A Two-Level, Discrete-Particle Approach for Simulating Ordered Colloidal Structures

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We devise a new, two-level discrete-particle model to simulate ordered colloidal structures with vastly different scales. We use the molecular dynamics paradigm with a Lennard-Jones-type potential to define colloidal particle system and dissipative particle dynamics (DPD) to model the solvent. The initially mixed, disordered particle ensemble undergoes a phase transition. We observe the spontaneous creation of spherical or rod-like micelles and their crystallization in stable hexagonal or worm-like structures, respectively. The ordered arrays obtained by using the particle model are similar to the two-dimensional colloidal crystals observed in laboratory experiments. The micelle shape depends on the ratio between the scaling factors of the colloid–colloid to colloid–solvent particle interactions. The properties of the DPD solvent, such as the strongly variable viscosity and partial pressure, determine the speed of crystallization. The intriguing features of colloidal arrays and their exotic symmetries, which persist also over two-dimensional domains, can be simulated numerically by using the two-level discrete-particle approach and are illustrated here.

Key Words: colloidal crystals; micelles; two-level particle model; dissipative particle dynamics; molecular dynamics.

1. INTRODUCTION

Complex fluids take on an homogeneous appearance at macroscopic scale but appear very disordered and heterogeneous on the microscopic scale. However, they possess an ordered structure over a mesoscopic length scale (1). For example, in polymer solutions, the intermediate length scale can be the size of a polymer chain. In a colloidal suspension, the mesoscopic length scale is the size involving colloid particles, i.e., 10–1000 nm. Typical examples of complex fluids with large molecular structures are micellar solutions, microemulsions, and colloidal suspensions such as ink, milk, foams, waste products, and emulsions. The properties of these systems are often determined by their mesoscale structures, thus endowing a complex fluid with unique and interesting features. Thus one of them is the ability to create ordered arrays and two-dimensional (2D) colloidal crystals (2–7) in colloidal suspensions. In these systems, the mesoscale structures influence the physical response to the external perturbations such as fluid flow, heat flow, electromagnetic waves, and acoustic waves. Controlling the microstructure of the colloidal systems is vital to the production of industrial materials and the development of new nanomaterials.

The classic numerical approaches used for studying fluid-like behavior, such as computational fluid dynamics (CFD) and molecular dynamics (MD), are inappropriate for describing mesoscale systems, whose spatiotemporal scale lies just between the scales covered by classic CFD and traditional MD. To obtain a better understanding of the unique phenomenon of ordering, which occurs in colloidal suspensions, reliable mesoscopic computational models are sorely needed.

Although MD is commonly used for simulating phenomena over atomic scales, a few orders of magnitude smaller than those occurring in colloidal suspension, we can match the MD model to the proper spatiotemporal scales. On the basis of the resemblance of the simulation results of similar processes on both the micro- and macroscale obtained by rescaling, changing the definition of the particle and interparticle potential, we find that we can employ the MD particle model to simulate some interesting physical phenomena on both the meso- and macroscale (8). Such scaling up of the MD method gives surprisingly good results in granular dynamics (9). We can extend this rescaling concept and thus interpret the DPD particle as a “lump of fluid.” The problems with defining the interparticle potential can be overcome by using the dissipative particle dynamics (DPD) method (10, 11), which is a mesoscopic counterpart to MD. Due to the soft character of the DPD force in comparison with the Lennard-Jones model, and the larger size of DPD particles corresponding to a particular coarse-grain level, much larger time steps can be used than for a typical MD simulation. Thus larger systems can be simulated over much longer periods. However, as is shown by Españoal et al. (12), the soft character of DPD potential has no distinct advantage. The advantages gained by increasing the size of time steps are lost for a much longer simulation period to obtain statistically significant results.

