 1064 nm infrared laser (Coherent Compass 1064-4000M) is used to provide a high intensity laser beam of up to 4 W. The beam is expanded as it passes through two lenses (L1, L2), and a $\lambda/2$ waveplate ensures the correct polarisation for the polarising beam splitter (PBS1) to act as a mirror. The back aperture of the AODs (AA Opto-Electronic DTSXY-250-1064) is intentionally overfilled by the expanded laser beam to maximise trapping and beam steering capability, and to create a symmetrical optical trap.

The 1st order beam leaving the AODs is collinear with the incoming laser beam. This means that only the 1st order beam is guided by M1 and M2 through subsequent optics. This is the strongest diffracted beam that can be controlled in both the x and y directions at the sample. The AODs are controlled with Aresis Tweez software, which has an in-built function to enable field flattening, ensuring traps created in the centre of the field of view have the same intensity as those at the edge of the field of view. The software also ensures that the optical traps are spatially calibrated.

The laser beam is subsequently reflected by two mirrors (M1, M2) before passing through a telescope (L3, L4) whilst being guided by mirrors (M3, M4) to the back of the trapping objective (O1, Leica 50 $\times$, NA=0.55). Note that the low NA of the trapping objective does not allow trapping in 3D. However, trapping is stable in 2D as particles are unable to undergo significant out-of-plane fluctuations due to their low gravitational height (see tables 2.1 and 2.2). The objective focusses the laser light at the sample plane where the sample cell is in order to maximise optical trapping capability. It then passes through the imaging objective (O2, Zeiss 40 $\times$, NA=0.50) and into the polarising beam splitter (PBS2). This acts to reflect half of the incoming light whilst allowing the rest of the light to pass straight through before being

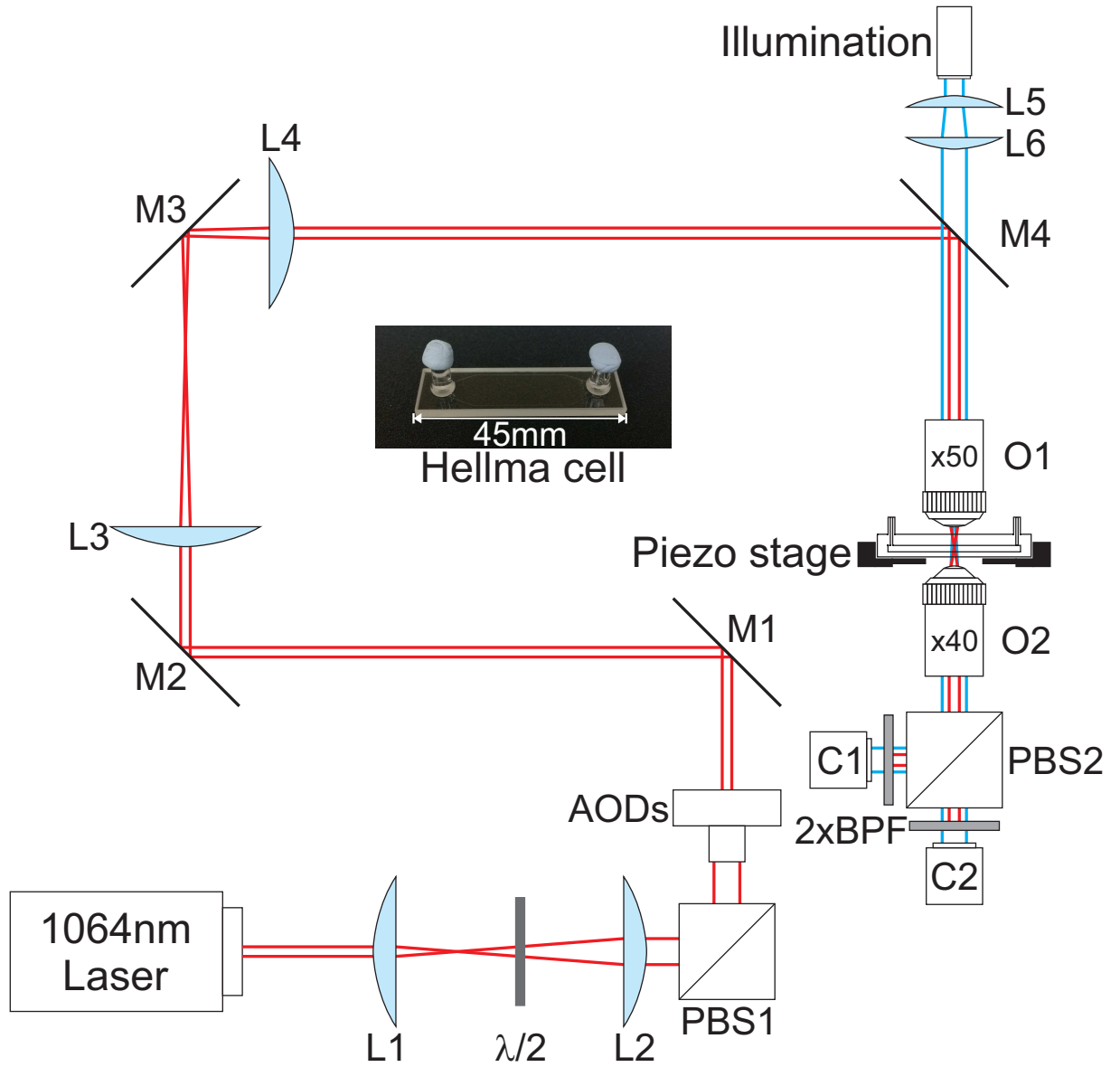


Figure 2.7: Diagram of optical setup that combines an optical trapping setup and inverted brightfield microscope. Laser beam path is displayed in red, with the illumination light path shown in blue. The laser beam is expanded by telescope (L1, L2) before overfilling the AOD aperture. The beam is then guided through a second telescope (L3, L4) and into the back aperture of the trapping objective (O1) to focus the laser at the sample plane. It is then filtered out by band pass filters (BPF) so that the laser light is not imaged. The illumination enters from above and is expanded by L5 and L6 to illuminate the sample before being focused onto the cameras (C1, C2) by the imaging objective (O2). Inset shows photo of a Hellma cell, which is held on the piezo stage.

selectively filtered out using two band pass filters (BPF). The beam waist of an optical trap can be calculated using $w_0 = \lambda/\theta\pi$ and $\text{NA} = n \sin \theta$. With the given experimental parameters, $w_0 = 0.79 \mu\text{m}$ corresponding to a laser spot size of $2w_0 = 1.58 \mu\text{m}$ in the sample plane.

Inverted brightfield microscope

The illumination for the microscope is generated by a white light LED. This provides an imaging light source, which is expanded using lenses (L5, L6) in such a way that it passes through a dielectric mirror (M4). At this point the illumination is coupled into the beam path of the optical trap. The white light is then focussed by the trapping objective below the sample plane to create a defocussed light spot at the sample plane and allow an even illumination of the sample. The light subsequently passes through the imaging objective (O2), where it is focused onto the two cameras to form an image of the sample. Two cameras are used (PixeLink PLB-741U and Ximea MQ013MG-E2) to allow the AOD software and live tracking software to run in parallel.

Piezo stage

A piezo-electric stage (PI-542.2CD) is used to provide the external driving of the colloids with respect to the optical landscape with sub-nanometre precision. Within the stage, there is a piezo crystal, which expands when a voltage is applied. Careful control of this allows fine adjustments to be made to the lateral positioning of the stage. This has a vast array of applications, but here the piezo-electric stage is fitted with a custom sample holder to drive the sample in one dimension. The driving velocity is always applied relative to the frame of reference, which is here defined as the stationary optical landscape. The stage has a total travel length of $200 \mu\text{m}$ with sub-nanometre precision. The response time of the stage is on the order of milliseconds, which is insignificant when compared to the Brownian time of a colloidal particle ($\tau_B \approx 15 \text{ s}$, see section 2.1). The stage is controlled using custom built LabVIEW software and is used to drive samples at velocities between $0.01\text{-}10.0 \mu\text{m s}^{-1}$. Calibration is achieved by driving a particle at a known velocity and measuring the average particle velocity, which produces a linear relationship with a unity gradient [59].

2.2.4 Magnetic fields

To control the interactions between the superparamagnetic particles as described in section 2.1.2, an external magnetic field is applied via two identical permanent magnets on the sample stage. This generates a magnetic field collinear with the direction of drive in the sample plane. By spacing the magnets such that they are equidistant from the sample, we ensure that we have a uniform field throughout the field of view. This setup is identical to that used in [59] and the calibration is given by $B = 2996 \times r^{-2} - 0.376$, where B is the magnetic field in mT, and r is the half separation of the magnets in mm.

2.2.5 LabVIEW interface

A custom written LabVIEW interface is used to communicate with the laser, AODs, piezo stage, and camera simultaneously during experiments. This allows the timing of all aspects to be synchronised, which is beneficial for post-experimental analysis.

Laser: The laser can be turned on, off and have its power adjusted through the LabVIEW software. During experiments, the laser is kept at the same power and the AODs are used to control any change in laser power. This is done to ensure laser power stability and to minimise the risk of any reduction in the lifetime of the laser.

AODs: The AODs are used to control the location and the intensity of individual optical traps. This can also be used to create time-dependent optical potential energy landscapes. The AODs are coupled with the PixelINK camera for calibration.

Piezo stage: The piezo stage can be controlled both in terms of position and velocity, which can be constant or modulated. This is used to automatically repeat hundreds of experimental runs in series.

Ximea camera: The Ximea camera is used for imaging and live particle tracking. For spheres, this is done through a convolution based particle finding method using an image of a single sphere as a template. The template is scanned through each image and the particle is located at the position at which the convolution returns the highest value. This method can be used to locate over 20 particles without any loss of speed. For rods, due

to their anisotropy, the tracking process is more complex and images are analysed using Mathematica after collecting experimental data (see Chapter 3).

Acknowledgments

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Chapter 3

Colloidal rods in optical potential energy landscapes

ABSTRACT

In this chapter we study the static and dynamic behaviour of colloidal rods in an optical potential energy landscape. First, we explore the stable states of a colloidal rod in a single optical trap close to a flat wall. Here two meta-stable states are observed, horizontal and vertical, both of which experience a parabolic potential energy landscape. Next we place a colloidal rod into a one-dimensional sinusoidal optical potential energy landscape and introduce a constant driving velocity. The equilibrium position of a particle is investigated as it is driven below the critical velocity and thus confined to a single potential energy minimum of the optical landscape. The equilibrium position of a rod is found to vary substantially from that of a sphere due to the friction coefficient of a rod, which is highly dependent on its proximity to an optical trap. Then, the driving velocity is increased to enable the particle to traverse the periodic landscape and above the critical velocity, the average particle velocity increases as the square root of the driving velocity. When introducing oscillations to the driving velocity we observe dynamic mode locking and characterise the nature of synchronised motion of the rod-like particles.

3.1 Introduction

Optical tweezers were first developed by Ashkin in the 1980s [91], after he initially observed the motion of microscopic particles when subject to a laser light source [39]. This has led to extensive research into the behaviour of a sphere in an optical trap [85, 92]. Due to its isotropy, this is the most studied geometry which has resulted in applications in optical sorting [51, 93], microrheology [94], and protein folding [43]. Over the past 30 years, the field of optical trapping has hugely evolved [41, 45] with the ability to impose angular momentum on particles with Laguerre-Gaussian modes [49] and create Bessel beams which are ‘diffractionless’ [45]. It is also now possible to create a vast number of different shapes of micron sized particles that can be optically trapped [38, 95], yet many remain unexplored due to their complexity [28, 29, 96, 97].

Anisotropic particles are more complex to study, but this complexity leads to phenomena that are unseen for spheres. The bulk properties of spherocylinders and rods have been greatly explored both theoretically and experimentally [24, 34, 98, 99]. The phase behaviour of rods differs from spheres due to their anisotropy [23, 89, 100]. For rods, the crystal and isotropic liquid phases are separated by a number of complex liquid crystal phases with varying degrees of translational and orientational order [101], which can have a complex interaction with light and cause birefringence [100]. Rods can be manipulated using a variety of external fields [27, 102] giving rise to further complex phase behaviour such as string formations [34]. In general, however, external fields such as gravitational fields [98], electric fields [35] or confinement [99] affect the entire sample and do not have the same single particle resolution that can be achieved with an optical trap. Gaining a deeper understanding of rods is particularly relevant due to the ubiquity of microscopic rod-like objects, from the liquid crystal make up of electronic displays [103] to bacteria and virus filaments [104].

Previous works have investigated the behaviour of rod-shaped objects in single [105, 106] and multiple optical traps [107], including nano-rods and nano-wires in optical fields [108, 109], where the anisotropy is shown to influence the trapping stability. Studies of colloidal spheres driven through an optical potential energy landscape have led to an array of rich dynamics including dynamic mode locking wherein particle motion synchronises with an external frequency [87]. However, for a rod driven through an optical potential energy landscape, synchronisation may be far more complex as the inherent anisotropy of a rod may lead to the potential for different

modes of synchronisation.

In this chapter we study the behaviour of a colloidal rod when confined in a single optical trap close to a flat wall. The arising meta-stable states are characterised, which correspond to a horizontal or vertical rod. We then introduce a colloidal rod to a periodic optical landscape formed of many optical traps and explore the motion in the case of a constant driving force. Here the effective friction of a rod and sphere greatly differ, which can be indirectly observed. Subsequently, a modulation to the driving force is introduced, leading to synchronisation. Particle motion is characterised for a dynamically mode locked particle and there is a clear similarity between rods and spheres in optical landscapes when driven above the critical velocity.

3.2 Theory

3.2.1 Optical trapping of colloidal rods

In section 2.1.4 the general concepts of optical trapping were introduced but only the behaviour of a sphere in an optical trap was discussed. Now a rod in an optical trap is considered, which may be expected to behave differently due to its inherent shape anisotropy. Using the arguments that were discussed in section 2.1.4, it is expected that the centre of the rod will be attracted to the point of highest laser intensity, which is the focus of the beam. However, this does not define the orientation of a rod. In this respect it is important to note that in three-dimensional (3D) space, an optical trap is not fully symmetrical, though it is in the two-dimensional (2D) cross-section perpendicular to the optical axis. Instead, a trap in 3D is elongated in the direction of the laser beam [49,86] due to inherent optical effects and optical aberrations and this effect is illustrated in figure 3.1. Provided that the rod length is greater than the beam width (Here $L \approx 4 \mu\text{m}$, $w_0 = 1.58 \mu\text{m}$) it maximises its overlap with the region of highest intensity by aligning its major axis parallel to the optical axis (See figure 3.2a).

Gravitational effects

Until now, the effect of gravity has been neglected. However, in this experimental system the rods have a much higher mass density than the solvent, meaning they are subject to a downward acting gravitational force that, for a perfect spherocylinder of length L and width W , is given

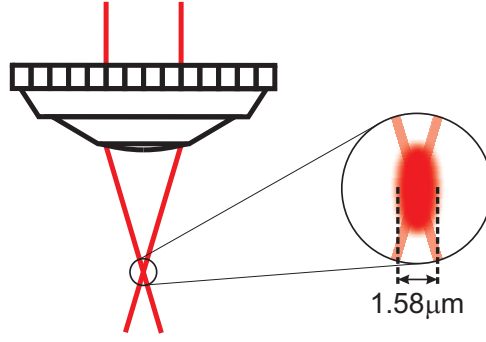


Figure 3.1: A schematic of laser light being focussed by an objective. An illustration of the point spread function of the light at the focus is also illustrated.

by [110]

$$F_g = mg = \Delta\rho\pi g \frac{W^2}{4} \left(L + \frac{2}{3}W \right). \quad (3.1)$$

Here $\Delta\rho$ is the mass density difference between the particle and the solvent. In the case of $\rho_{\text{particle}} - \rho_{\text{solvent}} > 0$, a larger rod will feel a greater gravitational force. If we consider the position of a rod under gravity within an optical trap close to a wall, we can identify two limiting cases, corresponding to either the optical forces or gravity dominating. When the optical forces dominate, a rod will maximise its overlap with the laser beam by aligning with the optical axis in a vertical configuration as shown in figure 3.2a. However, when gravity dominates, a particle will be confined to the plane next to the glass surface and be forced into a horizontal configuration as shown in figure 3.2b. Note that the rod is still drawn into the centre of the optical trap in the xy -plane but is unable to lie in the centre of the trap in the z direction. The gravitational potential energy difference between these states is $F_g\Delta h = F_gL/2$, and is therefore dependent on the particle size.

3.2.2 Friction of a rod

In a viscous fluid the motion of a rod is far more complex than that of a sphere due to its shape anisotropy. This anisotropy results in two possible modes of translational motion corresponding to parallel or perpendicular motion with respect to the long axis of the rod. The friction coefficient perpendicular to the rod's major axis is [111]

$$\zeta_{\perp} = \frac{4\pi\eta L}{(\sigma - \gamma_{\perp})}, \quad (3.2)$$

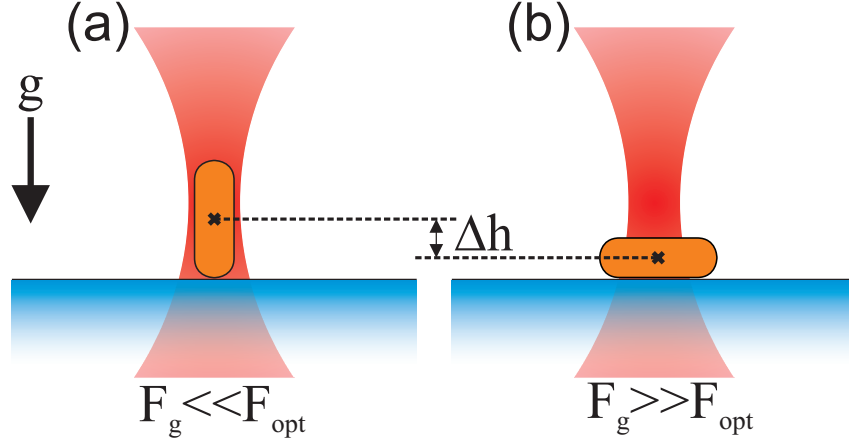


Figure 3.2: Schematic of a rod in an optical trap where $L \approx 4 \mu\text{m}$ and $w_0 1.58 \mu\text{m}$. (a) A rod is trapped vertically in the case where the optical forces dominate. (b) When gravity is the dominant force, a rod is trapped horizontally, where it minimises its gravitational potential energy. Δh shows the difference in height for the centre of mass of the rod. Note that in this system the height of the beam waist above the surface is not known.

where η is the viscosity of the solvent and $\sigma = \ln(2L/W)$. The value of $\gamma_{\perp} \approx 1$ is found to vary slightly amongst different theories but accounts for end-effects of a finite length rod as it translates and is obtained as a power series in $1/\sigma$ [112]. The friction coefficient for a rod moving collinear with the major axis is

$$\zeta_{\parallel} = \frac{2\pi\eta L}{(\sigma - \gamma_{\parallel})}, \quad (3.3)$$

where $\gamma_{\parallel} \approx -0.1$ and has the same origin as $\gamma_{\perp}$. It is worth noting from equations 3.2 and 3.3, that $\zeta_{\perp} > \zeta_{\parallel}$. As such, a rod will reduce the viscous drag it feels by aligning its long axis with the direction of solvent flow which is observed experimentally.

When a rod is brought close to a wall these expressions are no longer strictly valid as a wall restricts rod rotation and translation. Simulations have been carried out to study the behaviour of a rod in close proximity to a wall [113]. The extent to which a wall affects rod motion is dependent on the relative angle of a rod, however, by assuming that the normal vector of the wall is perpendicular to the long axis of the rod, as shown in figure 3.2b, the parallel friction coefficient $\zeta_{\parallel}$ can be approximated by

$$\zeta_{\parallel}(z) \approx \zeta_{\parallel}^B \left[1 + 0.1015 \frac{W}{z} \right], \quad (3.4)$$

where $\zeta_{\parallel}(z)$ is now dependent on z , the distance between the rod and the wall. $\zeta_{\parallel}^B$ is the bulk parallel friction coefficient. When a rod is driven through an optical landscape it remains

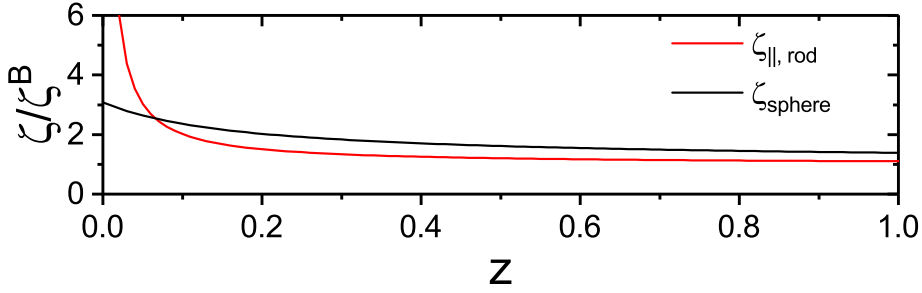


Figure 3.3: A plot of the normalised friction coefficient of a colloidal sphere and a colloidal rod as a function of distance from a flat wall, z . Here sphere radius and rod width are assumed to be equal. The bulk friction coefficient is denoted as ζ^B .

horizontal throughout experiments and motion is in the direction of the long axis so this is the only contribution that needs to be considered. In figure 3.3 the distance dependence of the friction coefficients for a sphere (equation 2.19) and a rod (equation 3.4) are shown. Here z is normalised by sphere radius and rod width, and at short distances the friction coefficient for a rod has a larger dependence on its proximity to the wall than for a sphere.

3.2.3 Motion of a colloidal rod in an optical potential energy landscape

In section 2.1.3 the Langevin equation was introduced to describe the motion of a particle:

$$\zeta \frac{dx}{dt} = F_{ext} + \xi(t), \quad (3.5)$$

where ζ is the friction coefficient and is here assumed to be constant, dx/dt is the velocity, F_{ext} describes external forces applied to the particle and $\xi(t)$ is a term to describe Brownian noise. For a colloidal particle in an optical potential energy landscape and driven by a constant driving force, F_{DC} , the Langevin equation takes the following form:

$$\zeta \frac{dx}{dt} = F_{DC} + F_{opt}(x) + \xi(t). \quad (3.6)$$

Here F_{opt} is the force due to the optical landscape. The notation here is such that ‘DC’ corresponds to a time-independent driving force and is used for an intuitive interpretation due to its analogy with a DC electric field.

In one dimension there is no difference between a sphere and a rod and the only distinction is the particle length scale. This length scale is simply the radius for a sphere, and for a rod

the equivalent length scale, assuming motion parallel to the long axis, is the rod length, L . For small trap spacings, a line of optical traps produces an optical landscape with the form (equation 2.31) [9, 47]

$$F_{opt}(x) = -\frac{2(2\pi V_0)^{3/2}}{\lambda^2 k^{1/2}} \exp\left(-\frac{2\pi^2 V_0}{\lambda^2 k}\right) \sin\left(\frac{2\pi x}{\lambda}\right), \quad (3.7)$$

where V_0 denotes the trap depth of each contributing optical trap, k is the associated trap stiffness, and λ denotes the trap spacing, which corresponds to the wavelength of the optical landscape.

The critical force of a particle in this type of potential energy landscape is considered following the work of Juniper [59]. As a particle is driven, the maximum opposing force is the point at which there is the largest barrier to forwards motion. This corresponds to when $dF_{opt}/dx = 0$ and $d^2F_{opt}/dx^2 > 0$, which for equation 3.7 occurs at $x^* = \lambda/4 \pm n\lambda$ (where $n = 0, \pm 1, \pm 2, \dots$). At this point the optical force is

$$F_{opt}(x^*) = -\frac{2(2\pi V_0)^{3/2}}{\lambda^2 k^{1/2}} \exp\left(-\frac{2\pi^2 V_0}{\lambda^2 k}\right), \quad (3.8)$$

hence the critical force is found to be

$$F_C = -F_{opt}(x^*) = \frac{2(2\pi V_0)^{3/2}}{\lambda^2 k^{1/2}} \exp\left(-\frac{2\pi^2 V_0}{\lambda^2 k}\right). \quad (3.9)$$

By combining equation 3.7 and 3.9, the following expression for F_{opt} is obtained:

$$F_{opt} = -F_C \sin\left(\frac{2\pi x}{\lambda}\right). \quad (3.10)$$

The assumption that a rod and a sphere will experience the same optical potential is tested throughout this chapter.

3.2.4 Subcritical driving

When driven below the critical driving force a particle is confined to a single optical trap and its average velocity, v_{AV} , is zero. However, the particle does not simply remain in the centre of an optical landscape minimum. The displacement from this minimum, Δ_r , is shown schematically

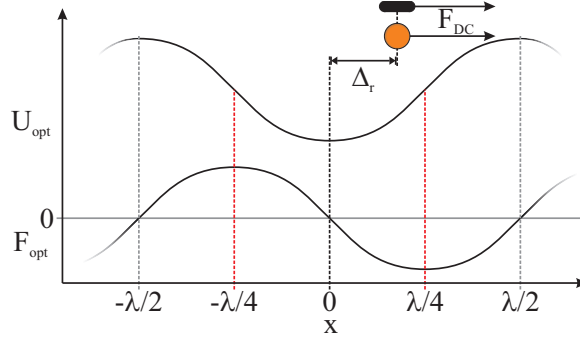


Figure 3.4: A schematic showing the optical potential energy landscape and the optical force landscape experienced by a rod or sphere. If F_{DC} is below the critical force then the particle is confined to a single minimum ($x = 0$) with an average displacement from that minimum equal to Δ_r .

in figure 3.4 and can be found by considering the force balance with $F_{DC} = -F_{opt}$ which can be written as

$$F_{DC} = F_C \sin\left(\frac{2\pi x}{\lambda}\right). \quad (3.11)$$

For a driving velocity $v_{DC} = F_{DC}/\zeta$, this equilibrium displacement, $\langle x(v_{DC}) \rangle \equiv \Delta_r(v_{DC})$, is found as

$$\Delta_r = \frac{\lambda}{2\pi} \arcsin\left(\frac{\zeta v_{DC}}{F_C}\right). \quad (3.12)$$

This distance can be directly calculated if $\zeta \neq \zeta(\Delta_r)$. However, in a regime where $\zeta = \zeta(\Delta_r)$ due to close proximity to a wall, as discussed in section 3.2.2, then this dependence can be probed by using the following relation:

$$\frac{\zeta}{F_C} = \frac{1}{v_{DC}} \sin\left(\frac{2\pi \Delta_r}{\lambda}\right), \quad (3.13)$$

which quantifies the friction coefficient as a function of distance from the centre of an optical trap.

3.2.5 Supercritical driving

The motion of a particle across this type of landscape is now considered when driven at $F_{DC} > F_C$ [9]. To this end the Langevin equation stated in equation 3.6 is rewritten as

$$\frac{dx}{dt} = \frac{F_{DC}}{\zeta} + \frac{F_{opt}(x)}{\zeta}, \quad (3.14)$$

where thermal noise is neglected. To find the average velocity, equation 3.14 is integrated over a single wavelength, λ , to find the time taken for a particle to move this distance:

$$\Delta t = \int_{t(x=0)}^{t(x=\lambda)} dt = \int_0^\lambda \frac{\zeta}{F_{\text{DC}} + F_{\text{opt}}(x)} dx = \int_0^\lambda \frac{\zeta}{F_{\text{DC}} - F_{\text{C}} \sin(2\pi x/\lambda)} dx, \quad (3.15)$$

which is solved to give

$$\Delta t = \frac{\lambda \zeta}{\sqrt{F_{\text{DC}}^2 - F_{\text{C}}^2}}. \quad (3.16)$$

The average particle velocity, v_{AV} then follows as

$$v_{\text{AV}} = \frac{\Delta x}{\Delta t} = \frac{\lambda}{\left(\lambda \zeta / \sqrt{F_{\text{DC}}^2 - F_{\text{C}}^2}\right)} = \frac{1}{\zeta} \sqrt{F_{\text{DC}}^2 - F_{\text{C}}^2}. \quad (3.17)$$

This is only defined for driving forces above the critical force and can be summarised as

$$v_{\text{AV}} = \begin{cases} 0, & F_{\text{DC}} \leq F_{\text{C}} \\ \frac{1}{\zeta} \sqrt{F_{\text{DC}}^2 - F_{\text{C}}^2}, & F_{\text{DC}} > F_{\text{C}}. \end{cases} \quad (3.18)$$

3.2.6 Modulated driving force

A time-dependency is now introduced such that the driving force is the sum of a constant and a modulated force contribution;

$$F_{\text{drive}} = F_{\text{DC}} + F_{\text{AC}} \sin(2\pi \nu t), \quad (3.19)$$

where ν is the frequency of oscillations and t is the time. F_{AC} quantifies the magnitude of the oscillations and in the limit of $F_{\text{AC}} = 0$ we reach the constant driving force regime. Here the notation ‘AC’ is used to correspond to the time-dependent contribution to the driving force due to its analogy with an AC electric field. The driving force from equation 3.19 leads to a Langevin equation of

$$\zeta v(x, t) = \zeta \frac{dx(t)}{dt} = F_{\text{DC}} + F_{\text{AC}} \sin(2\pi \nu t) - F_{\text{C}} \sin\left(\frac{2\pi x}{\lambda}\right) + \xi(t). \quad (3.20)$$

This is not directly soluble but has been studied in great detail due to its rich dynamics and direct application to condensed matter physics [47]. In particular, under certain conditions, synchronisation can be observed which manifests itself as ‘dynamic mode locking’ [47, 87].

Dynamic mode locking

A particle crossing a periodic landscape with a known average velocity, v_{AV} , can be described as an oscillator with a frequency

$$\nu_p = \frac{v_{AV}}{\lambda}. \quad (3.21)$$

When this frequency couples with an externally imposed oscillation, synchronisation may occur (as shown in figure 1.1) [65]. If the frequencies are labelled such that the particle has a frequency ν_p and the externally imposed oscillations have frequency ν then the expected synchronisation regime is given by

$$\nu_p \approx n\nu, \quad (3.22)$$

where n is an integer. The external frequency ν is fixed, but ν_p can vary slightly under the correct conditions. This means that when equation 3.22 is satisfied, ν_p ‘locks’ to ν such that

$$\nu_p = n\nu, \quad (3.23)$$

which can be combined with equation 3.21 to obtain the average particle velocity at dynamic mode locking:

$$v_{AV} = n\lambda\nu. \quad (3.24)$$

The range of $\Delta\nu = \nu - \nu_p$ over which synchronisation is observed depends sensitively on the coupling strength between the oscillators.

