May 2013

Hybrid Lattice Boltzmann - Molecular Dynamics Simulations With Both Simple and Complex Fluids

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A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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HYBRID LATTICE BOLTZMANN - MOLECULAR DYNAMICS SIMULATIONS WITH BOTH SIMPLE AND COMPLEX FLUIDS
(Thesis format: Integrated Article)

by

Frances Mackay

Graduate Program in Applied Mathematics

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

The behaviour and properties of colloidal suspensions strongly depend on the interactions arising between the immersed colloidal particles and the solvent. However, modelling such interactions is not at all straightforward; the larger time and length scales experienced by the colloidal particles compared to the solvent molecules makes all-atom molecular dynamics (MD) simulations of such systems completely impractical. Therefore a coarse-grained representation of the fluid is required, along with a method to couple this fluid to the colloidal particles.

In the first part of this thesis, we propose a new method for coupling both point and composite MD particles to an isotropic lattice-Boltzmann fluid. This coupling is implemented through the use of conservative forces, calculated by assuming elastic collisions between the particles and the fluid. With the implementation of a thermal lattice-Boltzmann method, the fluid acts as a heat bath for the MD particles without requiring external Langevin noise. This method has been implemented into the open source molecular dynamics package, LAMMPS, providing an efficient technique for explicitly including hydrodynamic interactions in MD simulations.

If a liquid crystal (LC) is used as a solvent instead of an isotropic fluid, anisotropic forces develop among the immersed colloidal particles even in the absence of flow. These forces arise due to a preferred orientation of the LC molecules on the colloidal surface, leading to the formation of topological defects in the bulk LC. A thorough understanding of the resulting forces is important, as their anisotropic nature could potentially be used to manufacture non-close packed photonic colloidal crystals.

In the second part of this thesis, we use a lattice-Boltzmann LC algorithm to investigate the interactions arising among colloidal particles in a LC. Using a cholesteric LC, we present results for a defect bonded particle chain, and a diamond colloidal crystal. In addition, as the defects and distortions generated in the LC result in a non-uniform pressure exerted on the particle surface, we also investigate the behaviour of 2D deformable particles in a nematic, as any potential shape change could have a significant impact on the resulting interactions.

Keywords: Lattice Boltzmann, Molecular Dynamics, Liquid Crystal, Hydrodynamics
Co-Authorship Statement

All articles presented in this thesis were co-authored with my supervisor, Dr. Colin Denniston. The work presented in Chapter 2 was additionally co-authored by Santtu Ollila (Ph.D. student at Aalto University School of Science and Technology, and co-supervised by Dr. Denniston), whose thermal lattice Boltzmann method was used in the code, and helped in testing the simulation package.
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Part I

Colloidal Particles in an Isotropic Fluid
Chapter 1

Introduction

Suspensions of colloidal particles are found abundantly in nature (eg. milk, blood) as well as in industrial applications such as paints, aerosols, and pharmaceuticals. Many technical applications, such as coatings and lubricants, rely on an understanding of the properties of such substances subject to shear. In addition, shear induced crystallization of confined colloidal particles can be used as a technique to manufacture photonic crystals [1].

A full understanding and study of the rheological properties of such suspensions necessarily requires the inclusion of hydrodynamic interactions, which arise as particles both generate and respond to flows in the host fluid. A prime example of the need to include these interactions is the high viscosity, shear thickened state of a colloidal system with large Péclet number [2] (this number relates the shear rate to the particle diffusion rate). For moderate shear rates, shear thinning occurs in the system, as the particles re-arrange themselves along fluid streamlines, thereby reducing the rate of inter particle collisions, and resulting in a decrease in the viscosity (see Figure 1.1(a)). Without considering hydrodynamic interactions, this state is expected to persist, even as the Péclet number approaches infinity. However, in reality, large shear rates lead to large hydrodynamic interactions, which couple the relative motion of the particles, resulting in the formation of highly concentrated particle clusters (see Figure 1.1(b)). Collisions and jamming of nearby clusters increases the viscosity in the system. This shear thinning/thickening behaviour has promising commercial applications, such as in the development of flexible soft body armour [3].

In addition to colloidal systems, hydrodynamic effects are important for a wide range of other applications, including confined polymers in solutions [4, 5], and protein folding [6]. Therefore, in order to accurately model solute/solvent systems, these hydrodynamic effects must be included, through the explicit inclusion of the fluid solvent.

Historically, computational approaches to fluid dynamics could be classified into one of two categories; either top-down, macroscopic approaches, or bottom-up microscopic approaches.
Figure 1.1: Shear thinning and thickening in confined colloidal systems.

In the top-down approach, the Navier-Stokes equations, governing the evolution of the fluid, are discretized, and modelled using either finite difference, finite element, finite volume, or spectral methods (see for example [7–9]). While these methods can be computationally efficient, they are difficult to apply to complex geometries. In contrast, the bottom-up approach uses Newton’s equations of motion to track the motion of the individual fluid molecules, with averaging performed in order to obtain their collective behaviour. This can easily be adapted to systems with complex geometries, however, the need to track the positions and velocities of every particle makes this approach completely impractical for simulations of colloidal systems, in which the vast majority of particles belong to the solvent, and a much smaller timestep is needed to resolve the motion of these solvent molecules than to track the colloidal particles.

Over the past few decades, several mesoscopic methods have been introduced, which lie somewhat in between the top-down and bottom-up approaches, allowing a speed up of computational time, without directly solving the Navier-Stokes equations. These include Dissipative Particle Dynamics (DPD) [10, 11], which is similar to MD, but uses very soft potentials to allow for a much larger timestep, multiparticle collision dynamics (MPCD) [12, 13], which treats the solvent as a set of particles with continuous space and velocity coordinates, but with free streaming between discrete “collision” events, and the lattice-Boltzmann method (LBM), which is the method used throughout this thesis.

The lattice-Boltzmann method treats the collective behaviour of the fluid molecules from a statistical point of view, through the use of a discretized Boltzmann equation. While its original, and most common application is modelling fluid flow governed by the Navier-Stokes
equations, this method has been applied to a range of other problems, including quantum mechanics [14, 15], magnetohydrodynamics [16, 17], the behaviour of a superconductor near the critical temperature [18], reaction-diffusion equations [19] and liquid crystal dynamics [20–22].

1.0.1 Origin of the Lattice Boltzmann Method

Historically, the lattice-Boltzmann method evolved from lattice gas cellular automata (LGCA) first successfully used in 1986 by Frisch, Hasslacher, and Pomeau [23]. This method uses a simplified microscopic model to treat the fluid, motivated by the fact that different microscopic interactions can lead to the same macroscopic behaviour provided they satisfy the same conservation laws [24]. Instead of allowing particles access to a continuous range of positions and velocities like in a classical MD simulation, space is discretized into a uniform lattice on which a set of particles with discrete velocities are confined, subject to a Pauli exclusion principle such that no two particles with the same velocity can occupy the same lattice site. At each timestep, the particles move to the nearest lattice site in the direction of their velocity, and a set of collision rules for particles approaching one another are used to determine their post-collision velocities. One might expect the resulting particle motion to satisfy the incompressible Navier-Stokes equations, provided the collisions conserve mass, momentum, and energy; however, while necessary, these are not sufficient conditions. This was observed by Hardy, de Pazzis, and Pomeau [25], who tried unsuccessfully to use this method on a uniform, square lattice. It took over 10 years for Frisch et al. [23] to realize the further requirement, that the lattice possess a sufficient symmetry; in 2D, a square lattice does not have enough symmetry to reproduce the Navier-Stokes equations, while a hexagonal lattice does. The precise reason for this symmetry requirement will be discussed in detail later, in the context of the lattice-Boltzmann algorithm.

LGCA provides an extremely computationally simple method for modelling the Navier-Stokes equations; it consists of purely local interactions, requiring only neighbouring grid point information, and the discrete nature of the particle velocities means that all the information about the system can be stored by a set of boolean occupation numbers. However, this method is not without it’s problems. These include a violation of Galilean invariance, the existence of spurious invariants, a non-physical dependence of the pressure on the fluid velocity, and a large amount of noise in the system, due to the use of the Boolean variables [26]. The lattice-Boltzmann method arose as a direct response to this last drawback, replacing the Boolean variables by a set of distribution functions. It was later discovered that the LBM could also solve all of the other problems plaguing LGCA, making it an extremely popular modelling method.
technique. See [26] for a detailed discussion of the historical steps involved in the evolution of LBM from LGCA.

1.0.2 Standard Lattice-Boltzmann Method

While the lattice-Boltzmann method historically evolved out of LGCA, it can simply be understood in terms of kinetic theory, discussed in Appendix A. The important result is the Boltzmann BGK equation given by,

$$\frac{df(x, p, t)}{dt} = \frac{\partial f(x, p, t)}{\partial t} + \frac{p}{m} \cdot \nabla f(x, p, t) + F \cdot \frac{\partial f(x, p, t)}{\partial p} = -\frac{1}{\tau} \left(f(x, p, t) - f^{eq}(x, p, t)\right).$$ (1.1)

Here, $f(x, p, t)$ is the single particle distribution function defined such that $f(x, p, t)d^3x$ corresponds to the total number of particles with position lying within $d^3x$ of $x$, and momenta within $d^3p$ of $p$, $m$ is the mass of the particles, $F$ is an external force acting on the fluid, and the right hand side of the equation represents the BGK [27] collision operator, corresponding to a single time relaxation towards the Maxwell-Boltzmann equilibrium distribution function, $f^{eq}$. Physical variables in the system correspond to velocity moments of the distribution function,

$$\int f(x, v, t)d^3v = \rho$$
$$\int f(x, v, t)v_\alpha d^3v = \rho u_\alpha.$$ (1.2)

By performing a suitable expansion it can be shown that the Boltzmann equation reproduces the macroscopic equations of fluid dynamics (see Appendix B).

The lattice-Boltzmann equation can be viewed as a discretized version of the Boltzmann equation [28], in which not only space and time are discretized (using a first-order finite difference scheme), but also velocity space. This velocity discretization amounts to choosing a quadrature such that moments of the distribution function can be expressed as,

$$\rho = \int f(x, v, t)d^3v = \sum_i w_i f(x, e_i, t) = \sum_i f_i(x, t)$$
$$\rho u_\alpha = \int v_\alpha f(x, v, t)d^3v = \sum_i w_i e_{i\alpha} f(x, e_i, t) = \sum_i e_{i\alpha} f_i(x, t),$$ (1.3)

where $e_i$ correspond to the discrete velocity vectors, and $w_i$ are the weights of the quadrature.

The discretized version of the Boltzmann equation used in the lattice-Boltzmann method
then reads,
\[
    f_i(x_\alpha + e_{i\alpha} \Delta t, t + \Delta t) - f_i(x_\alpha, t) = -\frac{\Delta t}{\tau} \left( f_i(x_\alpha, t) - f_i^{eq}(x_\alpha, t) \right) + p_i \Delta t,
\]
(1.4)

where \( p_i \) is an external forcing term.

As can be seen, modelling this equation requires a specification of the lattice velocity vectors, and corresponding weights, along with the equilibrium distribution, \( f_i^{eq} \), and forcing term, \( p_i \). Provided these unknown quantities are chosen appropriately (see discussion below), a Chapman Enskog expansion of equation 1.4 (see Appendix B for details) yields the continuity and Navier-Stokes equations,
\[
    \partial_t \rho + \partial_\beta (\rho u_\beta) = 0
\]
\[
    \partial_t (\rho u_\alpha) + \partial_\beta (\rho u_\beta u_\alpha) = \partial_\beta \sigma_{\alpha \beta} + F_\alpha + \partial_\beta \left( \eta_{\alpha \beta \gamma \nu} \partial_\gamma u_\nu \right),
\]
(1.5)

where \( \rho \) is the fluid density, \( u_\alpha \) is the velocity, \( \sigma_{\alpha \beta} \) is the stress tensor, which, for our purposes is set equal to \(-\rho a_0 \delta_{\alpha \beta}\), with \( a_0 \) corresponding to the square of the speed of sound in the fluid, \( F_\alpha \) is a local external force, and \( \eta_{\alpha \beta \gamma \nu} \) is the viscosity tensor,
\[
    \eta_{\alpha \beta \gamma \nu} = \eta \left[ \delta_{\alpha \gamma} \delta_{\beta \nu} + \delta_{\alpha \nu} \delta_{\beta \gamma} - \frac{2}{3} \delta_{\alpha \beta} \delta_{\gamma \nu} \right] + \Lambda \delta_{\alpha \beta} \delta_{\gamma \nu}.
\]
(1.6)

Here, \( \eta \) represents the shear viscosity, and \( \Lambda \), the bulk, given by,
\[
    \eta = \rho \left( \tau - \frac{\Delta t}{2} \right) v_c^2 / 3
\]
\[
    \Lambda = \eta \left( \frac{5}{3} - 3 a_0 / v_c^2 \right),
\]
(1.7)

with \( v_c = \Delta x / \Delta t \), where \( \Delta x \) and \( \Delta t \) are the lattice spacing and timestep respectively.

In order to choose the equilibrium distribution function, the following constraints must be used. First, as clearly indicated from equation 1.4, conservation of mass and momentum require,
\[
    \sum_i f_i^{eq} = \rho
\]
\[
    \sum_i f_i^{eq} e_{i\alpha} = \rho u_\alpha.
\]
(1.8)
In addition, the second velocity moment is chosen to control the stress tensor in the system,

$$
\sum_i f^e_i e_{i\alpha} e_{i\beta} = \sigma_{\alpha\beta} + \rho u_\alpha u_\beta.
$$

(1.9)

$f^e_i$ can then be written in the form,

$$
f^e_i = \rho w_i \left( A + B u_\alpha e_{i\alpha} + C u^2 + D u_\alpha u_\beta e_{i\alpha} e_{i\beta} + E_{\alpha\beta} e_{i\alpha} e_{i\beta} \right),
$$

(1.10)

with the above constraints used to determine the constants. The form of equation 1.10 can be obtained via a low-Mach number expansion of the Maxwell-Boltzmann equation (see for example [29,30]). Alternatively, one can intuitively pick this form by observing that the Navier-Stokes equations contain terms quadratic in velocity, and therefore, in order to model these equations, $f^e_i$ must contain terms up to this order as well.

The forcing terms, $p_i$, which control the external force $F_\alpha$ must also satisfy the following equations,

$$
\sum_i p_i = 0
$$

$$
\sum_i p_i e_{i\alpha} = F_\alpha
$$

(1.11)

$$
\sum_i p_i e_{i\alpha} e_{i\beta} = u_\alpha F_\beta + F_\alpha u_\beta,
$$

(1.12)

Finally an appropriate set of lattice velocity vectors, and corresponding weights must be chosen. As mentioned in the discussion of LGCA above, not all lattice choices will reproduce the Navier-Stokes equations; the lattice needs to have “enough” symmetry. In the derivation of the continuum equations from the lattice-Boltzmann equation, one encounters tensors composed of the lattice velocities up to 5th rank. It is essential that these tensors are isotropic in order to reproduce the rotationally invariant behaviour of the continuum equations. This
isotropy corresponds to the following set of conditions (see for example [24]),

\[
\begin{align*}
\sum_i w_i &= 1 \\
\sum_i w_i e_{i\alpha} &= 0 \\
\sum_i w_i e_{i\alpha} e_{i\beta} &= \delta_{\alpha\beta} \\
\sum_i w_i e_{i\alpha} e_{i\beta} e_{i\gamma} &= 0 \\
\sum_i w_i e_{i\alpha} e_{i\beta} e_{i\gamma} e_{i\eta} &= \delta_{\alpha\beta} \delta_{\gamma\eta} + \delta_{\alpha\eta} \delta_{\beta\gamma} + \delta_{\alpha\gamma} \delta_{\beta\eta} \\
\sum_i w_i e_{i\alpha} e_{i\beta} e_{i\gamma} e_{i\eta} e_{i\epsilon} &= 0.
\end{align*}
\]  

(1.13)

Using the notation of Qian et al. [31], the velocity lattices used in the lattice-Boltzmann method are labelled according to the scheme, \(DnQm\), where \(n\) corresponds to the number of spatial dimensions, and \(m\) is the number of velocity vectors. See Figure 1.2 for an example of a 2D, and 3D velocity lattice.

From a computational standpoint, the lattice Boltzmann algorithm provides an incredibly simple method for modelling fluid motion governed by the Navier-Stokes equations. As seen in equation 1.4, two basic steps are involved (see Figure 1.3 for an illustrative example): a
collision step in which the distribution function at a given grid point relaxes towards the local equilibrium distribution (Figure 1.3(b)), and a streaming of these new distributions to adjacent grid points, in the direction of the velocity vectors (Figure 1.3(c)). In addition, the fact that at any given timestep the update of the distributions requires only neighbouring grid point information makes this method ideally suited for parallelization.

It should be pointed out that although the lattice-Boltzmann method can be derived from the continuum Boltzmann BGK equation this is useful purely for an understanding of the form of the constituent equations (such as the velocity moments). The true power of the lattice-Boltzmann method as a computational tool simply lies in the fact that the continuum limit of the equation reproduces the Navier-Stokes equations; therefore, even if it wasn’t possible to derive the lattice-Boltzmann equation from the continuum Boltzmann BGK equation (which is a simplification itself, and not a fundamental equation), this would not diminish the viability of the method as a tool for numerical fluid dynamics.

1.0.3 Thermal Method

For simulations of micron-sized colloidal particles coupled to the lattice-Boltzmann fluid, the method described above is sufficient. However, for simulations at smaller length scales, the particles are expected to undergo Brownian motion [32]. This requires the inclusion of random noise in the system, such that the fluctuating stress tensor satisfies [33],

$$\left\langle s_{\alpha\beta}(r, t) s_{\gamma\nu}(r', t') \right\rangle = 2\eta_{\alpha\beta\gamma\nu}k_B T \delta(r - r') \delta(t - t').$$  \hspace{1cm} (1.14)
Fluctuations were first added to the lattice-Boltzmann method by Ladd [34], who simply added noise to the stress tensor. However, noise added in this manner was found to leak into the higher order distribution function moments. While these moments, known as “ghost” modes [26], are not involved in the Chapman Enskog expansion, this leakage results in a poor temperature reproduction. This can be improved through a thermalization of these modes [35]. The method of Ollila et. al. [36], which is used in this thesis, adds random noise to the system through the introduction of an additional forcing term, $\zeta_i$, to equation 1.4. The lower moments of $\zeta_i$ must satisfy,

$$\sum_i \zeta_i = 0$$

$$\sum_i \zeta_i e^{i\alpha} = 0$$ (1.15)

in order to conserve mass and momentum globally in the system. Higher moments are chosen in order to satisfy equation 1.14, with the resulting dissipation in the ghost modes compensated by corresponding fluctuations. Full details of this algorithm can be found in Ollila et. al. [36].

### 1.0.4 Hybrid LB-MD Methods

As mentioned previously, the large time and length scale differences encountered in simulations involving colloidal particles and solvent molecules necessitates the use of a coarse-grained solvent, which we model throughout this thesis using the lattice-Boltzmann algorithm described above. This allows for the use of a larger simulation timestep, while retaining the solvent properties that are relevant for the hydrodynamic time and length scales encountered by the colloidal particles, which are modelled simply by using a classical molecular dynamics algorithm.

Classical molecular dynamics (MD) simulations use Newton’s equations of motion in order to solve for the trajectories of a set of particles (see for example [37] for a detailed discussion). As this is a very common simulation technique, many MD simulation packages exist (eg. GROMACS [38], NAMD [39], LAMMPS [40], etc.). Throughout Part I of this thesis, the LAMMPS [40] (Large-scale Atomic/Molecular Massively Parallel Simulator) package is utilized extensively. This is an open-source package, which has been parallelized with MPI, using a spatial domain-decomposition. It is especially attractive, as it is very easy for a user to modify and extend the package.

Given a lattice-Boltzmann model for the fluid, and an MD algorithm for the colloidal particles, a method to couple the two techniques together is required. Incorporating a moving boundary (such as the surface of a colloidal particle) into a lattice-Boltzmann algorithm is not at all straightforward. Since the objects are potentially large and slowly moving, the spatial
discretization required in order to justify constraining the surface of the object to the lattice sites, and allowing discrete jumps of one lattice unit in position, is completely unfeasible; the object must be modelled off the lattice [41].

The original approach, taken by Ladd [34, 42–44], treats the colloidal particle as a surface, which, when placed on the lattice, intersects the links between adjacent lattice sites. Boundary nodes representing the particle surface are then placed half-way along these links (see Figure 1.4), and the fluid-particle interaction is treated at these nodes via a set of “bounce-back” rules in which velocities that would have crossed the colloidal surface are reflected back into the fluid. The resulting force and torque associated with these momentum changes are then used to update the center of mass velocity and angular velocity of the colloidal particle. This method works well for large particles, but discrepancies in the hydrodynamic behaviour occur for particles of radii $a < 2.4\Delta x$, where $\Delta x$ is the lattice spacing [41]. In addition, the hydrodynamic size of the particles is seen to depend on the viscosity, $\eta$, of the fluid.
As an alternative, Alrichs and Dünweg [45, 46] proposed using a velocity coupling method to treat point particles. This method applies a frictional force to both the particle and fluid proportional to their local velocity difference according to,

\[
\mathbf{F}_{\text{particle}} = \gamma (\mathbf{u} - \mathbf{v})
\]

\[
\mathbf{F}_{\text{fluid}} = \gamma (\mathbf{v} - \mathbf{u}),
\]

(1.16)

where \( \mathbf{v} \) is the particle velocity, \( \mathbf{u} \) is the velocity of the fluid at the particle location, and a linear interpolation is used to distribute the force to the fluid mesh. This method can also be applied to composite particles (extended objects whose surface is composed of a set of point particles) [47–49], in which case the force coupling constant, \( \gamma \), should be chosen so that the correct hydrodynamic behaviour (such as the Stokes drag force) is recovered for the particle.

As an alternative to a linear interpolation of the point particles onto the fluid mesh, Peskin and co-workers [50–52] have worked extensively on the incorporation of moving boundaries composed of point particles into a fluid. Their method, known as the immersed boundary method, uses a discrete representation of the Dirac delta function, with compact support in order to accomplish the interpolations, although for a somewhat different application than described here. This immersed boundary scheme has subsequently been used in lattice-Boltzmann simulations of both point [53], and composite [49] particles.

While the implementation of the frictional force coupling method is relatively straightforward in a simple lattice-Boltzmann fluid, issues arise when thermal fluctuations are included. Alrichs and Dünweg [45, 46] have found that in order for the thermally induced motion of the colloidal particles to satisfy a fluctuation-dissipation theorem consistent with the temperature of their fluid, an external Langevin thermostat needed to be applied to the particle phase. This was justified because of the dissipative nature of the coupling force. However, Ollila et. al. [49] have argued against the use of external Langevin noise on the grounds that the fluid alone should give rise to the Brownian motion of the colloidal particles. In addition, they suggest that the external noise may lead to unphysical thermal fluctuations and correlations in the fluid for close particle separations.

In the next chapter, a new method for coupling point and composite particles to a lattice-Boltzmann fluid is presented, which uses a conservative force, thereby eliminating the question of the need for external Langevin noise. This method, along with the frictional force coupling method, has been parallelized, and implemented into LAMMPS, as described in Chapter 3.
Bibliography


Chapter 2

Coupling MD Particles to a Lattice-Boltzmann Fluid Through the Use of Conservative Forces

This chapter corresponds to the published article:

2.1 Introduction

The lattice-Boltzmann algorithm [1, 2] is a popular method used to simulate the hydrodynamics of complex fluids on a grid. As this method requires only nearest neighbour grid point information, it is very straightforward to implement, and is ideally suited for large-scale parallel applications. Recently, it has become increasingly popular to use this method in conjunction with molecular dynamics simulations, to model situations where the dynamics of the MD particles depend on the hydrodynamic interactions between them. The resulting coupled lattice-Boltzmann, MD algorithms have been applied to a range of situations, including colloidal suspensions [3], blood flow [4, 5], polymers in solution [6–8], DNA translocation [9], flow through disordered media [10, 11], and colloidal particles in a liquid crystal [12].

Several different methods have been introduced to treat the coupling between the lattice-Boltzmann fluid, and the MD particles. The original approach of Ladd [13, 14] treated the interaction via a set of bounce-back rules at boundary nodes placed halfway along the links between fluid nodes cut by the particle surface. This has proven an effective method for large
particles, however discrepancies in the hydrodynamic behavior, dependent on the relaxation
time of the LB fluid, occur for radii smaller than $\sim 2.4\Delta x$ [3].

As an alternative, Alrichs and Dünweg [15] used a frictional force proportional to the local
velocity difference between the particle and the fluid, to couple point particles to the lattice-
Boltzmann fluid. In order to use this type of method for a larger particle, a representation of that
particle in terms of point particles is required. Peskin et al. [16–18] have worked extensively on
the treatment of such representations, creating the immersed boundary method to incorporate
moving boundaries into a fluid; however, for a somewhat different application than discussed
here. Composite particles were first modeled in the lattice-Boltzmann framework using the
force-coupling method by Lobaskin and Dünweg [19].

In order to model a particle in a fluctuating lattice-Boltzmann fluid using the frictional
force-coupling method, Alrichs and Dünweg [15] found they required the addition of external
Langevin noise to the forces in order for the particle motion to obey the fluctuation dissipation
theorem consistent with the temperature of their fluid. This was justified by the dissipative
nature of the coupling force. Here, we remove the question of the need for external Langevin
noise, by introducing a new force coupling method which uses conservative forces. With this
coupling method, the fluid alone acts as a heat bath for the particles. The theoretical details of
our method are described in Section 2.2, while Section 2.3 provides various tests of the method.

