Dissipative Particle Dynamics for Anisotropic Particles and Electrostatic Fluctuations: A Fully Lagrangian Approach

by

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Dissipative Particle Dynamics (DPD) is a Lagrangian type mesoscopic method widely applied in mesoscale hydrodynamics and complex fluids simulations. DPD can be understood as coarse-grained (CG) Molecular Dynamics (MD) method via the Mori-Zwanzig projection from bottom-up approach. In classical DPD, the stochastic evolution equations for CG variables, i.e., momentums and positions are constructed, however, additional CG variables and corresponding dynamical equations are required for more complicated systems with constraints existed. This thesis addresses several algorithmic issues and presents new DPD models with targeting different underlying systems and specific applications. In the first part, we give a quick introduction and specific application of classic DPD to inextensible fiber dynamics in stagnation-point flow, to show the capability of classic DPD in modeling mesoscopic complex fluids. In the second part, a novel single-particle DPD model is presented to study slightly anisotropic bluff bodies and colloidal suspensions, the dynamical equations for additional CG variables, i.e., angular momentum and rotation matrix are given due to the rigid body constraints in underlying system. Moreover, the compacted expressions of DPD forces between anisotropic DPD particles are formulated using a linear mapping from the isotropic model of spherical particles. The anisotropic DPD (aDPD) model is then applied to study the isotropic-nematic transitions, hydrodynamics and Brownian motion of ellipsoidal suspensions. The third part deals with long-range electrostatic interactions in mesoscopic simulations, where we address the importance of fluctuations in charged systems. First, we develop a “charged” DPD (cDPD) model for simulating mesoscopic electro-kinetic phenomena governed by the stochastic Poisson-Nernst-Planck and the Navier-Stokes (PNP-NS) equations. Specifically, the transport equations of ionic species are incorporated into the DPD framework by introducing extra degrees of freedom and corresponding stochastic evolution equations associated with each DPD particle. The electrostatic potential is obtained by solving the Poisson equation on the moving DPD particles iteratively. Subsequently, cDPD model is employed to study the electro-kinetic phenomena near charged surface in the mean-field regime. Moreover, the mesoscopic fluctuating electro-kinetics of electrolyte solutions at equilibrium are also investigated via cDPD and MD simulations, the results are then compared with linearized fluctuating hydrodynamics and electro-kinetics. Electrostatic fluctuations near charged planar surfaces are also systematically studied via field theory approach, with numerically solving the nonlinear 6-dimensional electrostatic self-consistent (SC) equations. Additionally, a new dynamic elastic network model (DENM) is also presented to describes the unfolding process of a force-loaded protein, and we further exploit the self-similar structure of pro-
teins at different scales to design an effective coarse graining procedure for DENM with optimal parameter selection.
This dissertation by Mingge Deng is accepted in its present form by the Division of Applied Mathematics as satisfying the dissertation requirement for the degree of Doctor of Philosophy.

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Publications


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Chapter 1

Introduction

1.1 Motivation

1.1.1 Complex Fluids and Mesoscale Modeling

Complex fluids or soft matter is a subfield of condensed matter, which includes a variety of materials, and broad applications in industrial technologies (lubricants, oil recovery, plastics, liquid crystals, and paints, etc.) and especially in the field of biological and biomedical sciences (blood flow, drug delivery systems). By definition, a complex fluid can be deformed or structurally altered by thermal fluctuations, which are of the same order as the characteristic energy of the mesoscale. Thus, the macroscopic properties and observable behaviors of complex fluids have significant dependency on the mesoscopic structures.

Computer simulations have beyond doubt become one of the most important research tools in modern physics, but it is only in the last two decades or so, that computer simulations have been able to approach the length and time scales relevant to complex fluids. In general there are three different approach for the simulation of complex fluids, namely, molecular dynamics (MD), continuum methods (i.e., Navier-Stokes solver) and mesoscopic methods, and each of these have their own characteristics, advantages and disadvantages. For example, the continuum approaches are able to capture the hydrodynamic behaviors well at the macroscale. However, these methods are based on natural constitutive equations which capture the microscopic details of the fluid in a phenomenological manner, and as a result are not suitable for many complex fluids applications; Meanwhile, although microscopic approaches have become increasingly successful in the simulation of small number of molecules, with the development of increasingly accurate, and complex force fields, they still remain limited to micro- length and time scales due to the expensive computational cost. It is
still far away to apply these detailed fully atomic MD techniques to large complex fluids systems and it would incur huge computational costs to reach time-scales over which hydrodynamic effects are significant. Such restrictions have driven the development of coarse-grained, or mesoscopic simulations that are able to follow the dynamical behavior of complex fluids for much longer length- and time-scale, i.e., microseconds to milliseconds. Thus in turn have motivated several mesoscopic approaches, such as Dissipative Particle Dynamics (DPD), the Lattice Boltzmann method (LBM), Brownian dynamics (BD), and Smoothed Particle Hydrodynamics (SPH), etc..

1.1.2 Overview of Dissipative Particle Dynamics

Mesoscopic simulation methods have been developed to overcome the aforementioned problems, aiming at modeling complex fluids with efficient computational costs. Dissipative particle dynamics (DPD), which describes clusters of molecules moving together in a Lagrangian fashion, is a typical mesoscopic simulation method for the dynamic and rheological properties of simple and complex fluids [2]. DPD combines Lagrangian features from MD and coarser spatial-temporal scales from lattice-gas automata (LGA), and, therefore it is faster than MD and more flexible than LGA. The first form of DPD was reformulated by Espa˜ nol and Warren so that it produces a correct thermal equilibrium state [3]. This is now considered as the standard form of DPD. Several improved DPD models [4, 5, 6, 7], which are capable of representing complicated fluid properties more accurately, as well as more efficient algorithms have also been developed. Rigorous foundations of DPD methodology have also been investigated by both top-down (from macroscopic description to mesoscopic description) and bottom-up (from microscopic to mesoscopic) approaches.

In a DPD simulation, a particle represents a cluster of molecules, and the position and momentum of the particle are updated in a continuous phase space at discrete time steps. The equation of motion and pairwise interacting forces of particles read

\[ \dot{r}_i = v_i, \quad m_i \dot{v}_i = \sum_{j \neq i} (F^C_{ij} + F^D_{ij} + F^R_{ij}), \]

where \( r_i, v_i \) and \( m_i \) are position, velocity and mass of particle \( i \), respectively. \( F^C_{ij} \) is referred to as conservative force obtained from a prescribed potential between particles \( i \) and \( j \). It is repulsive and leads particles to be evenly distributed in space. Roughly speaking, it can be understood as a pressure force; \( F^D_{ij} \) has a negative sign and is proportional to the velocity difference of two particles. Therefore, it is dissipative and resists velocity difference of any interacting pair of particles. Hence, \( F^D_{ij} \) dissipates the kinetic energy of the system. This amount of energy must be put back into the system, to keep the system at a constant temperature. \( F^R_{ij} \) is exactly for this purpose. It is a
random force and injects kinetic energy back into the system. Effectively, $F_D^{ij}$ and $F_R^{ij}$ implement a thermostat so that thermal equilibrium is achieved. The magnitudes and functional forms of the two forces are related by the so called fluctuation-dissipation theorem. The typical forms of the three forces are as follows [3, 8]

\[
F_C^{ij} = a_{ij} \omega^C(r_{ij}) e_{ij}, \quad (1.2a)
\]

\[
F_D^{ij} = -\gamma \omega^D(r_{ij})(e_{ij} \cdot v_{ij}) e_{ij}, \quad (1.2b)
\]

\[
F_R^{ij} = \sigma \omega^R(r_{ij}) \theta_{ij} \delta t^{-1/2} e_{ij}, \quad (1.2c)
\]

where $a_{ij}$, $\gamma$, and $\sigma$ reflect, respectively, the strength of conservative, dissipative and random forces. Here, $\theta$ is a Gaussian white noise ($\theta_{ij} = \theta_{ji}$), and $e_{ij}$ is the unit vector pointing from particle $j$ to $i$; also, $\omega^C$, $\omega^D$, and $\omega^R$ are unspecific weighting functions of relative distance $r_{ij}$. A common choice of the weighting functions is

\[
\omega^C(r_{ij}) = \begin{cases} 
1 - r_{ij}/r_c, & r_{ij} < r_c, \\
0, & r_{ij} \geq r_c,
\end{cases} \quad (1.3)
\]

\[
\omega^R(r_{ij}) = \begin{cases} 
(1 - r_{ij}/r_c)^s, & r_{ij} < r_c, \\
0, & r_{ij} \geq r_c,
\end{cases} \quad (1.4)
\]

where $s = 1$ is the most widely adopted for the classical DPD method. However, other choices (e.g., $s = 0.25$) for the envelopes have also been used. Also, $r_c$ is the cutoff radius, which defines the extent of the interaction range.

To satisfy the fluctuation-dissipation theorem, two conditions must be further enforced [3]:

\[
\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2, \quad \sigma^2 = 2\gamma k_B T, \quad (1.5)
\]

where $k_B$ is the Boltzmann’s constant and $T$ is the absolute temperature.

Two important implications of the DPD forces in Eqs. (1.2) must be explicitly noted: firstly, DPD is considered as a reduced model of the underlying microscopic dynamics. By construction, it focuses on the coarse-grained properties and intentionally ignores irrelevant degrees of freedom on the microscopic level. As a result, the inter-particle potential (the derivative of which is $-F_C^{ij}$) is much softer than that of MD method, hence, it can potentially access longer time and length scales than are possible using conventional MD simulations. Furthermore, $F_D^{ij}$ and $F_R^{ij}$ together account for the lost microscopic information. Secondly, by design, all three forces act along the
line of particle centers $e_{ij}$ and are symmetric by interchanging particle indices. Therefore, the momentum is locally conserved. The fulfillment of the conservation laws guarantees that a DPD system approaches the PDEs of fluid dynamics, such as Navier-Stokes equations, at the macroscopic scale.

For the purpose of modeling simple and complex fluids, $\alpha$, $\gamma$ (or $\sigma$) and $s$ are free parameters to calibrate so that the desired properties of a target system can be achieved. The time evolution of velocities and positions of particles is determined by Newton’s second law of motion similar to the MD method, which is usually integrated using a modified velocity-Verlet algorithm [8].

1.2 Objective and Main Contributions

The objective of this work is to reveal several open issues in mesoscopic simulations as follows.

- how to describe the interactions between mesoscopic anisotropic bluff bodies, which lead to the isotropic-nematic transitions and anisotropic Brownian motions in colloidal suspensions.

- how to describe the long-range electrostatic interactions effectively in mesoscopic simulations, and precisely capture the electrostatic fluctuations in mesoscopic systems, that are key to the origin of many unusual phenomena in charged systems.

In this thesis, we address the above two questions, and develop novel DPD models for the study of anisotropic bluff bodies and electrostatic interactions and fluctuations in mesoscopic simulations. The main novel contributions of this work are as follows.

- The inextensible filament model we built to describe the dynamics of single fiber at mesoscales.

  The numerical algorithm to enhance simulations of flows in complex geometries by DPD method when driven by body forces suitably tailored to the geometry. The analysis to describe the dynamic bifurcations using normal mode analysis and proper orthogonal decomposition (POD) analysis. We discuss these contributions in Chapter 2 and some details are given in the Appendices.

- The new formulation we developed to generalize the isotropic single-particle DPD model for slightly anisotropic bluff bodies. This new formulation includes the dynamical equations for angular momentum and rotation matrix for DPD particles, as well as a compact form description of forces between DPD particles. We introduce in detail this new formulation in Chapter 3.
• The cDPD model we proposed to describe the electro-kinetic phenomena governed by stochastic PNP-NS equations in mesoscales. This model captures the fluctuations around Mean-Field approximation. All the details about this work are described in Chapter 4 and 5.

• The field theory approach of electrostatic fluctuations near charged surface. The phase diagram of counterion condensation near planer surfaces and interactions between two likely charged surfaces are plotted. In Chapter 6, the model and results are explained in detail.

• The dynamic elastic network model (DENM) based on the $C_\alpha$ atoms coordinates of the protein backbone to describes the unfolding process of a force-loaded protein. The coarse-grained procedure to formulated the $C_\alpha$ atoms based DENM to various coarse-graining levels. Details of this work are discussed in Chapter 7.

1.3 Outline

In this section an outline of the thesis is provided along with a short description of the research work in each chapter as follows.

• In chapter 2, we investigate the dynamics of a single inextensible elastic filament subject to anisotropic friction in a viscous stagnation-point flow using classical DPD, the results are compared with a continuum model represented by Langevin type stochastic partial differential equations (SPDEs), to demonstrate the applications of DPD in complex fluids. It includes
  – the continuum and discrete inextensible elastic fiber model,
  – numerical schemes for stagnation-point flow in DPD,
  – numerical schemes for the governing stochastic partial differential equations,
  – normal mode analysis and proper orthogonal decomposition analysis of fiber dynamics,
  – theoretical analysis of the buckling instability of fiber dynamics

• In chapter 3, we develop a new single-particle dissipative particle dynamics model for slightly anisotropic particles (aDPD). This chapter contains,
  – the aPDD algorithm and descriptions,
  – the justification about the forces and thermostats of aDPD,
  – the static properties of suspensions of colloidal ellipsoids and the isotropic-nematic transitions captured by aDPD,
– the hydrodynamics and Brownian motion of single ellipsoidal particles.

• In chapter 4, we develop a charged dissipative particle dynamics (cDPD) model for simulating mesoscopic electro-kinetic phenomena governed by the stochastic Poisson-Nernst-Planck and the Navier-Stokes (PNP-NS) equations. This chapter includes,
  – derivation of PNP-NS equations, mean-field approach,
  – stochastic PNP-NS equations in mesoscale, generalized fluctuation-dissipation theorem,
  – algorithms and descriptions of cDPD model,
  – boundary conditions of cDPD,
  – electrostatic double layer (EDL),
  – electro-osmotic flow and electro-osmotic/pressure-driven flow,
  – dilute poly-electrolyte solution drifting by electro-osmotic flow,

• In chapter 5, we describe the fluctuations of electrolyte bulk solutions at equilibrium. It contains
  – derivation of the explicit formulas for linearized fluctuation hydrodynamics and electro-kinetics equations using perturbation theory,
  – verification by comparing with MD and cDPD simulation results,
  – fluctuations distributions in different scales,
  – spatial correlations.

• In chapter 6, we explore the electrostatic fluctuations effects around charged planar surfaces with field theory approach. This chapter contains,
  – derivation of electrostatic self-consistent (SC) equations and descriptions,
  – numerical algorithm for the nonlinear 6-dimensional SC equations,
  – comparison between numerical results of SC and mean-field theory,
  – counterion condensation phase-transition,
  – interactions between two likely charged surface,
  – phase diagrams.

• In chapter 7, we describe the general $C_\alpha$ atoms topology-based dynamic elastic network model and coarse graining procedure for DENM with optimal parameter selection. This chapter contains,
– $C_\alpha$ atoms topology-based elastic network model,
– non-covalent bond broken events: Karmers theory and the Bell model,
– essential dynamics coarse-graining scheme,
– self-similarity and fractal dimension of protein,
– minimization of Kullback-Leibler divergence

We conclude in Chapter 8 with a summary and a brief remarks about the future work.
Chapter 2

Fiber Dynamics: Application of Classic DPD Method

2.1 Introduction

Bio-polymers, such as F-actin, protein fibers, DNA, and microtubules are all semiflexible elastic filaments. There are two unique characteristic properties distinguishing them from most of the other natural and synthetic polymers: they possess a certain stiffness that energetically suppresses bending, and they are to a high degree inextensible, i.e., their back-bone cannot be stretched or compressed too much. The cytoskeletons of cells and tissues are mostly built by such bio-polymers, thus, studying the dynamics of inextensible elastic filaments subject to hydrodynamic forces can be a first step towards understanding the cytoskeleton networks and tissue motions. Previous works focused mainly on the stretching dynamics of filaments with tension applied lengthwise \([9, 10, 11, 12, 13, 14, 15, 16]\), both with and without hydrodynamics. However, recent works on the dynamics of elastic filaments subject to hydrodynamic forces has revealed complex nonlinear dynamical behavior both in simple shear flows \([17, 18, 19, 20, 21, 22]\) and in the neighborhood of a stagnation-point of stretching flows \([13, 23, 24]\). Specifically, the negative tension induced along the filament by simple hydrodynamic forces above some critical value can lead to buckling known as “stretch-coil” instability \([23, 25, 26]\). Hence, it is very important to fully understand the inextensible elastic filament dynamics for cell mechanics \([27]\).

Suspended in stretching flow, these filaments respond as mesoscopic entities (\(~ \mu m\)), and hence the forces on them, Brownian, hydrodynamic and elastic, are of the same order. This, in turn, implies the importance of thermal fluctuation so that the Brownian forces cannot be neglected.
However, to the best of our knowledge, only a few papers have addressed the thermal fluctuation effects [28, 17, 18, 19, 29]. Moreover, nonlinear response due to the thermal noise has become a central topic in studies of various dynamical systems. For example, as was shown recently, thermal noise is greatly amplified in a dynamical system due to the interaction between stochasticity and nonlinearity near bifurcation points [30, 31, 32, 33, 34], i.e., low dimensional models with a small number of modes are sufficient to capture the physics in these complex systems only up to the bifurcation points, after which, higher modes will make significant contributions to the full dynamics.

Figure 2.1: Sketches of (a) continuous filament with geometric parameter definitions and (b) bead-spring chain model.

The objective of the current work is to study the role of thermal fluctuations on the deformation of single linear filament subject to stretching and compression near a stagnation-point within a viscous flow (with the detailed implementation in DPD is included in Appendix B). The filaments are represented by two models. The first is the inextensible elastic filament described as a continuous curve for which the solvent flow acts through the anisotropic viscous resistance and thermal noise, and the dynamics of the inextensible filament is governed by Langevin type stochastic partial differential equations (SPDEs) [35, 19]. The second is a Dissipative Particle Dynamics (DPD) bead-spring chain model immersed in a solvent of DPD particles subject to the stagnation-point flow. Details about these two models are given in Sec. 2.2. These two models are then simulated by obtaining numerical solutions to the governing SPDEs and DPD equations, respectively.
Sec. 2.3). The main numerical results are obtained from each model in Sec. 2.4. We use normal mode analysis to identify the stretch-coil transition and amplification of thermal noise during filament dynamics. These physical phenomena can also be analyzed with Proper Orthogonal Decomposition (POD) analysis, which is included in the Appendix A. Finally, a short conclusion about the limitation of the current models and further work is included in Sec. 2.5.

2.2 Model Description

In this section, we present models for continuum inextensible elastic filaments and for bead-spring chains in stagnation-point flow.

2.2.1 Models of Linear Fibers

Most of the bio-polymers are generally modeled as inextensible elastic filaments whose deformations are dominated by elastic bending resistance. This contrasts with other long flexible molecules, which have little bending resistance, and are generally modeled as freely-jointed chains [18, 20, 21]. Two linear inextensible elastic filament models are simulated in our current work: a continuous elastic filament [36, 37] and a bead-spring chain.

The energy functional for a continuous filament, constrained to be inextensible, is expressible as a line integral along its contour, \( 0 \leq s \leq L \), as follows:

\[
E = \frac{1}{2} \int_{-L/2}^{L/2} ds \left( A(\kappa(s) - \kappa_0)^2 - \Lambda(s)(\partial_s r)^2 \right),
\]

(2.1)

where \( \theta \) and \( \kappa = \partial_s \theta(s) \) are the tangent angle and the curvature at arc length \( s \) as shown in Figure 2.1(a), respectively, and \( \kappa_0 \) is zero for a rigid rod filament. Bending resistance is characterized by the flexural rigidity, which in the theory of elastic beams is given by \( A = GI \), with a material modulus \( G \) and second moment of cross-section area \( I \) [38]. By definition a filament is very thin, and filament theory is applied to entities where the cross-section dimensions are not easily determined. Thus, \( A \) is the preferred elastic parameter to characterize the bending elasticity. The second term of the integrand introduces the Lagrange multiplier \( \Lambda(s) \) to impose the local constraint of inextensibility by the requirement that the tangent vector \( \partial_s r \) be of constant magnitude along the entire filament contour length. At the mesoscopic dimensions, where thermal fluctuations are an important alternative measure of bending resistance, the persistence length \( l_P \) is introduced as,

\[
l_P = \frac{2A}{k_BT(d-1)},
\]

(2.2)
where $d$ is the dimension of the deformation space. A Langevin type equation models the motion of an elastic inextensible filament immersed in a continuous Newtonian solvent. The neutrally buoyant filament, of radius $a \sim O(\mu m)$, $a/L \ll 1$, experiences hydrodynamic resistance governed by the Stokes equation, which exceeds inertia by several orders of magnitude; hence, inertial forces can be safely neglected. Also, the disturbance of the flow field by the filament motion is adsorbed into the Brownian force effects. Thus, the mesoscopic level equation of motion reduces to a balance between three forces: Brownian force ($\sim k_B T/L$), hydrodynamic force ($\sim \mu \dot{\gamma} L^2$) and elastic bending force ($\sim A/L^2$). The motion generated by these forces must satisfy the local inextensibility of the filament, which requires the magnitude of its tangent vector to be constrained locally to be $|dr/ds| = 1$ along its contour; the latter condition yields the line tension generated by the Lagrange multiplier. Finally, the governing equation can be written as the balance of three forces:

$$\eta D[\partial_t \mathbf{r} - \mathbf{u}(\mathbf{r})] = -\left( A \frac{\partial^4 \mathbf{r}}{\partial s^4} + \partial_s \left( \Lambda(s) \partial_s \mathbf{r} \right) \right) + f_{\text{stoch}}(s, t)$$  \hspace{1cm} (2.3)

where $D$ is the dimensionless anisotropic drag tensor, $D = I - \frac{1}{2} \partial_s \mathbf{r} \otimes \partial_s \mathbf{r}$, and $\eta = (2\pi)\mu/\ln(L/a)$ is the effective viscosity derived from the known Stokes resistance for a rigid rod of radius $a$. The latter is usually approximated by rough estimates, but the inaccuracy is tolerable since it appears only in the logarithm. This form of the hydrodynamic resistance is accurate provided the filament remains nearly straight, but as it departs from a linear configuration accuracy is lost. Also, the configuration of a compliant filament may depart so far from straightness as to induce significant hydrodynamic interactions between its parts. These restrictions are avoided for the DPD model since the DPD solvent accounts implicitly for hydrodynamic effects. The tensor Lagrange multiplier $\Lambda(s)$ is an unknown introduced to impose the inextensibility constraint, and is the one-dimensional analog of the pressure Lagrange-multiplier employed to impose incompressibility on a continuum velocity field. The Langevin equation is scaled with the contour length $L$, the hydrodynamic time $\dot{\gamma}^{-1}$ and a typical Brownian force $k_B T/L$ to yield the dimensionless equation,

$$\partial_t \mathbf{r} - \mathbf{\Gamma} \cdot \mathbf{r} = \frac{D^{-1}}{\alpha} \left( -\beta \frac{\partial^4 \mathbf{r}}{\partial s^4} - \partial_s \left( \Lambda(s) \partial_s \mathbf{r} \right) + f_{\text{stoch}}(s, t) \right)$$  \hspace{1cm} (2.4)

where $\mathbf{\Gamma}$ is the velocity gradient tensor to be explained below. The solution of the equation requires specification of two dimensionless parameters:

$$\alpha = \frac{\eta \dot{\gamma} L^3}{k_B T}, \quad \beta = \frac{A}{k_B T L} = \frac{l_p(d - 1)}{2L}$$  \hspace{1cm} (2.5)

Here $\alpha$ measures the hydrodynamic force relative to the thermal Brownian force, and $\beta$ measures
the elastic bending force relative to the thermal Brownian force, which is also the definition of relative persistence length in polymer science [35]. We define the ratio \( W_i = \alpha/\beta = \eta \gamma L^4/A \), and its limiting values indicate: \((W_i \rightarrow 0)\) a nearly-rigid rod dominated by bending elasticity and \((W_i \rightarrow \infty)\) a flexible string dominated by hydrodynamic forces. And in the limit of vanishing hydrodynamic force \((\alpha \rightarrow 0)\), the Langevin equation reduces to a linear problem, i.e, elastic bending vibrations forced by Brownian fluctuations. More discussions about these dimensionless parameters are included later. The Brownian force \( f_{stoch}(s,t) \) satisfies the fluctuation-dissipation theorem as follows:

\[
\langle f_{stoch}(s,t) \rangle = 0
\]

\[
(f_{stoch}(s,t) \otimes f_{stoch}(s',t')) = 2\alpha D \delta(s-s')\delta(t-t')
\]

Therefore, \( f_{stoch} \) represents white-noise excitation and can thus be expressed in terms of generalized derivatives of the multi-dimensional standard Wiener process,

\[
f_{stoch} = \sqrt{2\alpha} C \frac{\partial^2 W(s,t)}{\partial s \partial t}.
\] (2.7)

Here, \( C \) is a matrix satisfying \( CC^T = D \) and according to [32], \( C = I + (\sqrt{2} - 1)\partial s \otimes \partial s \).

The bead-spring chain model used in the particle-based simulations, as shown in Figure 2.1(b), is designed to mimic the continuous filament. The discrete elastic energy \( E_{bs} \) is a sum of angle-dependent bending energies and stretching energies for every consecutive pair of bonds,

\[
E_{bs} = \sum \frac{1}{2} k_a (\theta - \theta_0)^2 + \sum \frac{1}{2} k_s (b - b_0)^2,
\] (2.8)

where \( k_a \) and \( k_s \) are the elastic constants for bending and stretching, respectively. The deformation measures between consecutive bonds \( \theta - \theta_0 \) and \( b - b_0 \), for bending and stretching respectively, are taken relative to their equilibrium reference values \( \theta_0, b_0 \). In this work, \( \theta_0 \) is taken to be \( \pi \) along the entire contour, which sets the reference state to be a straight rod with \( b_0 \) determined by the number of bonds. The constraint of inextensibility is approximated locally with very stiff connectors (large \( k_s \)) between every pair of consecutive beads. Another equation incorporates the bending constant \( k_a \) into the persistence length \( l_P \) analogously to equation (2.2) of the continuous filament case as

\[
l_P = \frac{k_a b_0}{k_B T}.
\] (2.9)

Comparison of the two definitions of the persistence lengths, equations (2.2) and (2.9), suggests that the filament and the bead-spring chain models are elastically equivalent provided \( k_a b_0 = 2A/(d-1) \). In addition, the bond spring constant \( k_s \) needs to be large enough to approximate the
local constraints of inextensibility. This in turn limits the simulation time steps to very small value.

\[ \text{Figure 2.2: Numerical (weak) convergence of the solution of equation (2.4) as measured by the mean square error (MSE) of filament end-to-end distance as a function of time step } \Delta t. \text{ The exact solutions are computed with } \Delta t = 10^{-9}. \]

### 2.2.2 Stagnation-Point Flow

The stagnation-point flow has long been realized in the four-role-mill apparatus of Lagnado et al. and Yang et al., respectively [39, 40], and has been employed in the study of drops and other objects of macroscopic dimensions [41]. The stagnation-point flow can be realized in the cross micro-channel arrangement of Kantsler & Goldstein [23] to observe the response of mesoscopic particles such as actin molecules in the vicinity of the stagnation point. The micro-channel system requires smaller sample volumes, and hence appears to be more suitable for the observation of macromolecules, cells, etc. In the vicinity of the stagnation point the velocity field \( \mathbf{v}(\mathbf{r}) \) is spatially homogeneous, and can be written as,

\[
\mathbf{v}(\mathbf{r}) = \mathbf{\Gamma} \cdot \mathbf{r} , \quad \mathbf{\Gamma} = \dot{\gamma} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} , \quad V = \dot{\gamma} \sqrt{x^2 + y^2} ,
\]

with \( V \) the velocity magnitude, \( \dot{\gamma} \) the shear rate and \( \mathbf{\Gamma} \) the velocity field matrix. For particle-based simulation methods such as DPD, simple flows (i.e., shear flows) are commonly generated by imposing a constant driving force (Poiseuille flow), equivalent to a pressure gradient, or a driving velocity on the boundary shear planes (Couette flow). However, with a particle based
method it is not trivial to implement the stagnation-point flow together with periodic boundary conditions. Recently, Pan et al. [42] devised a periodic uniaxial stretching flow for DPD simulations in which a smaller box is placed inside an outer larger box. Periodic boundary conditions are applied on the surfaces of the latter, while the flow is driven by a distribution of velocities on opposing vertical surfaces of the inner box. By reversal of the direction of the driving velocities stretching/compressing can be imposed along the x/y-axes. Known analytic stretching flows are defined on infinite domains, and hence the box-inside-a-box is a convenient way to have fully periodic conditions with simplicity of implementation. However, the outer box size should be large enough to ensure minimal effect on the stagnation-point flow. Our experience is that the large size and slow convergence to the steady state makes the box-in-a-box scheme computationally expensive. Furthermore, the stagnation stretch rate cannot be specified, and has to be determined by trial.

