

Effect of transverse dissipative particle dynamics on dynamic properties of nanometer-thick liquid films on solid surfaces

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To ascertain the effect of transverse dissipative particle dynamics (DPD), which includes lateral dissipative forces in addition to the central ones in the standard DPD, on dynamics of systems involving interfaces, we compare dynamic properties derived from coarse-grained (CG) molecular dynamics simulations with the standard and transverse DPD for nanometer-thick liquid films on solid surfaces. The dynamic properties include relaxation times of the film thickness distribution and molecular rotational motion, and transport properties associated with molecular translational motion. Our results show that these dynamic properties are tuneable by changing friction coefficients in the transverse DPD, whereas this is not the case in the standard DPD. We also confirm that the transverse DPD applied to liquid–solid CG bead pairs can tune dynamic properties of nanometer-thick liquid films on solid surfaces, though it is less effective than when applied to liquid–liquid CG bead pairs. Moreover, we reveal that the dissipative forces are isotropic in transverse DPD, whereas the liquid–solid dissipative forces are highly anisotropic and nearly along the direction perpendicular to solid surfaces in standard DPD. This suggests that the transverse liquid–solid DPD might be crucial for modelling the in-plane energy dissipation at liquid–solid interfaces.

Keywords: coarse-grained molecular dynamics; transverse dissipative particle dynamics; dynamic property; liquid–solid interface; thin film

1. Introduction

As an effective tool to probe spatial and temporal scales at the atomic level, which are generally difficult to access by experiments, molecular dynamics (MD) simulations have been widely used in a variety of fields, ranging from life and materials sciences to engineering [1,2]. However, in spite of the tremendous advances in high performance computing, it is still computationally expensive to study systems over extended length and time scales using conventional all-atom (AA) MD simulations. One approach to circumvent this limitation is coarse graining which can reduce the computational cost

by mapping several atoms into one coarse-grained (CG) bead. The procedure for developing CG models includes the determination of a mapping scheme and determination of force fields which dictate interaction potentials between CG beads. While many general-purpose force fields for AA models, such as the universal force field, OPLS (optimized potentials for liquid simulations) [3], COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) [4,5], and AMBER (assisted model building with energy refinement) [6], etc., have been developed, the well-known generic CG force field that is commonly used is the MARTINI force field [7], which is for biomolecular simulations and basically employs the mapping scheme of four heavy atoms to one CG bead. One major reason for the lack of generic CG force fields is that, to achieve the best balance between computational accuracy and efficiency, CG models should be developed in accordance with the scales of the essential physics of target systems or phenomena.

CG models are usually constructed bottom-up by fitting reference physical quantities obtained from AA simulations. Commonly used methods include the iterative Boltzmann inversion (IBI) [8,9], inverse Monte Carlo [10,11], and force matching [12]. As references to be fitted, the former two approaches employ structural properties such as intermolecular radial distribution functions and intramolecular bond and angle distribution functions, and the latter approach employs potentials of mean force. Although these CG methods are able to reproduce static properties of AA systems, dynamic properties such as diffusion coefficients are difficult to retain, mostly because of the loss of friction effects between the eliminated degrees of freedom during coarse-graining [13]. One solution to address this issue is to compensate the lost friction in CG models by coupling CG beads with dissipative particle dynamics (DPD) [14,15]. In addition to conservative forces which are negative position derivatives of CG potentials

and govern both static and dynamic properties, dissipative (i.e., damping and random) forces, which only affect dynamic properties, are introduced in DPD. Hence DPD allows for the independent parameterization of dynamic properties while keeping static properties intact. Particularly, as an extension of the standard DPD, which contains only central forces, the transverse DPD, which also contains dissipative forces in the direction perpendicular to the central forces, has been proposed [14]. It was demonstrated that for bulk liquid systems, the transverse DPD can efficiently tune dynamic properties such as viscosity and diffusion coefficients. However, its effect on systems involving interfaces is yet to be ascertained.

In this study, aiming to clarify the effect of the transverse DPD on dynamic properties of systems with interfaces, we perform CG MD simulations for nanometer-thick liquid films on solid surfaces with both the standard and transverse DPD. The dynamic properties assessed include relaxation times of the film thickness distribution and rotational motion of individual liquid molecules, and transport properties associated with translational motion of individual liquid molecules in the in-plane and perpendicular directions. In particular, we developed an in-house package for LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) to implement the transverse DPD [16,17]. This allows us to separately analyse dissipative forces from the liquid and solid phases, thereby providing thorough insights into the effect of the DPD applied to liquid–liquid and liquid–solid bead pairs.

The paper is organized as follows. In Section 2, we describe the basic formulas for the transverse DPD, details of our simulation model and procedure, and techniques for deriving the various dynamic properties from our simulations. The derived dynamic properties are presented in Section 3, followed by a discussion on the comparison between the standard and transverse DPD and between the liquid–liquid and liquid–

solid transverse DPD in Section 4. Finally, the conclusions are summarized in Section 5.

