Invariance of experimental observables with respect to coarse-graining in standard and many-body dissipative particle dynamics

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Dissipative particle dynamics (DPD) is now a well-established mesoscale simulation method. However, there have been long-standing ambiguities regarding the dependence of its (purely repulsive) force field parameter on temperature as well as the variation of the resulting experimental observables, such as diffusivity or surface tension, with coarse-graining (CG) degree. Here we revisit the role of the CG degree in standard DPD simulations, derive a scaling of the input variables that renders the system properties invariant with respect to CG degree, and illustrate the versatility of the method by computing the surface tensions of binary solvent mixtures. We then extend this procedure to many-body dissipative particle dynamics (MDPD) and thus demonstrate that this newer method, which has not been widely applied so far, is capable of simulating real mixtures and other complex fluids of practical interest.

I. INTRODUCTION

Coarse-grained molecular dynamics (MD) contains, in addition to the usual force field- or thermostat-related parameters associated with atomistic MD, another parameter: coarse-graining (CG) degree, which provides the freedom to trade off between simulation speed and spatial or temporal resolution. As CG degree is a theoretical construct without experimental substance, the physical properties of a simulated system must be the same, or at least as similar as possible, at different scales, i.e., over a range of CG degrees.

Materials simulations are usually performed using reduced units in order to avoid extremely small or large numbers and prevent the arithmetic underflow or overflow. Some CG simulation methods, such as dissipative particle dynamics (DPD) widely used for soft matter, work in units where the length scale is defined from the reduced density and the CG degree, both of which one is free to choose.1 As a result, the conversion from real to reduced units while preserving the physical properties has been rather ambiguous, and the comparison of same physical settings simulated at different CG degrees nearly impossible. The purpose of the present paper is to address this challenge through a consistent scaling approach.

The standard version of DPD has been successfully applied to a wide range of soft matter systems in the past two decades.2 Besides, a many-body dissipative particle dynamics (MDPD) has been proposed by adding a density-dependent term into the force field.3–5 This version is thus capable of simulating non-ideal fluids and free surfaces, and hence covering a much wider range of systems of practical interest.6

Unfortunately, no general protocol for deriving the MDPD interaction parameters for real materials has been proposed so far. In case of standard DPD, the sole parameter a is obtained by matching the compressibility to an equation of state (EOS) of a pure liquid, and cross-interaction parameters for mixtures are based on some mean-field approximation, such as Flory-Huggins theory. However, in case of MDPD, the choice has so far been ad hoc.7–9

Furthermore, there has been much discussion about how the DPD interaction parameter should scale with the coarse-graining (CG) degree. Groot & Rabone10 originally suggested a linear dependence, but this was refuted independently by Maiti & McGrother11 and Füchslin et al.12 Maiti & McGrother also proposed linear scaling for the χ-parameter with the aim of reproducing the experimental surface tensions. However, we have found inconsistencies in their reasoning. In case of MDPD, to our knowledge there have been no predictions of the surface tension for real mixtures and consequently no discussion of the scaling.

The aim of this paper is to present a general protocol to determine the interaction parameters as a function of not only material properties, such as compressibility or surface tension, but also the coarse-graining degree and temperature. To achieve this, we first need to discuss the choice and role of the reduced units. We revisit and restate the derivation presented by Füchslin et al., and correct the temperature-dependence of the interaction parameter originally proposed by Groot & Warren. More importantly, we explain the derivation and the reasoning behind the scaling of the Flory-Huggins χ-parameter, a key variable determining the mixing properties of soft matter. Consequently, demonstrate the improved predictive accuracy of these methods across a range of CG degrees.

The paper is structured as follows. In Section II, we revisit Füchslin et al.’s arguments for the scaling in DPD
and the derivation of the interaction parameters as a function of temperature. In Section III, we present a method to achieve the scale-invariance of experimental observables. Section IV extends the parametrisation protocol to MDPD. Finally, in Section IV C, we verify that MDPD is capable of predicting the surface tension of binary solvent mixtures across a wide range of CG degrees.

II. SUMMARY OF REDUCED UNITS AND PARAMETERISATION IN DPD

Defining a set of reduced units $r_c = 1, m_0 = 1, k_B T = 1$, the DPD force field is linear:

$$F^c(r) = \begin{cases} a(1-r) \hat{r}, & r \leq 1, \\ 0, & r > 1, \end{cases}$$

(1)

In the simulation, the conservative force is complemented by a Langevin-type thermostat providing dissipative and random force:

$$F^D(r) = -\gamma w(r)^2 (\hat{v} \cdot \hat{r}),$$

(2)

$$F^R(r) = \frac{\sqrt{2\gamma k_B T}}{\sqrt{\Delta t}} r \theta,$$

(3)

where:

$$w(r) = \begin{cases} 1 - r, & r \leq 1, \\ 0, & r > 1 \end{cases}$$

(4)

is the weight factor, $\gamma$ the friction parameter, $v = v_i - v_j$ a relative particle velocity, $\theta$ a Gaussian random number with zero mean and unit variance, and $\Delta t$ a simulation step, i.e. $\theta \sqrt{\Delta t}$ is a Wiener process.

From this point, we denote all variables in reduced units by a diacritical tilde, following the convention used by Füchslin et al. The conversion is, for example, $\tilde{r} = r/r_c$, $\tilde{m} = m/m_c$, since all the masses are assumed to be same or very similar, and $k_B T = k_B T/k_B T_c$, where $k_B T_c$ is the energy scale based on the chosen temperature.