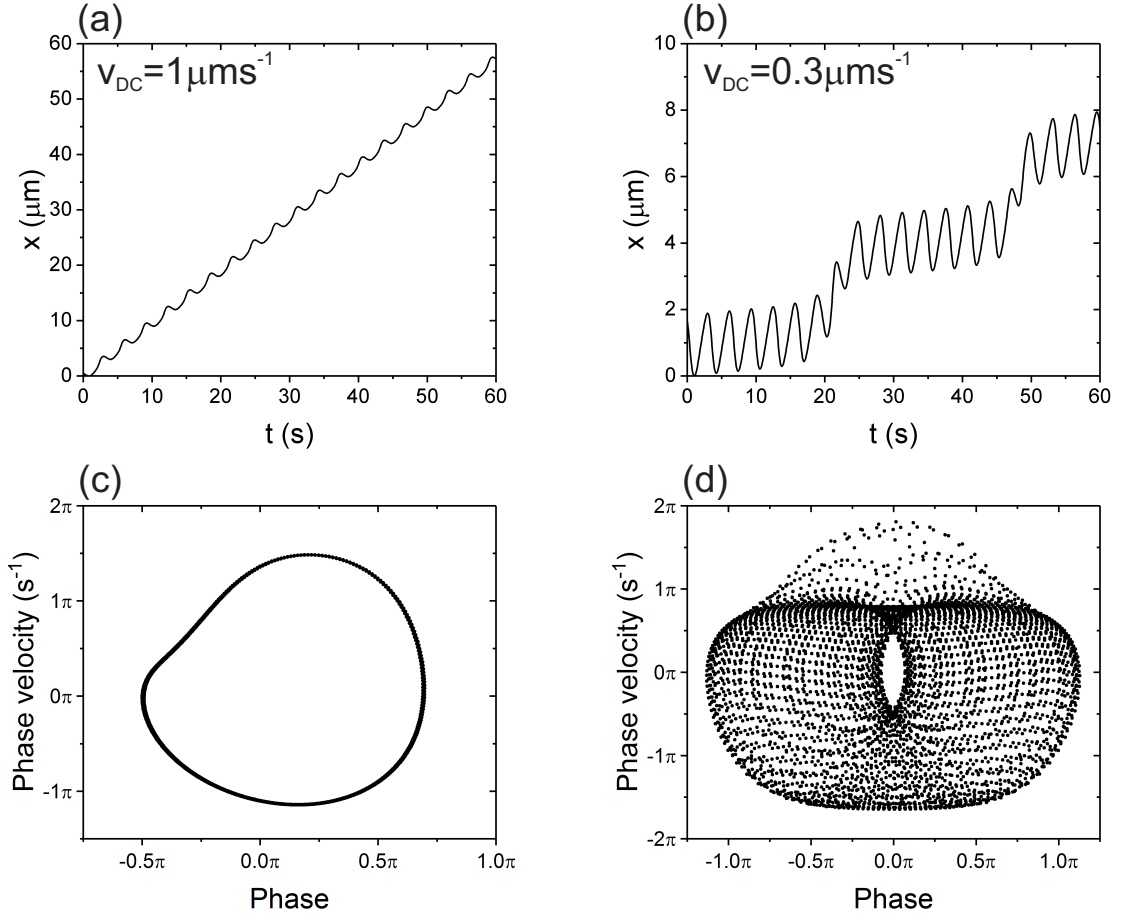


Figure 3.5: (a) Numerical mode locked trajectory from the deterministic Langevin equation (equation 3.20). (b) Numerical trajectory that is not mode locked. (c) Phase portrait of the trajectory shown in (a). (d) Phase portrait of the trajectory shown in (b). For these simulations, the parameters used are $\lambda = 3.0 \mu\text{m}$, $\nu = \pi\text{Hz}$, $v_C = 1 \mu\text{m s}^{-1}$, $v_{AC} = F_{AC}/\zeta = 2 \mu\text{m s}^{-1}$. The amplitude of both the phase and the phase velocity is sensitive to the exact experimental conditions.

Phase portraits

One form of illustrating synchronisation is with a Lissajous curve. In the context of a particle traversing an optical landscape, this takes the form of a phase portrait using the ‘phase’ given by

$$\varphi = \frac{2\pi}{\lambda} (x(t) - v_{AV}t), \quad (3.25)$$

and the ‘phase velocity’, which is simply the time derivative of the phase:

$$\frac{d\varphi}{dt} = \frac{2\pi}{\lambda} (v(t) - v_{AV}). \quad (3.26)$$

By plotting phase velocity as a function of phase, a phase portrait is obtained that will form a closed loop in the case of synchronisation as shown for a numerically generated particle trajectory in figure 3.5c. If no synchronisation is seen then the phase portrait will become quasi-periodic and lead to an open loop as illustrated in figure 3.5d.

3.3 Experimental methods

3.3.1 Colloidal model system

The colloidal model system used consists of silica rods dispersed in deionised water (see section 2.2.1) in a quartz glass Hellma cell. The system is sufficiently dilute to ensure that there is only a single particle in the field of view at any time. Rods vary in length and width, but typically rods are chosen to have $L \approx 4 \mu\text{m}$ and $W \approx 0.5 \mu\text{m}$ so that the rods can be imaged and optically manipulated.

Colloidal spheres are also used as a reference and these are Dynabeads M-270 Carboxylic Acid that have a diameter of $3 \mu\text{m}$ when dispersed in 20% EtOH(aq) (see section 2.2.1) in a quartz glass Hellma cell.

3.3.2 Equilibrium trap measurements

A thermal equilibrium method is used to find the stiffness constant of an optical trap by taking a long time series of a Brownian particle held by an optical trap close to a wall [40]. The images obtained are then analysed to give a probability distribution of the displacement of the particle from the trap centre. This is used to obtain a potential energy curve using $P(x) \propto \exp(-U(x)/k_{\text{B}}T)$. To achieve this a colloidal rod is trapped and imaged at 10 fps for 30 min. The optical trap used here has a laser intensity of 80 mW which was chosen to allow stable optical trapping of a rod in both the horizontal and vertical configurations. At higher laser powers, only the vertical configuration is seen while at lower laser powers, a rod cannot be confined within the optical trap.

The images of the rods are analysed to obtain the rod orientation. To this end, the particles are located using an initial binarisation with an ellipsoid fitted to the resulting image. The centre

of mass is found at the centre of the ellipsoid and vertical and horizontal rods are separated using the projected rod length. A rod is categorised as horizontal if the projected rod length is greater than $1.5\text{ }\mu\text{m}$ and vertical otherwise. This crude separation works well due to the fact that a rod spends almost all of its time either in a fully horizontal or vertical orientation.

3.3.3 Average velocity measurements

As a rod is driven through an optical landscape it is imaged at 10 fps. The rod is tracked to give $x(t)$ from which $v(t)$ and $v(x)$ can subsequently be determined. The optical landscape is made up of 12 optical traps with a spacing of $\lambda = 6\text{ }\mu\text{m}$ and a total laser intensity of $I_0 = 960\text{ mW}$. This results in the same laser intensity per trap as is used for single trap measurements. In experiments where the sample is subject to a driving velocity, $v_{\text{DC}} \leq 12\text{ }\mu\text{m s}^{-1}$, a rod is always in a horizontal configuration and if it moves into a vertical configuration the experiment is restarted because in this configuration the particle cannot pass through the landscape due to its greatly enhanced trap stiffness. A rod is driven using a constant driving force and subsequently with a modulated driving force according to equation 3.20. The magnitude of the oscillations used is $F_{\text{AC}}/\zeta = v_{\text{AC}} = 5.2\text{ }\mu\text{m s}^{-1}$ with an associated frequency of $\nu = 0.5\text{ Hz}$.

To enable a direct comparison, a sphere is driven with a constant driving velocity, $v_{\text{DC}} < v_{\text{C}}$, across an optical landscape consisting of 46 optical traps with a spacing of $\lambda = 4\text{ }\mu\text{m}$ and $I_0 = 350\text{ W}$. These experimental parameters lead to critical velocities with the same order of magnitude for both the rod ($v_{\text{C}} = 3.8\text{ }\mu\text{m s}^{-1}$) and the sphere ($v_{\text{C}} = 2.8\text{ }\mu\text{m s}^{-1}$).

3.4 Results and discussion

3.4.1 Equilibrium trapping of colloidal rods in a single optical trap

In this section, the trapping behaviour of a single rod in a single optical trap is characterised. An optically trapped colloidal rod close to a wall exhibits two ‘metastable’ trapping configurations, horizontal and vertical, which are shown in figure 3.6a–c. A schematic showing the relative stability of these configurations is shown in figure 3.6d and is such that a horizontal rod may overcome the effects of gravity and the scattering forces to leave it in a vertical configuration where it will remain. It is not possible to experimentally measure $U(\theta)$ using the technique

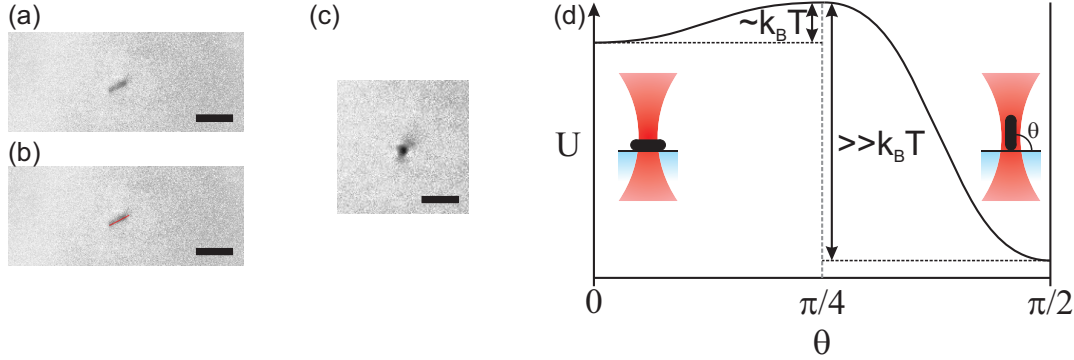


Figure 3.6: (a) Microscope image of a horizontal rod imaged from below, which is tracked in (b) with the rod's major axis shown in red. (c) Microscope image of a vertical rod. This appears roughly spherical as it is viewed from below with some distortion due to optical effects. Scale bars are 5 μm . (d) Schematic plot of potential energy as a function of the angle between the rod and the wall, θ .

described in section 3.3.2 due to the irreversibility of the transition from a horizontal to a vertical configuration. The transition from a horizontal to a vertical configuration is more prevalent for smaller rods where the effects of gravity and scattering are reduced so that the activation energy required to switch configurations is reduced.

A comparison between the optical potentials of the vertical and horizontal states is shown in figure 3.7a. Both states exhibit a parabolic optical potential energy landscape centered at the focus of the optical trap but clearly exhibit a differing trap stiffness. The fact that a vertical rod exhibits a parabolic optical potential energy landscape is expected, as it has a circular cross section, the same as for a sphere. A horizontal rod, however, has an anisotropic cross section, yet a parabolic potential energy curve is found when the particle is isolated in an optical trap. This is due to the fact that the rod can freely rotate in the xy -plane, meaning that on average it has a circular cross section similarly to a sphere. Assuming a harmonic potential (equation 2.23), a spring constant is extracted and is found to be seven times higher for the vertical rod than for the horizontal rod ($k_{\text{vertical}} = 3.7 \times 10^{-6} \text{ kg s}^{-2}$, $k_{\text{horizontal}} = 5.5 \times 10^{-7} \text{ kg s}^{-2}$). This is attributed to the fact that in the vertical state, there is a larger overlap between the particle and laser light, so it experiences a stronger optical force, leading to an increased trap stiffness.

3.4.2 Driven colloidal rods in optical potential energy landscapes

Next, we consider the behaviour of a colloidal rod in a more complex optical potential energy landscape composed of multiple equally spaced optical traps. First, the optical potential energy landscape is characterised by driving a rod well above the critical velocity and tracking the

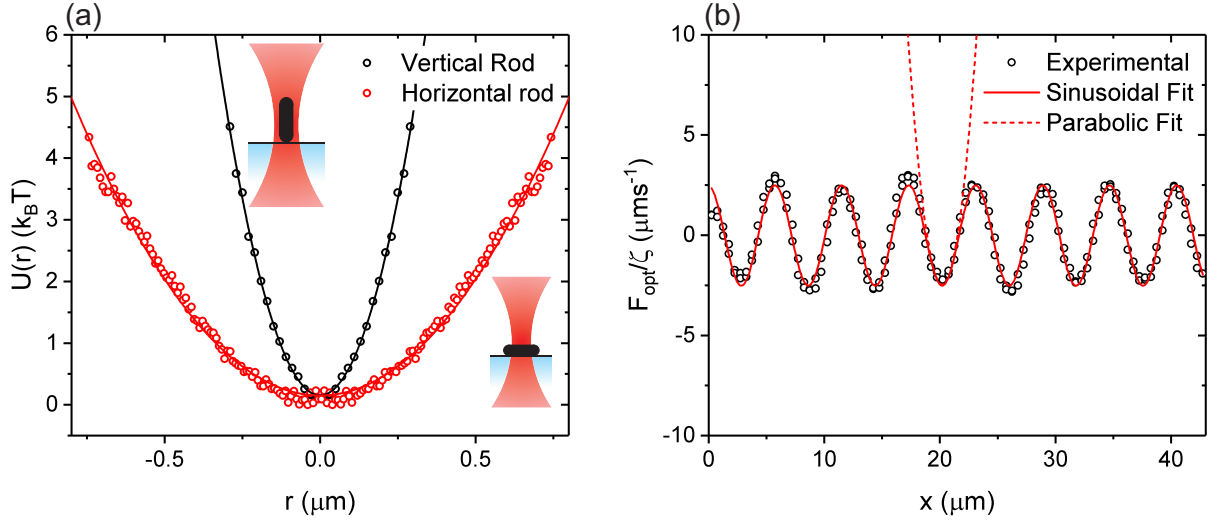


Figure 3.7: (a) A comparison of the optical potential experienced by a horizontal (red) and vertical (black) rod confined by a single optical trap. Experimental data is shown by points. Solid lines show a parabolic fit to both sets of data, from which the trapping stiffness can be extracted. This data is shown for a single rod, averaged over time. (b) The sinusoidal potential energy surface experienced by a rod driven through a line of optical traps with a spacing of $6 \mu m$. A parabolic fit is also shown for one potential well and close to the minima gives a good description of the true optical landscape.

observed velocity, from which F_{opt}/ζ can be calculated using equation 3.14 [47]. The resulting optical force is plotted as a function of position in figure 3.7b and is clearly sinusoidal as is seen for a sphere [114]. Potential minima are regularly spaced by a distance of $\lambda = 6 \mu m$, which is the spacing of optical traps as described in section 3.2.3.

Subcritical driving

A particle driven below the critical velocity, $v_{DC} < v_C$, will remain confined to a single optical trap. In this regime, the average particle velocity is $v_{AV} = 0$ but information can be gained about the friction coefficient of a particle, ζ , by plotting the average displacement from the centre of a trap as a function of the driving velocity as is shown in figure 3.8a. Here the results obtained for a sphere are also shown for comparison. The particle displacement, Δ_r , increases with the driving velocity for both a sphere and a rod as the particle can translate further from a landscape minimum before equilibrium is reached at $F_{DC} = -F_{opt}$. A sphere shows an increase in Δ_r as driving velocity is increased, and diverges as v_{DC} tends towards v_C . This behaviour is well described by equation 3.12, which is also plotted. Conversely, the value of Δ_r for a rod reaches a plateau as v_{DC} approaches v_C . This suggests that the friction coefficient of a rod is not simply a constant, but instead that $\zeta = \zeta(\Delta_r)$. This can be probed by noting that the

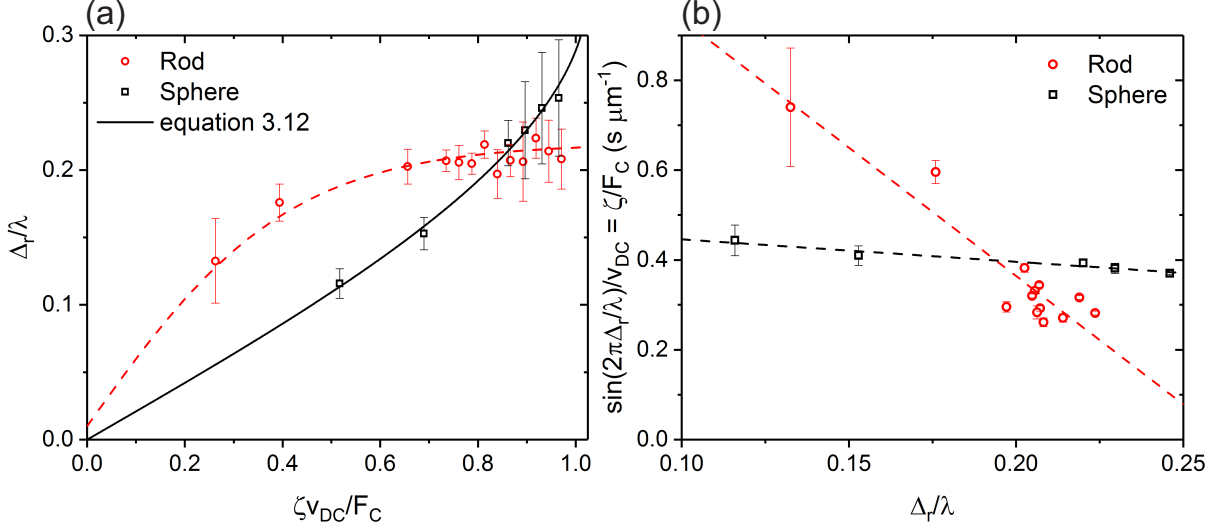


Figure 3.8: (a) A plot showing the driving velocity dependence of the equilibrium distance of a particle from the centre of an optical trap. For a sphere (black points) a fit to eq. 3.12 is shown (black line). For a rod (red points) the behaviour deviates from eq. 3.12 and the dashed red line simply acts as a guide to the eye. (b) A plot of the friction coefficient as calculated from equation 3.13 against distance from the centre of an optical trap. The dashed lines are guides to the eye. Note that only a horizontal rod is probed here.

right hand side of equation 3.13 can be calculated and is directly proportional to the friction coefficient, ζ :

$$\frac{\zeta}{F_C} = \frac{1}{v_{DC}} \sin\left(\frac{2\pi\Delta_r}{\lambda}\right).$$

As F_C is a feature of the optical landscape and constant, equation 3.13 can now be used to plot the change of the friction coefficient as a function of Δ_r as is shown for a rod and a sphere in figure 3.8b. The friction coefficient of the rod is highly dependent on its displacement from the centre of an optical trap, Δ_r . As the rod moves further from a minimum of the optical landscape, the friction coefficient reduces by a significant amount. We also note that the friction coefficient of the sphere is influenced by its proximity to an optical trap but to a far lesser extent than for the rod.

The friction coefficients of a sphere and a rod are influenced by the presence of a wall (equations 2.19 and 3.4) and this effect is enhanced when a particle is subject to scattering forces from an optical trap. The scattering forces (see section 2.1.4) act to push the particle towards the surface and therefore increase the interactions between the particle and the surface. The rods used here have a larger equilibrium distance from the wall than a sphere in the absence of an optical trap due to an increased gravitational height, l_g (tables 2.1 and 2.2). This means

that in the presence of an optical trap the reduction in distance between the rod and wall is greater than the equivalent reduction in distance for a sphere. This combined with a higher dependence on proximity to a wall for a rod as shown in figure 3.3 leads to a larger increase of the friction coefficient for a rod in the presence of an optical trap. Here a quantitative analysis of ζ is not possible due to a lack of information about the absolute distance between the particle and the wall.

Supercritical driving

A rod becomes mobile when driven through an optical landscape at velocities above the critical velocity, $v_{DC} > v_C$. By tracking the particle motion, trajectories are obtained such as those shown in figure 3.9a for four different driving velocities. For the lowest driving velocity shown, $v_{DC} = 2.5 \mu\text{m s}^{-1}$, the particle is below the critical velocity and is therefore confined to a single minimum in the optical landscape and does not deviate from $x = 0$ other than small fluctuations due to Brownian noise. As the driving velocity is increased to $v_{DC} = 4.0 \mu\text{m s}^{-1}$, the particle is able to escape the initial minimum in the optical landscape and travels a finite distance. As the driving velocity further increases to $v_{DC} = 5.0 \mu\text{m s}^{-1}$ and $v_{DC} = 8.0 \mu\text{m s}^{-1}$, so does the gradient of the trajectory, indicating a higher average particle velocity. In addition, there is evidence of the optical landscape in the trajectories, as there is a noticeable drop in the velocity of a rod at intervals of $6 \mu\text{m}$, corresponding to the wavelength of the optical landscape. At higher driving velocities, the particle spends less time on average being confined to a single minimum in the optical landscape.

From these trajectories the average particle velocity is obtained using $v_{AV} = \Delta x / \Delta t$. In figure 3.9b the average velocity is plotted as a function of the driving velocity. Particles remain stationary below the critical velocity, after which they show an increase in the average velocity as the driving velocity increases. At high driving velocities the behaviour tends towards that seen in the absence of any optical landscape because $F_{DC} \gg F_{opt}$. The average velocity is fitted using equation 3.18, which shows good agreement with the measured average velocity. Deviations from this deterministic equation for v_{AV} are seen close to the critical velocity due to Brownian noise. This provides the particle with enough thermal energy to overcome the barrier to motion slightly below the critical velocity as calculated by equation 3.18 for the deterministic case [9, 115].

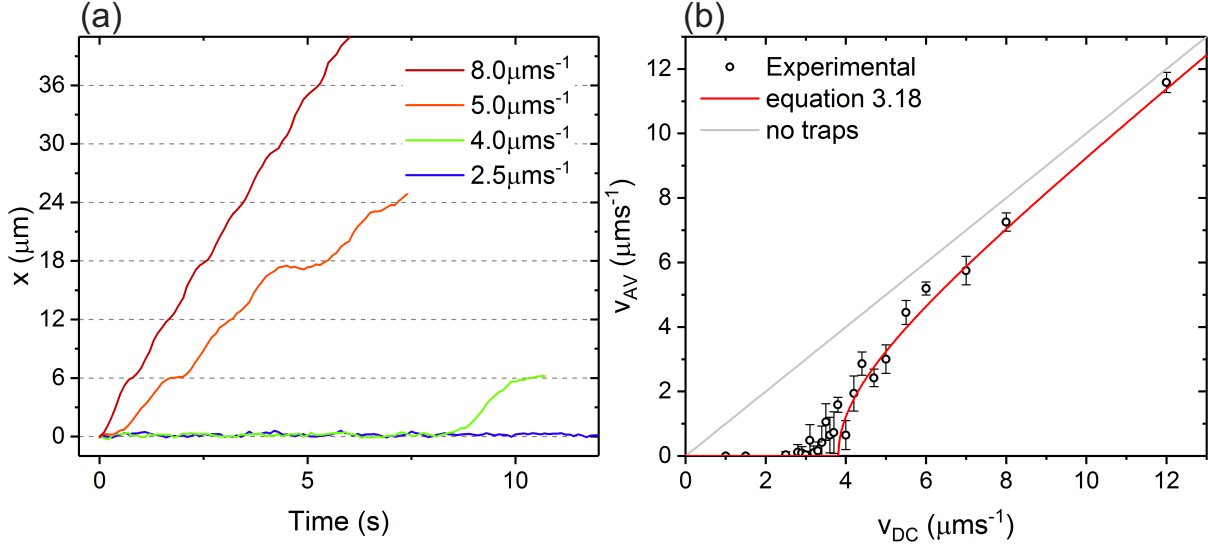


Figure 3.9: (a) Trajectories of a rod driven through an optical landscape, $\lambda = 6 \mu\text{m}$, at different driving velocities. (b) The average particle velocity plotted against the driving velocity. Experimental data (black circles) is fitted with equation 3.18 (red line). For reference, the behaviour expected in the absence of an optical landscape is shown (grey line) and shows $v_{AV} = v_{DC}$.

Modulated driving force

Next the motion of a rod driven by a more complex, time-dependent driving velocity (see section 3.2.6) over an optical landscape is described. Here the modulated component of the driving velocity has a magnitude $v_{AC} = 5.2 \mu\text{ms}^{-1}$, and a frequency $\nu = 0.5 \text{ Hz}$. Experimental trajectories of a rod are shown in figure 3.10a for three different average driving velocities. Each trajectory shows a clear signature of the oscillations in the driving velocity at $n \times t\nu$, where n is an integer. This is marked by the vertical dashed lines in figure 3.10a. For the lowest driving velocity shown here, $v_{DC} = 4.8 \mu\text{ms}^{-1}$, the particle exhibits some forward motion and moves the distance of $\Delta x = 2\lambda = 12 \mu\text{m}$ in the observed period. The imposed oscillations cause the particle to rock back and forth within a single minima before the particle escapes and passes to the next optical trap. As the driving velocity is increased to $v_{DC} = 8.0 \mu\text{ms}^{-1}$, a much more coherent motion is observed and within each period, the particle moves a distance of $\Delta x = \lambda$. This is highlighted in figure 3.10b for a single period and is termed the (1,0) mode to denote the fact that a particle moves forward one wavelength and has no backward motion per period [87]. At the highest driving velocity of $v_{DC} = 10.2 \mu\text{ms}^{-1}$, the particle is being driven at a high enough driving velocity to move $\Delta x = 2\lambda$ for each oscillation of the driving velocity. This causes the particle velocity to show a sharp rise as the particle begins to move out of the trap to which it is originally confined. It then slows as it passes into the first trap before the particle velocity

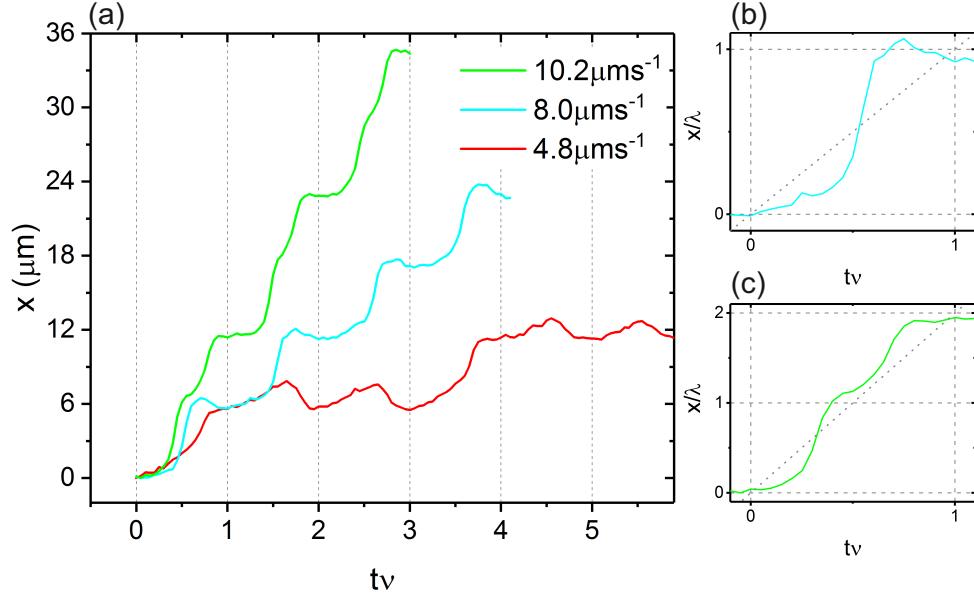


Figure 3.10: (a) An example of trajectories of a rod subject to an oscillating driving force where $\lambda = 6 \mu\text{m}$, $v_{AC} = 5.2 \mu\text{m s}^{-1}$ and $\nu = 0.5 \text{ Hz}$ for three different average driving velocities. Zoomed in trajectories are shown for (b) $8.0 \mu\text{m s}^{-1}$ and (c) $10.2 \mu\text{m s}^{-1}$ to highlight periodic motion of these trajectories.

increases again corresponding to the particle moving into the second trap. This motion is shown more clearly in figure 3.10c and corresponds to the $(2, 0)$ mode [87].

A plot of the average particle velocity as a function of the average driving velocity is shown in figure 3.11a. At a low average driving velocity, the average particle velocity is zero before an increase in average velocity above $v_{DC} \approx 4 \mu\text{m s}^{-1}$ is seen. The average particle velocity increases until $v_{DC} \approx 6.8 \mu\text{m s}^{-1}$, at which point the average particle velocity reaches a plateau until $v_{DC} \approx 8.8 \mu\text{m s}^{-1}$. Above this, the average particle velocity then steadily increases for measured values up to $v_{DC} = 10.2 \mu\text{m s}^{-1}$.

The trajectory for $v_{DC} = 8.0 \mu\text{m s}^{-1}$ in figure 3.10a already suggests the presence of dynamic mode locking and in this regime, the rod is expected to have an average velocity $v_{AV} = n\lambda\nu$, where n is an integer. This is initially seen at low driving velocities where $n = 0$, corresponding to $v_{AV} = 0$, and is termed the zeroth mode locked step. The first mode locked step is reached at $v_{DC} \approx 6.8 \mu\text{m s}^{-1}$, corresponding to $v_{AV} = \lambda\nu = 3 \mu\text{m s}^{-1}$. This physically corresponds to the particle travelling a distance equal to the wavelength (see figure 3.10b) of the optical landscape at a frequency identical to the externally imposed frequency, 0.5 Hz . As the driving velocity is further increased, it leaves the mode locked regime at $v_{DC} \approx 8.8 \mu\text{m s}^{-1}$ and again increases in

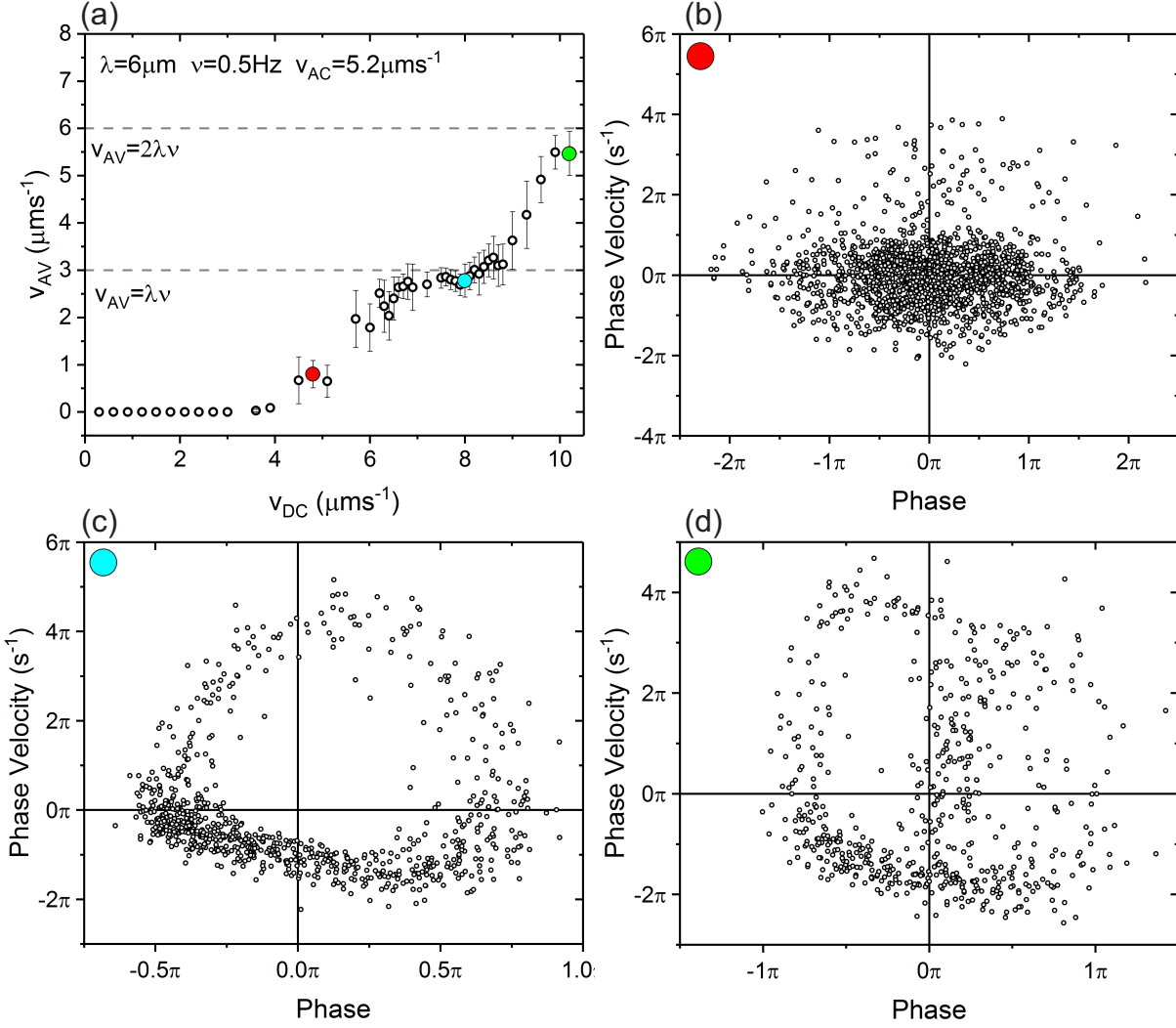


Figure 3.11: (a) The average particle velocity as a function of the average driving velocity in the presence of a modulated driving force. Experimental parameters are $\lambda = 6\mu\text{m}$, $\nu = 0.5\text{Hz}$, $v_{AC} = 5.2\mu\text{ms}^{-1}$. The dashed lines show the predicted average velocity of the mode locked steps. The phase portraits for (b) $4.8\mu\text{ms}^{-1}$, (c) $8.0\mu\text{ms}^{-1}$, and (d) $10.2\mu\text{ms}^{-1}$ are shown with the corresponding points in (a) highlighted by the filled data points.

average velocity where it approaches the average velocity predicted for the second mode locked step.