2. Simulation method and details

2.1. Transverse dissipative particle dynamics

Same as the standard DPD, the transverse DPD dictates motion of particles with

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i^C + \mathbf{F}_i^D + \mathbf{F}_i^R \quad (1)$$

where m_i and \mathbf{r}_i are the mass and position of the i th particle, and \mathbf{F}_i^C , \mathbf{F}_i^D , and \mathbf{F}_i^R are the conservative, damping, and random forces acting on the i th particle, respectively. The conservative force is calculated as a negative position derivative of interaction potentials. The damping and random forces are calculated as sums of pairwise forces:

$$\mathbf{F}_i^D = \sum_j \mathbf{f}_{ij}^D \quad (2)$$

$$\mathbf{F}_i^R = \sum_j \mathbf{f}_{ij}^R \quad (3)$$

In contrast to the standard DPD, the pairwise damping and random forces between the i th and j th particles are given by [14,18–20]

$$\mathbf{f}_{ij}^D = -\zeta^{\parallel} w_D^{\parallel}(r_{ij})(\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})\mathbf{e}_{ij} - \zeta^{\perp} w_D^{\perp}(r_{ij})[\mathbf{v}_{ij} - (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})\mathbf{e}_{ij}] \quad (4)$$

$$\mathbf{f}_{ij}^R = \sigma^{\parallel} w_R^{\parallel}(r_{ij})(\mathbf{e}_{ij} \cdot \boldsymbol{\theta}_{ij})\mathbf{e}_{ij} + \sigma^{\perp} w_R^{\perp}(r_{ij})[\boldsymbol{\theta}_{ij} - (\mathbf{e}_{ij} \cdot \boldsymbol{\theta}_{ij})\mathbf{e}_{ij}] \quad (5)$$

respectively. Here $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the i th and j th particles, $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is the unit vector pointing from the j th to i th particle, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity of the i th to j th particle. $\boldsymbol{\theta}_{ij}$ is a three-dimensional time-

variant vector whose elements are independent random numbers following the standard normal distribution, and it satisfies the following condition [14]

$$\langle \boldsymbol{\theta}_{ij}(t) \otimes \boldsymbol{\theta}_{kl}(t') \rangle = \mathbf{I}(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\delta(t - t') \quad (6)$$

where \mathbf{I} is a 3×3 unit matrix and \otimes represents the dyad product. ζ and σ are coefficients determining the magnitude of the damping and random forces, $w_D(r_{ij})$ and $w_R(r_{ij})$ are weight functions for the damping and random forces, and superscripts \parallel and \perp indicate directions parallel and perpendicular to \mathbf{e}_{ij} , respectively. Hereafter ζ is referred to as the friction coefficient. Note that the second term in Equations (4) and (5) is newly introduced to the transverse DPD, and setting $\zeta^\perp = \sigma^\perp = 0$ results in the standard DPD.

According to the fluctuation-dissipation theorem, the following relationships must be satisfied for both parallel and perpendicular components to ensure the canonical ensemble [21]

$$\sigma^2 = 2k_B T \zeta \quad (7)$$

$$[w_R(r_{ij})]^2 = w_D(r_{ij}) \quad (8)$$

where k_B is the Boltzmann constant and T is temperature. Consequently, undetermined parameters in the transverse DPD are the friction coefficients and weight functions in the parallel and perpendicular directions: ζ^\parallel , ζ^\perp , $w_D^\parallel(r_{ij})$, and $w_D^\perp(r_{ij})$.

2.2. Simulation model

The liquid used in this study was perfluoropolyether (PFPE), which has long been used to lubricate magnetic disk surfaces in hard disk drives [22]. The particular PFPE had a chemical structure of $\text{CF}_3\text{--O--}[\text{CF}_2\text{CF}_2\text{O}]_{21}\text{--}[\text{CF}_2\text{O}]_{21}\text{--CF}_3$ and a molecular weight of

3976.56 g/mol. As a simplified model of the carbon overcoats on the magnetic disk surfaces, a diamond crystal plate with (111) surface orientation was used as the solid surface. The liquid molecules and solid surface were described with CG models developed in our previous study [23,24]. Briefly, the former was modelled as a chain of 27 spherical liquid beads connected linearly using 26 springs and the latter was modelled using solid beads stacked in a simple tetragonal lattice with lattice constants of $a = b = 0.331$ nm and $c = 0.205$ nm. Interaction potentials included the bond-length potential for two consecutive liquid beads connected by a spring, bond-angle potential for three consecutive liquid beads connected by two springs, nonbonded liquid–liquid interaction potential for two of the other liquid beads, and nonbonded liquid–solid interaction potential for a liquid and solid bead. Note that, because the influence of thermal vibration of solid beads on the dynamics of liquid molecules can be equivalently described by damping and random forces between solid and liquid beads, we froze all the solid beads in our simulations for simplicity and thus solid–solid interaction potentials were not incorporated in the CG models. All the CG potentials were determined with the structure-based iterative Boltzmann method to match reference distribution functions derived from all-atom simulations. Figure 1 shows the nonbonded liquid–liquid and liquid–solid potentials. For both the potentials, the cutoff distance was set to 1.65 nm, which is 2.5 times the equilibrium distance of the nonbonded liquid–liquid potential.