In case of a single-component DPD fluid, this force field is sufficiently simple that its EOS can be easily reverse-engineered, as Groot & Warren (GW) did:\(^1\)

$$\tilde{p} = \tilde{p} + \tilde{a} \tilde{\rho}^2,$$

(5)

where $\tilde{p}$ is number density, and $\tilde{a}$ a fitting constant, which was shown to be approximately 0.1 for $\tilde{p} > 3$. To derive $\tilde{a}$, these authors matched the EOS to the isothermal compressibility $\kappa$. From definition,

$$\kappa^{-1} = \rho \left( \frac{\partial p}{\partial \rho} \right)_T,$$

(6)

and, in reduced units,

$$\kappa^{-1} = \tilde{p} \left( \frac{\partial \tilde{p}}{\partial \tilde{\rho}} \right)_{\tilde{T}},$$

(7)

Considering water with compressibility $\kappa \approx 4.5 \times 10^{-10} \text{ Pa}^{-1}$, which can be non-dimensionalised to $\kappa_{\text{mol}} = 1/(\kappa n k_B T) \approx 16$, where $T$ is the absolute temperature and $n$ is the number density, and making the choice that one DPD particle (bead) contains one molecule, the interaction parameter $\tilde{a}$ is then:

$$\tilde{a} = \frac{\kappa_{\text{mol}} - 1}{2\tilde{\rho}} = 25 \kappa_{\text{B}} T.$$

(8)

Groot & Rabone (GR) showed that the parameter $\tilde{a}$ should scale linearly with the number of molecules in a bead, i.e. the coarse-graining degree $N_m$: $\tilde{a}(N_m) = N_m\tilde{a}(1)$.

However, this argument was refuted by Füchslin et al., who showed that, in real units, the scaling is a power law: $a(N_m) = N_m^{2/3}a(1)$. More importantly, in reduced units the interaction parameter does not scale: $\tilde{a}(N_m) = 25$. This assumes that the length scale and interaction cutoff $r_c$ is defined as Groot & Rabone suggested:

$$r_c = (\tilde{p}N_mV_0)^{1/3},$$

(9)

where $V_0$ is the volume of a single water molecule.

A. Temperature dependence

Here, we show that the temperature scaling of GW needs to be reconsidered. Before that, we note that the are two ways to define the reduced units: either $k_B T$ is always held at 1, in which case the EOS is reduced to

$$\tilde{p} = \tilde{p} + \tilde{a} \tilde{\rho}^2,$$

(10)

as was already pointed by Maiti.\(^1\)\(^\dagger\)\(^\dagger\) A more practical approach is to decide a base temperature $T_e$, e.g. 300 K, and from it define the energy scale $k_B T_e = 1.0$. This enables varying the temperature in the simulation, as GW did, and the EOS is

$$\tilde{p} = \tilde{p}k_{\text{B}} T + \tilde{a} \tilde{\rho}^2,$$

(11)

where $k_{\text{B}} T = k_B T/k_B T_c$. In real units, the EOS looks the same: $p = \rho k_B T + \alpha a \rho^2$.

We can now obtain an unambiguous value of the interaction parameters in real units:

$$\kappa^{-1} = \rho \left( \frac{\partial p}{\partial \rho} \right)_T = \rho k_B T + 2\alpha a \rho^2,$$

(12)

from which it follows that

$$a = \frac{\kappa^{-1} - \rho k_B T}{2\alpha \rho^2}.$$

(13)

Consider here a DPD fluid where one bead corresponds to one molecule, so $N_m = 1$. Using dimensional analysis, the conversion to reduced units is as follows:

$$p = \tilde{p} \frac{k_B T_e}{r_c^2}, \quad a = \tilde{a} \frac{k_B T_e}{r_c^2}, \quad \alpha = \tilde{\alpha} r_c^4, \quad \rho = \tilde{\rho} \frac{1}{r_c^3}$$

(14)
To non-dimensionalise the compressibility we cannot use the same approach as GW, who took the molecular density \( n = 1/V_0 \) instead of the DPD density \( \rho \). These are only equal to each other in the special case \( N_m = 1 \).

To better illustrate this point and also reveal the strength of the dimensional analysis, we note that the inverse compressibility has the same dimensions as pressure, so:

\[
\tilde{\kappa}^{-1} = \kappa^{-1} \frac{r_c^3}{k_B T_c} = \kappa^{-1} \frac{\rho V_0}{k_B T_c}.
\]  

(15)

On the other hand,

\[
\kappa_{\text{nd}}^{-1} = \kappa^{-1} \frac{1}{nk_BT_c} = \kappa^{-1} \frac{V_0}{k_BT_c}.
\]  

(16)

By rearranging these equations we see that \( \tilde{\kappa}^{-1} = \tilde{\rho}\kappa_{\text{nd}}^{-1} \).

Non-dimensionalising eq. (13) by inserting eq. (14), we obtain the following expression for the interaction parameter in reduced units:

\[
\tilde{\alpha} = \frac{\tilde{\kappa}^{-1} - \tilde{\rho}k_BT}{2\tilde{\alpha}^2 \tilde{\rho}^2},
\]  

(17)

and, inserting \( \tilde{\kappa}^{-1} = \tilde{\rho}\kappa_{\text{nd}}^{-1} \):

\[
\tilde{\alpha} = \frac{\kappa_{\text{nd}}^{-1} - k_BT}{2\tilde{\rho}},
\]  

(18)

which, after setting \( k_BT = 1 \) and \( \kappa_{\text{nd}}^{-1} = 16 \), turns into the form due to GW: \( \tilde{\alpha} = 15/(2\tilde{\alpha}) = 75/\tilde{\rho} \). This proves that our derivation based on dimensional analysis is a generalised version of the approach first used by GW.

