Dynamics of diffusive and driven nanoparticles in fluids

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Abstract
The ability to make measurements and manipulate matter at micrometer and nanometer scales will have far-reaching applications. In the past decade, significant progress has been made in developing microscale and nanoscale motors that can be used for targeted delivery. These advances are not without complications, however, such as those brought about by thermal effects which are more apparent at the nanoscale.

Modeling microscale and nanoscale objects that interact with a fluid requires a fluid model that is quantitatively accurate and can capture macroscopically observed quantities without any adjustable parameters to make quantitative predictions of the dynamics. In this thesis, we have modeled diffusive and driven systems through the use of a recently developed numerical multiscale simulation method—a coupled fluctuating lattice-Boltzmann and molecular dynamics (LBMD) method—to study thermal effects on driven systems. The method was chosen because it is quantitatively accurate, it incorporates the full hydrodynamics and correct thermal fluctuations, it uses a consistent particle-fluid coupling scheme where the particle-fluid velocity boundary conditions can be controlled, and it allows simulation of particles with complex geometries.

Diffusion of fused colloids and colloidal aggregates, and propulsion of helical shapes are investigated using the LBMD method. We first show that the diffusion coefficients of complex aggregate clusters can be quantitatively described by the LBMD method. Then, the model is used to study the diffusive and driven dynamics of magnetic helices, which have been experimentally demonstrated to be applicable for targeted delivery. The geometrical properties—such as the cross-sectional shape, the number of turns, and the pitch length—are optimized for maximum propulsion and swimming efficiency. The dynamics of magnetic helices that are driven by a rotating magnetic field in the presence of thermal fluctuations is examined for varying propulsive strengths. We show that, even at the nanoscale, helices are a suitable candidate for targeted delivery because spatial and temporal precision can be preserved by meeting a Péclet number criterion. In particular, we show that velocities can be controlled for external field frequencies less than the object’s characteristic step-out-frequency and the direction of propulsion can be changed provided that the driving field and the helical rotation are synchronous. Finally, we show that self-propelled systems can also be modeled using this method.

Keywords Lattice Boltzmann, hydrodynamics, nanoparticles

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Espoo, September 1, 2017,

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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Shape and scale dependent diffusivity of colloidal nanoclusters and aggregates”

The author performed all the numerical simulations and analysis involving the lattice-Boltzmann method and wrote the first version of the manuscript.

Publication II: “Controlled propulsion and separation of helical particles at the nanoscale”

The author contributed significantly to the main idea of the work. The performed all the simulations and analysis of the data, and wrote the first version of the manuscript.

Publication III: “Propulsion and controlled steering of magnetic nanohelices”

The author contributed significantly to the main idea of the work. The author performed all the simulations and analysis of the data. The author wrote the first version of the manuscript.
1. Introduction

“Now let us talk about the possibility of making machines with movable parts, which are very tiny.”—Richard P. Feynman, *There’s Plenty of Room at the Bottom*

Richard Feynmann talked about small machines that can perform operations in the human body the way a medical surgeon would [1]. Contact-free and non-invasive control of matter at the micrometer and nanometer scales offers great potential for applications in physics, biology, chemistry, medicine, and nanoscience.

Advances in nanotechnology have opened new pathways to effective cancer diagnosis and treatment. Hyperthermia therapy is a treatment that damages cancer cells or targets body tissue through exposure to radiation; however, it also exposes healthy tissues to radiation. To minimize this damage of healthy cells in hyperthermia, gold nanoparticles can mediate by systematically administering the nanoparticles to the target site, such as a tumor. Through photo-excitation, the nanoparticle converts light to heat, and thereby destroys only cells close to the nanoparticle [2]. The range of utility of gold nanoparticles for targeted therapy is based on the tunability of the particles’ optical absorption and scattering properties through careful design of its shape [2].

In the field of medicine, the role of microrobots and nanorobots is broad. These can be used for localized delivery of therapeutic agents, for biopsy or for ablation of fatty deposits or blood clots, for reinforcement of microstructures in the body, and chemical analysis in hard-to-reach places [3–5]. Although the use of these tools in the human body is still far from being realized, significant progress has been made in recent years. Three-dimensional capture, transport and release of cargoes such as micron-sized beads [6] and microtransporters [7] or biological cells [8] and sperm (see Figure 1.1) [9] as well as in vivo use of micromotors in a mouse’s stomach [10] have been experimentally demonstrated. Others, meanwhile, have approached drug delivery through the use of the propulsive
power from nature. Bio-hybrid micromotors have been made by attaching flagellated bacteria or sperm to a cargo that interacts with an external field to guide the cargo for targeted delivery [11–15]. Observing that microrobots run the risk of being neutralized by the immune system before even reaching the target, one group created microtransporters of microrobots and nanorobots [7].

These are just a few examples of what has already been done in the microscale, and there is still plenty of room at the bottom with regard to applications, micro and nanomachine design and actual use of this technology. To facilitate further progress in this field, it is useful to consider the challenges both in the microscale and the nanoscale and recognize that some issues at the nanoscale may not be a problem at the microscale and vice versa.

One important concern present at both length scales is that viscous drag forces are more dominant than inertial forces; this dynamics is called low Reynolds number regime. In this regime, the forces and torques applied on an object are directly proportional to its velocity and angular velocity. Once the force is removed, the body stops almost instantaneously. Navigating in a fluid at low Reynolds number means that appropriate strategies to optimize are required when swimming at limited resources. This also means that time-symmetric movements will result in zero displacement [16]. Hence, micro- and nanomachines that are remotely controlled and those that are built to function autonomously require different mechanisms for navigating in the fluid.

The micromotor shown in Figure 1.1 is an example of a micromachine that is remotely guided through an external field. The field induces a torque on the
motor that drives its rotational motion, which propels it in the fluid. Here the 
translational and rotational movement is due to the application of an external 
force from the magnetic interaction of the motor with the rotating magnetic 
field. Autonomous motion is different because of the absence of an external 
force that can drive the motion. To translate or propel, the body must exert 
a force on its environment. Drag force counters the exerted force and inertia 
(which allows macroscopic organisms of the order of a millimeter to stream 
through the fluid) is insignificant. This is why time-symmetric movements 
will not result in any propulsion. Let us illustrate this difficulty regarding low 
Reynolds numbers in the length scale of the human body. The low Reynolds 
number regime at the microscale is equivalent to a human immersed in an 
incredibly thick fluid such as blackstrap molasses. If one waves one’s hand 
back and forth, displacements will display a forward and backward motion, but 
there will be very little, if any, significant progression in the movement. To 
advance, movements that are not the same forward and backward in time must 
be made (see the example in Figure 1.2). Edward Purcell provided an example 
of a simple swimmer at zero Reynolds number for a three-link swimmer [16]. 
The movement depicted in the top row of Figure 1.2 is not the same when the 
movements are reversed (bottom row). These series of configurations will result 
in a non-zero net displacement. It seems, therefore, that autonomous swimming 
at zero Reynolds number is complicated, but one can develop swimming protocols 
by mimicking the swimming strategies of many microorganisms that feed and 
navigate in fluid environments.

![Figure 1.2. Purcell’s three link swimmer is a simple example where time-symmetric motion can be broken. When the configurations in the top row are reversed, the resulting series of configuration (bottom row) are not the same as the series of configurations above [16].](image)

Moving from the micrometer to the nanometer length scale introduces effects 
that are less prominent in the larger time scale. Consider the Brownian motion 
or the random motion of two beads of radii 10 μm and 10 nm. The time it 
takes for the microbead and a nanobead to traverse an average distance of 100 
μm due to Brownian motion in water at 27°C are about 21 hours and about a
minute, respectively. To traverse an average distance that is equivalent to its body length, the microbead would require 12 minutes, while the nanobead only requires about 0.1 microseconds. It is therefore clear that when spatial precision and accuracy are paramount, the time constraints involved in controlling the motion are more pronounced at the nanoscale than at the microscale.

The challenges involving thermal effects are evident in the control of micromotors and nanomotors. One remarkable geometry that can be used for externally guided motors is the helix because of its coupled translational and rotational motion. Purcell explains this coupled motion by using the corkscrew illustration: as the corkscrew is rotated through the wine cork, it sinks deeper through the cork [16]. The helical shape translates when rotated (and vice versa) in a medium. Magnetic propellers, such as most of the microrobots mentioned in earlier examples, were developed using this fundamental principle. The helix, which is usually magnetic or coated with a magnetic material, interacts with an external field that drives its rotational motion. For the micromotors, thermal effects are minimal [6, 9, 17] but when the helices are scaled to the nanometer, steering in aqueous solutions was not possible because of Brownian motion [18]. Steering in viscoelastic fluids of the nanohelices, however, is not an issue because the viscoelastic fluid inhibits the strong fluctuations that were present in less viscous fluids [18]. For these driven helices, thermal fluctuations affect the motion by changing the orientation of the helix and interfere with the translational and rotational motion.