Another way to represent the periodic, mode locked motion is with the use of phase portraits (see section 3.2.6). In figure 3.11b-d the phase portraits associated with the coloured points in figure 3.11a are plotted, which also correspond to the trajectories shown in figure 3.10a. Figure 3.11b shows the phase portrait for $v_{AV} = 4.8\mu\text{ms}^{-1}$ where a particle is not dynamically mode locked. Here the phase portrait does not correspond to a closed loop as the particle does not exhibit synchronised motion. In contrast, figure 3.11c shows the phase portrait for $v_{AV} = 8.0\mu\text{ms}^{-1}$, which lies on the first mode locked step and clearly shows a closed loop, the

signature of dynamic mode locking. The closed nature denotes the periodic motion that corresponds to a particle translating to the neighbouring minimum each time the stage oscillates. This plot is formed from multiple trajectories, capturing a particle crossing 40 minima in the potential energy landscape while the stage oscillates. Each oscillation leads to a closed loop that, when overlaid, accentuates the predictable motion of the particle at this velocity. Figure 3.11d is the phase portrait for $v_{AV} = 10.2 \mu\text{m s}^{-1}$, which falls close to where the second mode locked step is expected. As this is not truly on a mode locked step, the noise greatly affects the phase portrait but the almost closed loop nature of the phase portrait gives evidence that this is the onset of the second mode locked step.

3.5 Conclusions

In this chapter the static and dynamic behaviour of colloidal rods in an optical potential energy landscape was studied. Initially the stable states of a single colloidal rod in a single optical trap close to a wall were explored. Here, two meta-stable states, corresponding to a horizontal or vertical rod were observed. A vertical rod was trapped more effectively than a horizontal rod with both experiencing a parabolic potential energy landscape. Next, the motion of a driven colloidal rod in a one-dimensional optical potential energy landscape was studied. The equilibrium position of a particle was investigated as it was driven below the critical velocity and confined to a single potential energy minimum of the optical landscape. The equilibrium position of a rod was found to vary substantially from that of a sphere due to the friction coefficient of a rod, which is highly dependent on its proximity to an optical trap. The driving velocity was then increased above the critical velocity to allow the particle to traverse the optical landscape. Here the average particle velocity increased as the square root of the driving velocity. Finally, oscillations were introduced to the driving velocity and rod trajectories were analysed. Dynamic mode locking was observed and the synchronised motion was characterised with the use of phase portraits.

Acknowledgments

This work was done in collaboration with Yongxiang Gao, James Spiers, Arthur Straube and Dirk Aarts. Louis Cortes and Arran Curran are thanked for useful discussions.

Chapter 4

Colloidal particles driven across an oscillating optical landscape

ABSTRACT

Colloidal particles are driven across a time-dependent one-dimensional optical potential energy landscape and particle motion is analysed. Different modes of dynamic mode locking are observed and are confirmed with the use of phase portraits. The effect of oscillation frequency on the mode locked step width is addressed and the results are discussed in light of a high frequency theory. Furthermore, the influence on mode locking of increasing the coupling between the particle and the optical landscape is probed, both by increasing the maximum depth of the optical landscape and also by only partially oscillating the optical landscape depth. Increased coupling is seen to increase the width of mode locked steps. Finally, transport across the time-dependent landscape is studied by measuring the effective diffusion coefficient of a mobile particle which is seen to be highly sensitive to the driving velocity and mode locking.

4.1 Introduction

Rough surfaces are inherent to everyday life, and on the macroscopic scale can range from tectonic plates [116] to the soles of running shoes [117]. Despite many surfaces seeming smooth, at the microscopic scale every surface has some level of roughness [118,119], which leads to phenomena that are often not obvious as an extension from the macroscopic world. Surface roughness gives rise to complex ad-atomic motion across a crystal surface [120,121], the creation of kinks and antikinks [122,123], and can act as a source of templated crystal growth [5,124]. At the microscopic scale, examples of rough surfaces appear in the form of sinusoidal potential energy landscapes in superconductors and have direct applications in Josephson junctions [14], vortex motion [13] and charge density waves [125]. These systems are inherently hard to image [126], making studying them challenging.

Creating a model system of colloidal particles in an optical potential energy landscape leads to a far more accessible system with increased control. Particle motion across random potential energy landscapes has led to observed subdiffusion [16,18,54,127–129], which can be controlled with surface roughness [18]. Exact particle motion has been shown to rely heavily on the form of the landscape and can give rise to freely diffusive as well as trapped particles [127]. Further to this, the study of colloidal particle transport across periodic potential energy surfaces has led to many interesting observations such as subdiffusion [6,10], superdiffusion [6,48,57,130], ballistic motion [48,131] and synchronisation [47,87]. Structured surfaces have also been created to achieve precise particle sorting [11,37] or directed transport [52,53].

On the colloidal scale, studies of time-dependent potential energy landscapes have exhibited rich dynamics such as accelerated motion with low dispersion [12,60] and a reduction in static friction [55] due to mode locking. Conversely, time-dependence can also cause enhanced diffusion [48,131,132] and, under the correct conditions, can lead to bidirectional particle transport [133]. Experiments carried out for large systems subject to a time-dependent optical potential energy landscape show that collective effects, such as kinks, can affect the dynamics [55]. Single particle behaviour in time-dependent potentials has also been probed theoretically in terms of velocity and diffusion [60], though experiments at the single particle level are lacking.

Here we drive colloidal particles through a time-dependent optical potential energy landscape and analyse trajectories to quantify the nature of transport. Synchronisation is exhibited

and can be directly observed in the form of phase portraits. We study the effect of the oscillation frequency as well as the effect of altering the coupling between the particle and the oscillating landscape on the synchronisation behaviour. This is achieved through changing the maximum depth of the optical potential energy landscape, and the extent to which it oscillates. We also characterise the efficiency of particle transport by analysing the effective diffusion coefficient whilst altering the driving velocity and the coupling between the particle and the oscillating landscape.

4.2 Theory

4.2.1 Langevin equation

Here the motion of a colloidal sphere when confined to a time-dependent one-dimensional optical potential energy landscape is discussed. As introduced in section 2.1.3, the motion of a Brownian particle in an external potential is described by the Langevin equation

$$\zeta \frac{dx}{dt} = F_{ext} + \xi(t), \quad (4.1)$$

where ζ is the friction coefficient and dx/dt is the velocity of the particle. F_{ext} describes all external forces that the particle is subject to, and $\xi(t)$ is an expression for the instantaneous forces that the particle feels due to Brownian noise. If a particle is driven with a constant force, F_{DC} , through an optical potential energy landscape then the external force can be expressed as

$$F_{ext} = F_{DC} + F_{opt}(x, t), \quad (4.2)$$

where F_{opt} is the force due to the optical landscape. In section 3.2.3, it was shown that a line of closely spaced optical traps leads to a static sinusoidal optical landscape, which has a resulting force that is given by equation 3.10:

$$F_{opt}(x) = -F_C \sin\left(\frac{2\pi x}{\lambda}\right). \quad (4.3)$$

Here F_C is the critical force of the optical landscape according to equation 3.9, and λ is the wavelength.

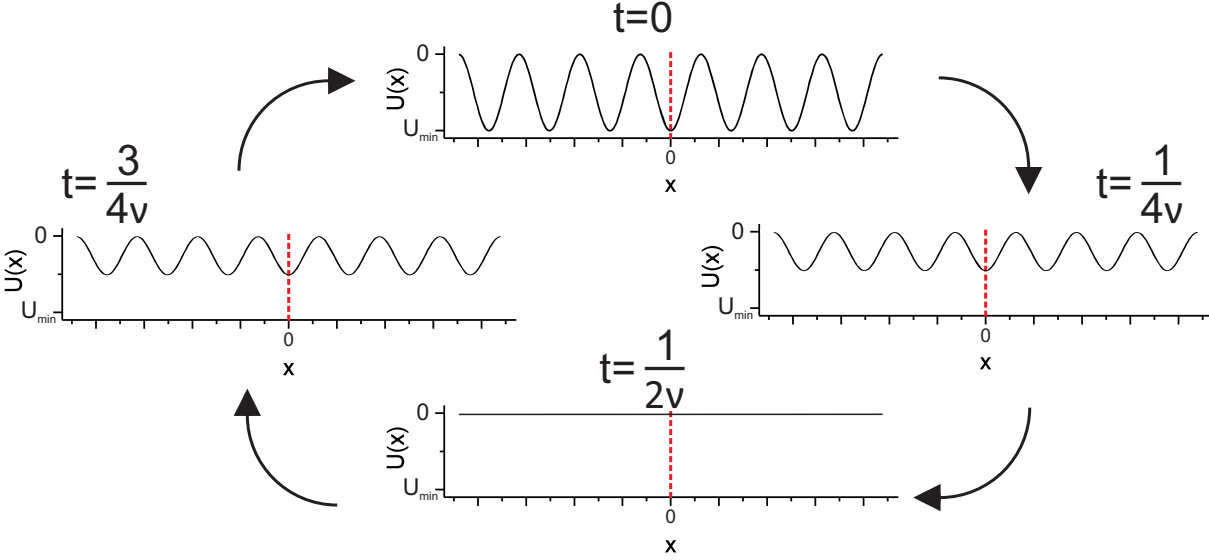


Figure 4.1: A schematic of the time-dependent optical potential described by equation 4.5.

Obviously, equation 4.3 corresponds to a time-independent optical landscape, but a time-dependent term can be introduced to give

$$F_{opt}(x, t) = -F_C \sin\left(\frac{2\pi x}{\lambda}\right) \times \frac{1}{2} (2 + \Delta_{osc} (\cos(2\pi\nu t) - 1)), \quad (4.4)$$

where ν is the frequency at which the amplitude of the optical landscape oscillates and $\Delta_{osc} \in [0, 1]$ denotes the extent to which the amplitude of the optical landscape varies with time. In the limit of $\Delta_{osc} = 0$, the time-independent regime is reached, however for the majority of this work, $\Delta_{osc} = 1$ is chosen, which corresponds to

$$F_{opt}(x, t) = -\frac{F_C}{2} \sin\left(\frac{2\pi x}{\lambda}\right) \times (1 + \cos(2\pi\nu t)). \quad (4.5)$$

Figure 4.1 shows a schematic of how this time-dependent term influences the nature of the optical landscape as time passes. Importantly, the time-dependent term is always positive meaning that the positions of the minima and maxima are stationary in space and do not interchange. At time $t = n/\nu$, for integer values of n , the depth of the potential is at its greatest and at time $t = 1/(2\nu) \pm n/\nu$, the optical potential is zero everywhere. The time averaged optical force corresponding to equation 4.5 is

$$\langle F_{opt}(x, t) \rangle = -\frac{F_C}{2} \sin\left(\frac{2\pi x}{\lambda}\right). \quad (4.6)$$

Now, the deterministic Langevin equation for the motion of a sphere in a time-dependent optical potential is obtained by combining equations 4.1, 4.2, and 4.5 and neglecting Brownian noise:

$$\zeta \frac{dx}{dt} = F_{\text{DC}} - \frac{F_{\text{C}}}{2} \sin\left(\frac{2\pi x}{\lambda}\right) (1 + \cos(2\pi\nu t)). \quad (4.7)$$

This can be written equivalently in terms of driving velocities using $\zeta v_i = F_i$:

$$\frac{dx}{dt} = v_{\text{DC}} - \frac{v_{\text{C}}}{2} \sin\left(\frac{2\pi x}{\lambda}\right) (1 + \cos(2\pi\nu t)). \quad (4.8)$$

In the case of a particle exhibiting mode locked motion, the average velocity over an integer number of oscillations is given by equation 3.24:

$$\left\langle \frac{dx}{dt} \right\rangle = n\lambda\nu, \quad (4.9)$$

where $\langle \dots \rangle$ denotes a time average and n is a positive integer. However, in the case of a particle not exhibiting mode locking but being close to a mode locked step, then the average velocity is

$$\left\langle \frac{dx}{dt} \right\rangle = n\lambda\nu + \delta v. \quad (4.10)$$

Here δv corresponds to a small velocity deviation from the velocity at the mode locked step.

As an ansatz for the particle position, we write

$$x(t) = n\lambda\nu t + \Delta x(t), \quad (4.11)$$

where the first term on the right hand side is the solution on a mode locked step for a given value of n and the second term, $\Delta x(t)$, denotes the deviation from the solution at step n . Taking the derivative of equation 4.11,

$$\frac{dx}{dt} = n\lambda\nu + \frac{d(\Delta x)}{dt}, \quad (4.12)$$

and combining equations 4.8, 4.11 and 4.12 leads to the full equation of motion:

$$\frac{d(\Delta x)}{dt} = v_{\text{DC}} - n\lambda\nu - \frac{v_{\text{C}}}{2} \sin\left(2\pi n\nu t + \frac{2\pi}{\lambda} \Delta x\right) (1 + \cos(2\pi\nu t)). \quad (4.13)$$

Note that the sine term is now written as a function of Δx using equation 4.11. Defining $\Delta v = v_{\text{DC}} - n\lambda\nu$ as the difference between the driving velocity and the mode locked step velocity gives

$$\frac{d(\Delta x)}{dt} = \Delta v - \frac{v_C}{2} \sin\left(2\pi n\nu t + \frac{2\pi}{\lambda}\Delta x\right) (1 + \cos(2\pi\nu t)). \quad (4.14)$$

4.2.2 High frequency regime

The time-dependent nature of the landscape leads to a particle trajectory that can be summarised as

$$\Delta x(t) = \overline{\Delta x} + \widetilde{\Delta x}, \quad (4.15)$$

where $\overline{\Delta x}$ denotes the linear component and $\widetilde{\Delta x}$ encompasses the oscillating, time-dependent component. In the limit of high frequency, $\nu \gg \nu_T$, where $\nu_T = v_C/\lambda$, we assume that this expression can be approximated by

$$\Delta x(t) \approx \overline{\Delta x}, \quad (4.16)$$

which holds at high frequencies, because the time-dependent term becomes insignificant, i.e. $|\overline{\Delta x}| \gg |\widetilde{\Delta x}|$, as $\widetilde{\Delta x} \propto 1/\nu$. Using the trigonometric identities

$$\sin(2\pi\nu nt) \cos(2\pi\nu t) = \frac{1}{2} [\sin((n+1)2\pi\nu t) + \sin((n-1)2\pi\nu t)],$$

$$\cos(2\pi\nu nt) \cos(2\pi\nu t) = \frac{1}{2} [\cos((n+1)2\pi\nu t) + \cos((n-1)2\pi\nu t)],$$

equations 4.14 and 4.16 can be combined:

$$\begin{aligned} \frac{d(\Delta x)}{dt} &\approx \frac{d(\overline{\Delta x})}{dt} \\ &= \Delta v - \frac{v_C}{2} \cos\left(\frac{2\pi}{\lambda}\Delta x\right) \left[\sin(2\pi\nu nt) + \frac{1}{2} \sin((n+1)2\pi\nu t) + \frac{1}{2} \sin((n-1)2\pi\nu t) \right] \\ &\quad - \frac{v_C}{2} \sin\left(\frac{2\pi}{\lambda}\Delta x\right) \left[\cos(2\pi\nu nt) + \frac{1}{2} \cos((n+1)2\pi\nu t) + \frac{1}{2} \cos((n-1)2\pi\nu t) \right]. \end{aligned} \quad (4.17)$$

This allows a closer analysis of average velocity at, or close to, a mode locked step in the time-dependent optical landscape, as n is varied.

Zeroth mode locked step: $n=0$

For $n = 0$, equation 4.17 reduces to

$$\frac{d(\Delta x)}{dt} = \Delta v - \frac{v_C}{2} \sin\left(\frac{2\pi}{\lambda} \Delta x\right) (1 + \cos(2\pi\nu t)), \quad (4.18)$$

and taking a time average of this expression over an integer number of oscillations leads to

$$\left\langle \frac{d(\Delta x)}{dt} \right\rangle = \Delta v - \frac{v_C}{2} \sin\left(\frac{2\pi}{\lambda} \Delta x\right), \quad (4.19)$$

which can be combined with equation 4.12 and $\Delta v = v_{DC} - n\lambda\nu$ for $n = 0$ to give the average velocity:

$$\left\langle \frac{dx}{dt} \right\rangle = \left\langle \frac{d(\Delta x)}{dt} \right\rangle = v_{DC} - \frac{v_C}{2} \sin\left(\frac{2\pi}{\lambda} \Delta x\right). \quad (4.20)$$

The step begins at $v_{DC} = 0$ and cannot be negative because only a positive driving velocity is considered. We now employ the same approach as used in section 3.2.5, and in particular equation 3.15, to obtain the average velocity on, or close to, the step where $n = 0$:

$$\left\langle \frac{dx}{dt} \right\rangle = v_{AV} = \begin{cases} 0, & 0 \leq v_{DC} \leq v_C/2 \\ \sqrt{v_{DC}^2 - (v_C/2)^2}, & v_{DC} > v_C/2. \end{cases} \quad (4.21)$$

This results in an average velocity of zero below $v_C/2$. As the driving velocity increases beyond this, the particle becomes mobile and exhibits a non-zero average velocity.

First mode locked step: $n=1$

For $n = 1$ the time average of equation 4.17 reduces to

$$\left\langle \frac{d(\Delta x)}{dt} \right\rangle = \Delta v - \frac{v_C}{4} \sin\left(\frac{2\pi}{\lambda} \Delta x\right), \quad (4.22)$$

which, when combined with equation 4.12 and $\Delta v = v_{\text{DC}} - n\lambda\nu$, leads to

$$\left\langle \frac{dx}{dt} \right\rangle = \left\langle \frac{d(\Delta x)}{dt} \right\rangle + \lambda\nu = v_{\text{DC}} - \frac{v_{\text{C}}}{4} \sin\left(\frac{2\pi}{\lambda} \Delta x\right). \quad (4.23)$$

This can be analysed to give a critical velocity as was done in equation 3.15, which gives rise to an average velocity at, or close to, the mode locked step where $n = 1$

$$\left\langle \frac{dx}{dt} \right\rangle = v_{\text{AV}} = \begin{cases} \lambda\nu, & |\Delta v| \leq v_{\text{C}}/4 \\ \lambda\nu \pm \sqrt{(\Delta v)^2 - (v_{\text{C}}/4)^2}, & |\Delta v| > v_{\text{C}}/4. \end{cases} \quad (4.24)$$

In this instance, $\Delta v = v_{\text{DC}} - \lambda\nu$ can take a positive or negative value. The critical points, denoting the limits of the mode locked step, are $v_{\text{DC}} = \lambda\nu \pm v_{\text{C}}/4$, which leads to a step width of $(\lambda\nu + v_{\text{C}}/4) - (\lambda\nu - v_{\text{C}}/4) = v_{\text{C}}/2$, the same as was found for the zeroth mode locked step.

Higher order mode locked steps: $n \geq 2$

For the case of $n \geq 2$, the time average of equation 4.17 is vastly simplified and only the first term remains:

$$\left\langle \frac{d(\Delta x)}{dt} \right\rangle = \Delta v. \quad (4.25)$$

When combined with equation 4.12, it is found that

$$\left\langle \frac{dx}{dt} \right\rangle = \Delta v + n\lambda\nu = v_{\text{DC}}, \quad (4.26)$$

which results in a step width of 0 for $n \geq 2$. This is very different to what is seen for a mode locked system with an oscillating driving force, as was studied in Chapter 3, and in [59,87] where mode locking steps have been experimentally observed for as high as $n = 6$.

The above information regarding mode locked steps can be summarised to predict the overall motion of a colloidal particle driven through a time-dependent optical potential energy landscape oscillating at a high frequency, as shown in figure 4.2. In the example shown, the critical velocity is defined as $v_{\text{C}} = \lambda\nu$. Both the zeroth and first steps have the same step width of $v_{\text{C}}/2$ and no higher order steps are seen.

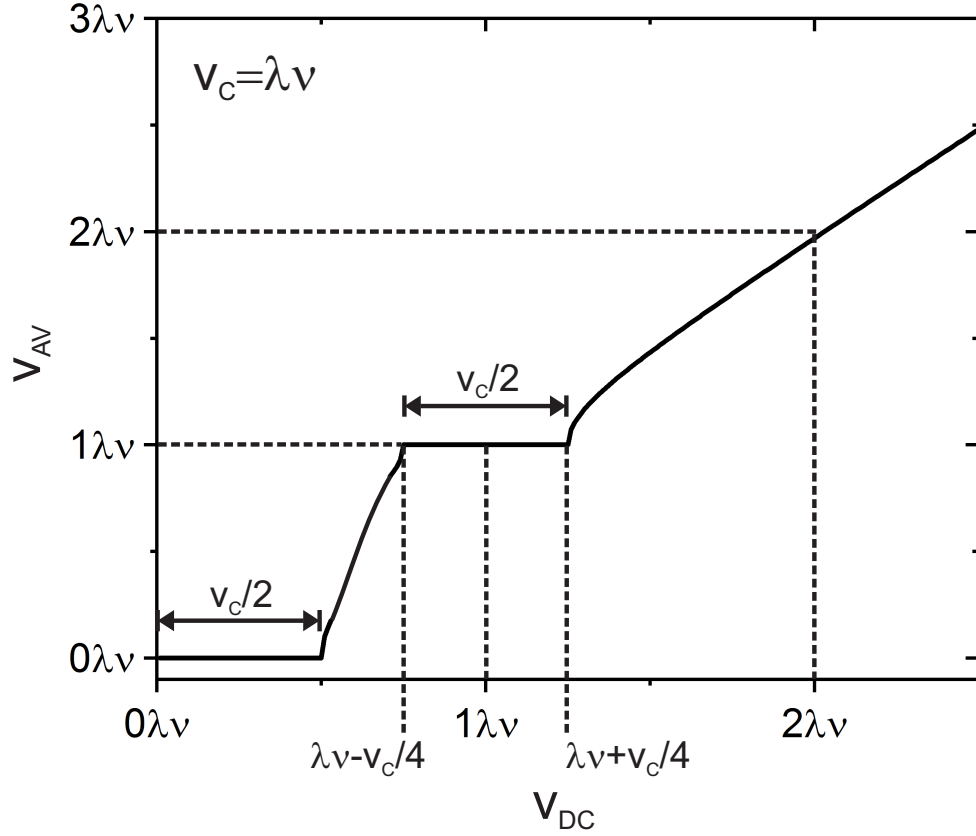


Figure 4.2: A schematic plot to summarise the predicted motion of a particle in a time-dependent optical potential energy landscape in the high frequency regime. Only the zeroth and first mode locked steps are observed.

High frequency validity

The high frequency assumption is only true if $\nu \gg \nu_T$, i.e. when the internal and external timescales are separated. Even though in this chapter no experiments fall into this limit, we use it as a reference for experimental results.

4.2.3 Effective diffusion coefficient

In a driven system, the mobility of a particle can also be probed by measuring an effective diffusion coefficient, D_{eff} , which is calculated by analysing the effective mean squared displacement, MSD_{eff} , of a particle. This is calculated in a similar fashion to the MSD for a Brownian particle, described in section 2.1, but now accounting for the driving of the system with an adjusted

second term:

$$\text{MSD}_{eff} = \left\langle [x(\Delta t) - \langle x(\Delta t) \rangle]^2 \right\rangle = 2dD_{eff}\Delta t, \quad (4.27)$$

where d is the dimensionality and Δt is the lag time. Both sets of angled brackets denote a time average. This can be rearranged to give the one-dimensional effective diffusion coefficient

$$D_{eff} = \lim_{t \rightarrow \infty} \frac{1}{2} \frac{d}{d\Delta t} \left\langle [x(\Delta t) - \langle x(\Delta t) \rangle]^2 \right\rangle. \quad (4.28)$$

4.3 Experimental methods

4.3.1 Colloidal model system

The colloidal model system used consists of Dynabeads M-270 Carboxylic Acid that have a diameter of $3\text{ }\mu\text{m}$ when dispersed in 20% EtOH(aq) (see section 2.2.1). These are held in a quartz glass Hellma cell with particles close to a wall. The system is sufficiently dilute to ensure that there is only a single particle in the field of view at any time.

4.3.2 Experimental setup

The sample is imaged and manipulated using the optical setup described in section 2.2.3. This consists of a brightfield microscope coupled to a 1064 nm infrared laser, which is focused at the sample plane and controlled using a pair of AODs. The particles are tracked in real time at 40 fps using a convolution method that outputs the particle position (see section 2.2.5). A line of optical traps is used to form a sinusoidal optical landscape with a wavelength of $\lambda = 3.5\text{ }\mu\text{m}$. The laser power is varied between $I_0 = 200 - 480\text{ mW}$, with the corresponding critical velocities summarised in table 4.1. The critical velocity corresponds to that which is seen for a time-independent optical landscape, $\Delta_{osc} = 0$, with a higher critical velocity corresponding to a deeper maximum optical potential energy landscape depth.

Table 4.1: Summary of laser powers used in this chapter. (*) denotes data points for which v_c is not directly measured but is instead extrapolated from a linear fit to measured data points using $F_C \propto I_0$ (equation 3.9).

Laser Power, I_0/mW	Critical velocity, $v_C/\mu\text{m s}^{-1}$	Trap frequency, ν_T/Hz
200	2.14 ± 0.03	0.6
240	2.52 ± 0.03	0.7
280	2.93 ± 0.03	0.8
320	3.23 ± 0.04	0.9
400	$4.00 \pm 0.04^*$	1.1
440	$4.37 \pm 0.04^*$	1.2
480	$4.74 \pm 0.04^*$	1.4

4.3.3 Oscillating the depth of the optical landscape

The landscape depth is oscillated sinusoidally as described in section 4.2.1 with a frequency of $\nu = 0.1 - 1.0 \text{ Hz}$, using $\Delta_{osc} = 1$. For each combination of laser power and frequency, a scan of driving velocities is carried out to obtain particle trajectories from which the average velocity is calculated, $v_{AV} = \Delta x / \Delta t$. Importantly, this calculation is carried out for a time period corresponding to an integer number of oscillations of the optical landscape depth.

An experiment was also carried out where the optical landscape depth was oscillated between 50 and 100% of its maximum depth equating to $\Delta_{osc} = 1/2$. This was done at $I_0 = 280 \text{ mW}$ and $\nu = 0.25 \text{ Hz}$ to allow a direct comparison to full oscillation experiments.

4.3.4 Step widths

The width of the mode locked steps is analysed from the experimentally measured average velocity. A mode locked step is here defined as having an average velocity equal to $v_{AV} = n\lambda\nu \pm 0.1 \times (n\lambda\nu)$ and containing at least two data points. This threshold is chosen to ensure that the full width of a step is captured. This criteria is only applied for $n < 2$ where mode locked steps are predicted, even at high frequencies.

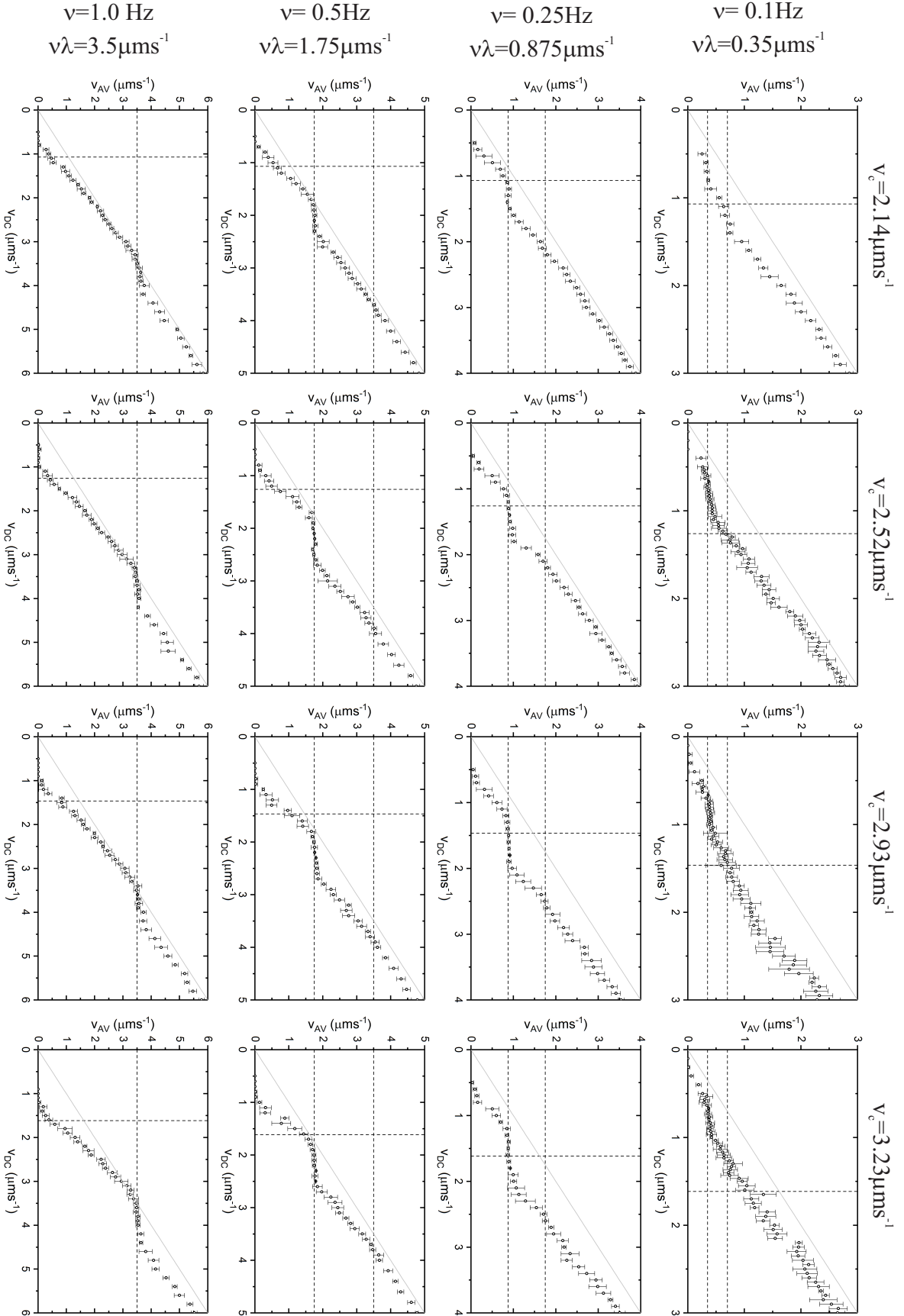


Figure 4.3: Summary of average velocity experiments with varying Critical velocity and frequency. Each plot shows average particle velocity as a function of driving velocity. Dashed horizontal lines show location of mode locked steps for reference. Dashed vertical lines denote $v_c/2$ which is the width of the zeroth step in the high frequency regime. In all experiments, the optical landscape wavelength is $\lambda = 3.5 \mu\text{m}$.