We have developed a driving-force field to yield a stagnation-point flow in a DPD computational box with periodic boundary conditions. The new scheme takes advantage of the well-known fact that the Navier-Stokes equation is satisfied by a potential flow. The $x-y$ plane of the box is a periodic square in a lattice of vortices. It is bounded by streamlines, and contains four counter-rotating vortices located at the centers of each quadrant. In potential flow, Bernoulli’s equation is $H = 1/2\rho v^2 + P + \rho\chi = \text{constant}$. The velocity field can be thought of as being driven by the body force per unit mass $\nabla(\chi + P/\rho)$, which by Bernoulli’s equation is $\nabla v^2$. The derivation of this driving force are included in Appendix B, where it will be shown that use of this driving force yields accurate simulations. Furthermore, excellent economy is achieved due to rapid convergence from a startup at rest to the steady state. The simulated streamline and pressure pattern is shown in Figure 2.3 (a), and the velocity-vector pattern in the vicinity of the center shows it to be a stagnation point; see the velocities along the centerlines $x = 0, y = 0$ plotted in Figure 2.3(b).

In DPD simulations, a single filament represented by the bead-spring model is placed and released at the center of the equilibrium stagnation-point flow, and the kinematics of filament are then recorded as a function of time.

2.3 Numerical Methods

With sufficient depth, the Yang et al.’s four-role-mill apparatus should allow a suspended object to move freely in any direction, and therefore it is appropriate to simulate the resulting disturbance flow as fully three-dimensional. However, in the crossed-channel configuration, the classical stagnation-point flow is realized only in the mid-vertical plane, and the small gap will tend to constrain a suspended object to move within that plane. This is the motivation for the 2D simulations
Figure 2.3: (a) dimensionless velocity along axes $y = 0$ and $x = 0$, DPD averages (points) compared to the analytical values (dashed lines). (b) DPD streamlines for the periodic box in a lattice of counter-rotating vortices calculated from the time-averaged DPD velocities. Colored background indicates number density. Prescribed average density: orange, other colors indicate depletion. Near the vortices depletion starts at about a radius of unit isothermal-Mach number.

2.3.1 Numerical Methods for Governing SPDEs

The numerical approach taken here was inspired by Chorin’s method for incompressible Navier-Stokes equation [43]. First, we introduce the auxiliary systems as follows

$$\partial_t \mathbf{r} - \mathbf{F} \cdot \mathbf{r} = \frac{D^{-1}}{\alpha} \left( -\beta \frac{\partial^4 \mathbf{r}}{\partial s^4} - \partial_s (\Lambda(s) \partial_s \mathbf{r}) + f_{stoch}(s, t) \right)$$

$$\frac{\partial(\delta \Lambda)}{\partial t} + \left( \frac{\partial \mathbf{r}}{\partial s} \right)^2 - 1 = 0$$

$$\Lambda(s = 0) = \Lambda(s = 1) = 0$$

$$\frac{\partial^2 \mathbf{r}}{\partial s^2}(s = 0, s = 1) = \frac{\partial^3 \mathbf{r}}{\partial s^3}(s = 0, s = 1) = 0$$

(2.11)

We shall call $\delta$ the artificial extensibility, and $t$ in the second equation is an auxiliary variable whose role is analogous to that of time in extensible fiber problem. Numerically, we choose $\delta \sim \mathcal{O}(\Delta t)$, and our auxiliary system indeed converges to inextensible filament system as $\Delta t$ goes to zero.

The auxiliary system (2.11) can be used with various difference schemes. Here, considering the stiffness introduced by the elastic term $\frac{\partial^4 \mathbf{r}}{\partial s^4}$, the SPDEs can be discretized by central finite difference in space and a stiffly-stable scheme in time. To this end, we consider $Nt + 1$ discrete points in time $t^i = i\Delta t$ with $i \in \{0, 1, 2, ..., Nt\}$, and the arc length in space is discretized uniformly by $Ns + 1$
Figure 2.4: First five normal modes (eigenfunctions) for the biharmonic operator with boundary conditions (Eq.2.18), black, red, blue, green and yellow lines represent 0th, 1st, 2nd, 3rd and 4th mode, respectively.

Nodes $s_k = k\Delta s$, $k \in 0, 1, 2, ..., Ns$ and $\Delta s = 1/Ns$. A staggered grid is used to calculate $\mathbf{r}$ and $\Lambda$ for stability reasons, i.e., the displacements $\mathbf{r}$ are calculated at the center points of each interval with total $Ns$ points, while the line tensions are updated every timestep on the boundaries of each interval with total $Ns + 1$ points. Ghost points are used to approximate the high-order derivatives near the boundaries. We approximate the stochastic force as piece-wise constant on distinct time and space intervals, $\Delta s$ and $\Delta t$, i.e., the discrete stochastic forces are Gaussian random numbers and are uniquely characterized by zero mean value and the covariance matrix:

$$f_{\text{stoch} k}^i \approx \sqrt{\frac{2\alpha}{\Delta t \Delta s}} C_{i k} N(0, 1) \quad (2.12)$$

with $N(0, 1)$ denoting the normalized Gaussian distribution. Finally, the discretized equations can be written using a third-order stiffly stable scheme [44] as

$$\mathbf{r}^{i+1} = \frac{18}{11} \mathbf{r}^i - \frac{9}{11} \mathbf{r}^{i-1} + \frac{2}{11} \mathbf{r}^{i-2} + \frac{6}{11} \Delta t (\mathbf{F}^i_k + f_{\text{stoch} k}^{i+1})$$

$$\Lambda^{i+1} = \frac{18}{11} \Lambda^i - \frac{9}{11} \Lambda^{i-1} + \frac{2}{11} \Lambda^{i-2} + \frac{6}{11} \Delta t \delta G^i_k \quad (2.13)$$

where $\mathbf{F}$ and $G$ are numerical discretizations of the terms $\mathbf{r} \cdot \nabla \mathbf{r} + \frac{D^{-1}}{\alpha} (-\beta \frac{\partial^4 \mathbf{r}}{\partial s^4} - \partial_s (\Lambda(s) \partial_s \mathbf{r}) )$ and $(1 - (\partial_s \mathbf{r})^2)$, respectively, with central differences. At each time step, these coupled two equations
are iteratively solved by fixed-point iteration. In equation (2.13), the stochastic terms are treated in the Ito sense. We then sample the stochastic trajectories with the Monte Carlo method. High order discretization formulas are used both in time and space, nevertheless, we can only achieve first-order convergence in the weak sense because of the Wiener process, as shown in Figure 2.2.

2.3.2 Dissipative Particle Dynamics Simulation

We then study the inextensible fiber dynamics subject to stagnation-point flow by employing DPD simulations. DPD is a mesoscale method for studying coarse-grained models of soft matter and complex fluid systems over relatively long length and time scales, see [2, 8, 45]. In DPD, the particles interact via pairwise additive forces, consisting (in the basic form) of three components:
(i) a conservative force $f^C$; (ii) a dissipative force, $f^D$; and (iii) a random force, $f^R$. Hence, the total force on particle $i$ is given by $f_i = \sum_{i\neq j} \left(f^C_{ij} + f^D_{ij} + f^R_{ij}\right)$, where the sum acts over all particles within a cut-off radius $r_c$. Specifically, in our simulations we have

$$f_i = \sum_{i\neq j} a_{ij} \omega(r_{ij}) \dot{r}_{ij} - \gamma \omega^2(r_{ij})(\dot{r}_{ij} \cdot \dot{v}_{ij}) \dot{r}_{ij} + \sigma \omega(r_{ij}) \frac{\zeta_{ij}}{\sqrt{\Delta t}} \hat{r}_{ij}$$

(2.14)

where $a_{ij}$ is a maximum repulsion between particles $i$ and $j$. We set $a_{ij} = a = 25.0$ for both solvent and filaments particles in our simulations. $r_{ij}$ is the distance with the corresponding unit vector $\hat{r}_{ij}$, $\dot{v}_{ij}$ is the difference between the two velocities, $\zeta_{ij}$ is a Gaussian random number with zero mean and unit variance, and $\gamma$ and $\sigma$ are parameters coupled by $\sigma^2 = 2\gamma k_B T$ [3]. Typically, the weighting functions $\omega(r_{ij})$ are given by

$$\omega(r_{ij}) = \begin{cases} 
1 - \frac{r_{ij}}{r_c}, & r_{ij} < r_c \\
0, & r_{ij} \geq r_c.
\end{cases} \quad (2.15)$$

The filaments are represented as bead-spring chains with $N = 32$ segments, with additional bond and angle forces ($-\nabla E_{bs}$) derived from equation (2.8). The average particle number density of the DPD solvent is $\rho = 3.0 r_c^{-3}$ and the temperature is set at $k_B T = 1.0$. The simulations are performed using a modified version of the DPD code based on the open source code LAMMPS, see [46]. Time integration of the equation of motion is obtained by a modified velocity-Verlet algorithm, first proposed by [8], with time step $\Delta t = 0.001$ (in DPD time units).

### 2.4 Results and Discussion

In order to obtain a quantitative understanding of fiber dynamics near the stagnation-point, normal modes analysis [47] is used to study the fiber configuration during its motion.

#### 2.4.1 Normal Modes Analysis

We can express the shape $\theta(s)$, as defined in Figure 2.1, as a superposition of normal “modes”,

$$\theta(s, t) = \sum_{q=0}^{\infty} u_q(t) \phi_q(s)$$

(2.16)

Here, the normal modes are sets of orthogonal basis functions, hence, it is natural to choose the eigen-functions of the biharmonic operator with natural boundary conditions ($\partial_s^2 \theta(-L/2) = \partial_s \theta(L/2) = 0$, $\partial_s \theta(-L/2) = \partial_s \theta(L/2) = 0$) as the normal modes since the leading contribution
governing filament dynamics is the fourth spatial derivative $\partial_{ssss}$ term. Thus, the normal modes are determined by

$$\phi_{ssss} - \Lambda_q \phi = 0, \quad \Lambda_q = k_q/(\pi AL)^4,$$

where $k_q$ is the $q$-th root of $\frac{1}{2} \cos(x)(e^x + e^{-x}) - 1 = 0$ and the eigenfunctions $\phi_q$ of this biharmonic operator are of the form,

$$\phi_q(s) = A \sin k_q s + B \sinh k_q s + D \cos k_q s + E \cosh k_q s$$

The coefficients are determined by the boundary conditions, and the first five normal modes are shown in Figure 2.4.

Here, we note the amplitudes $u_q(t)$ do not represent the true dynamical mode amplitudes due to the constraint in the governing equation. The true dynamical modes can be numerically calculated via proper orthogonal decomposition (POD) [48], however, the POD modes vary during the non-equilibrium dynamic process. A simple comparison between POD and normal modes is included in the Appendix. Here, the normal modes are proper for the shape deformation from the geometric aspect and computational convenience. For a simple scenario, if there are no interactions or correlations between each mode dynamics, i.e., the mode dynamics are all decoupled, the bending energy can be represented as quadratic summation of the normal modes amplitudes, i.e. $U = \frac{1}{2} A \sum_{q=1}^{\infty} k_q^2 u_q^2$. Then, each quadratic term contributes an $1/2k_B T$ from the equipartition theorem, thus, we have $u_q^2 = \frac{k_B T}{A} \frac{1}{k_q^2}$. However, it is not true for inextensible filament dynamics here due to the nonlinear interactions between different modes, which arise from the local inextensible constraint.

### 2.4.2 Numerical Results

First, we show that the spatial modes of the filament motion can be separated into symmetric (even) and antisymmetric (odd) relative to the mass center depending on whether under the transformation $r- \to -r$ they are even or odd functions. Our results show that for $W_i \leq 1$ odd modes are suppressed, which indicates fore-aft symmetry (Figure (2.5a)). As we increase $W_i$, the first mode is excited (Figure (2.5b)), further, for $W_i \gg 1$, odd modes are excited, which implies that symmetry is broken as in Figure (2.5c).

The average modal energies as functions of mode number $k_q$ display a sawtooth-trend due to the suppression of odd modes (two to three orders smaller than the even modes) and follow the equi-partition theorem for small $W_i \leq 1$, i.e., the modal energy exhibits $k_q^{-2}$ decay, as indicated
Figure 2.6: Time average normal modes energy as functions of mode number $k_q$, with $W_i = 100.0$ (red), $10.0$ (blue), $1.0$ (green). Data represented by solid symbols are derived from the numerical solution of continuum SPDEs, while data represented by open symbols are obtained from DPD simulations. The upper and lower dashed lines are reference lines for linear and quadratic decay, respectively.

by the dash line with slope = 2.0 in Figure 2.6. However, the modal energy decay is much slower for large $W_i \gg 1$, which is indicated by a dash line with slope = 1.0, and the sawtooth behavior disappears due to the excitation of odd modes (compared to even modes).

To further investigate the modal dynamics in time, we show the probability distribution functions (PDFs) of $\delta u_q$ defined as

$$\delta u_q (t) = u_q (t) - \langle u_q (t) \rangle$$

in Figure 2.7, compared to a normal distribution fitting. The corresponding variances increase continuously as we increase $\frac{1}{W_i}$, see inset in Figure 2.8. There is a three orders increase of variance within our parameters range, which implies that a significant amplification of thermal fluctuations is taking place. Another interesting physical property for studying modal dynamics is the autocorrelation function, which is defined in the usual way as,

$$C_q (t) = \langle \delta u_q (t_0 + t) \delta u_q (t_0) \rangle .$$

A useful observable to get insight into the stochastic behavior in time is the power spectral density (PSD) $P(f)$, which is the Fourier transform of the autocorrelation function $C_q(t)$, i.e.,

$P(f) := \text{FFTC}_q(t)$. In Figure 2.8, we show the PSD of the first mode $u_1$, at several values of $W_i$. For large frequencies (short time regime), the PSDs obey the same power law $P(f) \propto (\gamma f)^{-1}$. We
Figure 2.7: PDF of $\delta u_1$ with $W_i = 10.0$. (inset) PDF variance of $\delta u_1$ as a function of $W_i$.

Note that our results are from 2D simulation, thus the slopes here are different from previous 3D studies [19]. All of these PSD data with different parameters collapse onto a single line with a simple rescaling $f \sim f/W_i^{1/2}$. However, at small frequencies (long time regime), there is a pronounced increase in PSD with larger $W_i$, indicating stronger long-time correlations due to the interaction between nonlinearity and stochasticity.

To further quantify the Euler-buckling like instability and the transition point, we define $k^*$ motivated by a similar expression derived empirically as a wrinkling criterion for vesicle membranes in previous studies [30, 31]

$$k^* = \sqrt{\frac{12}{\sum_{q=2}^{12} q^2 |u_q|^2} / \sum_{q=2}^{12} |u_q|^2}$$

(2.21)

The results both from the continuous filament model and the bead-spring chain model show that a transition occurs with $W_i$ increasing to $O(1)$ as in Figure 2.10. This interesting transition can also be identified by the average end-to-end distance $R_f$ of the fiber as shown in Figure 2.9. This is the Euler-buckling like transition observed in previous experimental studies [23]. The departure into the flexible limit $\alpha/\beta \rightarrow \infty$ appears to be due to the use of steady flow Stokes resistance in continuous filament model Eq.(3)), which is valid only for rigid rods. In the coil regime, the hydrodynamic resistance is underestimated in the continuum model. Thus, the results from the continuum model will be closer to the DPD results if we increase the hydrodynamic resistance coefficient $\eta$ to $2\eta$. 

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Figure 2.8: Power spectral density function as a function of dimensionless frequency scaled with $\dot{\gamma}f/W_i^{1/2}$ and (inset) original data, red, blue and green lines represent $W_i = 100.0$, $W_i = 10.0$ and $W_i = 1.0$, respectively, with $\alpha = 10.0$. Data of solid and dashed lines are from solution of SPDEs and DPD simulations, respectively.

while keeping $W_i$ the same. These results and sensitivities are shown in Figures 2.10 and 2.9. Another difference between the two models originate from the hydrodynamics near the filament and the disturbance to the steady flow field by the filament deforming dynamics. The DPD model captures the instantaneous hydrodynamic interactions of the fluctuating flow field shown in Figure 9.2, and a more detailed video included as supplementary material.

Throughout this chapter, $W_i = \alpha/\beta$ is used to measure the system, which is also adopted by other deterministic models [23], i.e., models that do not include thermal fluctuations. However, a short discussion about these dimensionless parameters is needed for stochastic models, when the thermal energy dominates. We note that $\alpha = \dot{\gamma}\tau$ has the form of a Weissenberg number, with $\tau = \frac{\eta L^3}{k_B T}$ corresponding to the time the center of mass of the fiber takes to diffuse its own contour length, which is independent of the persistence length $l_P$. Thus, it seems more appropriate to consider the fiber relaxation time as the characteristic time, since we focus on fiber deformation dynamics. The characteristic relaxation time is widely used to study flexible polymer extension with hydrodynamic effects. For weak bending resistance, we can renormalize the semiflexible fiber into freely-jointed chain model with effective Kuhn length $l_P$ and number of segments $L/l_P$. Motivated
Figure 2.9: Relative end-to-end distance $R_f/L$ as a function of $W_i = \alpha/\beta$ determined from the planar motion of the Langevin filament (solid blue line) and the 2D motion of the DPD bead-spring chain (open red symbols) with $\alpha = 10.0$. The green symbols represent the variation of $R_f/L$ as the hydrodynamic resistance coefficients in the continuum model are changed from $\eta$ to $2\eta$ (upper symbol) and $0.5\eta$ (lower symbol) at constant $W_i$.

by the Zimm model for flexible polymers [49], we then define the relaxation time to be

$$\tau_R \propto \frac{\eta((L/P)^\nu L_P)^3}{k_B T} \propto \frac{\eta L^3 \beta^{3(1-\nu)}}{k_B T}$$

(2.22)

where $\nu$ is the Flory index and we take $\nu = 0.5$ for theta solvent in our simulation. Thus, we end up with another Weissenberg number $W = \alpha \beta^{3/2}$ and its limiting values indicate for: ($W \to \infty$) a nearly-rigid rod dominated by bending elasticity with negligible thermal fluctuations, while for ($W \to 0$) a flexible string dominated by Brownian forces. However, $W$ is only suitable for fiber under positive tension (extension relaxation). The effects of $W$ on fiber dynamics under negative tension are difficult to understand, hence, a new dimensionless number is required to capture accurately the physics of fiber dynamics under negative tension and thermal fluctuations.

### 2.5 Summary and Discussion

We considered here the dynamic response of a single inextensible, elastic filament subject to stretching/compression in a stagnation-point flow. We developed two different models, the first based on a stochastic PDE treating the filament as continuum, and the second based on dissipative particle dynamics (DPD) treating the filament as bead-spring chain. In the second model, the two-dimensional
stagnation-point flow is achieved by driving the particles with a body force derived from the pressure gradient of a potential flow in a lattice of vortices. In both models, the elastic properties are matched and the filament motion is constrained to the plane. In the DPD simulations the solvent is simulated explicitly and the corresponding particles are free to move in three-dimensions. On the other hand, in the continuum model, the solvent is simulated implicitly with the friction acting on the filament derived from the Stokes equation for a rigid rod subject to three-dimensional flow. The latter is subject to uncertainties, which we investigate by varying the magnitude of the friction coefficient by ±50%. In particular, we were interested in investigating the effect of thermal fluctuations on the dynamic response of the filament and the presence of a possible stretch-coil instability from two different modeling perspectives. We found that the filament displays a buckling instability induced by tension, analogous to the Euler beam, at Weissenberg number of order one. Above this values, both the temporal and spatial thermal noise are amplified due to interaction between the thermal fluctuations and the nonlinear filament dynamics. Normal mode analysis of the filament motion obtained by both models shows the response to be composed of the same modes, but the transition from nearly straight rods to loose coils suggests that constant resistance coefficients may overestimates the amplitude of the filament response. Although we have dealt only with the single continuous filament dynamics in an undisturbed stretching flow, the framework employed and
numerical schemes can be applied to concentrated filament solutions and filament networks with large disturbances of the flow field, where a Stokes or a Navier-Stokes solver should be employed together with our current frameworks [50].
Chapter 3

Anisotropic Dissipative Particle Dynamics Model

3.1 Introduction

The study of suspensions of Brownian colloids or nanoparticles encountered in biological and engineering applications has significantly advanced in recent years [51, 52, 53, 54, 55]. Colloidal particles can have a variety of shapes, including sphere, ellipsoid, rod, platelet, etc. A rather rich behavior of real colloidal systems can stem from the anisotropic shapes and interactions of colloidal particles [56, 57, 58, 59]. Hence, the dynamics of anisotropic particles is fundamental in many associated physical phenomena, such as sedimentation, coagulation, migration, and non-Newtonian rheology. Therefore, accurate and efficient models for suspensions of anisotropic particles are needed in many practical applications. Clusters of multiple particles commonly have been used to represent a single colloidal particle, a stiff fiber or other bluff bodies in dissipative particle dynamics (DPD) simulations to capture the correct hydrodynamics [60, 61]. However, such a representation may render a simulation inaccurate or prohibitively expensive.

Espanol et al. [5] proposed the fluid particle model (FPM) that sheds lights on possibly modeling colloid particles as single DPD particles by including torques and angular velocities of particles. Pan et al. [62] specified the general FPM formulation and demonstrated that the resulting model could capture the correct hydrodynamics of single DPD particles. The model was further extended to multi-sized particles to study colloidal suspensions [63], red blood cells [64], and also DNA [65]. However, all those formulations were restricted to isotropic spherical particles. In the present work, we propose a new DPD formulation that allows for modeling anisotropic particles by single DPD
particles. We then apply the new framework to study both static and dynamic behaviors of colloidal ellipsoid suspensions.

3.2 Formulation

We consider a canonical ensemble of single particles in three-dimensional (3D) space. The instantaneous state of the \(i\)th particle with fixed mass \(m_i\) and fixed-body frame inertia \(I^c_i\) is characterized by its position \(r_i(t)\), rotation matrix \(R_i(t)\), linear momentum \(P_i(t)\), and angular momentum \(L_i(t)\). These state variables provide the full spatial and velocity information. The \(\mu\)th column \((\mu = x, y, z)\) of \(R_i(t)\) represents the transformation of the \(\mu\)th axis of a particle from its fixed-body frame to the laboratory frame, which makes the rotation matrix satisfy \(R^T = R^{-1}\) and \(|R| = 1\). We define a state vector as \(Y_i(t) = (r_i(t), R_i(t), P_i(t), L_i(t))^T\), which is updated via the generalized Newton’s second law at each time step as:

\[
\frac{d}{dt} Y_i(t) = \begin{pmatrix}
\dot{r}_i(t) \\
\dot{R}_i(t) \\
\dot{P}_i(t) \\
\dot{L}_i(t)
\end{pmatrix} = \begin{pmatrix}
v_i(t) \\
\omega_i \times R_i(t) \\
F_i(t) \\
N_i(t)
\end{pmatrix}.
\]

Here, \(v_i(t) = m_i^{-1}P_i(t)\), \(\omega_i(t) = I_i(t)^{-1}L_i(t)\), \(F_i(t) = \sum_{j \neq i} F_{ij}\), and \(N_i(t) = \sum_{j \neq i} N_{ij}\), denoting the translational velocity, angular velocity, total force, and torque exerted on \(i\)th particle at time \(t\), respectively. \(I_i(t)\) is inertia in the laboratory frame and can be calculated via the rotation matrix as \(I_i(t) = R_i(t)I^c_iR_i(t)^T\).

In the present work, only two-body pairwise interactions are considered in the calculation of the total force and torque. Furthermore, the pairwise forces satisfy Newton’s third law, i.e., \(F_{ij} = -F_{ji}\). As such, the total linear momentum \(P = \sum_i P_i = \sum_i m_i v_i\) is a dynamical invariant with \(\dot{P} = 0\). In addition, the pairwise torque \(N_{ij}\) is defined as \(N_{ij} = -G_{ij}r_{ij} \times F_{ij}\). Here, the prefactor matrix \(G_{ij}\) is included to account for the different contributions from interacting particles with different sizes and shapes. It can be considered a generalization of the scalar factor defined in the isotropic single-particle DPD method [63, 66] as a weight to account for the size difference of interacting particles. The specific form of \(G_{ij}\) will be determined later. When \(G_{ij}\) satisfies \(G_{ij} + G_{ji} = I\) (\(I\): the \(3 \times 3\) identity matrix), it immediately follows that the total angular momentum \(J = \sum_i (r_i \times P_i + I_i \omega_i)\) is also conserved, i.e., \(\dot{J} = 0\).

The final expression of the corresponding Langevin equations for the examined particle system,
in the form of stochastic differential equations, can be written as:

\[
\begin{align*}
    d\mathbf{r}_i &= v_i dt = m_i^{-1} \mathbf{P}_i dt \\
    d\mathbf{R}_i &= \mathbf{\omega}_i \times \mathbf{R}_i dt = (I_i^{-1} \mathbf{L}_i) \times \mathbf{R}_i dt \\
    d\mathbf{P}_i &= \sum_{j \neq i} \left[ (F_{cj}^{ij} + F_{Tj}^{ij} + F_{Rj}^{ij}) dt + d\tilde{P}_{ij} \right] \\
    d\mathbf{L}_i &= -\sum_{j \neq i} G_{ij} \mathbf{r}_{ij} \times \left[ (F_{cj}^{ij} + F_{Tj}^{ij} + F_{Rj}^{ij}) dt + d\tilde{P}_{ij} \right].
\end{align*}
\]  

(3.2)

Here, as in Refs. [5, 62], the deterministic forces between particle \(i\) and \(j\) consist of four different terms: the conservative force \(F_{cj}^{ij}\), translational dissipative force \(F_{Tj}^{ij}\), rotational dissipative force \(F_{Rj}^{ij}\), and random force \(\tilde{F}_{ij} = d\tilde{P}_{ij}/dt\). The last term compensates for the effect of eliminating degrees of freedom during the coarse-graining procedure and is formulated to satisfy the fluctuation-dissipation theorem (FDT) given the expressions of the two dissipative forces. Previous studies [62, 63] have provided the specific formulations for the four force terms in the single-particle DPD model of isotropic spherical particles. In the present work, we aim to formulate the four force terms for slightly low symmetric (anisotropic) single particles in DPD.

To proceed, it is reasonable to assume that the mass density of an isotropic particle is Gaussian for computing the exclude-volume interactions, monopole and dipole hydrodynamic forces between isotropic particles. Hence, for anisotropic particles a generalized Gaussian function [67, 68, 69] is required. Specifically, if \(\mathbf{M}\) can be expressed as a quadratic form matrix, the density distribution of a single particle centered at \(\mathbf{r}_o\) can then be represented by a normalized Gaussian function as:

\[
    \rho(\mathbf{r}) = \frac{1}{\sqrt{8\pi^3|M|}} \exp \left[ -\frac{1}{2} (\mathbf{r} - \mathbf{r}_o)^T \mathbf{M}^{-1} (\mathbf{r} - \mathbf{r}_o) \right],
\]  

(3.3)

with \(\mathbf{M} = \mathbf{R}_i^T \mathbf{S}_i^2 \mathbf{R}_i\). Here, \(\mathbf{S}\) is the shape matrix indicating the particle size and shape. For example, for an ellipsoid particle with semi-principal axes of length \(R_a, R_b, \) and \(R_c\), \(\mathbf{S} = \text{diag}(R_a, R_b, R_c)\). We particularly interested in the interactions between two anisotropic particles \(i\) and \(j\), centered at \(\mathbf{r}_i\) and \(\mathbf{r}_j\), with the shape matrices \(\mathbf{S}_i\) and \(\mathbf{S}_j\), and the rotation matrices \(\mathbf{R}_i, \mathbf{R}_j\). We denote

\[
    \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \quad \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j, \quad \text{and} \quad \mathbf{\Omega}_{ij} = \mathbf{\omega}_i \times \mathbf{G}_{ij} \mathbf{r}_{ij} + \mathbf{\omega}_j \times \mathbf{G}_{ji} \mathbf{r}_{ij}.
\]

And we further define

\[
    \mathbf{M}_i = \mathbf{R}_i^T \mathbf{S}_i^2 \mathbf{R}_i, \quad \mathbf{M}_j = \mathbf{R}_j^T \mathbf{S}_j^2 \mathbf{R}_j, \quad \text{and} \quad \mathbf{H}_{ij} = \mathbf{M}_i + \mathbf{M}_j.
\]
The prefactor matrix in the pairwise torque (Eq. 3.2) between particles \(i\) and \(j\) is thus determined as \(G_{ij} = M_i^{-1}(M_i^{-1} + M_j^{-1})^{-1}\), which exactly satisfies \(G_{ij} + G_{ji} = I\). Moreover, \(H_{ij}^{-1}\) is a real symmetric \(3 \times 3\) matrix and can be decomposed as

\[
H_{ij}^{-1} = PQ^2P^T = (PQ)(PQ)^T.
\]

Based on this decomposition, the linear mapping operator is constructed as \((PQ)\), which thereby maps the anisotropic coordinates to isotropic ones as:

\[
r_{ij} = (PQ)\bar{r}_{ij}, \quad v_{ij} = (PQ)\bar{v}_{ij}, \quad \text{and} \quad \Omega_{ij} = (PQ)\bar{\Omega}_{ij},
\]

with \(\bar{r}\) indicating the isotropic coordinates. The main idea behind is that the forces between two single DPD particles can always be written as bilinear forms inner product (integration with respect to above Gaussian distributions), which further can be expressed as symmetric positive-definite matrix form, i.e. \(<X,Y> = XA Y\), with \(A\) the symmetric positive-definite matrix. Hence, a compact form for the deterministic forces between anisotropic DPD particles can be written as:

\[
F_C^C_{ij} = (PQ)a_{ij}W_c(\bar{r}_{ij})\bar{r}_{ij},
F_T^T_{ij} = -(PQ)W_d(\bar{r}_{ij})(\gamma_{ij}^e I + (\gamma_{ij}^c - \gamma_{ij}^s)\bar{e}_{ij} \otimes \bar{e}_{ij}) \cdot \bar{v}_{ij},
F_R^R_{ij} = -(PQ)W_d(\bar{r}_{ij})(\gamma_{ij}^e I + (\gamma_{ij}^c - \gamma_{ij}^s)\bar{e}_{ij} \otimes \bar{e}_{ij}) \cdot \bar{\Omega}_{ij},
\]

with \(\bar{e}_{ij} = \bar{r}_{ij}/|\bar{r}_{ij}|\). Here, \(a_{ij}, \gamma_{ij}^c,\) and \(\gamma_{ij}^s\) are the conservative, translational and rotational dissipative coefficients, respectively, while \(W_c\) and \(W_d\) are the kernel functions for the respective conservative and dissipative forces. In particular, the Gaussian function for both \(W_c\) and \(W_d\) is given as:

\[
W(\bar{r}_{ij}, H_{ij}) = \frac{1}{\sqrt{|H_{ij}|}} \exp(-\alpha \bar{r}_{ij}^T H_{ij} \bar{r}_{ij}),
\]

and can be obtained from the double integral of the Gaussian density distribution function in Eq. (3.3), i.e.,

\[
W(\bar{r}_{ij}, H_{ij}) = \int d\bar{r}' \int d\bar{r}'' \rho_c(\bar{r}')\rho_d(\bar{r}'')\delta(\bar{r}' - \bar{r}'')
\]

However, Eq. (3.5) can be replaced with other functions [70, 67, 69, 71, 72, 73, 74] by using different functions rather than the delta function in the above integral. Note that the parameter \(\alpha\) in \(W_c\) and \(W_d\) generally takes different values. In particular, \(\alpha_c\) in the conservative kernel \(W_c\) is larger, reflecting the rapid decay of excluded-volume repulsive force, while \(\alpha_d\) in the dissipative kernel \(W_d\) is smaller, capturing the long-range nature of hydrodynamic dissipation. In the present work, we
specifically use $\alpha_c = 1.3$ and $\alpha_d = 0.65$ throughout all the simulations.