The true advantage of DPD over MD consists of the possibility of matching the scale of discrete-particle simulation to the dominant spatiotemporal scales of the entire system. In MD simulation the time scales associated with evolution of heavy
colloidal particles are many orders of magnitude larger than the temporal evolution of solvent particles. We now consider the DPD droplets, as they evolve much more slowly and are able to match time scales close to those associated with the colloidal particles. A difficulty associated with applying DPD to simulate ordered colloidal structures lies in the repulsive character of the DPD interparticle force. Due to the Kirkwood–Alder transition (2), the DPD system “freezes” because of the very strong repulsive interactions. For weaker interactions, the lack of short-range attractions causes the DPD system of colloidal particles to behave like a fluid, thus creating a kind of disordered phase separation, foam-like or emulsion-like patterns (13–15).

We propose here a novel discrete-particle approach, which is based on a scaled up MD technique and the DPD method, to simulate ordering in colloidal suspensions. Within the framework of this model, we use molecular dynamics to define the colloidal particle system and dissipative particle dynamics to simulate the solvent. First, the 2D particle model and its assumptions are presented. On the basis of results obtained from numerical simulation of the particle colloidal system, we reveal the manner in which the ordering patterns change for various parameters of interaction potentials and simulation conditions. Finally, we summarize the results presented.

2. PARTICLE MODEL OF COLLOIDAL SUSPENSION

Let us consider a 2D binary system, which consists of colloidal particles (CPs) immersed in a solvent represented by an ensemble of dissipative particles (DPs). The dissipative particle can be viewed as a “droplet” of liquid with an internal structure and with some degrees of freedom. The DPs defined by mass $M_i$, position $r_i$, and momentum $p_i$ interact with each other via a two-body, short-range DPD force. It consists of the sum of conservative $F_C$, dissipative $F_D$, and Brownian $F_B$ components, where

$$F_C = \pi \cdot \omega(r_{ij}) \cdot e_{ij},$$  \(1\)

$$F_D = \gamma \cdot M \cdot \omega(r_{ij}) \cdot (e_{ij} \cdot v_{ij}) \cdot e_{ij},$$  \(2\)

$$F_B = \delta \cdot \theta_{ij} \cdot \omega(r_{ij}) \cdot e_{ij},$$  \(3\)

and $\omega(r_{ij})$ is a weight function dependent on the distance between particles $i$ and $j$, $e_{ij}$ is a unit vector pointing from particle $i$ to particle $j$, $\theta_{ij}$ is a random variable with zero mean and unit variance, and $\pi$, $\gamma$, and $\delta$ are the scaling factors for each type of interaction. The DPD force is mesoscopic in nature, because it resolves only the center-of-mass motion of the droplets and does not give any detailed description of their internal degrees of freedom.

Unlike the DP–DP dissipative interactions, we assume that the CP–CP and CP–DP interactions can be simulated by energy-conserving Lennard-Jones (L–J) two-body potentials. Thus, the collision operator for the whole particle system can be given by the formula

$$\Omega_{ij} = \pi_{kl} \cdot \omega_1(r_{ij}) - \gamma_{kl} M_i \cdot \omega_2(r_{ij}) \cdot (e_{ij} \cdot v_{ij}) + \frac{\delta_{kl} \theta_{ij}}{\sqrt{\Delta t}} \omega_1(r_{ij})$$

if $k$ and $l$ solvent particles,

$$\Omega_{ij}^n = \frac{24 \pi_{kl}}{r_{ij}^6} \left\{ \left( \frac{\sigma_{kl}}{r_{ij}^3} \right)^6 - 2 \left( \frac{\sigma_{kl}}{r_{ij}^3} \right)^{12} \right\}$$

if $k$ or $l$ colloidal particle,

[4]

and $\Omega_{ij}^n = 0$ for $r_{ij} \gg r_c$, where

$$v_{ij}^n = v_i^n - v_j^n,$$

$$\omega_1(r_{ij}) = \frac{3}{\pi r_c^2 n} \cdot \left( 1 - \frac{r_{ij}^n}{r_c} \right),$$

$$\omega_2(r_{ij}) = \frac{6}{\pi r_c^2 n} \cdot \left( 1 - \frac{r_{ij}^n}{r_c} \right)^2,$$  \(5\)