\section{2.2 Theoretical Background}

\subsection{2.2.1 The Lattice-Boltzmann Algorithm}

The fluid motion in our system is governed by the continuity and Navier-Stokes equations,

\begin{align}
\partial_t \rho + \partial_\beta \left( \rho u_\beta \right) &= 0 \\
\partial_t (\rho u_\alpha) + \partial_\beta \left( \rho u_\alpha u_\beta \right) &= \partial_\beta \sigma_{\alpha\beta} + F_\alpha + \partial_\beta \left( \eta_{\alpha\beta\gamma\nu} \partial_\gamma u_\nu \right),
\end{align}

(2.1)

where $\rho$ is the fluid density, $u_\alpha$ is the velocity, $\sigma_{\alpha\beta}$ is the stress tensor, $F_\alpha$ is a local external
force, and $\eta_{\alpha\beta\gamma\nu}$ is the viscosity tensor,

\begin{align}
\eta_{\alpha\beta\gamma\nu} &= \eta \left[ \delta_{\alpha\gamma} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\gamma} - \frac{2}{3} \delta_{\alpha\beta} \delta_{\gamma\nu} \right] + \Lambda \delta_{\alpha\beta} \delta_{\gamma\nu}.
\end{align}

(2.2)

Here, $\eta$ represents the shear viscosity, and $\Lambda$, the bulk. For the work presented here, we set
$\sigma_{\alpha\beta} = -\rho a_0 \delta_{\alpha\beta}$, where $a_0$ represents the square of the speed of sound in the fluid.
To solve these equations on a discrete grid of points we use a lattice-Boltzmann algorithm. This algorithm utilizes a velocity discretized version of the linearized Boltzmann equation, implemented here as a finite difference scheme,

\[
f_i(x + e_i \Delta t, t + \Delta t) = f_i(x, t) - \frac{\Delta t}{\tau} \left[ f_i(x, t) - \left[ f_i^{eq}(x, t) + \tau W_i(x, t) \right] \right]
\]  

(2.3)

in order to solve for the motion of a set of partial distribution functions, \( [f_i = 1...N] \), with each \( f_i \) corresponding to a discrete velocity direction, \( e_i \). These partial distribution functions can be thought of as direction specific fluid densities, with moments given by:

\[
\rho = \sum_i f_i \\
\rho u_\alpha = \sum_i f_i e_{i\alpha}.
\]  

(2.4)

We use an implementation of the algorithm in which each grid point is connected to its neighbouring points by a set of \( N = 15 \) velocity directions (D3Q15), with velocity vectors given by

\[
e_i = (0, 0, 0), (\pm v_c, 0, 0), (0, \pm v_c, 0), (0, 0, \pm v_c), (\pm v_c, \pm v_c, \pm v_c).
\]  

(2.5)

Here \( v_c = \Delta x/\Delta t \), and \( \Delta x \), and \( \Delta t \) are the lattice spacing, and the timestep respectively.

Equation 2.3 uses the BGK [20] model for the Boltzmann collision term, with \( \tau \), which is physically related to the viscosity in the fluid, representing the single time relaxation parameter, and \( f_i^{eq} \) corresponding to the local equilibrium distribution functions. External forcing terms are introduced through the functions, \( W_i \).

In order to enforce conservation of mass, momentum, and to control the stress tensor in the system, the equilibrium distributions are chosen according to

\[
\sum_i f_i^{eq} = \rho \\
\sum_i f_i^{eq} e_{i\alpha} = \rho u_\alpha \\
\sum_i f_i^{eq} e_{i\alpha} e_{\beta\gamma} = \sigma_{\alpha\beta} + \rho u_\alpha u_\beta,
\]  

(2.6)
while the forcing terms, $W_i$, which control the external force $F_\alpha$ are chosen to satisfy

$$
\sum_i W_i = 0 \\
\sum_i W_i e_{i\alpha} = F_\alpha \\
\sum_i W_i e_{i\alpha} e_{\beta} = u_\alpha F_\beta + F_\alpha u_\beta.
$$

(2.7)

With these constraints, a Chapman-Enskog expansion performed on equation 2.3 can be shown to reproduce equation 2.1, with viscosities given by

$$
\eta = \rho \left( \tau - \frac{\Delta t}{2} \right) \frac{v^2}{3} \\
\Lambda = \eta \left( \frac{5}{3} - 3a_0/v^2 \right).
$$

(2.8)

More details of these now standard methods can be found in [1, 2].

In addition, we have implemented the thermal lattice-Boltzmann method of Ollila et. al. [21] to treat situations in which the temperature induced random fluctuations in the fluid become important. With the implementation of this algorithm, the lattice-Boltzmann fluid acts as a heat bath for the MD particles.

In order to implement this algorithm, random noise is added to the system through the forcing term, $W_i$, which is now set equal to $W_i = p_i + \zeta_i$. The $p_i$ now take the place of $W_i$ in equation 2.7, while the $\zeta_i$ are chosen to satisfy

$$
\sum_i \zeta_i = 0 \\
\sum_i \zeta_i e_{i\alpha} = 0
$$

(2.9)

in order to conserve global mass and momentum in the system. Higher moments are chosen so that the fluctuating stress tensor, $s_{\alpha\beta}$, satisfies a fluctuation dissipation relation of the form,

$$
\left< s_{\alpha\beta}(\mathbf{r}, t) s_{\gamma\nu}(\mathbf{r}', t') \right> = 2\eta_{\alpha\beta\gamma\nu}k_B T \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'),
$$

(2.10)

with dissipation in the higher modes compensated by corresponding fluctuations. For complete details of the algorithm see Ollila et. al. [21].
2.2.2 Particle-Fluid Interaction

Extended objects are represented in our model by a surface consisting of a set of evenly distributed nodes. This type of surface discretization is illustrated in Figure 2.1 for spherical objects.

![Figure 2.1: Examples of spheres comprised of different numbers of nodes (92 on the left; 492 on the right [22]). The links between the nodes are fictitious and shown here only for clarity.](image)

In order to couple these objects to the lattice-Boltzmann fluid, we introduce energy and momentum conserving local forces which act on both the particle nodes and the fluid. These forces are computed by assuming a 3D elastic collision between each particle node (mass $m_v$, velocity $v$), and a representative mass of fluid located at the particle node location (mass $m_u$, velocity $u$), satisfying the usual conservation equations,

\[
\frac{1}{2} m_u u_i^2 + \frac{1}{2} m_v v_i^2 = \frac{1}{2} m_u u_f^2 + \frac{1}{2} m_v v_f^2
\]

\[
m_u u_i + m_v v_i = m_u u_f + m_v v_f,
\]

along with the additional assumption that the collision is head on, such that in a frame of reference where the particle node is initially at rest, the direction of its velocity immediately following the collision is dictated entirely by the incoming velocity direction of the fluid mass.
With this assumption, the fluid and particle node after-collision velocities are given by,

\[ u_f = u_i + \frac{2m_u}{m_v + m_u} (v_i - u_i) \]
\[ v_f = v_i + \frac{-2m_u}{m_v + m_u}. \] (2.12)

In order to obtain the fluid velocity, \( u_i \), at the node location, an interpolation of the velocities at nearby grid points is performed. This is accomplished by assigning weights, \( \xi_{\alpha i} = \phi_i(x_\alpha)\phi_i(y_\alpha)\phi_i(z_\alpha) \), which satisfy \( \sum_i \xi_{\alpha i} = 1 \), to the nearby lattice sites, labelled \( \alpha \), based on the distance between the site and the particle node, labelled \( i \), and using these weights to perform a weighted sum of the velocity. We have implemented two such interpolation schemes. The first, which we refer to as the trilinear stencil, assigns weights to each of the 8 nearest grid points according to

\[ \phi_j(r_\alpha) = 1 - |\Delta r|, \] (2.13)

where \( |\Delta r| \) corresponds to the scalar absolute value of \( \Delta r = (r_\alpha - r_j)/\Delta x \). Here, \( r_\alpha \) gives the position of the grid point, \( r_i \) is the position of the particle node, and \( \Delta x \) is the lattice spacing.

The second method we have implemented is based on the immersed boundary method [16, 17]. Here, a smoothing kernel is used to spread the influence of a point particle to a compact support. For this, we use a 4 point approximation to the dirac delta function, providing a support of 64 grid points, with grid weights given by [18],

\[ \phi_j(r_\alpha) = \begin{cases} 
\frac{1}{8}(3 - 2\Delta r + \sqrt{1 + 4\Delta r - 4\Delta r^2}), & 0 < \Delta r < 1; \\
\frac{1}{8}(5 - 2\Delta r - \sqrt{-7 + 12\Delta r - 4\Delta r^2}), & 1 < \Delta r < 2; \\
0, & 2 < \Delta r. 
\end{cases} \] (2.14)

In a manner similar to the velocity interpolation, the fluid mass is computed by performing an interpolation of the fluid density to the node location, and multiplying by the volume of space occupied by the particle node. For the spherical composite objects used in this work, this mass is given by,

\[ m_u = \rho \frac{4\pi R^2}{N} \Delta x, \] (2.15)

where \( R \) is the radius of the object, and \( N \) is the number of evenly distributed nodes used to represent its surface.

Equation 2.12 is used to determine the change in momentum (impulses) for both the particle node and the fluid occurring as a result of their collision. Assuming that the collision takes place...
over a time interval $\Delta_{\text{collision}}$, the forces associated with these impulses are calculated as:

$$
F_{\text{node}} = \frac{\Delta p_{\text{node}}}{\Delta t_{\text{collision}}} = \frac{m_v (v_f - v_i)}{\Delta t_{\text{collision}}}
$$

$$
F_{\text{fluid}} = \frac{\Delta p_{\text{fluid}}}{\Delta t_{\text{collision}}} = \frac{m_u (u_f - u_i)}{\Delta t_{\text{collision}}}. 
$$

(2.16)

It is important to note that $\Delta_{\text{collision}}$ is not necessarily equal to the lattice-Boltzmann timestep, $\Delta t$, as this collision time depends on the fluid parameters, and not the timestep chosen for the simulation. Since $\tau$ in equation 2.3 represents the time between successive collisions in the fluid, we assume collisions between the fluid and our particle nodes occur over this fluid relaxation time, such that $\tau/\Delta_{\text{collision}} = 1$.

The resulting fluid force is then redistributed to the associated lattice grid points, where it is applied to the fluid through the forcing term, $W_i$, in equation 2.3. The node forces are applied directly to the particle nodes. In order to track the motion of the particle nodes, we use the open source molecular dynamics code, LAMMPS [23], to which we have added our lattice-Boltzmann fluid.

### 2.3 Results

#### 2.3.1 Drag Force on a Single Particle

As a first test of the method, we consider the case of a particle moving at constant velocity through the fluid, and compare the resulting drag force acting on the particle to the known Stokes drag force,

$$
F_D = 6\pi \eta a U.
$$

(2.17)

Here, $\eta$ is the fluid viscosity, $a$ is the particle radius, and $U$ is the velocity of the particle measured relative to the far field fluid velocity. This situation corresponds to the motion of an infinitely massive particle moving though the fluid ($v_f = v_i$), in which case the impulses imparted to the particle nodes and the fluid via equation 2.12 dictate that

$$
F_{\text{node}} = 0
$$

$$
F_{\text{fluid}} = \frac{2m_u (v_i - u_i)}{\Delta t_{\text{collision}}}. 
$$

(2.18)

For the simulations presented here, we choose a fluid with density $\rho = 0.000998\text{ag}/(\text{nm})^3$, and viscosity $\eta = 1.000\text{ag}/(\text{nm} \cdot \text{ns})$ corresponding to $H_2O$ at STP. We use a lattice spacing
Figure 2.2: Drag force, normalized by the expected Stokes value, for spheres of various radii as a function of the lattice-Boltzmann timestep. Squares correspond to a radius $5.3\Delta x$, circles, a radius $4.3\Delta x$, and triangles, a radius $3.3\Delta x$. Filled symbols correspond to the Peskin interpolation stencil, while open symbols correspond to the trilinear stencil. The range of timesteps considered corresponds to values for $\tau/\Delta t$ from 0.70 to 1.25.

of $\Delta x = 2\text{nm}$, and a total system size of $(100\Delta x)^3$, with periodic boundary conditions in the $x$ and $y$ directions, and fixed boundary conditions in the $z$ direction. These $z$ walls are present in order to enforce a zero far field fluid velocity. While finite size effects will be present in this system, the walls reduce these from $1/L$ to $1/L^2$ [24], where $L$ is the linear system size, and the large system size used further diminishes their effect.

In order to represent the spherical particle in our simulation, we use a surface discretization of the form shown in Figure 2.1. It is important to choose the number of surface nodes large enough, so that the discretization of the particle surface is finer than the fluid mesh, thereby avoiding any holes in the mesh representation of the particle. For the results presented here, we use particles with 812 surface nodes.

Figure 2.2 shows the measured drag force, normalized by the expected Stokes drag, for a range of particle radii, as a function of the lattice-Boltzmann timestep, $\Delta t$. As can be seen, in all cases the measured drag force is slightly larger than the Stokes value. This is to be expected, as a result of discretization errors; the interpolation of the forces onto the fluid mesh results in a
Figure 2.3: Difference between the drag force at a range of lattice-Boltzmann timesteps, $\Delta t$, and its value at $\Delta t = \Delta t_{\text{collision}} = \tau$, normalized by the expected Stokes value. Triangles correspond to a radius of $3.3\Delta x$, circles, a radius of $4.3\Delta x$, and squares, a radius of $5.3\Delta x$. Filled symbols correspond to the Peskin interpolation stencil, while open symbols correspond to the trilinear stencil.
mesh representation of the particle that is somewhat larger than the size determined by the positioning of the particle nodes. As can be seen, this effect is greater for the Peskin interpolation stencil which uses a larger support, and therefore a larger mesh representation, compared with the trilinear stencil. In addition, there is a slight $\Delta t$ dependence to the hydrodynamic particle radius. This appears to be at least in part due to the mesh representation of the spherical particles. For the trilinear interpolation stencil, over the range of $\Delta t$ values considered, we see a $2.3\%$ change in hydrodynamic radius for the $5.3\Delta x$ particles, and a $3.8\%$ change for the $3.3\Delta x$ particles. However, when the Peskin stencil, which provides a much smoother mesh representation, is used, these values decrease significantly, down to $1.8\%$ for the $5.3\Delta x$ particles, and $2.5\%$ for the $3.3\Delta x$ particles. This behavior is illustrated in Figure 2.3.

The hydrodynamic radii calculated from the measured drag forces,

$$a_{\text{Drag}} = \frac{F_D}{(6\pi \eta U)},$$

are shown in Figure 2.4. For a value for $\tau/\Delta t$ of 1.0, corresponding to a timestep $\Delta t = 6.7 \times 10^{-3} ns$, the hydrodynamic radius is $\sim 0.2\Delta x$ larger than the positioning of the particle nodes for the trilinear interpolation stencil, and $\sim 0.43\Delta x$ larger for the Peskin stencil.

It is important that independent measures of the hydrodynamic radius produce the same result. To test this, we consider a stationary particle in shear flow. This flow is generated by moving the top wall at a speed $v_w = 0.00001 nm/ns$, while keeping the bottom wall stationary. Our particle is placed in the center of the simulation domain, far from the bounding walls. For this situation, in addition to a drag force, described by equation 2.17, the particle will also experience a drag torque, given by

$$T = 4\pi \eta a^3 (v_w/h)n,$$

where $h$ is the separation between the two walls, and $n$ is a unit vector perpendicular to the shear plane. Equations 2.17 and 2.20 provide two different means for calculating the hydrodynamic radius of the particle. Figure 2.5 shows the ratio of the radii calculated using these two methods over a range of $\Delta t$, corresponding to $\tau/\Delta t$ values from 0.7 to 1.25. As can be seen, these two methods agree within $1\%$ of one another over this $\Delta t$ range for both the trilinear and Peskin stencils, showing that the hydrodynamic radius is consistently defined using these methods.

In contrast, for the frictional force coupling method, the force coupling parameter needs to be chosen large enough in order to obtain this agreement, and recalibrated for any change in $\Delta t$.

Similar to the frictional force coupling method, our technique can also be applied to point
2.3. Results

Figure 2.4: Hydrodynamic radius of the particles obtained using the Stokes drag force, as a function of the lattice-Boltzmann timestep. Squares correspond to a node placement radius $5.3\Delta x$, circles, a node radius $4.3\Delta x$, and triangles, a node radius $3.3\Delta x$. Filled symbols correspond to the Peskin interpolation stencil, while open symbols correspond to the trilinear stencil. The range of timesteps corresponds to values for $\tau/\Delta t$ from 0.70 to 1.25.
Figure 2.5: Hydrodynamic radius of the particle determined from the drag force measurement divided by the hydrodynamic radius determined using the torque measurement. Squares correspond to a node placement radius of $5.3\Delta x$, while circles correspond to $3.3\Delta x$. Filled symbols correspond to the Peskin interpolation stencil, while open symbols correspond to the trilinear stencil.
particles. In this situation, we set the fluid mass interacting with the particle to

\[ m_u = \rho \Delta x^3, \tag{2.21} \]

where, as before, \( \rho \) is the fluid density interpolated to the particle node location. The interpolation of the particle onto the lattice mesh leads to an effective particle radius that is tied to the lattice resolution. Figure 2.6 shows this effective particle radius, calculated using equation 2.19, as a function of the chosen lattice-Boltzmann timestep, for both the Peskin and trilinear stencils. As can be seen, use of the trilinear stencil produces an effective radius of \( \sim 0.35\Delta x \), for \( \tau/\Delta t = 1 \), while the larger support of the Peskin stencil results in a radius of \( \sim 0.44\Delta x \). Just as in the case of the extended spherical object described above, there is a slight \( \Delta t \) dependence to the hydrodynamic radius, which is more prominent for the trilinear stencil. In addition, use of the trilinear stencil with a point particle gives rise to substantial mesh effects, in which the drag force oscillates with an amplitude of \( \sim 7\% \) its average value. These effects are negligible for the Peskin stencil (the oscillations amount to \( \sim 0.15\% \) of the mean values). Therefore, we strongly recommend the use of the Peskin stencil when simulating point particles.
2.3.2 Freely Moving Particle Near a Plane Wall

Next, we consider the motion of a freely moving particle near a stationary plane wall, in a system with a constant shear rate, $S$. Far from the stationary wall, the steady-state center of mass velocity, and angular velocity of the particle should obey,

\[ v_{CM} = hS \]
\[ \Omega = \frac{1}{2} S, \]

(2.22)

where $h$ is the distance of the particle from the wall. Closer to the wall, wall effects act to decrease both of these quantities.

For the simulations, we use the same fluid parameters as described above, and a sphere consisting of 812 nodes. Each node has a mass of 0.0083 ag. We use the trilinear interpolation method for the velocity, density, and force interpolations, as this allows the sphere to be placed closer to the lower wall. The motion of the nodes is integrated using the LAMMPS rigid integrator, which treats the collection of nodes as a single rigid body, so that they move and rotate together. We place the particle, initially at rest, at several distances from the stationary wall, and allow the system to equilibrate, at which point the center of mass and angular velocities are measured. The results are show in figure 2.7, along with the theoretical results presented in [25]. As can be seen, there is excellent agreement for the center of mass velocity. While the angular velocity exhibits noticeable mesh effects, this also agrees quite well with the theoretical prediction.

2.3.3 Velocity Autocorrelation Function

We next considered the velocity autocorrelation function,

\[ \text{VACF} = \frac{1}{3} \langle v(t) \cdot v(0) \rangle, \]

for a particle moving in a thermal lattice-Boltzmann fluid. According to the equipartition theorem, at time $t = 0$, the VACF should be equal to $k_B T / m$, where $m$ is the total mass of the particle. However, for a compressible fluid at short times, $t < t_s \sim a_H / v_s$, where $a_H$ is the hydrodynamic radius of the particle, and $v_s$ is the speed of sound in the fluid, acoustic damping of the particle velocity results in a decay from the $k_B T / m$ value to $k_B T / m^*$ [26]. Here, $m^* = m + M / 2$ is called the virtual mass of the particle, with $M$ corresponding to the mass of the fluid displaced by the particle. At longer times, fluid viscosity results in a much longer decay of the VACF down to zero, just like for the case of an incompressible fluid. The incompressible
Figure 2.7: Normalized center of mass velocity, $v_{cm}$, and angular velocity, $\Omega$, for a sphere in motion near a stationary plane wall in a system undergoing constant shear. The filled circles correspond to theoretical prediction of [25], while the hollow circles represent our simulation results.
Navier-Stokes equations have been used to predict this long term behavior, giving a power-law tail, \( k_B T (12 \rho \sqrt{\pi^3 \eta^3 / \rho^3})^{-1} t^{-3/2} \) \[26\].

To test the behavior of the VACF in our model, we placed a particle of radius \( 4.3 \Delta x \), initially at rest, in a periodic simulation domain of size \((100 \Delta x)^3\). The same fluid parameters were used as in the previous simulations, and a temperature of 300K was given to the fluid. After an initial equilibration time, the velocity of the particle at each timestep was measured, and the VACF was calculated.

Figure 2.8 shows the results for two different particle masses. Figure 2.8 (a), corresponds to a total particle node mass of 16.24ag, much larger than the mass of the fluid contained inside the particle, while Figure 2.8 (b) corresponds to a node mass of 0.32ag much smaller than that of the inside fluid. In both cases, we see good agreement with the long-time power law behavior.

To investigate the behavior at short times, we look at the VACF at \( t = 0 \), and compare this value to both \( k_B T / m \), and \( k_B T / m^* \). Here, \( m \) is calculated as the total mass of the particle nodes, plus the mass of the fluid inside the particle’s hydrodynamic radius that necessarily moves with it. We use a value of 4.49\( \Delta x \) for the hydrodynamic radius of the particle, determined using the drag force measurement. For the VACF shown in figure 2.8 (a), the total mass of the particle is dominated by the mass of the particle nodes, resulting in a small difference between \( m = 19.27ag \), and \( m^* = 20.78ag \). These correspond to values of \( k_B T / m = 0.21nm^2/\text{ns}^2 \), and \( k_B T / m^* = 0.20nm^2/\text{ns}^2 \), which are difficult to distinguish amongst when compared to the measured \( t = 0 \) VACF value, \( VACF(0) = 0.20nm^2/\text{ns}^2 \). In contrast, for Figure 2.8 (b), the mass of the particle is dominated by the mass of the fluid contained within its radius, and there is a substantial difference between \( m = 3.35ag \), and \( m^* = 4.86ag \), corresponding to \( k_B T / m = 1.24nm^2/\text{ns}^2 \), and \( k_B T / m^* = 0.85nm^2/\text{ns}^2 \). The measured value of \( VACF(0) = 1.27nm^2/\text{ns}^2 \), clearly corresponds to \( k_B T / m \), as expected. Indeed, looking at figure 2.8 (b), one can clearly see the initial decay from \( m \) to \( m^* \), where a plateau is observed in the VACF.

### 2.4 Summary and Conclusions

In this work, we have implemented a lattice-Boltzmann-MD coupling through the use of conservative forces applied to both the particles and the fluid. These forces are obtained by assuming an elastic collision between the MD particles, and a representative mass of fluid at the particle location. This method can be applied to point particles or composite objects created using collections of these point particles.

We have shown that the drag force and torque felt by a composite particle agree with the Stokes values, provided a slightly larger hydrodynamic radius is used for the particle. This is a
result of discretization errors, due to the representation of the particle on the fluid mesh. This hydrodynamic radius is, however, consistent among the different tests used to measure it.

When our method is used to couple particles to a thermal lattice-Boltzmann fluid, the particles pick up the correct temperature without the need for external Langevin noise. As a test of the thermal lattice-Boltzmann-particle coupling, we investigated the behaviour of the velocity autocorrelation function. We have shown that for arbitrary particle mass we are able to match the $t = 0$ equipartition result as well as the asymptotic long-time tail behaviour.
Figure 2.8: Velocity autocorrelation function of a particle in a thermal lattice-Boltzmann fluid. Open circles represent the particle data, while the line corresponds to the long-time, power-law tail, $k_B T (12 \rho \sqrt{\pi^3 \eta^3 / \rho^3})^{-1} t^{-3/2}$. Figure (a) corresponds to a total particle mass, $m = 19.27ag$, dominated by the mass of the particle nodes, while figure (b) corresponds to a mass, $m = 3.35ag$, dominated by the mass of the contained fluid.
Bibliography


Chapter 3

Hydrodynamic Forces Implemented into LAMMPS Through a Lattice-Boltzmann Fluid

The work presented in this chapter corresponds to the article:

3.1 Introduction

Hydrodynamic interactions, arising between particles in a fluid due to velocity fields created by their relative motion, play a key role in determining the dynamic behavior of a variety of systems. An illustrative example of hydrodynamics in containment at low Reynolds number is the inertial migration of confined particles [1], which has important applications to microfluidic systems [2]. Additional examples where hydrodynamic interactions are seen to be important include, but are not limited to, colloidal aggregation [3] and sedimentation [4], colloidal phase separation and gel formation [5], polymer migration in confined flow [6], and protein folding [7]. Therefore, accurate numerical modeling of such systems, performed using a classical molecular dynamics simulation code such as LAMMPS [8], requires the inclusion of hydrodynamic forces.

Due to their long range and many-body nature, however, the implementation of hydrodynamic forces is not at all straightforward, resulting in the existence of a variety of potential methods to incorporate them. For low Reynolds number flow, both Brownian dynamics [9] and Stokesian dynamics [10] treat the interactions using multipole type expansions. These methods
require only the particle positions and velocities, assuming an instantaneous propagation of the hydrodynamic interactions. However, as the number of particles, $N$, in the system increases, these methods quickly become impractical, scaling as $O(N^3)$, except in specialized geometries where Ewald-like sums can be used to speed up the computation \cite{11, 12}. An approximate Stokesian dynamics method, known as fast-lubrication dynamics has been implemented into LAMMPS, and treats the hydrodynamic interactions in a pair-wise fashion \cite{14}. However, the inclusion of many-body hydrodynamics has been recognized as being critical in the calculation of many quantities, such as the transport properties of suspensions \cite{13}. Implicit solvent methods such as this are also unable to reproduce several known experimental effects relevant to microfluidic devices, including the inertial migration of a sphere in Poiseuille flow to an equilibrium location $\sim 60\%$ of the way from the center of the channel to the wall \cite{1}. Modeling such behavior requires the explicit inclusion of the solvent degrees of freedom. The most straightforward explicit method, and the only one currently supported by LAMMPS, is simply to solve Newton’s equations of motion for both the colloidal and solvent particles. However, these purely MD simulations are also impractical for large systems, due to the large time and length scale differences encountered; in addition to the vast majority of particles in these simulations belonging to the solvent, a timestep much smaller than needed to track the colloidal particles is required in order to resolve the motion of the solvent molecules. Therefore, for larger systems, it is common to coarse-grain the fluid in order to speed up computational time, while retaining the solvent properties on the relevant hydrodynamic time and length scales. Examples of such coarse-grained methods include dissipative particle dynamics (DPD) \cite{15, 16}, which is similar to MD, but allows for a much larger timestep through the use of very soft potentials, multiparticle collision dynamics (MPCD) \cite{17, 18}, which treats the solvent as a set of particles with continuous space and velocity coordinates, but with free streaming between discrete “collision” events, as well as grid based methods such as finite-difference Navier-Stokes solvers, and the lattice-Boltzmann method. These explicit methods also have the advantage that they automatically include hydrodynamic retardation effects, which may be important, resulting from a finite momentum propagation time.

In this work, we implement a lattice-Boltzmann (LB) fluid into LAMMPS. This method, based on a discretized version of the Boltzmann equation, has several advantages. Since each computational step requires only nearest-neighbour information, the method is ideal for implementing into a parallelized code such as LAMMPS. In addition, in contrast to methods such as MD, and DPD, hydrodynamic flows can be created with or without the presence of thermal fluctuations, offering greater flexibility. In order to couple this fluid to the MD particles, a force proportional to the local velocity difference between the fluid and the particle is used. The method has been used extensively for colloidal and polymer simulations \cite{19–22}, and is
valid even for point particles [23].