Figure 3.1: (a) The magnitude contour of conservative forces between two identical ellipsoid particles with semi-axis lengths of 0.8, 0.4, and 0.4, at varying distances and orientation angles. Here, one particle is fixed while the other particle rotates around one of its short axes (around $y$ axis for (a) and $z$ axis for (b) plots, respectively) with a varying angle $\theta$. The two ellipsoid particles are initially positioned parallel along the short axes as sketched in (b).

To illustrate the orientational anisotropy of the interacting forces, Figure 3.1 shows the variation of the conservative forces between two identical ellipsoid particles with varying distances and orientation angles. As the conservative force is essentially a repulsive excluded-volume interaction, the two ellipsoid particles tend to be parallel with each other to minimize their free energy at any given center-to-center distance.

Finally, the random force is formulated as:

$$
\tilde{\mathbf{F}}_{ij}dt = (\mathbf{PQ}) W_r(\tilde{\mathbf{r}}_{ij}) \left[ \frac{\sigma^c_{ij}}{\sqrt{3}} \text{tr}[dW_{ij}] \mathbf{I} + \sqrt{2} \sigma^s_{ij} dW_{ij}^A \right] \cdot \tilde{\mathbf{e}}_{ij}. 
$$

(3.6)

Here, $dW_{ij}$ is a random matrix of independent Wiener increments, which is symmetric under particle interchange; $dW_{ij}^A$ is the antisymmetric random matrix with each element defined as $dW_{ij}^{\alpha\nu} = \frac{1}{2} (dW_{ij}^{\alpha\nu} - dW_{ij}^{\nu\alpha})$. The random force coefficients are $\sigma^c_{ij} = \sqrt{2k_B T \gamma^c_{ij}}$ and $\sigma^s_{ij} = \sqrt{2k_B T \gamma^s_{ij}}$. The kernel function in the random force satisfies $W^2_r(\tilde{\mathbf{r}}_{ij}) = W_d(\tilde{\mathbf{r}}_{ij})$. Based on this and due to
the invariant property of linear mapping, the FDT is automatically satisfied, which is also verified numerically by examining the kinetic temperature in each translational and rotational degree of freedom in the next section.

In summary, we have formulated the anisotropic single-particle DPD model with tunable effective parameters $\alpha_{ij}^c$, $\gamma_{ij}^s$, $\gamma_{ij}^c$, $\alpha_c$, and $\alpha_d$. The new formulation is essentially constructed via linear transformation from isotropic spherical interactions to anisotropic ones, and hence it can be readily reduced to that in the isotropic single-particle DPD model [62]. In the next section, the proposed framework is applied to study the static and dynamic properties of single ellipsoid particle (dilute suspension) and concentrated ellipsoid suspensions.

3.3 Results and Discussion

In all simulations presented in this section, the model of an ellipsoid suspension consists of suspended colloids represented as single ellipsoid DPD particles with a larger dimension and mass as well as a solvent bath of isotropic spherical DPD particles with a smaller radius and mass. Specifically, the solvent particle has a constant radius of 0.25, while the semi-axis lengths ($R_a$, $R_b$, and $R_c$) of the colloidal particle vary around 1.0, all in reduced DPD units. Without loss of generality, we consider ellipsoids with a pair of equal semi-axes and a distinct third semi-axis, i.e., prolate spheroids (two equal short axes and a long axis) and oblate spheroids (two equal long axes and one short axis).

First, we examine the solvation of a single colloid immersed in solvent at equilibrium. Figure 3.2

![Figure 3.2: Number density distribution of solvent particles with a solvation layer around an immersed single (a) spherical particle with a radius of 1.0, and (b) ellipsoid particle with semi-axis lengths of 1.5, 0.8165, and 0.8165. The black lines indicate the colloid-intrinsic boundaries.](image)
depicts the impenetrable area of the colloidal particle by the number density distribution of its surrounding solvent particles. By adjusting the parameters of conservative interactions between particles, i.e., $a_{ss} = 2.5$, $a_{cs} = 175.2$, and $\alpha_c = 1.30$, the calculated shape and dimensions for the impenetrable area of the colloidal particle are found to be consistent with the intrinsic shape and dimensions of the colloid as the input parameters in the shape matrix. This indicates that our conservative force can effectively preserve the size and shape of an anisotropic particle.

### 3.3.1 Microstructure in ellipsoid suspensions

Second, we use the proposed new DPD model to study the microstructure of colloidal ellipsoids in suspensions. Recently, Cohen and coworkers reported that compared to isotropic spherical colloids the rotational anisotropy of ellipsoids tends to smear out the shell structures of colloids in suspensions with moderate volume fractions [75]. This can be examined by computing the radial distribution function (RDF) $g(r)$ of colloidal particles. As shown in Figure 3.3, the peaks in the computed $g(r)$ of ellipsoids are much less pronounced than those of spherical colloids. This finding is consistent with the direct structural measurements by Cohen et al. [75]. Thus, our model captures accurately the microstructure of colloidal ellipsoids in suspensions. We note that $g(r)$ is not identically zero for $r < 2$, reflecting the fact that colloidal particles slightly overlap due to the soft Gaussian kernel function (Eq. 3.5).

![Figure 3.3: Radial distribution function $g(r)$ of prolate ellipsoids ($R_b = R_e$) with the aspect ratio $R_a/R_b = 2.0$ (blue line) and spherical colloids (red line) in suspensions with the same volume fraction $\phi = 0.31$. Here, $r$ is normalized by the short axis length ($R_b$) of prolate for ellipsoids or by the radius of sphere ($R_s$) for spherical colloids.](image-url)
The isotropic-nematic transition is another interesting phenomenon for concentrate suspensions of colloidal ellipsoids. In the isotropic phase, colloidal particles are randomly distributed without any orientational order. As the volume fraction of ellipsoids or the anisotropy of ellipsoids increases, the transition from isotropic to nematic phase takes place, in which colloidal particles tend to align in parallel to minimize the free energy of repulsive interactions. Figure 3.4 (a) and (b) show the

![Figure 3.4: Microstructures of colloidal ellipsoids in suspensions corresponding to the isotropic-nematic phase transition, with increase the volume fraction (upper, (a) isotropic phase $\phi = 5.3\%$, $R_a/R_b = 2.0$, (b) nematic phase $\phi = 70\%$, $R_a/R_b = 2.0$), or increase the axes ratio (lower, (c) isotropic phase $\phi = 31\%$, $R_a/R_b = 1.31$, (d) nematic phase, $\phi = 31\%$, $R_a/R_b = 3.71$).](image)

snapshots of both phases for ellipsoid particles with the same aspect ratio at different volume
fractions.

Figure 3.4 (c) and (d) illustrate the phase transition from one to the other due to the increased aspect ratio of ellipsoids at the same volume fraction. This phase transition can be characterized by the orientation order parameter $S$, which, by definition, is the largest eigenvalue of the second-rank ordering tensor $Q$ that can be calculated from

$$Q_{\nu\mu} = \frac{1}{N} \sum_i \frac{3}{2} \hat{n}_i \hat{n}_i \hat{n}_i - \frac{1}{2} \delta_{\nu\mu}. \quad (3.7)$$

Here, $\hat{n}$ is the unit vector along the ellipsoid long axis in the laboratory frame, and $\nu, \mu$ vary between $x, y, z$. Figure 3.5 (a) depicts the variation of $S$ as a function of the volume fraction $\phi$, given the fixed ellipsoid aspect ratio $R_a/R_b = 2.0$. In this example, $S$ is near zero when $\phi$ is small, and the transition takes place when $\phi$ reaches $50\% - 60\%$, followed by a gradual increase toward unity as $\phi$ further increases. The transition point at about $50\% - 60\%$ is found to agree with previous studies [76, 77]. However, we note that the transition is not as sharp as those predicted in the Percus-Yevick theory [76] or the Gay-Berne-potential based molecular dynamics simulation [78, 77], which can result from the soft Gaussian-type potential used in the model. In Figure 3.5 (b), varying $S$ is associated with the isotropic-nematic transition due to the increased aspect ratios $R_a/R_b$, even at a moderate volume fraction, i.e., $\phi = 31\%$.

In this section, the thermostat in the new anisotropic DPD model is verified by checking the translational, rotational, and total kinetic temperatures of a homogeneous particle system consisting of identical ellipsoidal DPD particles. In Figure 3.6 (a), the new DPD thermostat robustly yields fast
convergence for all kinetic temperatures to their desire values, indicating that the FDT is accurately satisfied. In addition, Figure 3.6 (b) depicts the total energy, including kinetic and conservative energies, converges fast to its equilibrium value. Moreover, both the linear and angular momenta are found to follow the Boltzmann distribution precisely, which is illustrated in Figure 3.6 (c) and (d).

![Figure 3.6: (a) Kinetic temperatures and (b) energies converge to their equilibrium values in a homogeneous particle system consisting of identical ellipsoidal DPD particles; (c) angular and (d) translational velocities follow the Boltzmann distribution.](image)

3.3.2 Hydrodynamics of ellipsoid in suspension

Notably, DPD was invented to accurately capture the dynamic properties of coarse-grained systems, including hydrodynamics and diffusion, which is the primary advantage of DPD compared to other coarse-grained methods. Thus, we examine the proposed model’s accuracy in reproducing the correct hydrodynamics and diffusion of colloidal ellipsoid in suspension.
We first study the hydrodynamics of flow around ellipsoid DPD particles. In particular, we test a uniform flow past a periodic array of oblate ellipsoids. The oblate ellipsoid was held stationary at the center of a cubic periodic domain. The flow then is driven by an external body force $F_{\text{ext}}$ exerted on all solvent particles, and the flow direction is along one of the ellipsoid’s short axes. The cubic lattice array was sized to ensure that the effect of the periodic neighboring colloids is negligible. This was verified by doubling the lattice dimension. Figure 3.7 (a) and (b) show the calculated velocity fields around the colloid along the flow direction for different-shaped oblate ellipsoids for a small portion of the cubic domain. The drag force $F_d$ exerted on the stationary particle was computed, and for the free particles an average superficial streaming velocity $U$ was calculated from $U = \frac{1}{V} \int_V u(x, y, z) dV$. At low Reynolds numbers, the drag force on the oblate satisfies the Stokes law: $F_d = 6\beta \pi \eta U R_s$. Here, $R_s$ is the effective Stokes radius of the oblate, and $\beta$ is the shape factor. The calculated superficial velocity as a function of the oblate aspect ratio is plotted in Figure 3.8, compared with the analytical prediction from the Stokes law [1]. Here, the calculated superficial velocities were normalized by that of the flow around a spherical colloid with the same volume and body force $F_{\text{ext}}$ exerted on solvent particles. In these simulations, we first determined the dissipative parameters $\gamma_c$ and $\gamma_s$ in simulating the flow around a spherical colloid to reproduce the correct hydrodynamics, and these parameters remain unchanged in the simulations of flow around ellipsoid particles with different aspect ratios.

![Figure 3.7](image-url)  
(a) 
(b)  

Figure 3.7: The velocity field of uniform flow past a periodic array of oblate ellipsoids with semi-axis lengths of (a) 1.414, 1.414, and 0.5; (b) 1.085, 1.085, and 0.85.
Figure 3.8: The calculated relative superficial velocity of flow around an oblate ellipsoid as a function of aspect ratio $R_a/R_b$ (symbol), compared with the analytical results [1] (solid line), with the Reynolds numbers are in the order of $10^{-3}$ to $10^{-2}$.

### 3.3.3 Diffusion of ellipsoid in suspension

Having demonstrated that the model can accurately capture the hydrodynamics of colloidal ellipsoid in flow, we next apply it to study the diffusion of ellipsoid particles. Diffusion of an ellipsoid particle can be described by its translational and angular mean-square displacements (MSDs), as previously studied by Han et al. [79, 80] for quasi-two-dimensional (2D) ellipsoids.

In the simulations, we recorded the ellipsoid particle trajectory in the laboratory frame, including the center of mass position $r(t)$ and rotation matrix $R(t)$ at each time step. At the $n$th time step, the particle’s translational displacement $\delta r(t_n)$ was mapped onto the fixed-body frame, i.e., obtaining the translational displacement along the principal axes denoted as $\delta \tilde{r}(t_n)$ by $\delta \tilde{r}(t_n) = R(t_n)\delta r(t_n)$.

The rotational displacement around the principal axes $\delta \tilde{\theta}(t_n)$ is approximated by the infinitesimal rotation matrix as $\mathbf{e} = R(t_{n+1})R^{-1}(t_n) - \mathbf{I}$, that is antisymmetric and has the form of

$$
\mathbf{e} = \begin{pmatrix}
0 & \delta \tilde{\theta}_c & -\delta \tilde{\theta}_b \\
-\delta \tilde{\theta}_c & 0 & \delta \tilde{\theta}_a \\
\delta \tilde{\theta}_b & -\delta \tilde{\theta}_a & 0
\end{pmatrix}.
$$

(3.8)

Thus, the total fixed-body frame displacements after $n$ time steps is the summation of all displacements in each time step, i.e., $\tilde{r}(t_n) = \sum_{k=1}^{n} \delta \tilde{r}_k$, and $\tilde{\theta}(t_n) = \sum_{k=1}^{n} \delta \tilde{\theta}_k$. Then, the displacements in the fixed-body frame of any duration $t$ at a starting time $\tau_0$ are calculated as $\Delta \tilde{r}(t) = \tilde{r}(t+\tau_0) - \tilde{r}(\tau_0)$ and $\Delta \tilde{\theta}(t) = \tilde{\theta}(t+\tau_0) - \tilde{\theta}(\tau_0)$, respectively. Figure 3.9 (a) and (b) depict the calculated transla-
Figure 3.9: (a) Translational and (b) rotational trajectories of an ellipsoid particle in the fixed-body frame with semi-axis lengths of 0.8, 0.4, and 0.4.

Translational and rotational trajectories of an ellipsoid particle in the fixed-body frame. As anticipated, the diffusion of an anisotropic particle varies with respect to direction, specifically, diffusion is significantly faster along the long axis than along the two short axes.

The MSDs in the fixed-body frame are statistically averaged (ensemble average) over all trajectories and different starting times $\tau_0$. They follow normal diffusion laws in long-time limit as

$$< [\Delta \tilde{r}_\mu(t)]^2 > = 2D_{t\mu}t, \text{ and } < [\Delta \tilde{\theta}_\mu(t)]^2 > = 2D_{r\mu}t, $$

with $\mu = a, b, c$ (axes in the fixed-body frame). We further define the overall average translational self-diffusion coefficient as

$$D_t = (D_{ta} + D_{tb} + D_{tc})/3$$

and the average rotational self-diffusion coefficient as

$$D_r = (D_{ra} + D_{rb} + D_{rc})/3.$$

The self-diffusion coefficients of a colloidal particle are related to its size and shape (effective hydrodynamical radius) via the Stokes-Einstein relation. Figure 3.10 (a) and (b) illustrate the computed MSDs in the fixed-body frame of a single ellipsoid with the aspect ratio $R_a/R_b = 2.0$. 

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Figure 3.10: (a) Translational MSDs of an ellipsoid particle with semi-axis lengths of 0.8, 0.4, and 0.4, along the fixed-body long axis (red) and the short axis (green). (b) Rotational MSDs around the fixed-body long axis (red) and the short axis (green).

The ratio between the translational diffusion coefficients along the long and short axes, i.e., $D_{ta}/D_{tb}$ ($D_{tb} = D_{tc}$), is estimated to be about 1.20 in our simulation, close to the theoretical result of about 1.15 [81]. The ratio between the rotational diffusion coefficients around the long and short axes, i.e., $D_{ra}/D_{rb}$ ($D_{rb} = D_{rc}$), is about 1.27.

The translational ($D_t$) and rotational diffusions ($D_r$) of a prolate particle relative to the corresponding diffusions ($D_{0t}, D_{0r}$) of a spherical particle with the same volume have been well established by Perrin [82, 83]. Therefore, we plot the normalized $D_t$ and $D_r$ by $D_{0t}$ and $D_{0r}$, respectively, as a

Figure 3.11: (a) The relative translational and (b) rotational diffusion coefficients as a function of aspect ratios (symbol), compared with Perrin’s analytical results (black solid line). Error bars are calculated as standard deviations of the ensemble average. The red and blue dots indicate low (number density $\rho = 3$) and higher ($\rho = 6$) resolutions, respectively.
function of the aspect ratio in Figure 3.11 (a) and (b). Our results agree very well with Perrin’s analytical results for up to moderate aspect ratios, i.e., $R_a/R_b \in (0.3, 3.5)$. As the anisotropy becomes more pronounced, leading to very elongated ellipsoid, the simulation results start to deviate from the analytical prediction. This can be alleviated by increasing the simulation resolution using smaller solvent particles, which results in more expensive computational cost. As shown in Figure 3.11 (a) and (b), the agreement with the analytical results improves using a doubled number density of solvent particles (blue dots). Alternatively, we in practice, can also make the dissipative parameters of anisotropic particles adaptive to their aspect ratios, instead of fixing their values as those of a spherical particle with the same volume.

### 3.4 Conclusion

An efficient new computational method was developed for modeling anisotropic bluff bodies using single particles in DPD, filling a gap in the current literature on mesoscopic methods. We have demonstrated the accuracy of the proposed method by capturing both static and dynamic properties of suspensions of colloidal ellipsoids. Three remarks bring further clarity to this new approach. First, the soft Gaussian excluded-volume repulsion between single DPD particles can be replaced by some hard potentials, such as the empirical Gay-Berne and RE-squared potentials used in molecular dynamics simulations, and other specifically-designed interaction potentials, which will make this model attractive to simulate self-assembly of nanoparticles in complex materials [84]. Second, to model particles with strong anisotropy, higher resolutions and hence more expansive computations are necessary to resolve the singularities at the sharp ends of particles. Alternatively, low-symmetric bluff bodies can be modeled as clusters of small anisotropic particles. Hence, we can extend our model to study both static and dynamic properties of suspensions of a broad range of low-symmetric bluff bodies, such as boomerang colloidal particles [85] that can be effectively constructed via two ellipsoids. Last, the present framework generalizes the standard isotropic DPD model to afford development of more efficient anisotropic coarse-grained models for macromolecules and proteins [86].
Chapter 4

Charged Dissipative Particle Dynamics Model

4.1 Introduction

Electro-kinetic phenomena refer to the coupling of hydrodynamic and electrostatic phenomena in the vicinity of a charged surface, which are ubiquitous in nature and in many engineering applications [87, 88, 89]. Understanding the electro-kinetic phenomena is of great practical importance in fields as diverse as micro-fluidics [90, 91, 92], colloid science [93], biological systems [94], oil exploration [95], etc.. From the modeling perspective, the challenge lies in the wide range of length and time scales involved in electro-kinetic phenomena, and several simulation methods have been applied from molecular dynamics (MD) [96, 97, 98, 99] and Classical Density Functional Theory (cDFT)[100] to continuum solvers of both deterministic and stochastic PNP-NS equations [101, 100, 102, 103, 104], aiming at different range of scales depending on the specific application.

In general, atomistic MD with proper force field can be viewed as the first-principle simulation of electro-kinetic systems that provide an accurate approach in quantifying and understanding electro-kinetic phenomena. However, the computational cost of atomistic MD simulations prevents their use to investigating large scale systems, especially due to extra cost in computing long-range electrostatic interactions. Moreover, there is a multi-scale nature associated with electro-kinetic phenomena; for example, the length scales vary several orders from micro-scales even to macro-scales in electro-kinetic systems, which involve atom/molecular size (effective Born radius of ion and solvent) [105, 106], charged objects size(effective hydrodynamic radius of colloids, polymers, cells, etc.) [107, 108], characteristic ion-ion interaction length (Bejerrum length) [109], ion-surface
interaction length (Gouy-Chapmann length) [110, 111], screening length (Debye length)[112], and hydrodynamic interaction lengths etc. The electro-kinetic phenomena associated with these length scales also occur over a wide range of time scales. Thus, the multi-scale nature makes it very challenging to model electro-kinetic phenomena in different scales using either single MD simulation or a single continuum solver of the PNP-NS equations.

To address this multi-scale challenge and develop a useful method for applications in micro-devices, a variety of mesoscopic approaches also have been proposed, including Dissipative Particle Dynamics (DPD) [113, 114, 115, 116, 117, 118, 119], Langevin Dynamics [120], Brownian Dynamics [121], Lattice Boltzmann[103] etc.. These mesoscopic simulation methods provide proper ways to bridge the gap between atomistic MD simulations and continuum solvers. Specifically, the description of solvent and ions can either be modeled explicitly as particles or implicitly as continuum fields. In particular, the explicit description of solvents and ions as particles is straightforward and could also capture the fluctuations and correlations accurately with enough samples, which are extremely important for mesoscopic electro-kinetic phenomena. However, the explicit description would tax computational resources heavily, especially for systems where long-range interactions dominate. In contrast, the implicit description of solvents and ions as continuum fields is much more efficient than the explicit descriptions. However, the implicit description is only valid when the characteristic length scales are above the continuum limits, and it is a non trivial task to take the discrete treatment of both thermal fluctuations and electrostatic correlations into account in implicit mesoscopic models.

Here, we propose an extension of classical DPD, which we name cDPD, to study the electro-kinetic phenomena. Specifically, the solvent is described explicitly in a coarse-graining sense as DPD particles, while the ion species are described semi-implicitly, i.e., using a Lagrangian description of ion species concentration fields, associated with every DPD particle. This provides a natural coupling between electrostatics and fluid motions. Moreover, the thermal fluctuations are carefully incorporated within this model.

The remainder of this chapter is organized as follows: the details of cDPD model are given in the Methodology section. In particular, we first discuss the evolution equations of cDPD state variables, which mimic the Lagrangian form of the stochastic PNP-NS equations. Subsequently, the methodology for imposing correct hydrodynamic and electro-kinetic boundary conditions is presented, including Dirichlet and Neumann boundary conditions for both ionic species concentration and electrostatic field. The mapping of DPD units to physical units is also briefly mentioned in this section. In the Results section, we validate the cDPD model and the corresponding boundary methodologies with simulations of the electrostatic double layer (EDL) in the vicinity of a charged...
surface, the parallel plate capacitor, and pure electro-osmotic and mixed electro-osmotic / pressure-driven flow in a micro-channel. The results are compared directly with well-known results from the mean-field theory. To show the flexibility and capability of the cDPD method, we also study a dilute poly-electrolyte solution in electro-osmotic flow in a micro-channel. Finally, we conclude with a brief summary and discussion in the last section.

4.2 Methodology

Mesoscopic electro-kinetic phenomena are usually described by fluctuating hydrodynamics and electro-kinetics, i.e., the stochastic PNP-NS equations. Essentially, the cDPD model we develop here is an extension of the classic DPD model to numerically mimic the stochastic PNP-NS equations, with the idea that the mesoscopic diffusion terms can be modeled via pairwise fluxes between DPD particles [122, 123].

4.2.1 Governing Equations

For a canonical (NVT) ensemble of cDPD particles with unit mass, the state vector of the \( i \)th cDPD particle can be written as \( (r_i, v_i, c_{\alpha i}, \phi_i) \), which is not only characterized by its position \( r_i \) and velocity \( v_i \) as in classic DPD, but also by ionic species concentration \( c_{\alpha i} \) (with \( \alpha \) representing the \( \alpha \)th ion type) and electrostatic potential \( \phi_i \) within this particle. The time evolution of the state vector of the \( i \)th cDPD particle with unit mass is governed by the following set of stochastic differential equations (SDEs):

\[
\begin{align*}
\frac{d^2 r_i}{dt^2} &= \frac{dv_i}{dt} = F_i = \sum_{i \neq j} (F_{ij}^C + F_{ij}^D + F_{ij}^R + F_{ij}^E) \\
\frac{dc_{\alpha i}}{dt} &= q_{\alpha i} = \sum_{i \neq j} (q_{\alpha ij}^D + q_{\alpha ij}^E + q_{\alpha ij}^R),
\end{align*}
\]

(4.1)

where \( F_i \) denotes the total force exerted on the \( i \)th particle, which consists of three pairwise forces between cDPD particles as in classical DPD method, i.e., the conservative force \( F^C \), dissipative force \( F^D \) and random force \( F^R \). Additionally, the electrostatic force \( F^E \) is also introduced to couple
the hydrodynamics and electro-kinetics following the DPD framework. In particular,

\begin{align}
F^C_{ij} &= a_{ij} \omega_C(r_{ij}) \hat{r}_{ij} \\
F^D_{ij} &= -\gamma_{ij} \omega_D(r_{ij}) (\hat{r}_{ij} \cdot \mathbf{v}_{ij}) \hat{r}_{ij} \\
F^R_{ij} &= \sigma_{ij} \omega_R(r_{ij}) \theta_{ij} \delta t^{1/2} \hat{r}_{ij} \\
F^E_{ij} &= \lambda_{ij} \rho_{ei} E_{ij},
\end{align}

(4.2)

where \( r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|, \hat{r}_{ij} = \mathbf{r}_{ij}/r_{ij} \) and \( \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j \). The conservative, dissipative and random forces are all pairwise forces with weighting functions \( \omega_C(r_{ij}), \omega_D(r_{ij}), \omega_R(r_{ij}) \), and corresponding strength \( a_{ij}, \gamma_{ij}, \sigma_{ij} \), respectively. Also, \( \theta_{ij} \) are symmetric Gaussian random variables with zero mean and unit variance, and they are independent for different pairs of particles at different times; \( \theta_{ij} = \theta_{ji} \) is enforced to satisfy momentum conservation. The dissipative and random forces together act as a thermostat with their coefficients and weighting functions satisfying the fluctuation-dissipation theorem (FDT)\[2, 3, 8\]

\[\sigma_{ij}^2 = 2k_B T \gamma_{ij} \quad \omega_D(r_{ij}) = \omega_R^2(r_{ij}),\]

(4.3)

where \( k_B T \) is the rescaled thermal energy in DPD units. The coupling parameter \( \lambda_{ij} \) in the electrostatic force is introduced by rescaling the PNP equations with DPD units, which is linearly related to macroscopic dimensionless coupling parameter \( \Lambda = \frac{k_B T \tau^2}{\rho_0 r_0^2 c_0} \), with \( c_0 \) and \( \rho_0 \) the reference concentration and mass density, which are chosen as the salt concentration and mass density of bulk solution, respectively; \( r_0 \) and \( \tau \) are the unit length and time in DPD. Here, \( \rho_{ei} = \sum_\alpha z_\alpha c_{ai} \) is the total charge density within the \( i \)th particle, and \( \mathbf{E}_{ij} \) is the relative electric fields between particle \( i \) and \( j \), which is determined by the electrostatic potential field difference

\[\mathbf{E}_{ij} = (\phi_i - \phi_j) \omega_E(r_{ij}) \hat{r}_{ij} \]

(4.4)

with \( \omega_E(r) \) a weighting function. It is very important to notice that the electrostatic forces here are essentially not pairwise, i.e., \( F^E_{ij} \neq F^E_{ji} \), however, \( \sum_{i,j} F^E_{ij} = 0 \) is always satisfied because of the charge neutrality condition \( \sum_i \sum_\alpha z_\alpha c_{ai} = 0 \), which further guarantees the global momentum conservation when there is no external electrostatic field.

