Dissipative Particle Dynamics interaction parameters from *ab initio* calculations

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ABSTRACT

Dissipative Particle Dynamics (DPD) is a commonly employed coarse-grained method to model complex systems. Presented here is a pragmatic approach to connect atomic-scale information to the meso-scale interactions defined between the DPD particles or beads. Specifically, electronic structure calculations were utilized for the calculation of the DPD pair-wise interaction parameters. An implicit treatment of the electrostatic interactions for charged beads is introduced. The method is successfully applied to derive the parameters for a hydrated perfluorosulfonic acid ionomer with absorbed vanadium cations.

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1. Introduction

Dissipative Particle Dynamics (DPD) is a meso-scale simulation technique that was first introduced by Hoogerbrugge and Koelman [1]. Further developments by Español and Warren included the stochastic differential equations and conservation of energy [2,3]. The method describes the system in terms of soft particles, or beads, whose motion is governed by certain collision rules [4]. The soft particles, or beads, represent groups of atoms or molecules in the system. The use of simplified potentials and the grouping of the atoms into particles permit simulations of large systems over long time-scales that are either impossible or difficult to perform in all atom methods such as molecular dynamics (MD) [5]. Since its development, the original formulation of DPD has been successfully applied to model a large variety of systems including: block copolymers [6,7], surfactant solutions [8], bilayer membranes [9], and ionomers [10–12].

The reliability of DPD simulations depends on the proper translation of the atomic-scale into the meso-scale interaction parameters. There have been different methods for the derivation of the interaction parameters between the various types of beads in order to link the actual physical system to the fictitious DPD particles. The most widely used method was introduced by Groot and Warren through mapping onto Flory–Huggins theory [4]. They used the Flory–Huggins χ-parameter to define the interactions between different components of the system. The χ-parameter may be related to the solubility [13] or approximated from mixing energy

calculations using a Monte Carlo approach [12,14]. However, χ is not available for every substance, and there are cases where the calculations via mixing energy are not fruitful. For instance, if the beads contain a net electrostatic charge both the solubility and mixing energy approximations fail to give a suitable value for χ and consequently the interaction parameters. Some authors have set the parameters based on the nature of the chemical groups that are lumped into each bead or the phase separation behavior of the system [15–17]. This technique requires a thorough understanding of the materials, specific experimental, and simulation results. Others started with MD simulations and extracted an effective coarse-grained potential, requiring the meso-scale simulations to match the structural data or pair-correlation functions of the atomistic simulations [18–20].

Groot developed a smeared-charge approach for the treatment of electrostatic interactions in which the charge is distributed within a sphere rather than being only on a point [21]. The inclusion of this long-range interaction increases the computational cost and violates the basic principle of DPD (that only considers the interactions to be short range). Therefore, it is necessary to provide a method for defining the interaction parameters that is versatile, does not rely on the experimental information, and still fits into the simple original DPD framework to ensure the expected high computational efficiency. The aim of this letter is to introduce a parameterization method that is capable of capturing the various types of interactions including strong electrostatics while preserving the simple form of the DPD potentials and high computational efficiency of the method.

In the following the overall DPD framework is briefly described (for a more detailed and complete description of the method the reader is referred elsewhere [1–4,22]). We then present a pragmatic

approach that uses ab initio electronic structure calculations for the development of the conservative interaction parameters. The average pairwise potentials derived from these quantum chemical calculations ensure the perseverance of the original framework. Finally, the parameterization method is applied to a system of interest, which consists of a hydrated perfluorosulfonic acid ionomer with absorbed ionic species.

2. DPD framework

The time evolution of the interacting particles is governed by Newton's equations of motion that are integrated using a modified velocity-Verlet algorithm [4]. The dimensionless equations of motion in the Hamiltonian form are:

$$\frac{dr_i}{dt} = v_i, \quad \frac{dv_i}{dt} = f_i \tag{1}$$

the r_i and v_i are the position and velocity of the ith particle and f_i is the net force acting on that particle. The net force contains three non-bonded terms. Bonded terms may also be included in order to make the simulation of polymers viable.

$$f_i = \sum_{j \neq i} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R \right) + f_i^{bonded} \tag{2}$$

The first three terms in the summation: F_{ij}^C, F_{ij}^D, and F_{ij}^R conservative, dissipative, and random forces which are the non-bonded components and are typically formulated as follows:

$$F_{ij}^C = a_{ij}(1 - r_{ij})n_{ij} \tag{3}$$

$$F_{ij}^D = -\gamma_{ij}(1 - r_{ij})^2(n_{ij}.v_{ij})n_{ij} \tag{4}$$

$$F_{ij}^R = \sigma_{ij}(1 - r_{ij})\xi_{ij}\frac{1}{\sqrt{\Delta t}}n_{ij} \tag{5}$$