In our simulations, damping and random forces were applied to both liquid–liquid and liquid–solid bead pairs. To clarify their individual effects, we employed four different combinations of DPD types, as listed in Table 1. These combinations are simply referred to as SS, ST, TS, and TT, where the first and second letters indicate the DPD types for the liquid–liquid and liquid–solid bead pairs, and S and T represent the

standard and transverse DPD, respectively. Until otherwise stated, for simplicity, we set the friction coefficients ζ for liquid–liquid and liquid–solid bead pairs to be identical, i.e., $\zeta_{ll} = \zeta_{ls} = \zeta$, and set $\zeta^{\parallel} = \zeta$ and $\zeta^{\perp} = 0$ for the standard DPD and $\zeta^{\parallel} = \zeta^{\perp} = \zeta$ for the transverse DPD. To investigate effects of the magnitude of the dissipative forces, we varied the value of ζ to be $20\zeta^*$, $60\zeta^*$, $200\zeta^*$, $600\zeta^*$, and $2000\zeta^*$, where $\zeta^* = 1$ (kcal/mol/Å)·(Å/fs)^{−1} = 0.69477 fN·(m/s)^{−1}. For the weight functions we used the standard choice:

$$w_D^{\parallel}(r_{ij}) = w_D^{\perp}(r_{ij}) = w_D(r_{ij}) = \left\{ \max \left[0, 1 - \frac{r}{r^{\text{DPD}}} \right] \right\}^2 \quad (9)$$

where r^{DPD} is the cutoff distance for the dissipative forces. Izvekov and Rice derived pairwise conservative and dissipative forces in a bottom-up manner and revealed that the dissipative force is likely to decay to zero more rapidly than the conservative force [25]. Hence in this study we set r^{DPD} to a distance where the conservative attraction forces started to decay, i.e., $r_{ll}^{\text{DPD}} = 0.81$ nm for liquid–liquid beads and $r_{ls}^{\text{DPD}} = 0.54$ nm for liquid–solid beads, as indicated in Figure 1. To discuss the effect of liquid–solid dissipative forces, $r_{ls}^{\text{DPD}} = r_{ll}^{\text{DPD}} = 0.81$ nm was also used for comparison, as will be described in Section 4.

2.3. Simulation procedure

We used a simulation box with the size of $x \times y \times z = 66.2$ nm \times 33.1 nm \times 21.23 nm and applied periodic boundary conditions to the x and y directions. A solid plate consisting of $200 \times 100 \times 6$ solid beads was set at the bottom of the simulation box, and then 1000 liquid molecules were inserted into the simulation box one by one with a time interval of 10 ps. Each liquid molecule was first randomly allocated within the region of 10.025 nm $\leq z \leq 12.025$ nm and then deposited onto the solid surface with an initial

velocity of -1 pm/fs in the z direction. During the deposition process, a Langevin thermostat was applied in the z direction to liquid beads within the region of $1.025 \text{ nm} \leq z \leq 3.025 \text{ nm}$. This thermostat reduced the velocity of the liquid beads in the z direction and thus effectively prevented liquid molecules from bumping outside of the simulation box upon collision with the solid surface. The liquid film formed upon deposition of all the liquid molecules on the solid surface was relaxed for 100 ns and the final result was used as the initial configuration for subsequent production simulations. Two initial configurations were prepared using the SS and TT DPD with $\zeta = 20\zeta^*$, respectively. The thickness of the deposited films on the solid surface was 1.57 nm. Figure 2 shows the snapshot of the initial configuration prepared with the SS DPD.

Production simulations were carried out under 40 conditions: two initial configurations, four combinations of DPD types (see Table 1), and five different values of friction coefficient ζ . Under most conditions, production simulations were run for 50 ns. However, for $\zeta = 600\zeta^*$ and $2000\zeta^*$ in the TS and TT DPD, simulations were run for 100 and 200 ns due to the relatively long relaxation time of the liquid molecules. During the production simulations, trajectories of liquid beads were recorded at a time interval of 0.1 ns. Sums of squared pairwise damping and random forces exerted on liquid bead, i , from other liquid and solid beads, i.e., $\sum_j \left[(f_{ij_v}^D)^2 + (f_{ij_v}^R)^2 \right]$ where j belongs to other liquid or solid beads and $v = x, y$, and z , were also recorded at a time interval of 50 fs. Hereafter these forces are simply referred to as liquid–liquid and liquid–solid squared dissipative forces, respectively.

All the simulations were conducted using LAMMPS with an in-house extended package to implement the transverse DPD. Temperature was set to 300 K. Timestep was set to 5 fs for nonbonded conservative forces and 1.25 fs for the other forces (i.e., bonded conservative, damping, and random forces) using the rRESPA (reversible

reference system propagator algorithms) multi-timescale integrator [26]. We found that reducing the timestep for the damping and random forces to a quarter of that for nonbonded conservative forces was essential to properly control the temperature when the friction coefficient was larger than $600\zeta^*$.