This thesis is organized as follows. Chapter 2 provides the theoretical framework of the general lattice Boltzmann method (LBM) while Chapter 3 presents the general features of the coupled lattice Boltzmann and molecular dynamics (LBMD) method that is implemented in LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator). Chapter 4 presents the results of cluster diffusion in Publication I. In Chapter 5, we model the propulsion of magnetic helices. The discussion in Chapter 5 covers the optimization of helices and the suitable conditions for controlled propulsion and steering at the nanoscale (Publication II and Publication III). Chapter 6 we present preliminary results of modeling biological microswimmers using the LBMD. Finally, Chapter 7 summarizes and concludes the results in this thesis.
2. Kinetic Theory for Liquids

The dynamics of fluids, which are composed of an extremely large number of atoms and molecules, may be investigated in different length scales. At the atomistic level, molecular dynamics (MD) can track the trajectories and interactions of the atoms in the system. The aim in MD is to obtain the macroscopic behavior of fluids from the microscopic interaction of the individual fluid particles [19]. Its implementation is straightforward because the trajectories of the individual particles are governed by Newton’s equations of motion. This, however, is also the reason why even if it were possible to numerically solve the dynamics of a large number of particles, calculating every particle-to-particle interaction in the system is computationally unrealistic. On the other end of the spectrum of models for fluid dynamics is continuum mechanics, which models only the macroscopic physical description of the fluid and involves numerically solving the governing fluid equations. While this representation of the system is rather useful in engineering applications, its accuracy is limited [20]. Better results may be obtained by using more fundamental concepts.

In between the length scales covered by atomistic models and continuum models, one can use mesoscopic models that are based on kinetic theory. Kinetic theory bridges the two different length scales and aims to explain physical phenomena at the macroscopic level regarding the properties of the evolution of the phase-space distribution function of the system [20, 21].

A numerical scheme based on this theory is the lattice-Boltzmann method (LBM), a widely used method for simulating fluid flows and colloid and polymer dynamics. The fundamental framework of the LBM method is based on the kinetic theory which incorporates the essential physics of microscopic and mesoscopic processes so that the macroscopic averages obey the continuum behavior of fluids [22]. The LBM solves the simplified Boltzmann equation and gives an accurate description of the macroscopic behavior without tracking the trajectories of each fluid particle.
**2.1 Kinetic Theory**

The starting point in obtaining the phase-space evolution of a fluid particle is the Hamiltonian dynamics of $N$ particles. The Hamiltonian is taken to be of the form [22]

$$
H = \frac{1}{2m} \sum_{i=1}^{N} p_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i<j}^{N} U(r_i - r_j), \quad (2.1)
$$

with the evolution of the momentum and the position of particle $i$ as

$$
\frac{\partial r_i}{\partial t} = \nabla_{p_i} H, \quad (2.2a)
$$

$$
\frac{\partial p_i}{\partial t} = -\nabla_{r_i} H. \quad (2.2b)
$$

Here, the $N$ particles are identical with mass $m$, $p_i$ and $V(r_i)$ are the momentum and external potential on the $i$th particle, while $U(r_i - r_j)$ is the interaction potential of the $i$th and $j$th particle for $i \neq j$.

Of particular interest in kinetic theory is the probability distribution function of the $N$ particles $f_N(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N, t)$, where $f_N$ contains the correlations between the particles. Because the distribution function is locally conserved, the continuity equation for $f$ must be obeyed:

$$
\frac{\partial f_N}{\partial t} + \sum_{i=1}^{N} \left( \nabla_{r_i} \left( \frac{\partial r_i}{\partial t} f_N \right) + \nabla_{p_i} \left( \frac{\partial p_i}{\partial t} f_N \right) \right) = 0, \quad (2.3)
$$

where $\nabla_r$ and $\nabla_p$ are the gradient operators for $r$ and $p$, respectively. Upon substitution of the Hamilton equations from eq. 2.2, the Liouville equation is obtained for the distribution function:

$$
\frac{\partial f_N}{\partial t} + \sum_{i=1}^{N} \left( \nabla_{r_i} f \cdot \nabla_{p_i} H - \nabla_{p_i} f \cdot \nabla_{r_i} H \right) = 0. \quad (2.4)
$$

In *Poisson bracket* notation, this is written as

$$
\frac{\partial f}{\partial t} = \{H, f\}. \quad (2.5)
$$

One can derive the evolution of the single-particle distribution function by integrating over the relevant phase-space volume of the $f_N$ distribution function to find that it depends on the interactions of the other particles in the system but here as a starting point, the $n$–particle distribution function is first considered to illustrate the hierarchy of distribution function dependence. The reduced $n$–particle distribution function $f_n(r_1, r_2, \ldots, r_n; p_1, p_2, \ldots, p_n)$ may be extracted from $f_N$ of the system by integrating over the relevant phase-space volume:

$$
f_n = \frac{N!}{(N-n)!} \int \cdots \int d^{N-n} r \int d^{n} p f(r_1, r_2, \ldots, r_N; p_1, p_2, \ldots, p_N; t). \quad (2.6)
$$
The factor \(N!/(N-n)!\) accounts for the fact that all particles in the system are considered identical. The aim is to find how the single particle distribution function evolves with time and, to do that, the evolution of the distribution function of the system from the Liouville equation (eq. 2.4) and the Hamiltonian (eq. 2.1) is used on eq. 2.6 to get

\[
\frac{\partial f_n}{\partial t} = -\frac{N!}{(N-n)!} \int \prod_{i=n+1}^N dr_i dp_i \sum_{i=1}^N (\nabla_{r_i} f \cdot \nabla_{p_i} H - \nabla_{p_i} f \cdot \nabla_{r_i} H)
\]  

(2.7)

which can be reduced to

\[
\frac{\partial f_n}{\partial t} = [H_n, f_n] + \int d\mathbf{r}_{n+1} d\mathbf{p}_{n+1} \sum_{i=1}^n \nabla_{\mathbf{r}_i} U(\mathbf{r}_i - \mathbf{r}_{n+1}) \cdot \nabla_{\mathbf{p}_i} f_{n+1}
\]

(2.8)

with the effective Hamiltonian

\[
H_n = \frac{1}{2m} \sum_{i=1}^n p_i^2 + \sum_{i=1}^n V(\mathbf{r}_i) + \sum_{i<j}^n U(\mathbf{r}_i - \mathbf{r}_j)
\]

(2.9)

through a series of integration by parts.

Eq. 2.8 is the BBGKY (Bogoliubov-Born-Green-Kirkwood-Yvon) hierarchy. To illustrate what this means, consider the single-particle distribution, abbreviated hereinafter as \(f\):

\[
\frac{\partial f}{\partial t} = [H_1, f] + \int d\mathbf{r}_2 d\mathbf{p}_2 \nabla_{\mathbf{r}_1} U(\mathbf{r}_1 - \mathbf{r}_2) \cdot \nabla_{\mathbf{p}_1} f_2,
\]

(2.10)

or equivalently

\[
\frac{\partial f}{\partial t} + \frac{1}{m} \nabla_{\mathbf{r}} f \cdot \mathbf{p} + \nabla_{\mathbf{p}} f \cdot \mathbf{F} = \int d\mathbf{r}_2 d\mathbf{p}_2 \nabla_{\mathbf{r}_1} U(\mathbf{r}_1 - \mathbf{r}_2) \cdot \nabla_{\mathbf{p}_1} f_2.
\]

(2.11)

The first term is the streaming term, where the effective Hamiltonian \(H_1\) depends only on the kinetic energy and the external potential of the single-particle. The second term is the correction term which accounts for the collisions. Naturally, this collision integral depends on the interaction of one particle with another, but it also depends on the two-particle distribution function. Consequently, to get information about the evolution of the single particle distribution, one needs the two-particle distribution. Similarly, when we require the two-particle phase space evolution, we end up with an integral expression with the three-particle distribution, and so on. Therefore, a closed form of the collision integral does not exist because the \(n\)th distribution function depends on the \((n+1)\)th distribution function. There is, however, significant progress from the BBGKY hierarchy (eq. 2.8) because, simply put, this means that the evolution of the distribution of \(n\)-particles evolves like the Hamilton’s equation (eq. 2.5) with a correction due to the collisions of the \(n\)-particles with the other \((N-n)\)-particles in the system.
For the kinetic theory to be useful in the LBM, we need the single particle distribution function \( f(\mathbf{r}, \mathbf{p}, t) \). In a system of volume \( V \) and \( N \) particles, this distribution function by definition satisfies the normalization condition

\[
\int f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p} = N. \tag{2.12}
\]

When particles are evenly distributed, the number density is given by

\[
\int f(\mathbf{r}, \mathbf{p}, t) d\mathbf{p} = \frac{N}{V}. \tag{2.13}
\]

