

SUPPORTING INFORMATION

Micelle Formation in Alkyl Sulphate Surfactants

Using Dissipative Particle Dynamics

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Dissipative Particle Dynamics (DPD)

DPD is a coarse-grained simulation methodology in which particles (beads) interact via soft repulsions and, in the most common version, with local pairwise friction and random forces which provide a thermostat.¹⁻³ The force acting on a DPD bead is

$$\vec{F}_i = \sum_{j \neq i} (\vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R) \quad (1)$$

where \vec{F}_{ij}^C , \vec{F}_{ij}^D and \vec{F}_{ij}^R are respectively the conservative, dissipative and random forces acting between pairs of beads (i and j).

The conservative force usually corresponds to a pairwise interaction potential such as the

soft truncated repulsive form proposed by Groot and Warren,³

$$\vec{F}_{ij}^C = \begin{cases} A_{ij}(1 - r_{ij}/R_{ij})\hat{e}_{ij} & r_{ij} < R_{ij}, \\ 0 & r_{ij} \geq R_{ij} \end{cases} \quad (2)$$

where $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ is the vector between beads i and j , r_{ij} is the distance between the beads, $\hat{e}_{ij} = \vec{r}_{ij}/r_{ij}$ is the unit vector, A_{ij} is the interaction strength (which is chosen to correspond to the bead types) and R_{ij} is a cutoff distance for beads i and j , beyond which a pair of particles do not interact. In much existing work a common value $R_{ij} = r_c$ is assumed, but in our parametrisation approach we allow R_{ij} to depend on bead types.⁴

The dissipative force corresponds to pairwise friction between the beads and depends on their relative velocity, $\vec{v}_{ij} = \vec{v}_j - \vec{v}_i$, as

$$\vec{F}_{ij}^D = -\gamma w^D(r_{ij}) (\hat{e}_{ij} \cdot \vec{v}_{ij}) \hat{e}_{ij} \quad (3)$$

where γ is the dissipative force strength and $w^D(r_{ij})$ is a distance-dependent weighting function.

The random force similarly takes the form

$$\vec{F}_{ij}^R = \Delta t^{-1/2} \sigma w^R(r_{ij}) \xi_{ij} \hat{e}_{ij} \quad (4)$$

where σ is the random force strength, $w^R(r_{ij})$ is another weight function, $\xi_{ij} = \xi_{ji}$ is a Gaussian-distributed random variable with zero mean and unit variance, and Δt is the time-step. To ensure the dissipative and random forces act as a momentum-conserving thermostat, the following conditions should be met,²

$$\sigma^2 = 2T\gamma, \quad w^D(r) = [w^R(r)]^2, \quad (5)$$

where T is the required system temperature (in DPD units). Most DPD simulations set the

random force weight function to have the same form as the conservative force law, *i. e.*

$$w^R(r) = \begin{cases} 1 - r/R_\gamma & r < R_\gamma, \\ 0 & r \geq R_\gamma \end{cases} \quad (6)$$

with $R_\gamma = r_c$. This minimises the computational cost since the same function can be used for each interacting pair of beads. In our work the cutoff in the conservative force law depends on species type but we choose not to mirror this in the thermostat; rather we use the above with the same value of R_γ for all pairs of particles, set equal to the maximum value of R_{ij} .

Other interaction forces can optionally be included alongside the conservative force, *e. g.* for bonds, angles and electrostatics (see below). The full force acting on a DPD bead in the present study is therefore

$$\vec{F}_i = \vec{F}_i^{E,L} + \sum_{j \neq i} \left(\vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R + \vec{F}_{ij}^B + \vec{F}_{ij}^{E,S} \right) + \sum_{k \neq j \neq i} \vec{F}_{ijk}^A \quad (7)$$

where \vec{F}_{ij}^B and $\vec{F}_{ij}^{E,S}$ are the forces acting between pairs of beads (i and j) due to bond stretching and short-range electrostatics (*e. g.* real space Ewald contribution) respectively, \vec{F}_{ijk}^A is due to bond angles between three beads (i, j and k), and $\vec{F}_i^{E,L}$ accounts for the long-range electrostatic force (*e. g.* reciprocal space Ewald contribution) acting on bead i . In the cases of bond stretching and angles, the associated forces are derived as $\vec{F} = -\nabla U$.

In this work we use the Slater-type charge smearing proposed by González-Melchor *et al.* in which the Coulomb potential for pairs of point charges is modified to eliminate the divergence at overlap.⁵ For the electrostatic pair potential therefore,

$$U_{ij}^E(r_{ij}) = \frac{\Gamma q_i q_j}{4\pi r_{ij}} [1 - (1 + \beta r_{ij}) e^{-2\beta r_{ij}}], \quad (8)$$

where r_{ij} is the ion separation, q_i and q_j are the ion charges (valencies), $\Gamma = e^2/(k_B T \epsilon_0 \epsilon_r r_c)$ is a dimensionless electrostatic coupling parameter which includes the relative background

permittivity, and β is a tuneable Slater smearing parameter.

Since the modified Coulomb interaction retains the long-range $1/r$ dependence, it is essential to account for the periodic boundary conditions. An appropriate approach is the Ewald summation method,⁶ in which the total electrostatic energy is

$$U_{total}^E = \frac{\Gamma}{4\pi} \left[\sum_i \sum_{j>i} \frac{q_i q_j}{r_{ij}} [\text{erfc}(\alpha r_{ij}) - (1 + \beta r_{ij}) e^{-2\beta r_{ij}}] + \frac{2\pi}{V} \sum_{\vec{k} \neq 0} \frac{e^{-k^2/4\alpha^2}}{k^2} S(\vec{k}) S(-\vec{k}) - \frac{\alpha}{\sqrt{\pi}} \sum_i^N q_i^2 \right]. \quad (9)$$

In this α is the parameter controlling the labor division between real and reciprocal space, \vec{k} are reciprocal space vectors concomitant with the periodic boundary conditions, and $S(\vec{k}) = \sum_i q_i e^{i\vec{k} \cdot \vec{r}_i}$ is the charge structure factor. Compared to the ‘vanilla’ Ewald method, the only change required due to charge smearing lies in the real space contribution. In this case, the associated pairwise short-range electrostatic force between beads i and j is

$$\vec{F}_{ij}^{E,S} = \frac{\Gamma q_i q_j}{4\pi r_{ij}^2} \left[\text{erfc}(\alpha r_{ij}) + \frac{2\alpha r_{ij}}{\sqrt{\pi}} e^{-\alpha^2 r_{ij}^2} - e^{-2\beta r_{ij}} [1 + 2\beta r_{ij} (1 + \beta r_{ij})] \right]. \quad (10)$$

Any standard method for dealing with the reciprocal space part of the Ewald sum, such as Smooth Particle Mesh Ewald (SPME),⁷ can be used without modification (including the associated expressions for reciprocal space force $\vec{F}_i^{E,L}$). For optimisation, a study of truncation effects due to choice of the values of α , β and the real-space cutoff is given by Vaiwala *et al.*⁸ In the case of SPME, the charge interpolation order is an additional parameter: this can be carefully selected to ensure the reciprocal space Ewald interactions are applied sufficiently accurately.

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