2.4. Calculation of dynamic properties

The thickness distribution and viscosity of PFPE films are critical factors affecting the recording performance and long-term reliability of hard disk drives. Hence, from the simulation results, we calculated relaxation times of the film thickness distribution and molecular rotational motion, and transport properties associated with molecular translational motion in the in-plane and perpendicular directions. The rotational relaxation time and transport properties are related to viscosity. Details of the calculation are described below.

2.4.1. Relaxation time of film thickness distribution

First, to obtain thickness distribution of the liquid films, we uniformly divided the simulation box into 100×50 grids in the x and y directions. The coordinates of the center of each grid were $x_i = i\Delta x$ and $y_j = j\Delta y$, where $\Delta x = \Delta y = 0.662$ nm, $i = 1, 2, \dots, 100$, and $j = 1, 2, \dots, 50$. For each snapshot outputted at time t , we computed the z coordinate of the envelope of the uppermost bead at the positions of (x_i, y_j) as

$$z_{\max}(t, x_i, y_j) = z_{\text{bu}}(t) + \sqrt{R_{\text{lb}}^2 - [x_{\text{bu}}(t) - x_i]^2 - [y_{\text{bu}}(t) - y_j]^2} \quad (10)$$

where x_{bu} , y_{bu} , and z_{bu} are the coordinates of the center of mass of the uppermost bead within the (i, j) grid and $R_{\text{lb}} = 0.33$ nm is the radius of liquid beads. The film thickness distribution was then computed as

$$h(t, x_i, y_j) = z_{\max}(t, x_i, y_j) - z_0 - \sigma_{\text{ls}} + R_{\text{lb}} \quad (11)$$

where $z_0 = 1.025$ nm is the z coordinate of the uppermost layer of the solid beads and $\sigma_{\text{ls}} = 0.49$ nm is the equilibrium distance of the nonbonded liquid–solid potential.

We then calculated the time correlation function (TCF) of the film thickness distribution, which is defined as

$$\text{TCF}_{\text{film}}(t) = \frac{\langle \iint [h(0, x_i, y_j) - \bar{h}(0)][h(t, x_i, y_j) - \bar{h}(t)] di dj \rangle}{\langle \iint [h(0, x_i, y_j) - \bar{h}(0)]^2 di dj \rangle} \quad (12)$$

where $\bar{h}(t)$ is the mean film thickness at time t . To reduce statistical uncertainty, we averaged TCFs calculated from seven sets of data for each production simulation, and then further averaged over two production simulations, which used the identical combination of DPD type and ζ value but different initial configurations. The average is indicated by angle brackets in Equation (12). Note that the average over two production simulations was also made for the analyses described in the following two subsections. The seven data sets started from the time point of two- to eight-tenths of the production simulations and had a time span equal to one-fifth of the production simulations. As described above, the DPD types and friction coefficients in the production simulations were different from those in the simulations for generating initial configurations. To eliminate the influence of such change, the data in the initial one-tenth period of the production simulations were not used for calculation of the TCFs.

Finally, relaxation times of the film thickness distributions, τ_{film} , were determined by fitting the following function to the TCFs

$$\text{TCF}_{\text{film}}(t) = \alpha \exp\left(-\frac{t}{\tau_{\text{film}}}\right) \quad (13)$$

where α is also a fitting parameter.

2.4.2. Relaxation time of molecular rotational motion

To characterize the dynamics of rotational motion of the liquid molecules, we defined a unit end-to-end vector \mathbf{u}_{ee} pointing from one end bead to the other of the liquid molecules and calculated the TCF of the vector $\langle \mathbf{u}_{ee}(t) \cdot \mathbf{u}_{ee}(0) \rangle$. Trajectory data in the last three-fifth period of the production simulations were used for the calculation. By fitting the TCF with the function given below, relaxation times of molecular rotational motion, τ_{rot} , were derived.

$$\text{TCF}_{rot}(t) = \exp\left(-\frac{t}{\tau_{rot}}\right) \quad (14)$$

2.4.3. Transport properties associated with molecular translational motion

Transport properties associated with translational motion of the liquid molecules were separately analysed in the directions parallel and perpendicular to the solid surface. For the parallel motion, self-diffusion coefficients, D , were calculated from mean squared in-plane displacement (MSD) of centers of mass of the liquid molecule, as given below:

$$D = \lim_{t \rightarrow \infty} \frac{\text{MSD}(t)}{4t} \quad (15)$$

$$\text{MSD}(t) = \langle [x(t) - x(0)]^2 + [y(t) - y(0)]^2 \rangle \quad (16)$$

where x and y are the x and y positions of the centers of mass, respectively. A factor of 4, rather than 6, is used in Equation (15) because the MSD is two-dimensional. To reduce statistical uncertainties, each production simulation average was made for MSDs calculated from three sets of data, which started from the time point of one-, two-, and three-fifths of the production simulations, and had a time span equal to two-fifths of the

production simulations. In this study, the in-plane self-diffusion coefficient was calculated from the slope of a straight line fitted to the latter half of the averaged MSD with respect to time.