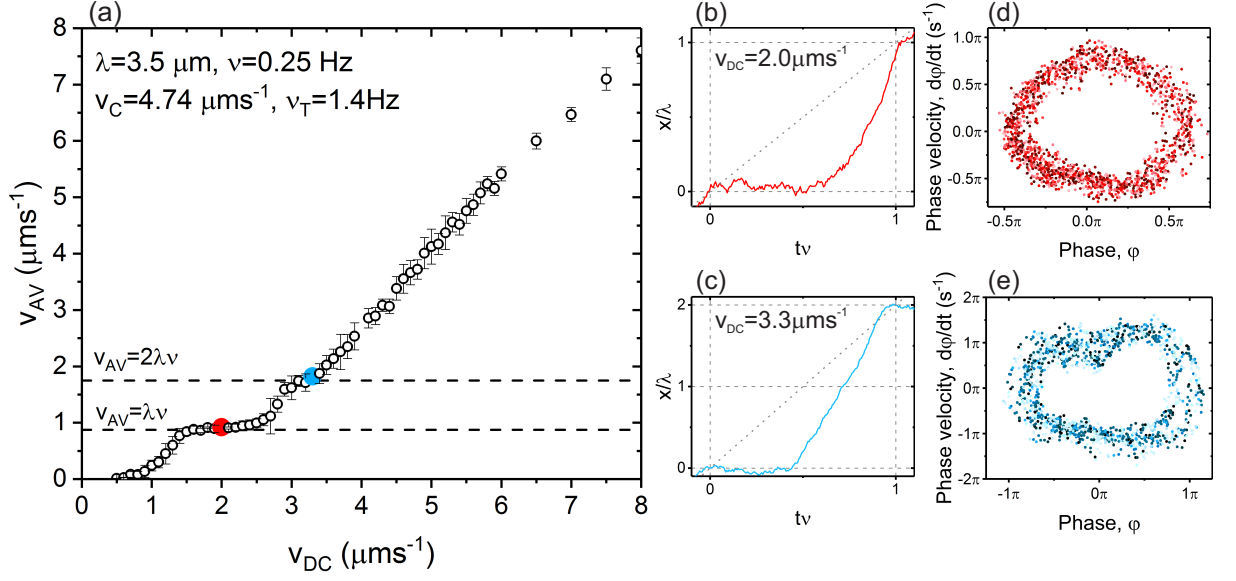


Figure 4.4: (a) A plot of average velocity against driving velocity for a sphere passing through an oscillating optical landscape. (b) $v_{DC} = 2.0 \mu\text{m s}^{-1}$ and (c) $v_{DC} = 3.3 \mu\text{m s}^{-1}$ show trajectories of points highlighted in (a), which correspond to the first and second mode locked steps. (d) (and (e)) shows a phase portrait for the trajectory shown in (b) (and (c)).

4.4 Results and discussion

4.4.1 Average velocity experiments

First, the average velocity, v_{AV} , as a function of driving velocity, v_{DC} , was measured for a wide range of frequencies and laser powers for $\Delta_{osc} = 1$, as is displayed in figure 4.3. Horizontal lines show the location of the expected mode locked steps according to equation 4.9 (for $n \leq 2$). While figure 4.3 presents an overview, in subsequent sections we perform a closer analysis on the frequency and laser power effects. Also note that some experiments were carried out at higher laser powers, up to $v_C = 4.74 \mu\text{m s}^{-1}$ but only for $\nu = 0.25 \text{ Hz}$.

First, we discuss the general behaviour of the average velocity of a sphere driven through a time-dependent optical landscape as a function of the driving velocity using the results from an experiment with $v_C = 4.74 \mu\text{m s}^{-1}$, and $\nu = 0.25 \text{ Hz}$ where the high frequency theory is not valid. As seen in figure 4.4a, there is a general increase in average velocity as the driving velocity is increased. For $v_{DC} < 0.8 \mu\text{m s}^{-1}$, the particle remains stationary despite having an applied driving velocity, because the driving velocity is not high enough for the particle to move to the subsequent potential well within an oscillation. For $v_{DC} > 0.8 \mu\text{m s}^{-1}$, the particle begins to move with a finite velocity. The average velocity increases until $v_{DC} = 1.5 \mu\text{m s}^{-1}$, at which point

it reaches a plateau up to $v_{\text{DC}} = 2.4 \mu\text{m s}^{-1}$ at $v_{\text{AV}} = \lambda\nu = 0.875 \mu\text{m s}^{-1}$. In this range of driving velocities, the particle is mode locked and every oscillation of the optical landscape corresponds to the particle crossing to the adjacent potential well, as displayed in figure 4.4b. As the driving velocity is further increased, the average velocity also increases until $v_{\text{DC}} = 3.0 \mu\text{m s}^{-1}$ where the second mode locked step is reached with $v_{\text{AV}} = 2\lambda\nu = 1.75 \mu\text{m s}^{-1}$. In this mode, each time the optical landscape oscillates, the particle traverses two optical minima as displayed in figure 4.4c. Note that in both individual particle trajectories, shown in figure 4.4b and c, the particle remains stationary for approximately half of the overall oscillation time, corresponding to the optical landscape being at, or close to, its maximum depth. For higher velocities, $v_{\text{DC}} > 3.4 \mu\text{m s}^{-1}$, the average velocity increases with driving velocity. At these higher driving velocities, $F_{\text{DC}} \gg F_{\text{opt}}$, so $v_{\text{AV}} \rightarrow v_{\text{DC}}$.

Phase portraits

To better visualise the nature of the mode locking observed in figure 4.4a, phase portraits (see section 3.2.6) are plotted from the particle trajectories corresponding to the first and second mode locked steps as shown in figure 4.4d and e. The phase portrait for the first mode locked step, $v_{\text{DC}} = 2.0 \mu\text{m s}^{-1}$, exhibits a closed loop due to the periodic motion of the particle. A single loop in the phase portrait corresponds to the particle moving forward one trap spacing, with this phase portrait containing data from 10 oscillations of the optical landscape. This can be compared to the phase portrait for a particle driven at $v_{\text{DC}} = 3.3 \mu\text{m s}^{-1}$, which corresponds to the second mode locked step and is shown in figure 4.4e. Here a closed loop as a result of periodic particle motion is again observed, but the phase portrait shows a small ‘indent’ in the centre of the upper half of the loop. This indicates a reduction in velocity as the particle is moving forward. This occurs because the particle must enter, and subsequently leave, a potential energy minimum as it crosses a distance of $\Delta x = 2\lambda$. This acts to reduce the particle velocity, though the effect is small because the optical landscape is relatively shallow when the particle passes through this minimum. As a consequence, this indent is less significant than is seen for the (2,0) mode for a time-dependent driving force where the optical landscape is time-independent [87]. Note that the variations in the amplitude of the phase and the phase velocity are sensitive to exact experimental conditions. A schematic summary of the hopping behaviour at the first and second mode locked steps is shown in figure 4.5.

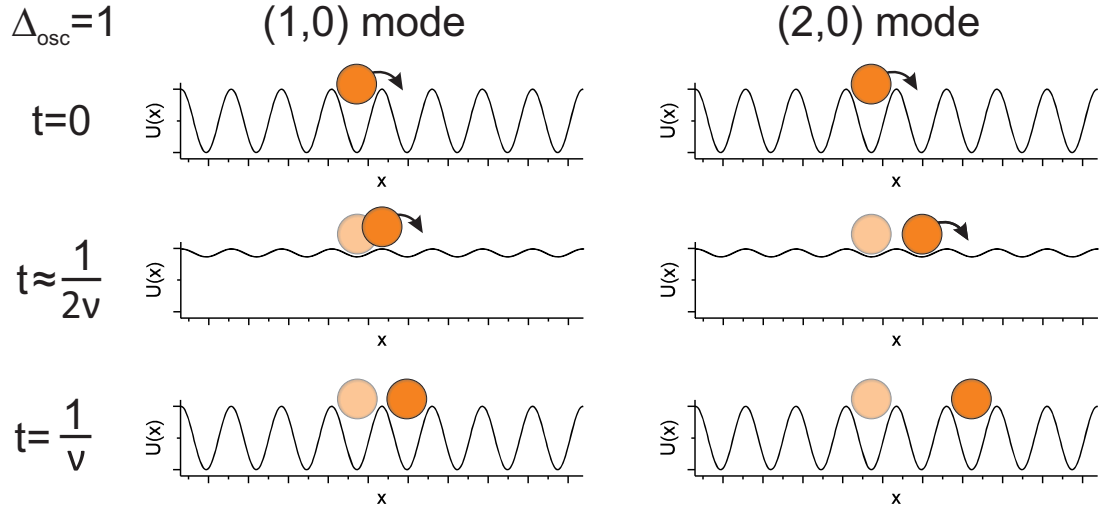


Figure 4.5: Schematic showing the mechanism for motion at the first mode locked step (left hand side), and the second mode locked step (right hand side). Bold particles show the instantaneous position with a shadow in place of initial particle position. In both cases, $\Delta_{osc} = 1$.

4.4.2 Frequency effects

Average velocity experiments

We now study the effects of changing the frequency with which the optical landscape is oscillated and show the average velocity as a function of driving velocity for four different frequencies in figure 4.6. This is shown for $v_C = 3.23 \mu\text{m s}^{-1}$. First of all, it is seen that the zeroth step width, corresponding to $v_{AV} = 0 \mu\text{m s}^{-1}$, is directly correlated with the frequency and as the frequency increases, so does the zeroth step width. Secondly, the average velocity corresponding to the first mode locked step at $v_{AV} = \lambda\nu$, changes with frequency as expected from equation 4.24. The horizontal dashed lines in figure 4.6 show the predicted locations of the mode locked steps as the frequency is changed and the experimental results match these predictions well.

Step widths

Next, we analyse the step widths of the observed mode locked steps (see section 4.3.4), where we note that the zeroth step width is equivalent to the critical velocity. The frequency dependence of the zeroth step width for four values of v_C is shown in figure 4.7a, and it is clear that the zeroth step width increases with frequency. A particle must overcome the optical landscape to give a non-zero average velocity and this movement occurs when the landscape is at its most shallow, at $t \approx 1/(2\nu)$ (see figure 4.1). The time period in which the optical landscape is

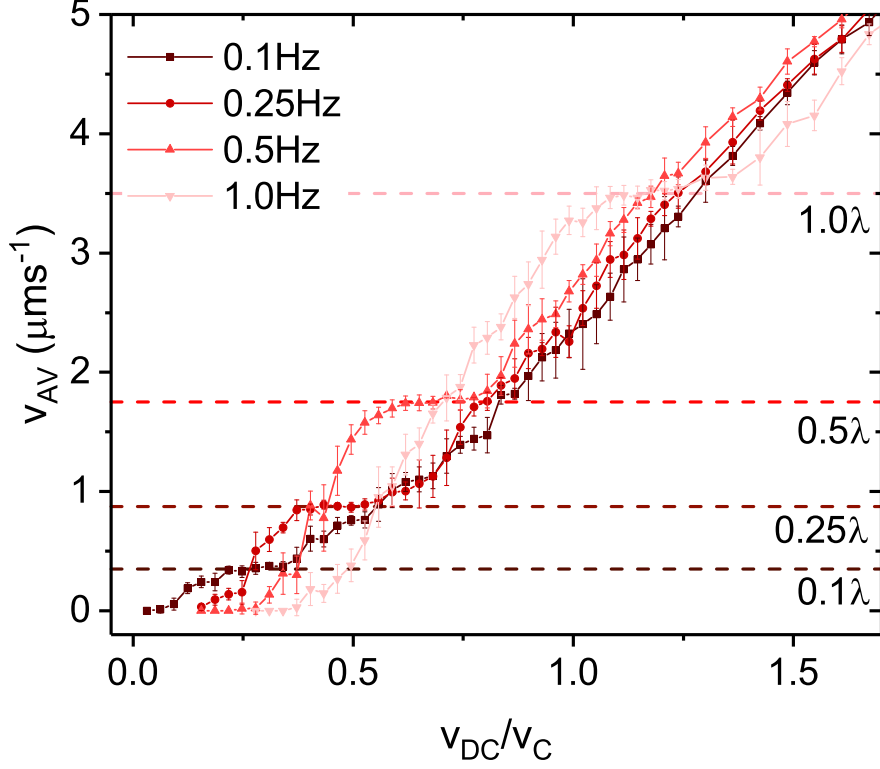


Figure 4.6: Average velocity as a function of normalised driving velocity for multiple frequencies. Horizontal dashed lines indicate the location of the first mode locked step, $v_{AV} = \lambda\nu$, for each frequency shown. These are measurements taken for $\lambda = 3.5 \mu\text{m}$ and $v_C = 3.23 \mu\text{s}^{-1}$ ($\nu_T = 0.9 \text{ Hz}$).

close to this ‘shallow’ state is inversely proportional to the frequency. This means that at low frequencies, where this time period is longest, the particle can move with least hindrance, leading to a smaller zeroth step width. Hence, the zeroth step width tends towards zero as $\nu \rightarrow 0$. In the high frequency regime (see section 4.2.2) the zeroth step width equals $v_C/2$, which ranges from $1.05 \mu\text{s}^{-1}$ – $1.6 \mu\text{s}^{-1}$ for the laser powers used here. While the high frequency regime has not been fully reached, the observed step widths appear to be plateauing towards higher frequencies.

Next, the frequency dependence of the first step width is shown in figure 4.7b. This shows a similar behaviour to that of the zeroth step, as the step width increases with frequency. At low frequencies, many closely spaced mode locked steps are expected with a separation of $\lambda\nu$. This means that the first step is inherently small as a large number of steps span a small range of v_{DC} . Tending towards a higher frequency leads to an increase in the step width, and in the high frequency limit, the step width is again predicted to be $v_C/2$ according to equation 4.24. This is observed for $v_C = 2.14 \mu\text{s}^{-1}$, and is closely approached for other values of v_C as the high frequency regime is approached.

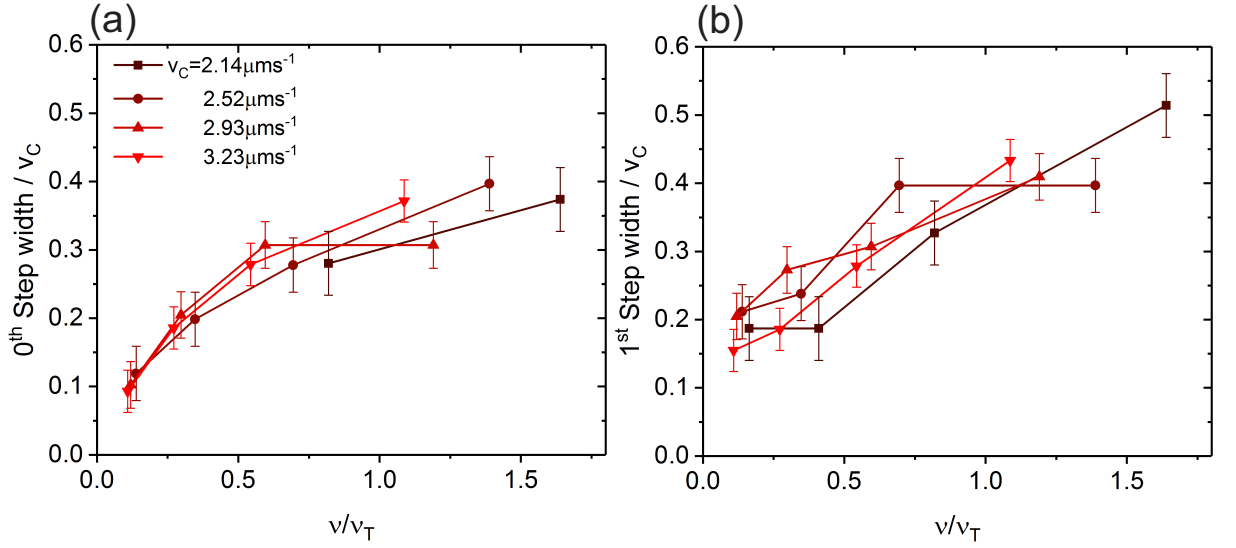


Figure 4.7: Normalised (a) zeroth and (b) first step width as a function of normalised frequency. The legend shown in (a) also applies to (b).

4.4.3 Laser power effects

Average velocity experiments

We now explore how the laser power, I_0 , and hence v_C affects the behaviour of a driven particle in a time-dependent optical landscape. I_0 is proportional to the maximum depth of the potential, $F_C \propto I_0$ (equation 3.9). A plot showing the average velocity as a function of the driving velocity for seven different values of v_C is shown in figure 4.8. Here the frequency of the optical landscape is $\nu = 0.25$ Hz, which leads to an observable zeroth and first step for all values of v_C . At higher v_C , the location of the first step is shifted to higher values of v_{DC} and the first step width increases. There is also a small second mode locked step present for $v_C = 4.74 \mu\text{ms}^{-1}$ that disappears at lower values of v_C where the high frequency theory is a better approximation ($\nu_T \propto v_C$). As v_C increases, there is also a greater deviation from $v_{AV} = v_{DC}$ at high driving velocities. This is because at high values of v_C , the coupling between the particle and the optical landscape is greater, which acts to slow the particle down as it travels across the optical landscape.

Step widths

Next we show how the zeroth step width changes with v_C in figure 4.9a. The step width generally increases with increasing v_C . This is because increasing v_C enhances the coupling between the

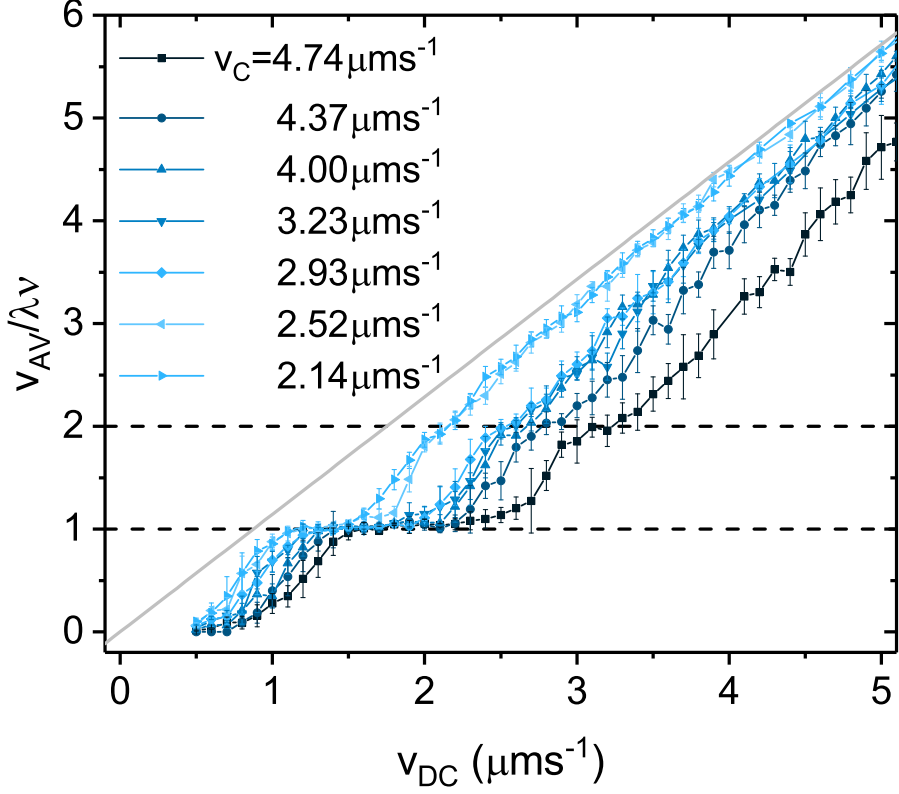


Figure 4.8: Normalised average velocity as a function of driving velocity for multiple values of v_C . Horizontal dashed lines indicate the average velocity of the first and second mode locked steps, which are not dependent on v_C . Grey line denotes $v_{AV} = v_{DC}$. These are measurements taken for $\lambda = 3.5 \mu\text{m}$ and a frequency of $\nu = 0.25 \text{ Hz}$.

oscillating optical landscape and the particle motion. An increased interaction between the optical landscape and the particle means that they can synchronise over a greater region of driving velocities (see figure 1.1), leading to a wider mode locked step. This step width increase also follows directly from equation 4.21, as in the high frequency regime the step width is equal to $v_C/2$.

For completeness we also inspect the effect of v_C on the first step width, which is plotted in figure 4.9b. As with the zeroth step, the first step width is predicted to increase with v_C as its width according to equation 4.24 is $v_C/2$ in the limit of high frequencies. This effect is not clearly observed however, which may be in part due to how the step width is measured (see section 4.3.4). This involves locating two critical points which increases the total level of noise and may mask any trend in the data.

It is also worth noting that the high frequency regime becomes less relevant at high values of v_C , where trap frequency ν_T is higher.

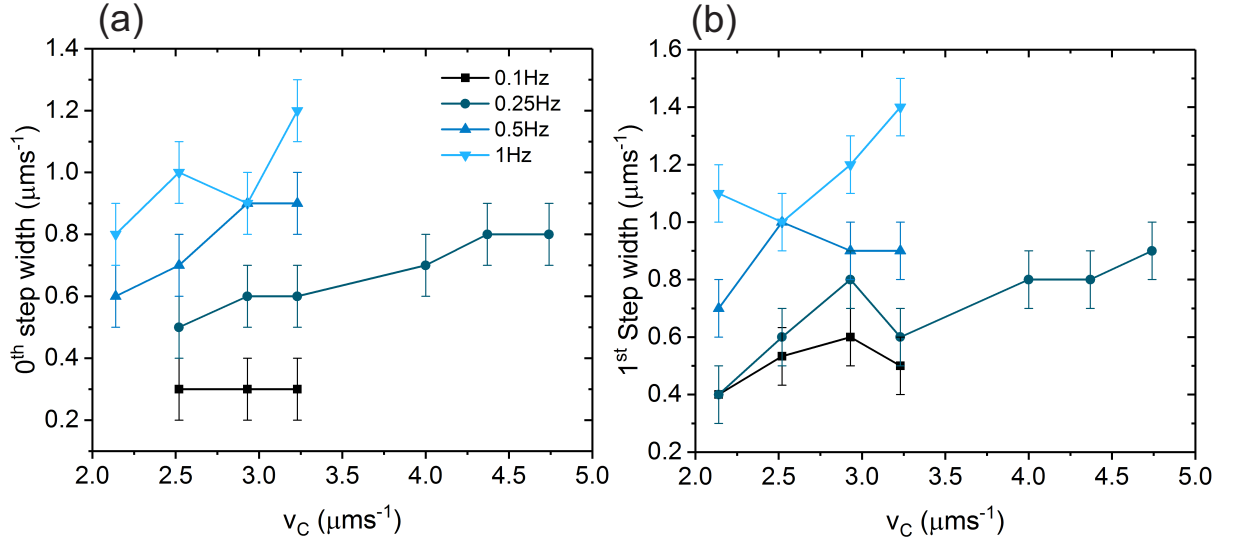


Figure 4.9: (a) Zeroth and (b) first step width as a function of v_C . The legend shown in (a) also applies to (b).

4.4.4 Oscillation amplitude effects

Average velocity experiments

To study the effect of oscillating the optical landscape to different extents, experiments with $\Delta_{osc} = 1$ and $\Delta_{osc} = 1/2$ are compared and the average velocity is shown as a function of the driving velocity in figure 4.10. The deterministic result for $\Delta_{osc} = 0$ according to equation 3.18 is also shown. There are clear differences between the two experimental results, starting with a very different critical velocity. There is a much larger critical velocity for $\Delta_{osc} = 1/2$ than for $\Delta_{osc} = 1$. In the case of $\Delta_{osc} = 1/2$, a particle must overcome a barrier to motion equivalent to $v_C/2$, which is higher than in the case of $\Delta_{osc} = 1$ where the barrier to motion is close to zero for a small but finite length of time. A schematic of this particle motion for $v_{DC} = 1.5 \mu\text{ms}^{-1}$ is shown in figure 4.11 where for $\Delta_{osc} = 1$ the optical landscape becomes shallow enough to allow particle motion. However, for $\Delta_{osc} = 1/2$ the particle does not have a sufficient driving force to overcome the non-zero optical landscape and remains confined with zero average velocity. The first step width for $\Delta_{osc} = 1$ is also much larger, and at a lower value of v_{DC} than that for $\Delta_{osc} = 1/2$. This reduction in step width can be understood by noting that the results for $\Delta_{osc} = 1/2$ are approximately the average of $\Delta_{osc} = 1$ and $\Delta_{osc} = 0$, which can be partly

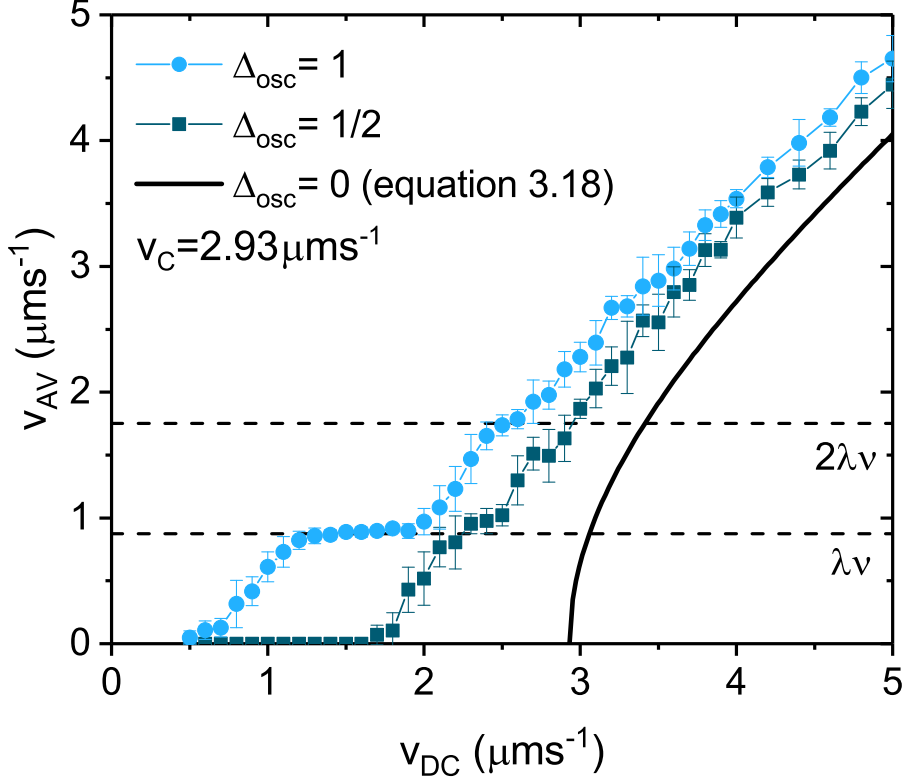


Figure 4.10: Average velocity as a function of driving velocity for experiments with $\Delta_{osc} = 1, 1/2$, and the deterministic result for $\Delta_{osc} = 0$. Experimental parameters are $\lambda = 3.5 \mu\text{m}$, $\nu = 0.25 \text{ Hz}$ and $v_C = 2.93 \mu\text{ms}^{-1}$. Horizontal dashed lines indicate the average velocity of the first and second mode locked steps.

accounted for by noting that the optical force is given by

$$F_{opt}(\Delta_{osc} = 1/2) = \frac{(F_{opt}(\Delta_{osc} = 1) + F_{opt}(\Delta_{osc} = 0))}{2}. \quad (4.29)$$

In the time-independent scenario, i.e. $\Delta_{osc} = 0$, there are no mode locked steps due to a complete lack of synchronisation and v_{AV} behaves according to equation 3.18 as was indeed observed for a colloidal rod in section 3.4.2 and for a sphere in [47, 87]. In other words, this reduction in step width can be accounted for by noting that decreasing Δ_{osc} leads to a reduced coupling between the particle motion and the time-dependent landscape so the range of v_{DC} where the system is synchronised is reduced (see figure 1.1).

4.4.5 Effective diffusion coefficient

Finally, we study the effective diffusion coefficient of a particle moving across a time-dependent optical landscape. The average velocity and the effective diffusion coefficient calculated from

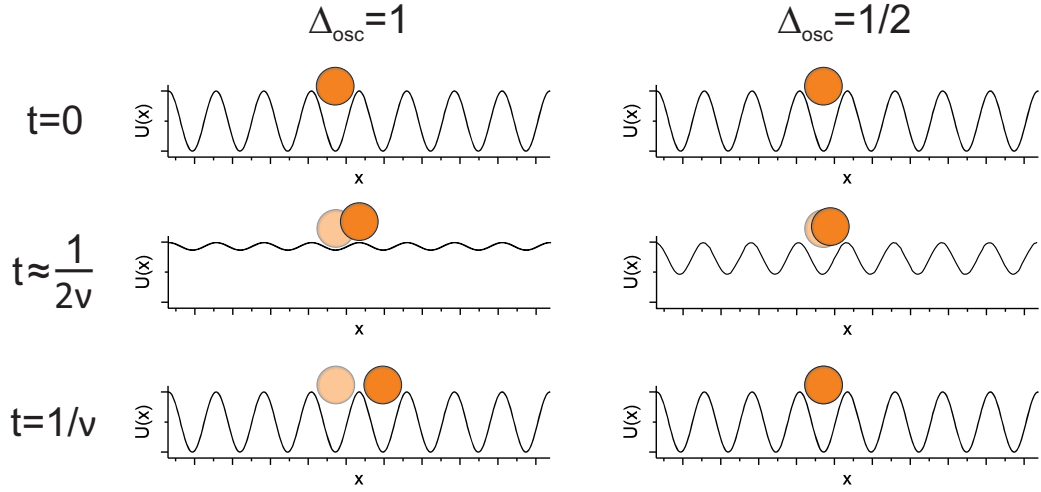


Figure 4.11: Schematic of particle motion in the case of $\Delta_{osc} = 1$ (left) and $\Delta_{osc} = 1/2$ (right). This corresponds to $v_{DC} = 1.5 \mu\text{m s}^{-1}$ in figure 4.10.

equation 4.28 are plotted against the driving velocity for three different laser powers in figure 4.12. In all three plots, we see that an initial rise in the average velocity corresponds to a sharp rise in the effective diffusion coefficient as the particle begins to exhibit a non-zero velocity. Upon approaching the first mode locked step at $v_{DC} = 1.1 \mu\text{m s}^{-1}$ in figure 4.12a, the effective diffusion coefficient is greatly reduced. This is due to the periodic motion that a particle experiences when it is mode locked, leading to very low levels of effective diffusion. The effective diffusion coefficient even drops below the diffusion coefficient measured for a free particle, $0.045 \mu\text{m}^2 \text{s}^{-1}$, indicating that Brownian fluctuations are less significant on this mode locked step, where particle motion is very well defined, than for a free particle. As the driving velocity is increased beyond $v_{DC} = 1.6 \mu\text{m s}^{-1}$, the particle is no longer mode locked, and the effective diffusion coefficient rises again before slowly decreasing as the driving velocity increases beyond $v_{DC} = 1.7 \mu\text{m s}^{-1}$, where the optical landscape has a diminishing effect on the particle motion.

In figure 4.12b, which shows results for a higher I_0 , the effective diffusion coefficient exhibits similar behaviour for the first mode locked step as that seen in figure 4.12a. At higher driving velocities there is an onset of a second mode locked step between $v_{DC} = 2.5\text{--}2.8 \mu\text{m s}^{-1}$, leading to a second reduction of the effective diffusion coefficient. This drop is not as pronounced as for the first mode locked step because the second mode locked step is not as broad as the first, and Brownian noise has a larger effect on the motion of the particle. As the laser power is further increased, see figure 4.12c, a wider second mode locked step causes a drop in the effective diffusion coefficient over a greater range of driving velocities between $v_{DC} = 2.9\text{--}3.4 \mu\text{m s}^{-1}$.

