Chapter 2

Computational Methodology

2.1 Dissipative particle dynamics simulaion method

For the simulation in the following chapters, we employ a technique that bridges the gap between atomistic and macroscopic scales, referred to as the *dissipative particle dynamics* (DPD) method. Firstly, this method was introduced by Hoogerbrugge and Koelman as a new simulation technique for studying hydrodynamic behavior [54]. It is an advanced and flexible simulation method for studying soft matter and complex fluids. It is known to be an advantageous technique for simulating systems over larger length and time scales compared to convensional MD simulations. Polymeric fluids and gels with linear dimensions up to 100 nm and timescales up to tens of microseconds are modeled well by this simulation technique [55,56]. A key feature of the DPD method is its highly coarse-grained approach, where a single bead represents a cluster of molecules or particles, and interactions occur via a soft-core potential [54–57].

In the recent past, DPD has been used to analyze a variety of complex systems, including polymer blends [58,59], biological systems [60–63], fluids confined by geometric constraints [64,65], fluids subjected to external trigger such as pH variations and photo-

reactions [59,66–69], as well as the pattern formation, and self-repairing mechanisms of gels or networks [67,70,71].

In this methodology, every bead experiences three pairwise additive forces within the cutoff distance r_c. Newton's equations of motion are integrated to determine its motion [55–57]:

$$\frac{d\vec{p}_i}{dt} = \sum_{j \neq i} \left[\vec{F}_{ij}^{C} + \vec{F}_{ij}^{D} + \vec{F}_{ij}^{R} \right] = \vec{f}_i(t). \tag{2.1}$$

Here, for the i^{th} bead with mass m_i, the total force and momentum vectors are denoted by $\vec{f}_i(t)$ and $\vec{p}_i = m_i \vec{v}_i$, respectively. Using the modified *velocity-Verlet* integration algorithm [56], we update the velocity vector $\vec{v}_i = d\vec{r}_i/dt$ and the position vector $\vec{r}_i$ at each time step. We model $\vec{F}_{ij}^{C}$, the conservative force, as a soft repulsive interaction, [56,57]

$$\vec{F}_{ij}^{C} = \begin{cases} a_{ij} \left(1 - r_{ij}/r_c\right) \hat{r}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c. \end{cases} \tag{2.2}$$

Here, a_{ij} represents the maximum repulsive interaction between i and j beads, which are separated by a distance $r_{ij} = |\vec{r}_{ij}|$, where $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$, and $\hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$ is the unit vector along the force direction. In Eq. (2.1), the dissipative force is given by

$$\vec{F}_{ij}^{D} = -\gamma \omega_D(r_{ij}) (\hat{r}_{ij} \cdot \vec{v}_{ij}) \hat{r}_{ij}, \tag{2.3}$$

where $\vec{v}_{ij} = \vec{v}_j - \vec{v}_i$, $\omega_D(r_{ij})$ is a distance-dependent weight function that vanishes at r_c, and γ represents the dissipation strength or friction coefficient.

The random force, $\vec{F}_{ij}^{R}$, is expressed in Eq. (2.1) as

$$\vec{F}_{ij}^{R} = \sigma \omega_R(r_{ij}) \xi_{ij} \hat{r}_{ij}. \tag{2.4}$$

Here, $\omega_R(r_{ij})$ is the weight function. The noise strength is denoted by σ. The parameter, ξ_{ij}, follows a Gaussian distribution with zero-mean and unit variance [56,57]:

$$\begin{aligned} \langle \xi_{ij}(t) \rangle &= 0, \\ \langle \xi_{ij}(t) \xi_{kl}(t') \rangle &= (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t'). \end{aligned} \tag{2.5}$$

The weight functions are typically related to modeling the correct canonical thermodynamic state at temperature T, given by [56,57],

$$\omega_D(r_{ij}) = \omega_R^2(r_{ij}) = \begin{cases} (1 - r_{ij}/r_c)^2, & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c. \end{cases} \tag{2.6}$$

The fluctuation-dissipation relation describes the coupling between the dissipative and random forces [56],

$$\sigma^2 = 2\gamma k_B T, \tag{2.7}$$

where, k_B is the Boltzmann constant. The $\vec{F}_{ij}^D$ and $\vec{F}_{ij}^R$ forces act along the line connecting the centers of the beads. The linear momentum conservation is guaranteed by the symmetry relations, $\vec{F}_{ij} = -\vec{F}_{ji}$ and $\xi_{ij} = \xi_{ji}$ [56,57].