The translational motion of the liquid molecules in the direction perpendicular to the solid surface cannot be effectively characterized by the diffusion coefficient because the motion is limited by the film thickness to 1.57 nm. Therefore, we counted the number of liquid beads staying within the liquid–solid interfacial region as a function of time, $N_{\text{inter}}(t)$. Specifically, $N_{\text{inter}}(t)$ is the number of liquid beads whose z coordinates are always less than a threshold value till time t . It is evident, from the definition, that N_{inter} is a monotonically decreasing function of time t . Rapidly decreasing N_{inter} means that liquid beads move into and out of the interfacial region frequently, i.e., rapid translational motion in the direction perpendicular to the solid surface. The threshold value was set to $z_0 + \sigma_{\text{ls}} + R_{\text{lb}} = 1.845$ nm. To reduce statistical uncertainties, we averaged five results of $N_{\text{inter}}(t)$, for which counting started at two- to six-tenths of the production simulations and had a time span of four-tenths of the production simulations. We used the half-life, which is defined as the time required for N_{inter} to decrease to half of its initial value, to quantitatively characterize the activity of the molecular translational motion in the perpendicular direction.

3. Results

It should be noted that the dynamic properties discussed in this section were derived from the simulations with $r_{\text{ll}}^{\text{DPD}} = 0.81$ nm, $r_{\text{ls}}^{\text{DPD}} = 0.54$ nm, and $\zeta_{\text{ll}} = \zeta_{\text{ls}}$, and those derived from simulation with $r_{\text{ll}}^{\text{DPD}} = r_{\text{ls}}^{\text{DPD}} = 0.81$ nm and $\zeta_{\text{ll}} \neq \zeta_{\text{ls}}$, which are plotted with a symbol of black star in Figures 5–9, will be discussed in Section 4.

3.1. Relaxation time of film thickness distribution

Figure 3 exemplifies the derived film thickness distributions at the start and end of two production simulations. The initial configurations at the start of the two production simulations were the same and prepared with the SS DPD, and the two production simulations were carried out with the SS DPD and friction coefficient of $20\zeta^*$ for 50 ns and with the TT DPD and friction coefficient of $2000\zeta^*$ for 200 ns, respectively. As can be seen in this figure, the distributions of film thickness are not uniform. The mean film thickness and standard deviation for all the simulations in this study are in the ranges of 1.569–1.572 and 0.336–0.341 nm, respectively. These similar results confirm that DPD types and friction coefficients do not affect the equilibrium thickness distribution, or in other words the static structural property, of thin liquid films on solid surfaces. It should be noted that the mean film thickness is 2.4 times the diameter of the liquid beads, indicating that the liquid films comprise two to three layers of liquid beads in the thickness direction.

Figure 4 shows the calculated TCFs of film thickness distributions. Though only those for the TT DPD and $\zeta = 200\zeta^*$, $600\zeta^*$, and $2000\zeta^*$ are shown for clarity, we confirmed that all the calculated TCFs exhibit common features of a sharp decrease to approximately 0.3 within 0.1 ns and a following tail. We suggest that the initial rapid decay of the TCFs is largely attributed to the individual motion of liquid beads rather than the collective motion of liquid films. Hence, to exclude the influence of the initial decay, only data at $t \geq 0.1$ ns were fitted by Equation (13) to derive relaxation times of film thickness distributions.

Figure 5 shows the relaxation time of film thickness distribution as a function of friction coefficient for different combinations of DPD types. Within the investigated range, increase in relaxation time is observed when applying the transverse DPD to

liquid–liquid beads (TS and TT) with $\zeta = 600\zeta^*$ and $2000\zeta^*$, whereas no obvious change is observed when applying the standard DPD to liquid–liquid beads (SS and ST). There are also no evident differences between the results of the SS and ST DPD and between the results of TS and TT DPD, indicating the weak influence of the type of the liquid–solid DPD. These results demonstrate that the relaxation of the thickness distribution of nanometer-thick films on solid surfaces can be tuned by the transverse DPD rather than the standard DPD, and the liquid–liquid DPD exhibits a dominant effect over the liquid–solid DPD under the condition $r_{ls}^{\text{DPD}} = 0.54 \text{ nm}$, $r_{ll}^{\text{DPD}} = 0.81 \text{ nm}$, and $\zeta_{ls} = \zeta_{ll}$.