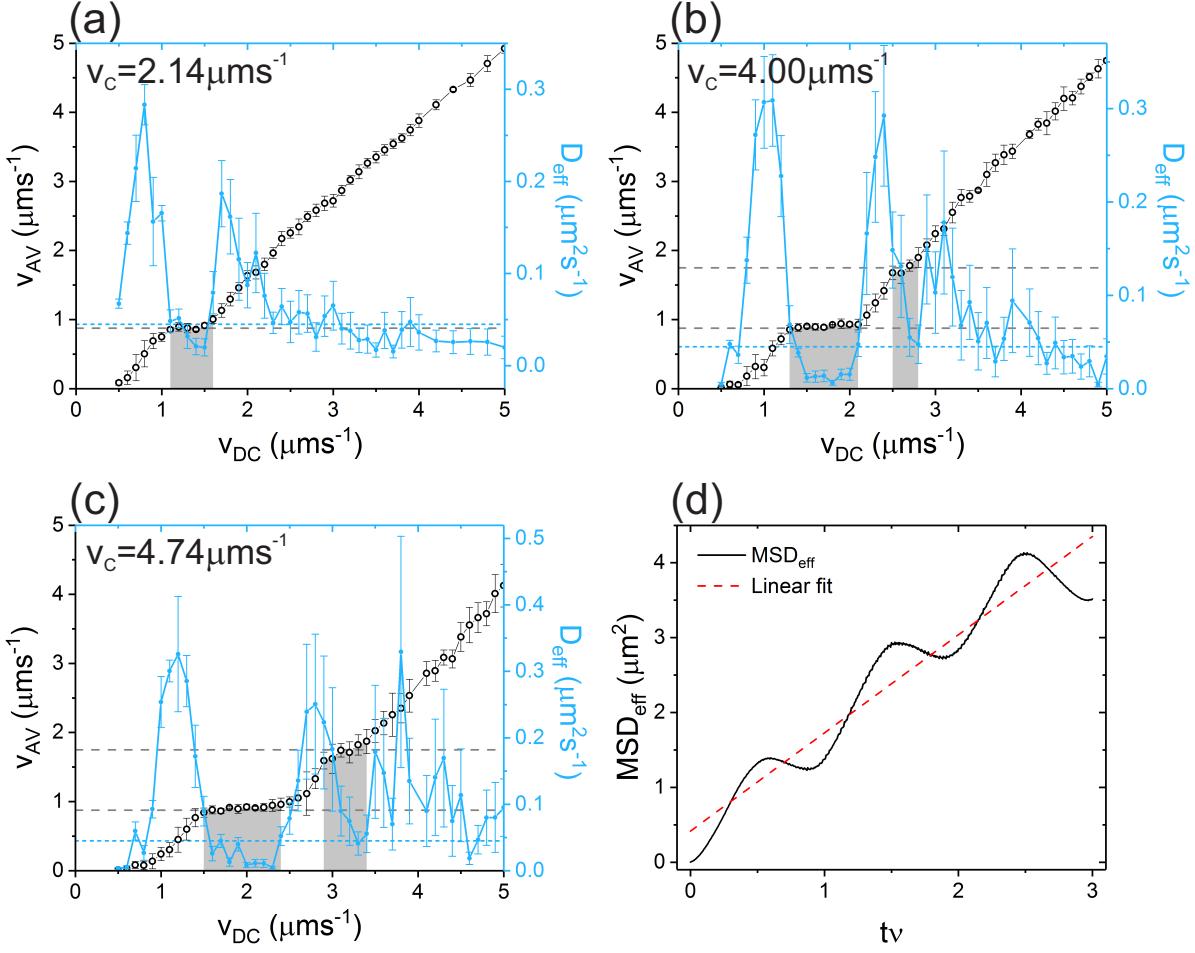


Figure 4.12: Effective diffusion coefficient (blue) and average velocity (black) shown for (a) $v_C = 2.14 \mu\text{m s}^{-1}$, (b) $4.00 \mu\text{m s}^{-1}$, and (c) $4.74 \mu\text{m s}^{-1}$. Here we use a frequency of $\nu = 0.25 \text{ Hz}$ and a landscape wavelength of $\lambda = 3.5 \mu\text{m}$. Grey horizontal dashed lines show the average velocity of first and, for (b) and (c), second mode locked steps with the grey regions denoting the mode locked steps using the criteria from section 4.3.4. Blue dashed lines indicate the diffusion coefficient of a free particle, $D_0 = 0.045 \mu\text{m}^2 \text{s}^{-1}$. (d) shows a typical plot of MSD_{eff} with a black line showing measured value and a linear fit shown in red, from which D_{eff} is extracted.

These plots show that when a particle is mode locked, its motion is greatly restricted and in many cases leads to an effective diffusion coefficient that is even lower than that of a freely diffusing particle.

4.5 Conclusions

In this chapter a colloidal sphere has been driven across a time-dependent one-dimensional optical potential energy landscape. Particle motion was seen to exhibit dynamic mode locking corresponding to periodic particle motion. This was visualised for the (1,0) and (2,0) modes with the use of phase portraits. The effect of the oscillation frequency on the step width was

studied with reference to a high frequency theory. The effect of the laser intensity on the step width was also probed and was shown to have a high correlation with the zeroth step width, however, no meaningful first step width dependence was extracted. The motion of a particle across an optical landscape with a partially oscillating amplitude was also explored and shown to behave very differently to its fully oscillating counterpart. The partially oscillating landscape can be treated as an average of the time-independent and the fully oscillating time-dependent optical landscapes. Finally, the effective diffusion coefficient was studied and was seen to be greatly reduced for a driving velocity corresponding to a mode locked step.

Acknowledgments

This work was done in collaboration with Arthur Straube and Dirk Aarts.

Chapter 5

Static Aubry-type transition and dynamic depinning in driven finite colloidal chains

ABSTRACT

In this chapter chains of interacting colloidal particles are studied as they are driven through a static optical potential energy landscape. A mismatch between length scales of the chain and the landscape gives rise to a freely sliding chain in an Aubry-type transition. In this regime a chain exhibits zero static friction despite being subject to a potential energy landscape. This transition is shown for a finite chain at regular and well defined chain lengths depending on the commensurability between the wavelength of the optical landscape and the particle spacing. The effect of changing the chain stiffness is studied and driven flexible chains are seen to exhibit breathing modes. Finally, oscillations are introduced in the driving force, leading to the observation of dynamic depinning of a chain for an average driving velocity below the critical velocity. Subsequently, the influence of the oscillation frequency and the average driving velocity on the chain motion is explored with oscillations lowering the depinning threshold of the chains.

5.1 Introduction

Friction is responsible for a huge loss of energy in sectors ranging from transport and power generation to the production of goods [3]. It can slow down processes, produce unwanted heat, and lead to wear and tear between counter-sliding surfaces [134, 135]. On the macroscopic scale friction is caused by local areas of contact due to surface roughness [136], but for microscopically smooth surfaces it is caused by areas of molecules or atoms that interact with a substrate [137]. One method of probing surface roughness is frictional force microscopy wherein the tip of a probe is driven across a surface from which local structure can be obtained. The inherent length scales and relative angle [138] between the driving direction of the probe and symmetry of the underlying surface have a significant impact on the exhibited friction and under the correct conditions can lead to a state of zero static friction, known as superlubricity. Superlubricity is known to be exhibited on the microscale for graphite [139–141] when layers are skew [138], due to the well defined structure of each layer. Graphene nanoribbons have been seen to exhibit superlubricity when subject to a gold substrate [142–144] and it has also been observed for carbon nanotubes [145].

A simple but useful model in the field of nanotribology is the Prandtl-Tomlinson model [137, 146] wherein a point mass is driven over a periodic potential. A more complex but still analytically accessible model is the Frenkel-Kontorova model [147, 148], in which a chain of particles have a spring-like interaction and are subject to a periodic potential as shown in figure 5.1. This system can either be commensurate or incommensurate depending on the ratio of the relevant length scales being the wavelength of the landscape, λ , and the particle spacing, s .

An interesting transition occurs for an infinitely long chain in the Frenkel-Kontorova model. If the ratio between the wavelength of the landscape and the particle spacing is irrational then a chain can freely slide below a critical landscape depth [148]. This is caused by the presence of an infinite number of degenerate ground states, separated by infinitesimally small displacements. As soon as the landscape depth exceeds the critical value the chain will deform to minimise its potential energy and there will be a finite number of ground-states, meaning that the chain will not freely slide. This is called the Aubry transition and was theoretically predicted by Aubry in 1983 [8, 149–151].

Experimentally, it is impossible to create an infinite chain, however an Aubry-type transi-

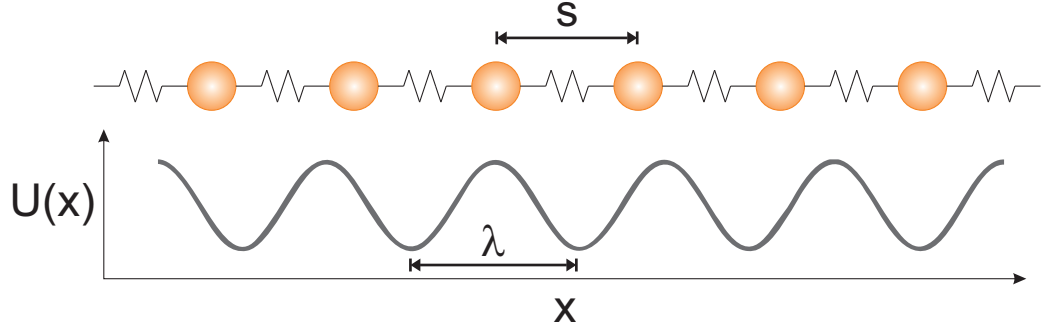


Figure 5.1: Schematic of the Frenkel-Kontorova model. Each particle interacts with the potential energy landscape and the neighbouring particles in the chain. The only two length scales in this model are the wavelength of the periodic potential, λ , and the particle spacing, s .

tion has been studied [152] and is seen to exist in cold ion traps [69–73]. Colloidal systems have also been used to model sample-substrate interactions and have successfully modelled a drop to zero static friction in two dimensions [58, 74, 75]. The one-dimensional analogue cannot have a mismatch angle between the driving direction and the symmetry of the landscape and instead the static friction is only governed by the length scales of the particle size and the underlying landscape and their interaction strength [153].

Here the motion of a finite colloidal chain driven through a static one-dimensional sinusoidal optical potential energy landscape is studied. A chain is driven at a constant velocity to probe an Aubry-type transition giving rise to zero static friction. The effects of the chain stiffness and commensurability on chain motion are then studied, and a model is developed for the case of a completely rigid chain. Next, breathing modes of a flexible chain driven across a periodic landscape are explored. Finally, oscillations are introduced to the driving velocity to probe dynamic depinning of a chain for an average driving velocity below the critical velocity. Here, the effect of the oscillation frequency and the average driving velocity on chain motion is explored with oscillations lowering the depinning threshold of chains.

5.2 Theory

Until now, the behaviour of a single driven particle in an optical potential energy landscape has been considered. Here, the behaviour of a finite chain in such a landscape when subject to a constant driving force is discussed with the aim of predicting the critical velocity of a chain. Finally, the constant driving force is set below the critical driving force and the effect of adding an oscillatory driving force on chain motion is explored.

5.2.1 Finite colloidal chains in an optical landscape

The potential energy experienced by a single particle in a sinusoidal optical landscape, U_1 , was derived in section 2.1.3 and was shown to be equivalent to

$$U_1(x) = -\frac{\sqrt{8\pi}V_0^{3/2}}{\lambda k^{1/2}} \left[\frac{1}{2} + \exp\left(-\frac{2\pi^2 V_0}{\lambda^2 k}\right) \cos\left(\frac{2\pi x}{\lambda}\right) \right], \quad (5.1)$$

where λ is the wavelength of the optical potential energy landscape, V_0 is trap depth, and k is trap stiffness. The first term in this expression has no spatial dependence and is here denoted as $U_0 = -\sqrt{2\pi}V_0^{3/2}\lambda^{-1}k^{-1/2}$. Using the expression for the critical force for a single particle, F_C , as derived in section 3.2.3, equation 5.1 can be rewritten as

$$U_1(x) = -\frac{\lambda F_C}{2\pi} \cos\left(\frac{2\pi x}{\lambda}\right) + U_0. \quad (5.2)$$

Next, the optical landscape experienced by a chain consisting of particles that are connected due to magnetic interactions is considered. To calculate the overall potential energy of a chain of n particles in an optical landscape, they are assumed to always be in contact, with a separation of $s = 2a$, where a is the particle radius. This means that the magnetic interactions between the particles remain constant for a given chain length, which is expressed as $U_{mag,n}$. The potential energy experienced by each particle and the magnetic contribution are summed for a chain of two particles to give

$$\begin{aligned} U_2(x) &= U_1(x) + U_1(x - 2a) + U_{mag,2} \\ &= -\frac{\lambda F_C}{2\pi} \left(\cos\left(\frac{2\pi x}{\lambda}\right) + \cos\left(\frac{2\pi(x - 2a)}{\lambda}\right) \right) + 2U_0 + U_{mag,2}, \end{aligned} \quad (5.3)$$

where x is the position of the first particle. If more particles are added to achieve a chain of length n then the overall potential energy landscape can be written as

$$U_n(x) = -\frac{\lambda F_C}{2\pi} \sum_{j=1}^n \cos\left[\left(\frac{2\pi x}{\lambda}\right) - \left(\frac{4\pi a}{\lambda}(j-1)\right)\right] + nU_0 + U_{mag,n}. \quad (5.4)$$

The identity $\sum_{k=0}^m \cos(ak + z) \equiv \csc(a/2) \sin(a(m+1)/2) \cos(z + am/2)$ is used to rewrite

equation 5.4 as

$$U_n(x) = -\frac{\lambda F_C \sin(2\pi na/\lambda)}{2\pi \sin(2\pi a/\lambda)} \cos \left[\left(\frac{2\pi x}{\lambda} \right) - \left(\frac{2\pi a}{\lambda} (n-1) \right) \right] + nU_0 + U_{mag,n}. \quad (5.5)$$

This can be differentiated to give a force using $F_n = -\partial U_n / \partial x$:

$$F_n(x) = F_{opt,n}(x) = -F_{0,n} \sin \left[\left(\frac{2\pi x}{\lambda} \right) - \left(\frac{2\pi a}{\lambda} (n-1) \right) \right], \quad (5.6)$$

where $F_{0,n} = F_C [\sin(2\pi na/\lambda) / \sin(2\pi a/\lambda)]$. Note that the force that a chain of n particles experiences, $F_n(x)$, is equal to the force due to the optical landscape only, $F_{opt,n}(x)$, as neither U_0 or $U_{mag,n}$ have a spatial dependence.

5.2.2 Static Aubry-type transition

For finite chains in a periodic landscape, the static Aubry-type transition corresponds to the emergence of a zero critical velocity. To probe this transition, an expression for the critical velocity must first be derived. This critical velocity is the driving velocity required to overcome the maximum opposing force due to the optical landscape, $-F_{opt,n}^{max}$, experienced by a chain composed of n particles in a sinusoidal landscape. Because $F_{0,n}$ changes sign as a function of the chain length the critical driving force, $F_{C,n}^*$, must be expressed as

$$F_{C,n}^* = |F_{0,n}| = F_C \left| \frac{\sin(2\pi na/\lambda)}{\sin(2\pi a/\lambda)} \right|. \quad (5.7)$$

A critical driving velocity, v_n^* , can now be written:

$$v_n^* = \frac{F_{C,n}^*}{\zeta_n}. \quad (5.8)$$

The friction coefficient of a chain, ζ_n , has been found to increase with the length of the chain both experimentally and theoretically [111, 154]. Here a simple expression is used to describe the friction coefficient of a chain made up of n particles:

$$\zeta_n = \frac{(n+1)}{2} \zeta_1, \quad (5.9)$$

where ζ_1 is the single particle friction coefficient, such that $\zeta(1) \equiv \zeta_1$. This equation is simple and concise, but is chosen as it encompasses the frictional behaviour of both long and short chains. By combining equations 5.7, 5.8 and 5.9 a full expression for the critical velocity for a rigid chain of n particles in a sinusoidal optical landscape is reached:

$$v_n^* = \frac{2F_C}{(n+1)\zeta_1} \left| \frac{\sin(2\pi na/\lambda)}{\sin(2\pi a/\lambda)} \right|. \quad (5.10)$$

Superlubric regime

From equation 5.10 the length of a chain where the predicted critical velocity is zero can be deduced. This occurs when

$$\sin\left(\frac{2\pi na}{\lambda}\right) = 0, \quad (5.11)$$

which is true for $n = \frac{k\lambda}{2a}$, where k is a positive integer. Physically it is only possible to have integer values for n , so solutions only exist if n and k are both integers, which implies that $\frac{\lambda}{2a}$ is a rational number for a finite chain. When this criterion is satisfied, equation 5.11 points to a superlubric regime at regular intervals of n . Interestingly, this drop to zero static friction is independent of optical potential energy landscape depth and relies only on the ratio between particle size, a , and the wavelength of the optical landscape, λ .

Equation 5.10 can only physically be interpreted when n is an integer. A technique called aliasing is used to change the frequency of equation 5.10, but still achieve the same results for integer values of n [155]. This can be done by changing the frequency as follows:

$$f = \frac{2a}{\lambda} \quad \rightarrow \quad f_{equiv} = \frac{2a}{\lambda} - f_s = \frac{2a - \lambda}{\lambda}, \quad (5.12)$$

where $f_s = 1$ is the sampling frequency as shown in figure 5.2. This gives a new, but equivalent expression for the critical velocity

$$v_n^* = \frac{2F_C}{(n+1)\zeta_1} \left| \frac{\sin(\pi n(2a - \lambda)/\lambda)}{\sin(\pi(2a - \lambda)/\lambda)} \right|. \quad (5.13)$$

This function is only true for integer values of n as is shown in figure 5.2.

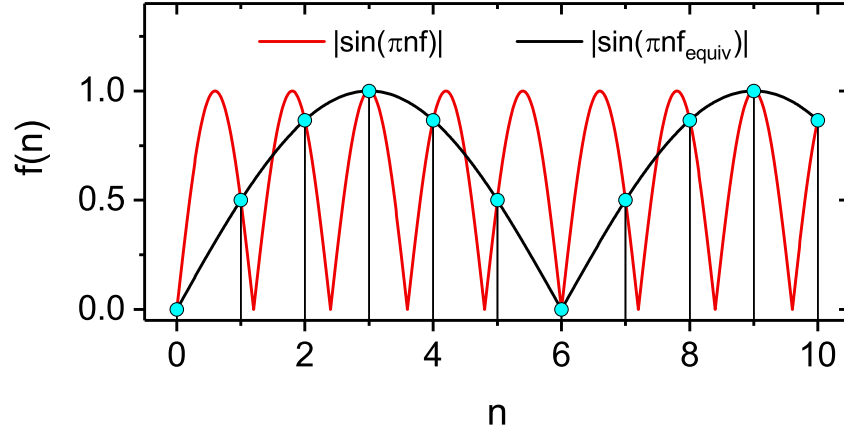


Figure 5.2: A schematic showing the effect of aliasing to convert equation 5.10 (red line) to equation 5.13 (black line). Though these plots have different frequencies, they are equivalent when sampled at integer values of n (Blue points).

5.2.3 Dynamic depinning

So far in this chapter we have considered a chain of colloidal particles subject to a time-independent driving force. Now, oscillations are introduced to the driving force so that the driving velocity consists of two terms:

$$v_{\text{drive}} = v_{\text{DC}} + v_{\text{AC}} \sin(2\pi\nu t), \quad (5.14)$$

where v_{DC} denotes the constant driving velocity, v_{AC} refers to the amplitude of the oscillations and ν is the frequency. Experimentally, ν is chosen to be on the same order of magnitude as the trap frequency $\nu_T \approx 1$ Hz in order to probe the frequency dependence of dynamic depinning. Note that the time averaged velocity $\langle v_{\text{drive}} \rangle = v_{\text{DC}}$. If $v_{\text{AC}} = 0$, then the time-independent scenario is reached and in the case of $v_{\text{DC}} < v_n^*$, no chain motion will be observed. If the amplitude of oscillations is now increased such that $v_{\text{AC}} > 0$ then a regime can be entered where despite $v_{\text{DC}} < v_n^*$, a finite average velocity is observed. This behaviour is exemplified in figure 5.3 where $v_{\text{drive}}(t)$ is shown for $v_{\text{DC}} < v_n^*$. Importantly, there are finite time periods denoted by the grey shaded areas corresponding to times where the instantaneous driving velocity is above the critical velocity. This can lead to the emergence of dynamic depinning, where motion is observed despite the fact that the average driving velocity is below the critical velocity.

To observe dynamic depinning, the inequality, $v_{\text{AC}} \geq v_n^* - v_{\text{DC}}$ must hold, though there are further necessary considerations. For a chain to move, it must be exposed to $v_{\text{drive}} > v_n^*$ for a long

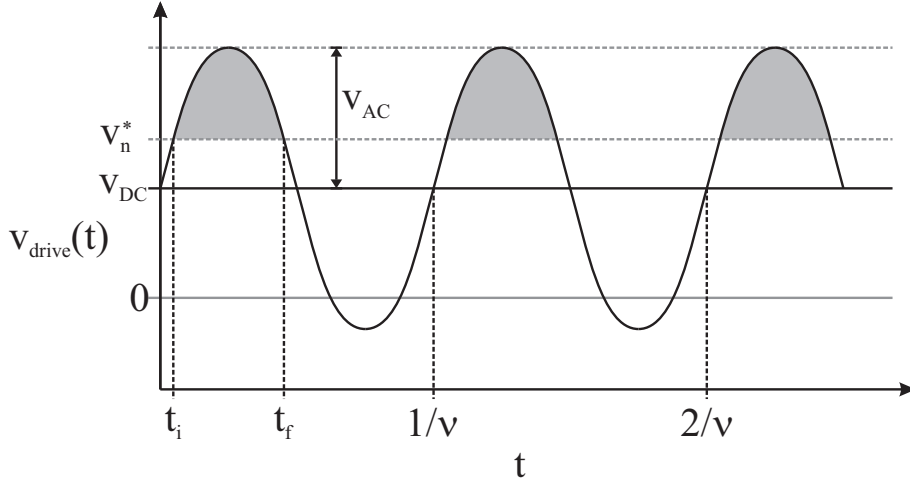


Figure 5.3: A plot showing the time dependent velocity as described in section 5.2.3. The average velocity is below the critical velocity but the imposed oscillations lead to a time where the instantaneous velocity exceeds the critical velocity and the chain has the possibility of moving (grey shaded area).

enough period so that it can move a critical distance, Δx^* that is on the order of the wavelength of the optical landscape, λ . To get an estimate for Δx^* we consider a chain in a sinusoidal optical potential energy landscape that is driven by the average driving velocity, $\langle v_{drive} \rangle = v_{DC}$ (see figure 5.4). The critical distance, Δx^* , corresponding to the distance over which the optical force is greater than the average driving force is indicated in figure 5.4. This distance is confined by the points where $v_{DC} = -F_{opt,n}/\zeta_n$, which can be written using equation 5.6 as

$$v_{DC} = v_n^* \sin\left(\frac{2\pi x}{\lambda}\right). \quad (5.15)$$

Here, only the x dependent part of equation 5.6 is used as this is the term required to calculate Δx^* . The first two solutions of equation 5.15 are

$$x_i = \frac{\lambda}{2\pi} \arcsin\left(\frac{v_{DC}}{v_n^*}\right), \quad \text{and} \quad x_f = \frac{\lambda}{2} - \frac{\lambda}{2\pi} \arcsin\left(\frac{v_{DC}}{v_n^*}\right),$$

and using $\Delta x^* = x_f - x_i$, the critical distance that needs to be crossed is found as:

$$\Delta x^* = \frac{\lambda}{2} \left[1 - \frac{2}{\pi} \arcsin\left(\frac{v_{DC}}{v_n^*}\right) \right]. \quad (5.16)$$

For constant λ , this expression only depends on the ratio between the average driving velocity and the critical velocity.

Thus for a chain to move, a critical distance of Δx^* needs to be crossed per oscillation of

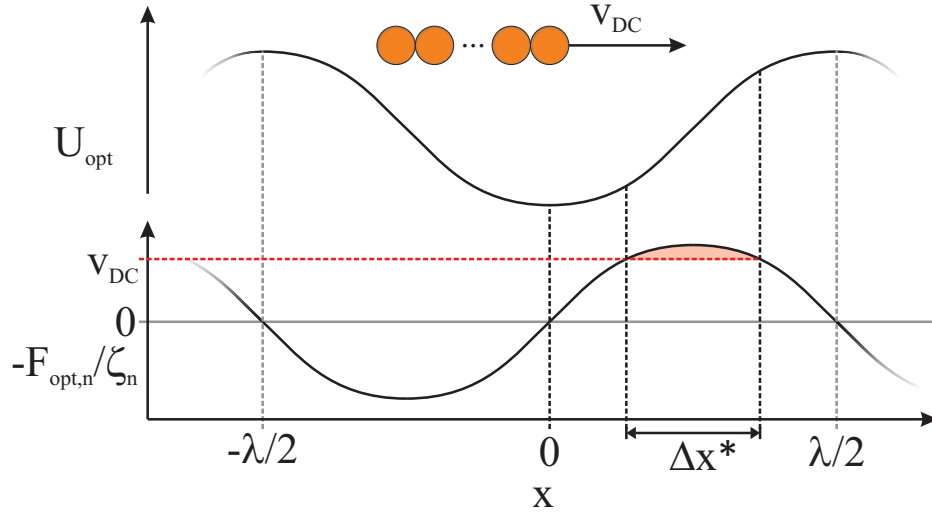


Figure 5.4: Optical potential and force are displayed for a chain of particles crossing an optical landscape (particles and optical landscape are not to scale). Δx^* corresponds to the distance where the optical force is greater than the average driving force and refers to the shaded red region of the force landscape. Note that here, $-F_{opt}$ is shown and is highest when the optical force opposes the driving force.

the driving velocity, and this distance can only be crossed when $v_{drive}(t) \geq v_n^*$, as indicated by the shaded region in figure 5.3. This shaded area can be directly calculated as

$$\int_{t_i}^{t_f} (v_{drive} - v_n^*) dt = \Delta x, \quad (5.17)$$

showing that it actually corresponds to the distance that the chain will move in that time period. Hence, chain motion is expected if $\Delta x > \Delta x^*$. Substituting equation 5.14 into the integral in equation 5.17 leads to

$$\Delta x = \int_{t_i}^{t_f} (v_{DC} - v_n^* + v_{AC} \sin(2\pi\nu t)) dt = \left[tv_{DC} - tv_n^* - v_{AC} \frac{1}{2\pi\nu} \cos(2\pi\nu t) \right]_{t_i}^{t_f}. \quad (5.18)$$

The values of t_i and t_f correspond to the two smallest solutions of

$$v_{DC} + v_{AC} \sin(2\pi\nu t) = v_n^*. \quad (5.19)$$

which are given by

$$t_i = \frac{1}{2\pi\nu} \arcsin\left(\frac{v_n^* - v_{DC}}{v_{AC}}\right), \quad \text{and} \quad t_f = \frac{1}{2\nu} - t_i = \frac{1}{2\nu} - \frac{1}{2\pi\nu} \arcsin\left(\frac{v_n^* - v_{DC}}{v_{AC}}\right). \quad (5.20)$$

Evaluating the integral in equation 5.18 with these limits leads to the following expression for

the distance Δx :

$$\Delta x = (v_{\text{DC}} - v_n^*) \left[\frac{1}{2\nu} - \frac{1}{\pi\nu} \arcsin \left(\frac{v_n^* - v_{\text{DC}}}{v_{\text{AC}}} \right) \right] - v_{\text{AC}} \left[\frac{1}{2\pi\nu} \cos \left(\pi - \arcsin \left(\frac{v_n^* - v_{\text{DC}}}{v_{\text{AC}}} \right) \right) - \frac{1}{2\pi\nu} \cos \left(\arcsin \left(\frac{v_n^* - v_{\text{DC}}}{v_{\text{AC}}} \right) \right) \right]. \quad (5.21)$$

Standard trigonometric identities are used to rewrite this as

$$\Delta x = (v_{\text{DC}} - v_n^*) \left[\frac{1}{2\nu} - \frac{1}{\pi\nu} \arcsin \left(\frac{v_n^* - v_{\text{DC}}}{v_{\text{AC}}} \right) \right] + \frac{v_{\text{AC}}}{\pi\nu} \sqrt{1 - \left(\frac{v_n^* - v_{\text{DC}}}{v_{\text{AC}}} \right)^2}. \quad (5.22)$$

This equation shows that $\Delta x \propto \nu^{-1}$ and that Δx increases with v_{AC} , though this is not a simple relationship. To gain a more insightful expression, we note that the grey shaded region in figure 5.3, corresponding to Δx , will be large in the case of $v_{\text{AC}} \gg v_n^* - v_{\text{DC}}$. This approximation is suitable for the experimental parameters used here and simplifies equation 5.22 to

$$\Delta x = \frac{1}{2\nu} (v_{\text{DC}} - v_n^*) + \frac{v_{\text{AC}}}{\pi\nu}. \quad (5.23)$$

Here Δx increases with v_{AC} and also with $v_{\text{DC}} - v_n^*$. The inverse relationship between Δx and ν is maintained, meaning that as the frequency is reduced, a chain moves further in each period and thus has an increased possibility of motion.

Finally equations 5.16 and 5.23 are combined to give the condition for movement corresponding to $\Delta x > \Delta x^*$:

$$\frac{1}{2\nu} (v_{\text{DC}} - v_n^*) + \frac{v_{\text{AC}}}{\pi\nu} > \frac{\lambda}{2} \left[1 - \frac{2}{\pi} \arcsin \left(\frac{v_{\text{DC}}}{v_n^*} \right) \right]. \quad (5.24)$$

The dependency on the amplitude of oscillations for chain motion can be given by rewriting equation 5.24 as

$$v_{\text{AC}}^* = \pi\nu \left[\frac{\lambda}{2} - \frac{1}{2\nu} (v_{\text{DC}} - v_n^*) - \frac{\lambda}{\pi} \arcsin \left(\frac{v_{\text{DC}}}{v_n^*} \right) \right], \quad (5.25)$$

where v_{AC}^* denotes the critical oscillation amplitude required to allow chain motion.

5.3 Experimental methods

5.3.1 Colloidal model system

The colloidal model system used consists of Dynabeads M-270 Carboxylic Acid that have a diameter of $3\text{ }\mu\text{m}$ when dispersed in 20% EtOH(aq) (see section 2.2.1). These are held in a quartz glass Hellma cell. The particles are subject to a uniform magnetic field in the sample plane, which causes particles to align due to an induced dipole in the direction of the magnetic field which is collinear with the one-dimensional optical landscape. In this way, chains of 2 – 25 particles can be formed with no other particles in the field of view. The magnetic field is varied from $0.6 - 1.5\text{ mT} \pm 0.05\text{ mT}$, which corresponds to a magnetic interaction parameter (equation 2.10) between $26 \leq \Gamma \leq 174$.

5.3.2 Optical landscape

A sinusoidal optical potential energy landscape is produced by creating 46 equally spaced optical traps. A laser power of 80 mW is chosen to give a single particle critical velocity of $v_C = v_1^* = 0.50\text{ }\mu\text{m s}^{-1}$ for $\lambda = 3.5\text{ }\mu\text{m}$. The wavelength of the optical landscape is varied between $3.20\text{ }\mu\text{m} \leq \lambda \leq 3.90\text{ }\mu\text{m}$.

5.3.3 Critical velocity experiments

Chains of particles are confined to an optical landscape and are then exposed to a driving velocity collinear with their major axis to locate the critical velocity. The critical velocity is defined as the minimum velocity at which a chain of particles moves from its original location after being subject to a driving velocity. The driving velocity is applied for 200 s or until the stage has moved $10\text{ }\mu\text{m}$ in the case of driving velocities smaller than $0.05\text{ }\mu\text{m s}^{-1}$. The critical velocity is found iteratively with a resolution of $0.01\text{ }\mu\text{m s}^{-1}$.

5.3.4 Chain length measurements

Individual particles are located using an image of a single particle as a template and then using a convolution method to find particle positions at 40 fps (see section 2.2.5). This gives coordinates of all particles, from which the end-to-end chain length can be calculated using $L = x_n - x_1$, where x_i is the position of particle i and n is the number of particles in the chain.

5.3.5 Dynamic depinning experiments

A chain of 13 particles is formed in an optical landscape with $\lambda = 3.5 \mu\text{m}$ and is subject to a magnetic field of 1.08 mT, corresponding to a critical velocity of $v_n^* = 0.19 \mu\text{m s}^{-1}$ for $n = 13$. The chain is driven at average velocities between $0.06 \mu\text{m s}^{-1} \leq v_{\text{DC}} \leq 0.18 \mu\text{m s}^{-1}$ with the oscillation amplitude varying between $0 \mu\text{m s}^{-1} \leq v_{\text{AC}} \leq 4.0 \mu\text{m s}^{-1}$. Using particle coordinates, the centre of mass of the chain is calculated, from which average chain velocity can be measured.