We now see clearly that \( \tilde{\alpha} \) decreases linearly with temperature, as opposed to the linear rise derived by GW. For a bead containing one water molecule at DPD density \( \tilde{\rho} = 3 \), the interaction parameter as a function of temperature is \( \tilde{\alpha} = (16 - k_BT)/0.6 \).

It must be noted that the temperature dependence is very weak and, for most practical purposes, can be neglected. For example, at 373 K, which is probably the highest temperature at which one would want to simulate liquid water, \( k_BT \approx 1.25 \), and \( \tilde{\alpha} \) changes to \( \approx 24.6 \), which is only a 2% difference from \( \tilde{\alpha} = 25 \) at 300 K. However, this temperature dependence becomes more relevant if one aims to explore different materials at extreme temperatures.

### III. SCALING WITH COARSE-GRAINING DEGREE

Having understood the temperature dependence of the DPD potential, we now turn to the scaling with respect to the coarse-graining degree \( N_m \), which is defined as the number of molecules in one bead. As mentioned above, Füchslin et al. have proposed that the interaction parameter scales with \( N_m^{2/3} \) in real units and remains scale-invariant in reduced units.\(^{12}\) We reproduce this derivation with simple arguments of dimensionality. Thus we will be able to intuitively track the scaling of separate variables, which would otherwise get complicated due to the fact that the length scale \( r_c \) depends on \( N_m \).

As a first step, we convert the density from reduced to real units. Knowing that the density of unscaled, \( N_m = 1 \) liquid is \( \rho(1) = 1/V_0 = n \), it follows that

\[
\rho(N_m) = \frac{\tilde{\rho}(N_m)}{\rho} = \frac{\tilde{\rho}(1)}{\rho} = \frac{n}{N_m},
\]  

(19)

where \( r_c \) is a function of \( N_m \) as well. We also note that the reduced density is set regardless of the CG degree, so \( \tilde{\rho}(N_m) = \tilde{\rho}(1) \). Knowing the relation between real and reduced variables, we can now figure out the EOS of a coarse-grained liquid:

\[
p = \frac{\rho}{N_m} k_B T + \alpha a \rho^2 \frac{N_m}{N^2_m}.
\]  

(20)

For \( N_m = 1 \), this simply reduces to the known form \( p = \rho k_B T + \alpha a \rho^2 \). For a general \( N_m \), we denote all the variables with a prime: \( p' = \rho' k_B T' + \alpha' a \rho'^2 \), where \( \rho' = \rho/N_m \). Now we need to decide which quantity is scale-invariant. Like Füchslin et al., we choose pressure, which is an experimental observable, so \( p = p' \). In principle, other variables can be thus chosen. Starting from \( r_c(N_m) = (\tilde{\rho}(N_m)V_0)^{1/3} \sim N_m^{1/3} \), we can derive how the quantities of interest change with the CG degree:

\[
\rho'(N_m) \sim N_m^{-1},
\]

(21)

\[
k_B T'(N_m) \sim N_m,
\]

(22)

\[
\alpha'(N_m) \sim N_m^{4/3},
\]

(23)

\[
a'(N_m) = a N_m N_m^{-1/3} \sim N_m^{2/3}.
\]

(24)

It might seem surprising that to keep the ideal gas term of the EOS scale-invariant, the energy \( k_BT \) should depend on the CG degree. To keep the temperature scale-invariant, this implies that the Boltzmann constant \( k_B \) must scale linearly with \( N_m \). This is correct, since the dimension of the Boltzmann constant is J/K, and energy was from the very beginning decided to scale linearly, whereas temperature was kept constant.

Importantly, and as already mentioned, the interaction parameter expressed in reduced units is scale-invariant:

\[
\tilde{\alpha}' = \frac{a' r_c(N_m)}{k_B T(N_m)} = \frac{a' r_c(N_m)}{k_B T(N_m)} \sim \frac{a r_c(N_m)}{k_B T(N_m)} = \tilde{\alpha}.
\]

(25)

This is the main and somewhat understated point from the paper by Füchslin et al.: assuming we do not enforce any constraints from the outside apart from the invariance of the compressibility, \( all \) the quantities in reduced units remain scale-invariant with respect to the coarse-graining. This means that any DPD simulation with water serving as the solvent should be done at \( \tilde{\alpha} = 25 \). What
matters is how we map the results back to the real units after the simulation. This has an important positive side effect in that the interaction parameter does not become too high at high CG degrees, which could lead to freezing, a generally undesirable phenomenon in simulations of liquids.\textsuperscript{13}

Finally, we derive the scaling of time and the friction constant $\gamma$ from dimensional analysis:

$$
\tau = \frac{m(N_m)^2(N_m')}{k_BT(N_m)} = \frac{N_m^{2/3}}{N_m^{1/3}} = N_m^{1/3}, \quad (26)
$$

$$
\gamma \sim \frac{m_0(N_m)}{\tau(N_m)} = \frac{N_m}{N_m^{1/3}} = N_m^{2/3}. \quad (27)
$$

Füchslin et al. wrote that there is a gauge freedom in choosing the scaling of time, but in fact this exponent is determined by the decision to keep pressure scale-invariant.

However, a problem now arises. Füchslin et al. decided to constrain the three basic units, length, mass, and energy, in such a way that pressure, compressibility, or any other quantity with the same dimension will be constant across all the scales. But liquid compressibility is not the only property that should be kept constant. In general, any experimental observable should behave so. This is not a priori guaranteed by Füchslin’s scaling scheme.

Consider surface tension and self-diffusivity, two important simulation outputs. The dimensional analysis reveals their scale dependence:

$$
\sigma \sim \frac{k_B T c(N_m)}{r_c^2(N_m)} = \frac{N_m}{N_m^{2/3}} = N_m^{1/3}, \quad (28)
$$

$$
D \sim \frac{r_c(N_m)^2}{\tau(N_m)} = \frac{N_m^{2/3}}{N_m^{1/3}} = N_m^{1/3}. \quad (29)
$$

Clearly, these experimental observables vary with the CG degree, which is undesirable, as CG degree is a simulation parameter without physical nature.