Earlier studies primarily used the Euler-type algorithm to update the position and velocity within an arbitrary time step Δt. During this short time interval, neither the position nor the velocity of the particles changes significantly. [54,57]. Over the decades, a modified version known as the *modified velocity-Verlet* algorithm has been employed [72],

$$r_i(t + \Delta t) = r_i(t) + \Delta t v_i(t) + \frac{1}{2}(\Delta t)^2 f_i(t), \tag{2.8}$$

$$\tilde{v}_i(t + \Delta t) = v_i(t) + \lambda \Delta t f_i(t), \tag{2.9}$$

$$f_i(t + \Delta t) = f_i(r(t + \Delta t), \tilde{v}(t + \Delta t)), \tag{2.10}$$

$$v_i(t + \Delta t) = v_i(t) + \frac{1}{2}\Delta t(f_i(t) + f_i(t + \Delta t)). \tag{2.11}$$

The mass of each DPD bead is set to $m_i = 1$, so the force acting on a particle equals its acceleration.

It is highly desirable to have a simulation where the equilibrium distribution corresponds to the Boltzmann distribution. By incorporating drag and noise, the system can map a suitable canonical ensemble (NVT). DPD is a well-known simulation method that preserves the *hydrodynamics* of the system. Therefore, for studying fluid systems with soft potential, DPD has an intrinsic advantage over other methods such as classical MD, dynamic density functional theory (DFT), or MC methods [56].

2.1.1 Modeling parameters

It is crucial to account for optimization parameters. Initially, parameteres like mass m, length r_c, time τ, and energy k_BT scales need to be defined. These are typically expressed in dimensionless reduced units: $m = 1$, $r_c = 1$, $k_BT = 1$, and $\tau = \sqrt{mr_c^2/k_BT}$.

For controlling the temperature, commonly reported values for noise strength and drag force strength are $\sigma = 3$ and $\lambda = 0.5$ from Eq. 2.9. With these optimized values, a favorable agreement with the time step is typically achieved in the $\Delta t \approx 0.02 - 0.04$ range, facilitating effective temperature regulation across the entire system [56,73]. In the modified velocity-Verlet Eq. 2.8, the term $\frac{1}{2}(\Delta t)^2 f_i(t)$ is crucial for maintaining the system's stable temperature. Without considering this term, the simulation will fail to control the temperature, similar to the Euler algorithm. Empirically adjusting the values of λ and σ can enable a more significant time step without compromising temperature control. Moreover, we can take a large time step upto $\Delta t \simeq 0.06$ for $\lambda = 0.65$ [56]. However, we have taken time step $\Delta t = 0.02\tau$ in our simulation work.

Characteristic length scale changes as one or more particles/molecules cluster into a single DPD bead. Considering a DPD bead comprises N_m water molecules, with r_c

representing the cube's side length. The cube volume r_c^3 contains ρN_m water particles/molecules, where ρ denotes the density of DPD beads. Consequently, the physical volume of the cube containing water molecules will be $30\rho N_m$Å^3. Thus, the following equation describes the characteristic length scale, r_c, in the DPD simulation method [74,75] as

$$r_c = 3.107(\rho N_m)^{1/3}\text{Å}. \tag{2.12}$$

To further estimate the density of the system, the following equation gives a good approximation for the pressure:

$$p = \rho k_B T + \alpha a \rho^2, \tag{2.13}$$

where ρ, T, and k_B are the density, the temperature, and the Boltzmann constant, respectively. The two constants α and a are related to the water compressibility, $\kappa^{-1} = 1 + 2\alpha a\rho/k_B T$. For compressibility of water $\kappa^{-1} = 16$ at $T = 298K$, the variation $(p - \rho k_B T)$ vs. ρ has a flat line along the ρ axis for the $\rho \geq 2$ limit [56]. For a fluid like water, density $\rho = 3$ is a reasonable choice, given the condition that the repulsive interaction parameter needs to be adjusted based on the chosen density values. The following section maps the repulsive interaction parameter using the Flory-Huggins parameter.