3.2. Relaxation time of molecular rotational motion

Figure 6 shows the relaxation time of molecular rotational motion as a function of friction coefficient for different combinations of DPD types. With increasing friction coefficient, the relaxation time increases up to roughly five times when applying the transverse DPD to liquid–liquid beads (TS and TT), whereas the increase in the relaxation time is only approximately 40 % when applying the standard DPD to liquid–liquid beads (SS and ST). Although the TT DPD results in slightly shorter relaxation times than the TS DPD at the largest friction coefficient, nearly identical relaxation times are obtained with the ST and SS DPD. These results lead to a conclusion similar to the one reached in Section 3.1; the relaxation of rotational motion of liquid molecules in nanometer-thick films can be tuned by the transverse DPD rather than the standard DPD, and the tuning effectiveness of liquid–liquid DPD is larger than that of liquid–solid DPD under the condition $r_{ls}^{\text{DPD}} = 0.54 \text{ nm}$, $r_{ll}^{\text{DPD}} = 0.81 \text{ nm}$, and $\zeta_{ls} = \zeta_{ll}$.

3.3. Transport properties associated with molecular translational motion

Figure 7 shows that the in-plane self-diffusion coefficient decreases with increasing

friction coefficient for all the combinations of DPD types. The standard DPD decreases the in-plane self-diffusion coefficient by up to approximately 20 %. This is again weaker than the effect of the transverse DPD, which decreases the in-plane self-diffusion coefficient by up to approximately 80 %. Upon comparison between SS and ST and between TS and TT, we infer that, same as for the rotational motion, the change in the in-plane translational motion of the liquid molecules is mostly induced by the liquid–liquid DPD rather than the liquid–solid DPD.

Figure 8 shows the half-life for liquid beads staying within the liquid–solid interfacial region as a function of friction coefficient. With increasing friction coefficient, the half-life increases by up to approximately three times for the TS and TT DPD, whereas it increases by only 18 % for the SS and ST DPD. The half-lives for the SS and TS DPD are identical to those for the ST and TT DPD within the resolution of 0.1 ns, respectively. These results demonstrate that the transverse DPD is useful for tuning the activity of perpendicular molecular motion, and translational motion of the liquid beads in the direction perpendicular to the solid surface is dominated by the liquid–liquid DPD rather than the liquid–solid DPD, even though the liquid film is composed of only 2 or 3 layers of liquid beads.

4. Discussion

To understand the reasons for the results described in Section 3, we averaged the recorded liquid–liquid and liquid–solid squared dissipative forces, i.e., $\sum_j \left[(f_{ij-v}^D)^2 + (f_{ij-v}^R)^2 \right]$ with j belonging to liquid or solid beads and $v = x, y$, or z , over liquid beads and simulation time. Figure 9 shows the in-plane component (i.e., average of the x and y components) and perpendicular component (i.e., z component) of the averaged squared dissipative forces as a function of friction coefficient. Notice that only data for the SS

and TT DPD are shown in the figure. This is because the liquid–liquid and liquid–solid squared dissipative forces in the ST DPD are identical to the liquid–liquid ones in the SS DPD and the liquid–solid ones in the TT DPD, respectively, and the liquid–liquid and liquid–solid squared dissipative forces in the TS DPD are identical to the liquid–liquid ones in the TT DPD and the liquid–solid ones in the SS DPD, respectively. Except for the data indicated by the black star, which will be described later in this section, for all friction coefficients and DPD types the squared dissipative forces between liquid beads are one to two orders larger than those between liquid and solid beads. This reveals that, under the condition $r_{ls}^{\text{DPD}} = 0.54 \text{ nm}$, $r_{ll}^{\text{DPD}} = 0.81 \text{ nm}$, and $\zeta_{ls} = \zeta_{ll}$, the dissipative forces acting on liquid beads are largely from liquid beads rather than from solid beads, which might explain why all the results presented in Section 3 showed a dominant effect from the liquid–liquid DPD rather than from the liquid–solid DPD. Furthermore, the total squared dissipative forces, i.e., sum of the liquid–liquid and liquid–solid squared dissipative forces, in the transverse DPD are approximately three times larger than those in the standard DPD. This is because the latter exerts only in one direction and the former in two additional orthogonal (i.e., a total of three) directions. Considering the factor of three difference in dissipative forces, it seems surprising that dynamical properties of nanometer-thick films on solid surfaces are tunable by the transverse DPD but not by the standard DPD. However, this conclusion is reasonable as it has also been reported for bulk liquid systems [14].

Let us focus our discussion on the standard DPD. The in-plane liquid–liquid squared dissipative forces (see the upper red circles in Figure 9(a)) are roughly 40 % larger than the perpendicular ones (see the upper red circles in Figure 9(b)), whereas the in-plane liquid–solid squared dissipative forces (see the lower red circles in Figure 9(a)) are one order smaller than the perpendicular ones (see the lower red circles in Figure