The way to rectify this problem is add an appropriate scaling of the reduced units $D, \tilde{\sigma}$ such that these will become scale-invariant after conversion to real units. To achieve this, we need to understand how these observables depend on the underlying simulation inputs, such as the interaction parameter $\tilde{a}$, the Flory-Huggins $\chi$-parameter, or the friction $\tilde{\gamma}$. To simplify our analysis as much as possible, we will restrict ourselves to either pure liquids or binary mixtures.

A. Surface tension

We first turn to the surface tension, which was extensively discussed by Maiti et al.\textsuperscript{11} Starting from the Hildebrand solubilities $\delta_i$ of species $i$, a simple model for the $\chi$-parameter is

$$
\chi_{ij} = \frac{V}{k_BT} (\delta_i^2 - \delta_j^2), \quad (30)
$$

where $V$ is the bead volume, Maiti derived a linear dependence of the $\chi$-parameter on $N_m$ from the fact that the bead volume varies linearly with the solubilities.\textsuperscript{11}

There are two problems with this line of reasoning, a technical and a theoretical one. Technically, these authors kept the energy scale $k_BT$ invariant. If we corrected this, we would find out that $\chi$ is invariant, which would lead, together with invariant $\tilde{a}$, to invariant surface tension $\tilde{\sigma}$. However, this would imply the scale dependence of $\sigma$, which is undesirable.

The theoretical objection is that mixing is a delicate interplay of various effects on the microscale and it is not a priori clear how these should vary on the number of molecules bundled into a bead. This bundling – the coarse-graining – is in itself an artificial process without any physical substance, the sole aim of which is speeding up the simulation.

In order to derive a plausible scaling of $\tilde{\sigma}$ we follow a different route, which will not require diving into the complex microscopic origin of mixing. We start from the dependence of surface tension on the $\chi$-parameter derived by GW in the context of the DPD (eq. (36) in their paper, with $\tilde{\rho}$ being density and assuming $k_BT = 1, r_c = 1$):

$$
\tilde{\sigma} = \begin{cases} 
0.75\tilde{\rho}^{0.26} \left( 1 - \frac{2.36}{\chi} \right)^{3/2} & \sigma > 2.36 \\
0, & \sigma \leq 2.36. 
\end{cases} \quad (31)
$$

To render $\tilde{\sigma}$ scale-invariant, we need determine the scaling of the $\chi$-parameter such that $\tilde{\sigma} \sim N_m^{-1/3}$. In other words, we are looking for the exponent $\beta$ such that

$$
\sigma = \tilde{\sigma} \frac{k_BT(N_m)}{r_c(N_m)^2} = 0.75\tilde{\rho}(\chi N_m^2)^{0.26} \left( 1 - \frac{2.36}{\chi N_m^2} \right)^{3/2} \sim \text{constant.} \quad (32)
$$

Due to the rather complex power law of eq. (31), we resort to numerical minimisation after defining the relevant range of CG degrees. Although it might be desirable to try to deliver a perfect analytical solution, given the overall qualitative nature of the DPD, a reasonably accurate approximation is sufficient for practical simulations.

We consider the mixtures explored by Maiti, that is water-benzene, water-CCl, and water-octane. Their $\chi$-parameters are computed from the Hildebrand solubilities, and the data are summarised in Table 1. Defining the range of CG degrees $N_m \in \{1, 2, ..., 10\}$ and the root mean-square error

$$
\text{RMSE} = \sqrt{\frac{1}{N_{N_m} - 1} \sum_{N_m} (\sigma_1 - \sigma_{N_m})^2}, \quad (33)
$$

we can minimise the RMSE across these mixtures. Hence, we arrive at the scaling of the χ-parameter \( \chi \sim N_m^{-0.22} \).

To test this scaling, we performed simulations in the LAMMPS software package.\(^{14}\) We set a \( 20 \times 10 \times 10 \) orthorhombic cell at density \( \tilde{\rho} = 3 \). The time step was set to 0.05. Taking water as the default liquid, the volume of a bead containing one molecule was \( V_0 = 30 \) Å, and the like bead repulsion \( \tilde{a}_{ii} = 25 \). We equilibrated the system for 20000 steps and collected data for another 50000 steps. The surface tension was calculated from the pressure tensor components:

\[
\tilde{\sigma} = \frac{\tilde{L}_{xx}}{2} \left( \langle \tilde{p}_{xx} \rangle - \frac{\langle \tilde{p}_{yy} \rangle + \langle \tilde{p}_{zz} \rangle}{2} \right). \tag{34}
\]

In parallel, we have reproduced the measurements by Maiti et al. These workers tested two various relations for \( \Delta a \) vs \( \chi \): a linear one derived by GW:

\[
\Delta a = \chi/0.286, \tag{35}
\]

which we used for our simulations as well, and a quadratic one derived by Wijmans et al. (WSG):\(^{15}\)

\[
\chi_{\Delta a} = 0.3 - \frac{0.3 - 0.2}{115 - 15} (\Delta a - 15). \tag{36}
\]

Both of these, if scaled linearly with \( N_m \), lead to extremely large excess repulsions \( \Delta a \) and allow CG degrees only up to \( N_m = 5 \) and 3, respectively.