Since the particles in the system are dynamic, \( f(\mathbf{r}, \mathbf{p}, t) \) varies with time. A particle in the system spends most of its time streaming until it finally collides with another particle. In the presence of an external potential which gives rise to a force \( \mathbf{F} \), a molecule that is initially at the phase-space volume \( d^3r d^3p \) at \((\mathbf{r}, \mathbf{p}, t)\) will be at the phase-space volume \( d^3r' d^3p' \) at \((\mathbf{r} + \frac{\mathbf{p}}{m} \delta t, \mathbf{p} + \mathbf{F} \delta t, t + \delta t)\)

\[
f\left(\mathbf{r} + \frac{\mathbf{p}}{m} \delta t, \mathbf{p} + \mathbf{F} \delta t, t + \delta t\right) d\mathbf{r}' d\mathbf{p}' = f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p}, \tag{2.14}
\]

or equivalently

\[
f\left(\mathbf{r} + \frac{\mathbf{p}}{m} \delta t, \mathbf{p} + \mathbf{F} \delta t, t + \delta t\right) = f(\mathbf{r}, \mathbf{p}, t), \tag{2.15}
\]

since the phase-space volume is conserved. When the molecules in the system collide, a correction term, similar to eq. 2.11, is added:

\[
f\left(\mathbf{r} + \frac{\mathbf{p}}{m} \delta t, \mathbf{p} + \mathbf{F} \delta t, t + \delta t\right) = f(\mathbf{r}, \mathbf{p}, t) + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \delta t, \tag{2.16}
\]

which can be reduced to

\[
\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} f + \mathbf{F} \cdot \nabla_{\mathbf{p}} f = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}, \tag{2.17}
\]

when a first order of expansion about \( \delta t \) for the right hand side of eq. 2.16 is done. This is of the same form as eq. 2.11 in the previous discussion. The last two terms in the left hand side represent the streaming term, while the right hand side represents the collision term. In this form, it seems that the evolution of the distribution function is simple and solvable, but one must recall, as shown in the previous section, that the collision term is coupled to the rest of the system. Boltzmann made two basic assumptions in order to arrive at a closed form for the collision term. First, the system is assumed to be dilute such that only the two-particle collisions are important. Second, molecular chaos is assumed such that the particles that interact are uncorrelated both before and after the collision (i.e. \( f_2 = f_1(\mathbf{r}, \mathbf{p}_1, t)f_1(\mathbf{r}, \mathbf{p}_2, t) \) and \( f'_2 = f_1(\mathbf{r}, \mathbf{p}'_1, t)f_1(\mathbf{r}, \mathbf{p}'_2, t) \) when the two particles are outside a region of collision) [23]. Molecular chaos is
a key assumption in kinetic theory and is a reasonable assumption for a dilute gas with short-range interactions [24]. In a dilute gas, molecules spend most of its time streaming in space only to have short-lived interactions through collisions with other molecules [24]. With these two assumptions, the collision operator can be expressed in terms of the scattering cross-section \((d\sigma/d\Omega)\) of the two-particle collision

\[
\langle \frac{\partial f}{\partial t} \rangle_{\text{coll}} = \int d\mathbf{p}_2 d\Omega (\mathbf{p}_1 - \mathbf{p}_2) \frac{d\sigma}{d\Omega}(f'_{p_1} f'_{p_2} - f_{p_1} f_{p_2}),
\]

where \(f'_{p_i} = f(\mathbf{r}, \mathbf{p}'_i, t)\) and \(f_i = f(\mathbf{r}, \mathbf{p}_i, t)\). \(^1\)

To summarize, the assumptions made for the kinetic theory are as follows [20]: the molecules of the dilute gas are identical; the system is dilute such that only binary collisions are taken into account; the external boundaries of the system are ignored and the physical interaction of the particles with the walls are assumed to be elastic collisions; the effects of the external force are neglected in the collision; a local equilibrium is imposed such that the distribution function does not vary significantly in between the molecular collisions and over the spatial distance of the intermolecular forces; and molecular chaos is imposed (the molecules before collision are uncorrelated outside the range of interaction).

\(^1\)Refer to Statistical Mechanics by Kerson Huang [23] for a detailed derivation of the collision integral.
3. Methods

The fluctuating LBMD method that was used in this thesis is a package in the classical molecular dynamics (MD) simulator, LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [25, 26]. The lattice-Boltzmann method is embedded in LAMMPS in such a way that the forces on the particles due to an implicit fluid (and vice versa) are calculated and updated to the MD particle positions and velocities, while also solving the evolution of the fluid distribution functions with the MD interactions. This section provides an overview of the fluctuating LBMD and highlights some important differences with other similar methods.

3.1 Standard Lattice-Boltzmann Method

One problem with the Boltzmann equation is the intricate nature of the collision operator, as shown in the previous discussion. The Boltzmann equation may be approximated and simplified by using the Bhatnagar-Gross-Krook (BGK) collision operator for which the Boltzmann equation reduces to,

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{F}{m} \cdot \nabla v f = -\frac{1}{\tau} (f - f_{eq}), \tag{3.1}
\]

where \(f_{eq}\) is the local equilibrium distribution function. In the BGK approximation, the distribution function relaxes to a Maxwell-Boltzmann equilibrium distribution function \(f_{eq}\) with a corresponding single relaxation time scale \(\tau\).

The Maxwell-Boltzmann equilibrium distribution function,

\[
f_{eq}(\mathbf{u}) = \rho \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m u^2}{2 k_B T}}, \tag{3.2}
\]

can be obtained by solving for \(f\) in the Boltzmann transport eq. 2.17 for non-interacting particles and zero external forces [20].

The discretized form of the lattice Boltzmann equation in eq. 3.1 is

\[
f_i(x_a + e_i \Delta t, t + \Delta t) - f_i(x_a, t) = -\frac{\Delta t}{\tau} (f_i(x_a, t) - f_{eq}^i(x_a, t)) + W_i(x_a, t), \tag{3.3}
\]
Methods

where \( x \) is the coordinate position in the grid, \( e_i \) is the velocity vector expressed in units of the lattice speed\(^1\), \( W_i \) is the forcing term and \( \alpha \) denotes the Cartesian component of the vectors \([25]\). The equilibrium distribution functions \( f_i^{eq} \) are constrained to be consistent with the weighted expansion of the Maxwell-Boltzmann distribution function, and the forcing terms \( W_i \) are the corresponding derivatives in the LBE equation. With the equilibrium distributions chosen to be

\[
\sum_i f_i^{eq} = \rho, \tag{3.4}
\]
\[
\sum_i f_i^{eq} e_{i\alpha} = \rho u_{\alpha}, \tag{3.5}
\]
\[
\sum_i f_i^{eq} e_{i\alpha} e_{i\beta} = P_{\alpha\beta} + \rho u_{\alpha} u_{\beta}, \tag{3.6}
\]
\[
\sum_i W_i = 0, \tag{3.7}
\]
\[
\sum_i W_i e_{i\alpha} = F_{\alpha}, \tag{3.8}
\]
\[
\sum_i W_i e_{i\alpha} e_{i\beta} = u_{\alpha} F_{\beta} + F_{\alpha} u_{\beta}, \tag{3.9}
\]

a Chapman-Enskog expansion can be performed on the lattice Boltzmann equation (eq. 3.3) to recover the the Navier-Stokes equation \([27]\) with the viscosity

\[
\eta = \rho \left( \tau - \frac{\Delta t}{2} \right) \frac{v_c^2}{3}, \tag{3.10}
\]

where \( v_c = \Delta x / \Delta t \).

The distribution function at each lattice point is discretized according to the velocity vectors \( e_i \). For example, in a D3Q13 LB model \(^2\), the three-dimensional LB model has 13 unit velocity vectors (as illustrated in Fig. 3.1) and 13 distribution functions with moments that correspond to the local quantities such as fluid density and momentum density:

\[
\sum_i f_i = \rho, \tag{3.11}
\]
\[
\sum_i f_i e_i = \rho u. \tag{3.12}
\]

The distribution functions for each point in the grid are updated via eq. 3.3. To illustrate this, consider the D2Q9 model in Fig. 3.2. In the absence of collisions, external forces and thermal fluctutations \( i.e. \) RHS of eq. 3.3 is zero), only the streaming term is left. Hence, the distribution function spreads out to the neighboring lattice points except for the distribution function which corresponds

\(^1\)For the 15 velocity model D3Q19 (which was used in this thesis) \( e_i = v_c((0,0,0),(\pm 1,0,0),(0,\pm 1,0),(0,0,\pm 1),(\pm 1,\pm 1,0),(\pm 1,0,\pm 1),(0,\pm 1,\pm 1)) \), where \( v_c = \Delta x / \Delta t \) is the lattice speed. \([25]\)

\(^2\)The LB schemes are labelled as \( \text{D}NQ\text{M} \) where \( N \) is the number of dimensions of the system and \( M \) is the number of the discrete velocity vectors.
to the unit velocity vector \((0, 0, 0)\) after a time step \(\Delta t\). However, from eq. 3.3, the evolution of the distribution function involves a collision and a streaming process. Although the linear Boltzmann equation in eq. 3.3 with the BGK approximation was not derived from the continuum Boltzmann transport equation, the choice of the BGK operator is justified since the role of the collision operator is to relax the system towards equilibrium. With the linear Boltzmann equation in eq. 3.3, the Navier-Stokes equations, which describes the behavior of fluids, are recovered.

**Figure 3.1.** Illustration of the lattice vector in a D3Q15 grid.

**Figure 3.2.** Streaming process of a lattice node in a D2Q9 LB model. The initial distribution functions (a) "streams" out to the neighboring lattice points after a time step (b).