In this cDPD framework, the evolution of ionic species concentrations (rescaled by reference concentration \( c_0 \)) associated with the \( i \)th cDPD particle is explicitly and seamlessly included to mimic the stochastic PNP equation with Lagrangian description. Specifically, the concentration dynamics is driven by three flux terms, i.e. the Fickian flux \( q^D \) induced by the concentration
gradient \( c_{\alpha ij} = c_{\alpha i} - c_{\alpha j} \), the electrostatic flux \( q^E \) induced by electrostatic potential gradient \( \phi_{ij} = \phi_i - \phi_j \), and the random flux \( q^R \), which can be written as

\[
\begin{align*}
q_{\alpha ij}^D &= -\kappa_{\alpha ij} c_{\alpha ij} \omega_{qD}(r_{ij}) \\
q_{\alpha ij}^E &= -\kappa_{\alpha ij} z_{\alpha} \tau_{\alpha ij} \phi_{ij} \omega_{qD}(r_{ij}) \\
q_{\alpha ij}^R &= \xi_{\alpha ij} \omega_{qR}(r_{ij}) \theta_{ij} \delta t^{-1/2},
\end{align*}
\]

where \( c_{\alpha ij} = (c_{\alpha i} + c_{\alpha j})/2 \) is the average ionic concentration and \( \kappa_{\alpha ij} \) are the diffusion coefficients of the \( \alpha \)th specie between particle \( i \) and \( j \), \( \omega_{qD}(r_{ij}) \) weighting functions of deterministic flux. The coefficient \( \xi_{\alpha ij} \) and weighting function \( \omega_{qR}(r_{ij}) \) of the random flux are determined via the generalized fluctuation-dissipation theorem (FDT) as

\[
\xi_{\alpha ij}^2 = \frac{\kappa_{\alpha ij}}{c_0 r_0^3}(c_{\alpha i} + c_{\alpha j}) \quad \omega_{qD}(r) = \omega_{qR}^2(r).
\]

Eq.(4.6) suggests that the variance of random flux is proportional to \( 1/r_0^3 \), and thus the random flux cannot be neglected in micro- and nano- scales with \( r_0 \approx 10^{-9} - 10^{-4} \text{m} \). Here, we ignore the relative small mutual-diffusions terms and only consider self-diffusions of ionic species. This assumption is only valid in dilute solutions, however, in concentrated solutions, the generalization of the current cDPD model to include mutual-diffusions of multi-type ionic species is rather straightforward.

The electrostatic potential \( \phi \) on each cDPD particle is determined by solving the Poisson equation at every DPD time-step. Usually, a grid-based Poisson solver is employed on top of the DPD framework. However, in order to use a grid-based Poisson solver one has to map a particle system onto a grid and then solve the Poisson equation on the grid. Subsequently, the resulting electrostatic field on the grid has to be redistributed back to the particles. Although the particle-to-mesh and then mesh-to-particle mapping/redistribution can solve Poisson equation for particle-based systems [113], its dependence on grid may contradict the original motivation for using a Lagrangian method, and additional computational complexity and inefficiencies are introduced. In the present work, we propose an alternative seamless Poisson solver on cDPD particles, such that the entire framework uses only one unifying Lagrangian description. In practice, in cDPD we consider the dimensionless Poisson equation rescaled by the DPD units

\[
\nabla \cdot \left( \epsilon(r) \nabla (\phi(r)) \right) = -\Xi \rho_e(r),
\]

where \( \Xi = e^2 c_0 r_0^2/\epsilon_0 k_B T \) with \( e \) the elementary charge, and \( \epsilon(r) \) the local relative permittivity rescaled by \( \epsilon_0 \), i.e., the reference permittivity of the bulk solution. The Poisson equation can be
viewed as the steady state of the diffusion equation, and again, the diffusion term can be modeled as a flux between cDPD particles. Thus, the Poisson equation can be solved at every time-step using the successive over-relaxation (SOR) iteration scheme, which can be integrated into the DPD framework seamlessly with corresponding boundary conditions. More specifically, the electrostatic potential $\phi_i$ on the $i$th cDPD particle is obtained iteratively as

$$
\phi_i^k = \phi_i^{k-1} + \vartheta \left[ \chi \rho_{ei} - \sum_{j \neq i} \tau_{ij} \phi_{ij}^k \omega_\phi(r_{ij}) \right],
$$

(4.8)

where $\chi$ is linearly related to the macroscopic parameter $\Xi$ defined above, which characterizes the strength electrostatic interactions, $\omega_\phi(r)$ is the weight function, $k$ represents an iteration step, and $\vartheta$ is the relaxation factor. $\tau_{ij} = (\epsilon_i + \epsilon_j)/2$ with $\epsilon_i$ and $\epsilon_j$ the permittivity of the $i$th and $j$th cDPD particle, respectively. In general, $\epsilon_i$ and $\epsilon_j$ can be different to model mixtures of heterogeneous solvents. The initial estimates of $\phi_i^{k-1}$ take the value of $\phi_i$ at the previous time step. The iteration stops when the absolute differences $|\phi_i^k - \phi_i^{k-1}|$ are smaller than a tolerance, i.e., $10^{-3}$ for all cDPD particles. In practice, the relaxation factor $\vartheta$ is adaptively selected during the iteration process to achieve faster convergence.

### 4.2.2 Boundary conditions

So far, we have described the framework of cDPD in open systems, however, most of the interesting electro-kinetic phenomena originate from the charge separation at interfaces and boundaries. Therefore, the implementation of correct boundary conditions is crucial for modeling electro-kinetic phenomena in charged surfaces bounded systems. Representation of solid objects using stationary particles has been widely used in classic DPD simulations. However, a solid wall made up of discrete particles may yield unwanted density and temperature oscillations in the vicinity of the wall. Alternatively, by assuming that the solid boundaries are made up of DPD particles with the same average distributions as in the bulk, the effective boundary forces are then obtained via integration with respect to the distribution function, and further employed to replace the presence of solid walls and impose the desired boundary conditions with negligible density and temperature oscillations near the boundaries in classic DPD \[124, 123, 122\]. Li etc. \[122\] further extended this idea to study transport phenomena in surface bounded systems by imposing an effective concentration flux from the surface. Here, by adopting the same methodology, we develop an effective and accurate boundary method for both hydrodynamics (velocity, mass density) and electro-kinetics (ionic concentrations, electrostatic potential) in cDPD. First, we define the weighting functions between wall and fluid cDPD particle as a function of the particle-to-surface distance $h$ \[124, 123, 122\], i.e., for
Dirichlet boundary conditions, we have

\[
\Phi_d(\omega, h) = \int_{z=h}^{r_c} \int_{x=0}^{\sqrt{r_c^2-z^2}} \omega(r) g(r) \frac{zx}{h} dx dz
\]

and

\[
\Phi_n(\omega, h) = \int_{z=h}^{r_c} \int_{x=0}^{\sqrt{r_c^2-z^2}} \omega(r) g(r) \frac{zx}{r} dx dz
\]

for Neumann boundary conditions. They are both integrals of the weighting functions \(\omega(r)\) with respect to the radial distribution function \(g(r)\) of cDPD particles in the bulk. Here, \(\omega(r)\) can be chosen as \(\omega_C, \omega_D, \omega_qD\) and \(\omega_\phi\) to compute the effective forces, concentration flux, and electrostatic potential contributions from the charged surface, respectively. We also further define the normalized \(\Phi_n(\omega, h)\) as

\[
\overline{\Phi}_n(\omega, h) = \frac{\Phi_n(\omega, h)}{\int_0^{r_c} \Phi_n(\omega, h') dh'}
\]

so that the integral of \(\overline{\Phi}_n(\omega, h)\) becomes unity.

**Hydrodynamic Boundary Conditions**

The hydrodynamic boundary conditions (no-slip and no artificial density fluctuations) are achieved via effective boundary forces, which are obtained by integrating the total forces between wall and fluid cDPD particles with respect to \(g(r)\). In particular, an effective conservative force \(F^C_{is}(h)\) between the \(i\)th cDPD particle and surface (represented by the symbol \(s\)) is imposed to eliminate the artificial density fluctuations near the surface, which is computed as

\[
F^C_{is}(h) = 2\pi \rho a \Phi_n(\omega_C, h) e_n,
\]

where the unit vector \(e_n\) represents the normal direction of surface and \(\rho\) the number density of the fluid cDPD particles. Further, the no-slip boundary conditions are exactly satisfied via the effective dissipative force \(F^D_{is}(h)\)

\[
F^D_{is}(h) = -\left(\gamma_\tau(h) \cdot v_\tau e_\tau + \gamma_n(h) \cdot v_n e_n\right),
\]

where \(v_n e_n = (\Delta v \cdot e_n) e_n\), \(v_\tau e_\tau = \Delta v - v_n e_n\), and \(\Delta v = v_i - v_s\) the velocity difference between a fluid particle \(i\) and the target surface velocity \(v_s\). The symbols \(\tau\) and \(n\) represent the tangential and normal directions of the wall surface, respectively. Also, \(\gamma_\tau(h)\) and \(\gamma_n(h)\) are functions of the...
particle-to-surface distance $h$ defined as
\[
\gamma_r(h) = \pi \rho \int_{x=0}^{r_c} \int_{z=h}^{\sqrt{r_c^2 - z^2}} \omega_D(r) g(r) \frac{zx^3}{hr^2} dx dz
\]
(4.14)
\[
\gamma_n(h) = \pi \rho \int_{x=0}^{r_c} \int_{z=h}^{\sqrt{r_c^2 - z^2}} \omega_D(r) g(r) \frac{xz^3}{hr^2} dx dz.
\]
Moreover, to eliminate the extra dissipation from the solid surface, additional effective random forces are also included in the effective boundary forces, which satisfy the fluctuation-dissipation theorem
\[
F_{R}^R(h) = \sigma_r(h) \xi_r \mathbf{e}_r + \sigma_n(h) \xi_n \mathbf{e}_n,
\]
(4.15)
where $\xi_r$ and $\xi_n$ are Gaussian random variables with zero mean and unit variance. To satisfy the fluctuation-dissipation theorem, the variances of random forces are related to the dissipative forces by $\sigma_r^2(h) = 2k_B T \gamma_r(h)$ and $\sigma_n^2(h) = 2k_B T \gamma_n(h)$. Since the effective boundary forces involve the particle density $\rho$ and radial distribution function $g(r)$ of the surface structure, which is the same as in the bulk, the DPD particle in the bulk cannot “feel” any difference as it approaches the boundary. Therefore, this boundary method eliminates erroneous fluctuations in the vicinity of wall boundaries and provides accurate no-slip boundary conditions.

**Electro-kinetic Boundary Conditions**

Besides the special treatment of mass density and velocity near boundaries via effective boundary forces, additional methodologies are also needed for electro-kinetic boundary conditions of ionic concentration and electrostatic potential in cDPD. Here, we adopt the same idea of effective boundary fluxes proposed by Li et al. [122] to impose Dirichlet and Neumann boundary conditions for both ionic concentrations and electrostatic potentials in cDPD. For instance, the Dirichlet boundary conditions of electrostatic potential $\phi(r) = \phi_s$ is specified when a charged surface is connected to a voltage source, while in the far field of the bulk solution we have $\phi(r) = 0$ and $c_\alpha(r) = c_{\alpha s}$. The Neumann boundary conditions for the electrostatic potential are imposed for a charged surface with known surface density $\sigma_s$, i.e., $\mathbf{n} \cdot (\epsilon \nabla \phi(r)) = -\Xi \sigma_s$. The Neumann boundary conditions are also adopted for ionic concentrations, when the simulation domain is subject to a constant ionic concentration flux $q_{\alpha s}$, i.e., $\mathbf{n} \cdot (\nabla c_\alpha(r)) = q_{\alpha s}$.

**Dirichlet Boundary Conditions:** We first consider the Dirichlet boundary conditions for both electrostatic potential and ionic concentrations in cDPD simulations, which are exactly satisfied by imposing additional effective concentration fluxes from the surface to cDPD particles in the vicinity
of a boundary, i.e.,

\[ q_{\alpha is}^D(h) = 2\pi \rho \kappa c_{\alpha is} \Phi_d(\omega_D, h) \]
\[ q_{\alpha is}^E(h) = 2\pi \rho \kappa z_{\alpha is} \phi_{\alpha is} \Phi_d(\omega_D, h) \]  

(4.16)

with \( q_{\alpha is}^D \) induced by the ionic concentration difference \( c_{\alpha is} = c_{\alpha s} - c_{\alpha i} \) and \( q_{\alpha is}^E \) induced by the electrostatic potential difference \( \phi_{\alpha is} = \phi_i - \phi_s \) between the \( i \)th cDPD particle and the surface \( s \). Here \( \bar{c}_{\alpha si} = \frac{1}{2}(c_{\alpha s} + c_{\alpha i}) \) is the average ionic concentration of the \( i \)th cDPD particle and the surface \( s \). Moreover, the presence of boundary conditions of the electrostatic potential appears not only in the above concentration flux terms, but also in the modified the Poisson solver. More specifically, for the \( i \)th cDPD particle in the vicinity of a Dirichlet boundary, the electrostatic potential \( \phi_i \) is updated according to the modified SOR iteration scheme by taking the Dirichlet boundary \( \phi(r) = \phi_s \) effect into account as,

\[ \phi_i^k = \phi_i^{k-1} + \theta \left[ \chi \rho_{ei} - \sum_{j \neq i} \tau_{ij} \phi_{ij}^k \omega(r_{ij}) + q_{\alpha is}^\phi(h) \right] \]  

(4.17)

with the extra contribution \( q_{\alpha is}^\phi(h) \) from the surface defined as

\[ q_{\alpha is}^\phi(h) = 2\pi \rho \tau_{is} \phi_{is} \Phi_d(\omega_D, h) \]  

(4.18)

with \( \tau_{is} = \frac{1}{2}(\epsilon_i + \epsilon_s) \) and \( \epsilon_s \) denoting the relative permittivity of the surface.

**Neumann Boundary Conditions:** We then consider the Neumann boundary condition for constant concentration fluxes from the surface \( \mathbf{n} \cdot (\nabla c_\alpha(r)) = q_{\alpha s} \), which is modeled as an additional effective concentration flux from the surface to the cDPD particles in the vicinity of a surface as,

\[ q_{\alpha is}^D(h) = \kappa q_{\alpha s} \rho \overline{\Phi}(\omega_D, h) \]  

(4.19)

with \( \overline{\Phi}(h) \) the normalized wall-to-particle weighting function defined before. For most of the solid boundaries, zero ionic concentration flux boundary conditions \( \partial c / \partial n = 0 \) are imposed by simply ignoring the concentration flux from the surfaces. The Neumann boundary conditions for the electrostatic potential \( \mathbf{n} \cdot (\epsilon \nabla \phi(r)) = -\Xi \sigma_s \) are achieved by modifying the Poisson solver for the cDPD particles in the vicinity of the surface as

\[ \phi_i^k = \phi_i^{k-1} + \theta \left[ \chi \rho_{ei} - \sum_{j \neq i} \tau_{ij} \phi_{ij}^k \omega(r_{ij}) + q_{\alpha is}^\phi(h) \right] \]  

(4.20)
with \( q_{ia}^b(h) = -\frac{\chi \sigma_s}{\epsilon_s} \rho \overline{P}_n(\omega_{ab}, h) \).

### 4.2.3 Mapping to Physical Units

It is non-trivial to map the DPD systems to real physical systems since all of the units as well as the parameters are dimensionless or scaled by DPD basic units (length, time and energy) in the DPD simulations. For a given cDPD simulation system, the macroscopic properties including viscosity \( \eta \), diffusivity \( D \), coupling parameter \( \Xi \) in DPD units are output properties, and related to the input parameters \( \gamma, \kappa \) and \( \chi \), respectively, which can be measured directly. For example, the viscosity \( \eta \) can be measured by imposing a reverse Poiseuille flow [125], and the diffusivity \( D \) can be measured in a similar way by imposing a reverse Poiseuille-like concentration sources; more details can be found in [122]. The coupling parameters \( \Lambda, \Xi \) can be calculated by measuring the flow and electrostatic potential in a straight 2D channel and imposing a constant external electric field. Moreover, these macroscopic properties can also be computed semi-analytically [8]. For example, the shear viscosity \( \eta \) of DPD system is computed as

\[
\eta = \eta^K + \eta^D
\]

\[
\eta^K = \frac{3k_B T \rho}{8\pi \gamma \rho \int_0^{r_c} r^2 \omega_D(r) g(r) dr}
\]

\[
\eta^D = \frac{2\pi \gamma \rho^2}{15} \int_0^{r_c} r^4 \omega_D(r) g(r) dr
\]

which include two parts, i.e., the kinematic viscosity \( \eta^K \) and dissipative viscosity \( \eta^D \). The diffusivity \( D \) of cDPD particle also includes two parts contributions, \( D^R \) due to the random movements of cDPD particles and \( D^F \) due to the Fickian concentration flux

\[
D = D^R + D^F
\]

\[
D^R = \frac{3k_B T}{4\pi \gamma \rho \int_0^{r_c} r^2 \omega_D(r) g(r) dr}
\]

\[
D^F = \frac{2\pi \kappa \rho}{3} \int_0^{r_c} r^4 \omega_D(r) g(r) dr.
\]

Similarly, the electrostatic coupling parameter \( \Xi \) is computed as

\[
\Xi = \frac{2\pi \chi \rho}{3} \int_0^{r_c} r^4 \omega_D(r) g(r) dr
\]

Throughout the chapter, the DPD parameters of our benchmark system are selected as \( \rho = 4.0 \), \( k_B T = 1.0 \), \( a = 18.75 \), \( \gamma = 4.5 \), \( \kappa = 0.025 \), \( \chi = 1.273 \), \( \lambda = 0.0282 \), \( r_c = r_{cc} = r_{ee} = 1.58 \),
and the weighting functions are chosen as \( \omega_C(r) = (1 - r/r_c) \), \( \omega_D(r) = \omega_R^2(r) = (1 - r/r_c)^2 \), \( \omega_{qD}(r) = \omega_{qR}^2(r) = (1 - r/r_{cc})^2 \), \( \omega_\phi(r) = (1 - r/r_{ec})^2 \), and \( \omega_E(r) = \frac{1}{2}(1 - r/r_{ec})^2 r \). The basic DPD units according to these parameters are \( r_0 = 21.358 \, \text{nm} \) and \( \tau = 3.276 \, \text{ns} \), \( k_BT = 4.14 \times 10^{-21} J \) and \( c_0 = 4.083 \times 10^{-3} M \). To simulate systems with different bulk concentration \( c_0 \), we also have to modify \( \chi \) and \( \lambda \), which are linearly depended on \( c_0 \). The macroscopic properties of these systems measured in DPD units are then directly mapped to real units.

4.3 Results

Throughout the chapter, for simplicity, we only consider two types of ion species, i.e., cation concentration \( c_+ \) and anion concentration \( c_- \), with charge valency \( z_+ \) and \( z_- \), respectively. Here, we also assume that the self-diffusion of ionic species is dominant and hence we ignore the mutual-diffusion between different species; however, the generalization to explicitly including mutual-diffusions of multi-type ionic species is straightforward. Moreover, there is only a small amount of additional computational cost for multi-type ion species case compared with the current model [122].

4.3.1 Electrostatic Structure near Planar Charged Surfaces

A solid surface in polar solvents is usually charged due either to dissociation of chemical groups from the solid surface into the solution, or due to chemical binding or physical adsorption of ions from the electrolyte. This surface charge is then balanced by an equal and opposite net charge of ions in the electrolyte. Although the counter-ions are definitely attracted to the oppositely charged surface, they still remain dispersed and mobile in the solvent in the vicinity of the surface due to the entropy effects. This spatial separation of charge is termed the electric double layer (EDL); so roughly speaking EDL refers to two parallel layers of ions near the surface. The first layer mainly comprises of ions tightly adsorbed on the surface, while the second layer is composed of ions loosely attracted to the surface by the first layer ions via an electrostatic force, which electrically screens the first layer. EDL is closely related to electrostatic phenomena as well as electrokinetic phenomena. For example, the interaction between two charged colloids is not simply given by Coulomb’s law because of the presence of EDL, which mediates the interactions between them. The EDL is well understood in the mean-field (MF) theory. For an infinite large planar surface immersed in salt solution, the solution of Debye-Huckel equation reads \( \phi(x) = \phi_s \exp(-x/\lambda_D) \), with \( x \) the distance from the surface, \( \phi_s \) the surface potential, \( \lambda_D = \sqrt{\frac{k_BT\epsilon}{e^2 z^2 c_0}} \) the Debye screening length and \( c_0 \) the salt concentration in the bulk, and the rescaled Debye screening length in DPD units \( \lambda_D/r_0 = \sqrt{\Xi} \). These well-known analytical results provide us a basic benchmark of the cDPD model. First, we
Figure 4.1: Scaled (a) total charge density $\rho_e(x)$, (b) positive ion density $\rho_+(x)$, (c) negative ion density $\rho_-(x)$ and (d) electrostatic potential $\phi(x)$ near charged surfaces. The charged surfaces are represented by constant electrostatic potential. The blue, red and black curves represent salt concentration $c_0 = 2.553 \times 10^{-5} M, 1.021 \times 10^{-4} M, 4.083 \times 10^{-4} M$, equivalently, the Debye length $\lambda_D = 85.43 nm, 42.72 nm, 21.36 nm$, respectively. The solid lines and open symbols are results from 1D mean-field theory and cDPD simulation, respectively. Here, the unit of horizontal axis is $r_0 = 21.358 nm$. 
study by cDPD the EDL near a single surface immersed in salt solution. We specify the boundary conditions \( \phi(x) = \phi_s \) and \( \partial_x c(x) = 0 \) at the surface \( x = 0 \), while \( \phi(x) = 0 \) and \( c(x) = c_0 \) far from the surface \( (x = L, \text{ making sure that } L \gg \lambda_D) \). Periodic boundary conditions are adopted in the directions. The simulation results are shown in Figure 4.1; the cDPD results are all in good agreement with the classical MF approximation at different bulk salt concentration or Debye screening length, which suggests that our cDPD model captures the electrostatic structure of ionic systems at least as accurately as the MF theory.

Figure 4.2: Scaled (a) total charge density \( \rho_e(x) \), (b) positive ion density \( \rho_+(x) \), (c) negative ion density \( \rho_-(x) \) and (d) electrostatic potential \( \phi(x) \) between two charged surfaces (upper surface positive charged and lower surface negative charged with the same surface charge densities). The black, red and blue curves represent salt concentration \( c_0 = 2.553 \times 10^{-5} M, 1.021 \times 10^{-4} M, 4.083 \times 10^{-4} M \), equivalently, the Debye length \( \lambda_D = 85.43 nm, 42.72 nm, 21.36 nm \), respectively. The surface charge density \( \sigma_s = 4.206 \times 10^{-4} C/m^2 \) is fixed. The solid lines and open symbols are results from the 1D mean-field theory and cDPD simulation, respectively. Here, the unit of horizontal axis is \( r_0 = 21.358 nm \).

Next, we study the electrostatic structures between two charged surfaces. Specifically, the cDPD
model is applied to study the infinite large parallel plate capacitor immersed in salt solution. The capacitor consists of two infinite large parallel surfaces (periodic in y and z directions) with a separation distance \( d = 20r_0 = 427.16 \text{nm} \) in the x direction. These two surfaces have opposite fixed charges with the same charge density \( \sigma_s = 4.206 \times 10^{-4} \text{C/m}^2 \), and are immersed in a salt solution with different salt concentrations. In the current simulation, we also consider a symmetric salt with valence \( z = 1 \) as before. The simulation results are compared with 1D mean-field theory results, which were obtained by numerically solving the equations below

\[
\begin{align*}
\partial_x (\epsilon \partial_x \phi(x)) &= -z e (c_+ - c_-) \\
c_+(x) &= n_+ \exp\left(-\frac{ze \phi(x)}{k_B T}\right) \\
n_+ &= \frac{n_0^+}{\int_{-d/2}^{d/2} \exp\left(-\frac{ze \phi(x)}{k_B T}\right) dx} \\
c_-(x) &= n_- \exp\left(-\frac{ze \phi(x)}{k_B T}\right) \\
n_- &= \frac{n_0^-}{\int_{-d/2}^{d/2} \exp\left(-\frac{ze \phi(x)}{k_B T}\right) dx}
\end{align*}
\]

(4.24)

where the first one in Eq.(4.24) is 1d Poisson equation, and the last two represent the ion distribution following the Boltzmann distribution, with \( n_0^+ = \int_0^d c(x) dx \) the total ion numbers between the plates, which is a conserved constant. The boundary conditions for the Poisson equation are \( \partial_x \phi(x) = \sigma_s / \epsilon \) at \( x = -d/2 \) and \( \partial_x \phi(x) = -\sigma_s / \epsilon \) at \( x = d/2 \), respectively. These equations are iteratively solved with a central finite difference scheme until convergence. We show the electrostatic structure between two charged surfaces in Figure 4.2 with the Debye screening length \( \lambda_D = 42.72 \text{nm}, 21.36 \text{nm}, 10.68 \text{nm} \). The simulation results are in perfect agreement with the 1D MF solutions when \( \lambda_D \) is small (high ionic concentration). However, there is a small deviation near the surface when \( \lambda_D \) is big (low ionic concentration), which is expected since the mean-field approximation is not valid when \( \lambda_D \) is big, while the thermal fluctuation in cDPD model will give us a small amount of correlation effects here. We also study the capacity density \( C = \sigma_s / V \) as a function of salt concentrations \( c_0 \) or Debye screening lengths \( \lambda_D \), where \( V \) is the voltage between two plates. The results are shown in Figure 4.3. Again, we observe good agreement for small \( \lambda_D \) and deviations for large \( \lambda_D \) as explained before. To fully understand the electrostatic structure and capacity density in the strong correlated regime of a mesoscopic capacitor, electrostatic correlation effects have to be introduced into the current model, and can be further compared with the modified Ginzburg-Landau field theory approach [126].
Figure 4.3: The capacity density of infinite large parallel plate capacitor as a function of Debye length in salt solution. The surface charge density $\sigma_s = 4.206 \times 10^{-4} \text{C/m}^2$ is fixed. The red and black symbols are results from 1D mean-field theory and cDPD simulation, respectively.

4.3.2 Electro-kinetic Flows

Micro- and nano-fluidic flows have attracted a great amount of interest in the past two decades, with electro-osmotic flow (EOF) and pressure-driven flow (PDF) the two main flow types [127, 99, 128, 89]. Thus, in this section, besides the electrostatic structure near the charged surfaces, we also simulate the electro-kinetic flows in micro-channels, and compare with continuum solvers to validate our cDPD model.

We first consider the problem of pure EOF in a micro-channel under the influence of an applied electric field [129, 130]. The dimensions of the micro-channel are $427.16 \text{nm} \times 427.16 \text{nm} \times 213.58 \text{nm}$ in $x - y - z$ directions. The no-slip boundary conditions are implemented at the walls located at $x = \pm 213.58 \text{nm}$. The walls are both positive charged with charge density $\sigma_s = 4.206 \times 10^{-4} \text{C/m}^2$. An external electrostatic field $E = 6.05 \times 10^9 \text{V/m}$ is applied in the $y$ direction. We vary the bulk salt concentration $c_0$ or Debye screening length $\lambda_D$ to obtain different EDL lengths, and compute the equilibrium velocity via time averaging. As shown in Figure 4.4 (a), a plug-like velocity profile is observed when the EDL length (small $\lambda_D$) is small and the effects of electrostatic structure vanish far from the wall. However, when the EDL length is large enough (e.g., $\sim 0.25 \times L$), a nearly parabolic shape velocity profile emerges. It is worth mentioned that the dispersion of large objects will be significantly decreased since there is zero velocity gradient in the plug-like flow, which will increase the transport efficiency. Thus, it is important to compute the ratio of EDL and micro-
channel width in the micro-device design. We also simulate the oppositely charged micro-channel with same charge densities. The flow profiles are shown in Figure 4.4 (b), where a nearly uniform shear flow far away from the wall is obtained when the EDL is small. All of these simulation results from cDPD model are compared with numerical solutions of the 1D PNP-NS equations, and good agreement is observed with the apparent viscosity of the electrostatic fluid $\eta = 0.898 \times 10^{-6}$ here.