These forces are pairwise and in the direction of $\mathbf{n}_{ij} = (r_i - r_j)/|r_{ij}|$ which is the unit vector toward the centers of particles i and j. The cut off distance for all the non-bonded forces is r_c, the length-scale, which is linked to physical units based on the system of study and degree of coarse-graining. The relative position and velocities are defined as $r_{ij} = r_i - r_j$ and $v_{ij} = v_i - v_j$. a_{ij} is the interaction parameter between two beads and is material or chemical compositional specific and therefore must be determined for each system. The dissipation constant, γ_{ij}, and the noise amplitude, σ_{ij}, are related by $\sigma_{ij} = \sqrt{\gamma_{ij}2k_BT}$ to control the temperature fluctuations as dictated by the fluctuation-dissipation theorem [2]. The dissipation constant has a typical value of 4.5 [4,12,14]. ξ_{ij} is a symmetric Gaussian random number with zero mean and unit variance chosen independently for each pair of interacting particles at each time step (Δt). The last term in Eq. (2) comes from the bonded potentials defined to describe polymeric systems. Beads of a polymer are usually connected to their nearest neighbor beads by harmonic springs [4,6]. However, another spring term to describe the second nearest neighbor beads may also be added in order to improve the structural properties of a polymer chain [19,23,24].

In this formulation, the only material parameters to be determined for the system of interest are the conservative interaction parameters, a_{ij}, and bonded potentials if present. It has been previously shown that the relative interactions affect the phase behavior of the system and not the absolute values [25,26]. Recent studies also underline the use of different like bead interactions for different bead types (i.e., $a_{ii} \neq a_{jj}$) and its effect on the correct prediction of phase behavior and local densities [27,28]. Hence, it is important to find the relative amount of the interactions between all pairs of beads (either like or unlike) as accurate as possible.

3. Parameterization of the conservative force

The conservative interaction potential is assumed to consist of two terms in the quadratic form:

$$U_{ij}^C = U_{ij}^R + U_{ij}^{ex} = \begin{cases} \dfrac{a_{ij}}{2}(1 - r_{ij})^2, & r_{ij} < 1 \\ 0, & r_{ij} \geq 1 \end{cases} \tag{6}$$

where $U_{ij}^R = \frac{a_{ij}^R}{2}(1 - r_{ij})^2$ and $U_{ij}^{ex} = \frac{a_{ij}^{ex}}{2}(1 - r_{ij})^2$ (this implies $a_{ij} = a^R + a_{ij}^{ex}$). The first term is the reference potential and is related to the compressibility of a reference material. The second term is the excess interaction and contains the information regarding the relative interactions among the beads excess to the reference. The intention is to reproduce the experimental compressibility of one pure reference material and then to obtain all the other interactions (either like or unlike) relative to this reference. The reference bead is a charge neutral species in the system with known experimental compressibility. The a^R is then obtained by matching the simulated compressibility of pure reference to that of the experiment, similar to the remarkable work by Groot and Warren (see Section IV of Ref. [4]).

The excess energy may be related to the interaction energy of the two beads which can be calculated using electronic structure calculations.

$$U_{ij}^{int} = U_{(i+j)} - U_{(i)} - U_{(j)} \tag{7}$$

where U_{ij}^{int} is the interaction energy and is obtained by subtracting the ab initio calculated electronic energy of the isolated beads (i.e., $U_{(i)}$ and $U_{(j)}$) from that of the interacting beads (i.e., $U_{(i+j)}$; the total electronic energy of a system containing the two interacting beads i and j). In order to correctly sample the interaction energy, $U_{(i+j)}$ should be calculated and averaged over many different spatial configurations of the two beads. Figure 1 illustrates the six spatial degrees of freedom that are varied in order to consider all the probable configurations of two objects in a three dimensional space. By varying these six geometric parameters, many different configurations are generated and consequently the interaction energies are fitted to a quadratic function of r_{ij} (the distance between the centers of mass of beads i and j). Overall, the procedure is similar to the derivation of classical two-body pair potentials from quantum chemical calculations [29–31]. However, in this case the calculations are performed on two large clusters of atoms or molecules (the selected beads with full atomistic resolution) instead of two atoms
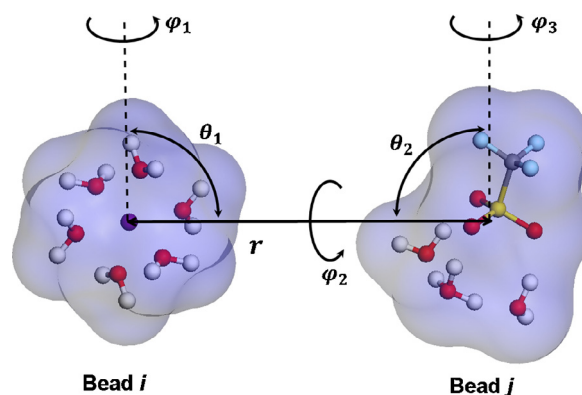

Figure 1. The six degrees of freedom that contribute different configurations to the two objects (beads). The atomic structures of the beads i and j are arbitrary. The angles can vary as $0° \leq \theta \leq 180°$ and $0° \leq \phi \leq 360°$ for each configuration. The lower limit for the $\mathbf{r}_{ij}$ is when the beads start to overlap and the upper limit is the cut off distance $\mathbf{r}_c$.