### 3.2 Thermal Lattice-Boltzmann Method

Thermal fluctuations are a necessary component in a fluid model to study systems in which Brownian motion of the particles is significant. The thermal fluctuations are integrated into the LBMD in the fluid model without adding stochastic forces on the MD particles [28]. This is done through the forcing term \(W_i = p_i + \xi_i\) (in eq. 3.3), which model the external forces \(p_i\) and the thermal fluctuations \(\xi_i\) in the fluid [28]. The forcing terms are constrained in such a way that the fluctuations generate local stresses that satisfy the fluctuation-dissipation relation. In the fluctuating LBMD, the fluid acts as a heat bath to
the MD particles and the desired fluid temperature is kept constant at all length scales in the system [25, 28].

### 3.3 Fluid-particle coupling

Coupled LBM and MD is a popular tool in studying polymer-solvent systems [27–30], colloids in binary solutions [31], DNA translocation [32], and charged colloidal systems [33, 34], to cite a few. The coupled LBM and MD is useful because it allows one to track the dynamics of colloidal particles without the need to calculate the equations of motion of all the fluid particles in the system.

**Other coupled LBMD methods**

In coupled LBM and MD methods, colloids are represented by MD particles (see Figure 3.3). The forces on the MD particles depend on the relative particle and fluid velocities, while the fluid velocities and the fluid masses are interpolated at the location of the MD particle.

![Figure 3.3](image)

**Figure 3.3.** Node representation of a spherical colloid in the lattice Boltzmann (LB) method and molecular dynamics (MD) hybrid. The nodes, which are evenly distributed on the surface of the colloid, interact with the fluid.

Lobaskin and Dünweg were the first to demonstrate that this approach can be done to quantitatively reproduce the physical dynamics of colloidal particles in the fluid [35]. In their *raspberry model*, the force on the colloid is given by

\[
\mathbf{F} = -\zeta (\mathbf{v} - \mathbf{u}) + \mathbf{f},
\]  

(3.13)

where \(\zeta\) is the bare friction coefficient, \(\mathbf{v}\) and \(\mathbf{u}\) are the velocities of the node and the fluid, respectively, and \(\mathbf{f}\) is a random force term that models thermal fluctuations with amplitudes that satisfy the fluctuation-dissipation theorem.
so that the particle has the correct temperature. This approach recovers the physical quantities of a particle through adjustable parameters.

**LAMMPS Thermal LBMD**

Ollila *et al.* improved on the raspberry model, ensuring that the fluid has the proper thermalization (as previously discussed in Section 3.2) and that the model has a consistent fluid-particle coupling scheme [25, 27, 36]. The fluid and the particles are coupled by adding forces that model an elastic collision. The MD particle of a specified mass $m_v$ and velocity $v$ interacts with a representative fluid “particle” with mass $m_u$ and velocities $u$ are interpolated at the location of the node. The applied force is calculated through energy and momentum conserving conditions and given by

$$F = -m_u m_v \frac{(v - u)}{m_u + m_v} \frac{\Delta t}{\Delta t} = -\zeta_{LBMD} (v - u). \quad (3.14)$$

![Figure 3.4. Schematic diagram of hydrodynamic drag measurement of a fixed colloid with respect to a fluid moving at velocity $v$.](image)

In the coupled LBM and MD method that was used, the fluid quantities such as the mass and velocity are interpolated using the trilinear stencil and Peskin stencil (Fig. 3.5). The Peskin stencil has a larger support for the interpolation of the fluid parameters than the Trilinear stencil. Each lattice point has a weighted contribution to the fluid-MD particle interaction (details of the weighting functions can be found in reference [25]), $F_\alpha = \zeta_{LBMD} (v - u)$ where $\alpha$ is an index that runs through the contributing nearest 8 and 64 grid points for the trilinear and Peskin interpolating schemes, respectively.

Drag test measurements of a fixed spherical particle in a fluid with a relative
methods

(a) Trilinear stencil  (b) Peskin stencil

Figure 3.5. Diagram of the interpolating stencils in the coupled LBMD method. The trilinear stencil interpolates the fluid mass and velocity from the eight nearest grid points of the MD particle (pink sphere) while the Peskin stencil interpolates the fluid quantities from 64 grid points\cite{25}.

velocity $v$ were made for varying area per node densities (see Figure 3.4). The trilinear stencil was observed to be unstable for high node-to-surface-area ratios. Hence, the Peskin interpolating stencil was employed throughout the study.

The mass of the colloid or the particle is specified by the user. Here, it is assumed that the mass density of the fluid and the mass density of the particle are the same. Hence, the individual node masses are fixed such that the total mass of the composite particle is equivalent to the mass of the fluid it occupies. Meanwhile, the representative fluid mass $m_u$ that interacts with the MD particle is set such that $m_u$ is equal to the interpolated fluid density times the volume of space occupied by the MD particle. With this particular coupling scheme, there is no need to guess parameters that will result in a good match to theory or experiments.

Another force coupling that can be used in the fluctuating LBMD, which was not used in this thesis, is a particle-fluid force given by $F = \gamma(v - u)$, where $\gamma$ is set by the user. This allows the user to artificially set the friction force coefficient of the colloid. Although this method offers versatility, it is not convenient to use when extended particles with complex shapes are studied.

Velocity boundary conditions

For a long time, fluid dynamics studies have relied on the assumption of a no-slip boundary condition (BC) where the fluid molecules at the fluid-solid interface are stationary. However, there has been no microscopic justification for this assumption \cite{38}. Fluid particles at the surface may have a non-zero velocity. Flows in micro- and nanochannels are affected by the velocity boundary
Figure 3.6. Navier model of slip in microchannels. The fluid velocity at the surface of the wall determines the velocity profile in the channel. In the Navier model, the slip length \( L_s \) is proportional to the slip velocity \( u_s \) through the shear rate \( \dot{\gamma}_s \) [37].

conditions at the walls. Factors that affect the BCs have been attributed to surface wettability, surface roughness, shear rate, and nanobubbles among others [38]. Figure 3.6 illustrates the Navier-model of slip in microchannels. In the Navier-model of slip, the slip-velocity \( u_s \), the fluid velocity at the bottom wall, is proportional to the slip length \( L_s \), by the shear rate \( \dot{\gamma}_s \) such that \( u_s = L_s \dot{\gamma}_s \). The slip-length \( L_s \) is the linear extrapolation for zero velocity (Fig. 3.6). A no-slip boundary condition would have \( L_s = 0 \) while a full-slip bound condition would have \( L_s = \infty \). The dynamics of colloidal particles is also affected by the velocity boundary conditions. While the Stokes-Einstein relation

\[
D = \frac{k_B T}{6\pi \eta R_H},
\]

applies to a diffusing no-slip colloid of hydrodynamic radius \( R_H \) in a fluid with viscosity of \( \eta \) and temperature \( T \), a slight modification can be made for colloidal particles with a partial or full-slip boundary condition by including a factor \( \gamma \) in the denominator \( (D = k_B T/(6\gamma \pi \eta R_H)) \) where \( 2/3 \leq \gamma < 1 \). \( \gamma = 2/3 \) and \( 2/3 < \gamma < 1 \) account for the full-slip and partial-slip conditions, respectively, while \( \gamma = 1 \) corresponds to the no-slip condition.

Two types of fluid boundary conditions can be set in the method: the no-slip and full-slip boundary conditions. This is done by imposing the bounce condition on both no-slip and full-slip BCs. The bounce condition models an impenetrable surface by imposing that the sum of the initial and final components of the relative velocity to zero. The no-slip condition is imposed by reversing the tangential relative velocity component, while, for the full-slip BC, the tangential components of the initial and final relative velocities are set to be equal (refer to

\[3\]The friction coefficient of a sphere with slip fluid boundary condition in Stokes flow is given by \( 4\pi \eta R_H \). Refer, for example, to reference [39] for the derivation.

\[4\]Full-slip boundary condition is not part of the current lattice-Boltzmann package in LAMMPS. The default boundary condition of the LBMD in LAMMPS is the no-slip BC, and the full-slip BC is implemented by modifying the code according to the geometry of the surface.
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Figure 3.7. Implementation of no-slip and full-slip velocity boundary conditions with arrows representing collisions between a surface node of the colloid and a fluid volume element.

In summary, the LBM uses a BGK collision operator in the Boltzmann equation which recovers the Navier-Stokes equations which describes the behavior of fluids. The thermal component in the model is designed in such a way that the local stresses satisfy the fluctuation-dissipation relation. Thus, as expected, the thermal LBMD is successful in modeling particles in a fluid with and without thermal fluctuations.

Colloid Node Representation

In using coupled LBM and MD methods, it is important that the nodes which represent the colloids of regular and irregular shapes must be evenly distributed on the surface. For the simulation of spheres and clusters of fused spheres, the nodes are distributed on the coordinates of a 320-fullerene [40]. Spheres with larger number of nodes are generated from the coordinates of isomers of fullerenes [40] and coordinates of the pixelized points generated by an icosahedron-based method in reference [41]. For helical particles (as shown in Figure 3.9), the nodes are systematically distributed on the surface such that each node is roughly equidistant with its neighboring nodes.

Using the consistent fluid-particle coupling described in the previous section, the hydrodynamic drag force is observed to be independent of the node per unit surface area, as shown in the drag force results in Figure 3.8.