9(b)). As is evident from Equations (4) and (5), the magnitudes of the in-plane and perpendicular squared dissipative forces in the standard DPD are determined by the direction of \mathbf{e}_{ij} (the vector connecting the mass centers of beads i and j). Therefore, the slightly larger in-plane liquid–liquid squared dissipative forces as compared with the perpendicular ones demonstrate that \mathbf{e}_{ij} for liquid–liquid beads is slightly toward the in-plane direction. This is because a liquid bead has more interacting liquid beads in the in-plane direction than in the perpendicular direction for thin liquid films. In contrast, \mathbf{e}_{ij} for liquid–solid beads is highly anisotropic and nearly along the perpendicular direction, which is manifested by the considerably larger perpendicular liquid–solid squared dissipative forces as compared with the in-plane ones. The strong anisotropy is induced by two factors. One is solid beads interacting with a liquid bead exist only in the lower half space, and the other is the short cutoff distance for the liquid–solid dissipative forces $r_{ls}^{\text{DPD}} = 0.54$ nm. As the equilibrium liquid–solid distance is $\sigma_{ls} = 0.49$ nm, we can calculate that, for most liquid–solid beads, the angle of \mathbf{e}_{ij} with respect to the perpendicular direction, θ , is smaller than $\cos^{-1}(\sigma_{ls}/r_{ls}^{\text{DPD}}) = 24.9^\circ$. From the results that perpendicular liquid–solid dissipative forces are one order larger than the in-plane ones, i.e., $\cos^2 \theta / \sin^2 \theta = 10$, we can also estimate that θ is approximately 17.5° .

Focusing our discussion on the transverse DPD, in contrast to the standard DPD, the in-plane and perpendicular components are equal for both liquid–liquid (see upper black crosses in Figure 9) and liquid–solid squared dissipative forces (see lower black crosses in Figure 9). Again, as is evident from Equations (4) and (5), the magnitudes of the in-plane and perpendicular squared dissipative forces in the transverse DPD with $\zeta^{\parallel} = \zeta^{\perp}$ are determined by the directions of \mathbf{v}_{ij} (the relative velocity between beads i and j) and $\boldsymbol{\theta}_{ij}$ (a random three dimensional vector). As $\boldsymbol{\theta}_{ij}$ is isotropic, the equal in-

plane and perpendicular squared dissipative forces demonstrate that \mathbf{v}_{ij} for both liquid–liquid and liquid–solid beads are isotropic.

It is clear from the above discussion that, for systems with anisotropic structures, dissipative forces are anisotropic in the standard DPD but can still be isotropic in the transverse DPD. This means that the transverse DPD can dictate the dissipation of kinetic energy in all directions, whereas this is not the case for the standard DPD. For instance, for nanometer-thick liquid films on solid surfaces, the standard DPD cannot dictate the in-plane dissipation between liquid and solid beads because the liquid–solid dissipative force is nearly along the perpendicular direction, but the transverse DPD can. This suggests that the transverse liquid–solid DPD might be crucial for modelling the in-plane energy dissipation at liquid–solid interfaces.

As described above, the ineffectiveness of liquid–solid DPD is probably due to the small magnitude of the liquid–solid dissipative forces in our simulations. To clarify this point, we increased liquid–solid dissipative forces by increasing the cutoff distance to $r_{ls}^{\text{DPD}} = r_{ll}^{\text{DPD}} = 0.81$ nm and setting the liquid–solid and liquid–liquid friction coefficients to $\zeta_{ls} = 2000\zeta^*$ and $\zeta_{ll} = 20\zeta^*$. Note that we set ζ_{ls} larger than ζ_{ll} to allow for a clear distinction of the influence of liquid–solid dissipative forces. Using these parameters and applying the transverse DPD to both liquid–liquid and liquid–solid beads (i.e., the TT DPD), we carried out an additional simulation. The liquid–solid squared dissipative force is plotted with a symbol of a black star in Figure 9. It is three orders larger than the liquid–solid squared dissipative force in the previous TT DPD simulation with $r_{ls}^{\text{DPD}} = 0.54$ nm, $r_{ll}^{\text{DPD}} = 0.81$ nm, and $\zeta_{ls} = \zeta_{ll} = 20\zeta^*$ (see the lower left black cross in Figure 9). As $r_{ll}^{\text{DPD}} = 0.81$ nm and $\zeta_{ll} = 20\zeta^*$ were used in the additional simulation, the liquid–liquid squared dissipative force is identical to that indicated by the upper left black cross in Figure 9. Hence, we know that, in the

additional simulation, the liquid–solid squared dissipative force is approximately 30 times larger than the liquid–liquid one. The total squared dissipative force (sum of the liquid–liquid and liquid–solid squared dissipative forces) in the additional simulation is comparable to that in the previous TT DPD simulation with $r_{ls}^{\text{DPD}} = 0.54$ nm, $r_{ll}^{\text{DPD}} = 0.81$ nm, and $\zeta_{ls} = \zeta_{ll} = 600\zeta^*$ (see the upper and lower second black crosses from the right in Figure 9), though in the previous simulation the liquid–solid squared dissipative force is approximately 60 times smaller than the liquid–liquid one.