In our simulation, we model a cluster of ten water molecules ($N_m = 10$) as a single DPD bead [56,76,77]. Each water molecule has a mass 18 Da and occupies a volume of 30 Å^3, leading to a total volume of 300 Å^3 for the cluster [24,74,78]. The mass of a DPD bead is $m = 180$ Da [67,68,78]. For $\rho = 3r_c^{-3}$ and applying Eq. 2.12, we determine the cutoff radius $r_c = 0.97$ nm. The characteristic time, τ can be calculated using the expression $\sqrt{mr_c^2/k_B T}$. At $T = 293.15$ K, the estimated value of τ is 8.33 ps.

2.1.2 Estimating a_{ij} using Flory-Huggins parameter

The repulsive interaction parameter (a_{ij}) in Eq. (2.2) is key for the soft potential. Various types of beads can be distinguished by varying the a_{ij} parameter between any two beads. Groot et al. [56] established a relationship between the repulsive interaction and Flory-Huggins parameters (χ),

$$a_{ij} = a_{ii} + b\chi_{ij}, \tag{2.14}$$

where, a_{ii} represents the repulsive interaction between same type of beads, b is the constant with values 3.5 for the density $\rho = 3$. The parameter χ_{ij} is temperature dependent and can be determined through the following relationship [56,75],

$$\chi_{ij} = \frac{V_{ij}}{RT}(\delta_i - \delta_j)^2. \tag{2.15}$$

Here, R is the gas constant, T is the absolute temperature ($298K$), V_{ij} represents the average molar volume of beads i and j; δ_i and δ_j are the solubility parameters for beads i and j.

2.2 Modeling the polymeric chain

For modeling the polymeric chains, we use the well-known *bead-spring model*, in which the beads are connected by spring. Various bead-spring models have been utilized in polymer rheology, such as the worm-like chain (WLC) model, finitely extendable nonlinear elastic (FENE) model, and harmonic spring model.

We use the harmonic spring model to connect the beads in a polymeric chain. In this model, beads are connected via harmonic bond potential. The potential energy

associated with a bond is given by

$$E_b(r) = \frac{\kappa_b}{2}(r - r_0)^2, \tag{2.16}$$

where, κ_b represents the bond strength, and $r_0 = 0.5$ is the equilibrium bond length [67,68,79,80]. The polymer chain stiffness is modeled using the angle potential

$$E_a(\theta) = \frac{\kappa_a}{2}(\cos\theta - \cos\theta_0)^2. \tag{2.17}$$

Here, κ_a represents the strength of the angle potential, and θ is the angle between two successive bonds along the chain. We set the equilibrium angle to $\theta_0 = 180°$ [81,82]. Higher values of κ_b and κ_b correspond to an increased polymer chain stiffness [83].

To prevent non-physical bond-crossing, which may occur due to the softcore interactions in our simulation. We employ the modified segmental repulsive potential (mSRP) [84]. This approach involves introducing pseudo beads at the midpoint of each bond, which interact through a soft repulsive force, as defined by the following equation

$$\vec{F}_{ij}^{mS} = \kappa_{mS}(1 - r_{ij}/r_c^{mS})\hat{r}_{ij}, \text{ for } r_{ij} < r_c^{mS}, \tag{2.18}$$

Here, κ_{mS} represents the force constant, and r_c^{mS} is the cutoff distance for the mSRP interaction. We set the coefficient $\kappa_{mS} = 100$ and cutoff distance $r_c^{mS} = 0.8$ [84].

2.3 Summary and conclusions

In this chapter, we describe the DPD simulation method. This method is designed for simulating mesoscopic systems and addresses the limitations of conventional MD. It is a highly coarse-grained model with a characteristic length scale on the order of nanometers and a characteristic time scale on the order of picoseconds. The time step,

$\Delta t = 0.02\tau$, is considerably more significant than the typical time step used in molecular dynamics. Modeling the polymeric chain employs a harmonic spring potential based on a bead-spring model. We use a modified SRP to prevent bond crossing within the chain. For simulations, we utilize the LAMMPS package [85] platform.