Fig. 1 shows the results of analytical predictions and simulations using the scaling arguments presented above, and the approach by Maiti et al. Our method gives satisfactory results for water-benzene and water-octane mixtures for CG degrees up to \( N_m = 10 \) and possibly even above. The water-CCl\(_4\) mixture starts from an incorrect position at \( N_m = 1 \), which might be due to the inability of the overly simple eq. (30) to describe real behaviour. Overall, our derived scaling of \( \chi \sim N_m^{-0.22} \) is able to capture the mixing properties over a wide range of CG degrees and improve the predictive accuracy of mixing in DPD.

### B. Self-diffusivity

The friction parameter \( \tilde{\gamma} \) from the dissipative and random force (eq. (3)) is another microscale parameter that influences the self-diffusivity \( D \), which can be measured experimentally. Overall, bead diffusion depends not only on \( \gamma \), but also on the particle repulsion \( a \). There have been attempts to analytically derive how \( \gamma \) should vary with the CG degree.\(^{16}\) Nonetheless, we can easily derive the scaling that renders the self-diffusivity constant across different CG degrees.

To understand the behaviour of a pure DPD liquid, we exploit the fact that the low number of simulation parameters enables fast exploration of a large portion of the parameter space. Defining the self-diffusivity from the MSD:

\[
\tilde{D} = \lim_{t \to \infty} \frac{\tilde{r}(\tilde{t})^2}{t}, \quad D = \tilde{D} \tilde{r}_c^2 \tilde{r}, \tag{37}
\]

we have measured the dependence of \( \tilde{D} \) for a wide range of \( \tilde{\gamma} \) values between 2 and 30, and \( \tilde{a} \) values between 0 and 55. Using \( 10 \times 10 \times 10 \) orthorhombic cell with 3000 beads, we have equilibrated for 40k steps and measured the MSDs for 1000 steps 10 times in succession to eliminate noise. We took a smaller time step 0.03 to maintain the temperature at \( k_B T = 1 \), as it tends to diverge with increased friction.

Firstly, we consider the case where \( \tilde{a} = 0 \), i.e. beads interact only via the dissipative and random force. In this case, GW derived analytically \( D = 45/(2\pi\gamma\rho c) \) or, in reduced units, \( \tilde{D} = 45/(2\pi\tilde{\gamma}\tilde{\rho}) \).\(^{1}\) From simulations we obtained systematically higher values, as shown on Fig. 2 (left). For all the interaction parameters \( \tilde{a} \), it is possible to fit the self-diffusivity with the power law of the form:

\[
\tilde{D}(\tilde{\gamma}, \tilde{a}) = c_1(\tilde{\gamma} - c_2)\tilde{a}^{c_3}, \tag{38}
\]

where \( c_i, i \in \{1, 2, 3\} \) are fitting parameters. We also tried to fit the self-diffusivities for both \( a \) and \( \gamma \) at once via

\[
\tilde{D}(\tilde{\gamma}, \tilde{a}) = c_1(\tilde{\gamma} - c_2\tilde{a})\tilde{a}^{c_3}, \tag{39}
\]

but this failed to achieve a desired accuracy, especially at low frictions. This is not an important obstacle, since most simulations are done with water as the default bead type with the repulsion \( \tilde{a} = 25 \). Hence, to derive the scaling of \( \tilde{\gamma} \) with the CG degree, it is sufficient to focus only on this value.

As before with the surface tension, our aim is to obtain the exponent \( \beta \) such that:

\[
D = D_{\text{ref}}(N_m)^2 \gamma(N_m) \tag{40}
\]

\[
= 3.303(\tilde{\gamma}N_m^3 + 21.275)^{-0.736}\frac{\tilde{r}_c^2 N_m^{2/3}}{\gamma N_m^{1/3}} \sim \text{constant}. \tag{41}
\]

Starting from \( \tilde{\gamma}(1) = 4.5 \) at \( N_m = 1 \) used by GW, we have minimised the RMSE defined as in eq. (33) for \( N_m \in \{1, \ldots, 10\} \), and obtained \( \beta = 1.13 \). To verify this, we have again simulated pure liquids at \( \tilde{a} = 25 \) with \( \tilde{\gamma} = \).
\( \chi \sim N_m^{-0.22} \)

FIG. 1: Variation of the surface tension for three mixtures with coarse-graining degree: (a) our derivation using the fine-tuned scaling of \( \chi \)-parameter, and (b) methodology by Maiti,\(^{11}\) working up to \( N_m = 5 \), for both Groot & Warren (GW) and Wijmans, Smit and Groot (WSG) \( \Delta a - \chi \) relation.

\( \tilde{a} = 0 \)
\[ \tilde{D} = 1.448(\tilde{\gamma} - 0.915)^{-0.561} \]

FIG. 2: Self-diffusivity dependence with error bars for (a) \( \tilde{a} = 0 \), i.e. no conservative interaction, and (b) \( \tilde{a} = 25 \) with power law fits (equations shown in inset).

\( \hat{\gamma}(1)N_m^{1.13} \). The results on Fig. 3 show a reasonably, if not perfectly flat curve, demonstrating the achieved scale invariance of water self-diffusivity in DPD.

Compared with the experimental self-diffusivity of water \( 2.3 \times 10^{-9} \) m\(^2\)/s at 300 K, the values from DPD simulations are about 20 times larger. This is expected due to the extremely soft nature of DPD potential. To precisely target the experimental value, we would need to take \( \hat{\gamma} \) of about 1500. Such a large value would severely impact the simulation efficiency in that the time step would have to be orders of magnitude smaller, and the speed of equilibration, which is one of the principal advantages of the DPD, would be lost. Nonetheless, having a method to generate scale-invariant, if shifted self-diffusivities can improve the insight into the dynamics of soft matter.