![Figure 4.4: Profiles of y-velocities between two charged surface with external electrostatic field $E = 6.05 \times 10^9 V/m$. The black, red and blue curves represent salt concentrations $c_0 = 2.553 \times 10^{-5} M, 1.021 \times 10^{-4} M, 4.083 \times 10^{-4} M$, equivalently, the Debye length $\lambda_D = 85.43 nm, 42.72 nm, 21.36 nm$, respectively. The surface charge density $\sigma_s = 4.206 \times 10^{-4} C/m^2$ is fixed, with the upper and lower surfaces both positive charged (a) and oppositely charged (b). The solid lines and open symbols are results from the 1D mean-field theory and cDPD simulation, respectively.](image)

We also studied the mixed electroosmotic and pressure-driven flows (PDF) in the same micro-channel, with additional pressure-gradient (body force) along the opposite direction of external electric field. The steady state solution of the velocity field for the mixed EOF-PDF in the periodic straight channel is the super-position of plug-like EOF and parabolic PDF. The simulation results compared with 1D mean-field theory solutions for different pressure gradient values are shown in Figure 4.5. As we increase the pressure-gradient, the flow in the center of micro-channel will first change direction while the flow in the vicinity of the surface is in the opposite direction, which represents a closed system in which there is no net flow rate, see blue symbols and curve in Figure 4.5. Achieving the proper pressure gradients is possible utilizing the closed systems due to the electroosmotic forces. Hence, it can be utilized for design and fabrication of micro-actuators [119, 131, 132]. By further increasing the pressure-gradient, the entire flow field will eventually change directions compared to the original EOF, see green symbols and curve in Figure 4.5. Our results from cDPD simulations are again in agreement with the 1D mean-field theory solutions with
slightly deviations around the sharp transitions of velocity gradients.

\[ \sigma_s = 4.206 \times 10^{-4} C/m^2 \]

Figure 4.5: Profiles of y-velocities between two positive charged surface with surface charge density \( \sigma_s = 4.206 \times 10^{-4} C/m^2 \), generated by an external electrostatic field \( E = 6.05 \times 10^9 V/m \) and different pressure gradients, with the black, red and blue curves represent \( dp/dx = 0, 3.109 \times 10^8, 6.218 \times 10^8 Pa/m \). The salt concentration is \( c_0 = 1.021 \times 10^{-4} M \) (Debye screening length \( \lambda_D = 42.72 nm \)). The solid lines and open symbols are results from the 1D mean-field theory and cDPD simulation, respectively.

### 4.3.3 Dilute Poly-electrolyte Suspension

In the last example, we model a dilute polyelectrolyte suspension in EOF, to demonstrate the capability of our cDPD method to study not only simple electro-kinetic flows, but also charged complex fluids. Here, we measure the poly-electrolyte mass distribution, as well as the configurations represented by its end-to-end distance, as a function of position across the micro-channel. The upper and lower surfaces of the micro-channel are both positive charged with surface charge density \( \sigma_s = 4.206 \times 10^{-4} C/m^2 \). The EOF is driven by the external electrostatic field \( E = 6.05 \times 10^9 V/m \).

Unlike the migration of polymer in pressure-driven flow [133], we find that the positive charged poly-electrolytes are likely to stay in the center of the channel due to the electrostatic repulsion from the charged surface, while the negative charged poly-electrolytes are drifted away from the center with double peaks as shown in Figure 4.6. However, the negative charged poly-electrolytes are not adsorbed onto the positive charged surface, mediated by the hydrodynamic interactions, i.e., the velocity gradient near the surface, as shown in Figure 4.4, induces additional hydrodynamic repulsion force from the wall to the charged objects. The configurations of poly-electrolytes at different positions across the micro-channel are very interesting; the polyelectrolytes are fully
extended in the center of channel due to the electrostatic repulsion between charged monomer. However, when the polyelectrolyte approaches the EDL near the surface, the end-to-end distance of poly-anions increases in the anion-rich regime and decreases in the cation-rich regime, and vice versa for poly-cations. This interesting polyelectrolyte configuration behavior further helps us to understand the layer structure of the EDL near charged surface.

Figure 4.6: Mass density distribution (a) and end-to-end distance (b) as a function of mass center location across the micro-channel for both positive (blue) and negative (red) charged polyelectrolytes drifting in EOF, which is generated between two positive charged surface with surface charge density \( \sigma_s = 4.026 \times 10^{-4} \text{C/m}^2 \), and external electrostatic field \( E = 6.05 \times 10^9 \text{V/m} \). The salt concentrations in the bulk is \( c_0 = 1.021 \times 10^{-4} \text{M} \) (or Debye length \( \lambda_D = 42.72 \text{nm} \)).

4.4 Summary and Discussion

Electro-kinetic phenomena involve a range of length and time scales, from the molecular to the macroscopic ones, and their description requires a multi-scale strategy combining different simulation techniques. Here, we develop a novel extension of DPD simulation method, aiming at applications involving electro-kinetic phenomena in mesoscopic scales, and bridging the molecular and macroscopic descriptions. We note that our simulation methodology inherits the multi-scale natural of DPD, and is suitable for modeling electro-kinetic systems and capturing the small scale electrostatic structures and larger scale hydrodynamic structures. The results we presented here are all in agreement with the 1D continuum mean-field theory approaches. Furthermore, we demonstrate the flexibility and capability of this methodology in the study of complex fluids in the last part of section 4.3.

The new model is designed to mimic the mean-field approach, i.e., PNP-NS equation description of electro-kinetic systems. We have assumed that the electrostatic correlation length is smaller than...
the coarse-grained DPD particle size, which suggests that our model will only be accurate when the thermal fluctuation is dominant and the electrostatic correlation is relatively weak. Besides the long-range correlation effects, we also ignore the ion size effects in our current model, which are extremely important in the high concentrated regime [126]. We are currently developing a new extension of the cDPD model, which takes correlation and ion-size effects into account, and we will present the corresponding numerical results in future work. The formulations in Sec 4.2 can also be derived from bottom up using the Mori-Zwanzig projection [134, 135, 136], thus such a derivation and justification of these formulas would be important and complementary to current model. Moreover, it will provide a practical way to coarse-grain the electrokinetic systems from molecular descriptions.
Chapter 5

Mesoscopic Fluctuating Electro-Kinetics of Electrolyte Solutions at Equilibrium

5.1 Introduction

Electrolyte solutions, consisting of a polarized solvent and ionic species, are extremely important in a wide range of fields including chemical physics, biology, and geochemistry [137, 138, 87, 139, 89, 140, 102, 141]. Despite a long history of electrolyte solution studies, there are still numerous open questions associated with fluctuations and correlations of electrolyte bulk solutions [138, 142, 143, 106, 144, 145]. At the mesoscale (i.e., nanometer to micrometer length scales), thermal energies of electrolyte solutions are of the same magnitude as the characteristic energies of the hydrodynamics and electro-kinetics. Therefore, thermal fluctuations should play an important role in both equilibrium and non-equilibrium electrolyte phenomena.

At continuum scales, fluctuating hydrodynamics and electro-kinetic theories have been used to describe thermally induced fluctuations through random tensor/flux terms in the governing equations, chosen to satisfy the fluctuation-dissipation theorem (FDT) [146, 147]. At the atomic scale, molecular dynamics (MD) simulations have also been used to study electrolyte solutions; however, the computational cost of MD simulations further prevents their use at large length- and time-scales [148, 96, 149, 150, 97, 99, 98]. In chapter 4, we presented the charged Dissipative Particle Dynamics (cDPD) model to bridge the gap between atomic-scale simulations and continuum the-
ories for electrolyte solutions. In this chapter, we employ the cDPD model to compute spatial and
temporal correlation functions for electrolytes and compare the results with both MD simulations
and continuum theory.

5.2 Continuum theories

This section present a brief review of fluctuating hydrodynamics and electro-kinetics theories in the
form of the stochastic Navier-Stokes (NS) and Poisson-Nernst-Planck (PNP) equations [102]. We
linearize the fluctuating hydrodynamics and electro-kinetics equations for a simple electrolyte bulk
solution and derive explicit closed form solutions of the linearized equations in Fourier space using
perturbation theory.

5.2.1 Fluctuating Hydrodynamics and Electro-kinetics

We consider an electrolyte solution as isothermal within a mesoscopic periodic domain Ω of fixed
volume containing m types of ionic species with concentration \( c_\alpha(r, t) \) and charge valency \( z_\alpha \)
for the \( \alpha \)th ionic specie. The charge neutrality condition \( \sum_\alpha \int_\Omega drc_\alpha(r, t) = 0 \), with \( e \) the elementary
charge, is imposed as a global constraint. The solvent molecules are represented implicitly through
their continuum properties: electrostatic permittivity \( \epsilon \), bulk viscosity \( \zeta \), and shear viscosity \( \eta \).
From a continuum perspective, this system can be described by classical fluctuating hydrodynamics
with an additional electrostatic body force

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot g = 0
\]

\[
\frac{\partial g}{\partial t} + \nabla \cdot (gv) = -\nabla p + \left( \frac{\eta}{3} + \zeta \right) \nabla (\nabla \cdot v) + \eta \nabla^2 v + \sum_\alpha e z_\alpha c_\alpha(r, t) E(r, t) + \nabla \cdot \delta \Pi
\]

for velocity \( v(r, t) \), pressure \( p(r, t) \), mass density \( \rho(r, t) \), momentum density \( g(r, t) = \rho(r, t)v(r, t) \),
and electric field \( E(r, t) \). The random stress tensor \( \delta \Pi \) is a matrix of Gaussian-distributed random
numbers with zero means and variances given by the fluctuation-dissipation theorem (FDT),

\[
\langle \delta \Pi_{ij}(r, t) \delta \Pi_{kl}(r', t') \rangle = 2k_B T \mathbf{C}_{ijkl} \delta(r - r') \delta(t - t') \tag{5.1}
\]

where \( \mathbf{C}_{ijkl} = \left[ \eta (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + (\zeta - \frac{2\eta}{3}) \delta_{ij} \delta_{kl} \right] \) is a rank-4 tensor. The fluctuating hydrodynamics
equations are closed with the equation of state (EOS); e.g., \( c_s^2 = (\partial p/\partial \rho)_T \) where \( c_s \) is the isothermal
sound speed.
The Ginzburg-Landau free energy functional for an electrolyte solution is 

\[ G = \int_{\Omega} d\mathbf{r} \left\{ k_B T \sum_{\alpha} c_\alpha \ln c_\alpha + \sum_{\alpha} e z_\alpha c_\alpha \phi - \frac{\epsilon}{2} \left( \nabla \phi \right)^2 \right\} \]  

(5.2)

where \( k_B T \) is the thermal energy. Variation of the free energy with respect to the electrostatic potential gives the Poisson equation

\[ -\nabla \cdot (\epsilon(r) \nabla \phi) = e \sum_{\alpha} z_\alpha c_\alpha \]  

(5.3)

by setting \( \delta G/\delta \phi = 0 \). Similarly, the electrochemical potential of the \( \alpha \)th ionic species can be derived by variation with respect to ionic concentration

\[ \mu_\alpha = \frac{\delta G}{\delta c_\alpha} = k_B T \ln c_\alpha + z_\alpha e \phi. \]  

(5.4)

Ionic species transport and dissipation are driven by the fluid velocity, electrochemical potential, and thermal fluctuations, which can be described in the terms of ionic concentration flux \( \mathbf{J}(\mathbf{r}, t) \),

\[ \frac{\partial c_\alpha(\mathbf{r}, t)}{\partial t} + \mathbf{v}(\mathbf{r}, t) \cdot \nabla c_\alpha(\mathbf{r}, t) = -\nabla \cdot (\mathbf{J}_\alpha(\mathbf{r}, t) + \delta \mathbf{J}_\alpha(\mathbf{r}, t)) \]  

(5.5)

where \( \mathbf{J}_\alpha(\mathbf{r}, t) \) is the dissipative flux and \( \delta \mathbf{J}_\alpha(\mathbf{r}, t) \) is the random flux when the system is near thermodynamic equilibrium. Therefore, the diffusion flux can be written as \( \mathbf{J}_\alpha = -\sum_{\beta} M_{\alpha\beta} \nabla \mu_\beta(\mathbf{r}, t) \) where \( \nabla \mu \) is the thermodynamic force for diffusion flux and \( M_{\alpha\beta} \) are the Onsager coefficients related to macroscopic ionic diffusion coefficients. In general, \( M_{\alpha\beta} = M_{\beta\alpha} \neq 0 \) as implied by reversal invariance [152, 153]. The off-diagonal terms \( M_{\alpha\beta} \) describe mutual-diffusion and are assumed to be relatively small compared to the diagonal self-diffusion terms. For example, the self-diffusion coefficients of the cation and anion in 1M NaCl solution are about \( 1.24 \times 10^{-9} m^2/s \) and \( 1.79 \times 10^{-9} m^2/s \), respectively, while the mutual-diffusion coefficient is one order of magnitude smaller: \( 0.12 \times 10^{-9} m^2/s \). Therefore, we assume that the mutual diffusion terms can be ignored in the present work for simplicity. This assumption is checked by computing the self- and mutual-diffusion coefficients from MD data using the Green-Kubo relations described below [154, 155]. By substituting the electrochemical potential expression into the diffusion flux, we obtain

\[ \mathbf{J}_\alpha = -M_\alpha \nabla \mu_\alpha(\mathbf{r}, t) = -\frac{M_\alpha k_B T}{c_\alpha} \nabla c_\alpha - M_\alpha z_\alpha e \nabla \phi \]  

(5.6)

In practice, it is more convenient to use the macroscopic diffusion coefficients \( D_\alpha = \frac{M_\alpha k_B T}{c_\alpha} \) in-
stead of the phenomenological coefficients $M_\alpha$. The ionic concentration transport equation can be rewritten as

$$\frac{\partial c_\alpha(r,t)}{\partial t} + \mathbf{v}(r,t) \cdot \nabla c_\alpha(r,t) = \nabla \cdot \left( D_\alpha \nabla c_\alpha + \frac{D_\alpha e z_\alpha c_\alpha}{k_B T} \nabla \phi + \delta \mathbf{J}_\alpha(r,t) \right). \quad (5.7)$$

Near thermodynamic equilibrium, the random fluxes can be modeled as Gaussian random vectors with zero means and variance given by the generalized FDT as

$$\langle \delta \mathbf{J}_\alpha(r,t) \cdot \delta \mathbf{J}_{\beta}(r',t') \rangle = 2k_B T M_{\alpha\beta} \delta(r-r') \delta(t-t') = 2D_\alpha c_\alpha \delta(r-r') \delta(t-t')$$

The coupled Eqs. 5.1, 5.1, 5.3, 5.7, and 5.8 form the fluctuating hydrodynamics and electro-kinetics equations.

5.2.2 Linearized Theory of Bulk Electrolyte Solutions

The stochastic partial differential equations (SPDEs) above could be solved through numerical discretization, with the FDT satisfied on the discrete level following the GENERIC framework [156, 157]. However, solution of such sPDEs can be very challenging. If the local hydrodynamic and electro-kinetic fluctuations are sufficiently small, then the relaxation of electrolyte solution towards equilibrium can be described by linearized equations. In the present work, we focus on the linearized equations and their closed-form solutions. The equilibrium state of a bulk electrolyte solution is characterized by constant mass density $\rho_0$, constant pressure $p_0$, constant bulk ionic concentration $c_\alpha_0$, zero momentum field $g_0 = 0$, and zero electrostatic potential field $\phi_0 = 0$. The local hydrodynamic field can be expressed as the perturbation around the bulk state: $\rho(r,t) = \rho_0 + \delta \rho(r,t)$, $g(r,t) = \delta g(r,t)$, and $p(r,t) = p_0 + \delta p(r,t)$. The local perturbation pressure can be related to density fluctuations via the equation of state $\delta p = c_0^2 \delta \rho$ under isothermal conditions. The local electrostatic fields can also be decomposed as $\phi(r,t) = \delta \phi(r,t)$, $c_\alpha(r,t) = c_\alpha_0 + \delta c_\alpha(r,t)$, and $\rho_e(r,t) = \delta \rho_e(r,t) = \sum_\alpha^m e z_\alpha \delta c_\alpha(r,t)$, by imposing the global electro-neutrality condition $\sum_\alpha^m e z_\alpha c_\alpha_0 = 0$. The fluctuating electrostatic potentials and charge densities are related via the Poisson equation. For small electrostatic field fluctuations, the linearized fluctuating hydrodynam-
ics and electro-kinetics equations can be written as

\[
\begin{align*}
\frac{\partial (\delta \rho)}{\partial t} &= -\nabla \cdot \delta \mathbf{g} \\
\frac{\partial (\delta \mathbf{g})}{\partial t} &= -c_s^2 \nabla \delta \rho + \eta \nabla^2 (\delta \mathbf{v}) + \left( \frac{\eta}{3} + \zeta \right) \nabla \cdot (\nabla \cdot \delta \mathbf{v}) \\
\frac{\partial (\delta c_\alpha)}{\partial t} &= \left( D_\alpha \nabla^2 (\delta c_\alpha) + \frac{e z_\alpha c_\alpha}{k_BT} \nabla^2 \delta \phi \right) \\
-\nabla \cdot (\epsilon \nabla \delta \phi) &= -\sum_{\alpha} e z_\alpha \delta c_\alpha (\mathbf{r}, t)
\end{align*}
\]  

(5.8)

where only first-order perturbation terms are kept in these linearized equations. It is important to note that the linearized hydrodynamics and electro-kinetics equations are explicitly decoupled. In particular, the electrostatic body force term \( \delta \rho \nabla \delta \phi \) (momentum equation) and the convection term \( \delta \mathbf{v} \cdot \nabla \delta c_\alpha \) (transport equation) are high-order perturbation terms and thus assumed to be negligible in the equations above. The linearized fluctuating hydrodynamics equations have been widely studied [158, 159, 160] with well-known mass-momentum correlations which characterize transport and dissipation in the fluctuating system:

\[
\begin{align*}
\langle \hat{\rho}(\mathbf{k}, t) \hat{\rho}(\mathbf{k}, 0) \rangle &= \exp(-\Gamma_T k^2 t) \cos(c_s kt) \\
\langle \hat{\mathbf{g}}_\parallel(\mathbf{k}, t) \hat{\mathbf{g}}_\parallel(\mathbf{k}, 0) \rangle &= \exp(-\Gamma_T k^2 t) \cos(c_s kt) \\
\langle \hat{\mathbf{g}}_\perp(\mathbf{k}, t) \hat{\mathbf{g}}_\perp(\mathbf{k}, 0) \rangle &= \exp(-\nu k^2 t) \\
\langle \hat{\mathbf{g}}_\parallel(\mathbf{k}, t) i \hat{\mathbf{g}}_\parallel(\mathbf{k}, 0) \rangle &= \exp(-\Gamma_T k^2 t) \sin(c_s kt)
\end{align*}
\]  

(5.9)

where \( \hat{\cdot} \) indicates Fourier components, \( \mathbf{k} = \frac{2\pi}{L} (k_x, 0, 0) \) is a Fourier mode along the (arbitrary) \( x \)-direction, \( \nu \) is the kinematic viscosity, and \( \Gamma_T \) is the sound absorption coefficient. The function \( \mathbf{g}_\parallel \) represents longitudinal momentum parallel to the wave vector \( \mathbf{k} \); \( \mathbf{g}_\perp \) represents the transverse components.

For simplicity in deriving closed-form solutions, we only consider two types of ionic species: the cation (denoted by \( p \)) and anion (denoted by \( n \)). By substitution of the Poisson equation into the linearized ionic transport equation, we obtain

\[
\begin{align*}
\frac{\partial (\delta c_p)}{\partial t} &= D_p \left( \nabla^2 (\delta c_p) - \kappa_p^2 \delta c_p + \left| \frac{z_n}{z_p} \right| \kappa_p^2 \delta c_n \right) \\
\frac{\partial (\delta c_n)}{\partial t} &= D_n \left( \nabla^2 (\delta c_n) - \kappa_n^2 \delta c_n + \left| \frac{z_p}{z_n} \right| \kappa_n^2 \delta c_p \right)
\end{align*}
\]  

(5.10)
where $\kappa^2_p$ and $\kappa^2_n$ are defined as

$$\kappa^2_p \equiv \frac{D_p z_p^2 c_p \epsilon^2}{k_B T \epsilon} \quad \kappa^2_n \equiv \frac{D_n z_n^2 c_n \epsilon^2}{k_B T \epsilon} \quad (5.11)$$

with units of inverse-squared distance. For a periodic system, we can expand the solution in Fourier modes: $\delta c(\mathbf{r}, t) = \sum \delta \hat{c}(\mathbf{k}, t)e^{i \mathbf{k} \cdot \mathbf{r}}$. The spatial Fourier transformation of Eq. 5.10 gives two coupled ordinary differential equations

$$\frac{\partial \delta \hat{c}_p(\mathbf{k}, t)}{\partial t} = -(k^2 + \kappa^2_p) D_p \delta \hat{c}_p(\mathbf{k}, t) + \frac{z_n}{z_p} \kappa^2_p D_p \delta \hat{c}_n(\mathbf{k}, t)$$

$$\frac{\partial \delta \hat{c}_n(\mathbf{k}, t)}{\partial t} = -(k^2 + \kappa^2_n) D_n \delta \hat{c}_n(\mathbf{k}, t) + \frac{z_p}{z_n} \kappa^2_n D_n \delta \hat{c}_p(\mathbf{k}, t). \quad (5.12)$$

The above equations can be written in matrix form as $\frac{\partial \mathbf{u}(\mathbf{k}, t)}{\partial t} + \mathbf{L} \mathbf{u} = 0$, with the vector $\mathbf{u} = (\delta \hat{c}_p, \delta \hat{c}_n)^T$, and $\mathbf{L}$ the $2 \times 2$ matrix defined as

$$\mathbf{L} = \begin{bmatrix} (k^2 + \kappa^2_p) D_p & -\frac{z_n}{z_p} \kappa^2_p D_p \\ -\frac{z_p}{z_n} \kappa^2_n D_n & (k^2 + \kappa^2_n) D_n \end{bmatrix}. \quad (5.13)$$
The matrix $\mathbf{L}$ can be further split as $\mathbf{L} = -\mathbf{L}_0 + k^2 \mathbf{L}_1$, where

$$
\mathbf{L}_0 = \begin{bmatrix}
\kappa_p^2 D_p & -|\frac{e_p}{z_p}| \kappa_p^2 D_p \\
-|\frac{e_n}{z_n}| \kappa_n^2 D_n & \kappa_n^2 D_n
\end{bmatrix}
$$

$$
\mathbf{L}_1 = \begin{bmatrix}
D_p & 0 \\
0 & D_n
\end{bmatrix}
$$

(5.14)

These equations can be solved by a linear combination of the eigenvectors $\xi^{(i)}(\mathbf{k})$, which satisfy the eigenvalue equation $[-\mathbf{L}_0 + k^2 \mathbf{L}_1] \xi^{(i)}(\mathbf{k}) = \lambda_i \xi^{(i)}(\mathbf{k})$. The conditions $\kappa_{p,n}^2 \gg k^2$ hold in the continuum limit, when either the domain size $L$ or the charge concentration $z_\alpha^2 c_{\alpha 0}$ are sufficiently large. In this limit, the eigenvalue equation can be solved perturbatively by expanding $\xi^{(i)}$ and $\lambda^{(i)}$ in powers of $k^2$:

$$
\xi^{(i)} = \xi^{(i)}_0 + k^2 \xi^{(i)}_1 + \ldots
$$

$$
\lambda^{(i)} = \lambda^{(i)}_0 + k^2 \lambda^{(i)}_1 + \ldots
$$

(5.15)

Substitution into the $\mathbf{L}$ eigenvalue equation gives the zero- and second-order perturbation theory equations:

$$
(\mathbf{L}_0 - \lambda^{(i)}_0 \mathbf{I}) \xi^{(i)}_0 = 0
$$

$$
(\mathbf{L}_0 - \lambda^{(i)}_0 \mathbf{I}) \xi^{(i)}_1 = (\mathbf{L}_1 + \lambda^{(i)}_1 \mathbf{I}) \xi^{(i)}_0
$$

(5.16)

where $\mathbf{I}$ denotes the identity matrix. The solution to the order $O(k^2)$ is given by two real negative roots approximated as $\lambda_1 \approx -(k^2 + \kappa_p^2) D_p + (k^2 + \kappa_n^2) D_n + k^2 D_s(k)$ (fast decay) and $\lambda_2 \approx -k^2 D_s(k)$ (slow decay). The collective diffusion coefficient of cation and anion pairs is defined as

$$
D_s(k) = \frac{(k^2 + \kappa_p^2 + \kappa_n^2) D_p D_n}{(k^2 + \kappa_p^2) D_p + (k^2 + \kappa_n^2) D_n}
$$

(5.17)

which has the same order as the diffusion coefficients $D_\alpha$. The solutions of Eq. 5.12 with initial conditions $\delta \hat{c}_p(\mathbf{k}, 0)$ and $\delta \hat{c}_n(\mathbf{k}, 0)$ can be written as

$$
\delta \hat{c}_p(\mathbf{k}, t) = A_1 \delta \hat{c}_p(\mathbf{k}, 0) + A_2 \delta \hat{c}_n(\mathbf{k}, 0)
$$

$$
\delta \hat{c}_n(\mathbf{k}, t) = A_3 \delta \hat{c}_n(\mathbf{k}, 0) + A_4 \delta \hat{c}_p(\mathbf{k}, 0)
$$

(5.18)

with the coefficients $A_1 = (\alpha_p e^{\lambda_1 t} + \alpha_n e^{\lambda_2 t})$, $A_2 = \beta_p (e^{\lambda_2 t} - e^{\lambda_1 t})$, $A_3 = (\alpha_n e^{\lambda_1 t} + \alpha_p e^{\lambda_2 t})$, $A_4 = (\alpha_n e^{\lambda_2 t} - \alpha_p e^{\lambda_1 t})$. 

66
\[ A_4 = \beta_n (e^{\lambda_2 t} - e^{\lambda_1 t}) \], where the dimensionless parameters are defined as

\[
\begin{align*}
\alpha_p &= \frac{(k^2 + \kappa_p^2)D_p}{(k^2 + \kappa_p^2)D_p + (k^2 + \kappa_n^2)D_n - 2k^2D_s(k)} - k^2D_s(k) \\
\alpha_n &= \frac{(k^2 + \kappa_n^2)D_n}{(k^2 + \kappa_p^2)D_p + (k^2 + \kappa_n^2)D_n - 2k^2D_s(k)} \\
\beta_p &= \frac{|\frac{z_n}{z_p}|\kappa_p^2D_p}{(k^2 + \kappa_p^2)D_p + (k^2 + \kappa_n^2)D_n - 2k^2D_s(k)} \\
\beta_n &= \frac{|\frac{z_p}{z_n}|\kappa_n^2D_n}{(k^2 + \kappa_p^2)D_p + (k^2 + \kappa_n^2)D_n - 2k^2D_s(k)}
\end{align*}
\] (5.19)

such that \( \alpha_p + \alpha_n = 1 \).

The fluctuations modeled by the equations above are transported and dissipated in time, and this can be shown via the time correlation of the fluctuating concentration field with different Fourier modes. Temporal correlations between species \( \alpha \) and \( \beta \) in the fluctuating concentration field are given by

\[
\Upsilon_{\alpha\beta} = \frac{\langle \delta \hat{c}_\alpha(k, t)\delta \hat{c}_\beta^*(k, 0) \rangle}{\langle \delta \hat{c}_\alpha(k, 0)\delta \hat{c}_\beta^*(k, 0) \rangle},
\] (5.20)

where, \( ^* \) denotes the complex conjugate. The temporal correlation function for specific ionic species
can then be expressed as

\[ \Upsilon_{pp} = \alpha_p e^{\lambda_1 t} + \alpha_n e^{\lambda_2 t} + \beta_p S_{np}(e^{\lambda_2 t} - e^{\lambda_1 t}) \]

\[ \Upsilon_{nn} = \alpha_n e^{\lambda_1 t} + \alpha_p e^{\lambda_2 t} + \beta_n S_{pn}(e^{\lambda_2 t} - e^{\lambda_1 t}) \]

\[ \Upsilon_{pn} = \alpha_p e^{\lambda_1 t} + \alpha_n e^{\lambda_2 t} + \frac{\beta_p}{S_{np}}(e^{\lambda_2 t} - e^{\lambda_1 t}) \]

\[ \Upsilon_{np} = \alpha_n e^{\lambda_1 t} + \alpha_p e^{\lambda_2 t} + \frac{\beta_n}{S_{np}}(e^{\lambda_2 t} - e^{\lambda_1 t}) \]

\[ (5.21) \]

The \( S_{pn}(k) \), \( S_{np}(k) \) are static structure factor-like terms defined as

\[ S_{pn}(k) = \frac{\langle \delta \hat{c}_p(k,0) \delta \hat{c}_n^*(k,0) \rangle}{\langle \delta \hat{c}_n(k,0) \delta \hat{c}_n^*(k,0) \rangle} \]

\[ S_{np}(k) = \frac{\langle \delta \hat{c}_n(k,0) \delta \hat{c}_p^*(k,0) \rangle}{\langle \delta \hat{c}_p(k,0) \delta \hat{c}_p^*(k,0) \rangle} \]

\[ (5.22) \]

In this linearized theory, the covariance between the initial ionic concentration fluctuations of cation and anion are nonzero due to the charge neutrality constraint. The structure factor terms \( S_{pn} \) and \( S_{np} \) can be obtained from experiment or more detailed simulations. The long time-behavior of both temporal auto-correlations and cross-correlations are dominated by slowly decaying terms which behave asymptotically as \( \exp(\lambda_2 t) \) where \( \lambda_2 \) is one of the two (negative) eigenvalues.