The same analyses as described in Section 2.4 were conducted for the additional simulation and the results are plotted with the symbol of a black star in Figures 5–8. They are close to the results obtained in the previous TT DPD simulation with $r_{ls}^{\text{DPD}} = 0.54$ nm, $r_{ll}^{\text{DPD}} = 0.81$ nm, and $\zeta_{ls} = \zeta_{ll} = 600\zeta^*$ (see the second black cross from the right in Figures 5–8). This is consistent with the above-described fact that the total squared dissipative forces in the additional and previous simulations are comparable. We thus conclude that the liquid–solid transverse DPD can also tune dynamic properties of nanometer-thick liquid films on solid surfaces. However, the tuning effectiveness of the liquid–solid transverse DPD is lower than that of the liquid–liquid one if identical friction coefficients are used. This is because liquid–solid dissipative forces act only on liquid beads close to the solid surface whereas liquid–liquid dissipative forces act on all the liquid beads. Nevertheless, the liquid–solid transverse DPD is still essential, because it, unlike the liquid–liquid one, tunes only the dynamic properties of liquid films on solid surfaces while leaving the dynamic properties of bulk liquid intact.

5. Conclusion

To clarify the effect of the transverse DPD on dynamic properties of systems involving interfaces, we conducted CG MD simulations for nanometer-thick liquid films on solid

surfaces using both the standard and transverse DPD. From the simulation results, we calculated 1) relaxation time of the film thickness distribution, 2) relaxation time of molecular rotational motion, 3) self-diffusion coefficient in the direction parallel to the solid surface, and 4) activity of molecular translational motion in the thickness direction. Our results demonstrate that the transverse DPD can effectively tune dynamics of nanometer-thick liquid films on solid surfaces whereas the standard DPD has almost no such effect, which is consistent with the previously reported results for bulk liquid systems.

We also investigated effects of the transverse DPD applied to liquid–liquid and liquid–solid bead pairs. Our results reveal that the liquid–solid transverse DPD can also tune dynamic properties of nanometer-thick liquid films, though it is less effective than the liquid–liquid one. Nevertheless, the liquid–solid transverse DPD is essential as it tunes only the dynamic properties of liquid films on solid surfaces while leaving the dynamic properties of bulk liquid intact. Moreover, we found that, for anisotropic systems such as nanometer-thick liquid films on solid surfaces, dissipative forces are isotropic in the transverse DPD, whereas in the standard DPD the liquid–solid dissipative forces are highly anisotropic and nearly along the direction perpendicular to solid surfaces. This suggests that the liquid–solid transverse DPD might be crucial for modelling the in-plane energy dissipation at liquid–solid interfaces, which is important in applications such as nano-lubrication, nanoimprint lithography, and nanofluidic devices.

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Table 1. Notation for combinations of DPD types used for liquid–liquid and liquid–solid bead pairs.

Figure 1. Nonbonded potentials with a cutoff distance of 1.65 nm for (a) liquid–liquid and (b) liquid–solid bead pairs. Cutoff distances for the liquid–liquid and liquid–solid dissipative forces are also indicated for comparison.

Figure 2. Snapshot of the initial configuration prepared with the SS DPD with $\zeta = 20\zeta^*$. The grey and sky blue represent the solid and liquid beads, respectively.

Figure 3. Examples of thickness distribution of the liquid films. (a) Initial film thickness distribution derived from the SS DPD simulation with $\zeta = 20\zeta^*$. (b) Film thickness distribution at the end of 50 ns production simulation with the SS DPD and $\zeta = 20\zeta^*$. (c) Film thickness distribution at the end of 200 ns production simulation with the TT DPD and $\zeta = 2000\zeta^*$.

Figure 4. Examples of time correlation functions of film thickness distributions. These were derived from the TT DPD simulations with friction coefficients of $\zeta = 200\zeta^*$, $600\zeta^*$, or $2000\zeta^*$. Black dotted lines are fits of data at $t \geq 0.1$ ns to Equation (13).

Figure 5. Relaxation time of film thickness distribution as a function of friction coefficient for different combinations of DPD types. Results indicated by symbols except the black star were obtained from simulations with $r_{ls}^{\text{DPD}} = 0.54$ nm, $r_{ll}^{\text{DPD}} = 0.81$ nm, and $\zeta_{ls} = \zeta_{ll} = \zeta$, whereas the result indicated by black star was obtained from an additional TT DPD simulation with $r_{ls}^{\text{DPD}} = r_{ll}^{\text{DPD}} = 0.81$ nm and $\zeta_{ls} = 2000\zeta^*$ and $\zeta_{ll} = 20\zeta^*$.

Figure 6. Relaxation time of molecular rotational motion as a function of friction coefficient for different combinations of DPD types. Symbols mean the same as in Figure 5.

Figure 7. In-plane self-diffusion coefficient as a function of friction coefficient for different combinations of DPD types. Symbols mean the same as in Figure 5.

Figure 8. Half time for liquid beads staying within the liquid–solid interfacial region as a function of friction coefficient for different combinations of DPD types. Symbols mean the same as in Figure 5.

Figure 9. (a) In-plane and (b) perpendicular components of squared liquid–liquid and liquid–solid dissipative forces as a function of friction coefficient. Symbols mean the same as in Figure 5.