IV. MIXING IN MANY-BODY DPD

A. Overview of MDPD

Having understood the scaling of standard DPD, we now turn its many-body version. First presented by Pagonabarraga et al. and Trofimov et al.,\(^3,4\) and thoroughly explored by Warren,\(^5\), MDPD builds on top of standard DPD by adding a density-dependent interaction at a new length scale \( r_d < 1 \). This modification leads to an EOS with a van der Waals loop, which enables the formation of
a liquid-vapour interface and increases the applicability to free surfaces. Compared with standard DPD, which contains only repulsive interactions, MDPD can support simulations in which the bead density varies widely across the simulation cell.

Adopting the reduced units $r_c = m_c = k_B T = 1$, as in standard DPD, the MDPD force field is:

$$F_{ij}(r) = Aw(r)\hat{r} + B(\tilde{\rho}_i + \tilde{\rho}_j)w_d(r)\hat{r},$$

(42)

where $A$ and $B$ are interaction parameters, $r = |r|$, $\hat{r} = r/r$. $w(r)$ and $w_d(r)$ are the weight functions:

$$w(r) = \begin{cases} 1 - r, & r \leq 1, \\ 0, & r > 1, \end{cases}$$

(43)

$$w_d(r) = \begin{cases} 1 - r/r_d, & r \leq r_d \\ 0, & r > r_d. \end{cases}$$

(44)

The local density $\tilde{\rho}_i$ of particle $i$ is defined as:

$$\tilde{\rho}_i = \sum_{j \neq i} \frac{15}{2\pi r_d^3} w_d(r_{ij})^2 \quad \text{for} \quad r_{ij} \leq r_d,$$

(45)

where we stress that index $j$ runs over all the particles, not just those of the same type as $i$th particle.

Warren showed that for $A < 0$ and $B > 0$, this force field leads to the liquid-vapour coexistence, and determined its equation of state:

$$p = \rho k_B T + \alpha A\rho^2 + 2\alpha Br_d^3(\rho^3 - c\rho^2 + d),$$

(46)

where $\alpha = 0.1$ comes from standard DPD, and $c = 4.16$, $d = 18$ are fitting constants. This EOS was further improved by Jamali et al.

$$p = \rho k_B T + \alpha A\rho^2 + 2\alpha Br_d^3(\rho^3 - c'\rho^2 + d'\rho) - \frac{\alpha Br_d^3}{|A|^{1/2}} \rho^2,$$

(47)

where $c' = 4.69$ and $d' = 7.55$. For further work, we decided to use the more accurate version of the EOS due to Jamali et al.

In the regime of the liquid-vapour coexistence, we can derive how the density and surface tension depend on the parameters $A, B, r_d$, and, by inverting thus obtained relations, determine $A$ and $B$ that would enable the simulation of a real liquid with a given experimental surface tension.

B. Parameterisation for real liquids

As before, from this point we denote the quantities in reduced units by a diacritical tilde. In our recent work we determined the regions of the phase diagram of an MDPD fluid that give rise to the liquid phase. Based on the measurements of liquid density and surface tension as a function of the interaction parameters $A, B$ and fixing $\tilde{r}_d$, for example at 0.75, we solved for the interaction parameters from the material properties, in this case compressibility and surface tension.

For any liquid defined by compressibility, surface tension and volume per molecule, and choosing CG degree $N_m$ and temperature defining the energy scale $k_B T_c$, we have four highly non-linear equations with four unknowns: $r_c, A, B$, and $\tilde{\rho}$. Considering, e.g., $\tilde{r}_d = 0.75$, the fitting coefficients from Table I and II in Ref. yield:
These equations can be solved numerically, either by a root-finding algorithm or by a brute-force search through the parameter space.

In a mesoscale simulation, one does not demand extreme accuracy, so rounding the interaction parameters to nearest integer can often suffice. Hence, working with resolution $\Delta \hat{A} = 1$, $\Delta \hat{B} = 1$, a brute-force search through the parameter space with range $[-100, 0]$ and $[0, 100]$ for $\hat{A}$ and $\hat{B} = 1$, respectively, requires only about 10k evaluations of eqs. (51) and an objective error term. On an average modern computer, this process takes less than a second.

We defined the error function as follows:

$$\text{Err} = w \left| 1 - \frac{\sigma}{\sigma_L} \right| + \left| 1 - \frac{\kappa^{-1}}{\kappa^{-1}_L} \right|,$$

where $\sigma_L$ and $\kappa^{-1}_L$ are experimental surface tension and compressibility, respectively. We chose the weight factor $w = 5$, putting more emphasis on reproducing the surface tension more accurately than compressibility.

We have determined the interaction parameters $\hat{A}, \hat{B}$ for water, which we later apply to water-solvent mixtures. We need to bear in mind that water is an outlier in that its surface tension is about three times higher and the volume per molecule is several times lower than in case of other common solvents. We have explored a range of many-body cutoffs $\tilde{r}_d$: 0.65, 0.75 and 0.85 and CG degrees $N_m$ from 1 to 10.

The resulting values of $\hat{A}, \hat{B}$ for $\tilde{r}_d = 0.65$, which are shown in Table II, are relatively small and marked by excessive inverse compressibilities. More importantly, the reduced density, which is a key parameter for simulation efficiency, is extremely high for any CG degree up to 10, as can be compared by the typical density $\bar{\rho} = 3$ used in standard DPD. We conclude that this many-body cutoff is useless for water simulations and decide not to proceed.

The parameter search for $\tilde{r}_d = 0.75$ yields more suitable results, with accurate surface tensions as well as compressibilities for all CG degrees, as shown in Table III. The density $\bar{\rho}$ is still rather high at $N_m = 1$ and 2, but other CG degrees are viable. $\tilde{r}_d = 0.85$ in Table IV produces reasonable parameter values and highly suitable reduced densities, almost on the level of standard DPD, but slightly low inverse compressibilities. Hence, both of these values of $\tilde{r}_d$ are suitable for simulations including water. This analysis also suggests that an intermediate value of $\tilde{r}_d$, such as 0.80, would provide both reasonable densities as well as accurate compressibilities.