### 5.3 Simulation methods

The results of the linearized model were tested against molecular dynamics (MD) and charged dissipative particle dynamics (cDPD) simulations as described below.

The fully-atomic MD simulation of an aqueous NaCl solution in the bulk consisted of 400 \( \text{Na}^+ \) ions, 400 \( \text{Cl}^- \) ions, and 64000 \( \text{H}_2\text{O} \) water molecules in a periodic cubic simulation box with box size \( L = 12.8\text{nm} \). The mass density is \( \rho^0 = 0.616 \text{ amu } \text{Å}^{-3} \) and the ion concentration is \( c_{\pm} = 0.3168 \text{M} \). The SPC/E model [161] was used for water and ion force field terms were obtained from Smith and Yoshida [96, 99]. The particle-mesh Ewald method [162] was used for computing electrostatic interactions with vacuum periodic boundary conditions and a direct space cutoff of 9.8 Å. The bond lengths of water were constrained using the SHAKE algorithm [163] to allow a 1 fs step size in the velocity-Verlet molecular dynamics integrator [164]. A constant number-temperature-pressure (NVT ensemble) simulation was simulated at \( T = 300K \) with a Nosé-Hoover thermostat. The system was relaxed for 0.5 ns and then sampled for another 10 ns with snapshots saved every 0.1 ps. The self- and mutual-diffusion coefficients of ionic species were computed from the MD velocity correlation functions via the Green-Kubo relationship [154, 155]. The calculated
self-diffusion coefficients were $1.3 \times 10^{-9}$ m$^2$ s$^{-1}$ for Na$^+$ and $2.1 \times 10^{-9}$ m$^2$ s$^{-1}$ for Cl$^-$. The mutual-diffusion coefficient was calculated as $1.2 \times 10^{-10}$ m$^2$ s$^{-1}$ which is very close to previous simulation and experiment results for NaCl solutions [155]. The mutual-diffusion coefficient is much smaller than the self-diffusion coefficients and thus is ignored in the current work.

The cDPD model is an extension of the classic DPD model to numerically mimic the fluctuating hydrodynamics and electro-kinetics equations in the Lagrangian framework. This model has been described in previously chapter 4. Throughout the paper, the DPD parameters are selected as $\rho = 4.0$, $k_B T = 1.0$, $a = 75.0$, $\gamma = 4.5$, $\kappa = 0.25$, $\lambda = 0.14378$, $\xi = 6.00$, $r_0^* = 26.224$, $r_c = 1.5$, $r_{cc} = 1.0$, $r_{ec} = 2.5$ and the weighting functions are chosen as $\omega_C(r) = (1 - r/r_c)$, $\omega_D(r) = \omega_R^2(r) = (1 - r/r_c)$, $\omega_QD(r) = \omega_Q^2B(r) = (1 - r/r_{cc})^2$, $\omega_\phi(r) = (1 - r/r_{cc})^2$ and $\omega_E(r) = \frac{1}{2}(1 - r/r_{cc})^2r$.

### 5.4 Results and Discussion

We examined the local fluctuations of mass density, momentum density, charge density and ionic concentration. For each of these quantities, we constructed the instantaneous function $n(r)$ on a grid $r^{i,j,k}$, using quintic splines $W(r_{ij}, h)$ with finite support $h$ as a smoothing function to project from particles to neighboring meshes according to $n(r) = \sum_i^N W(|r - r_i|, h)n_i$ with $h = 3.1$ Å for MD data and $h = 2.0r_0$ for cDPD data. According to central limit theorem, the local fluctuations in these quantities of interest should be Gaussian in the continuum regime; this is observed for
mass density, momentum density, charge density from both MD and cDPD results. However, the local concentration fluctuations for ionic species in the MD system follow gamma distributions and converge to Gaussian with large spacing $h$; these concentration fluctuations follow a Gaussian distribution in DPD systems (mesoscale) as shown in Fig. 5.2.

The spatial correlation for quantities of interest $n(r)$ were computed on the grid $r^{i,j,k}$ according to

$$CF(r) = \frac{1}{N(r)} \sum_{i=1}^{N(r)} \delta n(r) \delta n(r + r)$$  \hspace{1cm} (5.23)

where $N(r)$ is a normalization coefficient. We have assumed that the spatial correlations are isotropic in weakly charged electrolyte bulk solutions. We observed that the spatial correlations of mass density, momentum density, charge density and ion concentration are all very short ranged – approximately delta-correlated for large systems – in agreement with continuum fluctuating hydrodynamics results at equilibrium. However, as shown in Figure 5.4, there is small-scale anti-correlation structure for the charge densities obtained in the MD simulations.

This structure is observed on length scales comparable to the Bjerrum and Debye lengths for this system, suggesting that it could be related to solvent polarization and ionic screening.

The temporal correlation between two quantities $u$ and $w$ in Fourier space is defined by

$$\langle u(k,t)w(k,0) \rangle = \frac{1}{N(t)} \sum_{s=1}^{N(t)} \tilde{u}(k,t)\tilde{w}(k,0)$$  \hspace{1cm} (5.24)
Figure 5.5: Temporal transversal (red) and longitudinal (black) momentum auto-correlation functions in Fourier space from MD simulations, represented by open symbols, and compared against the linearized fluctuating hydrodynamics theory in solid lines.

Figure 5.6: Temporal transversal (red) and longitudinal (black) momentum auto-correlation functions in Fourier space from cDPD simulations, represented by open symbols, and compared against the linearized fluctuating hydrodynamics theory in solid lines.
with $k$ the Fourier mode, $\hat{u}$, $\hat{w}$ are the Fourier components, which are directly computed from particle trajectories as

$$\hat{u}(k, t) = \frac{1}{N_P} \sum_{i=1}^{N_P} u_i(r_i, t) \exp(-ik \cdot r_i(t)).$$  \hfill (5.25)

We do not project the particle variables onto the grid before Fourier transformation, as the average particle spatial distributions is uniform and isotropic at equilibrium.

Figure 5.6 shows the auto-correlation functions of momentum both from MD and cDPD simulations. The results are in agreement with the classical linearized theory of fluctuating hydrodynamics; i.e., the transversal autocorrelation function decays as $\exp(-\nu k^2 t)$, with $\nu$ the kinematic shear viscosity, while the longitudinal autocorrelation function decays as $\exp(-\Gamma_T k^2 t) \cos(cs_k t)$, with $\Gamma_T = 2\nu/3$ the isothermal sound absorption coefficient and $c_s$ the isothermal sound speed. We conclude that the fluctuating hydrodynamics model still follows the classical linearized theory, and is not explicitly affected by the electrolyte bulk solutions; the fluctuating hydrodynamics and electro-kinetics are explicitly decoupled. Next, we compare the auto-correlation and cross-correlation functions of ionic concentrations with the linearized theory derived above, as shown in Figure 5.8. We fit the MD and DPD results with the linearized theory by properly chosen structure factors $S_{pn}$ and $S_{np}$, which are around 1.0 and system dependent. The long time behavior of both auto-correlation and cross-correlation follow $\propto \exp(\lambda_2 t)$ decaying as shown by dashed lines in
5.5 Summary

We present both MD and DPD simulation results of bulk electrolyte solutions in about 10nm and 100nm scales, respectively. These simulation results are directly compared with the results of the linearized continuum theory. In a bulk electrolyte solutions at equilibrium, the fluctuating hydrodynamics and electro-kinetics are explicitly decoupled, and thus their behavior is not explicitly dependent on the electrolyte concentrations in the dilute regime. At length scales above 10 nm, the results obtained from both MD and cDPD simulations are in good agreement with the continuum-limit linearized theories.
Chapter 6

Electrostatic Correlations near Charged Surface: Field Theory Approach

6.1 Introduction

A fundamental description of charged systems is based on the well-known Poisson-Boltzmann (PB) theory, which was developed a century ago by Gouy [110] and Chapman [111]. However, being a mean-field (MF) theory, the PB formalism ignores fluctuations and correlations, which are important for the cases of low temperature, highly charged surfaces, or multivalent counterions. In mesoscopic systems, the fluctuations mainly due to the thermal noise, which is of the same order \((k_B T)\) with other characteristic interactions. Also, the roughness of surfaces and solvent inhomogeneities etc. may also create some fluctuations. These fluctuation and correlation effects, which may drastically alter the mean-field picture of PB theory, have been the focus of recent theoretical efforts [165, 166, 167, 97, 168, 103, 169, 170]. For example, one surprising phenomenon beyond MF theory is the so-called fluctuation-driven counterion condensation in a simple system with single charged surface and its oppositely charged counterions [171, 172, 173, 174]. Another interesting phenomenon is the attraction between two highly likely-charged surface immersed in electrolytes or polar solution [175, 176, 177, 178, 174], as observed in experiments and in computer simulations. These phenomena cannot be captured within PB theories [179, 180, 181] as PB theory only predicts pure repulsion between likely-charged surfaces. We will discuss these interesting phenomena further.
A simple perturbative expansion about the MF solution near a charged surface by Netz and Orland demonstrated the breakdown of MF theory with relatively high charge densities [168]. To go beyond the MF theory framework, nonlinear electrostatic self-consistent (SC) equations were first derived by Avdeev and Martynov within the Debye closure of the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchical equations [182]. Further, Netz and Orland re-derived the SC equations within the field theoretic formulation, using the Gaussian field variation ansatz [183]. However, as stressed by the authors, these coupled nonlinear SC equations are computationally very complex. The main difficulties come from the high dimensionality (6D) and the nonlinearity of the coupled equations. Here, we propose a numerical method to solve these equations at an affordable computational cost based on the specific properties of the SC equations.

We consider relative simple systems with positive charged planar surfaces immersed in a symmetric electrolytes solution with fixed surface charge densities $\sigma_s$ and salt valence $q$. The solvent is modeled implicitly as a continuous medium and the electric permittivity is a constant in the solution, hence, ignoring the solvent inhomegenities in space, i.e., these inhomegenty effects are considered as fluctuations. In general, there are three different length scales in such charged systems, i.e., the Debye-Hückel length $\kappa^{-1} = (8\pi q^2 l_B \rho_b)^{-1/2}$ which represents the salt screening effects in the bulk; the Gouy-Chapman length $l_G = 1/(2\pi l_B q \sigma_s)$, describing the interaction between ion charge and surface charge; and the Bejerrum length $l_B = e^2/(4\pi \epsilon_0 k_B T)$ representing the elementary charge interactions. Here, $\rho_b$, $e$, $k_B T$ and $\epsilon_0$ are the salt bulk concentration, elementary charge, thermal energy and solvent dielectric permittivity, respectively. As suggested by previous studies [183, 174], we can define a key dimensionless parameter in terms of two lengths as $\Xi = q^2 l_B / l_G$. On the one hand, the limit $\Xi \to 0$ is called weak coupling limit, where the thermal fluctuations overcome electrostatic interactions, thus the physical system can be precisely described within MF or PB theory. On the other hand, $\Xi \to \infty$ is the strong coupling limit, where the electrostatic correlations dominate the thermal fluctuations [165, 183]. A perturbative approach around the MF theory may not be valid, instead, non-perturbative approaches (e.g., the variational approach) remain accurate in this regime.

The central focus of the current work is to provide accurate numerical results from solving the nonlinear electrostatic SC equations. The simulation data cover a wide parameter range, and hence we can examine a complete counterion condensation phase diagram. We further explore other important features of the counterion condensation transition, such as the order of the phase transition, as well as the scaling properties of the order parameter and free energy near the transition point. We also investigate the interactions between two likely-charged surfaces as a function of
separation distance in salt solution with different coupling parameters.

This chapter is organized as follows: we start by re-deriving of the SC equations via the field theory approach. We then solve the equations numerically (see Sec. 6.2) with the help of selective inverse techniques [184], saving both memory storage and computational time. In Sec. 6.3, we describe the main numerical results obtained from the SC equations. In Sec. 6.4 A, we describe the counterion condensation phase diagram and analyze the associated scaling behavior near the transition point. In Sec. 6.4 B, we show the full interaction pictures between two-likely charged surfaces with electrostatic correlation effects. We conclude with a short discussion about the limitations and future studies are included in Sec. 6.5.

6.2 Self-Consistent (SC) Equations

In this section, we review the derivation of SC equations with the field theoretic variational approach [183]. The grand canonical partition function of $M$ ion species in a liquid of spatially varying dielectric permitivity $\epsilon(r)$ is

$$Z = \prod_i^{M} \sum_{N_i=0}^{\infty} \sum_{\mu_i} e^{N_i \mu_i} \int \prod_{j=1}^{N_i} dr_{ij} \chi(r_{ij}) e^{-\beta H},$$

(6.1)

where $r_{ij}$ is the position of $j-$th ion of type $i$, $\lambda_i$ is the thermal wavelength of point-like ions, and $N_i$ and $\mu_i$ are the total number and chemical potential of ions of type $i$, respectively. The indicator function $\chi(r)$ takes into account the presence of hard walls, $\chi(r) = 1$ in the solution, and $\chi(r) = 0$ inside the hard walls. In general, the hard surface can be represented by a hard potential as $\chi(r) = \exp(-V(r)/k_B T)$, $V(r) = \infty$, and we can adjust $V(r)$ to represent different surfaces. $H$ is the Hamiltonian of the charged system, which consists of two parts as follows:

$$H = \frac{1}{2} \int dr' d\rho(r) v_c(r, r') \rho(r') - \frac{v_c^b(0)}{2} \sum_{i=1}^{M} N_i q_i^2,$$

(6.2)

where the first part is the electrostatic energy with Coulomb potential defined as $v_c^{-1}(r, r') = -\frac{1}{\beta e^2} \nabla \cdot (\epsilon(r) \nabla \delta(r-r'))$, and the second part is self-energy of mobile ions, which should be subtracted from the total electrostatic energy with $v_c^b(r) = l_B / r$ the bare Coulomb potential. Here, we should note that the self-energy term is crucial for electrostatic correlations. As a first step, the LJ interactions are ignored for point charge ions, we will consider the LJ interactions or other short range interactions in our finite size ions model in the future. The charge density operator is introduced as $\rho(r) = \sum_{i=1}^{M} \sum_{j=1}^{N_i} q_i \delta(r - r_{ij}) + \rho_f(r)$, by assuming that all the ions are point-
like charges. To account for the ion size effects into the system, a general charge distribution function, i.e., a Gaussian distribution function $h(r, r')$, instead of $\delta(r, r')$, can be used for finite radius ions [103]. The grand-canonical partition function $Z$ is then transformed into a field-theoretic representation by the usual Hubbard-Stratonovich transformation, i.e., $Z$ is given by taking the form of a functional integral over the pure imaginary electrostatic auxiliary field $\phi(r)$; hence, $Z = \int D\phi e^{-S[\phi]}$, with the action functional defined as

$$S[\phi] = \int dr \left[ \frac{\epsilon(r)}{2\beta e^2} (\nabla \phi(r))^2 - i\rho_f(r)\phi(r) - \sum_i \chi(r)\lambda_i e^{(q_i^2\psi^2_0(0)/2 + iq_i\phi(r))} \right]$$ (6.3)

with $\lambda_i = e_i^\mu/\lambda_i^3$ is the fugacity of $i$th ion specie, here, we assume $\lambda_+ = \lambda_- = \lambda$ for symmetric salt solution. However, it is still impossible to calculate the above functional integral to obtain the partition function directly. Various approximations have been introduced in statistical physics to solve this problem. The simplest yet most popular approximation is to replace the functional integral over the electrostatic fields by the value of the integrand at the extremum or optimal value, i.e., the saddle point approximation, which determines the optimal values of the field given by $\frac{\delta S[\phi]}{\delta \phi} = 0$, then it yields the MF theory equations. Furthermore, for a weakly correlated system, a perturbative expansion around the mean field gives more accurate results, however, it breaks down for strongly correlated systems. Another common way to evaluate the partition function or equivalent equilibrium measure $dP(\phi) = \frac{1}{Z} \exp(-S(\phi))$ is to create a stochastic process generated by the Langevin equation $d\phi(\tau) = -\frac{\partial S}{\partial \phi(\tau)} d\tau + dW(\tau)$, with $W(\tau)$ the Wiener process, and with the ergodic stochastic process having the same measure $dP(\phi)$ as $t \to \infty$. However, this suffers from the long-time integration problem in solving numerically this stochastic partial differential equations. A more powerful and effective non-perturbative way is the standard Gibbs variational procedure. Based on the chosen proper reference action function $S_0$, the partition functional can be expressed as

$$Z = Z_0 \times \langle \exp\{-S[\phi] + S_0[\phi]\}\rangle_0 \geq Z_0 \times \exp\{-\langle S[\phi] - S_0[\phi]\rangle_0\}. \quad (6.4)$$

The above inequality holds due to Jensen’s Inequality [185]. Then, we approximate the partition function by the upper bound or optimizing the variational grand canonical free energy $F = F_0 + \langle S - S_0\rangle_0$, where averages $\langle \ldots \rangle_0$ are to be evaluated with respect to the most general Gaussian action function

$$S_0[\phi] = \frac{1}{2} \int dr dr' [\phi(r) - i\phi_0(r)] v_0^{-1}(r, r') [\phi(r) - i\phi_0(r)] \quad (6.5)$$
and with $F_0 = -\frac{1}{2} \text{tr} \ln v_0$. The variational Gibbs free energy $F$ is then given by

$$
F = -\frac{1}{2} \text{tr} \ln v_0 - \int dr \left[ \frac{[\nabla \phi_0(r)]^2}{8\pi l_B} - i\rho_f(r)\phi_0(r) \right] + \int \int dr dr' \frac{\nabla_r \nabla_r' v_0(r, r')}{8\pi l_B} - 2\lambda \int dr e^{q^2(v_0(r, r) - v_0^b(r, r))/2} \cos[q\phi_0(r)].
$$

By extremizing $F$ with respect to $v_0$ and $\phi_0$, i.e., $\delta F/\delta v_0^{-1}(r, r') = 0$ and $\delta F/\delta \phi_0 = 0$, we obtain the self-consistent (SC) equations. For simplicity, only two ion species with symmetric valency are considered here [183]:

$$
\begin{align*}
\nabla \cdot (\epsilon(r)\nabla \phi_0(r)) - 8\pi l_B q\lambda e^{-q^2\delta w(r)/2} \sinh[q\phi_0(r)] &= -4\pi l_B \rho_f(r) \\
\left[ \nabla \cdot (\epsilon(r)\nabla - 8\pi l_B q^2\lambda e^{-q^2\delta w(r)/2} \cosh[q\phi_0(r)]) \right] v_0(r, r') &= -4\pi l_B \delta(r - r'),
\end{align*}
$$

where $\delta w(r) = \lim_{r \to r'} [v_0(r, r') - v_0^b(r, r')]$, and $\epsilon(r) = \epsilon(r)/\epsilon_0$. We further rescale the SC equations with $l_G$, and by defining $\psi = q\phi_0$, $\rho_f = \rho_f l_G/\sigma_s$, $v_0 = v_0 l_G/l_B$, we obtain the dimensionless equations as

$$
\begin{align*}
\nabla \cdot (\epsilon(r)\nabla \psi(r)) - \Lambda e^{-\Xi \psi(r)/2} \sinh[\psi(r)] &= -2\rho_f(r) \quad (a) \\
\left[ \nabla \cdot (\epsilon(r)\nabla - \Lambda e^{-\Xi \psi(r)/2} \cosh[\psi(r)]) \right] v_0(r, r') &= -4\pi \delta(r - r') \quad (b)
\end{align*}
$$

Clearly, there are only two dimensionless parameters in this physical system from Equation 8, namely, the coupling parameter $\Xi$ defined in Sec. 6.1, and the rescaled fugacity $\Lambda = 8\pi l_B^2 \Xi \exp(-\Xi l_G/2)$. Here, it is worth mentioning that we define the ionic self-energy dressed with electrostatic correlations in the form $\delta v(r) = v_0(r, r) - v_0^b(r, r) + l_B \kappa = v_0(r, r) - v_0^b(r, r)$, with $v_0^b(r) = \frac{l_B}{r} \exp(-\kappa r) = \lim_{r \to \infty} v_0(r, r)$, the Debye-Hückel potential in the homogeneous salt solution (i.e., $\Xi = 0, \psi = 0$) [165, 166]. That is, the reference system is chosen as the far field, such that we can obtain $v_0(r, r)$ and $v_0^b(r)$ simultaneously with same numerical accuracy, thus, the numerical errors for $\delta v(r)$ are exactly canceled.

### 6.3 Numerical Methods

The first of the SC equations is a modified PB equation for the fluctuating external potential induced by the fixed surface charge, while the second is a modified Debye-Hückel equation that accounts for the local screening of the electrostatic propagator by mobile ions. Before we proceed to numerically solve the SC equations, we discuss their properties and subsequently we develop our
numerical method based on these properties. First of all, we note that these two equations can only be decoupled in the limits $\Xi \rightarrow 0$ and $\Xi \rightarrow \infty$; and that an iterative method is needed for general $\Xi$. Second, these equations resemble the typical “Bratu problem” $\Delta u + \alpha e^u = 0$ [186], the highly nonlinear term $e^u$ creates difficulties near bifurcation points for numerical methods. We note that most of the iterative methods, i.e., fixed point iteration method or Newton iteration method only work well before the bifurcation point. However, the bifurcation point is isolated, thus we can approach the point from one side of parameter space with the continuation method. Physically, the bifurcation point corresponds to the famous counterion condensation phase transition. Another important aspect and also the greatest difficulty in solving the SC equations arise from the 6D $(\mathbf{r}, \mathbf{r}')$ modified Debye-Hückel equation; however, only the diagonal information $(\mathbf{r} = \mathbf{r}')$ is needed for calculating $\delta v(\mathbf{r})$. Thus, the problem reduces to finding the diagonal elements of the inverse of the discrete Debye-Hückel operator. Since the discrete Debye-Hückel operator is a symmetric and positive definite matrix, we can use Cholesky or LDL factorization to fully invert the matrix, but the computational time cost ($\mathcal{O}(n^3)$) and storage $\mathcal{O}(n^2)$ are extremely expensive for multi-dimensional problems. However, the problem is greatly simplified if only the diagonal elements are needed, which can be achieved by using the recently developed SelInv package to extract the diagonals of a matrix inverse [184], with much smaller computational time cost ($\mathcal{O}(n^2)$) and storage $\mathcal{O}(n)$.

We employ a fixed-point iteration scheme for the solution of coupled SC equations following two alternating steps: first, for given $\delta v(\mathbf{r})$, we solve the modified PB equation for $\psi(\mathbf{r})$ given the boundary conditions $\psi(\mathbf{r} \rightarrow \infty) = 0$; next for given $\delta v(\mathbf{r})$ and $\psi(\mathbf{r})$, we invert the discrete Debye-Hückel operator for $v(\mathbf{r}, \mathbf{r}')$, and then obtain a new $\delta v(\mathbf{r})$. These two steps are iteratively performed until the convergence criterion of the solution is reached; here, we use the relative free energy as the convergence criterion $|F^{(k)} - F^{(k-1)}| < \delta$, with $k = 1, 2, \ldots$ the iteration step and $\delta$ a small pre-set value.

We consider numerical solutions of the nonlinear modified PB equation and the discrete form of the Debye-Hückel operator. The former is often approximated by the linearized PB equation, obtained by taking $\sinh(\psi(\mathbf{r})) \approx \psi(\mathbf{r})$ when $\psi(\mathbf{r}) << 1$. The nonlinear modified PB equation presents several numerical difficulties due to the rapid exponential nonlinearities, discontinuous coefficients, delta functions (point charge distribution), etc.. The finite volume method has been one of the standard approaches for discretizing 2D and 3D interface problems which enforce conservation of certain physical quantities even for the discrete systems. First, we partition the domain $\Omega$ into 3D non-uniform Cartesian mesh, $\Omega = \bigcup_{j=1}^{M} \tau^j$ with $\tau^j$ the $j$th finite volume. It is important to notice that all the discontinuities in the coefficients are taken to lie along the boundaries of $\tau^j$. Then, by integrating the modified PB equation over an arbitrary finite volume, and employing the
Figure 6.1: (a) Electrostatic potential $\psi(x)$, (b) correlation potential $\delta v(x)$, (c) negative ion density $\rho_-(x)$ and (d) positive ion density $\rho_+(x)$ near one charged surface with $\Lambda = 0.3$. The black, red, blue, green and purple lines represent PB results and $\Xi = 0.50, 2.50, 3.80, 4.20$, respectively. The charged surface is at $x/l_G = 0$. 
Figur 6.2: Numerical solution for the critical coupling parameter $\Xi_c$ represented by circles, at the phase boundary between weak adsorption and counterion condensation phases, as a function of the parameter $\Lambda$. The solid line is a polynomial fit through the data points (circles).

divergence theorem for the first term in the equation, we obtain the algebraic equations in the form $A\psi + N(\psi) - f = 0$. We then solve the algebraic equation with inexact-Newton method for the modified PB equation [187, 188]. A small trick is used during discretization for the “Bratu” type problem, i.e., we approximate the second-order derivative using a nonlinear denominator function, $(\Delta x)^2 = 2.0 \ln(\cosh(\Delta x)) + O((\Delta x)^4)$ (Mickens Discretization) [189], which works well near bifurcation points.

For simple systems with charged planar interfaces located at the $(y, z)$ plane, the translational symmetry will greatly simplify the problem. In such cases, the electrostatic potential becomes simply a function of the coordinate $x$, and the electrostatic Green’s function can be expanded in 2D Fourier basis, with the Fourier transform of circularly symmetrical function (Hankel transform) as

$$v_0(r, r') = \int_0^\infty \frac{dk}{2\pi} J_0(k|r||r'|)|\tilde{v}_0(x, x', k)$$

with $J_0$ the Bessel function. Then, the modified Debye-Hückel equation can be decoupled as a series of one-dimensional equations for each $k$

$$\left[\partial_x \epsilon(x) \partial_x - \epsilon(x) k^2 - \Lambda e^{-\Xi \delta v(x)/2} \cosh(\phi(x))\right] \tilde{v}_0(x, x', k) = -4\pi \delta(x - x').$$

Here $\delta v(x)$ is calculated using Eq. (10) with $|r||r'| = 0$, and the integral is obtained numerically.
via Gauss quadrature integration by a cutoff at a certain number, which is sufficiently large to account for the contribution from the smallest correlation length.

Once we solve the above SC equations, the local ion densities are given by

$$\rho_{\pm}(r) = \rho_{0} \chi(r) e^{-\frac{q^2}{2} \delta \nabla \phi(r) \mp \phi_0(r)}. \quad (6.11)$$

To further investigate the physical phenomena near the charged surface, we define a proper order parameter $\rho$ for ion adsorption by the charged surface as

$$\rho = \int_{0}^{L_{\text{z}}} (\rho_{+}(r) - \rho_{-}(r)) \, dr.$$
6.4 Results and discussion

A. Single planar surface in symmetric electrolytes solution

First, we consider one planar charged surface case with fixed charge density $\rho_f(x) = \delta(x)$. The results from numerically solving the SC equations with different coupling parameters, such as electrostatic potential, correlation potential and ion density distribution near one charged surface are shown in Figure 6.1. Clearly, when $\Xi$ is small, the results from the SC equations approach the same results as the one from the PB equation. However, as $\Xi$ increases, the results differ from the PB results, especially for larger value of $\Xi$. One of the interesting phenomena is that there is a peak in the positive ion density profile near the positive charged surface. This is due to the strong correlations, which cause overcompensation of surface charge by negative ions close to or at the surface. Then, the positive ions which are away from the surface will “feel” a negative apparent charged surface. Therefore, they will be attracted toward the wall. This is the so called "charge inversion" which was observed by previous studies. [190, 191, 192]

As we already discussed at the end of Section 6.2, the state of the simple charged systems is determined by two parameters: the coupling parameter $\Xi$, and the rescaled fugacity $\Lambda$. For various rescaled fugacity values, we change $\Xi$ from small to large values with small increments and we measure the free-energy and the adsorbed amount of ions within a Gouy-Chapmann length near the wall $\rho$. There is obviously a phase transition when $\Xi$ become bigger corresponding to the bifurcation point of the SC equation. Above this point, simple fixed point iteration method will blow up. All of the data near the transition point are then carefully analyzed.

The numerical results for the phase transition between the weak ion adsorption and counterion condensation states based on the analysis of the free energy are displayed in Figure 6.2. The phase boundary curve is constructed by simulation data within three orders of magnitude in parameter space. The fact that the counterion condensation transition is a first-order phase transition is established. As a result, going from the weak adsorption state, the free energy and ion adsorbed amount follow some scaling behavior near the transition point. To demonstrate the first-order phase transition, we plot $(\rho(\Xi, \Lambda) - \rho_c)$ as a function of $(\Xi/\Xi_c - 1)$ in a double logarithmic plot in Figure 6.3(a). A dashed line representing slope of 1 has also been included. All data collapse and approach a single scaling power law as shown in Eq. 12.

$$\frac{(\rho(\Xi, \Lambda) - \rho_c)}{\Xi_c} \propto \frac{(\Xi/\Xi_c - 1)}{(\Xi/\Xi_c - 1) << 1}. \quad (6.12)$$

To confirm the first-order nature of the transition, we further examine the dependence of the free
Figure 6.4: Electrostatic potential $\psi(x)$ (a), correlation potential $\delta v(x)$ (b), negative ion density $\rho_-(x)$ (c) and positive ion density $\rho_+(x)$ (d) near two charged surface for $\Lambda = 1.0, \Xi = 1.0$ with different separation distances. The black, red, blue and green lines represent separation distance $h/l_G = 0.5, 1.0, 2.0$ and $4.0$, respectively.
energy per unit volume as a function of \((\Xi/\Xi_c - 1)\) near the transition point. For a first-order transition, we expect that

\[
(F(\Xi, \Lambda) - F_c) / (\Lambda \Xi_c) \propto (\Xi/\Xi_c - 1), \quad (\Xi/\Xi_c - 1) \ll 1.
\]  

(6.13)

The power law exponent 1 is characteristic of the first-order transition. Figure 3(b) demonstrates that all \(\Lambda\) cases display the above power law near the transition point; for comparison, a dashed line has been drawn with the anticipated power-law exponent 1. Our numerical results are consistent with previous studies [171].