Molecular Dynamics

The other component of the fluctuating LBMD is the molecular dynamics part of the method which is implemented in LAMMPS [26]. Molecular dynamics is
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\[
\frac{\text{Force}}{(\gamma \dot{c} \rho V)} = \begin{cases} 
0 & \text{no-slip fluid--colloid boundary condition} \\
\text{full-slip fluid--colloid boundary condition} & \gamma_{\text{no-slip}} = 1, \gamma_{\text{full-slip}} = \frac{2}{3}
\end{cases}
\]

**Figure 3.8.** Hydrodynamic drag of a fixed sphere of radius \( R = 2.718 \) nm in a fluid with relative velocity \( v \) and viscosity \( \eta \) for varying number of nodes.

**Figure 3.9.** Node representation of helical particles in a fluid (green). The arrows show a section of the surrounding fluid velocities, while the white helical curve traces the center-of-mass trajectory of the helix.

...a widely used simulation method for studying the dynamics of an ensemble of particles in a fluid or solid state. The implementation of the method is rather simple because each MD particle obeys Newton’s equation of motion:

\[
F_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2},
\]

(3.16)

where \( F_i \) is the force on particle \( i \) with mass \( m_i \) and coordinate \( \mathbf{r}_i \). The force on the MD particle \( i \) may arise from applied external potentials and interactions with other particles in the system or, in the case of the fluctuating LBMD, from the coarse-grained fluid. The trajectories of rigid particles are integrated in such a way that the total force and torque on the constituent nodes or MD particles of the rigid particle is calculated. The rigid body moves as one entity according to the total force and torque on it.
4. Diffusive Systems

Brownian motion is the random motion of large particles in a fluid comprised of much smaller solvent particles. The term was named after Robert Brown, a biologist, who discovered the phenomena while observing pollen suspended in a fluid under a microscope. He initially thought that since the pollen particles were from a living organism, the motion was due to the active motion of the biological specimen. He ruled out this possibility when he observed a similar behavior in many inorganic particles of varying sizes and shapes [42, 43]. The phenomenon was unexplained until 78 years later, when Einstein formulated a theory for the stochastic motion of solute particles in a solvent [44].

4.1 Brownian motion

Consider an isothermal system with a volume $V$, side length of $L$, and cross-sectional area $A$ as shown in Figure 4.1. A higher concentration of solute particles is found in the left side of the vessel at $t = 0$. $N$ Brownian particles are
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located at \((x, x + \Delta x)\). Due to the collision of the solute particles with the solvent particles, the large particles will diffuse in the fluid, leading to a net transfer of particles from the region of higher concentration \((0, x)\) to the region of lower concentration \((x + \Delta x, L)\). The driving force for this process is attributed to osmotic pressure. To calculate the osmotic force \(F\) on the \(N\) Brownian particles within the volume element \(V\) for \((x, x + \Delta x)\), consider the pressure differences at the surfaces \(A_1\) and \(A_2\) for \(A_1 = A_2 = A\):

\[
P(x) - P(x + \Delta x) = \frac{NF}{A}. \tag{4.1}
\]

As \(\Delta x \to 0\),

\[
\frac{\partial P}{\partial x} = -CF, \tag{4.2}
\]

where \(C = N/V\) is the number density. The system of \(N\) Brownian particles in the volume \(V\) satisfies the equation of state

\[
PV = Nk_B T, \tag{4.3}
\]

where \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature. Differentiating eq. 4.3 with respect to \(x\) and using the relation in eq. 4.2, a linear differential equation for the number density is obtained:

\[
\frac{k_B T}{V} \frac{\partial N}{\partial x} = k_B T \frac{\partial C}{\partial x} = -CF. \tag{4.4}
\]

By Fick’s law of diffusion,

\[
C_v = -D \frac{\partial C}{\partial x}, \tag{4.5}
\]

which states that the solute flux \(C_v\) is proportional to the concentration gradient, with a constant of proportionality \(D\) as the diffusion coefficient. Eq.4.4 reduces to

\[
 \frac{k_B T v}{D} = F. \tag{4.6}
\]

At equilibrium, the osmotic force \(F\) on each Brownian particle is counteracted by the hydrodynamic drag \(F_D = \kappa v\) where \(v\) is the particle speed and \(\kappa\) is the frictional coefficient. For spherical particles of radius \(R\) in a fluid of viscosity \(\eta\), this frictional coefficient is \(\kappa = 6\pi\eta R\). This hydrodynamic drag is known as Stokes’ drag, \(F_D = 6\pi\eta R v\). Using the equilibrium condition, \(F = F_D\), the Stokes-Einstein relation is obtained

\[
D = \frac{k_B T}{F_D} = \frac{k_B T}{\gamma 6\pi\eta R^2}. \tag{4.7}
\]

Here, the factor \(\gamma\) was included to account for the velocity boundary conditions: \(\gamma = 1\) for the no-slip BC and \(\gamma = 2/3\) for the full-slip BC.
4.2 Cluster diffusion

The diffusion of single-particle spheres and fused spheres (Figure 4.2) in a fluid with the parameters of water at $T = 300$ K was simulated in a cubic box with periodic boundaries and side length $L$. A 320-icosahedron was used to model the surface of the spheres and fused spheres.

In order to obtain the diffusion coefficient (DC) from the simulations, the center-of-mass displacements $\mathbf{r}(t)$ were tracked. The DCs for a given system length are then calculated through the relation

$$D = \lim_{\Delta t \to \infty} \frac{\langle |\mathbf{r}(t + \Delta t) - \mathbf{r}(t)|^2 \rangle}{2N_D \Delta t},$$

where $N_D$ is the number of translational degrees of freedom.

4.2.1 Finite size effects

Finite size effects are present in the simulations because the diffusing particle interacts hydrodynamically with its periodic images; this is typically observed in models that incorporate full hydrodynamics [28, 35, 45–48]. Unlike the single sphere in Stokes’ flow, which has a drag force of $6\pi \eta R v$, a simple cubic array of spheres with an inter-particle distance of $L$ has a reduced drag [49],

$$F_D = \frac{6\pi \eta R v}{1 - B \frac{R}{L}},$$

where $B = \frac{R}{L}$ and $L$ is the lattice spacing.

---

\footnote{LB lattice discretization, with MD timestep $\Delta x = 1.2$ nm and $\Delta t = 2.25 \times 10^{-4}$ ns and fluid viscosity 1 cP.}
where $B = 2.8373$. Including the correction to the frictional coefficient in diffusing particles in the periodic system, the DC is given by

$$D(L) = \frac{k_B T}{\gamma 6 \pi \eta} \left( \frac{1}{R_H} - \frac{B}{L} \right). \tag{4.10}$$

![Graph](image)

**Figure 4.3.** Variation of diffusivities of single particle colloidal nanoclusters in Figure 4.2 for the (a) no-slip and (b) full-slip velocity boundary conditions a periodic cubic simulation domain with length $L$. The values of $B = 2.835 \pm 0.025$ and $B = 2.882 \pm 0.045$ obtained for the no-slip and full-slip velocity boundary conditions respectively are close to the theoretical prediction of $B = 2.8373$ [49].

The single-particle diffusion coefficient of nanosized monomers and fused monomers for varying system-sizes are in good agreement with eq. 4.10, as shown in Figure 4.2. Additionally, the $B$ values in eq. 4.10 are close to the theoretical prediction of $B = 2.8373$, with $B = 2.835 \pm 0.025$ and $B = 2.882 \pm 0.045$ for no-slip and full-slip velocity boundary conditions, respectively [49].

The values for the diffusion coefficient are then extrapolated for $R/L \to \infty$. The measured effective radius or the hydrodynamic radii, $R_H$, obtained from the diffusion coefficient calculations were slightly larger (by 0.7 nm) than the effective sizes of the clusters. Nevertheless, the fluid model recovers a consistent hydrodynamic radius without any adjustable parameters.
4.2.2 Comparison with other models and experiments

In principle, the diffusion tensor (which is proportional to the inverse of the resistance tensor) of colloids with complex shapes can be obtained using bead models [50, 51]. In this model, the resistance tensor is calculated from truncated hydrodynamic interactions by setting the friction coefficients of each bead in the composite particle. Again, through adjustable parameters, one can recover good agreement with theory or experiment but, under these conditions, one cannot make quantitative predictions about the dynamics of a complex shape without the help of experimental or theoretical values.

Thus, these truncated many-body hydrodynamic interaction methods require adjustable parameters to obtain the experimental colloidal diffusivities. Being able to adjust the friction coefficients of the individual beads in a composite particle so as to recover either the experimental or theoretical result may be useful in some circumstances, but making quantitative predictions will be impossible in some variants of bead models.

![Figure 4.4](image_url)

Figure 4.4. Normalized diffusion coefficients of colloidal fused spherical colloidal clusters from the LBMD simulations and from the experiments. The bare radius of the fused spheres are given by $R$.

In reference [52], Hoffmann and colleagues report the diffusion coefficients of nanoparticle clusters with spherical building blocks and compare it with the theoretical expressions for ellipsoids [53] and with the shell model [50, 51]. Both provided excellent agreement with the experiment, but required adjustable parameters, such as approximate geometrical ratios for the former and friction coefficients of bead radii for the shell models for the latter. Meanwhile, the colloidal diffusivities of the smaller submicron clusters using the LBMD method gave good qualitative agreement with the experiments (see Figure 4.4). A difference of $\sim 0.7$ nm between the hydrodynamic radius obtained from the
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diffusion simulations and the bare radius is attributed to the LBMD resolution that was used. Thus, the results are much closer to the experimental values when the particle size increases because of the increase in the resolution, as shown in Figure 4.5.