### Table II: Derived interaction parameters for water at various CG degrees and $\tilde{r}_d = 0.65$

| $N_m$ | $\bar{\rho}$ | $\hat{A}$ | $\hat{B}$ | $\sigma$ (mN/m) | $\kappa^{-1}$ (10^9 Pa) |
|-------|-------------|---------|---------|-----------------|-----------------|
| 1     | 13.33       | -16     | 5       | 71.6            | 4.41            |
| 2     | 14.49       | -15     | 4       | 72.4            | 3.95            |
| 3     | 21.17       | -14     | 2       | 69.2            | 3.27            |
| 4     | 21.17       | -14     | 2       | 76.2            | 3.27            |
| 5     | 16.37       | -14     | 3       | 70.3            | 3.47            |
| 6     | 16.37       | -14     | 3       | 74.7            | 3.47            |
| 7     | 13.85       | -14     | 4       | 70.6            | 3.65            |
| 8     | 13.85       | -14     | 4       | 73.9            | 3.65            |
| 9     | 12.29       | -14     | 5       | 70.6            | 3.82            |
| 10    | 12.29       | -14     | 5       | 73.1            | 3.82            |

### Table III: Derived interaction parameters for water at various CG degrees and $\tilde{r}_d = 0.75$

| $N_m$ | $\bar{\rho}$ | $\hat{A}$ | $\hat{B}$ | $\sigma$ (mN/m) | $\kappa^{-1}$ (10^9 Pa) |
|-------|-------------|---------|---------|-----------------|-----------------|
| 1     | 15.71       | -19     | 2       | 70.7            | 2.33            |
| 2     | 14.37       | -17     | 2       | 71.0            | 1.94            |
| 3     | 8.23        | -20     | 6       | 71.5            | 2.50            |
| 4     | 7.97        | -19     | 6       | 70.7            | 2.33            |
| 5     | 7.36        | -19     | 7       | 70.6            | 2.35            |
| 6     | 7.71        | -18     | 6       | 72.1            | 2.16            |
| 7     | 7.13        | -18     | 7       | 70.3            | 2.19            |
| 8     | 7.13        | -18     | 7       | 73.5            | 2.19            |
| 9     | 6.68        | -18     | 8       | 71.3            | 2.22            |
| 10    | 6.68        | -18     | 8       | 73.8            | 2.22            |

### C. Mixing in MDPD

Having provided a general liquid parametrisation protocol for MDPD and derived the interaction parameters and densities of coarse-grained water, we now turn to the mixing properties of liquids. In simulating binary
mixtures, we keep the parameter $\tilde{B}$ constant across liquid species, as required by the no-go theorem derived by Warren.\textsuperscript{20} Thus, only varying $\Delta \tilde{A}$ controls the phase separation.

In the context of standard DPD, mixing was related to the Flory-Huggins theory.\textsuperscript{1} In order to bridge the experiments to mesoscale simulation, the Flory-Huggins $\chi$-parameter, which can be computed \textit{a priori} for a given mixture from Hildebrand solubilities $\delta$ via eq. \eqref{eq:flory_huggins} or through a more sophisticated Monte Carlo sampling,\textsuperscript{21} was related to the excess repulsion $\Delta \tilde{A}$.

Denoting $\chi = \nu \Delta \tilde{A}$, $\nu = 0.286$ in standard DPD at $\tilde{\rho} = 3$ and 0.689 at $\tilde{\rho} = 5$.\textsuperscript{1} In the context of MDPD, Jamali \textit{et al.} derived three values of $\nu$ at three different densities, considering positive values of $\tilde{A}$ only and hence describing a purely repulsive liquid (eqs. \eqref{eq:dpd_fit_1}--\eqref{eq:dpd_fit_3} in their paper).\textsuperscript{17} Since density in MDPD is not decided \textit{a priori} but arises by choosing the liquid and the specific CG degree, we need to understand the general dependence of $\nu$ on density. These three points obtained by Jamali \textit{et al.} can be fitted by a line:

$$\nu(\tilde{\rho}) = -0.259 + 0.196 \tilde{\rho}. \quad \eqref{eq:dpd_fit_1}$$

Here, we derive how $\nu$ depends not only on density but also many-body cutoff $\tilde{r}_d$ for negative values of $\tilde{A}$. Following the protocol presented by GW (Section V and Fig. 7), we set up a simulation cell $20 \times 8 \times 8$, varied excess repulsion $\Delta \tilde{A}$ between 0 and 15 and measured the $\chi$-parameter from the phase-separated density profiles via:

$$\chi = \frac{\ln[(1 - \tilde{\rho}_A)/\tilde{\rho}_A]}{1 - 2\tilde{\rho}_A}, \quad \eqref{eq:dpd_fit_2}$$

where $\tilde{\rho}_A$ is the density of component A (for illustration, see Fig. 6 in GW). Consequently, we fitted this dependence of $\chi$ on $\Delta \tilde{A}$ by a line. Fig. 5 shows that that the region of linear dependence is limited for the values of $\chi$ between about 2 and 6 and depending on the density, which should be carefully taken into consideration in simulating binary mixtures.