The remainder of the paper is organized as follows. In Section 3.2, we describe the method used, which is based on the work of [22, 24]. Sections 3.3 and 3.4 describe the implementation of the method into the LAMMPS MD code, while Section 3.5 provides several test examples of the method.

3.2 Theoretical background

3.2.1 The Lattice-Boltzmann Algorithm

Lattice-Boltzmann algorithms [25, 26] are a popular method used to model fluid motion governed by the Navier-Stokes equations,

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} \left( \rho u_i \right) &= 0, \\
\frac{\partial \left( \rho u_i \right)}{\partial t} + \frac{\partial}{\partial x_j} \left( \rho u_i u_j \right) &= \frac{\partial}{\partial x_j} \sigma_{ij} + F_i + \frac{\partial}{\partial x_j} \left( \eta_{ij \ell} \delta_{\ell j} u_\ell \right),
\end{align*}
\] (3.1)

with summation over repeated indices assumed. Here \( \rho \) is the fluid density, \( u_i \) is the \( i \)-component (\( x, y \) or \( z \)) of the local fluid velocity, \( \sigma_{ij} \) is the stress tensor, \( F_i \) is a local external force, which for our purposes results from the presence of the MD particles, and \( \eta_{ij \ell} \) is the viscosity tensor, given by:

\[
\eta_{ij \ell} = \eta \left[ \delta_{ij} \delta_{\ell j} + \delta_{ij} \delta_{\ell j} - \frac{2}{3} \delta_{ij} \delta_{\ell j} \right] + \Lambda \delta_{ij} \delta_{\ell j},
\] (3.2)

where \( \eta \) and \( \Lambda \) represent the shear and bulk viscosities respectively. For this work, we choose \( \sigma_{ij} = -P_{ij} \), with \( P_{ij} = \rho a_0 \delta_{ij} \), where \( a_0 \) is the square of the speed of sound. By default, \( a_0 \) is set to a value of \( (1/3) \Delta x^2 / \Delta t^2 \), although a different value may be specified by the user.

The algorithm involves tracking the time evolution of a set of partial distribution functions, \( f_i \), whose moments define physical variables in the system,

\[
\begin{align*}
\rho &= \sum_i f_i, \\
\rho u_i &= \sum_i f_i e_{i\alpha}.
\end{align*}
\] (3.3)

These partial distribution functions, each corresponding to a discrete velocity direction, \( e_i \), evolve according to a velocity discretized version of the linearized Boltzmann equation,

\[
(\partial_t + e_{i\alpha} \partial_{\alpha}) f_i = -\frac{1}{\tau} \left( f_i - f_i^{eq} \right) + W_i.
\] (3.4)
The first term on the right hand side of this equation is the BGK collision operator [27], which represents a single-time relaxation towards the equilibrium distribution function, \(f^e_i\), \(\tau\) is the relaxation parameter, which is physically related to the fluid viscosity, and \(W_i\) is an external forcing term. By default, the implementation presented here uses a 15 velocity model (D3Q15), with velocity vectors, \(e_i = (0, 0, 0), (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)\), expressed in lattice units with \(\Delta x = \Delta t = 1\); however, the user also has the option to switch to a 19 velocity (D3Q19) model, with velocity vectors

\[
\begin{align*}
& e_i = (0, 0, 0), (\pm 1, 0, 0), (0, \pm 1, 0), (\pm 1, \pm 1, 0), (0, \pm 1, \pm 1), (\pm 1, 0, \pm 1), (0, \pm 1, \pm 1), (0, \pm 1, \pm 1), (0, 0, \pm 1), (0, \pm 1, \pm 1)
\end{align*}
\]

Using a Chapman-Enskog expansion, it can be shown that equations 3.1 can be obtained from equation 3.4 provided that the equilibrium distribution function and forcing terms are constrained in an appropriate fashion. In order to impose conservation of mass and momentum, and to control the stress tensor, the equilibrium distribution functions, \(f^e_i\), are chosen to satisfy

\[
\begin{align*}
\sum_i f^e_i &= \rho, \\
\sum_i f^e_i e_{i\alpha} &= \rho u_\alpha, \\
\sum_i f^e_i e_{i\alpha} e_{i\beta} &= \sigma_{\alpha\beta} + \rho u_\alpha u_\beta
\end{align*}
\]

while the forcing terms, \(W_i\), are chosen to control the external force \(F_\alpha\),

\[
\begin{align*}
\sum_i W_i &= 0, \\
\sum_i W_i e_{i\alpha} &= F_\alpha, \\
\sum_i W_i e_{i\alpha} e_{i\beta} &= u_\alpha F_\beta + F_\alpha u_\beta.
\end{align*}
\]

In practice, to solve equation 3.4, a finite difference method is required. Our fix provides the choice between two such algorithms. The first,

\[
f_i(x + e_i \Delta t, t + \Delta t) = f_i(x, t) - \frac{1}{\tau} \left( f_i(x, t) - f^e_i(x, t) \right) + W_i(x, t)
\]

is the standard LB scheme [28]. This algorithm gives

\[
\begin{align*}
\eta &= \rho \left( \tau - \frac{\Delta t}{2} \right) v_c^2 / 3, \\
\Lambda &= \eta \left( \frac{5}{3} - 3a_0 / v_c^2 \right)
\end{align*}
\]
3.2. Theoretical background

where \( v_c = \Delta x / \Delta t \). In order to remove physically unrealistic, non-Galilean invariant terms which appear in the momentum equation, we have also added corrections to the scheme, in the form of density gradient terms incorporated into the pressure tensor [29].

The second algorithm is that used by Ollila et. al. [22],

\[
\begin{align*}
    f_i (x + e_i \Delta t, t + \Delta t) &= e^{-\Delta t/\tau} f_i (x, t) + \left(1 - e^{-\Delta t/\tau}\right) g_i^{eq} (x, t) \\
    &+ \left(\Delta t - \tau (1 - e^{-\Delta t/\tau})\right) D_i g_i^{eq} (x, t) \\
    &+ \left(\tau^2 (1 - e^{-\Delta t/\tau}) - \Delta t \tau + \Delta t^2 / 2\right) D_i^2 g_i^{eq} (x, t) \\
    &+ O(\Delta t^4),
\end{align*}
\]

(3.9)

with,

\[
D_i g_i^{eq} = \frac{g_i^{eq} (x, t) - g_i^{eq} (x - e_i \Delta t, t - \Delta t)}{\Delta t}
\]

(3.10)

and

\[
D_i^2 g_i^{eq} (x, t) = \frac{g_i^{eq} (x + e_i \Delta t, t) - g_i^{eq} (x, t - \Delta t) - g_i^{eq} (x, t) + g_i^{eq} (x - e_i \Delta t, t - \Delta t)}{\Delta t^2}.
\]

(3.11)

Here \( g_i^{eq} = f_i^{eq} + \tau W_i \). This algorithm was obtained from the exact solution of equation 3.4 at time \( t + \Delta t \),

\[
f_i (x + e_i \Delta t, t + \Delta t) = e^{-\Delta t/\tau} \left( f_i (x, t) + \int_t^{t + \Delta t} \frac{1}{\tau} e^{(s-t)/\tau} g_i^{eq} (x + e_i s, t + s) \, ds \right),
\]

(3.12)

by performing a Taylor series expansion on the \( g_i^{eq} \) term, about \( s = 0 \). Ollila et. al. [22] found that this algorithm was more stable than the standard LB algorithm with regards to the treatment of stiff terms introduced into the equations by the colloidal forces. The shear and bulk viscosities obtained with this algorithm are similar to equation 3.8, but with \( \tau - \Delta t/2 \) replaced simply by \( \tau \).

\subsection*{3.2.2 Thermal Lattice-Boltzmann}

In a real fluid, a finite temperature gives rise to fluctuations which are not present in the basic LB algorithm described above. These fluctuations produce spontaneous local stresses in the fluid, governed by a fluctuation dissipation relation of the form,

\[
\left\langle s_{ab} (r, t) s_{yy} (r', t') \right\rangle = 2\eta_{a'b'} k_B T \delta (r - r') \delta (t - t').
\]

(3.13)
In practice, we add random noise to the system through the forcing terms $W_i$ in equation 3.4, which we now generalize to $W_i = p_i + \zeta_i$. Here the $p_i$ are chosen to satisfy equations 3.6, while the $\zeta_i$ must satisfy,

$$
\sum_i \zeta_i = 0,
\sum_i \zeta_i e_{\alpha} = 0
$$

(3.14)

in order to conserve mass and momentum globally in the system. The higher moments of $\zeta_i$ are chosen so that the fluctuating stress tensor satisfies equation 3.13, and dissipation in the higher modes is compensated by corresponding fluctuations. With the noise implemented in this manner, the fluid acts as a heat bath for the MD particles [24]. See Ollila et al. [22], for complete details of the algorithm.

### 3.2.3 Coupling MD Particles to the Fluid

In order to couple a moving object to the LB fluid, a pixelized representation of the object on the fluid lattice is required. This is accomplished by dividing the surface of the object into a set of nodes (done a priori by the user, with each node treated as an individual MD particle by the main LAMMPS program), and then distributing these nodes to the nearby lattice sites, by assigning weights, $\zeta_{\alpha j} = \phi_j(x_\alpha)\phi_j(y_\alpha)\phi_j(z_\alpha)$ to these sites. We provide the user with the choice between two different distribution methods. The first we refer to as the trilinear interpolation method, or trilinear stencil, which assigns weights to each of the nearest lattice sites according to a linear interpolation,

$$
\phi_j(r_\alpha) = 1 - |\Delta r|,
$$

(3.15)

where $|\Delta r|$ corresponds to the scalar absolute value of $\Delta r = (r_\alpha - r_j)/\Delta x$. Here $r_\alpha$ gives the position of the particle node, while $r_j$ gives the position of the fluid lattice site, and $\Delta x$ is the lattice spacing. It is easily seen that these weights vary smoothly from 1 to 0 for a given lattice site, as a particle initially located on that lattice site moves to a neighboring site. Therefore, as an object composed of many nodes moves through the fluid, it affects the fluid in a continuous manner.

The second method we have implemented is based on the immersed boundary method [30,31], which uses a smoothing kernel to spread the influence of a point particle to a compact support. Here, the smoothing kernel is a 4-point approximation to the Dirac delta function, and
3.2. Theoretical background

The associated grid weights are given by \[32\],

\[
\phi_j(r_\alpha) = \begin{cases} 
\frac{1}{8} (3 - 2\Delta r + \sqrt{1 + 4\Delta r - 4\Delta r^2}), & 0 < \Delta r < 1; \\
\frac{1}{8} (5 - 2\Delta r - \sqrt{-7 + 12\Delta r - 4\Delta r^2}), & 1 < \Delta r < 2; \\
0, & 2 < \Delta r. 
\end{cases} \tag{3.16}
\]

We refer to this interpolation method as the Peskin stencil. This stencil provides a larger support of 64 lattice sites, compared to the 8 provided by the trilinear interpolation, and is seen to be more stable and exhibit fewer lattice artifacts when used in simulations compared with the trilinear stencil. For these reasons, the Peskin stencil has been set as the default interpolation method. However, due to its smaller support, the trilinear stencil may be better suited for simulations of objects close to walls or other surfaces.

As an object moves through the lattice-Boltzmann fluid, an interaction between the two must occur. This is accomplished by applying forces to both the fluid lattice sites and the particle nodes. The contribution to the force on a given lattice site \(j\), due to particle node \(\alpha\) is calculated as:

\[
F_j = \gamma (v_n - u_f) \zeta_{j\alpha}, \tag{3.17}
\]

where \(v_n\) is the velocity of the particle node, \(u_f = \sum u_j \zeta_{j\alpha}\) is the velocity of the fluid interpolated to the particle node location, and \(\gamma\) is a proportionality constant. Since \(\sum \zeta_{j\alpha} = 1\), the total force acting on the fluid due to the particle node \(\alpha\) is \(\gamma (v_n - u_f)\). Therefore, an equal and opposite force is then applied to this particle node,

\[
F_\alpha = -\gamma (v_n - u_f). \tag{3.18}
\]

One might assume that \(\gamma\), the coupling constant, should be set at \(6\pi\eta a\), to give the Stokes drag force; however this is not correct, as the velocity in equation 3.17 is not the far field velocity. Due to the discrete nature (in time) of numerical simulations, it is possible to show that \(\gamma\) in a discrete simulation can be chosen so that it conserves the net kinetic energy [24]. This corresponds to

\[
\gamma = \frac{2m_\alpha m_v}{m_v + m_\alpha} \left( \frac{1}{\Delta t_{\text{collision}}} \right), \tag{3.19}
\]

where \(\Delta t_{\text{collision}}\) is the collision time, chosen so that \(\tau/\Delta t_{\text{collision}} = 1\), \(m_v\) is the mass of the particle node, and \(m_\alpha\) is a representative fluid mass at the node location. This fluid mass is calculated by performing an interpolation of the fluid density to the node location, and multiplying by the volume of space occupied by the particle node (calculated as the object surface area associated with the node multiplied by the lattice spacing). This is the default choice for \(\gamma\); however, we also allow the user to specify their own value. A detailed description of the method by which
the user can choose an appropriate value for $\gamma$ is described below in the test run section.

When $\gamma$ is set by default, using equation 3.19, we have found that the built-in LAMMPS velocity-Verlet type integrators work well to solve for the resulting particle motion. However, large, user-set values of $\gamma$ result in stiff equations, and poor stability. Therefore, for these cases, we have created our own integration algorithm, utilizing the velocity-dependent nature of the forces. This algorithm reduces to velocity-Verlet as $\gamma$ tends to zero. It is important to note that the algorithm requires a constant value of $\gamma$ for a given group of particles; therefore it should not be used when $\gamma$ is set by default. Our algorithm is similar to the LAMMPS rigid fix, which integrates the motion of extended rigid objects composed of a set of individual particles, which are assumed to move and rotate as a single body. For our algorithm, we assume that the single body is a solid, spherical object represented by a shell of $N$ point particles. We have also included an integration routine for a single point particle; however since this is fairly obvious, we will not go into the details here. In the description that follows, we refer to our rigid object as a “composite particle”, and the individual point particles comprising it as “particle nodes”.

Our algorithm is based on the exact solutions to the equations of motion for the center-of-mass, and angular velocities,

$$M \frac{d\mathbf{v}_{CM}}{dt} = \mathbf{F}_{ext} - \gamma \sum_n (\mathbf{v}_n - \mathbf{u}_f);$$

$$I \frac{d\omega}{dt} = \tau_{ext} - \gamma \sum_n (\mathbf{r}_n \times (\mathbf{v}_n - \mathbf{u}_f)), \quad (3.20)$$

namely,

$$\mathbf{v}_{CM}(t + \Delta t) = e^{-\gamma N \Delta t / M} \left[ \mathbf{v}_{CM}(t) + \int_0^{\Delta t} e^{\gamma N s / M} \left( \frac{\mathbf{F}_{ext}^{TOT}(t + s)}{M} + \frac{\gamma N \mathbf{u}_{CM}^{L}(t + s)}{M} \right) ds \right],$$

$$\omega(t + \Delta t) = e^{-\gamma I \Delta t / mI} \left[ \omega(t) + \int_0^{\Delta t} e^{\gamma \gamma s / mI} \left( \frac{\tau_{ext}(t + s) + \tau_{fluid}(t + s)}{I} \right) ds \right], \quad (3.21)$$

where $M$ is the mass of the composite particle, $m$ is the mass of an individual particle node (note all the nodes which interact with the fluid must have the same mass in the current implementation), $\mathbf{u}_{CM}^{L} = (1/M) \sum_n m \mathbf{u}_f^n$, $\mathbf{F}_{ext}^{TOT}$ is the sum of the external, non-hydrodynamic, LAMMPS forces acting on the particle, $I$ is the moment of inertia of a spherical shell of mass $M$, $I$ is the moment of inertia of a solid sphere of mass $M$, $\tau_{ext}$ is the torque acting on the sphere due to the external LAMMPS forces, and $\tau_{fluid} = \gamma \sum_n \mathbf{r} \times (\mathbf{u}_f^n - \mathbf{v}_{CM})$. The distinction between the moment of inertia of the shell and the solid is made due to the fact that we are assuming that the composite particle rotates as a solid rigid body, while only the nodes on the surface contribute to the hydrodynamic force. Tracking the motion of a hollow shell would simply require
3.2. Theoretical background

replacing the moment of inertia of the solid with that of the shell.

It is important here to clarify what we mean by the mass of the particle, $M$, in equation 3.20. Our algorithm assumes that this mass is simply the sum of the masses of all of the individual particles nodes (this would correspond to what is sometimes called the excess mass). However, one should realize that the actual composite particle, consisting of the shell with mass $M$, plus the fluid inside, which necessarily moves with it, responds as a particle with total mass to be the mass of the nodes plus the mass of the fluid inside the particle. For example, by measuring the velocity autocorrelation function of a single particle with total node mass, 66.9 ag, and contained fluid mass, 82.1 ag, diffusing in a thermal LB fluid, Ollila et al. [22] used Zwanzig's calculation of the VACF at time $t = 0$ [33], to determine a total particle mass of 150 ag, in excellent agreement with the 149 ag calculated sum of the node mass and contained fluid mass.

Our algorithm proceeds as follows. The position of the particle is first updated according to,

$$
\mathbf{r}^{CM}(t + \Delta t) = \mathbf{r}^{CM}(t) + \mathbf{v}^{CM}(t)\Delta t + \left( \frac{(\mathbf{F}^{TOT}_{ext}(t) + \mathbf{F}^{TOT}_{fluid}(t))\Delta t^2}{2M} \right),
$$

where $\mathbf{F}^{TOT}_{fluid} = \gamma \sum_{n} (\mathbf{v}_n - \mathbf{u}_n^p)$, with all quantities evaluated at time $t$. Approximations to $\mathbf{v}^{CM}$, and $\omega$ are made by performing a Taylor series expansion of equations 3.21 about $s = 0$, in a manner similar to the derivation of the LB algorithm given in equations [3.9-3.11]. $\mathbf{v}^{CM}$ and $\omega$ are calculated as,

$$
\mathbf{v}^{CM}(t + \Delta t) = e^{-\gamma N\Delta t/M} \left[ \mathbf{v}^{CM}(t) - \frac{\mathbf{F}_{ext}(t)}{N\gamma} - \mathbf{u}_f^{CM}(t) \right] + \frac{\mathbf{F}_{ext}(t)}{N\gamma} + \mathbf{u}_f^{CM}(t);
$$

$$
\omega(t + \Delta t) = e^{-\gamma I\Delta t/mI} \left[ \omega(t) - \frac{m}{\gamma I} (\tau(t) + \tau_{fluid}(t)) \right] + \frac{m}{\gamma I} (\tau(t) + \tau_{fluid}(t)).
$$

Using these new velocities, the positions of the individual particle nodes are then updated, and the fluid velocities at the new particle node locations are calculated. Corrections are then made to the center of mass, and angular velocities according to
\[
v_{\text{final}}^{CM}(t + \Delta t) = v^{CM}(t + \Delta t) + \left( \Delta t - \frac{M}{N\gamma} \left( 1 - e^{-\gamma N \Delta t / M} \right) \right) \times \\
\left[ \frac{(F_{\text{ext}}(t + \Delta t) - F_{\text{ext}}(t))}{\gamma N \Delta t} + \frac{(u_{f}^{CM}(t + \Delta t) - u_{f}^{CM}(t))}{\Delta t} \right] ; \\
\omega_{\text{final}}(t + \Delta t) = \omega(t + \Delta t) + \left( \Delta t - \frac{mI}{\gamma I} \left( 1 - e^{-\gamma I \Delta t / mI} \right) \right) \times \\
\left[ \frac{(\tau(t + \Delta t) - \tau(t)m)}{\gamma I \Delta t} + \frac{(\tau_{\text{fluid}}(t + \Delta t) - \tau_{\text{fluid}}(t)m)}{\gamma I \Delta t} \right] .
\]

Finally, using the updated particle node velocities, the force from the particles is applied to the fluid.

As mentioned previously, this algorithm reduces to velocity-Verlet for non-hydrodynamic, conservative forces (\(\gamma = 0\)). This can be seen by performing a Taylor series expansion of the exponential terms in both equations 3.23 and 3.24, and taking the \(\gamma \to 0\) limit.

### 3.3 Description of the individual software components

The lattice-Boltzmann fluid and particle integrators described above have been implemented into LAMMPS through the creation of a series of fixes, which, in the formalism of LAMMPS, are operations performed during the normal timestepping of the program.

The main such fix, \(lb_{\text{fluid}}\), is used to create the LB fluid on a user defined grid covering the LAMMPS simulation domain. This fix allows for the presence of walls in the \(z\)-direction, which can either be stationary, or moving with constant velocity along the \(y\)-direction. Periodic boundary conditions are required in the \(x\) and \(y\) directions. At each timestep, the forces from the MD particles that the fix acts on are applied to the fluid, and the fluid properties are calculated.

If the fluid and particle hydrodynamic forces are calculated, by default, with the force coupling constant set according to equation 3.19, a built-in LAMMPS integrator should be used to track the resulting particle motion. This requires the addition of these hydrodynamic forces to the total forces acting on the individual particles. This is accomplished through the use of the \(viscous_{lb}\) fix, which we have created as an analogue to the built-in \(viscous\) LAMMPS fix. However, if the user chooses to specify a value for the coupling constant themselves, this may lead to instability when using the built-in LAMMPS integrators. Therefore, we have provided two integration fixes to treat these cases, \(rigid_{pc_{sphere}}\), which integrates the motion of rigid spherical objects, and \(pc\), which integrates the motion of individual MD particles. The \(rigid_{pc_{sphere}}\) fix was created to integrate the motion of solid, spherical particles, represented...
by a spherical shell of nodes. This fix assumes that the spheres rotate as solid bodies, with
uniform density and total mass obtained from a sum of the masses of all the contributing
nodes, both those on the particle surface which interact with the fluid, and those inside the
particle which do not (see the description of atom style \textit{lb}, which follows).

A new atom style \textit{lb}, has also been included, to assign an additional attribute to each MD
particle (\textit{interiortag}), allowing the user to specify whether the specific MD particle contributes
to the hydrodynamic force (\textit{interiortag} = 0), or not (\textit{interiortag} = 1). For example, particles on
the inside of a non-porous object should not normally contribute to this force. Those particles
which do not contribute to the hydrodynamic force will, however, contribute to the total object
mass, and any non-hydrodynamic LAMMPS forces acting on them will contribute to the total
force acting on the composite object. This is a desirable feature because, while a large number
of nodes are required to represent the surface of a spherical object, non-hydrodynamic forces
such as hard-core interactions, require properties such as the position of the center of mass
and the sphere radius, but not the locations of the individual particle nodes. Therefore, it
will usually make sense to assign non-hydrodynamic forces (\textit{e.g.} Coulomb forces) between
two spheres simply by placing an MD particle at the center of each sphere, and assigning
interactions between these central atoms, as opposed to the computationally intensive task of
assigning interactions between all of the surface atoms.

Finally, we have also included the fix, \textit{momentum\_fluid}. This is analogous to the built-in
\textit{momentum} fix for particle momentum only, but additionally includes the fluid momentum,
thereby allowing the user to subtract off the total (particle plus fluid) linear momentum from
the system.

3.4 Installation instructions

All of the source files contained in the package can be found in the /\textit{src\_lbfluid} directory. As
documented in the LAMMPS manual, the installation of a new feature simply requires the user
to copy the source and header files into the LAMMPS /\textit{src} directory, and recompile the code.
We have provided all code for the May 23, 2012 version of LAMMPS, and a \textit{readme.txt} file
with some tips that may prove helpful for future versions.

Documentation for the individual components can be found in the /\textit{doc\_lbfluid} directory,
which is in a format compatible with the standard LAMMPS documentation.
3.5 Test run descriptions

As previously discussed, by default, the force coupling constant used in equations 3.17 and 3.18 is set according to equation 3.19. Numerous tests of this method have been presented in Mackay et al. [24]. Therefore, here, the majority of examples we present provide simple tests to illustrate the use of a user specified coupling constant. More complex examples of polymer simulations performed using the method can be found in [22].

It should be noted that while this method is much faster than using individual MD particles to represent the fluid (with a gain of up to several orders of magnitude in timestep obtained by coarse-graining the fluid), the majority of the computational time is still spent updating the lattice-Boltzmann fluid. Therefore, the limiting factor in these simulations is the number of lattice sites required to discretize the fluid; additional MD particles could be added to these simulations with a relatively minimal increase in computational cost, while increasing the simulation domain to model larger systems/objects could potentially be quite costly. However, any increases in wall clock time can be substantially minimized through the use of additional processors, as this method parallelizes quite well. The final example we present illustrates this scalability for a realistic implementation of the method using the default force coupling constant.

3.5.1 Single Spherical Particle

As described above, any surface interacting with the LB fluid must first be discretized into a set of nodes. This is done outside of the code by the user, with each of the nodes implemented into the main LAMMPS program as an individual LAMMPS particle. For spherical particles we typically use fullerenes composed of various numbers of nodes, obtained from [34], to represent the particle surface. Examples of fullerenes with 20 and 240 nodes respectively are shown in Figure 3.1.

The number of nodes used for the fullerene should be chosen so that the discretization of the particle surface is finer than that of the fluid lattice, thereby avoiding gaps in the mesh representation of the surface, when the particle nodes are interpolated onto the fluid lattice. In general, the nodes should be chosen closer than $\Delta x$ apart, with closer spacings potentially reducing mesh effects; however, in practice we have found minimal improvement for spacings smaller than $\Delta x/2$ for the Peskin, and $\Delta x/4$ for the trilinear stencil. A single node could also be used to represent the particle; however, due to the interpolation of the node onto the fluid mesh, the effective size of the particle is then tied to the mesh resolution. In addition, mesh effects observed for a single particle node are substantially larger than those for a composite object.
3.5. Test run descriptions

Figure 3.1: Example fullerenes used to represent the spherical particle surface. The fullerene on the left is composed of 20 nodes, while the fullerene on the right consists of 240 nodes.