![Figure 4.5](image)

**Figure 4.5.** Diffusion coefficient from the simulations of the fused clusters normalized by the Stokes-Einstein diffusion coefficient. The monomers in the clusters have bare radii 2.718, 4.330, and 7.210 nm.

### 4.2.3 Continuum limit

In the limit of a large number $N$ of spherical monomers in an aggregate, the hydrodynamic scaling for the diffusion coefficients should be $D_N/D_1 = 1/N^{1/3}$ by using volume arguments. Brownian clusters with a large number of aggregates were simulated using Brownian Dynamics with the Yamagawa-Rotne-Prager tensor (BD-YRP) method, stochastic rotational dynamics (SRD) method, Brownian dynamics, and LBMD. In the BD-YRP, each colloidal particle in the aggregate experiences random forces, representing Brownian dynamics, with a constant of friction given by $6\pi \eta R$. The hydrodynamics are included in the simulation through the Yamakawa-Rotne-Prager tensor, which dictates the resulting friction due to the colloid-colloid hydrodynamic interactions [54]. The stochastic rotational dynamics method is also a coarse-grained fluid model where the solvent consists of explicit MD particles that capture the macroscopic Navier-Stokes equations [54, 55]. With the Brownian dynamics without the hydrodynamic interactions, the scaling is given by $1/N$, as expected. BD-YRP and LBMD, meanwhile, captured the proper scaling of $D_N/D_1$ in the continuum limit.
Remarks

From the diffusion coefficients obtained in the simulations, one is able to obtain a value for the hydrodynamic radius of the colloidal particle which is close to the theoretical values. Although an increase in the resolution, particle size, and lattice spacing ratio would provide better accuracy, what is useful in this method is that the Brownian motion of the particle is applied in a consistent way without the need for adjustable parameters. Thus, LBMD can be utilized in studies where the strengths of thermal fluctuations and driving forces are compared.
5. Externally Driven Systems

The past decade has seen substantial development in the field of micro- and nanomotors, due to the advances in nanoscale fabrication techniques like glancing angle deposition and direct laser writing [56]. Micro- and nanomotors can be used for targeted delivery, wherein ease of spatial and temporal control of the motors are desirable. At the micron scale, two types of motors are being investigated: catalytic motors and magnetic propellers. Catalytic micromotors are driven by chemical gradients generated from chemical reactions on the anisotropic surface of the particle. These micromotors can be guided magnetically or chemically; however, they require fuels that are typically bio-incompatible like hydrogen peroxide, or acidic or alkaline solutions [57]. Thus, research on catalytic micromotors has shifted towards the fabrication of propellers that can propel at significant speeds using low fuel concentrations [57–59] or bio-compatible fuels [60–66]. On the other hand, unlike the self-autonomous propulsion of catalytic micromotors, magnetic micro- and nanopropellers rely on external driving from a rotating magnetic field. Hence, they do not require fuel for propulsion, making them suitable candidates for \textit{in vivo} applications.

5.1 Propulsion of Helices

The macroscopic mass and momentum conservation equations for an isothermal and compressible fluid, or otherwise known as the Navier-Stokes equations, are given by

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (5.1)
\]

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla P + \mathbf{F} + \eta \nabla^2 \mathbf{u}. \quad (5.2)
\]

A scaling of \( r' = r/L, \ u' = u/U, \ t' = tU/L \) and \( P' = \rho P L/\eta U \) can be made for creeping flows with characteristic velocity of \( U \) and length of \( L \) on eq. 5.2 to
obtain the dimensionless Navier-Stokes equation

$$\frac{\rho UL}{\eta} \left( \rho \frac{\partial u}{\partial t} + \rho u \cdot \nabla u \right) = \left( -\nabla P + F + \nabla^2 u \right). \quad (5.3)$$

For length scales that are in the order of magnitude of a micrometer or smaller in an aqueous fluid like water, with $\eta = 10^{-3}$ mPa s and $\rho = 1.0 \times 10^3$ kg/m$^3$, the inertial terms become insignificant because of the factor $Re = \rho UL/\eta$ on the left hand side. This factor is called the Reynolds number. At zero Reynolds number, the remaining terms are the pressure force, the external force, and the viscous force. The dynamics of simple surfaces such as spheres and ellipsoids for a given external force and torque are exactly solvable for $Re = 0$ [53]. However, for objects with complex shapes, analytical solutions are difficult to obtain, even if the Stokes equation (eq. 5.3 for $Re = 0$) is simpler than the full Navier-Stokes equations. Since the inertial terms have no contribution to the dynamics, we are guided by the fact that the external force is linear with the motion. To be more precise, the external force and torque are linear with the velocity and angular velocity of the body, respectively. This linear behavior does not necessarily mean that the directions of the forces and the motion are the same, however. Hence, a general expression that captures the relationship of the forces with the motion is given by [16, 67]

$$\begin{pmatrix} F \\ \tau \end{pmatrix} = \begin{pmatrix} \xi_{TT} & \xi_{TR} \\ \xi_{RT} & \xi_{RR} \end{pmatrix} \begin{pmatrix} v \\ \omega \end{pmatrix}, \quad (5.4)$$

where the tensor in the right side of the equation can be simplified for different kinds of symmetry (e.g. spherically symmetric particles would have zero non-diagonal terms, while helical particles would have non-zero non-diagonal terms with $\xi_{TR} = \xi_{RT}$). This means that the translational and rotational terms are coupled. The direction of the torque, therefore, depends on the handedness or the helicity of the particle (i.e. a left-handed helix (right-handed helix) will translate in the negative (positive) direction when a positive torque is applied).

The resistive force theory and slender body theory can be used to calculate the propulsive thrust from the rotational motion of helices. The resistive force theory works by assuming that the segments of the helices do not influence the motion of the other segments of the helices through hydrodynamic interactions while the hydrodynamic drag on the infinitesimal segment is assumed to be proportional to the local body velocity [68]. Evidently, the main weakness of the resistive force theory lies in the neglect of the hydrodynamic interactions. The slender body theory incorporates these hydrodynamic interactions by considering the fluid response from each helical segment [68–72]. The helical segments are represented by Stokeslets that are distributed along the helical body [68–72]. Helical propulsion can be studied through the slender body theory but
the analyses is limited only to microscale low Reynolds number regime where thermal fluctuations can be ignored.

5.1.1 Shape optimizations

![Graph](image)

**Figure 5.1.** Propulsion and swimming efficiencies of helices as a function of the number of turns.

Helical particles, similar to the one shown in Figure 3.9, were driven with a constant torque along the direction of the long axis’ initial orientation. As the helix rotates in the fluid, a non-zero displacement along its long axis is observed, with the translational displacements at constant torques dependent on the shape. Helices with more turns experience more drag and, thus, the propulsion is expected to decrease as the number of turns increase. However, we also find that helices with less than a full turn wobbled as these rotated and translated due to the helical asymmetry. Figure 5.2 shows the displacements with respect to time of helices with $N = 0.5$ and $N = 1.25$ turns at varying torque strengths. The wobbling of the $N = 0.5$ helix is exhibited by the periodic forward and backward motion with a non-zero net displacement. At higher torque strengths, it is clear that helices with less than a full turn can propel (See Figure 5.2b), while helices with stable rotation ($N > 1$) had a constant propulsion velocity.

The optimal values for propulsion and swimming efficiency—which we defined
as $\epsilon = v/(\omega R)$ where $v$, $\omega$ and $R$ are the propulsion velocity, angular velocity and helical radius—are reported in Publication II. We find that achieving the optimal propulsion and swimming efficiency is a balance between achieving stability in motion, from having a sufficient number of turns, and minimizing drag (See Figure 5.1).

### 5.2 Magnetic driving

The propulsion of magnetic helices with a magnetization $\mathbf{M}$, as shown in Figure 5.3b, is driven by the interaction of the magnetic field $\mathbf{B}$. Ideally, the magnetization $\mathbf{M}$ is uniform and perpendicular to the nanopropeller’s easy axis of rotation. The resulting interaction is given by $\tau = \mathbf{M} \times \mathbf{B}$. When the magnetic field rotates on a plane perpendicular to the long axis, a stable rotation along the long axis
is observed which drives the propulsion through the coupled translational and rotational motion.

![Figure 5.3](image_url)

**Figure 5.3.** (a) Scanning electron microscope image of magnetic propeller in the experiments [73]. (b) Schematic diagram of the helix that was simulated using the LBMD method. The magnetic field is rotated about a plane perpendicular to the long-axis of the helix. Image in (a) reprinted with permission from *Optimal Length of Low Reynolds Number Nanopropellers*. D. Walker, M. Kübler, K. I. Morozov, P. Fischer, and A. M. Leshansky. *Nano Letters*. 2015 15 (7), 4412-4416

![Figure 5.4](image_url)

**Figure 5.4.** External torque on a helix without attached cargo due to the interaction between the magnetic moment and the external magnetic field. (b) Phase difference between the magnetic moment of a helix and the magnetic field for the step-out frequency $f_{SO} = (149 \pm 3) \times 10^4$ Hz.