5.4 Results and discussion

5.4.1 Static Aubry-type transition

Critical velocity measurements

In order to probe a static Aubry-type transition, the critical velocity of colloidal chains, v_n^* , is measured as a function of the number of particles in a chain, n . This is shown in figure 5.5 for an optical landscape wavelength of $\lambda = 3.9 \mu\text{m}$ and a magnetic field of 1.465 mT corresponding to a magnetic interaction parameter of $\Gamma = 174$. The first important feature to note is that at higher chain lengths, the critical velocity, v_n^* , tends to have a lower value. This is a direct result of the fact that longer chains have a larger friction coefficient (equation 5.9), which means that, at the same driving velocity, they are subject to a larger driving force than for shorter chains, $F_{\text{C},n}^* = \zeta_n v_n^*$. A second striking feature is that there are chain lengths with a critical velocity of $v_n^* = 0$, which corresponds to a free sliding chain. This occurs for $n \approx 5k$ where k is a positive integer. The experimental data can be compared with equation 5.13 which predicts v_n^* . While equation 5.13 works relatively well for short chains, this relationship breaks down as the chain

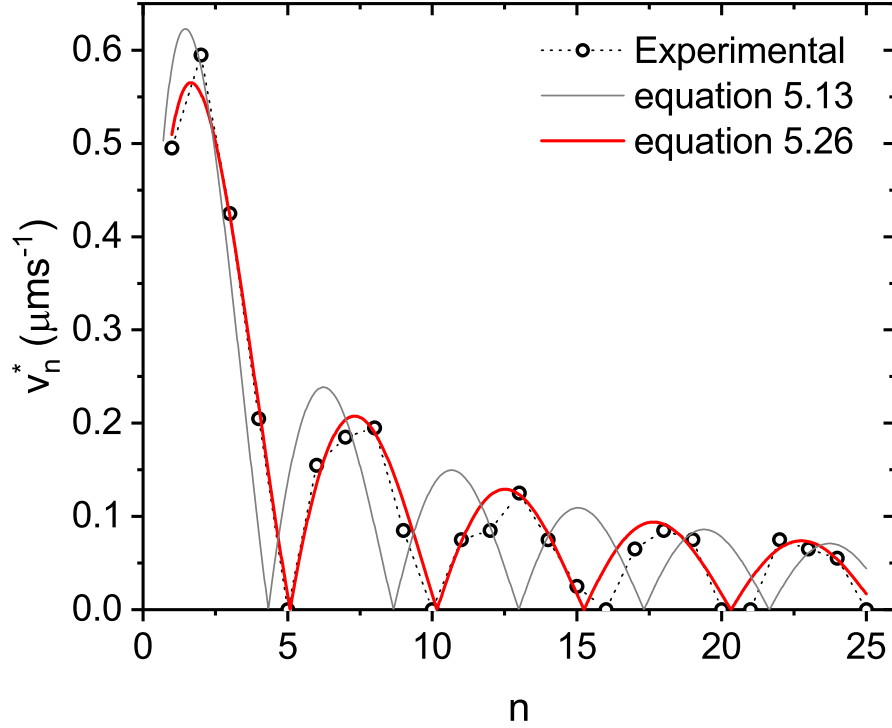


Figure 5.5: Plot of critical velocity, v_n^* against chain length, n for $\lambda = 3.9 \mu\text{m}$ and $\Gamma = 174$. Equation 5.13 is shown (grey line). Equation 5.26 is also shown where $2a$ is replaced with s and is used as a fitting parameter (red line).

becomes longer, beyond $n = 4$.

Chain commensurability

While equation 5.13 captures the qualitative behaviour well, it quantitatively predicts the location of $v_n^* \rightarrow 0$ incorrectly due to the assumption that the chain is completely rigid. At high magnetic fields, this is a reasonable assumption, but at lower magnetic fields where chains become more flexible, this assumption may break down. To improve this, the $2a$ in equation 5.13 is replaced with the average particle spacing, s , which may be extracted from the experimental data using the following expression:

$$v_n^* = \frac{2F_C}{(n+1)\zeta_1} \left| \frac{\sin(\pi n(s-\lambda)/\lambda)}{\sin(\pi(s-\lambda)/\lambda)} \right|. \quad (5.26)$$

The critical velocity thus becomes zero when

$$\frac{\pi n(s-\lambda)}{\lambda} = q\pi \quad \rightarrow \quad n = \frac{q\lambda}{(s-\lambda)}, \quad (5.27)$$

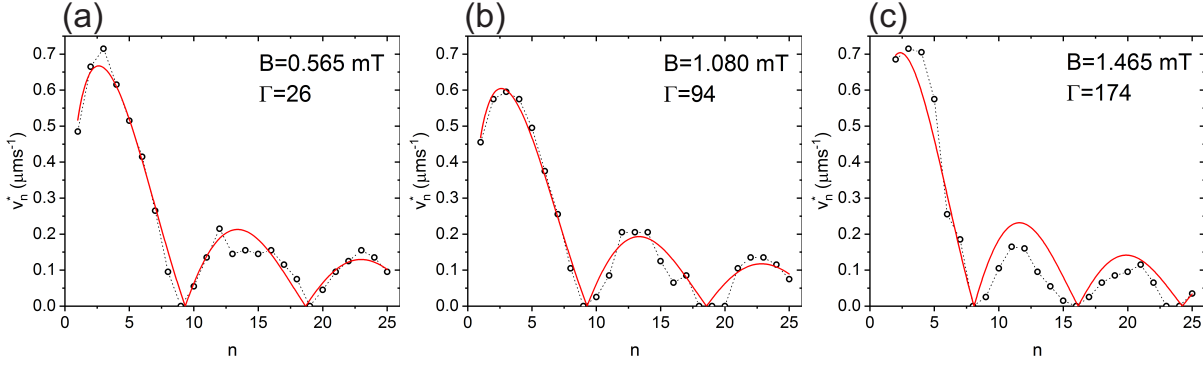


Figure 5.6: Plots of the critical velocity as a function of the chain length for three different magnetic field strengths. Here the landscape wavelength remains constant at $\lambda = 3.5 \mu\text{m}$.

where q is any integer. The smallest non-zero value that corresponds to $v_n^* = 0$ is thus

$$n_0 = \begin{cases} \lambda/(s - \lambda), & s > \lambda \\ \lambda/(\lambda - s), & s < \lambda \\ \text{undefined}, & s = \lambda. \end{cases} \quad (5.28)$$

This parameter, n_0 , is the critical chain ‘length’ and is the shortest non-zero chain length for which there is zero static friction. The critical chain length is a fitting parameter and as such is allowed to deviate from integer values, allowing an accurate estimate of the particle spacing. Due to the periodicity of equation 5.26, $v_n^* = 0$ for $n = qn_0$, as is indeed seen in figure 5.5, where equation 5.26 gives an excellent quantitative description of the data, even for n up to 25, and the critical chain length is found to be $n_0 = 5.09$. For the optical landscape wavelength used in figure 5.5, $\lambda = 3.9 \mu\text{m}$, we obtain a particle spacing of $s \approx 1.04 \times 2a = 3.13 \mu\text{m}$. This shows that a chain subject to an optical landscape slightly adjusts its length to accommodate free sliding at well defined values of n .

Magnetic field effects

Next the influence of the magnetic field upon the critical velocity of a chain in an optical landscape is considered. Changing the magnetic field affects the interaction strength between particles in a chain. Plots of the critical velocity against the chain length for three different magnetic field strengths for a landscape wavelength of $\lambda = 3.5 \mu\text{m}$ are shown in figure 5.6. The shape of each plot is similar to what was observed before with a general decrease in v_n^* as n increases and periodic chain lengths for which $v_n^* = 0$. The data are also very well described by

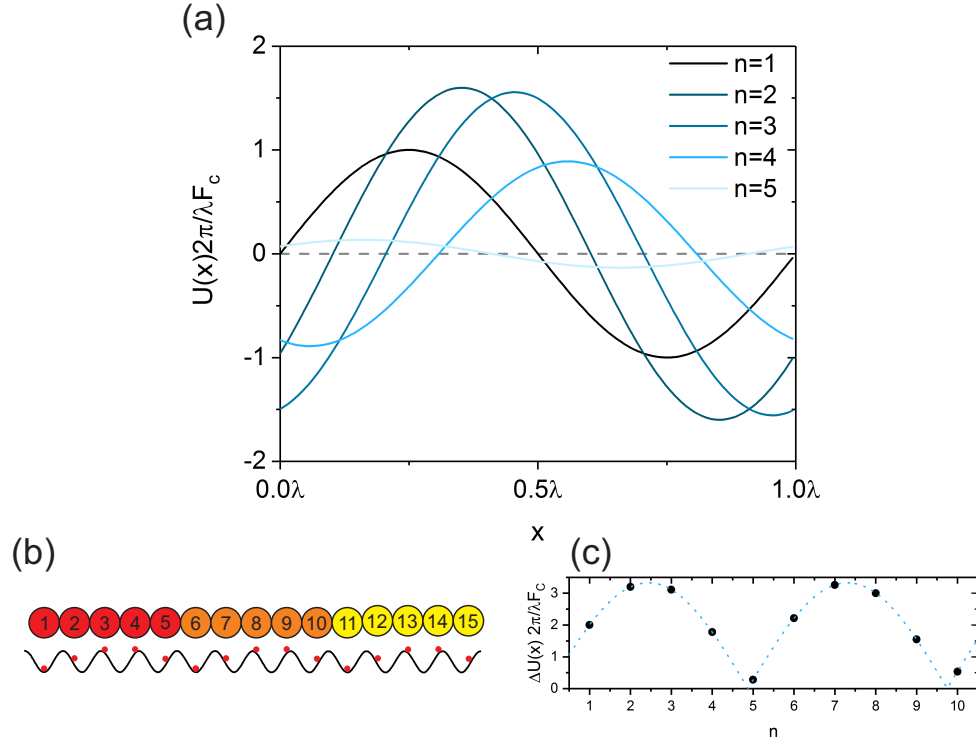


Figure 5.7: (a) Plot showing optical landscape as formed in equation 5.4 using $\lambda = 3.9 \mu\text{m}$ and $s \approx 3.1 \mu\text{m}$ for a chain length of $n = 1 - 5$. The optical potential almost disappears in the case of $n = 5$. (b) Schematic of a chain with the same length scales probed in (a). Different coloured particles highlight the repeating 5 particle units in the chain. (c) Plot of well depth as a function of chain length extracted from (a). Dotted line acts as a guide to the eye.

equation 5.26. An increased field strength leads to a reduced particle spacing and therefore a reduced value of n_0 , however this effect is relatively small (14% change in n_0 measured).

Physical interpretation

The physical nature of a freely sliding chain can be visualised using figure 5.7. The potential energy curves experienced by chains with $n = 1 - 5$ as calculated from equation 5.4, neglecting U_0 and $U_{mag,n}$, are plotted in figure 5.7a. Whilst the depth of the landscape increases from one to two particles, it then decreases until $n = 5$, where the depth of the potential is almost zero over all displacements, x . The critical force corresponds to the largest gradient in U_{opt} which, for a sinusoidal landscape, is proportional to the depth of the landscape. It can therefore be seen that a chain of five particles will freely slide, and exhibit superlubricity, if Brownian motion provides enough energy for it to overcome the small force barrier observed in figure 5.5. Figure 5.7b shows that for this commensurability, using $\lambda = 3.9 \mu\text{m}$, every fifth particle will be roughly in the same position of the optical landscape relative to its closest potential minimum (i.e. particle

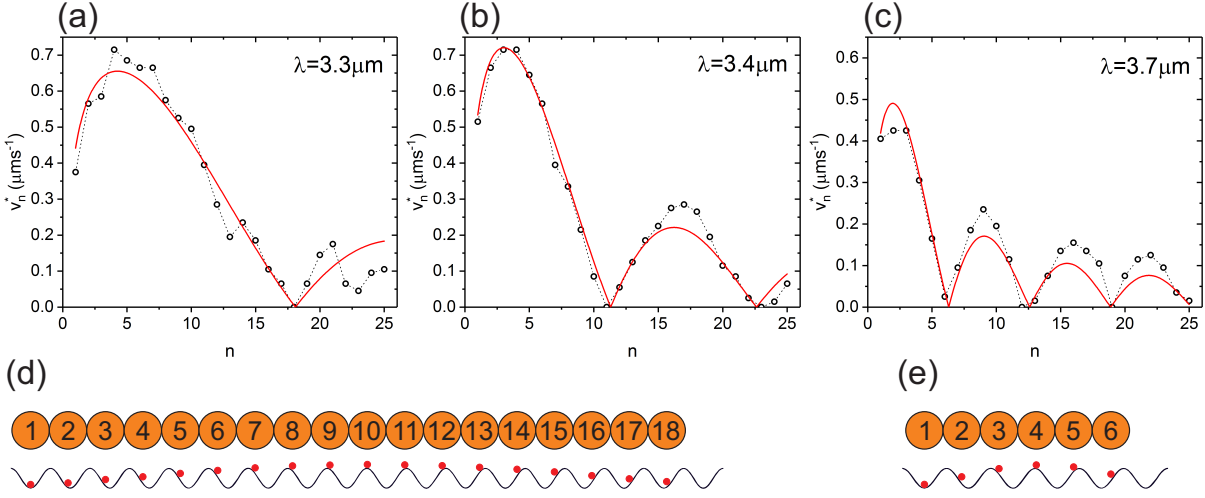


Figure 5.8: Plots of critical velocity as a function of chain length for landscape wavelengths of (a) $\lambda = 3.3 \mu\text{m}$, (b) $\lambda = 3.4 \mu\text{m}$ and (c) $\lambda = 3.7 \mu\text{m}$. As the commensurability of the chain in the landscape changes, so does the appearance of this plot. This is displayed schematically for (d) $\lambda = 3.3 \mu\text{m}$ and (e) $\lambda = 3.7 \mu\text{m}$ using a particle spacing experimentally found to be $s \approx 3.10 \mu\text{m}$.

1, 6, 11 etc.). This means that each unit of five particles (shown in figure 5.7b) will freely slide and this is what causes the periodicity predicted in equation 5.26 and seen experimentally in figures 5.5 and 5.6.

Wavelength effects

The effect of altering the wavelength of the optical potential energy landscape on the critical velocity of a chain being driven across an optical landscape is now addressed. Plots of the critical velocity as a function of the number of particles in a chain, n , are shown for three different landscape wavelengths in figure 5.8a–c. The general shape of these plots is consistent with what was shown in figure 5.5, however, the first value at which $v_n^* = 0$ changes dramatically. This is a direct result of the changing commensurability of λ and s and is visualised in figure 5.8d and e. The relative length scales for $\lambda = 3.3 \mu\text{m}$ (figure 5.8d) and $\lambda = 3.7 \mu\text{m}$ (figure 5.8e) are schematically shown, for the experimentally found particle spacing of $s = 3.10 \mu\text{m}$. In both cases, an additional particle would take the same relative position in the optical landscape as the first particle, which in this case is a minimum in potential energy. This means that the displayed chains will freely slide corresponding to $v_n^* = 0$ for $n = 18$ and $n = 6$.

For each wavelength, the average particle spacing, s , can be obtained via equation 5.26. The critical chain length, n_0 , can then be extracted using equation 5.28, which corresponds to the shortest chain length at which $v_n^* = 0$. Figure 5.9 shows that n_0 decreases as the wavelength

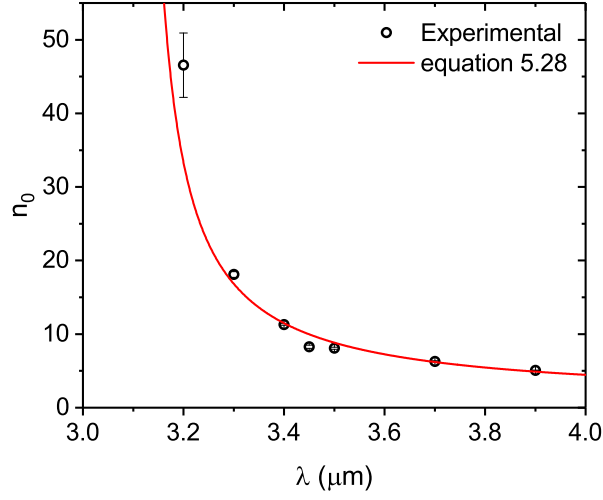


Figure 5.9: Plot of the critical chain length against the wavelength of the optical landscape. This is fitted to equation 5.28 and from this an average particle spacing of $s = 3.10 \mu\text{m}$ is extracted.

of the optical landscape increases. Fitting this with equation 5.28 gives an average particle spacing of $s = 3.10 \pm 0.01 \mu\text{m}$, which works well for all values of λ and confirms that $s \approx 2a$.

Breathing modes

As $s > 2a$, a colloidal chain has some flexibility within the optical landscape and the chain length is expected to fluctuate as it traverses the landscape. To probe this, a chain is driven across an optical landscape at a relatively low magnetic field corresponding to $B = 0.565 \text{ mT}$ and $\Gamma = 26$. The position of its centre of mass is tracked as well as its length, which is shown in figure 5.10 for two different values of n . For a chain of 9 particles (figure 5.10a) there is a clear correlation between the chain velocity and its length corresponding to caterpillar motion wherein the chain first compresses as the rear-most particle is driven forward. When the chain length is approximately $L = 25.25 \mu\text{m}$, corresponding to an average particle spacing of $s = 3.16 \mu\text{m}$, the front end of the chain moves forward causing the centre of mass to move whilst allowing the chain to extend to its original length, $L = 25.5 \mu\text{m}$. This process is shown in figure 5.10c and repeats itself each time there is chain motion. For a chain of $n = 11$ (figure 5.10b), there is a slightly different breathing mode wherein the chain extends before moving. Here, as the chain is driven, the leading particle moves forward, causing the chain to increase in length until the chain length reaches approximately $L = 31.5 \mu\text{m}$, corresponding to $s = 3.15 \mu\text{m}$. At this point, the rear-most particle is pulled forward and the chain can recoil to its original length of $L = 31.25 \mu\text{m}$, as illustrated in figure 5.10d. Breathing modes are often seen for chains driven at

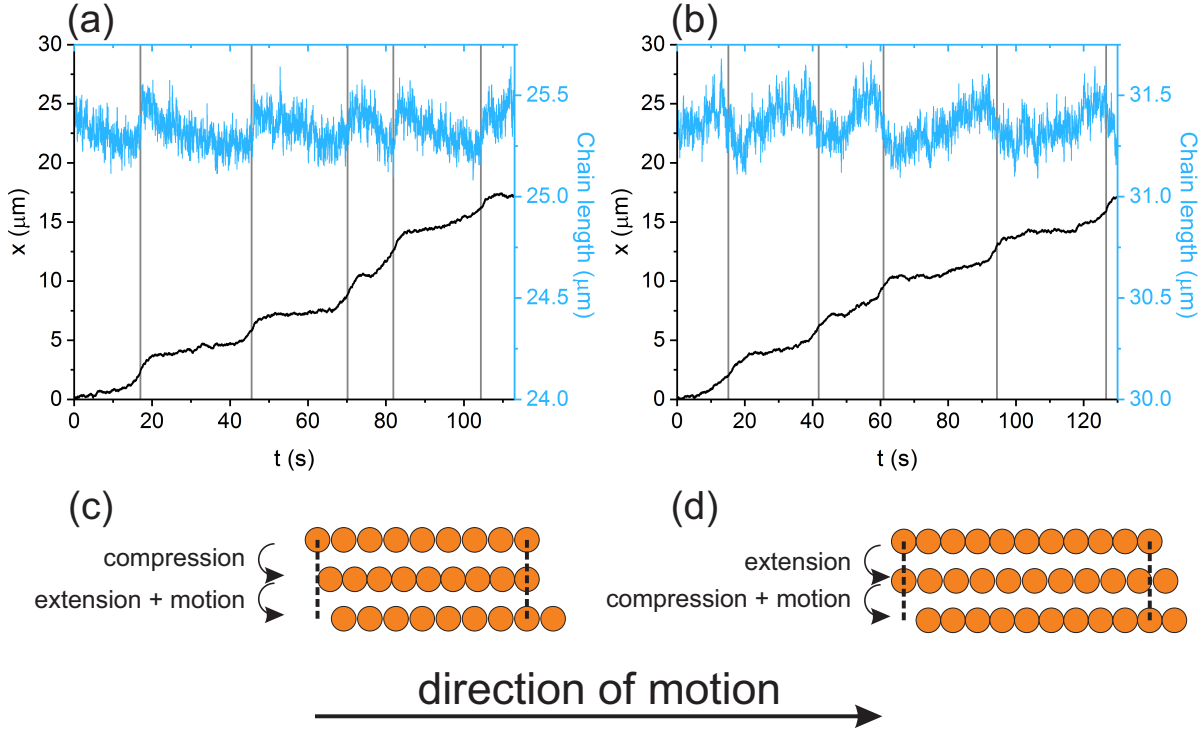


Figure 5.10: Chain position and chain length tracked for a chain consisting of (a) 9 and (b) 11 particles. Vertical lines denote chain motion and have been overlaid to ease identification of correlations between chain length and chain position. Here a magnetic field of $B = 0.565$ mT and a wavelength of $\lambda = 3.5$ μm are used. (c) Schematic of caterpillar motion via initial compression for a chain of 9 particles corresponding to motion displayed in (a). (d) Schematic of motion via initial extension for a chain of 11 particles corresponding to motion displayed in (b).

a driving velocity slightly above the critical velocity, however we find no systematic parameters that determine if a chain will move via initial compression or extension. Multiple chains of different lengths were tested and the breathing mode mechanism showed no dependence on n .

5.4.2 Dynamic depinning

Average velocity experiments

We now introduce an oscillation to the driving velocity and study how varying the AC amplitude, frequency and average driving velocity affects the depinning of a chain. Note that what was previously termed the driving velocity is, in this section, referred to as the average driving velocity, v_{DC} which is equal to the time-averaged driving velocity, $v_{DC} = \langle v_{drive} \rangle$. The average velocity, v_{AV} , is measured directly from the experiments and is the velocity of the chain. Importantly, for these experiments an average driving velocity is chosen such that $v_{DC} < v_n^*$ so in the absence of oscillations, there is no observed motion.

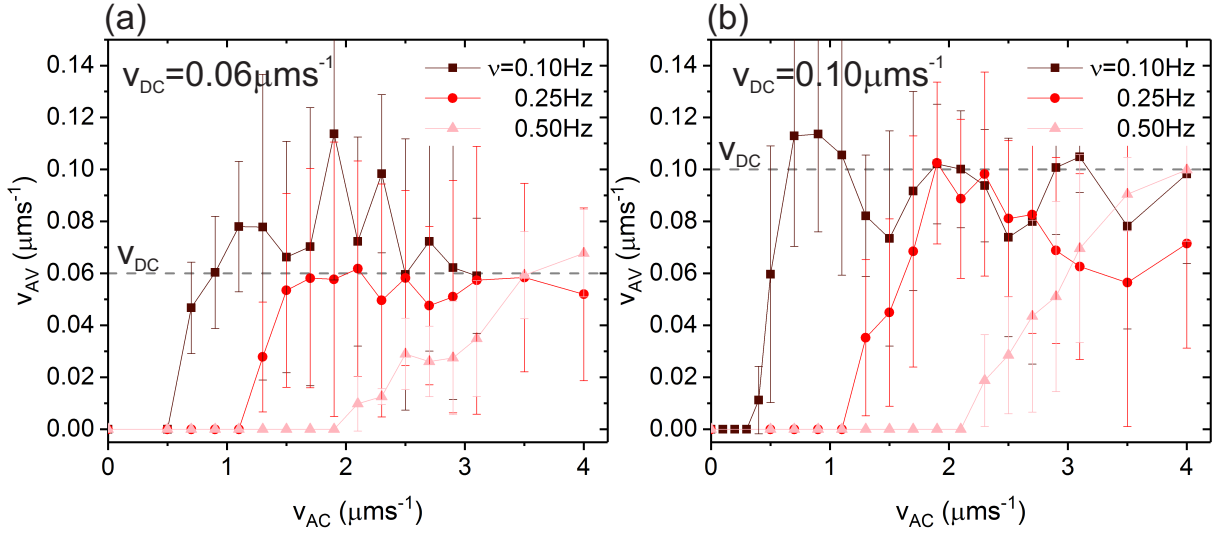


Figure 5.11: Average velocity measured as a function of v_{AC} for three different frequencies, $0.1 \text{ Hz} \leq \nu \leq 0.5 \text{ Hz}$, with an average driving velocity of (a) $0.06 \mu\text{m s}^{-1}$ and (b) $0.10 \mu\text{m s}^{-1}$. The average driving velocity, v_{DC} , is indicated by a horizontal dashed line. Here the chain length is $n = 13$, and $v_{13}^* = 0.19 \mu\text{m s}^{-1}$.

Initially, a typical experiment such as that shown for $v_{DC} = 0.06 \mu\text{m s}^{-1}$ and $\nu = 0.25 \text{ Hz}$ in figure 5.11a (red circles) is inspected with $v_n^* = 0.19 \mu\text{m s}^{-1}$ with $n = 13$. The average velocity of the chain, v_{AV} , is plotted as a function of the oscillation amplitude, v_{AC} . There is no motion for low values of v_{AC} corresponding to $v_{AV} = 0$. As the oscillation amplitude is increased, the chain becomes mobile at the critical oscillation amplitude, $v_{AC}^* = 1.3 \mu\text{m s}^{-1}$. This corresponds to the oscillations increasing the instantaneous driving velocity by a sufficient amount to overcome the critical velocity. The average velocity then increases as the oscillation amplitude increases until it reaches a plateau at $v_{AV} = v_{DC}$ for $v_{AC} \geq 1.5 \mu\text{m s}^{-1}$. At this point, the oscillations are so large that the chain is driven back and forth at such a high velocity that the optical landscape becomes insignificant and the chain simply moves at $v_{AV} = v_{DC}$, the average driving velocity.

Frequency effects

The effect that the frequency of oscillations, ν , has on the average velocity is shown for two average driving velocities in figure 5.11. Each experimental run shows the same general trends as were previously described but, importantly increasing the frequency of oscillations increases the critical oscillation amplitude. This is consistent with equation 5.25

$$v_{AC}^* = \pi\nu \left[\frac{\lambda}{2} - \frac{1}{2\nu} (v_{DC} - v_n^*) - \frac{\lambda}{\pi} \arcsin \left(\frac{v_{DC}}{v_n^*} \right) \right],$$

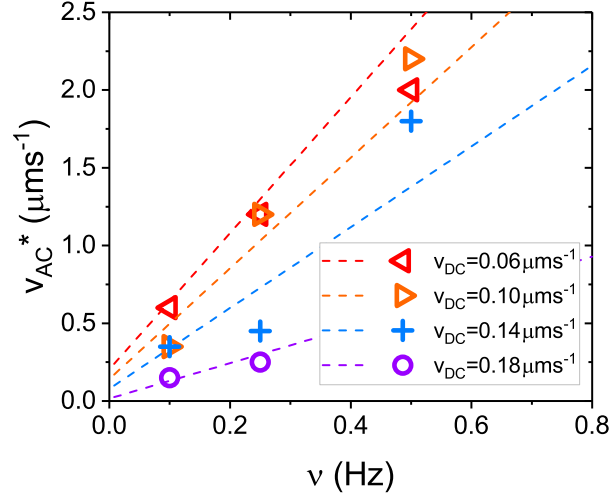


Figure 5.12: A graph showing the dependence of critical oscillation amplitude, v_{AC}^* on oscillation frequency, ν . Data points show experimental results for $0.06 \mu\text{s}^{-1} \leq v_{DC} \leq 0.18 \mu\text{s}^{-1}$ and dashed lines show equation 5.25.

from which it can immediately be seen that $v_{AC}^* \propto \nu$. The dependence of the critical oscillation amplitude on the frequency is shown in figure 5.12. Here the analytical expression for the critical oscillation amplitude as given by equation 5.25 is also plotted and is shown with dashed lines. While there is some deviation, this analytical expression gives a remarkably good estimate for the critical oscillation amplitude, especially in the absence of any fitting parameters.

Average driving velocity effects

We now study the effect of changing the average driving velocity, v_{DC} , on the average velocity, v_{AV} and the critical oscillation amplitude, v_{AC}^* . To this end, the normalised average velocity is plotted against the oscillation amplitude and this is shown for four different average driving velocities at two frequencies in figure 5.13. It is important to note that for all driving velocities, $v_{DC} < v_n^*$. Here the average velocity is normalised by the average driving velocity to ensure all graphs tend towards unity at high oscillation amplitude. Again, a similar general shape is seen for each data set as was shown in figure 5.11, but increasing the average driving velocity reduces the critical oscillation amplitude. Inspecting equation 5.25 reveals that the effect on v_{AC}^* of increasing v_{DC} is twofold. The first contribution is due to an increased average driving velocity decreasing v_{AC}^* due to the $(v_{DC} - v_n^*)/2\nu$ term in equation 5.23. The second and more substantial, effect is that increasing the average driving velocity lowers the $\arcsin(v_{DC}/v_n^*)$ term in equation 5.23, which originates from the expression for Δx^* in equation 5.16.

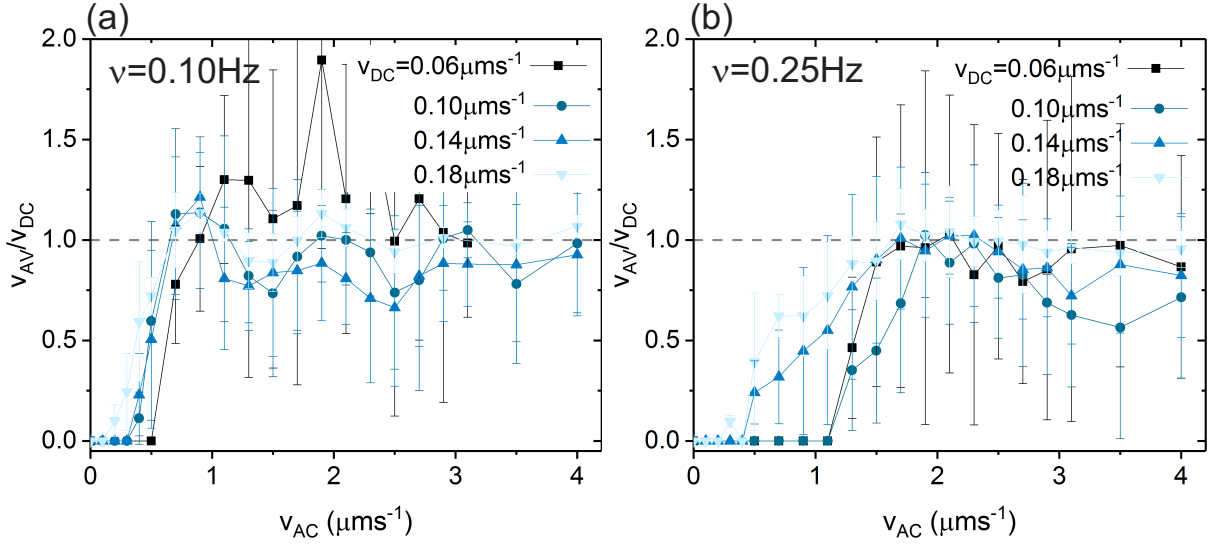


Figure 5.13: Normalised average velocity measured as a function of v_{AC} for four different velocities with an oscillation frequency of (a) 0.10 Hz and (b) 0.25 Hz. Here the chain length is $n = 13$, and $v_{13}^* = 0.19 \mu\text{m s}^{-1}$.

Finally we directly test the prediction for Δx^* given by equation 5.16 by measuring Δx^* using equations 5.22 (full expression) and 5.23 (approximation) with the experimentally measured value of v_{AC}^* such that $\Delta x^* = \Delta x(v_{AC} = v_{AC}^*)$. As Δx^* is only a function of the average driving velocity, v_{DC} (see equation 5.16), the experimentally measured values of Δx^* from equation 5.23 can be averaged over different experimental runs at the same average driving velocity, v_{DC} . In figure 5.14, Δx^* is plotted against the average driving velocity, with experimentally obtained results using equations 5.22 (full expression) and 5.23 (approximation) plotted as triangles and the line showing the predicted value of Δx^* from equation 5.16. Here, there is good agreement seen between experimental and theoretical values for Δx^* .