Setting the Force Coupling Constant

The first step in any simulation in which the user chooses to specify a value for the force coupling constant, $\gamma$, is to calibrate its value. Theoretically, in the absence of thermal noise (appropriate at larger length scales $\sim 1\mu m$ in a water-like solvent), the force and torque experienced by a stationary, infinitely thin shell of nodes, interacting with the fluid through the forces described by equations 3.17 and 3.18, are given by [35, 36],

$$\frac{F}{F_S} = \frac{2\beta^2}{2\beta^2 + 9}$$

$$\frac{T}{T_S} = \frac{\beta^2}{\beta^2 + 9}$$

where $F_S = 6\pi\eta RU_0$, $T_S = 4\pi\eta R^3 S$, $R$ is the radius of the particle, $\eta$ is the fluid viscosity. $U_0$ and $S$ are what the velocity and shear rate of the fluid would be at the shell location if the shell were not there. $\beta$ is a dimensionless parameter given by $\beta = R \sqrt[3]{\gamma \lambda / \eta}$, where $\lambda = N / (4/3\pi R^3)$, and $N$ is the number of surface nodes. Using these equations, one could therefore, theoretically calculate the value for $\gamma$ required to produce a force and torque within a small, predefined error of the Stokes values. Ollila et. al. [37] have found quite good agreement between these equations and simulation results obtained using the trilinear stencil. We have found that the level of agreement is lower when using the Peskin stencil. This makes sense, since the theoretical results are for an infinitely thin shell, while the Peskin stencil distributes...
the nodes to the nearest 64 grid points, resulting in a substantial shell thickness. In addition, for large values of $\gamma$, the simulation results can be sensitive to the value used for $\tau$, given in equation 3.4. However, in all situations, good agreement is found for the case of porous particles, where $\gamma$ is of a lower value. In this case, the simulations generally produce forces which are only slightly larger than those obtained with equation 3.25.

Here, we use the Peskin stencil, and calibrate $\gamma$ simply by requiring that the fluid force acting on a particle moving at constant velocity, $U$, is equal to the Stokes drag force, $F_D = 6\pi\eta RU$. In this section, we provide an example, showing in detail how this is accomplished. The input and data files for the example, in.drag and data.drag, can be found in the /testruns/dragforce directory.

For our example, we have chosen to simulate a particle of radius 16.2 $\mu$m in a fluid with density $\rho = 1.0$ g/cm$^3 = 1.0$ pg/µm$^3$, and viscosity $\eta = 1.0$ g/(cm s) = 1.0 pg/(µm µs). In order to use units of µm, µs, and pg in the code (with all other units set to SI values), we have edited the update.cpp file, creating an lb_micron units type (we have also created an lb_nano units type for simulations with units of nm, ns, and attg). The lattice parameters are chosen to be $\Delta x = 4.0\mu$m, $\Delta t = 4.0\mu$s, and $\Delta m = 10.0$ pg, resulting in scaled LB parameters on order unity. This gives a radius of 4.05$\Delta x$ for the particle, whose surface we represent using a fullerene consisting of 320 nodes. The size of our system is taken to be $(80\Delta x)^3$, with periodic boundary conditions used in the $x$ and $y$ directions, and fixed boundary conditions used in the $z$ direction, as stationary $z$ walls are required to enforce a zero far field fluid velocity. For simulations like these, a large system size is required, in order to reduce finite size effects which, for systems containing 2 walls, are expected to scale as $1/L^2$, where $L$ represents the linear system size [38].

To set up the simulation, the fullerene is placed in the center of the simulation domain, and given a velocity of $0.0001\Delta x/\Delta t \hat{y}$, by assigning this velocity to each of the individual particle nodes. In order to print the fluid forces acting on the particle at each timestep, the lb_fluid fix is used with the calcforce option (documentation for the fix options have been provided in LAMMPS format in the /doc_lbfluid directory). With this option, the forces and torques acting on the particle are output to the screen at each timestep, as a row of six numbers. The first 3 numbers correspond to the $x$, $y$, and $z$ components of force acting on the particle, while those remaining correspond to the $x$, $y$, and $z$ components of torque, which for this example should be negligible. Since the particle is required to move at a constant velocity, the fluid forces should not actually be applied to it. In any situation where the user does not want the fluid forces to act on the particles, an integrator other than rigid_pc_sphere or pc should be used. For this particular situation, where the non-fluid LAMMPS forces are all zero, the choice of alternate integrator is arbitrary, and we simply use the nve integrator.
Several simulations with different values of $\gamma$ were performed. These simulations were allowed to run until the system reached equilibrium, and the drag force was seen to oscillate around a constant value. These oscillations are present due to mesh effects, but are quite small, $\sim 0.001\%$ of the average, for the parameters considered here. In general, mesh effects depend on several parameters including, (1) the number of nodes used; point particles experiencing larger mesh effects than composite objects, (2) the interpolation stencil employed; mesh effects are smaller for the Peskin stencil compared with the trilinear stencil, and (3) the physical size (in lattice units) of the object; the larger the lattice representation, the smaller the mesh effects. Figure 3.2 shows the particle velocity divided by the drag force as a function of $1/\gamma$, which produces a straight line. From this, the value of $\gamma$ required to produce the correct drag force, (i.e. $6\pi \eta a U$), can be obtained. Here, we calculate this to be 13.65 $\text{pg}/\mu\text{m}$.

It is worth pointing out that in order for the drag force and torque to give consistent results with spheres of different numbers of nodes or radii, one should follow the relation,

$$\frac{\gamma N_v}{4\pi a^2 \tau / \Delta t} = \text{Const}, \quad (3.26)$$

where $N_v$ is the number of nodes on the fullerene. This relation indicates that $\gamma$ is proportional
Figure 3.3: Geometry used for the sphere positioned a distance $h$ from a stationary plane wall in a system undergoing Couette flow, with shear rate $S$. 

to the surface area per node of the composite object, which makes sense, since spheres of the same size but different numbers of nodes should contribute the same total force, in addition to being proportional to $\tau$, which is the relevant timescale in the fluid. Therefore, once $\gamma$ has been calibrated for a given radius and number of nodes, changing either of these quantities will produce consistent results if $\gamma$ is altered in order to obey this relation.

**Free Motion of a Particle Near a Plane Wall**

As a test of our particle integrator, *rigid_pc_sphere*, we next consider the free motion of a particle near a stationary plane wall, in a system undergoing Couette flow (see Figure 3.3). The input files for this example can be found in the /testruns/planewall directory. We use the same parameters as described above for the fluid and particle, however now the particle is allowed to move freely, and we move the upper wall at a constant velocity of $0.0001 \Delta x / \Delta t$, corresponding to a shear rate of $S = 1.25 \times 10^{-6} \Delta t^{-1}$.

The particle is placed, initially at rest, at several distances, $h$ above the stationary, lower wall. To do this using the input files provided, in which the particle is located at $(0,0,0)$, the positions of the z walls given in the *data.planewall* file are varied, keeping a constant spacing of $80 \Delta x$ between them. We allow the system to equilibrate, and the resulting center of mass
3.5. Test run descriptions

and angular velocities of the sphere are measured. Far from the wall, the center of mass, and angular velocities are expected to be,

\[ v_{CM} = hS, \]
\[ \Omega = S/2. \]  

(3.27)

However, as the sphere is brought closer to the wall, wall effects act to decrease both of these quantities. Figure 3.4 shows both the normalized center of mass and angular velocities for a range of distances, \( h \), along with a comparison to theoretical results presented in [39]. As can be seen, the agreement is quite good.

3.5.2 Hydrodynamic Interaction Between Four Spherical Particles

Next, we investigate the hydrodynamic forces acting between particles. We use the same fluid and lattice parameters as the previous test, and a particle radius of \( 2.05\Delta x \). For this test, we set up a situation as shown in Figure 3.5. Particles 1 and 2 are moved in the negative y-direction with constant velocity, while particles 3 and 4 are moved in the positive y-direction. This set-up ensures that no net velocity, or vorticity is added to the fluid. In order to reduce finite-size effects, a system size of \( (120\Delta x)^3 \) is used, with the particles restricted to the central region, of size \( 15\Delta x \times 30\Delta x \). The input files for this test can be found in the /testruns/fourspheres directory.

For this test, the particles are allowed to pass through one another, allowing us to investigate a full range for the hydrodynamic forces. However, in practice, it is very straightforward to implement a hard sphere type interaction between the particles (described in the next test), to prevent this.

To test the validity of our results, we compare them to theoretical results obtained using the Rotne-Prager tensor, \( \mathbf{M} \). This tensor represents an improvement, at short range, to the Oseen hydrodynamic mobility tensor, \( \mathbf{H} \), obtained based on linearized hydrodynamics, relating the hydrodynamic forces on identical spheres to their velocities [40],

\[ V = \mathbf{H}F. \]  

(3.28)

Here, \( V \) is a column vector of the particle velocities, and \( F \) is a column vector of the forces.
Figure 3.4: Normalized center of mass velocity, $U$, and angular velocity, $\Omega$, for a sphere in a system undergoing Couette flow, with shear rate $S$, as a function of its height, $h$, from a stationary plane wall. The grey lines represent the simulation results, while the black circles correspond to the theoretical prediction given in [39].
3.5. Test run descriptions

Figure 3.5: Setup of the 4 particle system in the $x – y$ plane. The particles are positioned at $(-7.5\Delta x, 15.0\Delta x, 0)$, $(7.5\Delta x, 15.0\Delta x, 0)$, $(-7.5\Delta x, -15.0\Delta x, 0)$ and $(-7.5\Delta x, -15.0\Delta x, 0)$ in a system of size $(120\Delta x)^3$. 
The Rotne-Prager tensor takes the form [41],

\[
M_{ii} = \frac{I}{6\pi \eta a}
\]

\[
M_{ij} = \frac{1}{8\pi \eta R_{ij}} \left( I + \hat{R}_{ij}\hat{R}_{ij} \right) + \frac{2a^2}{3R_{ij}^2} \left( I - 3\hat{R}_{ij}\hat{R}_{ij} \right),
\]

(3.29)

where \(a\) is the particle radius, \(\eta\) is the fluid viscosity, and \(\hat{R}_{ij}\) is a unit vector parallel to \(R_{ij} = r_i - r_j\). Since our simulation contains an infinite number of periodic images, in addition to using a large system size, we also include one shell of periodic images when computing results using the Rotne-Prager tensor.

Figure 3.6 presents results for two different particle velocities, 0.0001\(\Delta x/\Delta t\) (solid circles), and 0.005\(\Delta x/\Delta t\) (open circles), which we compare to the theoretical prediction (grey line). For the faster velocity, there is an asymmetric lag in the force perpendicular to the velocity, \(F_x\), compared with the theoretical result. This discrepancy is due to the fact that in both the Oseen and Rotne-Prager formulations, the hydrodynamic interactions are assumed to propagate instantaneously, which is not the case for the simulation. However, with the slower velocity, this lag is seen to disappear, and good agreement between the Rotne-Prager tensor is obtained.

While the forces do not diverge as the particles approach one another, as predicted by the theory, they do become very large, and as mentioned previously, it is easy to put a hard-sphere type interaction between the particles so that they would not actually overlap.

### 3.5.3 Two Particle Microrheology

As a further test of the method, we consider two-particle microrheology. This example is presented to illustrate both the use of the thermal LB method, as well as the implementation of hard sphere interactions between particles.

Two particle microrheology was proposed by Crocker et. al. [42] as an extension of single-particle microrheology, with the advantage that it does not depend on the size or shape of the tracer particles. Instead of measuring the mean square displacement of a single thermally fluctuating tracer particle, this method measures the correlated fluctuations of pairs of particles, given by the pair displacement correlation tensor,

\[
D_{\xi\psi}(r, dt) = \left( \Delta r_{\xi}^i(t, dt) \Delta r_{\psi}^j(t, dt) \delta \left[ r - R_{ij}^t \right] \right)_{i \neq j, t},
\]

(3.30)

where \(\xi, \psi\) label different coordinates, \(\Delta r_{\xi}(t, dt) = r_{\xi}(t + dt) - r_{\xi}(t)\), and \(R_{ij}\) is the separation of the two particles. For an incompressible, visco-elastic medium, with \(r \gg a\), where \(a\) is the particle radius,
Figure 3.6: Forces both perpendicular and parallel to the particle velocities for the situation shown in Figure 3.5. Filled circles represent results obtained with particle velocities of $0.0001 \Delta x / \Delta t$, while the open circles correspond to $0.005 \Delta x / \Delta t$. The grey line corresponds to the theoretical prediction obtained from the Rotne-Prager tensor.
\[ \tilde{D}_{rr}(r, s) = \frac{k_B T}{2\pi rs \tilde{G}(s)}. \]  

(3.31)

Here \( \tilde{D}_{rr} \) is the Laplace transform of \( D_{rr} \), and \([s^{-1} \tilde{G}(s)]\) is a frequency-dependent viscosity. For a purely viscous fluid, which we consider here, \( D_{rr}(r, dt) \) takes the form,

\[ D_{rr}(r, dt) = \frac{k_B T dt}{2\pi r \eta}, \]  

(3.32)

where \( \eta \) is the fluid viscosity.

For the simulations, we use a lattice spacing of 1.2\,nm, and a timestep of 0.00045\,ns in a fluid with \( \rho = 998.2\,kg/m^3 \), \( \eta = 1.0\,gm^{-1}s^{-1} \), and \( T = 300\,K \). A system size of \((80\Delta x)^3\) was used along with particles either of radius 1.0\,\Delta x, or 2.0\,\Delta x. To prevent the particles from overlapping, a node was placed at the center of each sphere, using the atom style \textit{lb}, and a Lennard-Jones interaction, cut off at its minimum in order to provide a purely repulsive force, was implemented between the two particles, for situations when their surfaces were within one lattice unit of another. For larger distances, the interaction is purely hydrodynamic. In addition, the \textit{momentum fluid} fix was used in order to subtract off any net system momentum that might develop.

Several hundred different runs, tracking the positions of the two particles were performed. The input files for one such run can be found in the \texttt{/testruns/microrheology} directory, illustrating the implementation of the hard-sphere interaction between our particles. \( D_{rr}(r, dt) \) was measured, using equation 3.30 for a range of particle separations, where bins of size 1.0\,nm were used for the separations. For a given separation, the slope of \( D_{rr}(r, dt) \) vs \( dt \) was measured. The results are presented in Figure 3.7, where separations up to 17.5\,nm use results from the 1.0\,\Delta x particles, while the larger separations use the 2.0\,\Delta x particles. The error bars give a measure of the error due to the noise in the slopes, and vary in accordance with the amount of data available for each particle separation. As can be seen, the results agree within error with the theoretical prediction given by equation 3.32. It should be stressed that this agreement was achieved without the use of any adjustable parameters.

### 3.5.4 Confined Colloids

While the previous examples have consisted of simple tests with known theoretical solutions, as a final example, we consider a more complex simulation consisting of confined colloidal particles subject to shear. Using this example, we are able to provide timing and scalability data for a representative, realistic implementation of the method.
Figure 3.7: Slope of the radial component of the pair displacement correlation tensor as a function of particle separation. Simulation results are given by the black circles, while the grey line represents the theoretical prediction of equation 3.32.
Chapter 3. Lattice-Boltzmann Method Implemented Into LAMMPS

Figure 3.8: Geometry used for the confined colloid simulation. Left: view of the four layers in the $z$-$y$ plane. Right: view of a single layer in the $x$-$y$ plane. For simplicity, the spheres shown simply indicate the location of the central atoms for each particle. (In the simulation, each colloidal particle is composed of 3613 MD particle nodes).

The physical system we consider consists of 480 composite colloidal particles, of radius $r = 0.726 \mu m$, arranged in four layers in a system of total size $16.8 \mu m \times 16.8 \mu m \times 6.0 \mu m$ (see Figure 3.8). The system is periodic in both the $x$ and $y$ directions, with walls located at $z = 0$, and $z = 6.0 \mu m$. We use a fluid with density $\rho = 1.0 \, pg/\mu m^3$, and viscosity $\eta = 1.0 \, pg/(\mu m \cdot \mu s)$. Shear is established in the system by moving the $z$ walls in opposite directions, with velocities $v = \pm 20.0 \mu m/\mu s$.

For this simulation, we use the default method for calculating the force coupling constant, $\gamma$, and utilize the Peskin stencil for all interpolations. Since the Peskin stencil requires data from the two nearest lattice sites in each direction, it does not make sense to initialize our system with any surface to surface particle separations closer than $2\Delta x$. Therefore, for a given particle radius, and system density, this sets a maximum value for $\Delta x$ ($\Delta x$ must be less than half the minimum surface to surface separation found in the system). Here, we use $\Delta x = 0.06 \mu m$. The choice for $\Delta x$ also somewhat constrains the value used for the LB timestep, $\Delta t$, as we would like $\tau/\Delta t \sim O(1)$ for stability, which can be calculated from equation 3.8 for the standard LB scheme as,

$$\tau \Delta t = \frac{3\eta \Delta t}{\rho \Delta x^2} + \frac{1}{2} \tag{3.33}$$

Therefore, a simulation with a larger particle density (closer surface to surface separation) would require a smaller value for $\Delta x$, to ensure a minimum surface to surface separation of $2\Delta x$, and may also require a smaller LB timestep, to keep $\tau/\Delta t \sim O(1)$. Here, we choose
\[ \Delta t = 0.0006 \, \mu s. \]

With \(\Delta x\) set at 0.06 \(\mu m\) the colloidal particles we wish to represent have a radius of 12.1\(\Delta x\). Therefore, in order to obtain a finer discretization of the particle surface than that of the fluid mesh, we use 3612 surface nodes to represent the particle surface, resulting in an area per node of 0.0018\(\mu m^2\) or 0.51\(\Delta x^2\).

Similar to the situation described in Section 3.5.3, we place an additional node at the center of each colloidal particle and implement particle-particle hard-sphere interactions between these nodes, using a Lennard-Jones interaction cut off at its minimum such that a repulsive force is generated for situations when the surface to surface distance between particles is less than 2\(\Delta x\). In addition, we place Lennard-Jones walls at \(z = 0\), and \(z = 6.0 \mu m\), which interact with the central nodes, providing a repulsive force if the distance from the colloid surface to the wall is less than 3\(\Delta x\).

The input files for this example can be found in the /testruns/confined_colloid directory. With the choices for \(\Delta x\), and the number of surface nodes per colloidal particle described above, the resulting system contains 1734240 MD particle nodes, and 280\(\Delta x \times 280\Delta x \times 100\Delta x\) lattice sites. To test the performance of our method, we performed several different simulations, with various numbers of processors, on two different HPC clusters, Requin on SHARCNET (Shared Hierarchical Academic Research Computing NETwork), and Nestor on WestGrid (Western Canada Research Grid). The Requin cluster uses a Quadrics Elan4 interconnect, and consists of 768 nodes, each with an Opteron Dual-Core processor @ 2.6 GHz, and 8.0 GB of memory, while the Nestor cluster consists of 288 nodes, each with eight 2.67 GHz Xeon x5550 cores and 24 GB of memory, with an InfiniBand interconnect. Simulations were performed for a total of 400 timesteps. In all runs it was found that approximately 55 – 60% of the total computational time was spent updating the lattice-Boltzmann fluid.

Figure 3.9 shows both the speedup, \(T_1/T_p\), and efficiency, \(T_1/(p \cdot T_p)\), obtained with both clusters. Here \(T_1\) is the execution time obtained with 1 processor, and \(T_p\) is the time for \(p\) processors. As can be seen, good scalability is obtained with this method, with efficiencies greater than \(\sim 70\%\) for up to 400 processors.

3.6 Summary

We have implemented a thermal lattice-Boltzmann algorithm into the open source molecular dynamics package, LAMMPS, which uses a velocity dependent force to couple the MD particles to the fluid. We have provided several test examples illustrating the use of the method, along with their results, which show good agreement to theory, thereby providing a validation of the method.
Figure 3.9: Scalability results for the $280\Delta x \times 280\Delta x \times 100\Delta x$ lattice site, 1734240 MD particle node system. Solid circles correspond to simulations run on the SharcNet cluster, Requin, while hollow squares correspond to simulations run on the WestGrid cluster, Nestor. Left: speedup $= T_1 / T_p$, with the solid line showing ideal, linear speedup. Right: efficiency $= T_1 / (p \cdot T_p)$. 
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Part II

Colloidal Particles in a Liquid Crystal
Chapter 4

Introduction

Colloidal crystals have attracted substantial attention over the past several years due to their potential use as photonic band gap materials [1]. These materials, which control the propagation of light in a manner analogous to electrons in semiconductors [2], have a wide range of applications including optical telecommunication fibers, and photonic integrated circuits [3].

A major challenge in photonic crystal technology, however, is the fabrication of 3D crystals. One technique used to manufacture such crystals is to allow colloidal particles in a fluid to self-assemble [4–6]. However, the isotropic nature of most fluids leads to close-packed structures, which are not ideal, as non-close packed structures, such as a diamond lattice, provide better optical performance. If instead the colloidal particles are placed in a liquid crystal, non-isotropic forces develop among the particles, leading to the formation of new colloidal structures not seen in isotropic fluids. This has led to a substantial interest in the use of liquid crystals as the host medium in the hope that various self-assembled, ordered 3D crystals can be generated.

The remainder of this introduction presents a mathematical description of liquid crystals, and discusses the origin of the non-isotropic forces experienced by dispersed colloidal particles.

4.1 Liquid Crystal Basics

4.1.1 History

Prior to the late 1800’s, the scientific community knew only of three states of matter: solid, liquid, and gas. This all began to change in 1888, with Friedrich Reinitzer’s peculiar observation of a compound formed from a carrot cholesterol and benzoic acid [7]. To his surprise, this cholesteryl benzoate compound did not melt like a normal substance. Rather, Reinitzer
observed two distinct melting points, the first from a solid to a cloudy liquid, and at higher temperature a transition to a translucent liquid. After examining this cloudy liquid, Otto Lehmann described this new state of matter as a “flowing crystal” [8]. In 1922, Georges Friedel wrote a ground breaking article describing the potential structure of these liquid crystals, and introducing a classification scheme for their various phases [9]. While the discovery of liquid crystals generated substantial initial research, interest gradually declined, as few saw any practical applications for these substances. However, renewed interest in the field arose in the 1960’s and 70’s, most notably with the development of the first LC display prototype [10, 11], and the publication of P.-G. de Gennes’ now famous book [12].

### 4.1.2 Types of Liquid Crystals

As their name suggests, liquid crystals are a state of matter somewhat between a crystalline solid, and a liquid (see figure 4.1). These substances display a certain degree of liquid fluidity, yet at the same time exhibit strongly anisotropic properties. The transition to the liquid crystalline phase is controlled either by temperature (thermotropic liquid crystals), or solvent concentration (lyotropic liquid crystals) [13].

The molecules comprising a liquid crystal are necessarily non-spherically symmetric in shape, as required in order to produce the anisotropic properties of the liquid crystalline phase. In general, these molecules can be classified as either rod-like, or disc-like in shape. Liquid crystals composed of rod-like molecules will be used exclusively throughout this thesis. Two well known examples are shown in figure 4.2.
4.1. **Liquid Crystal Basics**

(a) PAA:

![Chemical structure of PAA](image)

(b) MMBA:

![Chemical structure of MMBA](image)

Figure 4.2: Examples of rod-like liquid crystal molecules (chemical structures obtained from de Gennes [12]).

Figure 4.3: Liquid crystal phases for rod-like constituent particles.

4.1.3 **Liquid Crystal Phases**

Rod-like constituent molecules can produce several different phases of liquid crystal, illustrated in Figure 4.3. The nematic phase, shown in Figure 4.3(a) lacks any long-range positional ordering of the centers of gravity of the molecules; however, long-range orientational order is observed, with the molecules on average oriented along a common axis. This axis, referred to as the “director”, is represented by a unit vector $\hat{n}$ (with $+\hat{n}$ and $-\hat{n}$ assumed indistinguishable due to the non-polar nature of the liquid crystalline phases; while liquid crystals tend to be composed of polar molecules [14], these molecules arrange themselves such that on average there are as many dipole moments pointing along $\hat{n}$ as there are along $-\hat{n}$). If the liquid crystal molecules are chiral (i.e. not super-imposable on their mirror images), or if chiral molecules...
are dissolved into the nematic phase, the director is seen to undergo a helical twist. This helical phase, shown in Figure 4.3(b) is called a cholesteric liquid crystal. The third phase of liquid crystal is known as the smectic phase. This phase, which represents a more ordered state than the nematic, typically occurs for temperatures below the nematic phase and is characterized by an arrangement of the molecules into layers, with no long-range positional ordering of the molecules in the direction parallel to the layers. This phase of liquid crystal can be further classified as either the smectic A phase (shown in Figure 4.3(c)), in which the molecules in a given layer are oriented along a direction perpendicular to the layer, or the smectic C phase, in which the director is tilted with respect to the layers.

### 4.1.4 Topological Defects

Topological defects are a common feature of condensed matter physics (eg. vortices in superfluid helium [15, 16], dislocations in a periodic crystal [17, 18]), and even appear in theories of the early universe [19]. These defects occur in systems in which a continuous symmetry is broken, and are characterized by a core region in which order is destroyed [20]. In the context of liquid crystals, defects correspond to singularities in the director field, and are responsible for many of the well known optical features of these substances. For example, the name nematic itself, originating from the Greek word for thread, was coined by Friedel [9] after observing the thread-like appearance of defects in a liquid crystal sample.

Defect lines in a liquid crystal are referred to as disclinations, and are classified by an integer or half-integer, \( s \), known as the strength of the defect. This number gives the multiple of \( 2\pi \) by which the director rotates when traversing a closed loop counter-clockwise around the disclination. Several examples are shown in Figure 4.4. The presence of these defects clearly costs energy, which can be shown to be proportional to the square of their strength [12].

Point defects can also occur, appearing in capillaries [21], liquid crystal droplets [22, 23], and, as will be discussed below, around immersed colloidal particles. Equal and opposite strength defects attract one another, annihilating each other if possible [24, 25].

### 4.2 Mathematical Description

#### 4.2.1 Order Parameter

In comparing the nematic and isotropic phases, it is clear that the nematic liquid crystal is “more ordered”. In order to quantify this order, it is common to introduce an order parameter, defined to be zero in the disordered, isotropic phase, and non-zero in the liquid crystalline...
Figure 4.4: Examples of topological defects in a liquid crystal. $s$ corresponds to the multiple of $2\pi$ by which the director rotates when traversing a closed loop counter-clockwise around the defect.
phase. The simplest order parameter, first introduced by Tsvetkov [26], is the scalar order parameter, $S_0$, defined as a coarse-grained average of the 2nd order Legendre polynomial,

$$S_0 = \frac{1}{2} \left< 3 \cos^2 \theta - 1 \right>.$$  \hspace{1cm} (4.1)

Here $\theta$ is the angle the molecular axis makes with the director. (Note that the 1st order Legendre polynomial evaluates identically to zero due to the equivalence of $+\hat{n}$, and $-\hat{n}$). This makes sense as an order parameter, since in an isotropic fluid, $\left< \cos^2 \theta \right> = 1/3$ leading to a value of $S_0 = 0$, while in a crystalline solid, in which the molecules are perfectly aligned, $\left< \cos^2 \theta \right> = 1$, and $S_0 = 1$. However, the scalar order parameter suffers from two main shortcomings. First, it assumes the constituent molecules are uniaxial (cylindrically symmetric about their molecular axis) [13]. It is however also possible for the molecules to either be biaxial in shape (think of a plank of wood), or for uniaxial molecules to form a biaxial distribution [27]. Secondly, the scalar order parameter requires knowledge of the overall director orientation, which may not be known beforehand, especially in the case of simulation.