Figure 6.5: Electrostatic potential \(\psi(x)\) (a), correlation potential \(\delta\nu(x)\) (b), negative ion density \(\rho_-(x)\) (c) and positive ion density \(\rho_+(x)\) (d) near two charged surface for \(\Lambda = 1.0, \Xi = 2.0\) with different separation distances. The black, red, blue and green lines represent separation distance \(h/l_G = 0.5, 1.0, 2.0\) and 4.0, respectively.
B. Two planar surfaces in symmetric electrolyte solution

We now consider the case of two charged planar surfaces immersed in salt solution with separation distance \( h \), and fixed charged density \( \rho_f(x) = \delta(x - 0.5h) + \delta(x + 0.5h) \).

Figure 6.6: Free energy (a) and osmotic pressure (b) as a function of distance between two likely-charged planar surface in weakly charged regime \( (\Lambda = 5.0, \Xi = 0.5) \).

First, we show electrostatic potential, correlation potential and ion density profiles in Figure 6.4 and Figure 6.5. For small separation distance \( h \), or strong confinement, the osmotic pressure is extremely big, pushing the ions into the middle of the confinement layer, see black lines of Figure 6.4(c) and (d).

Figure 6.7: Free energy (a) and osmotic pressure (b) as a function of distance between two likely-charged planar surface in strongly charged regime \( (\Lambda = 5.0, \Xi = 1.2) \).

The osmotic pressure is a key parameter in understanding the thermodynamics and the interactions in colloidal systems. Here, we calculate the osmotic pressure from \( \Pi(h) = -\frac{\partial F}{\partial h} \) as a function of separation distance. The results are shown in Figure 6.6 and Figure 6.7. For a weakly charged system, the access free energy decreases by increasing the separation distance \( h \), while the osmotic
pressure is pure repulsion. However, in strongly charged systems, the access free energy decreases when we increase the separation distance only within a small regime, i.e., $h \sim l_G$, and the access free energy then increases by increasing the separation distance for large $h$, which corresponds to an attractive osmotic pressure as shown in Figure 6.7.

![Figure 6.8: Phase diagram for two likely-charged wall interactions as a function of parameters $\Xi$ and $\Lambda$. Here, red and blue symbols represent purely repulsive osmotic pressure and attractive osmotic pressure with certain distance, respectively. The phase boundary is plotted with black dash line here.](image)

Finally, by calculating all the osmotic pressure data in the parameter space, we obtain the global phase diagram for the interactions between two likely-charged surfaces as shown in Figure 6.8. The phase boundary shape here is similar to the one of the counterion condensation phase diagram (Figure 6.2) with a shift on the log-log plot due to the confinement effects.

### 6.5 Conclusions

In this work, we have developed a numerical method for solving the electrostatic SC equations in order to explore the parameter space for simple charged planar surfaces immersed in salt solution. We quantified the physical picture beyond MF theory, i.e., we established the first-order phase transition properties of counterion condensation and the phase diagram, and we calculated the osmotic pressure between two likely-charged planar surface. For the latter case, we found that the surfaces may attract each other for a certain separation distance in strongly charged systems.

For the moment, we only consider very simple geometry systems, however, the extension to
complex geometry systems is straightforward. From our current studies, we observe that the electrostatic correlation energies are mainly located near the charged surface, thus, an adaptive mesh refinement scheme should be constructed with most of the grid points distributed near the charged surfaces. Alternatively, a high-order Discontinuous Galerkin (DG) method or extensions of the finite volume method employed here may result in higher accuracy and efficiency.

Due to the bifurcation nature of the SC equations, our current fixed point iteration method will blow up above the bifurcation point, thus, there remains one problem, namely, what should we do after the bifurcation point? To this end, we propose the recursive projection method (RPM) [193] to deal with these situations. On the other hand, physically, we can always renormalize the charge densities and the condensation ions into a new charge density, such that the renormalized system can be solved with our current method again.

Another important aspect is to account for the ion size effects [194, 195, 196] in SC equations [103], i.e., the charge on an ion is assumed to have a finite spread around its center, instead of point charge \( \delta(r - r') \). A convenient choice is the Gaussian distribution with Born radius \( a \),

\[
    h(r - r') = \left( \frac{1}{2a} \right)^{3/2} \exp \left[ -\frac{\pi (r - r')^2}{2a^2} \right].
\]

The LJ interactions are ignored for point charges here as a first step, we plan to include the LJ interactions or other short range interactions in our finite size ions model.
Chapter 7

Coarse-Grained Modeling of Protein Unfolding Dynamics

7.1 Introduction

A major challenge in molecular biology is to understand the regulatory mechanisms in large protein complexes that are abundant in multi-cellular organisms, as most proteins perform their function through structural deformation driven by mechanical loading. In general, atomistic MD simulation has played a significant role in gaining insight into protein dynamics [197, 198], however, systematic computational characterization of protein complex dynamics is still far beyond current computational capabilities. This has motivated efforts for developing efficient but physically realistic methods for deriving dynamic properties based on structures and mechanical properties. Indeed, coarse-graining approaches have proven to be useful in elucidating the functionality of important collective motions of large proteins [199].

Proteins in living cells can fold quickly into a unique native-state of minimum free energy, which conceals a wealth of information about the folding/unfolding processes [200]. The free-energy landscapes of a protein can basically be mapped-out by its native-state structure [201], so it has been concluded that the protein dynamics mechanisms are largely determined by its native-state structures [202, 203]. Previous experimental and simulation studies also suggested that the dominant motion of a protein structure is mainly represented by its carbon backbone chains [204]. Based on these arguments, coarse-grained protein models, which delineated by $C_\alpha$ atoms along protein backbone chains have been suggested. For example, Flory first proposed and Tirion then formulated and improved the popular elastic network model (ENM) for conformational
fluctuations of proteins [205, 206], which then inspired many successful studies of protein dynamics and mechanics with high computational efficiency [207]. The model reduction scheme (coarse-graining) of ENM has also been employed for large protein structures because cooperative motions between $C_\alpha$ atoms are largely obtained during protein dynamics [208, 209, 210, 211, 212].

Computational studies based on ENM have been successful in exploring the molecular motions of proteins around the folded native-state, when considered a harmonic approximation to the free-energy surface of the protein around native state. However, there remains a very simple yet fundamental question: can the simple ENM be used to describe the protein folding/unfolding process, given that the folding/unfolding pathways in globular proteins are mainly determined by their native topologies [213]. Experimental and theoretical studies have shown that the protein unfolding process can be mimicked through breaking the native contacts (including hydrogen bonds, salt bridges, hydrophobic contacts, etc.) one-by-one between the residues [214, 215, 216]. Inspired by these findings, here, we extend the widely used ENM, and propose a multi-scale dynamic elastic network model (DENM) at various coarse-graining scales. The idea behind the extension of ENM is simple, i.e., as suggested by the well-known Levinthal paradox, the protein folds or unfolds through a series of meta-stable intermediate states instead of a random conformational search. Hence, we can approximate the entire energy landscape (simply 1D, along the unfolding path) as perturbed harmonic potential, where all perturbations are considered as local minima (meta-stable) on the energy surface. The transition rate between these meta-stable states with force loading can be described with the Bell model [217]. Our approach is a general framework to construct a bottom-up coarse-graining model to capture the protein unfolding dynamics mechanism. We apply this approach to Fibrinogen (PDB ID is 1M1J; total number of protein atoms and heterogen atoms is 16117) and Titin Immunoglobulin (PDB ID is 1TIT; total number of protein atoms and heterogen

Figure 7.1: Atomistic level visualizations of (a) Titin Immunoglobulin and (b) Fibrinogen Protein, respectively.
Figure 7.2: (a) $C_{\alpha}$-based ENM and (c) coarse-grained ENM representations of Titin Immunoglobulin. The contact maps of residues for (b) $C_{\alpha}$-based ENM and (d) coarse-grained ENM model are also shown here with the red and black symbols representing the covalent and non-covalent contacts, respectively.

atoms is 1377) proteins, see Figure 7.1. We will show that the proposed method can reproduce accurately the force-extension curve of a single protein compared against atomistic MD simulations as well as AFM experimental results [218, 219].

7.2 Materials and Methods

The standard ENM describes a three-dimensional protein structure as an elastic network of $C_{\alpha}$ atoms connected by harmonic-spring bonds within a cutoff distance $r_c$. The potential energy in
the elastic network is given by

$$\frac{U}{k_B T} = \sum_{i \neq j}^n h(r_c - r_{ij}^0) \left( \frac{\gamma}{2} (\Delta r)^2 \right)$$

where \( h(r) \) is the heaviside function, \( \Delta r = r_{ij} - r_{ij}^0 \), with \( r_{ij} \) the distance between node \( i \) and \( j \), \( r_{ij}^0 \) the original distance in the native-state structure, \( n \) the total number of residues (or total number of \( C_\alpha \) atoms) and \( \gamma \) a spring force constant. However, in our model, the spring force constants for the covalent (i.e., peptide bonds, disulfide bonds, etc.) and non-covalent (i.e., hydrogen bonds, salt bridges, etc.) interactions are different for capturing the nonlinear extension of the protein.
network. Here, we set the spring force constants of covalent bonds and non-covalent bonds as $c\gamma$ and $\gamma$, respectively, with the new constant $c$ typically greater than 1. The potential function of the ENM can be expanded to second-order about the minimum near the saddle point by computing its Hessian matrix $H$, which includes the second derivatives of the potential function and contains $n$-by-$n$ super-elements each of size $3 \times 3$. Correspondingly, the mean-square fluctuations of each node are given by the pseudo-inverse of the Hessian matrix $H^{-1}$ as

$$<\Delta r_i^2> = \left(\frac{3k_BT}{\gamma}\right) \text{Tr} \left([H^{-1}]_{ii}\right).$$  \hfill (7.2)

The pseudo-inverse is constructed based on the $3n - 6$ nonzero eigenvalues $\lambda_i^2$ of the full Hessian matrix (quadratic vibrational degrees of freedom) and corresponding eigenvectors $u_i$, i.e.,

$$H^{-1} = \sum_{i=7}^{3n} \frac{1}{\lambda_i^2} u_i u_i^T. \hfill (7.3)$$

The values of the force spring constants $c\gamma$ and $\gamma$ are determined by comparing the theoretical B-factor, $B_i = 8\pi^2 <\Delta r_i^2>/3$, with the x-ray experimental data in the PDB file of the protein. It is worth pointing out that because the magnitude of $\gamma$ does not affect the distribution (or relative size) of residue fluctuations, it has no influence on the correlation between the computed and experimental B-factors. So, the value of $\gamma$ was set to 1 at first and the value of $c$ was determined by maximizing the correlation between the computed and experimental B-factors. Then, the value of parameter $\gamma$ was determined by normalizing the computed fluctuation with the experimental B-factors.

To capture the unfolding processes of a protein (i.e., to overcome the local energy barrier) as well as to cover the timescale of unfolding events in MD simulation, we combine the well-known dynamic bond model within the standard ENM here, which we call dynamic elastic network model (DENM). As we mentioned above, the unfolding event is mimicked through breaking non-covalent bonds, i.e., all of the network non-covalent bonds may break reversibly under force loading with a certain probability. The probability for the bond to break with an extension $\Delta r$ is computed from

$$P_{off} = 1 - \exp \left(-k_{off} \cos \theta \Delta t \exp \left(\frac{\gamma(\Delta r)^2}{k_BT}\right)\right). \hfill (7.4)$$

At the same time, the broken non-covalent bonds may also be formed again if they are in close proximity, with the formation probability computed from

$$P_{on} = 1 - \exp \left(-k_{on} \cos \theta \Delta t \exp \left(\frac{-\gamma(\Delta r)^2}{k_BT}\right)\right). \hfill (7.5)$$
According to the Bell model, the dissociation and formation reaction rates of non-covalent bonds are estimated as
\[ k_{\text{off}} \propto \frac{1}{2\pi \eta} \exp\left(-\frac{\Delta G_{\text{off}}}{k_B T}\right) \]
and
\[ k_{\text{on}} \propto \frac{1}{2\pi \eta} \exp\left(-\frac{\Delta G_{\text{on}}}{k_B T}\right), \]
respectively. Here, \( \eta \) is the friction coefficient in the MD simulation, \( k_B T \) is the unit of energy, and \( \Delta t \) is the time step for MD simulation; \( \theta \) is the angle between the bond direction and the pulling force direction. In general, these dynamic bond model parameters are used to describe the non-covalent bond breaking, i.e. mainly for hydrogen bonds. Hence, the typical values for hydrogen bond formation and dissociation energy barrier \( \Delta G_{\text{on}} \) and \( \Delta G_{\text{off}} \) can be used; \( k_{\text{off}} \) and \( k_{\text{on}} \) are chosen on the order \( 10^{-1} \) and \( 10^{-2} \), respectively, in previous papers.

So far, we have constructed a DENM of a protein by assigning every \( C_\alpha \) atom to the node, and subsequently we mapped the \( C_\alpha \) atoms based DENM to a consistent Coarse-Grained-DENM (CG-DENM). In general, for coarse-grained models of relatively small bio-molecules or in cases that the coarse-grained and fine-grained models have similar resolution, the construction of mapping is relatively straightforward. However, it is more challenging to construct a coarse-grained map when large and complex domains of bio-molecules have to be represented by a few coarse-grained sites. Here, we use the essential dynamics coarse-graining (ED-CG) scheme [204, 220, 221] to define the CG-DENM nodes from the original \( C_\alpha \) atoms based DENM. The \( C_\alpha \) atoms based DENM system is specified by the values of \( n \) nodes position vectors as \( r^n = r_1, r_2, ..., r_n \). These nodes are then
separated into $N$ dynamic domains, and each domain is a group of nodes that move together in a highly correlated fashion, whose motion can be obtained by minimizing the residual as follows:

$$
\chi^2 = \frac{k_B T}{3N} \sum_{i=1}^{N} \sum_{i \in I} \sum_{j \leq i \in I} \left( \text{Tr}[H^{-1}_{ii}] - 2\text{Tr}[H^{-1}_{ij}] + \text{Tr}[H^{-1}_{jj}] \right). 
$$ (7.6)

Figure 7.5: B-factors along Fibrinogen (right) protein backbones from experimental measurements (black), $C_\alpha$-based ENM calculation (red) as well as coarse-grained ENM calculation (green). The insets are the zoom in of the corresponding plots for a more clear comparison.

where $N$ is number of dynamic domains, $I$ denotes the CG node and $i, j$ denote the atoms in node $I$. Here, the same numerical algorithm (simulated annealing method) as in Zhang et al. [220, 221] is used to obtain the best CG model that reflects the low-frequency functional dynamics characterized by the ENM. First, $N$(coarse-grained nodes number) dynamic domains are randomly partitioned. For example, these domains are chosen to be continuous on the primary sequence, so they can be chosen by determining $N-1$ boundary atoms located randomly along the primary sequence. Using a global simulated annealing, at each temperature, we adjust variationally the locations of these boundary atoms using Monte Carlo method based on the Metropolis criterion, i.e., if residual of the new partition domains is smaller than the previous one, then the new partition is accepted. If it is higher than the previous one, then it is accepted with a probability $\exp(-\chi^2/T)$. We use large temperature $T$ at the beginning, and then gradually decrease it during the annealing process, allowing the calculation to settle into the global minimum of the residual. After the dynamic
domains are determined, we set the node that is closest to the center of each domain as a coarse-graining node, also called master node, while the other nodes are called slave nodes. Now the \( C_\alpha \) atoms based DENM nodes are decomposed into two regions such that master nodes are denoted as residues belonging to a region that is maintained during model reduction, whereas the other residues (or slave nodes) are the residues that could be eliminated during coarse-graining. Based on such decomposition, the potential energy of the (coarsened) network model can be represented in the form

\[
U(r_0 + \Delta r) \approx U(r_0) + \frac{1}{2} \begin{bmatrix} \Delta r_m^T \\ \Delta r_s^T \end{bmatrix} \begin{bmatrix} H_{mm} & H_{ms} \\ H_{sm} & H_{ss} \end{bmatrix} \begin{bmatrix} \Delta r_m \\ \Delta r_s \end{bmatrix}.
\]

(7.7)

\[ \text{Figure 7.6: Force-extension profile of Titin Immunoglobulin stretched at 0.0025 nm/ps. The black, red, and green lines represent the results from full-atomistic MD simulation, } C_\alpha \text{ based DENM and CG-DENM, respectively. The blue line represents the failure of DENM at large coarse-graining level. The insets are the zoom in of the corresponding plots for a more clear comparison.} \]

Model condensation (for the master nodes "m" and the slave nodes "s") reduces the Hessian matrix \( H \) into the condensed Hessian matrix \( \tilde{H} \) for a coarse-grained structure as \( \tilde{H} = H_{mm} - H_{ms}H_{ss}^{-1}H_{sm} \), and its corresponding pseudo-inverse matrix can be calculated similarly as before, i.e.,

\[
\tilde{H}^{-1} = \sum_{i=7}^{3N} \frac{1}{\tilde{\lambda}_i^2} \tilde{u}_i \tilde{u}_i^T.
\]

(7.8)

Here, \( \tilde{\lambda}_i^2 \) are its \( 3N - 6 \) nonzero eigenvalues and \( \tilde{u}_i \) are the corresponding eigenvectors.

At the same time, based on the above decomposition approach, the CG-DENM is constructed by \( N \) nodes less than the total number of residues belonging to such protein structures, the contact
Figure 7.7: Force-extension profile of Fibrinogen proteins stretched at 0.05 nm/ps. The black, red, and green lines represent the results from full-atomistic MD simulation, C\textalpha based DENM and CG-DENM, respectively. The blue line represents the failure of DENM at large coarse-graining level. The insets are the zoom in of the corresponding plots for a more clear comparison.

maps of C\textalpha-based ENM and coarse-grained ENM representations of 1IIT and 1M1J proteins are shown in Figure 7.2 and 7.3, respectively. The average cutoff distance $r_c^\Gamma$ for CG-DENM is in the form of $r_c^\Gamma = r_c p^b = r_c \left( \frac{n}{N} \right)^{1/b}$, where $b$ is the fractal dimension based on the self-similarity principle of complex networks theory. The self-similarities of the protein structure can be observed in Figure 7.2 and Figure 7.3, i.e., the shapes of contacts map are conserved during coarse-graining. This self-similarity property is extremely important for our coarse-graining procedure. Here, the fractal dimension $b$ is calculated by the so-called cluster growing method [222], and $\Gamma$ represents the coarse-grained model. Then, the spring constant for CG-DENM is determined from the Kullback-Leibler divergence [223, 224] as shown below while the other parameters remain the same as the ones with the C\textalpha atoms based DENM, i.e.,

$$\gamma(\Gamma) = \frac{1}{3N} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \frac{\lambda_i^{(\Gamma)}^2}{a_j^{(\Gamma)^2}} \left| u_i^{(\Gamma)^T} u_j \right|^2.$$  \hspace{1cm} (7.9)

Here, $\lambda_i^{(\Gamma)^2}$ and $u_i^{\Gamma}$ are eigenvalues and corresponding eigenvectors of the CG-DENM Hessian matrix $H^\Gamma$, and $a_j^{(\Gamma)^2} = \frac{\lambda_i^{(\Gamma)^2}}{\gamma(\Gamma)}$ are independent of $\gamma(\Gamma)$ since the eigenvalues $\lambda_i^{(\Gamma)^2}$ are proportional to $\gamma(\Gamma)$. In total, there are five parameters in our DENM, i.e., the cutoff distance $r_c$, spring constants $\gamma$ and $c_\gamma$, dissociation rate $k_{off}$ and association rate $k_{on}$. 

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7.3 Results and Discussion

Next, we apply our DENM to two well-known proteins, Titin Immunoglobulin and Fibrinogen Protein, whose fractal dimension $b$ are 0.42 and 0.50, respectively. The former plays an important role in muscle contraction and elasticity [225], while the systematic assembly or polymerization of the latter forms the main component of a blood thrombus [226].

We employ coarse grained molecular dynamics in these simulations with a time step $\Delta t = 10^{-4} ps$. This selection is based on the observation that the rate of the force extension response is of the order $0.1 nm/ps$. We start the simulation by fixing one end of the protein network and moving the other with constant velocity along the line in opposite direction, and we compute the force exerted on the moving bead as well as the distance between that bead and the fixed one. In the MD simulation, a velocity Verlet scheme is used to integrate the system, at each time step, and the dynamic bond interactions are considered. In the MD, all existing bonds are checked for a potential dissociation according to probability $P_{off}$; a bond is ruptured if $\xi < P_{off}$ and left unchanged otherwise, where $\xi$ is a random variable uniformly distributed on $[0, 1]$. Second, we check all the free nodes for possible bond formation according to the probability $P_{on}$. Finally, the forces of all remaining bonds are calculated and applied.

All parameters used in applying this DENM approach to these two proteins are shown in Table 1. First, we developed a $C_\alpha$ atoms based DENM of these two proteins from the all-atom PDB file by choosing the cutoff distance $r_c$ of 10.0 Å and 9.0 Å for 1M1J and 1TIT protein, respectively. Then, we obtained the best ENM of these proteins by carefully choosing the values of $c$ and $\gamma$ shown in Table 7.1, yielding patterns of $C_\alpha$ atoms B-factors that are similar to those of the experimental data as shown in Figure 7.4 and Figure 7.5, respectively. Next, we consider the force-extension unfolding process of these two proteins with the help of coarse-grained MD simulation. The sequence of unfolding events depends strongly on the network structure or native contact topology. Figure 7.6

<table>
<thead>
<tr>
<th>ID</th>
<th>N</th>
<th>$\gamma$</th>
<th>c</th>
<th>$r_c$</th>
<th>$k_{off}$</th>
<th>$k_{on}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M1J</td>
<td>1984</td>
<td>27.06</td>
<td>10.0</td>
<td>10.00</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>1M1J</td>
<td>1001</td>
<td>26.60</td>
<td>10.0</td>
<td>13.33</td>
<td>0.04</td>
<td>0.8</td>
</tr>
<tr>
<td>1M1J</td>
<td>228</td>
<td>26.0</td>
<td>10.0</td>
<td>24.81</td>
<td>0.02</td>
<td>0.4</td>
</tr>
<tr>
<td>1TIT</td>
<td>89</td>
<td>64.50</td>
<td>5.0</td>
<td>9.0</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>1TIT</td>
<td>44</td>
<td>63.27</td>
<td>5.0</td>
<td>12.66</td>
<td>0.025</td>
<td>0.5</td>
</tr>
<tr>
<td>1TIT</td>
<td>22</td>
<td>61.13</td>
<td>5.0</td>
<td>18.10</td>
<td>0.012</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 7.1: Effective parameters of DENM at different levels of coarse graining of the Fibrinogen (1M1J) and Titin Immunoglobulin (1TIT) proteins. The unit of $\gamma$ is $(k_B T/\AA^2)$, while the unit of $r_c$ is Å; other parameters are dimensionless quantities. The highest value of $N$ is the number of residues, $N_0$, of the fine-grained system.
Figure 7.8: Contact maps of residues for fine-grained (upper) and coarse-grained model (lower) of Titin Immunoglobulin during unfolding (total extension of protein is 0 nm, 15 nm and 25 nm, respectively form left to right). The red and black symbols representing the covalent and non-covalent contacts, respectively.

and Figure 7.7 show the forces as functions of cantilever displacement. For the Titin Protein, the curves are terminated when the protein is fully extended, and the sharp rise in force at the end of the curves reflects stretching of the covalent bonds along the backbone, which in our DENM, strongly depends on the constant $c$. We can also see that the force curves show a series of upward ramps followed by rapid drops where local contacts break. Both the $C_\alpha$ based DENM and CG-DENM can predict force-extension curves which match well with the atomistic MD simulation results below a certain coarse-graining limit. Besides the force-extension curves, the unfolding events, which are marked by the bonds breaking can be clearly understood from the contact map of residues with different stretch length as shown in Figure 7.8 and Figure 7.9. Results from the coarse-grained models are in agreement with the fine-grained models for both 1M1J and 1TIT proteins.

The key assumptions behind the coarse-grained scheme are the cooperative motion between $C_\alpha$
Figure 7.9: Contact maps of residues for fine-grained (upper) and coarse-grained model (lower) of Fibrinogen during unfolding (total extension of protein is 0 nm, 37.5 nm and 62.5 nm, respectively from left to right). The red and black symbols representing the covalent and non-covalent contacts, respectively.

atoms during the folding/unfolding process and the shape conservation of the contacts map during coarse-graining. The $L_2$ error between our coarse network model and full atomistic simulations is of the order 10% but increases rapidly at extreme coarse-graining levels; for example it reaches order 50% for Fibrinogen for 228 nodes, which is the coarsest graining we attempted. Correspondingly, we found our results start to deviate from the experimental results when the number of nodes is smaller than 22 and 228 for the Titin and Fibrinogen proteins as shown in Figure 7.6 and Figure 7.7, respectively. Clearly, we cannot coarse-grain our model to as small number of nodes as we want, because when the $C_\alpha$ atoms in a coarse-graining node are not moving in a highly correlated fashion, the model cannot capture the real dynamics any more. In other words, the CG-DENM works well only when the relative minimal residual is relative small. As shown in Figure 7.10, the minimal relative residual error ($L_2$ error), which represents the cooperative motion in coarse-graining nodes,
increases proportional to $C(N_0/N)^2$ for both proteins, consistent with the scaling first documented in [227]. The constant $C$ is different for different proteins with small values for stiffer proteins with large persistent length.

Figure 7.10: Minimal relative residual error (normalized by the biggest Residual when $N = 1$) as a function of coarse-graining level $N_0/N$ for Titin (black) and Fibrinogen (red) protein. $N_0$ is the protein residues number and $N$ is the coarse grained network nodes number.

7.4 Conclusion

In summary, we have developed a general $C_\alpha$ atoms topology-based dynamic elastic network model (DENM) to describe the mechanical unfolding of proteins with force loading, which yields quantitative agreement with full-atomistic MD simulations. By combining different techniques, e.g., ED-CG, the Kullback-Leibler divergence, and exploiting the self-similar structure of proteins at different scales, we formulated the $C_\alpha$ atoms based DENM to various coarse-graining levels, which can be used with particle-based methods to model the dynamic properties of proteins.

Here we have used hydrogen bond values for all the dynamic bond parameters for both examples presented. However, in principle, we can employ an adaptive procedure to update them based on the large deviation theory, i.e. to minimize the distance of the coarse-grained and fine-grained force-excitation responses by considering them as stochastic processes. Our results suggest that we can coarse-grain with reasonable accuracy about ten residues to one CG node, which taken together
with the elimination of the atoms per residue (of the order of ten, see Table 7.1), yields a total reduction in degrees-of-freedom of about *two orders* of magnitude. This is a rather aggressive coarse-graining, which can have a tremendous effect on speeding-up simulations of cell-protein interactions in biological systems. An example is blood flow where simulating accurately the cross-linking of fibrin fibers and their interactions with blood cells (e.g., platelets and red blood cells) is critical in producing physiologically correct results for the formation of thrombus [226]. The computational complexity of such CG-MD simulations is of the order of $O(N\log N)$, where $N$ the number of protein network nodes. However, there is an initial cost associated with the coarse graining procedure due to the eigenvalue problem for constructing the pseudo-inverse of the Hessian matrix and also due to simulated annealing for parameter selection. While this cost is substantial it is relatively small if many simulations are pursued based on this coarse grained model.
Chapter 8

Concluding Remarks

8.1 Summary

In this thesis we have achieved the following goals:

- We investigate the dynamics of a single inextensible elastic filament subject to anisotropic friction in a viscous stagnation-point flow, by employing both a continuum model represented by Langevin-type stochastic partial differential equations (SPDEs) and a Dissipative Particle Dynamics (DPD) method. The kinematics of the filament is recorded and studied with normal modes analysis. The results show that the filament displays an instability induced by tension, which is analogous to Euler buckling of a beam. Symmetry breaking of normal modes dynamics and stretch-coil transitions are observed above the threshold of the buckling instability point. Furthermore, both temporal and spatial noise are amplified resulting from the interaction of thermal fluctuations and nonlinear filament dynamics. Specifically, the spatial noise is amplified with even normal modes being excited due to symmetry breaking, while the temporal noise is amplified with increasing time correlation length and variance.