5.5 Conclusions

In this chapter, chains of magnetically interacting colloidal particles have been driven through sinusoidal optical potential energy landscapes. Rigid colloidal chains were driven across an optical potential energy landscape at a constant driving velocity, leading to a critical velocity with a complex chain length dependence. This gave rise to an Aubry-type transition where zero static friction was exhibited at well defined values of n , where a chain freely traverses the optical landscape. The effect of commensurability between the particle size and the wavelength of the optical landscape was explored and used as a way to experimentally measure the average

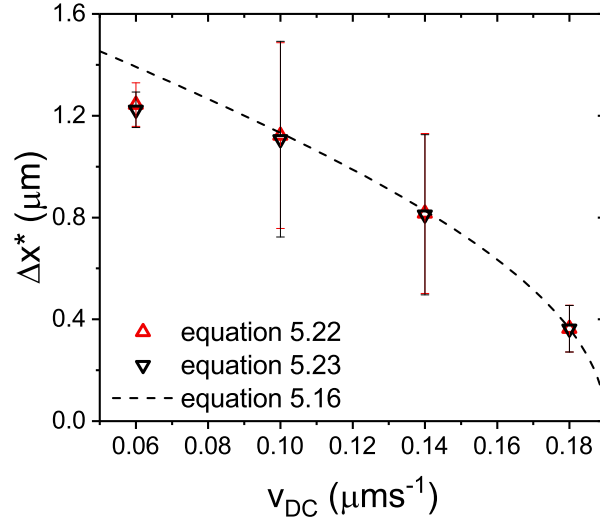


Figure 5.14: Plot comparing the experimentally measured value for Δx^* both for the full expression given by equation 5.22 (red triangles), and for the approximate solution given by equation 5.23 (black triangles). We also show the theoretically predicted value for Δx^* from equation 5.16 (Dashed line), which closely matches experimental results.

particle spacing in a chain. The nature of chain motion for a flexible chain was explored and two distinct breathing modes were observed. The motion of a colloidal chain when subject to an oscillating driving force was then studied. In this regime a chain can become depinned when driven at an average driving velocity below the critical velocity. We explored the behaviour of critical oscillation amplitude both as a function of the oscillation frequency and the average driving velocity where good agreement was found between theory and experiments.

Acknowledgments

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Chapter 6

Stochastic thermodynamics of driven colloidal particles

ABSTRACT

The stochastic thermodynamics of colloidal particles driven across one-dimensional optical potential energy landscapes is considered. Initially, a time-independent optical landscape is studied and the work due to the optical landscape is extracted from a particle trajectory. The timescales used to calculate the optical work are carefully considered to ensure that it is zero for a periodic time-independent optical landscape. The optical work is then combined with the work due to an external driving force, and the time dependence of the total work distributions is studied. Next, the stochastic thermodynamics of a particle as it is driven through a time-dependent optical landscape at a driving velocity corresponding to mode locked motion is studied. Here the optical work is non-zero and its time dependence is considered. The magnitude of the optical work and the total work is then considered in light of the mechanism of particle motion.

6.1 Introduction

Thermodynamics is of paramount importance to the world we live in. The first law states that a change in internal energy can be described in terms of heat and work, where heat denotes energy in the form of ‘random’ motion, and work describes ‘organised’ motion [82]. Its inception aimed to improve the efficiency of engines [156], but its applications range from calculating chemical equilibria to predicting phase changes [157].

Thermodynamics can be applied to macroscopic systems, whereby a thermodynamic transformation will always result in the same change in thermodynamic quantities as fluctuations are insignificant [158]. However, at the microscopic scale, local fluctuations mean that the same measurement will provide slightly different results [159, 160] and stochastic thermodynamics needs to be considered. This can be readily done in a colloidal system, which has the benefit of being easily manipulated, observable, and also subject to thermal noise. In this way, thermodynamic quantities have been measured for single colloidal particles [161–166] as well as for proteins [166–170] and in electronic systems [171, 172]. Thermodynamic quantities have also been extracted from larger systems consisting of two particles [173] up to samples of over 500 colloidal particles [174].

The stochastic thermodynamics of driven colloidal systems is particularly rich as they cannot reach true thermodynamic equilibrium. However, they can exhibit a so-called non-equilibrium steady state (NESS), the dynamic analogue of equilibrium. A system in NESS is not at equilibrium, meaning there is some net flow of energy or matter, however, it reaches a steady state whereby energy or matter is being transferred at a constant rate. In colloidal systems, viscous drag due to the solvent can be used to apply a non-conservative driving force [175], either using constant [159, 176, 177] or random forces [166], and in this way they may reach a NESS [178].

Here, we use a previously established framework to extract stochastic thermodynamic quantities from a colloidal particle driven across an optical landscape. Initially, a particle driven across a time-independent optical landscape is considered. The work due to the optical landscape is calculated from a particle trajectory and is shown to be zero. Timescales are carefully considered to obtain distributions for both the optical work and the total work. Next, the stochastic thermodynamics of a mode locked particle driven across a time-dependent optical

landscape is explored. This exhibits a finite amount of optical work, the magnitude of which is studied in the light of the nature of the particle motion.

6.2 Theory

6.2.1 Stochastic thermodynamics

Here, we follow the work of Sekimoto [160] as a means of extracting stochastic thermodynamic quantities from the trajectory of a driven colloidal particle in an optical potential energy landscape. This starts with the description of particle motion using the Langevin equation (see section 2.1.3):

$$\zeta \frac{dx}{dt} = F_{ext}(x, t) + \xi(t), \quad (6.1)$$

where ζ is the friction coefficient and $\xi(t)$ denotes thermal noise. Here, F_{ext} describes the external forces which, in these experiments, is composed of an optical force, $F_{opt}(x, t)$, and a constant driving force, F_{DC} ,

$$\zeta \frac{dx}{dt} = F_{opt}(x, t) + F_{DC} + \xi(t). \quad (6.2)$$

This Langevin equation can be rearranged into the following force balance:

$$0 = -\zeta \frac{dx}{dt} + \xi(t) - \frac{\partial U_{opt}(x, t)}{\partial x} + F_{DC}, \quad (6.3)$$

where it is noted that the conservative optical force can be written in terms of the optical potential, U_{opt} , as $F_{opt} = -\partial U_{opt}(x, t)/\partial x$. The driving force, F_{DC} , however, is non-conservative, meaning that a particle subject to F_{DC} leads to non-zero work over a closed loop, due to the fact that a particle moving in a solvent experiences viscous drag. The force balance in equation 6.3 is now converted into an energy balance by multiplying each term by ‘ $-dx$ ’:

$$0 = -\left(-\zeta \frac{dx}{dt} + \xi(t)\right) dx + \left(\frac{\partial U_{opt}(x, t)}{\partial x} - F_{DC}\right) dx. \quad (6.4)$$

Next, the concepts of the ‘system’ and the ‘heat bath’ are introduced. The system refers to the colloidal particle under study and the heat bath denotes the surrounding solvent. Importantly, $-\zeta \frac{dx}{dt} + \xi(t)$ denotes the heat that the heat bath transfers to the system [160], so by extension, the first term in equation 6.4, $-\left(-\zeta \frac{dx}{dt} + \xi(t)\right)$ is the heat that the system transfers to the heat bath. This is here denoted as positive heat and is defined as [160]

$$dQ \equiv -\left(-\zeta \frac{dx}{dt} + \xi(t)\right) dx. \quad (6.5)$$

With this definition, equation 6.4 simplifies to

$$0 = dQ + \left(\frac{\partial U_{opt}(x, t)}{\partial x} - F_{DC}\right) dx. \quad (6.6)$$

As the only external potential is due to the optical landscape and the following total differential can be written:

$$dU(x, t) = \left(\frac{\partial U_{opt}(x, t)}{\partial x}\right)_t dx + \left(\frac{\partial U_{opt}(x, t)}{\partial t}\right)_x dt, \quad (6.7)$$

from which equation 6.6 can be expressed as

$$0 = dQ + dU - \left(\frac{\partial U_{opt}(x, t)}{\partial t}\right)_x dt - F_{DC} dx. \quad (6.8)$$

This can now be compared with the first law of thermodynamics [160]:

$$dU = dW - dQ. \quad (6.9)$$

Note that the sign convention here is such that work is positive when it is done on the system and heat is positive when it is transferred to the heat bath. This convention is displayed in figure 6.1. Finally, by comparing equations 6.8 and 6.9, the work can be identified as [160]

$$dW \equiv \left(\frac{\partial U_{opt}(x, t)}{\partial t}\right)_x dt + F_{DC} dx. \quad (6.10)$$

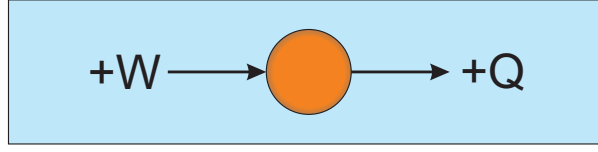


Figure 6.1: Schematic showing sign convention of work, W , and heat, Q , between the system (particle) and heat bath (solvent). Work is positive when done by the heat bath on the system and heat is positive when dissipated into the heat bath from the system.

6.2.2 Work from particle trajectories

The work as defined by equation 6.10 is now considered in more detail. To this end, the total work is split into the conservative ‘optical work’, W_{opt} , due to the time-dependent optical potential, and the non-conservative ‘DC work’, W_{DC} , due to a constant driving force,

$$W = W_{opt} + W_{DC}. \quad (6.11)$$

The optical work can be extracted from the particle trajectories as follows

$$W_{opt} = \int \frac{\partial U_{opt}(x, t)}{\partial t} dt = - \int F_{opt}(x, t) \frac{dx}{dt} dt = - \int_t^{t+\tau} F_{opt}(x, t) v(t) dt, \quad (6.12)$$

where τ is the lag time over which the integration is calculated and we have used

$$F_{opt}(x, t) = - \frac{\partial U_{opt}(x, t)}{\partial x} = - \frac{\partial U_{opt}(x, t)}{\partial t} \frac{dt}{dx}. \quad (6.13)$$

The integral in equation 6.12 can be obtained experimentally where both $F_{opt}(x, t)$ and $v(t)$ are known. Note that in the case of a time-independent optical landscape, where $U \equiv U(x)$, the optical work is zero, as $\partial U_{opt}(x)/\partial t = 0$. Importantly, this means that the lag time, τ , is restricted by the periodicity of the landscape as will be discussed in detail in section 6.4.1.

The second, non-conservative, contribution to the total work comes from the DC work, which is calculated from the particle trajectory as

$$W_{DC} = \int F_{DC} dx = \int F_{DC} \frac{dx}{dt} dt = \int_t^{t+\tau} F_{DC} v(t) dt. \quad (6.14)$$

The DC work, W_{DC} , increases with time for a mobile particle, but the more insightful contribution to the work comes from W_{opt} , which describes the work corresponding to a colloidal particle interacting with a spatially and time-dependent optical landscape.

6.3 Experimental methods

6.3.1 Colloidal model system

The colloidal system used here consists of Dynabeads M-270 Carboxylic Acid that have a diameter of $3\text{ }\mu\text{m}$ when dispersed in 20% EtOH(aq) (see section 2.2.1) and is held in a quartz glass Hellma cell. The system is sufficiently dilute to ensure that there is only one particle in the field of view at any time. Images are captured for all experiments at a frame rate of 40 fps.

6.3.2 Time-independent optical landscapes

A sinusoidal optical potential energy landscape is formed by creating 46 equally spaced optical traps where $\lambda = 4\text{ }\mu\text{m}$. A laser power of $I_0 = 350\text{ mW}$ is chosen, corresponding to $v_C = 2.8\text{ }\mu\text{m s}^{-1}$, and the sample is driven at a constant velocity of $v_{DC} = 4.0\text{ }\mu\text{m s}^{-1}$.

6.3.3 Time-dependent optical landscapes

Experimental data from Chapter 4 is used to study the stochastic thermodynamics of colloidal particles driven through time-dependent optical landscapes and a full experimental description is given in section 4.3.2. In short, a sinusoidal optical landscape with $\lambda = 3.5\text{ }\mu\text{m}$ is produced with a laser power of $I_0 = 320\text{ mW}$, corresponding to $v_C = 3.2\text{ }\mu\text{m s}^{-1}$. The amplitude of the optical landscape is oscillated according to equation 4.5 at a frequency of $\nu = 0.25\text{ Hz}$. The sample is driven at a constant velocity between $1.3\text{ }\mu\text{m s}^{-1} \leq v_{DC} \leq 1.7\text{ }\mu\text{m s}^{-1}$.

6.4 Results and discussion

6.4.1 Time-independent optical landscape

Optical work

Initially, the optical work distribution is considered for a particle being driven across a time-independent optical landscape using a constant driving velocity. To calculate the optical work

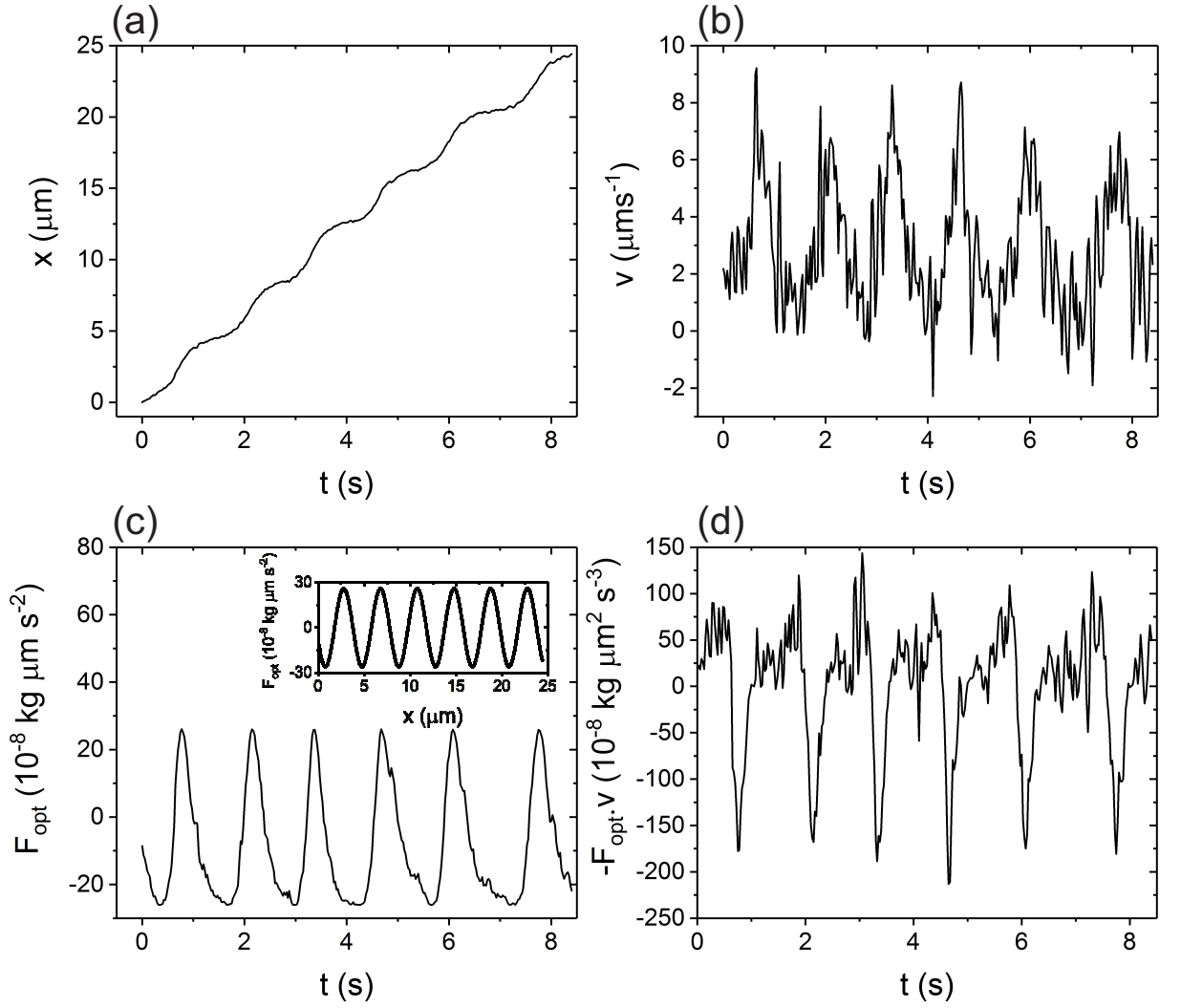


Figure 6.2: (a) A particle trajectory of a particle driven at $v_{\text{DC}} = 4 \mu\text{m s}^{-1}$ through a time-independent optical potential energy landscape where $\lambda = 4 \mu\text{m}$. (b) The velocity of the particle trajectory shown in (a). (c) The optical force that a particle is subject to as a function of time and inset: as a function of x . (d) The negative of the product of (b) and (c), $-F_{\text{opt}}(x, t)v(t)$.

according to equation 6.12,

$$W_{\text{opt}} = - \int_t^{t+\tau} F_{\text{opt}}(x, t)v(t) dt,$$

the instantaneous velocity and the optical force must first be obtained for a particle trajectory. An example of such a particle trajectory is shown in figure 6.2a, with the particle driven above the critical velocity of the optical landscape. The particle shows a non-zero average velocity, but is influenced by the optical landscape as can be seen from plateaus in the trajectory as a particle passes through the optical potential energy minima at intervals of $\lambda = 4 \mu\text{m}$. The instantaneous velocity, $v(t)$, is then calculated as the derivative of the particle trajectory and

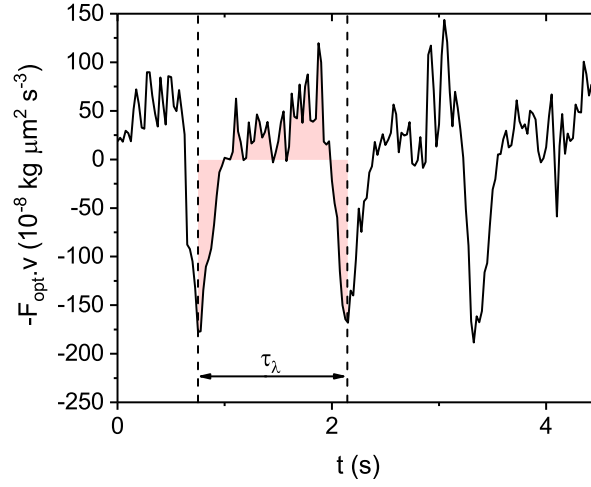


Figure 6.3: A plot of $-F_{opt}v$ against time, showing a graphical demonstration of the timescale, $\tau_\lambda \approx 1.4$ s and the associated optical work integral. This plot shows a zoomed in section of figure 6.2d.

is shown in figure 6.2b. Here the reduction in velocity as a particle passes through a minimum of the optical landscape is clear, though there is a significant amount of noise due to thermal fluctuations, allowing us to probe the stochastic nature of these experiments. The next quantity required to calculate the optical work is $F_{opt}(x, t)$ experienced by the particle moving through the optical landscape, which is shown in figure 6.2c as a function of time. This is calculated from $F_{opt}(x)$ given by equation 2.31 and shown as an inset in figure 6.2c, using the particle trajectory, $x(t)$. A particle experiences both a positive and a negative optical force as it crosses the optical landscape with $F_{opt}(t)$ being less ‘symmetrical’ than $F_{opt}(x)$ because $F_{opt}(t)$ is dependent on the particle trajectory, $x(t)$, which is non-linear and contains noise. The product of figure 6.2b and c gives $F_{opt}(x, t)v(t)$, and the negative of this, $-F_{opt}(x, t)v(t)$, which is integrated to give the optical work using equation 6.12, is shown in figure 6.2d. This plot shows a clear periodicity, with a large negative value when both the force and the velocity are large and positive. The periodicity of $-F_{opt}(x, t)v(t)$ corresponds to the frequency at which the particle crosses the optical landscape.

For a time-independent optical landscape, $\partial U_{opt}(x)/\partial t \equiv 0$, and because of this $\langle W_{opt} \rangle \equiv 0$ according to equation 6.12. To ensure this, the lag time, τ , in equation 6.12 is set to the time corresponding to the particle travelling a distance equal to $\Delta x = \lambda$. This is now referred to simply as τ_λ , and is calculated as $\tau_\lambda = \lambda/v_{AV}$. Graphically, this can be viewed as the average time between minima in figure 6.2d and is visualised more clearly in figure 6.3. Examples of optical work distributions, calculated from equation 6.12 for $\tau = \tau_\lambda$ and $\tau \neq \tau_\lambda$, are shown in figure 6.4a–c. Note that each graph shows a distribution because many integrals are calculated for different

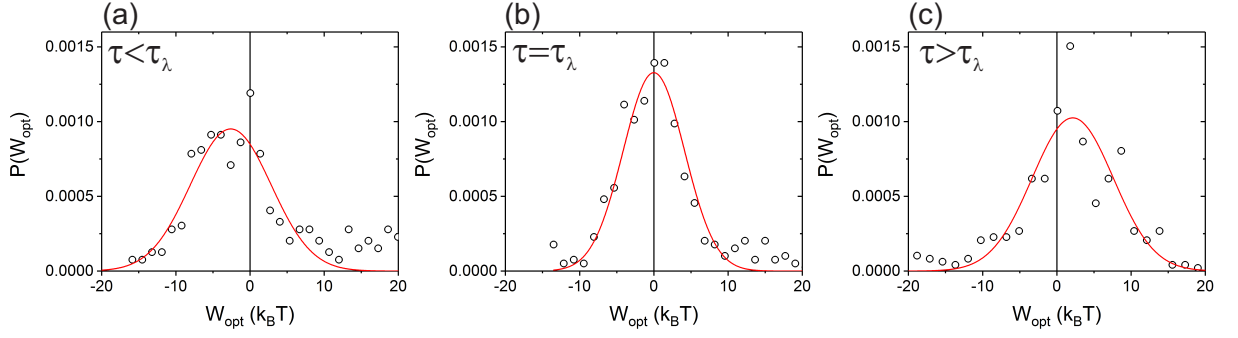


Figure 6.4: Optical work distributions shown for (a) $\tau < \tau_\lambda$, (b) $\tau = \tau_\lambda$, and (c) $\tau > \tau_\lambda$ (and $\tau < 2\tau_\lambda$). The experimental data is shown as points and a Gaussian fit to the data is shown as a red line. Vertical lines denote $W_{opt} = 0$.

starting times along the particle trajectory. Each work distribution shown in figure 6.4 is fitted with a Gaussian distribution due to the thermal noise in the system. For $\tau = \tau_\lambda$, shown in figure 6.4b, the distribution is centred at zero corresponding to no optical work done on average as expected. For $\tau < \tau_\lambda$, shown in figure 6.4a, the optical work distribution is centred at a negative value and for higher values of $\tau > \tau_\lambda$, shown in figure 6.4c, the distribution is centred at a positive value of optical work. The non-zero average optical work seen for $\tau \neq \tau_\lambda$ is due to incorrectly sampling the trajectory, which leads to oversampling of the negative and positive parts of the integral in figure 6.3.

The average optical work is zero over a time of τ_λ , and this should also be the case for $\tau_{n\lambda} = n\lambda/v_{AV}$. This is tested in figure 6.5 where the optical work distributions are shown for four values of $\tau_{n\lambda}$. Note that here only the Gaussian fits to the data are shown for clarity. All

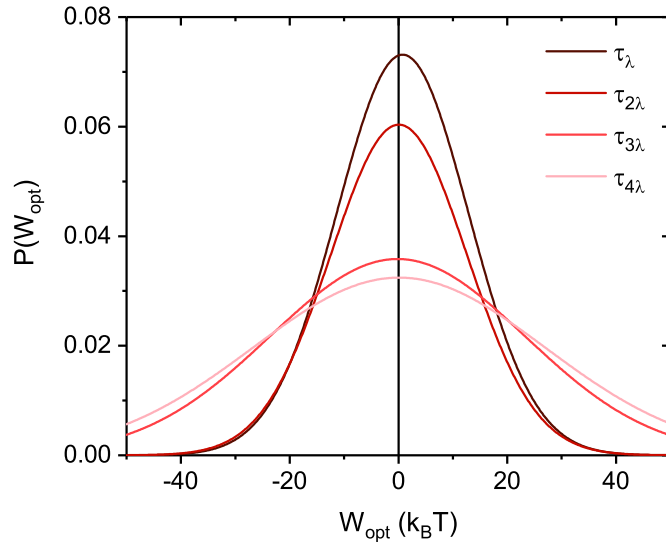


Figure 6.5: Optical work distributions shown for $\tau_{n\lambda}$, for $n = 1-4$. A vertical line is shown at $W_{opt} = 0$ which marks the centre of all four distributions.

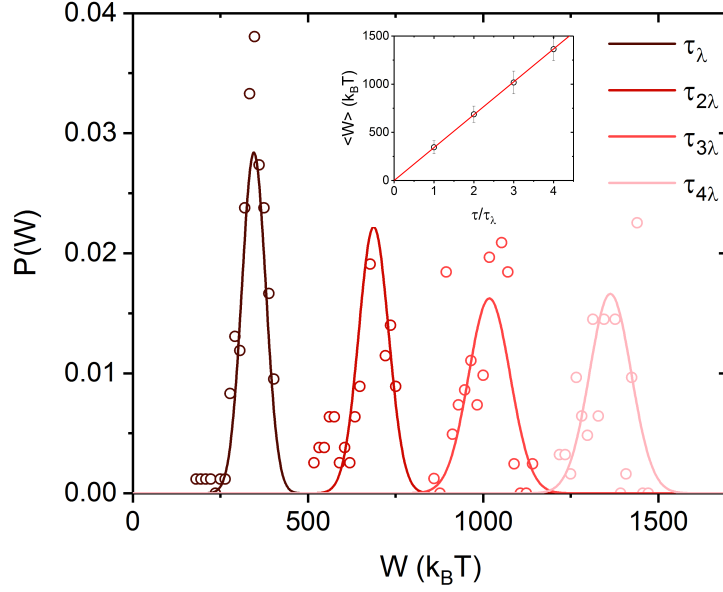


Figure 6.6: Total work distributions for four different times which correspond to the same distributions shown in figure 6.5. Inset: the mean total work as a function of time.

four optical work distributions are centred at zero due to the time-independent nature of the optical landscape. The distributions are, however, clearly different and as τ increases, so does the width of the distribution. Each distribution has a finite width due to the thermal noise in the system, and at longer lag times more noise is sampled. The distributions for $\tau_{3\lambda}$ and $\tau_{4\lambda}$ are very similar due to a lack of statistics when calculating the optical work distributions over finite-length trajectories.

Total work

Next, the total work, including both the conservative optical work and non-conservative DC work, is considered according to equation 6.11:

$$W = W_{opt} + W_{DC}.$$

As $\tau_{n\lambda}$ is defined as $\tau_{n\lambda} = n\lambda/v_{AV}$, the DC work can be expressed as

$$W_{DC} = \int_t^{t+\tau} F_{DC} v(t) dt \approx \int_t^{t+\tau} F_{DC} v_{AV} dt, \quad (6.15)$$

where F_{DC} and v_{AV} are both positive and constant. This approximation is, on average, true and shows that the DC work will increase linearly with time. In this thesis, however, the

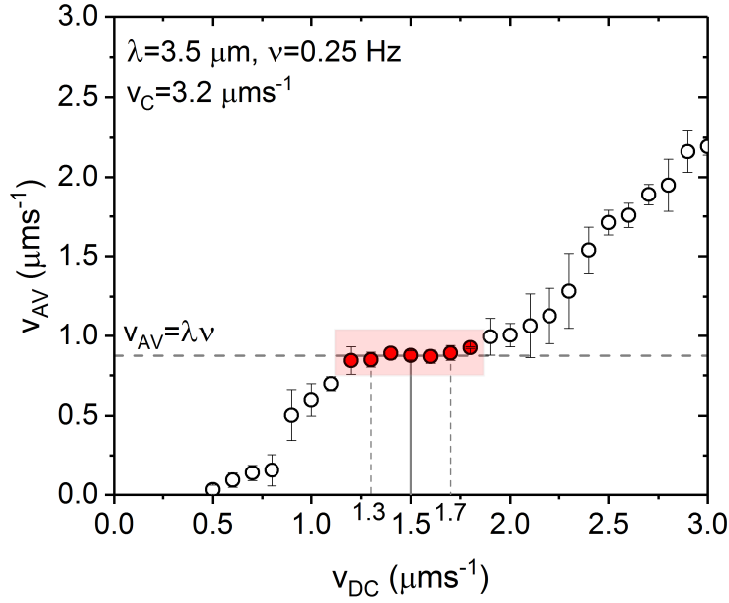


Figure 6.7: Average velocity plotted against driving velocity for a colloidal particle in a time-dependent optical landscape. This plot corresponds to the data shown in figure 4.3 for $\lambda = 3.5 \mu\text{m}$, $\nu = 0.25 \text{ Hz}$ and $v_C = 3.2 \mu\text{ms}^{-1}$. The highlighted region denotes the mode locked region, where $\tau_\lambda = \tau_{osc} = 4 \text{ s}$.

approximation is not used to ensure that a work distribution with a finite width is seen. The total work distributions are shown in figure 6.6 for four different lag times with Gaussian fits. Here the distributions become wider for longer lag times, and also show an increase in their average value. The inset shows the average work as a function of τ , which has a clear linear dependence. The increasing width of the distributions has the same origin as that for the data in figure 6.5 with the thermal noise having a greater effect at longer lag times, $\tau_{n\lambda}$. The increase in the average total work is due to the contribution from the DC work which is shown to increase linearly with time in equation 6.15.

6.4.2 Time-dependent optical landscape

Optical work

Next we consider a driven colloidal particle in a time-dependent optical landscape with $\lambda = 3.5 \mu\text{m}$, $v_C = 3.2 \mu\text{ms}^{-1}$ and $\nu = 0.25 \text{ Hz}$. Here, a finite amount of optical work is expected to be observed because $\partial U_{opt}(x, t)/\partial t \neq 0$. To do this, experimental results, previously presented in Chapter 4, are used in which the amplitude of the optical landscape is oscillated with a frequency, $\nu = 0.25 \text{ Hz}$. Figure 6.7 shows the average particle velocity as a function of the driving velocity. Above $v_{DC} = 0.5 \mu\text{ms}^{-1}$ the particle is mobile and as the average velocity reaches

$v_{AV} = \lambda\nu = 0.875 \mu\text{m s}^{-1}$, the particle becomes mode locked, exhibiting periodic motion for $1.2 \mu\text{m s}^{-1} \leq v_{DC} \leq 1.8 \mu\text{m s}^{-1}$ (highlighted). At higher driving velocities the average velocity increases and no further mode locked steps are seen.

When calculating the optical work for a particle driven through a time-independent optical landscape, the time of integration was carefully chosen to be $\tau_{n\lambda} = n\lambda/v_{AV}$. With a time-dependent optical landscape, a new timescale is introduced corresponding to $\tau_{osc} = 1/\nu$. As such, three driving velocities are considered where these two timescales are equal to each other, which corresponds to the first dynamic mode locking step, highlighted in figure 6.7. Here, $v_{AV} = \lambda\nu$, and hence $\tau_{\lambda} = \lambda/v_{AV} = 1/\nu = \tau_{osc}$. Initially, the ‘centre of the mode locked step’ is considered, where $v_{DC} = 1.5 \mu\text{m s}^{-1}$ and the same process is followed as in section 6.4.1 to obtain the optical work for a driven colloidal particle in a time-dependent optical landscape (figure 6.8). First, a particle trajectory is shown in figure 6.8a which has a periodic nature due to the mode locked motion of the particle. From this, the particle velocity is calculated (figure 6.8b), and similarly to the particle trajectory, shows a periodic nature. Note that a smoothed line is shown to highlight the periodicity in figure 6.8b, however, in all subsequent calculations the raw data is used. The optical force is then shown as a function of time in figure 6.8c. The optical force, $F_{opt}(x, t)$, is a function of both space and time, so importantly the optical force shown in figure 6.8c is the optical force as experienced by a single particle following the trajectory, $x(t)$. The particle experiences both a positive and a negative optical force, with a zero optical force at intervals of $\tau_{osc} = 4 \text{ s}$, corresponding to the amplitude of the optical landscape being zero. The product of figures 6.8b and c gives $F_{opt}(x, t)v(t)$, and the negative of this is shown in figure 6.8d. This is an essential step as the integral of this curve gives the optical work, W_{opt} , according to equation 6.12. The envelope of this graph shows a periodicity due to the oscillating nature of the optical landscape. Figure 6.8d has a high level of noise due to the noise in $v(t)$, so in figure 6.9 we show a zoom of the velocity, optical force, and the resulting $-F_{opt}(x, t)v(t)$ for a time period corresponding to $\Delta t = \tau_{2\lambda}$. Due to the time-dependence of the optical landscape, there are time periods corresponding to $F_{opt} \approx 0$. The exception to this is a large negative region of $-F_{opt}(x, t)v(t)$ (shaded red), which denotes a high and positive optical force and a positive velocity corresponding to the optical landscape ‘pushing’ the particle forward.