A more general order parameter, applicable to arbitrary molecular shape, and determined solely by the orientation of the individual liquid crystal molecules, $\hat{m}$, is the tensor order parameter, $Q$,

$$Q_{\alpha\beta} = \frac{1}{2} \left< 3 \hat{m}_\alpha \hat{m}_\beta - \delta_{\alpha\beta} \right>.$$  \hspace{1cm} (4.2)

$Q$ is a symmetric, traceless tensor, and similar to the scalar order parameter, is identically equal to 0 in the isotropic phase, with non-zero components in the liquid crystalline phase. Since $Q$ is symmetric, it has 3 orthogonal eigenvectors, corresponding to real eigenvalues. The eigenvector associated with the principal eigenvalue is the director $\hat{n}$, while the principal eigenvalue is itself the scalar order parameter, $S_0$ [27]. Diagonalizing $Q$ yields the following tensor,

$$Q_{\alpha\beta} = \begin{bmatrix} S_0 & 0 & 0 \\ 0 & -(S_0 + P)/2 & 0 \\ 0 & 0 & -(S_0 - P)/2 \end{bmatrix},$$  \hspace{1cm} (4.3)

where $P$ is a measure of the biaxiality. The form of this tensor can be understood by considering a rotation of the system about the director. If the system is symmetric about such a rotation, then $P = 0$, and the liquid crystal is uniaxial. If the rotation is not a symmetry then there is an overall preference for one of the two directions orthogonal to the director, $P \neq 0$, and the liquid crystal is biaxial [27]. While a uniaxial symmetry is usually assumed for nematic liquid crystals, the cores of defects are generally considered to be biaxial [28, 29].
4.2. Mathematical Description

4.2.2 Free Energy Description

In order to mathematically describe the liquid crystal system, a free energy approach is used. To describe the isotropic-nematic transition, de Gennes [12] proposed a phenomenological description based on the Landau theory of phase transitions [31], writing the free energy in the following form,

\[ F = F_0 + \frac{1}{2} A (T - T_c) Q_{\alpha\beta} Q_{\beta\alpha} - B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + C (Q_{\alpha\beta} Q_{\beta\alpha})^2. \] (4.4)

Here, \( T \) is the temperature, \( T_c \) is the critical temperature for the transition, and \( A, B, C \) are constants. A term linear in the order parameter is absent from eq. 4.4 due to the traceless nature of \( Q \) (this also ensures that \( F \) is minimized by \( Q = 0 \) in the isotropic phase). The presence of the cubic term distinguishes between systems \( Q_1 = Q \), and \( Q_2 = -Q \) which correspond to different molecular alignments. It is this cubic term which leads to the first order nature of the phase transition (characterized by a discontinuous jump in the order parameter from the isotropic to nematic phase, illustrated by Figure 4.5).

If the director varies locally, the free energy of the system must also include the energy associated with these local distortions. The three principal distortions in a liquid crystal, illustrated in Figure 4.6, are described as splay, twist, and bend distortions, and correspond to a Frank elastic free energy of the form [32]

\[ F_{\text{elastic}} = \frac{1}{2} K_1 (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_2 (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_3 ((\hat{n} \cdot \nabla) \hat{n})^2. \] (4.5)

Here \( K_1, K_2, \) and \( K_3 \) are the splay, twist and bend Frank elastic constants respectively. In terms of the tensor order parameter, the distortion energy can be written as,

\[ F_{\text{elastic}} = \frac{L_1}{2} (\partial_\alpha Q_{\beta\gamma})^2 + \frac{L_2}{2} (\partial_\alpha Q_{\gamma\gamma})(\partial_\beta Q_{\beta\gamma}) + \frac{L_3}{2} Q_{\alpha\beta}(\partial_\alpha Q_{\gamma\epsilon})(\partial_\beta Q_{\gamma\epsilon}), \] (4.6)

where the elastic constants, \( L \), can easily be shown to map onto the Frank elastic constants, \( K \) [33].

While the above energy contributions can be used to describe the bulk liquid crystal, a complete theory must also include boundary energy contributions associated with a preferred anchoring of the liquid crystal molecules at a boundary surface. A simple form for this energy is given by,

\[ F_{\text{surface}} = \frac{\alpha_s}{2} (Q_{\alpha\beta} - Q^0_{\alpha\beta})^2, \] (4.7)

where \( Q^0 \) is the preferred value of the order parameter at the surface, and we typically choose \( \alpha_s \) large enough so that \( Q \) is essentially fixed to the value of \( Q^0 \) at the surface.
Figure 4.5: Example of a first order phase transition. Above the critical parameter the system is minimized by the isotropic phase (scalar order parameter $S_0 = 0$). At the critical temperature there is a co-existence between the isotropic and nematic phases, while below the critical temperature the system is minimized by the nematic phase (non-zero scalar order parameter). The transition from the isotropic to the nematic phase is discontinuous, signifying the first order nature of the phase transition.

Figure 4.6: The splay, twist, and bend elastic distortions found in a liquid crystal. Figure adapted from de Gennes [12].
4.2.3 Liquid Crystal Hydrodynamics

The hydrodynamic behaviour of liquid crystals is more complex than that of isotropic fluids due to a coupling between the director and the fluid flow; flow typically disturbs the alignment of the molecules, while any externally generated change in alignment will tend to induce a flow [12].

The first commonly used theory of liquid crystal hydrodynamics was developed by Ericksen and Leslie [34–37] in the 1960s, and is based on the dynamics of the director, \( \hat{n} \). This theory assumes a constant order parameter, and a uniaxial liquid crystal. In the bulk liquid crystal, far from any defects these assumptions are valid; however, the order parameter rapidly changes in the vicinity of a defect, which is biaxial in the defect core [28, 29]. Therefore, this method is inadequate for simulations treating the hydrodynamics of defects [38, 39].

A varying order parameter, and potential biaxiality, can automatically be accounted for in a hydrodynamic description based on the order parameter, \( Q \). Such a method has been developed by Beris and Edwards [33, 40–42]. In this theory, the order parameter evolves according to the following equation,

\[
(\partial_t + \mathbf{u} \cdot \nabla) Q - S(\mathbf{W}, Q) = \Gamma H,
\]

with

\[
S(\mathbf{W}, Q) = (\xi D + \Omega)(Q + I/3) + (Q + I/3)(\xi D - \Omega) - 2\xi (Q + I/3) \text{Tr}(Q\mathbf{W}),
\]

where \( D = (\mathbf{W} + \mathbf{W}^T)/2 \), and \( \Omega = (\mathbf{W} - \mathbf{W}^T)/2 \) are the symmetric and antisymmetric components, respectively, of the velocity gradient tensor, \( W_{\alpha\beta} = \partial_{\beta} u_{\alpha} \), and \( \xi \) is related to the effective aspect ratio of the liquid crystal molecules. \( S(\mathbf{W}, Q) \) is present in order to take into account stretching and rotations of the distributions by flow gradients, arising from the rod-like nature of the constituent molecules. Equation 4.8 has the form of a Ginzburg-Landau type equation, augmented to include advection of the order parameter; the right hand side of the equation is present in order to drive the system towards the minimum of the free energy, with \( H \) related to the functional derivative of the free energy as,

\[
H = -\frac{\delta F}{\delta Q} + (I/3) \frac{\delta F}{\delta Q},
\]

and \( \Gamma \) corresponding to a collective rotational diffusion constant.

In addition, the liquid crystal obeys both the continuity and Navier-Stokes equations, with
a stress tensor generalized to describe the liquid crystal, consisting of both symmetric,

\[
\sigma_{\alpha\beta} = -P_0 \delta_{\alpha\beta} - \xi H_{\alpha\gamma} (Q_{\gamma\beta} + \frac{1}{3} \delta_{\alpha\beta})
- \xi (Q_{\alpha\gamma} + \frac{1}{3} \delta_{\alpha\gamma}) H_{\gamma\beta} + 2\xi (Q_{\alpha\beta} + \frac{1}{3} \delta_{\alpha\beta}) Q_{\gamma\epsilon} H_{\gamma\epsilon}
- \partial_\beta Q_{\gamma\nu} \frac{\delta F}{\delta Q_{\gamma\nu}},
\]  

(4.11)

and antisymmetric,

\[
\tau_{\alpha\beta} = Q_{\alpha\gamma} H_{\gamma\beta} - H_{\alpha\gamma} Q_{\gamma\beta}
\]  

(4.12)

collections. Numerically, these equations can be solved using a lattice-Boltzmann algorithm [43, 44]. Details of this algorithm are presented in Appendix C.

### 4.3 Colloidal Particles

The presence of colloidal particles in a liquid crystal induces the formation of topological defects. These defects arise due to a preferred orientation of the liquid crystal molecules on the colloidal surface (such a preference can be created through the use of a surfactant [54,55]). For example, if perpendicular (or homeotropic) anchoring is preferred at the surface of the particle, topological theory (the Gauss-Bonnet theorem) dictates that this particle carries a topological charge of +1 [56]. Boundary conditions at infinity require a net topological charge of zero in the system, leading to the generation of defects around the particle [48]. Two possible defect structures can arise, illustrated in Figure 4.7. The first, known as a hyperbolic hedgehog, corresponds to a single point defect of topological charge −1, located near the surface of the particle. As required, this particle-defect pair has no net topological charge. The second potential structure consists of a −1/2 disclination ring encircling the particle, which, for obvious reasons is known as a Saturn-ring defect. This defect structure is topologically equivalent to the hyperbolic point defect, which can be seen by shrinking the radius of the ring down to zero. The deciding factor in which structure arises is the particle radius; for large particles the hyperbolic hedgehog structure is energetically favourable, while for smaller particles the Saturn ring defect is the stable structure [48,49]. If instead tangential anchoring is preferred at the particle surface, the Euler-Poincare theorem allows for only one possible defect structure [56]. This corresponds to a pair of surface defects, known as boojums, located at the poles of the particle (see Figure 4.7).

The elastic distortions in the liquid crystal generated by these particle-defect pairs result in the presence of long range forces among the particles that would not be present in an isotropic
Figure 4.7: Defects around colloidal particles in a nematic.
fluid. For the hyperbolic hedgehog defects, the resulting particle interactions are dipolar in nature [49–51], while for both the Saturn ring defect [52, 53], and boojum pair [54] the interaction is quadrupolar. At closer separations, the particles tend to experience attractive forces along preferred directions, allowing them to share regions of distortion, and thereby minimize the elastic energy. This leads to a variety or self-assembled structures including linear and kinked chains [49, 55, 57], 2D colloidal crystals [50], hexagonal arrays of particles formed near interfaces [58, 59] and various anisotropic particle arrangements [54, 60]. More recently, a close-packed, ordered 3D crystal was produced in a nematic using directed self-assembly [61].

If a cholesteric liquid crystal is used as the host medium instead of a nematic, the defect structure around the particle changes, depending on the pitch in the cholesteric (see Figure 4.8). In the case of the Saturn ring defect obtained for perpendicular surface anchoring, this defect simply becomes twisted around the particle [62]. However, if tangential anchoring is preferred at the surface, the +1 boojums present at the poles of the particle in a nematic split into +1/2 defects on the particle surface, connected by a 1/2 defect line in the bulk liquid crystal [63]. When the pitch in the cholesteric is comparable in size to the particle diameter, these defect lines have the appearance of handles emerging from the particle surface. As the pitch decreases, these lines wind around the particle with an increasing degree. Experimentally, particle-stabilized defect gels [64], as well as 2D planar structure [65] have been produced using particles in a cholesteric.

In the remainder of this section we numerically investigate the interactions and possible structures that can be formed by colloidal particles with both perpendicular and tangential
anchoring in a cholesteric. In addition, since the defects and distortions generated by the immersed particles result in a non-uniform pressure exerted on the particle surface, we also investigate the behaviour of 2D deformable particles in a nematic liquid crystal.
Bibliography


Chapter 5

Modelling defect-bonded chains produced by colloidal particles in a cholesteric liquid crystal

This chapter corresponds to the published article:

5.1 Introduction

Colloidal crystals have recently attracted considerable attention, particularly with regards to their photonic properties. Self-assembly as a practical means of generating such structures is therefore of great interest. The potential for colloidal particles to self-assemble is, however, limited by the symmetry of the constituents; for spherical particles in an isotropic fluid, hard sphere interactions lead to close-packed structures, most commonly fcc. In order for more complex structures to form, constituents with a lower symmetry are required. The anisotropic nature of liquid crystals (LCs) make them an ideal candidate. LC droplets can be created in an isotropic host (see for example [1, 2]), which exhibit various symmetries including bipolar. This arises from preferential planar anchoring of the LC molecules at the particle surface, thus requiring two point defects, known as boojums, to form on the particle surface [3]. In 2002 Nelson proposed [4] using a LC shell (spherical particle coated with LC) instead of a drop arguing that the shell should have a ground state surface configuration where the two +1 boojums split into four +1/2 topological defects yielding a tetrahedral symmetry. He then suggested that chemical linkers could be attached creating 4-fold valence similar to sp³ hybridized
bonds of carbon, presumably opening up the possibility to construct crystals with analogous structures. This tetrahedral defect structure has been seen experimentally for thin LC shells in double emulsion drops [5]. Zhang et al. [6] have shown that colloidal particles with tetragonally positioned attractive patches should self-assemble from an initially disordered state to a diamond structure; however such tetravalent colloidal self-assembly has not yet been reported.

Here, we focus instead on the use of LC as the host medium. While LC droplets and shells in an isotropic fluid would require chemical linkers to join them together, the defect structures produced by colloids in a bulk LC generate long range elastic forces among the particles. For colloidal particles in a nematic LC, these interactions can be dipolar or quadrupolar in nature, depending on the type and strength of the surface anchoring [7–10]. In nematic LCs a variety of 2D structures have been produced, including linear and kinked chains [8, 11, 12], 2D colloidal crystals [9], hexagonal arrays of particles near interfaces [13, 14], and various anisotropic particle arrangements [15, 16]. In cholesteric LCs, disordered colloidal structures have been produced, in the form of particle-stabilized defect gels [17]. It is also possible for colloidal particles in a cholesteric to self-organize into more ordered structures, as seen through the formation of 2D planar structures [18].

In this work, we investigate the interactions arising among colloidal particles with tangential surface anchoring placed in a cholesteric LC. In this case, the +1 boojums present for such particles in a nematic split into two +1/2 defects on the particle surface [19], similar to the case of a thin LC shell, however, here pairs of defects are connected to one another by a +1/2 defect line in the bulk. As shown by Lintuvuori et al. [19], when the pitch in the cholesteric is comparable in size to the particle diameter, these defect lines have the appearance of handles emerging from the particle surface. As the pitch in the cholesteric decreases, the degree of winding of these lines around the particle increases. Hijnen et al. [18] have shown that for large diameter to pitch ratios the colloids are seen to self-organize, forming 2D plates as opposed to the chains seen in a nematic. Here, using a substantially lower diameter to pitch ratio of 2/3, we observe a more fundamental change in behavior when switching from a nematic to a cholesteric, marked by the appearance of two distinct interaction regions. In addition to a non-bonded interaction occurring for moderate to large particle separations, we also find a defect mediated harmonic bonding occurring between closely spaced particles, which is not observed in the presence of a nematic. The resulting defect bonded chains resemble double bonded carbon chains. Additionally, we see evidence supporting the formation of planar structures via an observed phase-locking to the cholesteric twist.
5.2 Theoretical Background

To model the LC-colloid systems, we use Landau-de Gennes free energy approach [20]. A tensor order parameter, $Q_{\alpha\beta} = \langle \hat{m}_\alpha \hat{m}_\beta - \frac{1}{3} \delta_{\alpha\beta} \rangle$ is used to describe the LC, where $\hat{m}$ gives the local orientations of the individual molecules and the angular brackets denote a coarse grained average. $Q$ is a symmetric, traceless tensor, whose largest eigenvalue, $2/3 q$, gives the magnitude of order along the principle eigenvector, or director $\hat{n}$, which describes the average orientation of the LC molecules. Within this framework, the free energy takes the form,

$$F = \int [f_{\text{bulk}} + f_{\text{elastic}}] dV + \int f_{\text{surface}} dS,$$

where,

$$f_{\text{bulk}} = A Q_{\alpha\beta}^2 - B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + C \left( Q_{\alpha\beta}^2 \right)^2$$

$$f_{\text{elastic}} = \frac{L_1}{2} \left( \partial_\alpha Q_{\beta\gamma} \right)^2 + \frac{L_2}{2} \left( \partial_\alpha Q_{\alpha\gamma} \right) \left( \partial_\beta Q_{\beta\gamma} \right) + \frac{L_3}{2} Q_{\alpha\beta} \left( \partial_\alpha Q_{\gamma\epsilon} \right) \left( \partial_\beta Q_{\gamma\epsilon} \right) + \frac{4\pi L_1}{P} \epsilon_{\alpha\beta\gamma} Q_{\alpha\gamma} \left( \partial_\beta Q_{\gamma\epsilon} \right)$$

$$f_{\text{surface}} = \alpha S \left( Q_{\alpha\beta} + 2 Q_{0\alpha\beta} \right)^2.$$  \hspace{1cm} (5.2)

$f_{\text{bulk}}$ describes the bulk free energy in the system, where $A$, $B$, and $C$ are constants chosen to ensure the system is in the liquid crystalline phase\textsuperscript{1}. $f_{\text{elastic}}$ is the elastic free energy associated with distortions in the LC. The last term in this contribution is present in order to model a cholesteric LC; the free energy is minimized when the helical pitch in the cholesteric is equal to $P$. The elastic constants $L$ in this equation can easily be shown to map to the usual Frank elastic constants, $K$ [21]. The last contribution to the free energy, $f_{\text{surface}}$, is the energy associated with the anchoring of the LC molecules on the colloid surface. With $Q^0$ chosen as $Q_{0\alpha\beta} = q^0 \left( \hat{n}_0^0 \hat{n}_\beta^0 - \frac{1}{3} \delta_{\alpha\beta} \right)$, where $q^0$ is set to the equilibrium bulk value of $q$, and $\hat{n}^0$ is the normal to the colloid surface, this contribution creates a preference for the LC molecules to lie tangentially to the colloidal surface. In the simulations that follow, $\alpha S$, the strength of this anchoring potential, is chosen large enough to ensure we are in the strong anchoring limit.

Using the Beris-Edwards formulation of liquid crystal hydrodynamics [21], the order parameter evolves according to the convective-diffusion equation,

$$\left( \partial_t + u \cdot \nabla \right) Q - S(W, Q) = \Gamma H.$$  \hspace{1cm} (5.3)

\textsuperscript{1}$A = \frac{A_0}{2} (1 - \frac{7}{2})$, $B = A_0 \frac{7}{2}$, $C = A_0 \frac{7}{2}$, with $A_0$ set to 0.5 atm, and $\gamma = 3.2$
The first term in this equation is the usual material derivative for a fluid with velocity \( u \). This is supplemented by a term \( S \), taking into account stretching and rotation of the distributions by flow gradients, given by

\[
S(W, Q) = (\xi D + \Omega)(Q + I/3) + (Q + I/3)(\xi D - \Omega) - 2\xi (Q + I/3) Tr(QW).
\]

Here \( D = (W + W^T)/2 \), and \( \Omega = (W - W^T)/2 \) are the symmetric and antisymmetric components, respectively, of the velocity gradient tensor, \( W_{\alpha\beta} = \partial_\beta u_\alpha \), and \( \xi \) is a constant related to the molecular details of the given LC. On the right of this equation, \( \Gamma \) is the collective rotational-diffusion constant, and \( H \) is the molecular field, given by,

\[
H = -\frac{\delta F}{\delta Q} + (I/3) \frac{\delta F}{\delta Q}. \tag{5.5}
\]

This term is present in order to drive the system towards the minimum of the free energy. In addition, the fluid obeys the continuity and Navier-Stokes equations. Full details of the algorithm used can be found in [22, 23].

### 5.3 Results

Our simulations are performed in a periodic box with the period chosen commensurate with the pitch of the cholesteric. To reduce finite-size effects the system size is also chosen to be at least four particle radii in all directions. For most of the simulations, we first initialize the LC with a twist compatible with the cholesteric pitch, and add particles to the system by turning on the sphere surface potential. The system is then allowed to relax, according to the above evolution equations, till the minimum free energy is obtained. Due to the large system size, far from the spheres the cholesteric remains in a uniform phase; therefore, experimentally this system is equivalent to a cholesteric twisted between two aligning walls with a separation corresponding to our \( z \)-system size. We have also tried initializing the system with a random director orientation resulting in the same final state, for all cases examined here.

Here, we investigate the interaction energies generated by colloidal particles in a cholesteric with a pitch approximately 1.5 times the particle diameter. We choose a particle radius of \( 0.625\mu m \), and a cholesteric pitch of \( \sim 1.8\mu m \). While it is common to model LCs using a one elastic constant approximation, real cholesterics often have a small \( K_2 \) compared to \( K_1 \) and \( K_3 \) (for example, doped 5CB [25]). Therefore, we have chosen \( K_1 = K_3 = 15pN, K_2 = 6.7pN, \)
5.3. Results

Figure 5.1: Defect structure around a single particle of radius 0.625 \( \mu m \) in a cholesteric with pitch 1.833 \( \mu m \). The solid black lines, representing the defects, correspond to a contour plot indicating the location where the scalar order parameter has dropped by \( \sim 20\% \) of its value in the bulk. (a) View along the twist (\( z \)) axis. (b) View along \( x \)-axis. (c) View along \( y \)-axis, along with the director orientation on the surface of the particle.

which produces a stable cholesteric phase; in contrast, the one elastic constant approximation typically generates a blue phase \([26, 27]\).

As seen in fig. 5.1, our prescribed diameter to pitch ratio of \( \sim 2/3 \) leads to +1/2 defect lines winding around the particle that have the appearance of handles emerging from its surface. This image was produced using a contour plot of the maximum eigenvalue of \( Q \), shown in black. This eigenvalue describes the magnitude of order along the director, and is a minimum at the defect locations. The location of the particle is also shown (grey sphere). The defect line handles cost energy, proportional to their length, which is balanced by an energy benefit from a reduction in the surface energy. For ultra-thin spherical shells the energy of the nematic state is known to be minimized by a configuration similar to that seen in fig. 5.1(c) (the “baseball seam” pattern) \([24]\). However, for a sphere in a nematic this surface energy is overcome by the price paid to create the handle defects that necessarily accompany the +1/2 defects on the surface of the sphere so the typical +1 boojums, which do not require defects in the bulk LC, are the preferred state. On the other hand, the director pattern for the +1 boojums, similar to the lines of longitude on the globe, is incompatible with the cholesteric twist which wants these lines to rotate along the twist axis. This twist is what the “baseball seam” director pattern of the four +1/2 defect-state produces thus making it more energetically favorable.

In a nematic, the two +1 boojums result in a quadrupolar particle interaction at large distances \([10]\). At particle surface to surface separations comparable to the particle radii the force weakens somewhat due to finite surface anchoring and possible deviations from the quadrupolar to lower symmetries \([10]\). For even closer particle separations, Mozaffari et al. \([28]\) have
Figure 5.2: Defect bonded chain viewed (a) perpendicular to the twist (z) axis, (b) along the twist (z) axis. The solid black lines correspond to a contour plot indicating the location where the scalar order parameter has dropped by $\sim 20\%$ of its value in the bulk.

shown that the interparticle force actually reverses sign for particles whose separation is along the nematic direction. However, the force in a nematic is a continuous function of particle separation. In contrast we show below that in a cholesteric the force is a discontinuous function of particle separation, taking a discrete jump to much stronger forces at close distances, a behavior similar to the colloidal capillary interaction experienced by particles in the isotropic phase of a nematic LC [29]. This jump occurs when the defects on adjacent particles join together, forming defect bonded particle chains (see Fig. 5.2).

To investigate the energy associated with this interaction, we consider a system consisting of two colloidal particles. For these simulations, a system size of $2.75 \times 7.5 \times 2.75 \mu m$ is used, with a lattice spacing of $0.03125 \mu m$. This corresponds to particles with a radius of 20 lattice units. Figure 5.3(a) shows the effect of the inter-particle spacing on the free energy of the system. The smallest separation considered corresponds to three lattice units separating the sphere surfaces, which coincides with the minimum distance at which the interpolation of the spheres onto the lattice mesh does not overlap. As can be seen, the free energy consists of two distinct regions. Up to a separation of $\sim 0.41 \mu m$ the particles are connected by a pair of defect lines, and the free energy can be fit using a quadratic form. At $\sim 0.41 \mu m$, the defect bonds break, the defects on the particle surfaces move significantly closer together (see Fig. 5.3(b)),...
Figure 5.3: (a) Free energy (relative to minimum) for a system of two colloidal particles (see insets) as a function of their inter-particle separation (surface-to-surface distance). Points correspond to simulation results, while the solid line is a quadratic fit in the bonded region (excluding the two endpoints). (b) Angular separation $\alpha$ of the points on the surface of the sphere where the defect lines terminate (for one of the two spheres in the inset of (a)) as a function of the inter-particle separation.
and there is a kink in the free energy as a function of particle separation. The force required to separate particles should be related to the derivative of this curve. Thus the kink at the point where the defect bonds break corresponds to a jump in the force (from $\sim 34pN$ just before the bond breaks to $2pN$ after it has broken). This discontinuous behaviour is not experienced by particles in a nematic (see for example Smalyukh et al. [10]), which only share regions of distortion, and are not directly connected by disclinations. The separation at which the bonds breaks corresponds, approximately, to the point at which the length of a handle defect is longer than a single defect bond, and it is energetically favorable for particle bonding to occur. As can be seen, the energy associated with defect bonding is several orders of magnitude greater than $k_B T$; therefore, once bonding occurs it is stable against thermal effects. While it would appear that the energy should be minimized at contact, strong anchoring can also lead to a very short-range repulsive interaction which would be below the resolution of our simulations [30] and would require a more detailed knowledge of the anchoring energy to model accurately.

The harmonic nature of the bond is somewhat surprising. It would appear that the dominant term in the free energy should be related to the defect lines, whose lengths are directly proportional to the particle separation. However, if this was the case, the interaction energy would be linear in the separation. The explanation for this lies in the angular separation $\alpha$ of the points on the surface of the sphere where the disclination lines terminate, shown in Fig. 5.3(b) as a function of the sphere separation. As previously noted, these angular separations for the bound state, which are all greater than 60°, are considerably larger than that for the handles of a single colloid, in which case the ends of the defect handle are $\sim 30°$ apart (cf. Fig. 5.1(c)). That is, by sharing the disclination lines in a bond the $+1/2$ defects on the surface can move further apart, thus lowering their interaction energy [24] (the defects repel each other so the surface energy would be minimized if they were separated by 109°). This surface energy gain from the defects moving further apart compensates for the longer defect lines as the spheres move apart which results in the quadratic dependence of the free energy versus separation (rather than linear).