Exploring four different densities, we obtained a linear dependence of $\nu$ on density similar to Jamali \textit{et al.}:

$$\nu = -(0.233 \pm 0.019) + (0.188 \pm 0.003)\tilde{\rho}, \quad \eqref{eq:dpd_fit_3}$$

for $\tilde{r}_d = 0.75$, and

$$\nu = -(0.285 \pm 0.019) + (0.196 \pm 0.003)\tilde{\rho}, \quad \eqref{eq:dpd_fit_4}$$

for $\tilde{r}_d = 0.85$. The influence of $\tilde{r}_d$ on $\nu$ is small and for practical purposes can be neglected.

\section{Surface tension}

Having determined the dependence of the $\chi$-parameter on excess repulsion $\Delta \tilde{A}$, we now turn our attention to surface tension, a key quantitative descriptor of behaviour of a binary mixture.
Firstly, we verify how surface tension varies on $\chi$-parameter. We note that Jamali et al. have also computed this dependence (Fig. 12b in\textsuperscript{17}) but did not provide a functional form. We decided to revisit their results due to a different choice of interaction parameters $A > 0$ by these authors. As in Section III, we used the pressure tensor components for surface tension calculation via eq. (34).

Fig. 4a and 4b show the surface tension vs $\chi$-parameter for $\hat{r}_{d} = 0.75$ and 0.85, respectively. We do not observe the collapse of the ratio $\hat{\sigma}/\hat{p}$ onto one curve, as GW claimed, beyond $\chi > 5$, as there still remains a small density dependence. Furthermore, our absolute values of the surface tension are lower by about a factor of three from the values obtained by Jamali et al. (Fig. 12b), but in agreement with Fig. 1b from Yong.\textsuperscript{22} GW suggested a fitting form $\hat{\sigma} = \mu_{i}/\hat{p}^{2}(1 - \mu_{3}/\chi)^{3/2}$. In order to find a universal scaling where all the surface tension curves collapse onto one, we relaxed this form via coefficient $\xi$:

$$\hat{\sigma}/\hat{p}^{\xi} = \mu_{i}/\chi^{\mu_{2}}(1 - \mu_{3}/\chi)^{3/2}.\quad (57)$$

Searching for $\xi$ that minimises the standard deviation on $\mu_{i}$, which is a signature of universal scaling, we found that the best fit is provided by $\xi = 1.38$ for $\hat{r}_{d} = 0.75$ and 1.24 for $\hat{r}_{d} = 0.85$.

As in the case of standard DPD, in order to enable reliable simulations of real mixtures at various scales, we need to derive the scaling of the $\chi$-parameter with CG degree in order to keep surface tension in real units scale-invariant. Fitting for $\mu_{i}$ in eq. (57) and computing surface tension for the three mixtures considered by Maiti et al.\textsuperscript{11}, namely: water-benzene, water-CCl$_4$ and water-octane, at CG degrees 1-10, we found that $\chi \sim N_{m}^{-0.2}$ yields the smallest RMSE with respect to experimental values in Table I, an exponent similar to -0.22 for standard DPD.

Finally, to verify the predictive ability of MDPD, we computed via simulation surface tensions of the mixtures for a range of CG degrees and the two viable many-body cutoffs, 0.75 and 0.85. We remark that the $\chi$-parameters computed by eq. (30) of these mixtures are all on the top end of the range of validity in Fig. 5 at low CG degrees. We setting the simulation cell $20 \times 10 \times 10$ and timestep $\Delta t = 0.02$, we simulated in DL-MESO version 2.6 for 150k steps, using first 50k for equilibration and collecting 10k pressure tensor components for averaging. The interaction parameters $B_{ij}$ were the same for all pairs of species due to the Warren’s no-go theorem, and $A_{ij}$ were different only for unlike species:

$$\hat{A}_{ij} = \hat{A} + \nu(\hat{p}) \chi_{ij},\quad (58)$$

$$\hat{B}_{ij} = \hat{B},\quad (59)$$

where $\hat{A}, \hat{B}$ were taken from Tables III or IV for appropriate CG degree.

For $\hat{r}_{d} = 0.75$, the results on Fig. 6a show a satisfactory albeit not perfect agreement apart from $N_{m} = 1$ and 2. At these low CG degrees, the densities are very high and already out of the range of validity of the density fit,\textsuperscript{18} resulting in incorrect liquid behaviour. Increasing many-body cutoff to $\hat{r}_{d} = 0.85$, Fig. 6b shows good agreement of up to 10% in case of water-CCl$_4$. Considering that due to lower density $\hat{p}$ the simulations took about a third of the time required by the configurations employing $\hat{r}_{d} = 0.75$, this setting is suitable for water-solvent simulations. Illustrative density profiles of water and benzene at $N_{m} = 5$ are provided on Fig. 7.

V. CONCLUSIONS

In this work, we explored the freedom in tuning the force field of both standard and many-body dissipative particle dynamics. We reviewed the derivation of the temperature-dependence of the interaction parameter, first proposed by Groot and Warren.\textsuperscript{1} Consequently, we theoretically revisited the scaling of the simulation variables and elucidated the role of the coarse-graining degree, an important ingredient of a mesoscale simulation. We derived the scaling of the friction and interaction parameters so that the experimental observables emerging from the simulation would remain invariant with respect to the coarse graining.

For the many-body DPD, we explored a range of the many-body cutoffs and derived the interaction parameters simulating water at correct surface tension and compressibility while preserving simulation efficiency by minimising the number of particles in a simulation cell. Building on this, we derived the scaling of the Flory-Huggins $\chi$-parameter, which controls the mixing of liquids, on excess repulsion as well as coarse-graining degree. Our findings will enable the application of the many-body DPD to more complex soft matter systems.
including pores, liquid/solid or liquid/vapour interfaces on the length scales of 10-100 nm, such as, for example, polymer electrolyte membranes, and raise the predictive accuracy vis à vis experimental data.

VI. ACKNOWLEDGMENTS

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