Computing the optical work according to equation 6.12 corresponds to calculating the area underneath the curve shown in figure 6.9c, which leads to the optical work distributions shown

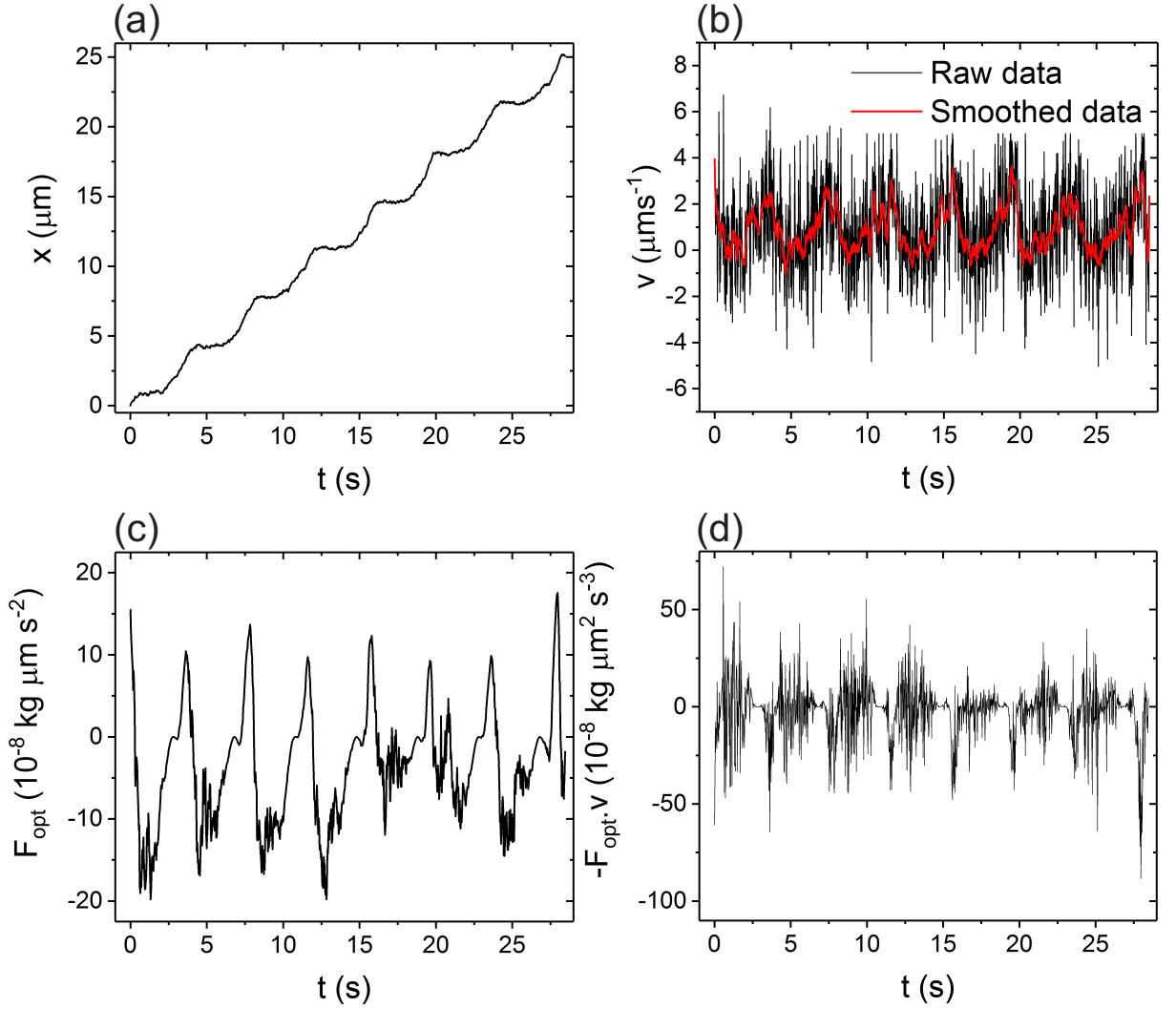


Figure 6.8: (a) A particle trajectory of a particle driven at $v_{\text{DC}} = 1.5 \mu\text{m s}^{-1}$ through a time-dependent optical potential energy landscape where $\lambda = 3.5 \mu\text{m}$, and $\nu = 0.25 \text{ Hz}$. (b) The velocity of the particle trajectory shown in (a) both for the raw data, $dt = 0.025 \text{ s}$ (black line) and the data smoothed over 10 frames, $dt = 0.25 \text{ s}$ (red line). (c) The optical force that a particle is subject to as a function of time. (d) The negative of the product of (b) and (c), $-F_{\text{opt}} v$.

in figure 6.10a for four different lag times. Here, unlike the time-independent optical landscape studied in section 6.4.1, there is a finite amount of negative optical work done, which corresponds to the particle doing work on the surrounding heat bath as it is ‘pushed’ forwards by the optical landscape. At longer lag times, there is a more negative value of optical work. This is because the work is measured over a longer time period so increases in magnitude.

The DC work distributions can also be calculated according to equation 6.15, and are shown in figure 6.10b for the same lag times as in figure 6.10a. The magnitude of DC work increases with time and is always positive as it denotes the heat bath doing work on the particle as it ‘pushes’ the particle forwards.

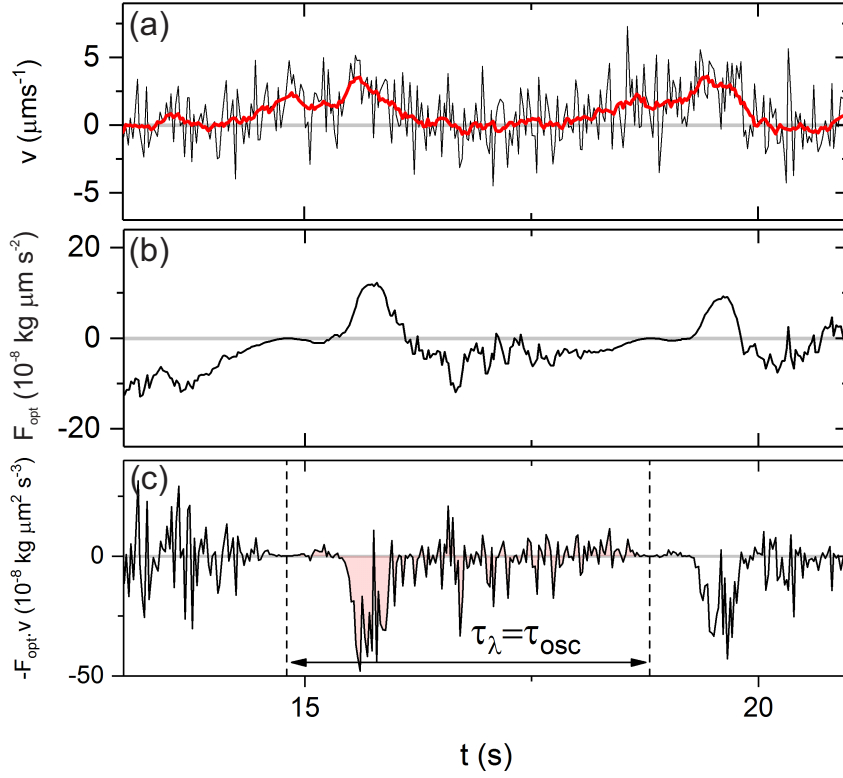


Figure 6.9: A zoomed in plot of (a) $v(t)$, (b) $F_{opt}(t)$, and (c) $-F_{opt}v(t)$ (figures 6.8b–d), with a graphical demonstration of the timescale, $\tau_\lambda = \tau_{osc} = 4$ s and the associated optical work integral (shaded region).

The total work distributions are shown in figure 6.10c and the total work increases with lag time. The inset in figure 6.10c shows the mean values of optical work, DC work, and total work. The magnitude of all values increases linearly with lag time as a longer lag time increases the magnitude of the measured work. We also note that the magnitude of the DC work is greater than the optical work as the driving force has a larger effect on the particle than the optical landscape. The total work is always positive denoting that, on average, the heat bath does more work on the particle than the particle does on the heat bath. The statistics of experimental data is low and therefore the widths of the Gaussian fits do not contain conclusive information about the random diffusive noise.

Stochastic thermodynamics at mode locking

At dynamic mode locking, the average velocity, v_{AV} remains constant, however, the instantaneous dynamics may vary substantially. The optical work can be interpreted as the amount of work that is required to maintain v_{AV} for a given v_{DC} , hence maintaining the mode locked motion. To probe this, the optical work is measured at three different driving velocities within

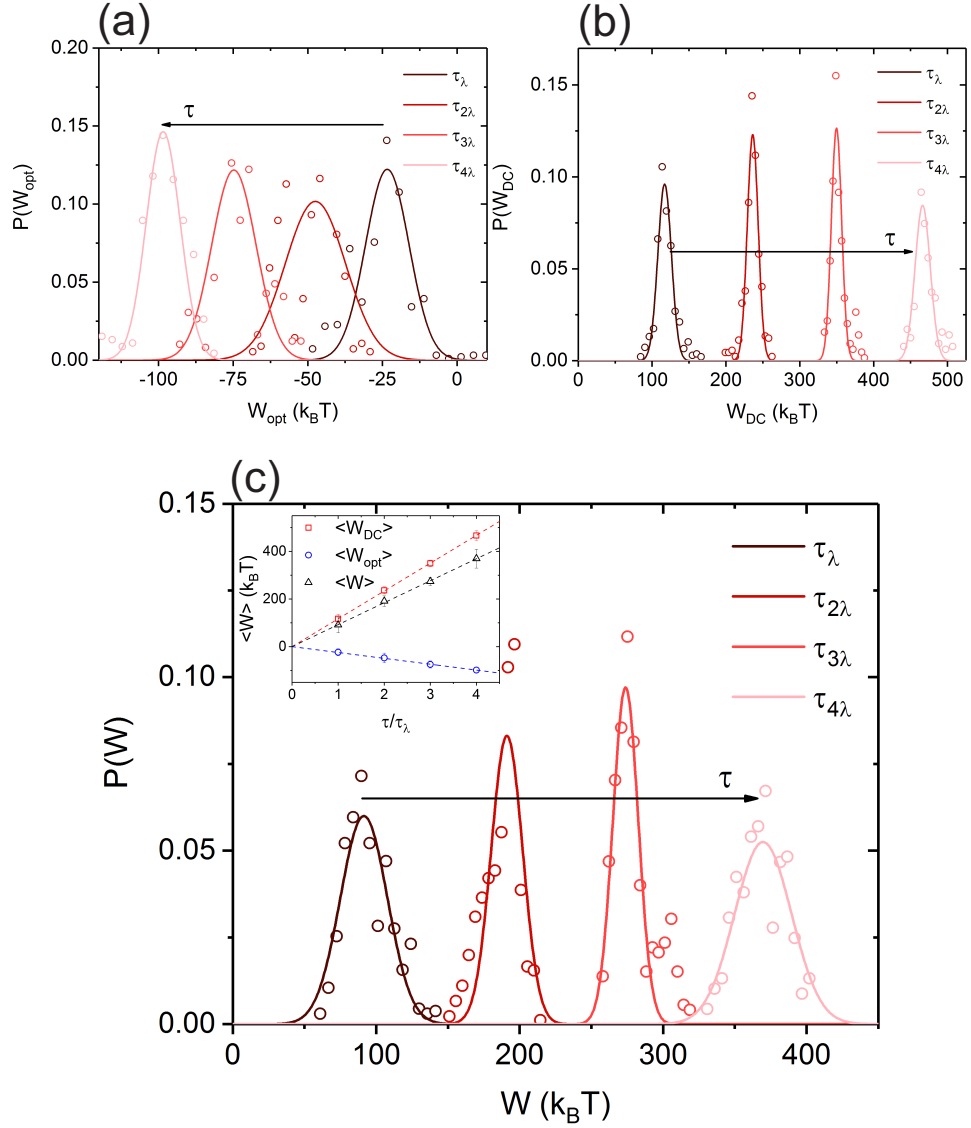


Figure 6.10: (a) Optical work, (b) DC work and (c) total work distributions for $\tau_{n\lambda}$, for $n = 1-4$, where $v_{\text{DC}} = 1.5 \mu\text{m s}^{-1}$. (c) Inset: the mean optical work, DC work and total work as a function of time.

the first mode locked step, as shown in figure 6.7. The velocities explored here all exhibit mode locked motion, and have the same average velocity of $v_{\text{AV}} = 0.875 \mu\text{m s}^{-1}$ (see figure 6.7), but correspond to the beginning of a mode locked step ($v_{\text{DC}} = 1.3 \mu\text{m s}^{-1}$), the centre of a mode locked step ($v_{\text{DC}} = 1.5 \mu\text{m s}^{-1}$), and the end of a mode locked step ($v_{\text{DC}} = 1.7 \mu\text{m s}^{-1}$). The essential values for calculating work, v_{DC} , $F_{\text{opt}}(x, t)$, and $F_{\text{opt}}(x, t)v(t)$ are shown for these three different driving velocities in figure 6.11 for $\tau = \tau_\lambda$.

Each plot of $v(t)$ (figure 6.11a, d, and g) shows the same form, with a positive velocity as the particle moves forward, followed by a period where $v(t) \approx 0$ as the particle is confined in a minimum of the optical landscape. The optical force $F_{\text{opt}}(x, t)$ varies substantially between

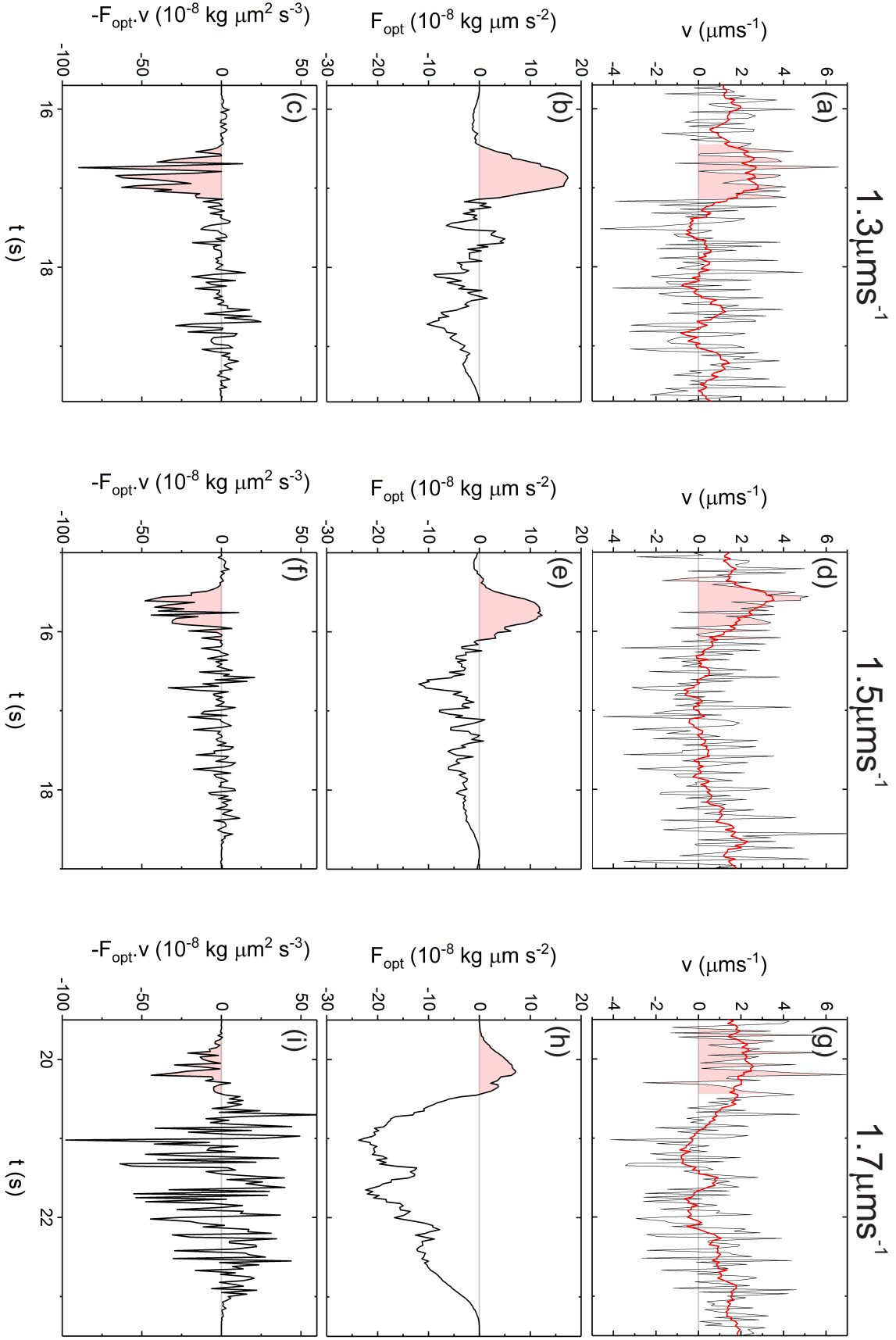


Figure 6.11: Particle velocity, optical force and $-F_{\text{opt}}v$ for driving velocities of (a)–(c) $1.3 \mu\text{m s}^{-1}$, (d)–(f) $1.5 \mu\text{m s}^{-1}$, and (g)–(i) $1.7 \mu\text{m s}^{-1}$. Highlighted regions correspond to a positive optical force. Only one oscillation of the optical landscape is shown for clarity, $\tau = \tau_\lambda = 4 \text{ s}$.

different driving velocities. At the beginning of the mode locked step, when $v_{\text{DC}} = 1.3 \mu\text{m s}^{-1}$, $F_{\text{opt}}(t)$ (see figure 6.11b) is large and positive before dropping to $F_{\text{opt}} \approx 0$. The physical meaning of this is that the optical force acts to ‘push’ the particle forwards to maintain its mode locked motion. In the centre of the mode locked step, when $v_{\text{DC}} = 1.5 \mu\text{m s}^{-1}$, $F_{\text{opt}}(t)$ (see figure 6.11e) is positive before becoming negative with a smaller amplitude. This corresponds to the particle being ‘pushed’ forwards by the optical landscape before being slightly ‘pulled’ backwards by the optical landscape. At this driving velocity, the particle is ‘pushed’ forward to a lesser extent than for $v_{\text{DC}} = 1.3 \mu\text{m s}^{-1}$ as it is being driven at a higher velocity than at the beginning of the mode locked step. At the end of the mode locked step, when $v_{\text{DC}} = 1.7 \mu\text{m s}^{-1}$, $F_{\text{opt}}(t)$ (see figure 6.11h) is small and positive before becoming large and negative. This corresponds to the particle being slightly ‘pushed’ forwards before being significantly ‘pulled’ backwards by the optical landscape to maintain the same v_{AV} . These effects are echoed in figure 6.11c, f, and i, where the highlighted region shows $-F_{\text{opt}}(x, t)v(t)$ at its largest magnitude which corresponds to a high particle velocity. A summary of this behaviour is shown schematically in figure 6.12 with the arrows denoting the approximate magnitude of the optical force experienced by a colloidal particle as it is driven across a time-dependent optical landscape.

The integral of $-F_{\text{opt}}(x, t)v(t)$ over τ_{λ} corresponds to the optical work, and the optical work distributions for the driving velocities studied in figures 6.11 and 6.12 are shown in figure 6.13a. As the driving velocity increases, the average optical work also increases and becomes less negative. At low driving velocities, the particle is mainly ‘pushed’ by the optical landscape, meaning it does work on the solvent corresponding to negative work. At higher driving velocities, the particle experiences less of a ‘push’ by the optical landscape, which means it does less work on the solvent and less negative work is exhibited, even to the point where for $v_{\text{DC}} = 1.7 \mu\text{m s}^{-1}$, $\langle W_{\text{opt}} \rangle > 0$. This means that on average, the particle is ‘pulled’ backwards by the optical landscape more than it is ‘pushed’ forwards. Despite this ‘pushing’ and ‘pulling’, on average the optical landscape acts to slow the particle down, $v_{\text{AV}} < v_{\text{DC}}$. The optical landscape leads to time periods where the particle velocity is low meaning that the work contribution from this is small because $W_{\text{opt}} = \int F_{\text{opt}}v dt$. The DC work distributions are calculated using equation 6.15 (see figure 6.13b). The average value of the DC work increases with the driving velocity which can be directly seen from equation 6.15 where v_{AV} remains constant but $F_{\text{DC}} = \zeta v_{\text{DC}}$ increases and the solvent does more work on the particle.

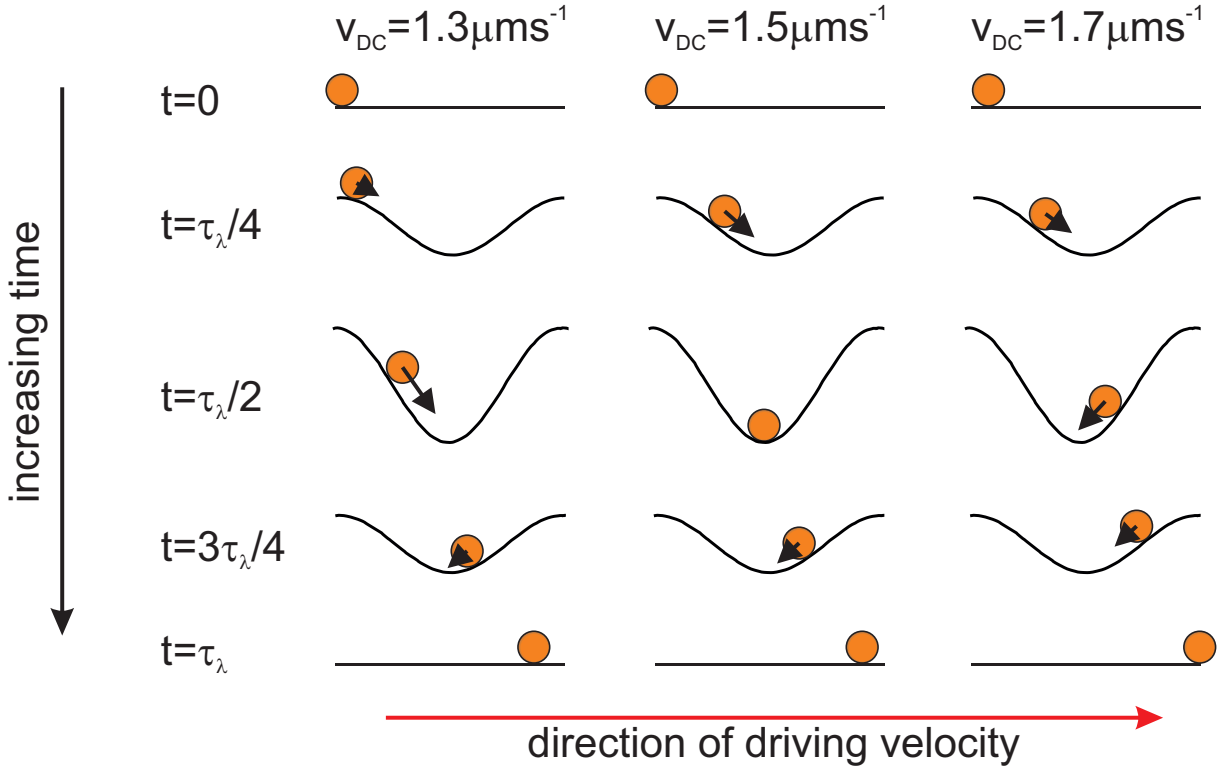


Figure 6.12: Schematic of mode locked motion at three different driving velocities over one wavelength of the optical landscape which also corresponds to $\tau = \tau_\lambda$. Snapshots of particle position are shown as the time-dependent optical landscape oscillates (top to bottom). Arrows denote the approximate amplitude of the optical force as the particle is driven from left to right.

The resulting total work distributions are shown in figure 6.13c. Each distribution shows a similar shape, but as v_{DC} increases, the centres of the distributions become more positive. This is due to the DC work, W_{DC} , and the optical work, W_{opt} , both increasing with driving velocity as shown in figure 6.13d where the mean work is plotted as a function of driving velocity for the DC work, the optical work and the total work. At a lower driving velocity, $v_{DC} = 1.3 \mu\text{m s}^{-1}$, the system is most efficient with the particle travelling at $v_{AV} = 0.875 \mu\text{m s}^{-1}$ whilst $+60 k_B T$ of total work is done on the particle for a distance of $x = \lambda$. At the highest driving velocity considered on this mode locked step, $v_{DC} = 1.7 \mu\text{m s}^{-1}$, the particle clearly travels at the same average velocity, $v_{AV} = 0.875 \mu\text{m s}^{-1}$, but here over double the amount of work is done on the particle over the same distance, $+135 k_B T$. This corresponds to a particle being ‘pushed’ forward strongly by the solvent, and leads to the optical landscape ‘pulling’ the particle backwards to maintain the mode locked average velocity.

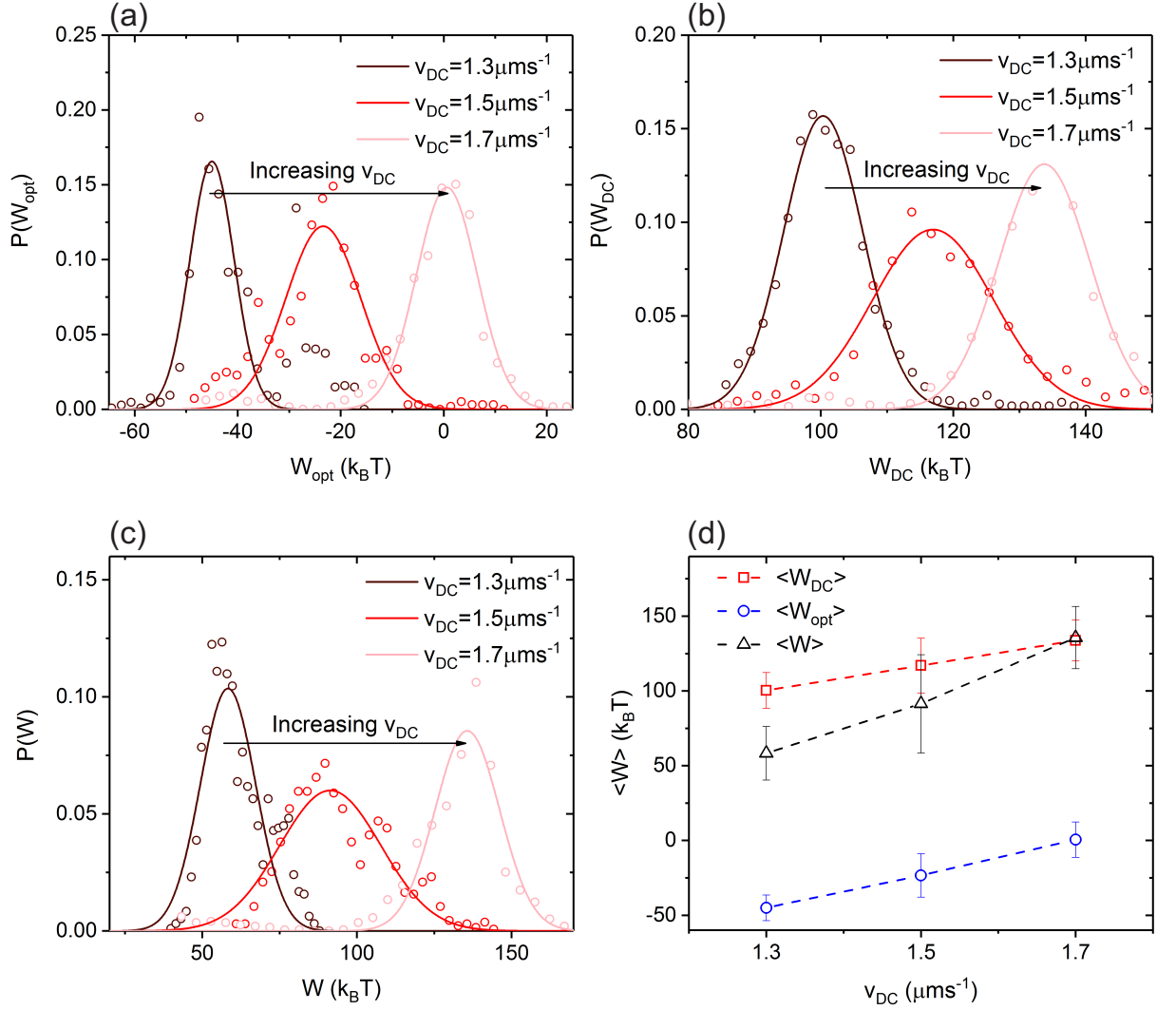


Figure 6.13: (a) Optical work, (b) DC work and (c) Total work distributions for three driving velocities, all located on a mode locked step. Work distributions are calculated for $\tau_\lambda = 4$ s. (d) The mean optical, DC and total work as a function of driving velocity. All data is shown for $\tau = \tau_\lambda$

6.5 Conclusions and outlook

In this chapter a particle has been driven through a time-dependent and a time-independent optical landscape. Initially, the ‘optical work’ done by a particle in a time-independent optical landscape was calculated. The work distribution was centred at zero, denoting that no optical work was done on average, though the width of the distribution increased with lag time. The ‘DC work’ was then considered and shown to increase linearly with time. A mode locked particle in an time-dependent optical landscape was then studied, from which a non-zero optical work was extracted. The work exhibited a strong time dependence and was also seen to vary strongly with exact conditions of motion, even in the presence of mode locked motion.

This chapter has introduced the concept of stochastic work for a colloidal particle driven through a one-dimensional time-dependent optical landscape, and particularly in the case of mode locked motion. Future works may focus on the work done by a particle that does not exhibit synchronised motion wherein the issue of timescales becomes far from trivial, as $\tau_\lambda \neq \tau_{osc}$. This work may also have implications on other synchronised systems, however for a non-zero work to be extracted the system must be subject to a time-dependent conservative force, which is here manifested in the time-dependent optical landscape. Further to this, the behaviour of two or more particles may be studied in this system, which introduces an extra term in the equation of motion to account for particle interactions [174]. In this way, multiple particle transport could be studied and motion aided by interactions could be probed.

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Summary

In this thesis the dynamic behaviour of colloidal particles driven across optical potential energy landscapes has been studied. The meta-stable horizontal and vertical states of colloidal rods in a single optical trap close to a wall have been characterised before exposing a horizontal colloidal rod to a driving force through an optical landscape. Below the critical velocity, the equilibrium position of a rod was found to vary substantially from that of a sphere due to its enhanced interaction with a wall greatly altering its friction coefficient. At higher velocities, a colloidal rod was seen to behave similarly to a sphere, exhibiting dynamic mode locking. Colloidal spheres were then driven across a time-dependent optical landscape where different modes of mode locking was observed. The mode locked step widths were shown to vary with the oscillation frequency and the coupling strength between the particle and the optical landscape. The particle transport was also studied by measuring the effective diffusion coefficient which showed a large dependence on driving velocity and mode locking. Next, chains of interacting colloidal particles were driven across an optical landscape. A mismatch between the length scales of the chain and the optical landscape gave rise to a freely sliding chain in an Aubry type transition. In this regime a chain exhibited zero static friction despite being subject to a potential energy landscape. Chain motion was inspected for a driven flexible chain that exhibited breathing modes. Introducing oscillations in the driving force led to dynamic depinning, which was affected by both the frequency and amplitude of the oscillations. Finally, the stochastic thermodynamics for particles driven across an optical landscape was considered. The work done by a particle in both a time-independent and a time-dependent optical landscape was measured. The optical work in a time-independent landscape was shown to be zero. However, the time-dependent counterpart exhibited a finite amount of work due to the optical landscape. The magnitude of the observed total work was considered in light of the mechanism of particle motion along with analysis of the contributing optical work and driving work.

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