In order to determine the preferred orientation of the defect bonded chains relative to the twist axis, we investigate the dependence of the free energy on the angular positioning of the particles relative to one another along the twist axis, for a center to center particle separation of 1.431$\mu m$ (see inset of fig. 5.4 for a schematic). Figure 5.4 shows this free energy angular dependence. The error bars in the plot give a measure of the error due to lattice effects. From $\sim 0° - 25°$ defect bonding is maintained between the particles, while at $\sim 25°$, the defect bonds break, and for larger angular separations the free energy begins to level off. Clearly the free energy is minimized for $\theta = 0°$, corresponding to a preference for alignment in a plane perpendicular to the twist axis.
Figure 5.4: Free energy (relative to minimum) as a function of the angular positioning of the particles relative to the twist axis (see inset), for a pair of particles held at a constant separation of 1.431 $\mu$m. The error bars represent the error in the measurement due to lattice effects.
5.4 Summary and Conclusions

To conclude, we have investigated the interactions occurring among colloidal particles in a cholesteric LC when the pitch of the cholesteric is approximately 1.5 times the particle diameter. At this pitch, the defect lines around the particles have the appearance of handles emanating from their surfaces. In order to minimize the system free energy, handles from adjacent particles join together, thereby reducing the total length of the defect lines, and allowing the defects on the particle surface to move further apart from one another. We find that the resulting interaction energy is characterized by both a non-bonded region as well as a harmonically defect-bonded region found for small particle separations, leading to a discontinuous force as a function of particle separation. In addition, for these defect bonded particles, we observe a phase-locking to the twist axis, a potential precedent to the plates seen in experiments [18] for much larger particle diameter to pitch ratios.
Bibliography


Chapter 6

Investigating the Stability of a Diamond Colloidal Crystal Formed in a Cholesteric Liquid Crystal

6.1 Introduction

The ability of colloidal particles to form ordered, three-dimensional dielectric structures has important technological applications, due to the photonic band gap such materials possess [1]. Self-assembly provides a convenient route for manufacturing such colloidal crystals, and has been used to produce opaline-type crystal structures [2–4]. However, the large-scale production of colloidal crystals with minimal imperfections remains a challenge [5], as is the ability to form non-close packed, self-assembled crystal structures.

Recently, substantial interest has grown in the use of a liquid crystal as the host medium for such self-assembly. Due to the anisotropic nature of the liquid crystalline phases, immersed colloidal particles generate defects and distortions which lead to forces among the particles that are not present in an isotropic fluid [6–11]. In a nematic liquid crystal, in which the defect structure around an isolated particle corresponds to either a hyperbolic hedgehog point defect, a Saturn ring defect loop, or a pair of surface defects known as boojums, the self-assembly of colloidal particles has been shown to produce a variety of 2D structures, such as chains, clusters, and crystal structures [6, 7, 11–16]. Recently, directed assembly has also been used to produce close-packed, ordered 3D colloidal crystals [17]. In a cholesteric, the helical twist in the liquid crystal modifies the defect structure around a particle from that found in a nematic. For example, the +1 surface boojums are observed to split into a pair of +1/2 surface defects, connected by a defect line in the bulk [19], while the Saturn ring defect becomes twisted
around the particle [18]. This results in a range of potential defect structures, depending on the size of the colloid, and the pitch in the cholesteric. Colloidal particles in a cholesteric have been observed to self-assemble into plates [20], and 2D defect-bonded particle chains have been predicted to form [21]. In addition, by using the liquid crystalline blue phase, which is characterized by an ordered network of defect lines, simulation has shown the potential for 3D self-assembly in which these defect lines are used as a template [22].

In this paper we numerically investigate the stability of a 3D colloidal diamond lattice in a cholesteric liquid crystal, using a lattice-Boltzmann algorithm. The approach we take is to assume a crystal structure for the colloids, determine the cholesteric pitch commensurate with our system size that gives rise to the most energetically favorable particle-defect structure, and investigate the stability of this resulting structure using its phonon spectrum. We use this approach as opposed to simply allowing a large number of colloidal particles to self-assemble into a crystal structure, due to imposed computational limitations. First, as defects play a key role in determining the interparticle interactions, a fine enough grid resolution is required in order to accurately model them. This places constraints on the total system size that can realistically be modelled. Secondly, as it takes time for the defect lines to develop, during any potential system relaxation it is possible for the system to become stuck with a defect configuration above the ground state, if long enough relaxation times are not considered. While it is not possible with our approach to determine the most stable equilibrium ground state configuration, if we are able to produce a locally stable structure (i.e. one that is stable under thermal fluctuations), it should be possible (for example, by manipulating the particles using optical tweezers), to experimentally form the structure, even if it does not correspond to the global minimum.

The remainder of the paper is organized as follows. The theoretical details of the model, and a description of the phonon spectrum calculation are presented in Section 6.2. Section 6.3 presents results for the defect structure obtained using a diamond colloidal lattice, investigating the stability of this colloid-defect system using calculated phonon frequencies, and comparing this structure to those formed using both BCC and FCC colloidal crystals. Conclusions are presented in Section 6.5.

6.2 Theoretical Background

6.2.1 Liquid Crystal Simulation Method

To model the liquid crystal, we use a coarse-grained approach, introducing the standard tensor order parameter, $Q$, defined as an average of the individual molecular orientations, $\hat{m}$, accord-
6.2. Theoretical Background

To

\[ Q_{\alpha\beta} = \left\{ \hat{m}_\alpha \hat{m}_\beta - \frac{1}{3} \delta_{\alpha\beta} \right\}. \quad (6.1) \]

Using this order parameter, we describe the total system in terms of a Landau de-Gennes free energy of the form,

\[ \mathcal{F} = \int (\mathcal{F}_{\text{bulk}} + \mathcal{F}_{\text{elastic}}) dV + \int \mathcal{F}_{\text{surface}} dS. \quad (6.2) \]

Here, \( \mathcal{F}_{\text{bulk}} \) represents the bulk free energy in the system, given by

\[ \mathcal{F}_{\text{bulk}} = \frac{A_0}{2} \left( 1 - \frac{\gamma}{3} \right) Q^2_{\alpha\beta} - \frac{A_0 \gamma}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{A_0 \gamma}{4} (Q^2_{\alpha\beta})^2, \quad (6.3) \]

where \( A_0 \) is a constant, and \( \gamma \) controls the transition between the isotropic and liquid crystalline phases. A value of \( \gamma = 3.2 \) is used throughout this work, corresponding to the liquid crystalline phase. The elastic free energy, \( \mathcal{F}_{\text{elastic}} \), associated with distortions in the liquid crystal is given by

\[ \mathcal{F}_{\text{elastic}} = \frac{L_1}{2} \left( \partial_\alpha Q_{\beta\gamma} \right)^2 + \frac{L_2}{2} \left( \partial_\alpha Q_{\beta\gamma} \right) \left( \partial_\beta Q_{\gamma\alpha} \right) + \frac{L_3}{2} Q_{\alpha\beta} \left( \partial_\alpha Q_{\gamma\epsilon} \right) \left( \partial_\beta Q_{\gamma\epsilon} \right) + \frac{4\pi L_1}{P} \epsilon_{\alpha\beta\gamma} Q_{\alpha\nu} \left( \partial_\beta Q_{\gamma\nu} \right). \quad (6.4) \]

The first three terms in this expression are associated with the usual distortions in a nematic liquid crystal; the elastic constants, \( L \), are easily shown to map onto the more familiar Frank elastic constants, \( K \) [23]. The last term is necessary in order to model a cholesteric, creating a preference for a liquid crystal with a helical pitch, \( P \), in the director. To simulate the surfaces of the colloidal particles, which we assume prefer a homeotropic alignment of the liquid crystal molecules, we introduce a surface free energy term of the form,

\[ \mathcal{F}_{\text{surface}} = \frac{\alpha_s}{2} \left( Q - Q^0 \right)^2. \quad (6.5) \]

Here, \( Q^0 \) is set equal to \( Q^0_{\alpha\beta} = q^0 (n^0_\alpha n^0_\beta - \delta_{\alpha\beta} / 3) \), where \( n^0 \) corresponds to the particle surface normal, and \( \alpha_s \) is chosen large, effectively constraining \( Q \) to \( Q^0 \) on the surface.

Using the above expressions for the free energy, we model the evolution of the order parameter according to the Beris-Edwards formulation [23],

\[ (\partial_t + \mathbf{u} \cdot \nabla) \mathbf{Q} - \mathbf{S}(\mathbf{W}, \mathbf{Q}) = \Gamma \mathbf{H}. \quad (6.6) \]

This equation has a Ginzburg Landau form, augmented to take into account advection of the
order parameter. Here,

\[
S(W, Q) = (\xi D + \Omega)(Q + I/3) + (Q + I/3)(\xi D - \Omega)
- 2\xi (Q + I/3) \text{Tr}(QW),
\]  

(6.7)

where \( D = (W + W^T)/2 \), and \( \Omega = (W - W^T)/2 \) are the respective symmetric and antisymmetric components of the velocity gradient tensor, \( W_{\alpha\beta} = \partial_{\beta} u_{\alpha} \), and \( \xi \) is related to the effective aspect ratio of the liquid crystal molecules. The right hand side of equation 6.6 which is present in order to drive the system towards the minimum free energy state, is related to the functional derivative of the free energy, according to

\[
H = -\frac{\delta F}{\delta Q} + (I/3) \frac{\delta F}{\delta Q},
\]  

(6.8)

with \( \Gamma \) in equation 6.6 representing a collective rotational diffusion constant.

The fluid also necessarily satisfies the continuity and Navier-Stokes equations, with a stress tensor modified to take into account the additional complexities of liquid crystal hydrodynamics. This stress tensor now contains both symmetric,

\[
\sigma_{\alpha\beta} = -P_0\delta_{\alpha\beta} - \xi H_{\alpha\gamma}(Q_{\gamma\beta} + 1/3\delta_{\gamma\beta})
- \xi(Q_{\alpha\gamma} + 1/3\delta_{\alpha\gamma})H_{\gamma\beta} + 2\xi(Q_{\alpha\beta} + 1/3\delta_{\alpha\beta})Q_{\gamma\epsilon}H_{\gamma\epsilon}
- \partial_{\beta}Q_{\gamma\nu}\frac{\delta F}{\delta a_{\alpha} Q_{\gamma\nu}},
\]  

(6.9)

and antisymmetric,

\[
\tau_{\alpha\beta} = Q_{\alpha\gamma}H_{\gamma\beta} - H_{\alpha\gamma}Q_{\gamma\beta}
\]  

(6.10)

components. This set of equations is modelled on a uniform grid using a lattice-Boltzmann algorithm, with simulation parameters provided in Table 6.1. See Denniston et. al. [24, 25] for full details.

### 6.2.2 Liquid Crystal Forces

In order to test the stability of a colloidal crystal in the cholesteric, it is necessary to compute the forces from the liquid crystal acting on the colloidal particles. This is accomplished by integrating the symmetric component of the stress tensor over the colloidal surface, according to

\[
F_\alpha = \int n_\beta \sigma_{\alpha\beta} dS,
\]  

(6.11)
Table 6.1: Simulation parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
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<td>atm</td>
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<td>-</td>
</tr>
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<td>pN</td>
</tr>
<tr>
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<td>pN</td>
</tr>
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<td>pN</td>
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<tr>
<td>$\Gamma$</td>
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<td>$(atm \cdot \mu s)^{-1}$</td>
</tr>
<tr>
<td>$\xi$</td>
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<td>-</td>
</tr>
<tr>
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<td>$\mu m$</td>
</tr>
<tr>
<td>$dt$</td>
<td>1.0</td>
<td>$\mu s$</td>
</tr>
<tr>
<td>$P_0$</td>
<td>1.0</td>
<td>atm</td>
</tr>
</tbody>
</table>

where $n$ is the unit surface normal. However, a subtlety occurs here, owing to the discrete nature of the simulation; the interpolation of the particle surface (which is represented by a set of nodes) onto the lattice-Boltzmann grid results in a grid representation of the particle as a spherical shell of thickness $\sim 2\Delta x$ [26]. Therefore on the LB grid, the particle has an effective radius $\sim 1\Delta x$ larger than that given by the placement of the particles nodes. It is the surface corresponding to this larger radius that should be used when performing the integration of equation 6.11.

### 6.2.3 Phonon Frequencies

The diamond colloidal crystal we model corresponds to an FCC lattice, with lattice vectors,

$$ a_1 = \frac{a_0}{2} (0, 1, 1), \quad a_2 = \frac{a_0}{2} (1, 0, 1), \quad a_3 = \frac{a_0}{2} (1, 1, 0) \quad (6.12) $$

and a two point basis

$$ (0, 0, 0), \quad \frac{a_0}{4} (1, 1, 1). \quad (6.13) $$

Any unit cell in the crystal can be expressed in terms of the lattice vectors, as

$$ r_i = l_1 a_1 + l_2 a_2 + l_3 a_3, \quad (6.14) $$

with each unit cell containing the two basis particles, where the basis particles lie at a position $\Delta r_k$ (given by either expression in equation 6.13), relative to the origin of the unit cell. Therefore, the equilibrium position of each particle in the crystal can be written as

$$ r_{ik} = r_i + \Delta r_k. $$
Noise in the system results in the particles displaced by a value \( \mathbf{u}_{lk} \) from their equilibrium positions. Therefore at any given time, the position of a particle in the crystal is given by
\[
\mathbf{R}_{lk} = \mathbf{r}_{lk} + \mathbf{u}_{lk}.
\]

Assuming the harmonic approximation, and working in Fourier space, the potential energy in the system can be written in terms of a dynamical matrix, \( D_{k\alpha,k'\beta}(\mathbf{q}) \), as
\[
V = \frac{1}{2} \sum_{k,k',\alpha\beta} \tilde{u}_{k\alpha}^* D_{k\alpha,k'\beta} \tilde{u}_{k'\beta},
\]
(6.15)
where \( \tilde{u}_{k\alpha} \) are the Fourier-transforms of the displacements, given by
\[
\tilde{u}_{k\alpha} = \frac{1}{\sqrt{N}} \sum_{l} u_{l\alpha} e^{-i \mathbf{q} \cdot \mathbf{r}_l}.
\]
(6.16)
Here \( \mathbf{q} \) is the wave vector, \( N \) is the number of unit cells, \( \alpha \) corresponds to a Cartesian component (i.e. \( x, y, \) or \( z \)), and \( l \) labels the unit cells. By diagonalizing the dynamical matrix, the potential energy can be written as
\[
V = \frac{1}{2} \sum_{i} \lambda_i |Q_i|^2,
\]
(6.17)
where \( \lambda_i \) correspond to the eigenvalues of the dynamical matrix, and \( Q_i \) correspond to symmetry-adapted coordinates computed from the eigenvectors, and the \( \tilde{u}_{k\alpha} \). Therefore, in the harmonic approximation, the system can be viewed as a set of independent harmonic oscillators vibrating with frequencies \( \sqrt{\lambda_i} \). Thus, in order for the crystal to be stable, one clearly must have all \( \lambda_i \geq 0.0 \), other than those corresponding to translation.

To measure the phonon spectrum of the colloidal system, we add noise to the liquid crystal, and allow the colloidal particles to move, updating their positions using the forces calculated with equation 6.11. Our noise takes the form of a term, \( N_{\text{amp}} \delta \), added to each component of the molecular field, \( \mathbf{H} \), where \( N_{\text{amp}} \) is the noise amplitude, and \( \delta \) is a standard, normally-distributed random number.

Using the resulting particle positions, we calculate the dynamical matrix, by applying the equipartition theorem to equation 6.15, requiring that
\[
D_{k\alpha,k'\beta} = \frac{k_B T}{\langle \tilde{u}_{k\alpha}^*(t) \tilde{u}_{k'\beta}(t) \rangle_t},
\]
(6.18)
where \( \langle ... \rangle_t \) corresponds to a temporal average.
6.3 Results

6.3.1 Defect Structure for a Diamond Colloidal Crystal

In order to model a diamond lattice, we place 8 particles of radius $17\Delta x$, in a periodic system of size $88 \times 88 \times 88\Delta x$, at locations specified by equations 6.12 and 6.13. Physically, this corresponds to particles of radius $\sim 1.1\mu m$ arranged with closest surface to surface separations of $\sim 4\Delta x$. This separation is small enough so that the defects and distortions associated with neighboring particles have an influence on one another (i.e. the defect structure differs from that of an isolated particle), yet large enough to prevent an overlap of the interpolated particle surfaces. Experience with defect-bonded chains [21] suggests that the cost of defect lines (which is proportional to their length), will result in optimum structures having close nearest-neighbor separations. Typically colloids will have a close-range repulsive force which we do not explicitly model here, other than assuming the $4\Delta x$ separation.

To obtain the equilibrium defect structures, simulations were performed for a range of values of the cholesteric pitch, $P$, until the free energy converged to a minimum. Commensurability with the periodic lattice Boltzmann grid (and unit cell of the colloidal lattice) limits the values $P$ can take; the director can only rotate by multiples of $\pi$ in the direction of the cholesteric twist in order for the directors at the system boundaries to line up. Since it is possible for the system to become stuck in a defect configuration not necessarily corresponding to the global minimum, we also ran several simulations with the same cholesteric pitch, but with the initial twist shifted up and down along the twist-axis. Due to the highly symmetric nature of the diamond lattice, we simply considered twists along the $z$-axis (i.e. the system was initialized with different values for the angle, $\theta$, between the director and the $x$-axis at $z = 0$). Figure 6.1 shows the effect of different values of $\theta$ on the resulting defect structure for a system with pitch $P = 5.5\mu m$. Here, the lowest free energy corresponds to a system initialized with $\theta = 90^\circ$. However, for all $\theta \geq 60^\circ$, the system reaches a very similar defect structure, with similar energy, which appears to be the lowest energy configuration. Therefore, the final configuration does not seem to be too dependent on $\theta$, provided the system is not initialized very far away from the ideal configuration, becoming stuck in a higher energy state.

The resulting lowest energy defect structures as a function of the pitch in the cholesteric are presented in Figure 6.2. In order to determine the colloid-defect system most likely to result in a stable configuration, we measured the decrease in total energy per particle obtained by having a particle in the diamond lattice, compared to an isolated particle in a liquid crystal with the same pitch. This decrease in energy, shown in Figure 6.3, was calculated as the difference between the free energy increase per particle in the diamond lattice over a pure liquid crystal, and the free energy increase of an isolated particle over the pure liquid crystal.
Figure 6.1: Effect of the initial angle between the director and the $x$-axis at $z = 0$ on the resulting defect structure in the system. These images correspond to a cholesteric with pitch $= 5.5 \, \mu m$. The lowest free energy state occurs at $\theta = 90^\circ$. 
Figure 6.2: Various views of the defect structure around particles in a diamond lattice, as a function of the pitch of the cholesteric (corresponds to 0, 1, 2, 3 and 4 total twists of the director in the system).
Figure 6.3: Decrease in energy over an isolated particle, for a particle in the diamond lattice, as a function of the pitch in the cholesteric.

As can be seen, the largest free energy decrease per particle over an isolated particle occurs for a system with pitch $P = 5.5\mu m$. The resulting defect structure with and without the colloidal particles for the entire system, as well as the defect structure found locally around a single particle in the lattice are shown in Figure 6.4. As can be seen, the defect lines associated with this pitch travel along symmetry axes of the diamond lattice, in contrast to the other defect structures shown in Figure 6.2.

### 6.3.2 Stability Analysis

In order to investigate the stability of the energetically favorable colloid-defect diamond structure found above, we consider its phonon spectrum. As this spectrum corresponds to vibrational modes in the crystal, a large number of colloidal particles should be used in order to accurately describe these vibrations. Ideally, a system composed of many units cells in each spatial direction should be considered. However, computational constraints place limits on the maximum system size that can realistically be modeled, which, for our purposes corresponds to $\sim 8$ times the original system size used in Section 6.3.1. Therefore, we consider three different systems of total sizes, $176 \times 176 \times 176\Delta x$, $352 \times 176 \times 88\Delta x$, and $704 \times 88 \times 88\Delta x$. While
Figure 6.4: Defect structure for a system with pitch = 5.5 µm (corresponding to the system with the largest energy decrease per particle over an isolated particle). Top: Full colloid and defect system, Middle: defect structure around a single particle in the diamond lattice, Bottom: Same as the top panel, but with the colloidal particles removed, thereby simply showing the defect structure.
we expect finite size effects to be present in these simulations, the increasing size in $x$ should allow us to somewhat quantify these effects in the $x$-direction.

For the simulations, we initialized the system using periodic images of the converged $88 \times 88 \times 88\Delta x$, $5.5\mu m$ pitch system found in Section 6.3.1, added noise to the system as described in Section 6.2.3, and allowed the particles to move based on the resulting liquid crystal forces. Approximately 700,000 sets of positions were measured for each system. After noise is first added, it takes time for both the liquid crystal and colloidal particles to equilibrate, with the average positions of certain particles observed to shift up to $\sim 0.5\Delta x$. Therefore, we have discarded the first 100,000 positions of each simulation, to ensure equilibration had occurred. (This number was chosen by calculating the phonon frequencies over bins of the simulation data. The frequencies calculated using the first $\sim 50,000$ positions were found to differ substantially from the average, which we attribute to the equilibration.)

In all cases, the eigenvalues of the dynamical matrix are positive, corresponding to real phonon frequencies, a necessary condition for stability. Figure 6.6 presents a comparison of the frequencies for the allowed wave-vectors, $\mathbf{q}$, common to all systems, along paths in the irreducible wedge of the Brillouin zone (see Figure 6.5). The resulting frequencies can be understood as follows. Each wave vector corresponds to 3 high frequency optical modes (corresponding to out of phase vibrations of the lattice and basis particles), and 3 somewhat lower frequency acoustic modes (corresponding to in phase vibrations), with each set composed of one longitudinal mode, and two transverse modes. Looking at the path from $\Gamma$ to $X$, it is clear that finite size effects are present in the systems, as the acoustic modes do not all approach zero at the $\Gamma$ point (which should correspond to purely translational, zero frequency acoustic modes). However, as the system size in the $x$-direction increases, it is clear that one of these acoustic modes does begin to approach zero linearly near the $\Gamma$ point, as is expected for these modes. Therefore, this portion of the spectrum does appear to behave as expected for a stable diamond lattice. Looking at the remaining portion of the phonon spectrum, the lowest frequency acoustic mode at $W$ also appears to approach zero for the $704 \times 88 \times 88\Delta x$ system, potentially indicating the presence of a soft mode associated with a transition to a more stable crystal structure. However, while the largest component of this wavevector is along $x$, it does have a component along $y$ (of which the spatial component has been reduced in this simulation), making the exact cause of this frequency decrease difficult to determine conclusively. Therefore, further future analysis is required in order to determine if this diamond structure is truly stable, or if it would prefer to transform into a different crystal structure.
Figure 6.5: Irreducible wedge of the Brillouin zone for the diamond lattice, illustrating the independent wave-vectors. (Note, periodicity of the lattice reduces the number of independent wave-vectors to those in the Brillouin zone, while point symmetries of the lattice further reduce these to the irreducible wedge).
Figure 6.6: Phonon frequencies with error bars. Triangles correspond to the 176x176x176 lattice point system, circles correspond to 352x176x88, and diamonds correspond to 704x88x88. Here, the data for each system size is slightly offset from only another along the x-axis, so that all of the data is visible. The size of the error bars is based on the standard deviation of the frequencies computed when the data set is split up into the specified number of bins, and the frequencies are calculated for each bin. The data points themselves correspond to the frequencies calculated over the entire data set.
6.3.3 Comparison to BCC and FCC Colloidal Lattices

It is instructive to compare the diamond lattice to other common crystal lattices such as the BCC, or FCC lattice, to determine if either of these offers a more energetically favorable configuration. For these simulations we kept the same particle separation as the nearest-neighbour diamond separation used above, resulting in system sizes of $44 \times 44 \times 44\Delta x$ for the BCC unit cell, and $54 \times 54 \times 54\Delta x$ for FCC. Similar to the diamond simulations, we determined the lowest energy defect configurations for cholesteric pitches commensurate with our periodic grids. Figure 6.7 shows the lowest energy defect structure found for each lattice.

It is difficult to directly compare the energies among the different lattices, due to the different system sizes and particle densities, as well as the incommensurability of the FCC grid with the diamond grid. Figure 6.8 shows the per unit volume energy of each of the systems. While the diamond lattice corresponds to the lowest energy density, this is most certainly due to the lower particle density of this lattice. Therefore, this provides little information as to the lowest energy structure a given number of particles will self-assemble into.

As an alternative approach, we measured the energy decrease per particle obtained by having one particle in the given crystal lattice, compared to an isolated particle in a system with the same pitch, similar to what was done for the diamond simulations. A comparison of these per particle energy decreases among the different lattices is presented in Figure 6.9 as a function of cholesteric pitch. It is clear that larger per particle energy decreases are obtained by having a particle in either the BCC and FCC lattices compared to the diamond lattice, however
Figure 6.8: Per unit volume system energy for the diamond (filled triangles), BCC (hollow squares) and FCC (filled circles) crystal lattices. The solid line corresponds to a pure liquid crystal system.
6.4 Conclusions

In this work, we have investigated the stability of a diamond colloidal crystal in a cholesteric liquid crystal, with the value for the helical pitch chosen in order to give rise to the most energetically favorable defect configuration. The phonon spectrum of the resulting colloidal crystal appears somewhat promising, as the presence of real phonon frequencies suggests that if formed, the crystal should not immediately break apart. However, the spectrum also hints at the presence of a soft mode, potentially indicating a desire to transform into a lower energy structure, such as a BCC lattice. Indeed, both the BCC and FCC crystal lattices do appear to correspond to lower energy configurations. However, we have also shown that with the presence of a repulsive interaction between the particles it should be possible for the diamond lattice to become the lower energy configuration, due to fewer nearest-neighbour interactions.
Figure 6.9: Comparison of the decrease in energy over an isolated particle, for a particle in the various crystal structures, as a function of the pitch in the cholesteric. Filled triangles correspond to the diamond lattice, hollow squares correspond to the BCC lattice, and filled circles correspond to the FCC lattice.
Figure 6.10: Effect of an additional particle-particle interaction on the largest energy decrease per particle found in Figure 6.9. The thick solid line corresponds to the diamond lattice, the dashed line corresponds to the BCC lattice, while the dotted line corresponds to the FCC lattice.
Therefore, future work will involve measuring the phonon spectrum with this repulsive interaction implemented, to ascertain whether or not this has any noticeable effect on the spectrum.
Bibliography


Chapter 7

Deformable Vesicles Interacting in a Nematic Liquid Crystal

The work presented in this chapter corresponds to the article:

7.1 Introduction

The photonic applications of colloidal crystals have generated substantial interest in efficient manufacturing methods. Self-assembly of colloidal particles into a crystal structure would be an ideal method; however, particles in an isotropic fluid tend to form close-packed structures which do not exhibit a complete band gap. In order for non-close-packing to occur, the particles need to experience non-isotropic interactions. The anisotropic nature of liquid crystals has therefore led to interest in their use as the host medium (see for example [1, 2]).