In the simulations, the magnetization and the magnetic field are initially
aligned; as the magnetic field rotates with a frequency of \( f \), the torque from the interaction increases from zero up to a certain value if the magnetic frequency is below a certain threshold, as shown in Figure 5.4a. Figure A.I in the Appendix A, meanwhile, shows the alignment of the magnetization and the magnetic field in the synchronous regime. For helices with geometries optimized for propulsion, there was minimal wobbling from the magnetic torque when the torques were applied along the long axis. At steady state, the external torque and the hydrodynamic drag are equal; thus,

\[
f \kappa_\parallel = |M||B| \sin \theta,
\]

where \( \kappa_\parallel \) is the viscous rotational drag and \( \theta \) is the phase difference between the magnetization and the magnetic field. Maximum torque is achieved at a certain frequency called the step-out frequency

\[
f_{SO} = \frac{|M||B|}{\kappa_\parallel}.
\]

The synchronous regime is characterized by \( f \leq f_{SO} \). Here, the phase difference of the magnetization and the magnetic field are constant. One can see in Figures 5.4b and A.I that the alignments of the magnetic field and the magnetization have a constant phase. Beyond the step-out frequency is the asynchronous regime, \( f > f_{SO} \), where the helix undergoes a complicated damped and driven dynamics as demonstrated in Figure A.II and 5.4a. In particular, we see in Figure 5.4b that, at the asynchronous regime, the phase difference “steps-out” of \( \pi/2 \). Consequently, the torques vary periodically for frequencies beyond the step-out frequency.

### 5.2.1 Propulsion velocities

![Figure 5.5. Propulsion velocities of helices driven at \( MB = 1.5 \times 10^{-18} \text{ Nm} \) (triangles) and \( MB = 2.0 \times 10^{-18} \text{ Nm} \) (circles). The blue and red vertical lines mark the step-out frequency for the operating magnetic field interactions, \( MB \). The corresponding Péclet numbers for a given propulsion velocity are marked on the \( y \)-axis on the right side.](image-url)
At steady-state and for $f < f_{SO}$, since the angular frequency of the rotation matches the field frequency, field frequency is linear with the propulsion velocity (see Figure 5.5). Here, the propulsion velocities are easily adjusted by the field frequencies, but this is limited by the step-out frequency. To achieve greater propulsive strengths, therefore, either the field strength interaction should be increased or the viscous rotational drag should be decreased (eq. 5.6) The latter is accomplished by fabricating helices with geometries that optimize propulsion. Figure 5.6 shows a plot of the propulsive velocities of helices with and without attached cargo for a magnetic interaction of $MB = 2.0 \times 10^{-18}$ Nm. The addition of cargo, which was chosen to have an ellipsoidal shape that minimizes the drag, increases the rotational viscous drag without increasing its propulsive efficiency. As expected, the step-out frequency is smaller for the helix with cargo than for the helix without cargo. Moreover, since there is greater drag, the propulsion velocities are remarkably smaller for the one with the attached cargo.

Thus, the ease of tuning the propulsion velocities by varying the field frequencies makes the magnetic micro- and nanopropellers a more suitable candidate for in vivo applications, especially since the propulsion speed of catalytic propellers is controlled by the (typically bio-incompatible) fuel concentration in the fluid.
that steering is possible even for nanoscale helices.

5.2.2 Thermal Effects

At the nanoscale, thermal effects can diminish spatial and temporal control. In order to determine whether Brownian motion will dominate the dynamics of the driving of nanohelices, it is important to compare the diffusive and propulsive timescales.

**Péclet number**

The Péclet number (Pe) is the ratio of the diffusive and propulsive time scales. This dimensionless number is typically used in the context of mixing in microfluidics. A simple micro-channel with a T-junction (Figure 5.7) mixes two different solutions at laminar flows (or at low Reynolds number) through diffusion alone. While fast diffusive mixing may or may not be desirable depending on the application, control of the dispersion of the fluids is useful for all applications. The length $L$ (Figure 5.7) along the channel for which the fluid would be homogenous through passive diffusive mixing is given by $L \propto u w^2 / D = w Pe$, where $u$ is the speed of the fluids in the channel and $w$ is the width of the channel.

![Figure 5.7](image)

**Figure 5.7.** Laminar fluid mixing in microfluidic channels. For the two fluids to be homogenous through passive diffusive mixing, the characteristic length $L$ is related to the Péclet number by $L / w \sim (u w^2 / D) = Pe$, where $u$ is the fluid velocity and $D$ is the diffusion coefficient of the solute particles.

For nanoscale helical propulsion, the Péclet number may be used to quantify the strength of the driving over the thermal effects: $Pe > 1$ indicates that the external driving is greater than the random forces due to the thermal fluctuations, while $Pe < 1$ indicates that Brownian motion dominates the external driving. The rotational and translational Péclet numbers are $Pe_R = \omega / D_R$ and $Pe_T = v L / D_T$, respectively, where $\omega$ is the angular frequency of the field, $v$ is the propulsion velocity in the absence of thermal fluctuations, and $L$ is the characteristic length of the helix.

In Publication II, we show how thermal fluctuations can interfere with the
direction of the propulsion of the helices. As discussed, the handedness of the helix dictates the direction of the propulsion with respect to the external applied torque; however, when the translational Péclet number is greater than 12, the direction of the propulsion is consistent with its handedness. While the experimental steering of nanomotors (helical radius of 35 nm) in viscoelastic media has been successful [18], this has not been the case for fluids with viscosities that are close to that of the viscosity of water. In Publication III, the steering of nanohelices in an aqueous fluid has been demonstrated. Trajectories of steering with 45° and 90° turns are shown in Figure 5.9, with the diffusive spreading plotted against the steering with and without thermal fluctuations. The possible effects of thermal fluctuations on the propulsion and steering of nanohelices are as follows: (1) interference with the induced rotation and propulsion, (2) alteration of the direction of motion, and (3) hindrance of spatial control. (1) can be overcome by ensuring that the rotational and Péclet numbers are much larger than unity (in our simulations, it was > 100). When the rotational and translational Péclet numbers are greater than unity, this also means that the magnetic interaction is stronger than thermal effects (\(MB > k_B T\)), such that the magnetization will always tend to follow the rotating magnetic field and consequently preventing (2). Lastly, Brownian motion (3) is unavoidable, but it can be mitigated by ensuring that velocity of the helix should be larger than \(6D_T L/R_0^2\), where \(R_0\) is the radius of diffusive spreading.

In Publication III we report the protocols for changing the direction of the helices. To summarize, in addition to driving the helices at high Péclet numbers, it is also important to keep the magnetic interaction in the synchronous regime. This is done by applying gradual changes in the direction of the field. Changing the direction of propulsion with abrupt changes in the direction of the fields
will force the helix to rotate about an axis perpendicular to its long axis, which causes the helix to have large jumps in displacement (see Publication III).

It is crucial to compare the simulation results with the experiments and the conditions that were set to achieve controlled propulsion and steering. Here we have used field strengths of $MB = (1.5 - 2.5) \times 10^{-18}$ Nm. The state-of-the-art helices have a magnetization of $2 \times 10^{-14}$ emu [18]. Therefore, the magnitude of the rotating field should be 75 – 125 mT, which is about 10 times stronger than the magnetic fields in the experiments. We also note that the fastest micropropellers that have been developed so far have propulsion speeds $\sim 40 \mu m/s$ [74]. Scaling down the size of the helices provides access to higher speeds, and thus providing spatial- and temporal control in the presence of thermal fluctuations.
Remarks

We conclude that if the magnetic fields are driven at the specified field strengths and frequencies, nanohelices would be excellent nanopropellers for targeted nanoscale delivery applications.
6. Future outlook: Self-driven systems

The low Reynolds number regime was discussed in Section 5.1, wherein it was mentioned there that inertial effects are insignificant at that scale. Additionally, at zero Reynolds number, the dynamics are time-independent. This presents a different set of challenges for autonomous locomotion, because time-symmetric motion will result in a zero net displacement. In this environment, it is thus important for microorganisms to develop swimming strategies that are optimized for escaping predators and maximizing swimming efficiency with limited resources. In nature, for example, *Borrelia burgdorferi* has flagella within its inner and outer cellular membrane that rotate and cause undulations along its cellular body [75], a sperm cell has a single flagellum that performs periodic sinusoidal patters that propel it, *Chlamydomonas reinhardtii* has a pair of flagella that move in an anti-symmetric "breast-stroke" fashion for propulsion [76], and star fish larvae have cilia that generate vortices that allow them to feed and swim [77]. In the interest of building micro- and nanomachines that are capable of autonomous movement, therefore, it would be advantageous to exploit the salient strategies for locomotion that nature has streamlined through eons of evolution.

This chapter presents preliminary work on simulating microswimmers that have thin movable parts that model autonomous motion using the coupled lattice Boltzmann and molecular dynamics (LBMD) method, and recommendations for future objectives concerning this work.