- We develop a new single-particle dissipative particle dynamics (DPD) model for anisotropic particles and different shapes e.g., prolate spheroids, oblate spheroids, etc. In particular, the conservative and dissipative interactions between anisotropic single DPD particles are formulated using a linear mapping from the isotropic model of spherical particles. The proper mapping operator is constructed between each interacting particle pair at each time step. Correspondingly, the random forces are properly formulated to satisfy the fluctuation-dissipation theorem (FDT). Notably, the model exactly conserves both linear and angular momentum. We demonstrate the proposed models accuracy and efficiency by applying it to ellipsoidal
particles. Specifically, we show that it efficiently captures the static properties of suspensions of colloidal ellipsoids and the isotropic-nematic transition in ellipsoidal suspension are reproduced by increasing the volume fraction or aspect ratio of ellipsoid particles. Remarkably, the hydrodynamics and diffusion of a single colloidal ellipsoid (prolate or oblate with moderate aspect ratios) are accurately captured. The calculated drag force on the ellipsoid and its diffusion coefficients (both translational and rotational) agree quantitatively with the theoretical predictions in the Stokes limit.

- We develop a charged dissipative particle dynamics (cDPD) model for simulating mesoscopic electro-kinetic phenomena governed by the stochastic Poisson-Nernst-Planck and the Navier-Stokes (PNP-NS) equations. Specifically, the transport equations of ionic species are incorporated into the DPD framework by introducing extra degrees of freedom and corresponding evolution equations associated with each DPD particle. Diffusion of ionic species driven by the ionic concentration gradient, electrostatic potential gradient and thermal fluctuations are captured accurately via pairwise fluxes between DPD particles. The electrostatic potential is obtained by solving the Poisson equation on the moving DPD particles iteratively at each time-step. For charged surfaces in bounded systems, an effective boundary treatment methodology is developed for imposing both the correct hydrodynamic and electro-kinetics boundary conditions in cDPD simulations. To validate the proposed cDPD model and the corresponding boundary conditions, we first study the electrostatic structure in the vicinity of a charged solid surface, i.e., we perform cDPD simulations of the electrostatic double layer (EDL), and show that our results are in good agreement with the well-known mean-field theoretical solutions. We also simulate the electrostatic structure and capacity densities between charged parallel plates in salt solutions with different salt concentration. Moreover, we employ the proposed methodology to study the electro-osmotic and electro-osmotic/pressure-driven flow in a micro-channel. In the latter case, we simulate the dilute poly-electrolyte solution drifting by electro-osmotic flow in a micro-channel, hence demonstrating the flexibility and capability of this method in studying complex fluids with electrostatic interactions at the micro- and nano-scales.

- We describe the fluctuations of electrolyte bulk solutions at equilibrium with an emphasis on mesoscale length- and time-scales. We derived explicit formulas for linearized fluctuation hydrodynamics and electro-kinetics equations using perturbation theory. We also performed computer simulations of electrolyte bulk solution using both molecular dynamics (MD) and charged Dissipative Particle Dynamics (cDPD) method. Simulated temporal correlations
due to fluctuating hydrodynamics and electro-kinetics from both MD and cDPD trajectories show good agreement with the linearized theory. This agreement indicates that temporal correlations from electro-kinetics decay much more slowly than those from hydrodynamics. Local ionic concentration fluctuations follow gamma distributions at small length scales and converge to Gaussian distributions in the continuum limit. Spatial correlations of charge density demonstrate finite range and non-trivial structure at nanometer length scales but can be viewed as delta functions in the continuum limit.

- Electrostatic correlation effects near charged planar surfaces immersed in a symmetric electrolyte solution are systematically studied by numerically solving the nonlinear 6-dimensional electrostatic self-consistent (SC) equations. We compare our numerical results with widely used mean-field (MF) theory results, and found that MF theory remains quantitatively accurate only in weakly charged regimes, whereas, in strongly charged regimes, the MF predictions are drastically changed by the electrostatic correlation effects. Hence, a first order like phase-transition is observed corresponding to the counterion condensation phenomenon in strongly charged regimes, we then compute the phase diagram numerically within a wide parameters range. We also investigate the interactions between two likely charged planar surfaces, which repulse each other as MF theory predicts in weakly charged regimes, however, our results show that they attract each other at some distance in strongly charged regimes due to electrostatic correlations.

- We present a new dynamic elastic network model (DENM) that describes the unfolding process of a force-loaded protein. The protein interaction network and its potentials are constructed based on information of its native-state structure obtained from the Protein Data Bank, with network nodes positioned at the $C_{\alpha}$ coordinates of the protein backbone. Specifically, to mimic the unfolding process, i.e., to simulate the process of overcoming local energy barrier on the free energy landscape with force loading, the non-covalent protein network bonds (i.e., hydrogen bonds, salt bridges, hydrophobic contacts, etc.) are broken one-by-one with a certain probability while the strong covalent bonds along the backbone (i.e., peptide bonds, disulfide bonds, etc.) are kept intact. The jumping event from local energy minimums (bonds breaking rate) are chosen according to the famous Karmer’s theory and the Bell model. Moreover, we exploit the self-similar structure of proteins at different scales to design an effective coarse graining procedure for DENM with optimal parameter selection. The robustness of DENM is validated by coarse-grained molecular dynamics (MD) simulation against atomistic MD simulation of force-extension processes of the Fibrinogen and Titin Immunoglobulin proteins.
We observe that the native structure of the proteins determines the total unfolding dynamics (including large deviations) and not just the fluctuations around the native state.

### 8.2 Future Directions

In concluding this thesis, we will now suggest some areas of future research which follow from some of the work presented herein.

- **More applications of the anisotropic DPD model.**
  - Study the self-assembly of nanoparticles in complex materials with specifically-designed interaction potentials.
  - Study the sharp isotropic-nematic transition, by replacing the soft Gaussian excluded-volume repulsion by empirical Gay-Berne and RE-squared potentials. Investigate the phase boundaries.
  - Model more complicated low-symmetric bluff bodies as clusters of isotropic spherical and anisotropic ellipsoidal particles.

- **More theoretical justifications and applications of charged DPD model.**
  - Justifications of cDPD formulations from bottom up Mori-Zwanzig projection.
  - Consider the ion-size and solvent-size effects in charged DPD model, to study the concentrated ionic solution with broad applications in battery simulations. For example, to modeling the sedimentation of ion-battery with both perturbation analysis and modified charged DPD model.
  - Consider the mutual-diffusion between different ionic species in charged DPD model, to study ion-pairing and more complicated phenomena in concentrated ionic solutions.

- **Follow up in Field theory approach.**
  - Derivation of finite ion size modified SC equations with the field theoretic variational approach, with assuming charge on an ion to have a finite spread around its center, instead of point charge as in current model, i.e., A convenient choice is the Gaussian distribution with its Born radius.
  - Re-investigate the ion-condensation and interactions between likely-charged planner surfaces phase diagram with numerically solving the modified SC equations.
– Use alternative directions method to study 2d or even 3d charged systems, i.e., interactions between likely-charged cylinders and spheres.
Proper Orthogonal Decomposition (POD) is a spectral analysis tool often employed for data compression and low-dimensional modeling, which is also known as principal component analysis (PCA), singular value decomposition (SVD). Here, POD decomposes the time-space fiber configuration $\theta(t,s)$ into an expansion of orthogonal temporal and spatial modes, i.e.,

Figure 9.1: POD modes energy as functions of mode number $q$, with $Wi = 100.0$ (red), 10.0 (blue), 1.0 (green).
\[ \theta(t, s) = \sum_{q=1}^{N_{pod}} \phi_q(s)a_q(t) \]  

(9.1)

To compute the space-time POD modes, a temporal auto-correlation covariance matrix \( C \) is constructed from the inner product of \( \theta(\tau^i, s) \) and \( \theta(\tau^j, s) \) as

\[ C_{ij} = \int \theta(\tau^i, s)\theta(\tau^j, s)\,ds, \quad i, j = 1, 2, ..., N_{POD} \]  

(9.2)

The temporal modes \( a_q(t) \) are the eigenvectors of \( C \), and the spatial modes \( \phi_q(s) \) are computed via orthogonality relations, i.e.,

\[ \phi_q(s) = \int a_q(t)\theta(\tau, s)\,d\tau \]  

(9.3)

The eigenvalues \( \lambda_k \) of the autocorrelation matrix \( C \) (with \( \lambda_1 > \lambda_2 > ... > \lambda_{N_{pod}} \)) represent the energy level associated with the POD mode \( q \), as shown in Figure (9.1).

As expected, we observe a typical power-law decay of high-order POD modes in all simulations. For \( Wi \leq 1 \), the power-law decay corresponds to a thermal white-noise energy spectrum indicated by black dashed line (slope = 2.0) in the plots, and a few POD modes are enough to characterize the fiber dynamics. However, the power-law decay becomes slower as we increase \( Wi \), which shows that the fiber dynamics are accompanied by the excitement of high-order deformation modes, and hence more degrees of freedoms are needed to describe such motions. In general, POD and normal modes analysis reveal the same physics as described above.
Figure 9.2: Instantaneous streamlines and velocity vectors showing the disturbance of the stagnation-point flow caused by the bead-spring chain constrained to deform in the plane. (see video)
Chapter 10

Appendix B: Implementation

Details of Stagnation-Point Flow in DPD

Fluid flows simulated by Dissipative Particle Dynamics (DPD) have been successfully demonstrated for several geometries. However, efficient convergence starting from rest is achievable mainly in regular geometries, such as rectilinear channel flow driven by a spatially uniform body force, essentially the gravity force of arbitrary strength applied to each DPD particle. Examples of successful DPD simulations of this kind include: flow in small tubes of a blood suspension of multi-scale model red cells [228], flow past a sphere fixed on the axis of a tube by Chen et al. [229], and flow of a DNA suspension in a micro-channel with rectangular side cavities by Fan et al. [230]. However, in a study of blood flowing through a Y-junction [231], convergence is not always possible. A continuum solution of such flows is achievable with equal ease whether with a body force driver or by specification of normal tractions across the channel section. Generally, a continuum flow is driven by prescription on its boundary of some combination of velocities and tractions; It may also be driven by body forces. Traction on boundaries are a consequence of the divergence theorem, which permits the net force due to stress at interior points to be transformed onto the boundary. The equivalent operation does not exist for particle based methods. Furthermore, for particle methods inflow/outflow specifications for channel flows, so easily carried out with continuum methods, do not converge nearly as well as with body-force drivers. Random fluctuations, a crucial feature of DPD, impel particle motion in all directions. Hence, the hypothesis to be tested here is whether a
body force field, derived by continuum methods in the same domain, can serve to guide the particles in the general direction of the motion defined by the boundaries. In this work the required body force potential is taken as the pressure field of the corresponding Navier-Stokes (N-S) flow governed by,

$$\frac{\partial \mathbf{V}}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{V} - \frac{\mu}{\rho} \nabla^2 \mathbf{V} = -\nabla \left( \frac{P}{\rho} + \chi \right), \quad (10.1)$$

where the viscosity $\mu$ and the density $\rho$, are constants. To be isothermal constants, while the density $\rho$ may be slightly variable due to weak imposition of incompressibility. This corresponds to the typical conditions of DPD flow simulations, although compressibility effects may appear where large pressure gradients exist. The curl of the Navier-Stokes equation (10.1) eliminates the Bernoullian, $1/2 \mathbf{V}^2 + P/\rho + \chi$, and yields the vorticity equation in terms of the velocity field, and its gradients. For interior flows with velocity boundary conditions the velocity field is governed by the vorticity equation, and therefore remains unchanged for any choice of the scalar potential $\chi$ on the right-hand side of equation (10.1). If required, with the velocity field in hand, the scalar potential $P/\rho + \chi$ can be found by integration of equation (10.1). Usually, it is determined as the single variable $P/\rho$, and when $\chi$ is the gravitational potential it is said to be absorbed into the ‘modified’ scalar pressure. In experimental fluid mechanics the fluid pressure is obtained by subtraction of the gravitational potential from the measured modified pressure. It may also be driven by body forces. Traction on boundaries are a consequence of the divergence theorem which permits the net force at a point due to stress to be transformed onto the boundary. The equivalent operation does not exist for particle methods $\chi$, and hence with the same velocity boundary conditions its solution will yield the same the $\mathbf{V}$ field.

A homogeneous Non-Newtonian fluid with extra stress $\mathbf{T}$, given by a constitutive equation expressible in terms of the velocity field, has the equation of motion,

$$\frac{\partial \mathbf{V}}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{V} - \nabla \cdot \mathbf{T} = -\nabla \left( \frac{P}{\rho} + P_{NS}/\rho \right), \quad (10.2)$$

where $P_{NS}$ is the N-S pressure field derived from the solution of equation (10.1), and in equation (10.2) functions as body force. The continuum algorithms for solving Non-Newtonian flows generally proceed by iteration starting from the linearized $N-S$ equation. The Newtonian pressure gradient imposed as a body force is not usually a feature of such algorithms whose primitive variables are $\mathbf{V}, P$. It is displayed in equation (10.2) to emphasize that the unknown $P$ is then the disturbance pressure due the Non-Newtonian character of the fluid. The term ‘complex fluids’ is to be understood here to describe those fluids which, in addition to exhibiting nonlinear extra-stress, become spatially inhomogeneous when subjected to flow. Typically, these are suspensions of
small particles and macromolecules such as those found in bio-fluids, e.g. blood. The development of constitutive equations for such heterogeneous materials is fraught with theoretical and experimental difficulties, and in some circumstances the heterogeneous continuum description becomes invalid [228]. The alternative is the particle description where the suspended bodies are modeled as mesoscopic entities, and for the DPD method employed in this work the solvent is likewise modeled with such particles. However, flow simulations with DPD have convergence limitations, which are usually manifested by failure of the thermostat to maintain temperature uniformity. For complex domains, convergence failure generally appears at lower flow rates than would be expected for the corresponding flows in simple geometries such as straight channels and tubes. The difficulties appear to stem from the thermal fluctuations, a crucial feature of DPD, which drive the particles in random directions. The purpose of this work is to explore the use of body force fields as local drivers to guide the particles towards the direction of the local average motion.

Here this concept is demonstrated in the DPD simulation of flow in an irregular geometry, which consists of four counter-rotating vortices inside a periodic box bounded by streamlines with stagnation points at each corner and edge midpoint. This box is a unit cell of an infinite lattice of counter-rotating, equally-spaced line vortices whose irrotational velocity field satisfies the N-S equation, and its periodicity avoids the need to model real-wall boundaries. Furthermore, since strain rates are determined by the line-vortex strength, the uniform strain rates in the stagnation region are then prescribed, and thus satisfy the design goal of the periodic box.

In a number of papers [232, 233] Leal and co-workers have experimentally realized the classical stagnation flow in the central region of a four-roll mill. Here this apparatus is idealized by four line vortices within a periodic square bounded by streamlines. This potential flow without solid boundaries satisfies the N-S equation for incompressible flow, and from it will be derived the body force needed to drive the DPD simulation of the equivalent flow. Before the complete complex potential is constructed the regions near the vortices and near the stagnation points are reviewed. For a single line vortex and for the stagnation-point flow complex potentials are respectively

$$ W = \phi + i\psi = -\frac{\kappa}{2\pi} \ln(z), \quad W = 1/2\dot{\epsilon} z^2, \quad z = x + iy = re^{i\theta}, \quad (10.3) $$

where $\kappa$ is the vortex strength measured as its circulation, and $\dot{\epsilon}$ the stagnation stretch rate; the real and imaginary parts of $W$ are the scalar velocity potential $\phi$ and the stream function $\psi$. The complex velocity is derived from $dW/dz = U - iV$ so that $d/dz$ corresponds to the vector operator $\nabla$, and also $(e^{i\phi}, ie^{i\theta})$ correspond to the base vectors $(k_r, k_\theta)$ in cylindrical-coordinates. With the overline to indicate the complex conjugate, the body force per unit mass $\nabla \chi$ is determined by Bernoulli ’s equation to be the gradient of $-(q^2)/2$, and is obtained for each case from equations
(10.3), respectively, as

\[
q^2 = \frac{dW}{dz} \frac{d\overline{W}}{dz} = \left(\frac{\kappa}{(2\pi r)}\right)^2, \quad q^2 = \dot{\epsilon} r^2, \tag{10.4}
\]

\[
-\frac{dq^2}{dz} = \nabla \chi = \left(\frac{\kappa}{(2\pi)}\right)^2 (k_r/r^3), \quad \nabla \chi = -\dot{\epsilon} r k_r. \tag{10.5}
\]

Figure 10.1: Lattice of vortices with alternating signs and spacing \(a\). The dashed lines define a typical periodic square of side \(2a\); the vortices labeled with two-digits refer to the construction of the potential, equation (10.14), described in Appendix. Alternating signs (shown) yield the stagnation-point flow, and same signs (not shown) the circulation flow in each periodic square.

Hence, the effective body force per unit mass is radial and repulsive relative to the vortex and radial and attractive relative to the stagnation point. In viscous flow the vortex strength can be characterized by the Reynolds number \(\text{Re} = \kappa \rho / \mu\). The torque per unit length \(L\) imposed by the vortex is \(2\kappa \mu\) so that the Reynolds number is also expressible as \(\text{Re} = L\rho/(2\mu^2)\). The complex potential for four vortices arranged symmetrically in a square defined by streamlines requires the construction of the potential for a square lattice of vortices. The starting point is Milne-Thomson's [234] potential for an infinite row of positive vortices equally-spaced along the real axis,

\[
W_0(z) = -i(\kappa/2\pi)\ln(\sin(\pi z/a)), \tag{10.6}
\]

where \(\kappa\) is the vortex strength, \(a\) is the vortex spacing along \(x\), \(z\) gives the field-point position.
relative to the reference vortex at \(z = 0\). The vortex positions then proceed to the left(-) and right(+) as: \(-na, -2a, -1a, 0, +1a, +2a, \ldots, +na\). Milne-Thomson’s result holds for a linear row at any orientation by taking the vortex spacing \(a\) to be any complex constant \(A\).

In what follows below the reference origin will lie at the center of symmetry of a square, and the following definitions will be needed for the construction of the potential of the lattice of vortices,

\[
2z = 2z_{jk} = z_j + z_k, \quad \pi(z_j - z_k)/A = \pi 2b/A = \pi(n + im), \tag{10.7}
\]

where \(n, m\) are real integers for a square lattice (see Appendix). The reference origin \(z_{jk}\) is the midpoint between any two reference vortices \((j, k)\) separated by \(z_j - z_k = 2b\) along the same row \((m = 0)\), or when \(j\) and \(k\) lie on separate parallel rows \((m \neq 0)\) then \(z_{jk}\) lies between the rows at the midpoint of \(z_j - z_k\). For both cases, the construction of the total potential requires the sums of row potentials referred to the midpoint \(z_{jk}\).

Let \(W_j\) and \(W_k\) be the Milne-Thomson vortex row potential (10.6) with origins at vortices \(j\) and \(k\) respectively, and with the real line spacing \(a\) replaced by a complex spacing \(A\), a vector oriented in any direction. The sum of these potentials \(W_{jk} = W_j + W_k\) introduces sine products in \(z_j\) and \(z_k\) which must be transformed to the midpoint reference origin \(z_{jk}\). This is accomplished by standard identities for products of trigonometric functions [235] as,

\[
\sin(\pi z_j/A) \sin(\pi z_k/A) = \sin(\pi((z_{jk} - b)/A)) \sin(\pi((z_{jk} + b)/A)
\]

Figure 10.2: Periodic square of a lattice of counter-rotating vortices: (left) dimensionless stream function, and (right) pressure contours, unit arrows indicate direction of the pressure gradient field derived from equation (10.14). Arrows point away from vortices and towards stagnation points as suggested by equations (10.5)
The dimensionless potential $(2\pi/\kappa)W_{jk}(z_{jk})$ referred to the origin $z_{jk}$ at midpoint of $z_j - z_k$ is then,

$$W(z) = -i \ln(\sin(\pi z_j/A) \sin(\pi z_k/A)) = -i \ln(\sin(z^*)^2 - \sin(\pi b/A)^2), \quad (10.9)$$

where $z^* = \pi z/A$, and henceforth the subscript of $z_{jk}$ is dropped to indicate that the sum of every pair of vortex rows will be referred to the center of a typical lattice square as shown in figure(10.1).

This is the starting point for all the potentials given below. When $(j, k)$ lie on the same row ($m = 0$) the contributions of each vortex are doubled in equation (10.9); accordingly, to be a term in a sum over all vortices counted once, that $W(z)$ must be weighted by half. The potential (10.9) and its first two derivatives are now written with the condensed notations:

$$Z_s(z^*, m), \quad Z_c(z^*, m) = \sin(z^*)^2 + \sinh(m\pi/2)^2, \quad - \cosh(m\pi/2)^2, \quad (10.10)$$

here the subscripts $s$ and $c$ indicate respectively that the second term is either $\sinh(m\pi/2)$ for $n$ even, or $- \cosh(m\pi/2)$ for $n$ odd. Thus for $n$ even,

$$W_s(z^*, m) = -i \ln(Z_s(z^*, m)), \quad (A/\pi) \frac{dW_s(z^*, m)}{dz} = -i \frac{\sin(2z^*)}{Z_s(m, z^*)},$$

$$\frac{d^2W_s(z^*, m)}{dz^2} = i\{\frac{\sin(2z^*)^2}{Z_s(m, z^*)^2} - \frac{2\cos(2z^*)}{Z_s(m, z^*)}\}, \quad (10.11)$$

and for $n$ odd $W_c$ and its derivatives are obtained from equations (10.11) by replacing $Z_s$ with $Z_c$. The definitions (10.10) are insensitive to the signs of $A$, $n$, and $m$, consequently so are these potentials and their derivatives. For the important case $n$ odd, $m = 0$, they simplify to,

$$W_c(z^*, 0) = -i \ln(\cos(z^*)) \quad (A/\pi) dW_c(z^*, 0)/dz = i \tan(z^*) \quad (A/\pi)^2 d^2W_c(z^*, 0)/dz^2 = i \sec(z^*)^2, \quad (10.12)$$

where the extraneous constant $\ln(-1)$ has been omitted from $W(z)$ which is normalized by $1/2$ to satisfy equal weighting of vortices.

Figure 10.1 depicts the lattice of vortices with alternating signs whose structure consists of periodic squares bounded by streamlines and containing four vortices. The vortex positions define squares of side $a$; the red circle marks the center of a typical vortex square. The periodic squares of side $2a$ have corners, marked with open circles, at the centers of diagonally neighboring squares along each passing through the vortex square centers. The center of each square is a stag-
nation point near which the motion is the stagnation-point flow treated above. When all vortices have one sign a circulating flow is produced in each periodic square. The diagonals of the lattice are vortex rows of entirely one sign with intersecting right and left diagonals of the same sign passing through each vortex. Successive vortices along the diagonals are connected by the vectors:

\[ A_r = a + ia, \quad A_l = -a + ia, \quad A_r A_l = -2a^2, \quad A_r/A_l = -i = -A_l/A_r, \]  

(10.13)

where the subscripts \( r \) and \( l \), respectively, indicate right and left vectors connecting diagonally adjacent vortices. Thus, the notations \( z^*_r \), \( z^*_l \) imply from its definition (10.10) that \( z^* \) is to be constructed with \( A_r \) or \( A_l \), respectively. The complete potential for the lattice of vortices is constructed as a weighted sum of the row potentials (10.11) for the diagonals passing through the labeled vortices in figure (10.1). The weights are chosen so that each vortex is counted once only. The details of this construction are given in Appendix, and from the terms given there the total dimensional potential follows by induction to be,

\[
W = -i\kappa/(2\pi) \left\{ \ln \{\cos(z^*_r) \prod_{k=1}^{\infty} W_s(z^*_l, (2k-1)) W_c(z^*_r, 2k)\} \right.
\]

\[
\left. \mp i\ln \{\cos(z^*_l) \prod_{k=1}^{\infty} W_s(z^*_r, (2k-1)) W_c(z^*_l, 2k)\} \right\} ,
\]

(10.14)

where \( \mp \) indicates the stagnation-point flow and the circulation flow respectively. Shear flow is realized by elimination of the negative vortices following \( \mp \). The potential is then obtained from
equations (10.6) to (10.14) by omission of all terms following the $\mp$ signs from equation (10.14). The stagnation-point flow and the shear flow can be superposed to yield mixed stretching-shear flows in arbitrary proportions in the vicinity of the origin $z = 0$. Likewise, the derivatives $dW/dz$ and $d^2W/dz^2$ can be represented as infinite sums. The infinite products in equation (10.14) converge rapidly so that only four or five terms are sufficient for an accurate representation of $W$ in the periodic square whose center is $z = 0$.

Figure 10.2(left) displays streamlines derived from the imaginary part of the complex potential (10.14). In potential flow the Bernoullian, $H = 1/2\rho q^2 + P + \rho \chi$, is constant, and hence $-1/2q^2$ is effectively the pressure depicted in Figure 10.2(right), which is derived from the derivatives of $W$, as in the limiting cases discussed above (see equation (10.5)). The arrows on the pressure contours are unit vectors indicating the direction of the driving body force. Due to the singularities at the vortex positions, contours plot as an almost continuous band, and hence for clarity are omitted in their vicinity. This emphasizes their circular form as expected from the well-known single vortex results summarized in equation (10.5). The elementary potentials and their derivatives (10.3), (10.5) suggest that a contour plot of $P/\rho$ should show concentric circles in the vicinities of the vortices and the stagnation point with arrows pointing radially outward from the vortices and inward towards the stagnation points.

In the stagnation region near $z = 0$, the potential $W$ approaches the elementary stagnation-point potential 1/2$\dot{\epsilon}z^2$. As $z \to 0$ the expansion of expression (10.15) yields,

$$ W = \left(\kappa/(2\pi)\right)(\pi z/a)^2 \{1/2 + \sinh(\pi/2)^{-2} + \cosh(\pi)^{-2} + \sinh(3\pi/2)^{-2} + \cosh(2\pi)^{-2} + ... \} = 0.6966... (\kappa/(2\pi)(\pi z/a)^2) . \quad (10.15) $$

The very small contribution of the last term suggests that contributions from image vortices outside the periodic square are well-captured by this truncation of $W$, equation (10.14) at $W_4$ (see Appendix). From equation (10.3), the stagnation-point strain rate, $\dot{\epsilon} = 2.1884\kappa/a^2$, is specified by the choice of the vortex strength and spacing.

Standard DPD particles occupy a periodic box. On the $XY$ planes of the domain, the body force field is imposed, derived from the gradient of the analytical pressure field for a lattice of vortices shown in Figure (10.2). Since the analytical potential flow and the periodic boundary conditions satisfy the $N - S$ equation this system of DPD particles is expected to respond macroscopically as a Newtonian fluid. Hence, verification of the driving force hypothesis implies that the DPD results should agree closely with the analytical fields. In Figures (10.2) the near-vortex regions were left blank since there the $V, P$ fields are singular with circular contours. Figure 2.3 shows the stream-
lines calculated from the DPD velocity fields to be very similar to their analytical counterparts, except in the near-vortex regions. Likewise the number density, indicated by the background color of Figure 2.3, shows it to be the prescribed value of 3.0 (orange) over most of the domain. In equation (10.5) the pressure gradient, and hence the DPD driving force, is \( O(r^{-3}) \) directed away from the vortices. This implies that the near-vortex regions will suffer depletion as indicated by the background colors of the plot. However, when the density gradient is normal to the circular streamlines \( \nabla \cdot (\rho \mathbf{V}) = \rho \nabla \cdot \mathbf{V} = 0 \), and hence the single-vortex velocity field continues to satisfy the equation of motion for a compressible viscous fluid with constant viscosity. For the single-vortex flow of an isentropic compressible gas Milne-Thomson ([234], p382) argues that within the circle of unit Mach number the motion is rigid rotation. However, in isothermal gas flow this argument does not hold; none-the-less in Figure 2.3 significant depletion begins with the approach to the circle of unit isothermal-Mach number surrounding the vortices.

The anti-symmetry of the streamlines of Figure 10.2 implies that the \( x,y \)-velocity components \( U_V \) along the \( x,y \)-axes satisfy \( U(x,0) = -V(0,y) \). Likewise, the strain-rate difference \( D_{xx} - D_{yy} \) and the Newtonian stress difference \( T_{xx} - T_{yy} \) are the same along those axes. Figure 10.3 compares the average of \( U(x,0) \) and \( -V(0,y) \) calculated by DPD (points) with their analytical counterparts (continuous curves) for several Reynolds numbers, \( \kappa \rho/\mu \). The average DPD velocity is differentiated numerically along the axes to yield the strain rate which is also plotted against its analytical values. Also shown (see Figure 9.5) is the stress difference \( T_{xx} - T_{yy} \) calculated with the virial (Kirkwood) formula from the DPD simulation compared to the analytical stress calculated as the analytical strain rate times the DPD viscosity measured in a separate shear flow simulation [236]. The plotted stresses collapse onto a single curve because \( \kappa \) and \( \mu \) were chosen to satisfy \( \kappa \mu = \text{constant} \) to verify that the DPD model satisfies the analytical scaling. The agreement between the DPD results and the analytical solution of the \( N - S \) system is clearly good, and excellent in the vicinity of the axes.
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