Particles immersed in a liquid crystal generate defects and distortions which result in long-range interactions among the particles. The type of interaction depends on the preferred orientation of the liquid crystal molecules on the colloidal surface, and the phase of the liquid crystal. For particles in a nematic liquid crystal, homeotropic anchoring of the liquid crystal molecules on the particle surface results in the formation of either a hyperbolic hedgehog defect with an associated long-range dipolar interaction, or a Saturn ring defect, which, at long-range, generates quadrupolar interactions [3–8]. Tangential surface anchoring results in a pair of +1 boojums at the poles of the particles, also leading to long-range quadrupolar interactions [4]. At close range, the particles tend to experience attractive forces along preferred directions, leading to the formation of a variety of self-assembled structures [3, 4, 6, 8–10], in
which the particles share regions of distortion. Changing the phase of the liquid crystal used also changes the type of interaction experienced. For example, in a cholesteric liquid crystal, harmonically defect bonded particle chains have been modeled, in which the particles not only shared regions of distortion but also the defects themselves [11].

The majority of research into liquid crystal mediated particle interactions has been performed using spherical colloidal particles; however, the shape of the particle has a strong influence on the resulting interactions it experiences. Using ellipsoidal particles, Mondiot et. al. [12] have found that above a certain aspect ratio, aggregation of the particles no longer occurs. For polygonal particles the type of symmetry produced, either quadrupolar or dipolar, depends on whether the number of sides comprising the particles are odd or even [13, 14]. These polygonal platelets have been used to produce 2D periodic lattices [14].

In addition, previous work has, in general, focused on the use of rigid particles; however, deformable vesicles could also be used. Since the defects and distortions generated by the particles result in non-spherically symmetric local forces, the vesicles should deform in an attempt to minimize the distortion energy. By constraining the shape to either circular or elliptical, Silvestre et. al. [15] theoretically investigated the preferred shape of a colloidal particle with tangential surface anchoring in a smectic membrane, observing, for small particles, a strong preference for elliptical shapes. This preference was confirmed by Dolganov et. al. [16], who observed the formation of elongated, spindle-like shapes produced from nematic droplets in a smectic. Lishchuk, and Care [17], have calculated the single particle shapes that would result for 2D deformable particles with homeotropic anchoring in a nematic liquid crystal, ignoring the effect of the particle on the liquid crystal (which is a reasonable approximation for very small particles). They found the formation of lens-like particle shapes. Similar to the case of liquid crystal droplets in an isotropic fluid, this deformation occurs only if \( K/\sigma a > 1 \), where \( K \) is the elastic constant, \( \sigma \) is the surface tension, and \( a \) is the particle radius [3, 17]. Here, we investigate the behavior of pairs of interacting deformable vesicles in a nematic. Since the vesicle shape influences the type of interaction, these deformable particles may experience substantially different interactions compared to their rigid counterparts, potentially generating quite different packing structures. Here we focus on 2D deformable vesicles, and investigate the interactions between pairs of vesicles for a range of surface elasticities.
7.2 Simulation Method

7.2.1 Liquid Crystal

In order to mathematically describe the liquid crystal, it is natural to introduce a tensor order parameter, $Q$, given by

$$Q_{\alpha\beta} = \left\langle \hat{m}_\alpha \hat{m}_\beta - \frac{1}{3} \delta_{\alpha\beta} \right\rangle,$$  \hfill (7.1)

where $\hat{m}$ describes the orientation of the individual liquid crystal molecules, and the angular brackets denote a coarse grained average. With this order parameter, the liquid crystal system can then be described using a Landau-de-Gennes free energy of the following form,

$$F = \int \left[ \frac{A_0}{2} \left( 1 - \frac{\gamma}{3} \right) Q_{\alpha\beta}^2 - \frac{A_0 \gamma}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{A_0 \gamma}{4} (Q_{\alpha\beta}^2)^2 + \frac{\kappa}{2} \left( \partial_{\alpha} Q_{\beta\gamma} \right)^2 \right] dV.$$  \hfill (7.2)

Here the first three terms represent the bulk free energy, where $A_0$ is a constant, and $\gamma$ is a parameter controlling the transition from the isotropic to the nematic liquid crystalline phase. For the simulations that follow, we use a value of $\gamma = 3.2$, well within the nematic regime. The last term in equation 7.2 corresponds to the elastic energy associated with distortions in the liquid crystal. For simplicity, we employ the one elastic constant approximation, with $\kappa$ representing this constant.

At the surfaces of our deformable vesicles, we assume homeotropic anchoring of the liquid crystal molecules. To accomplish this, we introduce a surface free energy term,

$$F_{\text{surface}} = \int \frac{1}{2} \alpha_s \left( Q_{\alpha\beta} - Q^0_{\alpha\beta} \right)^2 dS,$$  \hfill (7.3)

where $Q^0_{\alpha\beta} = q(n_0^\alpha n_0^\beta - \delta_{\alpha\beta}/3)$ corresponds to the preferred orientation, $\hat{n}$, of the liquid crystal molecules on the surface, and $\alpha_s$ is chosen large enough so that $Q$ is essentially fixed at $Q^0$ on the colloidal surface.

To track the evolution of the order parameter, we use the Beris-Edwards equations of motion [18],

$$\left( \partial_t + \mathbf{u} \cdot \nabla \right) Q - S(W, Q) = \Gamma \mathbf{H},$$  \hfill (7.4)

with

$$S(W, Q) = (\xi D + \Omega) (Q + I/3) + (Q + I/3) (\xi D - \Omega)$$

$$- 2 \xi (Q + I/3) \text{Tr}(QW),$$  \hfill (7.5)
where \( D = \left( W + W^T \right)/2 \), and \( \Omega = \left( W - W^T \right)/2 \) are the symmetric and antisymmetric components, respectively, of the velocity gradient tensor, \( W_{\alpha\beta} = \partial_{\beta} u_{\alpha} \), and \( \xi \) is related to the effective aspect ratio of the liquid crystal molecules. The right hand side of equation 7.4 is present in order to drive the system towards the minimum of the free energy; \( H \) is related to the functional derivative of the free energy,

\[
H = -\frac{\delta F}{\delta Q} + \left( \frac{1}{3} \right) \frac{\delta F}{\delta \xi},
\]

(7.6)

while \( \Gamma \) corresponds to the collective rotational diffusion constant.

In addition to the evolution of the order parameter, the fluid should also obey the continuity and Navier-Stokes equations. Here, however, the additional complexities of the liquid crystal appear in the stress tensor, which contains both symmetric,

\[
\sigma_{\alpha\beta} = -P_0 \delta_{\alpha\beta} - \xi H_{\gamma\gamma}(Q_{\gamma\beta} + \frac{1}{3} \delta_{\gamma\beta}) - \xi(Q_{\gamma\gamma} + \frac{1}{3} \delta_{\gamma\gamma})H_{\gamma\beta} + 2\xi(Q_{\alpha\beta} + \frac{1}{3} \delta_{\alpha\beta})Q_{\gamma\epsilon}H_{\gamma\epsilon} - \partial_{\beta} Q_{\gamma\gamma} \frac{\delta F}{\delta \partial_{\alpha} Q_{\gamma\gamma}},
\]

(7.7)

and antisymmetric,

\[
\tau_{\alpha\beta} = Q_{\alpha\gamma}H_{\gamma\beta} - H_{\alpha\gamma}Q_{\gamma\beta}
\]

(7.8)

contributions.

We model these evolution equations on a uniform mesh using the 3D lattice-Boltzmann algorithm of Denniston et. al. [19, 20]. This method introduces two sets of partial distribution functions, the scalars \( f_i \), which sum at each lattice site to give the fluid density, and the tensors \( G_i \), which sum to give the order parameter \( Q \), both of which evolve according to single time relaxation Boltzmann equations, with relaxation times, \( \tau_f \), and \( \tau_G \) respectively. This is quantitatively equivalent to recent hybrid-LB methods [21, 22], which use the lattice-Boltzmann method for the fluid density, and a finite-difference scheme for the order parameter. For our simulations, we use two mesh points along the direction perpendicular to the plane of the 2D particle, in order to avoid constraining the liquid crystal alignment to this plane. The parameters we have used for our simulations are provided in Table 7.1.

### 7.2.2 Deformable Vesicles

In our model, we represent each vesicle as a deformable surface in the liquid crystal, with preferred homeotropic anchoring, and liquid crystal filling all space inside and outside the vesicle.
Table 7.1: The liquid crystal simulation parameters used.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>0.5</td>
<td>atm</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>3.2</td>
<td>-</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>24.35</td>
<td>pN</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>0.33775</td>
<td>$(atm \cdot \mu s)^{-1}$</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.52</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>0.03125</td>
<td>$\mu m$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>0.25</td>
<td>$\mu s$</td>
</tr>
<tr>
<td>$P_0$</td>
<td>1.0</td>
<td>atm</td>
</tr>
<tr>
<td>$\tau_f/\Delta t$</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>$\tau_G/\Delta t$</td>
<td>0.25</td>
<td>-</td>
</tr>
</tbody>
</table>

Physically, this could correspond a vesicle composed of a lipid bilayer, with perpendicular alignment of the surrounding liquid crystal preferred at the lipid head.

Similar to previous methods which have modeled deformable objects and surfaces in isotropic lattice-Boltzmann fluids [23, 24], we use a bead-spring model to represent our particles. Each vesicle surface is composed of 200 nodes, with each node, $i$, connected to it’s neighbouring nodes, ($i + 1$, and $i - 1$), by both linear and angular springs corresponding to total elastic energies,

\[
E_{\text{linear}} = \sum_{i} \frac{1}{2} k_1 (|x_i - x_{i-1}| - l_0)^2
\]

\[
E_{\text{angular}} = \sum_{i} \frac{1}{2} k_2 (\theta_i - \pi)^2.
\]  

(7.9)

Here $l_0$ is the equilibrium linear spring length, and $\theta_i$ is the angle between the vectors $(x_{i-1} - x_i)$, and $(x_{i+1} - x_i)$. It is straightforward to show that these spring constants correspond to a local surface tension, $\sigma_i = (1/2) k_1 (l_i - l_0)^2/l_i$, and, in the continuum limit, a bending rigidity, $\kappa = k_2 l_0$. Together, these springs create the preference for a circular particle shape with a constant perimeter.

In addition, we require our vesicles to maintain a constant particle volume, $V$, (the area enclosed by the springs) throughout the simulations. To accomplish this, we introduce a volume constraint force, corresponding to the energy,

\[
E_{\text{volume}} = \frac{1}{2} (V - V_0)^2,
\]

(7.10)

where $V_0$ is the starting volume of our initially circular vesicles. Since at each timestep we only have information about the locations of our surface nodes, we employ the method of Hong et. al. [25] in order to calculate the volume of these particles. This method utilizes the divergence
theorem to express the volume of a particle in terms of an integration over its surface,

\[
\int \int \nabla \cdot \mathbf{r} \, dV = \int \mathbf{r} \cdot \hat{n} \, dS \quad \Rightarrow \quad 2V = \int \mathbf{r} \cdot \hat{n} \, dS. \quad (7.11)
\]

Here \( \mathbf{r} \) is the position vector, and \( \hat{n} \) is the surface normal. If we calculate the surface normal at the midpoint locations between the nodes, and convert this integral to a sum at those locations, the volume can be expressed as

\[
V = \sum_i \frac{1}{4} \left( (y_{i+1} - y_i)(x_{i+1} + x_i) - (x_{i+1} - x_i)(y_{i+1} + y_i) \right). \quad (7.12)
\]

In contrast to the case of rigid particles in an isotropic fluid, which can be coupled to the fluid simply through the use of forces proportional to the particle-fluid velocity difference (see for example [26, 27]), the presence of the liquid crystal and the deformable nature of our particles necessitate the use of local forces which are present even in the absence of particle motion or fluid flow. These forces arise due to the anisotropic nature of the liquid crystal, and its preferred anchoring on the colloidal surface.

As previously mentioned, we assume perpendicular anchoring of the liquid crystal at the particle surface by introducing the surface free energy term given by equation 7.3. This requires a representation of the colloidal surface on the lattice-Boltzmann grid. In order to accomplish this, the colloidal nodes are distributed to nearby grid points by assigning weights at those grid points based on a linear interpolation in each dimension. The resulting grid representation for a circular colloidal particle is shown in Figure 7.1, which can be seen to correspond to a circular shell with thickness \( \sim 2\Delta x \).

The preferred anchoring at the colloidal surface results in a local torque, \( \Gamma \), applied to a volume element, \( \Delta V \), of the liquid crystal, given by

\[
\Gamma_\alpha = 2\tau_{\beta\gamma}^{\text{applied}} \Delta V. \quad (7.13)
\]

Here \( \alpha, \beta, \gamma \) represents a cyclic permutation of \( x, y, z \), and \( \tau_{\beta\gamma}^{\text{applied}} \) is the contribution to the antisymmetric stress tensor (equation 7.8), from the surface anchoring free energy term (equation 7.3) (see for example [28]). While the liquid crystal molecules are allowed to align out of plane in our simulations (we are using a 3D lattice-Boltzmann algorithm), in practice this is not observed. Therefore, since we are considering vesicles in the \( xy \)-plane, with the liquid crystal molecules aligned in this plane, \( \Gamma_z \) is the only relevant component of the torque. Since our colloidal surface applies a torque to the liquid crystal, we would like to apply an equal and
Figure 7.1: Lattice-Boltzmann grid representation of a circular colloidal particle. Greyscale corresponds to the magnitude of the linear interpolation weights (darker = larger) at each grid point. The interpolation onto the grid results in a shell of thickness $\sim 2\Delta x$, with the dashed lines denoting the outer and inner edges of the shell.
opposite local torque to the colloid. To accomplish this, we calculate $\Gamma_z$ at the midpoint locations between particle nodes, and apply forces to pairs of adjacent nodes $i$, and $i+1$, according to

$$F_i = \frac{\Gamma_z \hat{n}}{l},$$

$$F_{i+1} = \frac{-\Gamma_z \hat{n}}{l},$$

(7.14)

in order to produce an equal and opposite torque acting on the local surface element between the two nodes. Here $l$ is the distance between the particle nodes, and $\hat{n}$ is the surface normal at the midpoint location (see Figure 7.2). This results in zero net force acting on the particle, but may lead to deformations of the particle shape.

In addition to the forces that result directly from the particle surface anchoring, distortions in the liquid crystal generate forces that would be felt even by particles with neutral surface anchoring. These forces are calculated using the symmetric liquid crystal stress tensor according to

$$F_{\alpha,i} = n_\beta \sigma_{\alpha\beta} \Delta S_i,$$

(7.15)

where $\Delta S_i$ is the portion of the colloidal surface represented by node $i$, and $\hat{n}$ is the surface normal. One might expect this calculation to be performed directly at the node locations; however, as illustrated in Figure 7.1 the interpolation of the colloidal surface onto the lattice Boltzmann grid results in a grid representation of the surface with a thickness of $\sim 2\Delta x$. Therefore, we calculate the force contribution from equation 7.15 at the outer edge of the surface, by stepping out one lattice-Boltzmann distance unit, $\Delta x$, along the surface normal, to the outer dashed line shown in Figure 7.1. In addition, since there is liquid crystal throughout the simulation domain, in particular, inside the vesicles, we also include the force contribution from the inner surface. As a test of this method, we evaluated the total forces generated between two interacting rigid particles, and found excellent agreement with the theoretical result given for long-range interactions [29].

The final equilibrium shapes for our vesicles are determined by balancing the spring, liquid crystal, and volume constraint forces. Our algorithm proceeds as follows. (1) We begin with an initially circular arrangement of particles nodes which we interpolate, along with the surface normal, onto the lattice-Boltzmann grid. (2) Using the grid representation of the particle, we update the liquid crystal, and determine the new liquid crystal forces acting on the particle nodes. (3) These forces, along with the spring and volume constraint forces are used to update the particle node locations, using an implicit integration scheme. (4) Using the new node
Figure 7.2: Geometry used to determine the liquid crystal force contribution to the colloidal nodes, based on the local torque, $\Gamma_z$, applied to the liquid crystal by the colloidal surface.
locations, the surface normals are recalculated, and (5) we repeat the process until the liquid crystal free energy has converged to a minimum, and the particle shape no longer changes.

7.3 Results

7.3.1 Single Vesicle

As a first step, we considered the equilibrium shapes obtained by a single, isolated deformable vesicle in a nematic liquid crystal aligned along the $y$-axis. Here, we use a particle of radius $15\Delta x$, represented by 200 nodes, and an equilibrium linear spring length of $l_0 = 0.471\Delta x$. This particle was placed in a simulation box of size $100 \times 100 \Delta x$, and allowed to deform until its equilibrium shape was obtained. Figure 7.3 shows the resulting shapes for a range of linear and angular spring constants. As can be seen, the smaller the linear spring constant, the more oval-shaped the vesicles become. In addition, for small values of the angular spring constant, the vesicles have a lens like appearance, with peaks on either end, which smooth out as that spring constant increases. These shapes agree well with previously calculated single particle shapes [17].

The reason that these shapes are obtained can be seen by considering the liquid crystal orientation and defect locations around the particles, as illustrated in Figure 7.4. Here, the equilibrium liquid crystal director orientations are shown for a rigid circular particle (left), along with a deformable vesicle (right). As can be seen, for the deformable particle case, the defects are brought closer to the surface of the vesicle, reducing the total volume of distortion in the bulk liquid crystal. In addition, as the particles flatten out, the normal to the particle surface becomes more closely aligned with the bulk liquid crystal orientation also reducing the distortion energy.

7.3.2 Interaction Between Vesicles

Next, we consider the interaction between pairs of deformable vesicles. We use the same simulation parameters for the particles as the single particle case, however, we now consider a system of size $100 \times 240 \Delta x$. Figure 7.5 shows a representative free energy landscape for a pair of vesicles with linear spring constant, $k_1 = 0.2$, and angular spring constant, $k_2 = 4.0$, which is qualitatively similar to that obtained using a range of spring constants. One vesicle was fixed at the origin, and the free energy of the system was measured for various locations of the second vesicle, with the bulk liquid crystal aligned along the $y$-axis. The resulting total system energy (liquid crystal energy plus elastic spring energy) is quite similar to that obtained
Table 7.3: Single vesicle equilibrium shapes as a function of the linear ($k_1$), and angular ($k_2$), spring constants. In all cases the bulk liquid crystal is aligned along the $y$-axis (vertically, in the plane of the page).

Figure 7.4: Liquid crystal director orientation and defect locations (greyscale) for a rigid circular particle (left), and a deformable vesicle (right).
for two rigid interacting particles [29, 30]. In the discussion that follows, we consider three angular orientations of the particles measured relative to the $x$-axis: $0^\circ$, $45^\circ$, and $90^\circ$. For large separations, the interaction is repulsive for all orientations of the vesicles. As the vesicles are brought closer together, the interaction becomes attractive for angular orientations of $0^\circ$, and $45^\circ$, but remains repulsive for $90^\circ$. However, for even closer separations, which are not accessible in our simulations, we expect a short range repulsion for all angles, similar to the rigid cylinder case [30].

Figure 7.5: Total interaction energy between a pair of deformable vesicles, with spring constants $k_1 = 0.2$ and $k_2 = 4.0$, in the $xy$-plane. One vesicle is fixed at $(0, 0)$, and the system energy (in $f g \cdot \mu m^2/\mu s^2$ relative to the minimum attained value) is measured for various positions of the second particle. The solid white areas correspond to regions that were not measured.

The individual components of the free energy are provided in the supplementary material, along with a Mathematica notebook of the data, which provides a 3D viewing of the energy surfaces. It is clear that there is a correspondence between regions where the liquid crystal free energy is minimized, and maxima in the elastic spring energy. Before we investigate this behavior in detail, it is instructive to first consider the well known case of two interacting, rigid cylinders (see for example, [29]). Here, we reproduce results for cylinders with the same radius, $15\Delta x$, as our initially circular deformable particles, measuring the system free energy.
as a function of separation along the $x$-axis in a nematic with a bulk director orientation along the $y$-axis. Figure 7.6 shows the changes in free energy as a function of the separation, along with examples of the defect structure and liquid crystal orientation around the cylinders. For large separations, the particles experience a repulsive, quadrupolar interaction, with the defect structure around each particle the same as would occur around an isolated particle, namely a pair of $-1/2$ defects located on diametrically opposite sides of the cylinder. As the cylinders are brought closer together, the locations of the inner defects shift off axis, and the interaction becomes attractive; the particles are able to reduce the total volume of the distortion in the system by decreasing the space between them, as the distortion region of a given particle is essentially shielded by the surface of the other particle.

Keeping this behavior in mind, we now consider an equivalent simulation using deformable particles. Figure 7.7 presents representative results for two different sets of spring constants. Additional examples are provided in the supplementary material. Similar to the rigid particle situation, for large separations the particles have the same shape as would be obtained by an isolated particle which has deformed in the direction of the diametrically opposite defects. As the particles are brought closer together the inner defects again shift off axis, however, now the particles change shape as they continue to deform in the direction of these defects. The result is a smooth total free energy curve consisting of a repulsive interaction for large separations, and an attractive portion for smaller separations. This behavior is the same as that experienced by the rigid particles, however for the cases considered, the repulsive interaction now occurs sooner (i.e. for closer center to center separations) than in the rigid case. While the deformation of the particles results in a smaller separation between their surfaces for a given center to center separation, which would act to increase the range of the attractive interaction, the particle deformation results in a curvature at the sides of the particles that would correspond to a circular rigid particle of smaller radius. This, coupled with the fact that the deformation of the particles in the attractive region corresponds to a higher spring energy, acts to decrease the range of attraction.

While the total energy curves are a smooth function of particle separation, the individual components of the spring and liquid crystal energies, in most cases, clearly are not. These two components act in direct competition with one another; the inner defects would like to be close to minimize the liquid crystal distortion energy between the particles, however the closer these defects are, the larger the particle deformation, and the higher the spring energy. For example, in all cases, the change from the anti-symmetric shapes generated by the off axis locations of the defects in the region between the particles, to the large separation, symmetric particle shapes results in a decrease in elastic spring energy, while increasing the liquid crystal free energy. The position at which this change occurs corresponds to the point at which the
Figure 7.6: Interaction between two rigid particles in a nematic. Top panel: defect structure and liquid crystal orientation for sample particle separations (the outlines of the particle surfaces have been added for clarity). Bottom panel: changes in the system free energy as a function of the cylinder separation. The arrows indicate the particle separations corresponding to the images on the left.
Figure 7.7: Interaction between deformable particles separated along the $x$-axis, with the bulk liquid crystal director orientation along the $y$-axis. Plots I(a), and II(a) show the relative changes in the free energy as a function of particle separation, with the associated particle shapes given in plots I(b), and II(b). Hollow circles represent the elastic energy of the springs, which has been shifted so that the closest particle separation corresponds to a value of $-0.5 \, \text{fg} \cdot \mu m^2/\mu s^2$, hollow squares correspond to the liquid crystal free energy, shifted to $0.5 \, \text{fg} \cdot \mu m^2/\mu s^2$ for the closest separation, and the total system energy, which is set to $0.0 \, \text{fg} \cdot \mu m^2/\mu s^2$ at closest separation, is denoted by filled circles. Plots I: spring constants: $k_1 = 0.1$, $k_2 = 4.0$. Plots II: $k_1 = 0.2$, $k_2 = 4.0$. 

$\begin{align*}
\text{Relative Energy (fg \cdot \mu m^2/\mu s^2)} \\
\text{Separation (\mu m)}
\end{align*}$

$\begin{align*}
\text{Distance (\mu m)}
\end{align*}$
decrease in elastic energy is enough to overcome the resulting increase in liquid crystal energy. This can be seen by considering the difference between Figure 7.7 I, and II. For these two simulations, the particle shapes appear quite similar, however Figure 7.7 I corresponds to a smaller linear spring constant than Figure 7.7 II. Therefore, for Figure 7.7 I, the change to the symmetric particle shapes occurs at a larger separation, since the smaller spring constant implies that any decrease in the elastic energy resulting from an earlier shape change would not be enough to overcome the resulting increase in liquid crystal energy.

Figure 7.7 I also exhibits an additional shape change compared to Figure 7.7 II, the change from region C to region B, illustrated more clearly in Figure 7.8. The particles in region B have a larger perimeter ($\sim 99.7\mu m$), compared to those in region C ($\sim 98.6\mu m$), resulting in a higher elastic energy for the particles in region B; however, the particle shapes in this region are flatter, and the inner defects are closer, leading to a smaller volume of distortion between them, and a decrease in the liquid crystal free energy. This change is not observed in plot II, because with a higher linear spring constant, any decrease in liquid crystal energy would not be enough to overcome the resulting increase in spring energy.

![Figure 7.8: Comparison of the particle shapes occurring in region B (black), and region C (gray) of Figure 7.7 I. Plot (a) shows the actual orientation of the particles in the $xy$-plane, while the shapes in plot (b) have been rotated so that the inner defects lie along the $x$-axis, to allow a more direct shape comparison.](image)

In addition to particles separated along the $x$-axis, we also considered separations along the $y$-axis. Detailed results are presented in the supplementary material. In all cases, the resulting interactions are repulsive for all separations considered. This occurs because the outer defects associated with the particles are of like sign, which repel one another, and contrary to the previous case, these defects are now located on the tops of the particles and therefore the region of distortion around them can no longer be shielded by the surface of the other particle. However, similar to the previous case, there is again a direct competition between the spring and liquid crystal energies, resulting in a range of particle shapes. These can be classified into
three general groups shown in Figure 7.9. For large separations (ex. Figure 7.9(a)), the shapes are the same as would be obtained for isolated particles. For closer separations (ex. Figure 7.9(c)), the inner facing sides are flattened, reducing the distortion in the region between the particles, while increasing the spring energy. The location at which this shape change first occurs, and the extent of the deformation, both depend on the strength of the spring constants. For small enough spring constants, an additional shape change to tilted particle shapes also occurs (ex. Figure 7.9(b)). In these situations, the total distance between all like pairs of defects, which repel one another, is increased, resulting in a decrease in the liquid crystal energy, which is enough to overcome the increase in spring energy associated with the larger perimeters of these shapes.