**Modeling flagellar swimming**

Tiny hair-like structures like cilia and flagella are some of the most ancient cellular structures that provide motility to prokaryotic and eukaryotic cells in aqueous environments [79]. The inner structure of the flagella is composed of a set of nine pairs of microtubules (doublet microtubules) surrounding a central
Future Outlook

Figure 6.1. (a) Cross-sectional diagram of a flagellum courtesy of [78] (b) Triangular crane-like structure of the flagellum model. Adjacent nodes interact through harmonic bonds. The equilibrium distances of the harmonic bonds (represented by grey links) are fixed, while the equilibrium distances of outer bonds (represented by orange links) vary periodically to bend the flagellum.

Microtubule pair (see Figure 6.1a). Microtubules have dynein arms that attach to the adjacent doublet microtubules. The bending motion of the flagella is a result of two doublet microtubules sliding past each other by way of the dynein arm “walking” on the adjacent microtubule [78, 80, 81]. The central doublet is believed to control the activation of the surrounding dyneins.

In order to model the bending motion of the flagellum, a structure that can replicate the mechanical bending is needed. Elgeti and co-workers have successfully modeled the swimming motion of sperm by using a crane-like structure to model the flagellum [82, 83]. In our model, we add a central node to the triangular crane for added support and added control of the bending angle of the central nodes. The connecting links between the adjacent nodes in Figure 6.1b represent harmonic bonds

$$U_{\text{harmonic}} = E(r - r_0)^2,$$

where $r$ is the distance between the nodes and $r_0$ is the equilibrium distance. The equilibrium distances are kept constant for all connecting links, except for the outer links (in orange) in the figure. The equilibrium distances are varied periodically. The cell body is assumed to be a rigid structure and the flagellum is flexible and able to move freely. The nodes which interact with the fluid are the surface nodes of the cell body and the three outer nodes in the crane model. Since Brownian motion does not play a major role in the dynamics for large systems, the thermal fluctuations are not included in the model.
Spermatozoa model

![Figure 6.2](image)

**Figure 6.2.** Node representation of a sperm cell in the LBMD method.

Spermatozoon is a reproductive cell with a single flagellum that it uses to navigate in fluid. The undulations of the flagellum resemble a travelling wave; this can take the form of a three-dimensional wave which looks like a helix, a two-dimensional wave, or a planar wave. We simplify the model by implementing a pattern that resembles a planar wave.

Here, the cell body of the sperm has a radius of 3 \( \mu m \) and the flagellum has a length of \( L_F = 80 \mu m \). The central nodes and outer nodes of the flagellum have a separation of \( r_0 = 1 \mu m \). To implement a travelling wave on the flagellum that is constrained on a plane, the equilibrium distance \( r'_0 \) of one edge of the outer nodes is varied periodically such that

\[
r'_0(s, t) = r_0 - A \sin(ks - 2\pi t/T),
\]

where \( s \) is the \( s \)th central node bead of the flagellum from the cell head, \( k = 2\pi/L_F \), \( T \) is the period of the beat frequency, and \( A = 0.08 \mu m \). The stiffness \( E \) from the harmonic bonds (eq. 6.1) is kept at \( E = 100k_B T \) in units of J/m\(^2\).

The equilibrium distance of the outer nodes were tested for \( r'_0(s, t) \) in eq. 6.2, but did not result in significant net displacements of the center-of-mass (COM) of the cell head. On the other hand, \( r'_0(s, t) = r_0 - A(\sin(ks - 2\pi t/T) + \sin(ks - 4\pi t/T)) \) resulted in a cell head COM shown in Figure 6.3.
Figure 6.3. Center-of-mass position of the cell head of a sperm with the flagellum bending in such a way that a wave travels along the tail. For one edge of the outer nodes in the flagellum, the equilibrium bond distances are varied as $r'_0(s,t) = r_0 - A(\sin(ks - 2\pi t/T) + \sin(ks - 4\pi t/T))$.

Figure 6.4. Node representation of the *Chlamydomonas reinhardtii*. 

**Chlamydomonas reinhardtii**

*Chlamydomonas reinhardtii* is a unicellular green alga which has two flagella as shown in Figure 6.4. This organism performs “breast-strokes” which are characterized by an anti-symmetric beat pattern that can either be synchronous or asynchronous. The synchronous beat pattern causes a bi-directional motion that typically results in a non-zero net displacement. Unlike the helical or sinusoidal trajectories of the sperm, the motion of *Chlamydomonas reinhardtii* is rather straight, unless asynchronous beat patterns are made to change its swimming direction [84]. Here, we simulate the anti-symmetric synchronous
beat pattern of the flagella. For the beat patterns to be time-asymmetric, the swimming stroke of the organism should maximize the force that it imparts on the fluid to pull its body forward. After the swimming stroke, the flagella should return to the unbent position, minimizing the drag that would push the body backward. It is with this series of motions that we obtain the COM displacement shown in Figure 6.5.

![Figure 6.5](image)

**Figure 6.5.** Center-of-mass position of the cell head of *Chlamydomonas reinhardtii* performing a synchronous “breast-stroke” swimming.

**Recommendations for future objectives**

The preliminary work establishes that the LBMD can be used for modeling the swimming of biological microorganisms. There are, however, several issues concerning the motion of the sperm in the LBMD. Imposing a wave pattern in eq. 6.2 does not provide significant non-zero displacements even if the generated wave pattern is non-symmetric with time. It should be investigated if it is due to the cell head to flagellar length ratio or if it is the wave curvature or amplitude $A_0$ that will provide better agreement with the sperm movement. Elgeti et al. used stochastic rotation dynamics (SRD) to model the swimming of a sperm and they were able replicate the circular, planar sinusoidal and helical trajectories of sperm in the bulk [82] and we expect that the LBMD to capture this swimming behavior as well. Sperm and *Chlamydomonas reinhardtii* generally perform different beat patterns for swimming. For building microrobots with self-autonomous propulsion, it is useful to understand what kind of beat patterns generated by the flagella result in optimal swimming efficiencies and changing directions using the LBMD.
7. Conclusions

This thesis has focused on diffusive and driven dynamics of particles in regimes where thermal fluctuations play a major role. To this end, a simulation method that models accurately the hydrodynamics and thermal fluctuations, a fluctuating lattice Boltzmann and molecular dynamics method (LBMD), was chosen. With this method, we first studied the diffusion of nanoscale particles and verified that colloidal particles with complex shapes can be simulated with the fluctuating LBMD. Then, we modeled the propulsion and steering of magnetic helices in the presence of thermal fluctuations. Lastly, we provided an outlook of the use of the LBMD for modeling swimming of biological microorganisms at low Reynolds number.

In Publication I, nanosized spheres, fused spheres, and colloidal aggregates were simulated using the LBMD method, and the results of no-slip and full-slip boundary conditions were compared with the theory. The diffusion coefficients of fused spheres were found to be in good agreement with the experiment. In addition, the method recovered the diffusion coefficients of colloidal aggregates at the continuum limit.

In Publication II, the coupled translational and rotational motion of helices was investigated. The shape- and size-dependent optimal propulsion and swimming efficiencies (defined as the ratio between the propulsion velocity and the angular velocity) were obtained by applying a constant torque along the long axis of rotation of the helix. However, since the helices with less than a full turn have unstable rotational motion due to helical asymmetry, the propulsion is also unstable. On the other hand, while stable rotation is achieved for turns more than unity, an increase in the number of turns contributes to additional translational and rotational drag. Thus, optimal propulsion is achieved through a balance between increasing the number of turns and minimizing the drag effects.

In Publication III, the optimal geometries were used to model the propulsion
of magnetic helices that are driven by an external rotating field. The linear dependence of the propulsion on the field frequencies is consistent with the experiments. However, for driven helices, thermal fluctuations can (1) interfere with the induced rotation and interfere with the propulsion, (2) alter the direction of motion, and (3) hinder spatial control through Brownian motion. Driving at frequencies of the order of $10^4$ Hz addresses (1). Similarly, the strong magnetic interaction between the helix and the field maintains the direction of motion, addressing (2). Lastly, although Brownian motion (3) is unavoidable, this can be mitigated by tuning the propulsion velocity to a value that minimizes the diffusive spreading. We also show that propulsion and steering is possible at the nanoscale where thermal fluctuations are significant. To have spatial and temporal control of the changes in the direction of motion, a $< \pi/2$ phase difference should be maintained between the magnetic interaction of the helix and the field through gradual changes in the field directions.

For the work presented here, we found that the LBMD method can potentially be used to study the locomotion of microorganisms. The results suggest directions for further improvements, such as effective mimicry of the beat patterns of the microorganisms in the simulations, as well as a comparison of the simulations with the swimming behavior of these microorganisms in a fluid bulk and in the presence of wall or surface interactions.
References


References


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References


A. Magnetic Alignment

The helix and the magnetic field were initially aligned. At $t > 0$, a rotating magnetic field with an angular frequency of $f$ is applied inducing a rotational motion on the helix. For frequencies greater than the step-out frequency, the helix undergoes a periodically driven and damped dynamics.
Figure A.I. Components of the normalized alignment of the magnetic moment of the helix (blue) and normalized magnetic field (orange) along the (a) x-, (a) y- and (a) z-directions for field $f = 100 \times 10^4 < f_{SO}$. 
Figure A.II. Components of the normalized alignment of the magnetic moment of the helix (blue) and normalized magnetic field (orange) along the (a) x-, (a) y- and (a) z-directions for field $f = 600 \times 10^4 < f_{SO}$. 

(a)

(b)

(c)