Figure 7.9: Example particle shapes obtained for separations along the y-axis. Plots (a) and (c) correspond to spring constants, $k_1 = 0.2, k_2 = 4.0$, while plot (b) corresponds to $k_1 = 0.1, k_2 = 4.0$. 
7.4 Conclusions

We have investigated the interactions between 2D deformable particles with homeotropic anchoring, immersed in a nematic liquid crystal. Each particle, which is associated with the usual pair of $-1/2$ defects, deforms in the direction of the defects, in order to reduce the region of distortion around the particle. This potentially results in antisymmetric particle shapes for interacting particles, in which the defects have shifted away from the diametrically opposite locations observed for isolated particles.

While the resulting free energy behaves in a qualitatively similar way to that of two rigid interacting particles, the shape the particles obtain, and the locations of any shape changes depend strongly on the particle elasticities, determined by the spring constants. These shapes, and associated shape changes are determined by a direct competition between the liquid crystal free energy, and the elastic spring energy.


Chapter 8

Conclusions

In this thesis, we have investigated techniques for modelling colloidal particles in both isotropic and liquid crystalline fluids by coupling these particles to coarse-grained, lattice-Boltzmann representations of the fluids.

In Part 1 of the thesis, a new method for coupling molecular dynamics objects to an isotropic lattice-Boltzmann fluid was presented. Alternative coupling methods exist, however these either cannot be applied to simulations of point particles, or they treat the coupling using a frictional force. While the frictional force coupling method works well in systems without noise, the dissipative nature of the coupling force has led to a disagreement about the potential need to add external Langevin noise to the particle phase, in simulations where the Brownian motion of the particles is important. In contrast, our method uses conservative forces, obtained by assuming elastic collisions between the MD particles and a representative mass of fluid at the particle location. This method can be applied to both point, and composite MD particles, and the conservative nature of the force eliminates the question of the need for external Langevin noise. We have implemented this method, along with the frictional force coupling method into the open source, molecular dynamics package, LAMMPS, and have presented numerous tests illustrating its validity.

In the second part of the thesis, we investigated the interactions experienced by colloidal particles in a liquid crystal. A preferred orientation of the liquid crystal molecules on the colloidal surface leads to anisotropic forces among the particles that are present even in the absence of flow. This has generated substantial recent interest, as it may be possible to use these anisotropic forces to produce non-close packed colloidal crystals.

Using a cholesteric liquid crystal (one in which the average orientation of the liquid crystal molecules is seen to undergo a helical twist) we have modelled the formation of harmonically defect-bonded, linear chains of particles. This illustrates the potential for significantly different particle interactions in a cholesteric compared to a nematic liquid crystal; in a nematic such
particles simply share regions of distortion, and do not exhibit defect bonding. Therefore, we have focused on the use of a cholesteric liquid crystal, in an attempt to produce stable, non-close packed 3D structures. To this end, we have investigated the stability of a diamond colloidal crystal produced in a cholesteric, with the helical twist chosen in order to obtain the most energetically favourable defect configuration. Initial results suggest that this structure may correspond to a stable configuration, provided an additional repulsive force is present among the particles; however more analysis is required.

Finally, as the anisotropic forces which develop among particles in a liquid crystal result in a non-uniform pressure acting on the particle surface, we have also investigated the effect of a deformable particle surface on the resulting interactions experienced by 2D particles in a nematic. This is of interest, as a change in particle shape could potentially lead to quite different particle packing structures. While we have found that the resulting particle interactions are qualitatively similar to those experience by rigid interacting particles, there is a direct competition between the liquid crystal energy, and the elastic deformation energy, resulting in the existence of a variety of potential particle shapes.
Appendix A

Kinetic Theory and the Boltzmann Equation

A.1 Single Particle Distribution Function

Consider a gas consisting of N interacting particles of mass, m. The microstate of this system can be described by providing the positions and momenta of all the particles, resulting in a 6N dimensional point in phase space. This phase space point evolves according to Hamilton’s equations of motion,

\[
\begin{align*}
\frac{dx_i}{dt} &= \frac{\partial H}{\partial p_i}, \\
\frac{dp_i}{dt} &= -\frac{\partial H}{\partial x_i},
\end{align*}
\]

where \(x_i\) are the particle positions, \(p_i\) are the particle momenta, and \(H(x_1, x_2, \ldots, x_N; p_1, p_2, \ldots, p_N)\) is the Hamiltonian, describing the total energy of the system.

From a computational standpoint, for even a small volume of gas consisting of Avagadro’s number of particles, (~ \(10^{23}\)), tracking the time evolution of this phase space point is completely unfeasible. Fortunately, we are rarely interested in the microstate of the system, but rather the macrostate it represents, which is described by a small number of variables such as the temperature, pressure, energy, etc. of the gas. Therefore, instead of tracking the motion of the individual particles, it makes sense to approach their collective behavior from a statistical point of view.

At the most basic level, this involves the introduction of the single particle distribution function, \(f_1(x, p, t)\), or simply, \(f(x, p, t)\). Here, \(f(x, p, t)d^3xd^3p\) corresponds to the number of particles with position in the range \(x\) and \(x + d^3x\), and momentum between \(p\) and \(p + d^3p\) at
time \( t \). After a time interval, \( \Delta t \), the number of particles in this initial volume element develops into

\[
f \left( x + \frac{p}{m} \Delta t, p + F \Delta t, t + \Delta t \right) d^3x d^3p',
\]

where \( F \) is an external force field acting on the fluid. This particle number can only differ from the original through the action of collisions, adding or removing particles. Therefore the following equation must be satisfied,

\[
\left[ f \left( x + \frac{p}{m} \Delta t, p + F \Delta t, t + \Delta t \right) - f(x, p, t) \right] d^3x d^3p = C_{12} \Delta t d^3x d^3p,
\]

where \( C_{12} \) is a collision term, and we have made use of the fact that phase space volume is conserved (i.e. \( d^3x d^3p = d^3x' d^3p' \)) \[1\]. Expanding this equation leads to the distribution function evolution equation,

\[
D_t f(x, p, t) \equiv \left[ \frac{\partial}{\partial t} + \frac{p}{m} \cdot \nabla_x + F \cdot \nabla_p \right] f(x, p, t) = C_{12}.
\]

In order to solve equation A.4, the collision term, \( C_{12} \) must be specified. In order to provide a closed-form equation for \( C_{12} \), Boltzmann made a number of key assumptions. First, he assumed a dilute gas, comprised of point-like particles, experiencing short-range interactions described by a two-body potential. Under this assumption, interactions between the particles can be described by binary collisions, the effect of which is expressed through a differential cross section, \( \sigma(\Omega, |p_2 - p_1|) \). This leads to the following form for the collision term,

\[
C_{12} = \frac{1}{m} \int (f_{1'2'} - f_{12}) |p_2 - p_1| \sigma(\Omega, |p_2 - p_1|) d\Omega dp_2.
\]

(See Reichl \[2\] for a discussion and derivation of the differential scattering cross section in this context.) Here, \( f_{1'2'} \), and \( f_{12} \) are two-body distribution functions. \( f_{12} \) expresses the probability of finding one particle at position \( x_1 \) with momentum \( p_1 \), and a second particle at position \( x_2 \) with momentum \( p_2 \), both at time \( t \). \( f_{1'2'} \) in equation A.5 is present to take into account the gain of particles scattered into particle stream lines, while \( f_{12} \) considers the loss of particles scattered out. While it is not difficult to write down an expression for \( f_{12} \), this in turn depends on \( f_{123} \), and so on, in an infinite series of equations (the BBGKY hierarchy \[3\]). Therefore, in order to close equation A.5, Boltzmann introduced his second main assumption, that of molecular chaos, or \textit{Stosszahlansatz}. Under this assumption, the particles are considered to be completely uncorrelated prior to a collision (a reasonable assumption provided the gas is relatively dilute), such that the two-body distribution function can be written as the product of two single particle
distribution functions, (i.e. \( f_{12} = f_1 f_2 \)). The Boltzmann equation then reads,

\[
\left[ \partial_t + \frac{p}{m} \cdot \partial_q + F \cdot \partial_p \right] f(x, p, t) = \frac{1}{m} \int (f_1 f_2 - f_{12}) |p_2 - p_1| |\sigma(\Omega, |p_2 - p_1|)| d\Omega dp_2. \tag{A.6}
\]

### A.2 Maxwell-Boltzmann Equilibrium Distribution Function

Another important statistical mechanical concept is the idea of a local equilibrium distribution function. In local equilibrium, collisions adding particles to the volume \( d^3x \) should exactly balance those removing particles, such that \( C_{12} = 0 \), and

\[
f_{1'}^{eq} f_{2'}^{eq} = f_1^{eq} f_2^{eq}, \tag{A.7}
\]

the condition of detailed balance. Taking the logarithm of both sides yields,

\[
\ln f_{1'}^{eq} + \ln f_{2'}^{eq} = \ln f_{1}^{eq} + \ln f_{2}^{eq}. \tag{A.8}
\]

Thus, in local equilibrium, \( \ln f \) is an additive collision invariant. Therefore, it must be possible to express this in terms of the known quantities that are conserved in a binary collision, namely mass, momentum, and energy. Thus,

\[
\ln f = A + B_\alpha p_\alpha + \frac{1}{2m} C p^2, \tag{A.9}
\]

for some constants \( A, B_\alpha, \) and \( C \), where \( \alpha \) corresponds to a cartesian coordinate, \( x, y, \) or \( z \), and summation is implied over repeated indices. Using the following expectation values for the local equilibrium fluid properties,

\[
\begin{align*}
m \int f dv &= \rho \\
m \int f v_\alpha dv &= \rho u_\alpha \\
m \int f \frac{1}{2} v^2 dv &= \rho e,
\end{align*} \tag{A.10}
\]

where \( \rho \) is the fluid density, \( u_\alpha \) is the fluid velocity, and \( \rho e \) is the energy density, yields the familiar Maxwell-Bolzmann equation for the equilibrium distribution function

\[
f^{eq} = \rho \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[ -\frac{m(v - u)^2}{2k_B T} \right], \tag{A.11}
\]
where $T$ is the temperature of the fluid.

### A.3 Bhatnagar-Gross-Krook Collision Term

For ease of computation, it is common to replace the non-linear collision term in the Boltzmann equation A.6 by a simpler expression. One popular choice, is the Bhatnagar-Gross-Krook (BGK) collision operator [4], given by the following expression,

$$C_{BGK} = -\frac{f - f^{eq}}{\tau}.$$  \hspace{1cm} (A.12)

This collision operator corresponds to a single-time relaxation of the distribution function to its local equilibrium value, with $\tau$ corresponding to the time scale.

Using this collision operator, a Chapman-Enskog expansion of the Boltzmann equation (provided in Appendix B, for the discretized version), can be shown to reproduce the Navier-Stokes equations, with $\tau$ physically related to the viscosity of the fluid.
Bibliography


Appendix B

Chapman-Enskog Expansion of the Lattice Boltzmann Equation

For simplicity, we present the expansion in the absence of external forces; however, this can easily be generalized to the case where a forcing term, $p_i$ is present in the lattice-Boltzmann equation.

As a starting point, consider the standard lattice-Boltzmann BGK equation,

$$ f_i(x_\alpha + e_{i\alpha} \Delta t, t + \Delta t) - f_i(x_\alpha, t) = -\frac{1}{\tilde{\tau}}(f_i(x_\alpha, t) - f_{eq_i}(x_\alpha, t)), \quad (B.1) $$

where $\tilde{\tau} = \tau/\Delta t$ is the dimensionless relaxation time, of order $O(1)$, and moments of the distribution function, $f_i$ correspond to physical system variables, according to,

$$ \sum_i f_i = \rho $$
$$ \sum_i f_i e_{i\alpha} = \rho u_\alpha. \quad (B.2) $$

Here $\rho$ is the fluid density, and $\mathbf{u}$ is the local fluid velocity. The equilibrium distribution, $f_i^{eq}$ is constrained by the following equations

$$ \sum_i f_i^{eq} = \rho $$
$$ \sum_i f_i^{eq} e_{i\alpha} = \rho u_\alpha $$
$$ \sum_i f_i^{eq} e_{i\alpha} e_{i\beta} = P_{\alpha\beta} + \rho u_\alpha u_\beta $$
$$ \sum_i f_i^{eq} e_{i\alpha} e_{i\beta} e_{i\gamma} = \frac{\rho}{3}(u_\alpha \delta_{\beta\gamma} + u_\beta \delta_{\alpha\gamma} + u_\gamma \delta_{\alpha\beta}). \quad (B.3) $$
Replacing the first term of equation B.1 by its Taylor series expansion yields,

\[ \Delta t D_t f_i + \frac{\Delta t^2}{2} D_t^2 f_i = -\frac{1}{\bar{\tau}} (f_i - f_i^{eq}) + O(\Delta t^3), \] (B.4)

where \( D_t = (\partial_t + e_{ia} \partial_a) \), and the arguments of \( f_i(x_a, t) \) have been omitted. The main assumption of the Chapman Enskog expansion is that the \( f_i \) can be expanded as a series according to,

\[ f_i = f_i^{(0)} + \Delta t f_i^{(1)} + \Delta t^2 f_i^{(2)} + \ldots \] (B.5)

Using this expression in equation B.4, and grouping terms of the same order in \( \Delta t \), we obtain the following set of equations,

\[ f_i^{(0)} = f_i^{eq}, \]
\[ D_t f_i^{(0)} = -\frac{f_i^{(1)}}{\bar{\tau}}, \]
\[ D_t f_i^{(1)} + \frac{1}{2} D_t^2 f_i^{(0)} = -\frac{f_i^{(2)}}{\bar{\tau}}. \] (B.6)

Thus, \( f_i \) can be expressed as,

\[ f_i = f_i^{eq} - \tau D_t f_i^{eq} + \tau \left( \tau - \frac{\Delta t}{2} \right) D_t^2 f_i^{eq} + O(\Delta t^3), \] (B.7)

where the derivative terms clearly correspond to the higher order terms in the expansion.

Summing equation B.7 over the lattice vectors, \( i \), i.e.

\[ \sum_i f_i = \sum_i f_i^{eq} - \tau \sum_i (\partial_t + e_{ia} \partial_a) f_i^{eq} + \tau \left( \tau - \frac{\Delta t}{2} \right) \sum_i (\partial_t + e_{ia} \partial_a)^2 f_i^{eq}, \] (B.8)

and using the definitions of the distribution function moments given in equation B.3, yields the following equation,

\[ \partial_t \rho + \partial_a (\rho u_a) = \left( \tau - \frac{\Delta t}{2} \right) \partial_t \left[ \partial_t \rho + \partial_a (\rho u_a) \right] + \left( \tau - \frac{\Delta t}{2} \right) \left[ \partial_t (\rho u_a) + \partial_{\bar{a}} \sum_i e_{ia} e_{ib} f_i^{eq} \right]. \] (B.9)

The RHS of this equation is clearly 2nd order in derivatives. Therefore, the first term in brackets on the RHS is \( O(\partial^2) \) making the entire term \( O(\partial^3) \), which we neglect, leading to the following equation,

\[ \partial_t \rho + \partial_a (\rho u_a) = \left( \tau - \frac{\Delta t}{2} \right) \left[ \partial_t (\rho u_a) + \partial_{\bar{a}} \sum_i e_{ia} e_{ib} f_i^{eq} \right] + O(\partial^3). \] (B.10)
Multiplying equation B.7 by $e_{i\alpha}$, and summing over the lattice vectors produces the following equation,

$$\partial_t(\rho u_\alpha) + \partial_\beta \sum_i e_{i\alpha} e_{i\beta} f_i^{eq} = \left( \tau - \frac{\Delta t}{2} \right) \partial_\beta \left[ \partial_t(\rho u_\alpha) + \partial_\gamma \sum_i e_{i\alpha} e_{i\gamma} f_i^{eq} \right] + \left( \tau - \frac{\Delta t}{2} \right) \partial_\beta \left[ \partial_\gamma \sum_i e_{i\alpha} e_{i\beta} f_i^{eq} + \partial_\gamma \sum_i e_{i\alpha} e_{i\gamma} e_{i\beta} f_i^{eq} \right]. \quad (B.11)$$

To first order in derivatives, this equation reads,

$$\partial_t(\rho u_\alpha) + \partial_\beta \sum_i e_{i\alpha} e_{i\beta} f_i^{eq} = 0 + O(\partial^2). \quad (B.12)$$

Plugging this result into equation B.10 generates the continuity equation to second order in derivatives (equivalently, second order in $\Delta t$).

$$\partial_t \rho + \partial_\alpha(\rho u_\alpha) = 0 + O(\partial^3). \quad (B.13)$$

Plugging equation B.12 into the first term on the RHS of equation B.11, and evaluating all of the distribution function moments, leads to

$$\partial_t(\rho u_\alpha) + \partial_\beta (\rho u_\alpha u_\beta) = -\partial_\beta P_{\alpha\beta} + \left( \tau - \frac{\Delta t}{2} \right) \partial_\gamma \left( \frac{\rho}{3} (u_\alpha \delta_{\beta\gamma} + u_\beta \delta_{\alpha\gamma} + u_\gamma \delta_{\alpha\beta}) \right) + \partial_\gamma (P_{\alpha\beta} + \rho u_\alpha u_\beta). \quad (B.14)$$

Consider the last term on the RHS of this equation, namely, $\partial_\gamma (P_{\alpha\beta} + \rho u_\alpha u_\beta)$. First, assume the stress tensor can be approximated by an equilibrium pressure, such that $P_{\alpha\beta} = -P_0 \delta_{\alpha\beta}$. Then, the time derivative of the pressure tensor can be expressed as

$$\frac{\partial P_{\alpha\beta}}{\partial t} = -\frac{\partial P_0}{\partial t} \delta_{\alpha\beta} = -\frac{\partial P_0}{\partial \rho} \frac{\partial \rho}{\partial t} \delta_{\alpha\beta}. \quad (B.15)$$

Assuming incompressibility of the fluid, and using the continuity equation to replace the time derivative of the density leads to

$$\partial_t P_{\alpha\beta} = \rho(\partial_\rho P_0)(\partial_\gamma u_\gamma) \delta_{\alpha\beta}. \quad (B.16)$$
Next, re-write the term, $\partial_t(\rho u_\alpha u_\beta)$ as

$$\partial_t(\rho u_\alpha u_\beta) = \partial_t(\rho u_\alpha)u_\beta + u_\alpha \partial_t(\rho u_\beta). \quad (B.17)$$

Using the terms of $O(\partial)$ from equation B.14, and again, assuming $P_{\alpha\beta} = -P_0 \delta_{\alpha\beta}$, equation B.17 can be re-written as

$$\partial_t(\rho u_\alpha u_\beta) = -\partial_\gamma(\rho u_\alpha)u_\gamma u_\beta - u_\alpha \partial_\gamma(\rho u_\beta)u_\gamma. \quad (B.18)$$

As this term is clearly 3rd order in velocity, we will neglect it in our expansion. With these above results, equation B.14 transforms into the Navier-Stokes equation, as desired,

$$\rho \partial_t u_\alpha + \rho \partial_\beta(u_\alpha u_\beta) = \partial_\gamma P_{\alpha\beta} + \frac{\rho(\tau - \Delta t/2)}{3} \partial_\beta \left[ (\delta_{\alpha\beta} - 3\partial_\rho P_0 \delta_{\alpha\beta}) \partial_\gamma u_\gamma + \partial_\beta u_\alpha + \partial_\alpha u_\beta \right]. \quad (B.19)$$
Appendix C

Lattice-Boltzmann Algorithm for Liquid Crystals

In order to model the liquid crystal equations of motion (presented in Chapter 4; for brevity we will not repeat them here), we use the lattice-Boltzmann algorithm of Denniston et al. [1, 2]. This is similar to the standard lattice Boltzmann algorithm for an isotropic fluid (see Chapter 1 for details), however, instead of simply requiring a single set of distribution functions, $f_i$, to model the fluid density, a second set of distribution functions, the tensors $G_i$, are introduced, in order to model the liquid crystal order parameter, $Q$.

Both the $f_i$ and $G_i$ evolve according to discretized versions of the Boltzmann equation, with forcing terms $p_i$, and $M_i$ respectively,

$$
(\partial_t + e_i \partial_\alpha) f_i(x_\alpha, t) = -\frac{1}{\tau_f} \left( f_i(x_\alpha, t) - f_i^{eq}(x_\alpha, t) \right) + p_i
$$

$$
(\partial_t + e_i \partial_\alpha) G_i(x_\alpha, t) = -\frac{1}{\tau_G} \left( G_i(x_\alpha, t) - G_i^{eq}(x_\alpha, t) \right) + M_i.
$$

The equilibrium distribution function, $f_i^{eq}$ is defined according to,

$$
\sum_i f_i^{eq} = \rho
$$

$$
\sum_i f_i^{eq} e_i = \rho u_\alpha
$$

$$
\sum_i f_i^{eq} e_\alpha e_\beta = -\sigma_{\alpha \beta} + \rho u_\alpha u_\beta,
$$

(C.1)
where \( \sigma_{\alpha\beta} \) is the symmetric portion of the liquid crystal stress tensor. The forcing term \( p_i \), is chosen to control the antisymmetric portion of the stress tensor, \( \tau_{\alpha\beta} \), with moments defined as

\[
\sum_i p_i = 0 \\
\sum_i p_i e_{ia} = \partial_\beta \tau_{\alpha\beta} \\
\sum_i p_i e_{ia} e_{i\beta} = 0.
\] (C.3)

Moments of the equilibrium order parameter distribution, \( G_{eq}^i \), are chosen according to

\[
\sum_i G_{eq}^i = Q \\
\sum_i G_{eq}^i e_{ia} = Qu_\alpha \\
\sum_i G_{eq}^i e_{ia} e_{i\beta} = Qu_\alpha u_\beta,
\] (C.4)

in order to ensure that the order parameter is convected with the flow, while the forcing term \( M_i \) is used to model the order parameter evolution, with

\[
\sum_i M_i = \Gamma H(Q) + S(W, Q) \\
\sum_i M_i e_{ia} = \left( \sum_i M_i \right) u_\alpha,
\] (C.5)

where \( \Gamma, H, W, \) and \( S \) are defined in Chapter 4. With the equilibrium distributions chosen to satisfy the above constraints, a Chapman-Enskog expansion can be performed in order to obtain the liquid crystal equations of motion described in Chapter 4 (see Denniston et. al. [1] for details).
Bibliography


Appendix D

Supplementary Material for Chapter 7: Deformable Vesicles Interacting in a Nematic Liquid Crystal

Figure D.1 is an expanded version of Figure 7.5 in the main manuscript, showing not only the total interaction energy (top panel), but also the individual components, consisting of the liquid crystal free energy (middle panel), and the spring energy (lower panel). Note the correspondence between regions where the liquid crystal energy is minimized, and maxima in the spring energy.

Figure D.2 is similar to Figure 7.7 in the main manuscript, providing further examples of the interaction energies and particle shapes for particles separated along the \( x \)-axis. As can be seen, the behavior is quite similar to that shown in Figure 7.7; for large separations, the shapes are the same as for an isolated particle, and the change to these symmetric shapes occurs at a larger separation for the particles in Figure D.2 I. In addition, a further shape change, from Region A to B is also observed in Figure D.2 I. The locations of the various shape changes, and whether or not a change occurs results from a direct competition between the spring and liquid crystal energies. (See the main manuscript for further detail).

Figure D.3 provides detailed results for the interaction of particles separated along the \( y \)-axis, which corresponds to the shapes presented in Figure 7.9 of the main manuscript, and discussed there in more general terms. As can be seen, the interaction is purely repulsive for all separations considered. However, similar to separations along the \( x \) axis, there is again a
Figure D.1: Interaction energy between a pair of deformable vesicles, with spring constants $k_1 = 0.2$ and $k_2 = 4.0$, in the $xy$-plane. One vesicle is fixed at $(0, 0)$, and the system energy (in $fg \cdot \mu m^2/\mu s^2$ relative to the minimum attained value) is measured for various positions of the second particle. The solid white areas correspond to regions that were not measured. The plots correspond to: the total (liquid crystal plus spring) energy (top panel), the liquid crystal free energy (middle panel), and the spring energy (lower panel).
Figure D.2: Additional example of the interaction between deformable particles separated along the $x$-axis, with the bulk liquid crystal director orientation along the $y$-axis. Plots I(a) and II(a) show the relative changes in the free energy as a function of particle separation, with the associated particle shapes given in plots I(b) and II(b). Hollow circles represent the elastic energy of the springs, which has been shifted so that the closest particle separation corresponds to a value of $-0.5 \, fg \cdot \mu m^2/\mu s^2$, hollow squares correspond to the liquid crystal free energy, shifted to $0.5 \, fg \cdot \mu m^2/\mu s^2$ for the closest separation, and the total system energy, which is set to $0.0 \, fg \cdot \mu m^2/\mu s^2$ at closest separation, is denoted by filled circles. Plots I: spring constants: $k_1 = 0.1$, $k_2 = 2.0$. Plots II: $k_1 = 0.2$, $k_2 = 2.0$. 
Figure D.3: Interaction between deformable particles separated along the y-axis, with the bulk liquid crystal director orientation along this same axis. Here, hollow circles represent the elastic energy of the springs, which has been shifted so that the closest particle separation corresponds to a value of $-0.75 \, fg \cdot \mu m^2/\mu s^2$, hollow squares correspond to the liquid crystal free energy, shifted to $0.75 \, fg \cdot \mu m^2/\mu s^2$ for the closest separation, and the total system energy, which is set to $0.0 \, fg \cdot \mu m^2/\mu s^2$ at closest separation, is denoted by filled circles. Panel I: spring constants $k_1 = 0.2$, $k_2 = 4.0$. Panel II: $k_1 = 0.1$, $k_2 = 4.0$. 
direct competition between the spring and liquid crystal energies. As can be seen, in Figure D.3 I., the inner facing sides in region A are somewhat flattened, in comparison to region B. This reduces the distortion in the region between the particles, but increases the spring energy. The transition from region A to B corresponds to the point where the decrease in spring energy that would occur by having a rounder particle side overcomes the resulting increase in liquid crystal energy. For the particles in Figure D.3 II., such a shape change at the larger separations we have considered does not occur, since these particles have a smaller linear spring constant, and therefore would experience a smaller change in spring energy with the shape change which would not be enough to overcome the increase in liquid crystal energy at these separations. This lower spring constant does however allow for additional shape changes at closer separations. As can be seen, in moving from region A to region B, there is a shape change, as the particles become tilted. This change in shape is associated with an increase of \( \sim 0.2 \, \mu m \) in perimeter length, resulting in an increase in the spring energy; however there is also an increase of \( \sim 0.1 \, \mu m \) in the total distance between all pairs of the like defects (compared to particles at the same locations, but with the same shapes as those in region A), resulting in a decrease in the liquid crystal energy. Since the linear spring constant is smaller in this case compared to that of Figure D.3 I., the decrease in liquid crystal is enough to overcome the increase in spring energy associated with this shape change.
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