$$e_{ij} = \frac{r_{ij}^n - r_i^n}{r_{ij}^n},$$

$$r_{ij}^n = \sqrt{(r_i^n - r_j^n)^2},$$  \(6\)

where

$n =$ superscript denoting time step number,

$i, j =$ subscripts for particle numbers,

$\pi_{kl} =$ scaling factor for conservative part of collision operator,

$\gamma_{kl} =$ dissipative force coefficient,

$\sigma_{kl} =$ scaling factor for Brownian motion,

$\theta_{ij} =$ a random variable with zero mean and unit variance,

$r_c =$ cutoff radius, for which $\omega_1(r) = \omega_2(r) = 0,$

$r_{ij}^n$, $v_{ij}^n =$ position and velocity of particle $i$ in $n$th time step, respectively,

$n_D =$ average particle density in $D$-dimensional particle system ($D = 2, 3$),

$r_{ij} =$ distance between particles $i$ and $j$,

$e_{ij} =$ unit vector pointing from particle $j$ to particle $i$.

$\omega_1(\cdot)$ and $\omega_2(\cdot)$ are the weight functions defined such that

$$n_D \cdot \int_0^1 \omega_m(r) \, dr = 1 \text{ for } m = 1, 2.$$  \(7\)

Let us further assume that the particle system is confined within a periodic box to ensure pseudo-infinity of the sample considered and colloidal particles are scattered randomly in the box; i.e., this binary system is perfectly mixed initially. The temporal evolution of the particle system can be represented in a discretized format as

$$\Delta p_i^n = \sum_{j \neq i} \Omega_{ij}^n e_{ij}^n \cdot \Delta t,$$  \(7\)

$$\Delta r_i^n = \frac{p_i^n}{M_i} \Delta t,$$  \(8\)
where $\Delta r_i, \Delta p_i$ are the changes in position and momentum for particle $i$ in the time $n \Delta t$, and $\Delta t$ is the time step. To solve these equations of motion, we have employed the “leap-frog” algorithm for the particle positions $r_i^n$ and a second-order Adams–Bashforth scheme for the particle velocities $v_i^n$ and momenta $p_i^n$ (14). Two-dimensional lattice-gas automata, molecular simulations. On the other hand, the conservative part dictates the role played by the repulsive character of the DPD collision operator.

As shown in (15), the scaling factor $\pi$ of conservative DPD forces is responsible for the thermodynamic properties of the particle system. By increasing the $\pi$ value we can induce the gas–fluid–solid phase transitions. We set the value of $\pi_1$ such that it maintains the DPD particle system in liquid phase; i.e., the radial distribution function (RDF) for DPD particle system is characteristic of the ordering in liquids (15).

Groot and Warren (18) devised the equation of state of a simple DPD fluid, which is used to map out the conservative part of DPD interactions onto a mean-field theory of polymer mixtures, i.e., the Flory–Huggins theory. As shown in (19), comparing the free energy of a DPD fluid with the Gibbs free energy equation obtained from mean-field theory of polymer mixtures, we find the scaling factor of the enthalpic component of Gibbs free energy to be proportional to the scaling factor of conservative DPD forces, while the entropic component does not depend on the conservative-force interactions. Therefore, the liquid/liquid separation comes from the conservative (repulsive) part of the DPD interactions. In the case of spinodal decomposition, the thermodynamic driving force is strong enough to induce an upward diffusion so that any concentration fluctuation, no matter how small, will grow by mass transport along the concentration gradient. This physical situation was first realized by Cahn and Hilliard in the 1950s.

Since colloidal particles interact with each other also via DPD forces, the colloid will like liquid. It will separate from the solvent, resulting in foam-like or emulsion-like phase separations (13–15). The character of these patterns depends mainly on the value of $\pi_{1,2}$—the scaling factor of conservative forces acting between solvent–colloid particles (15). While $\Delta = \pi_{1,2} - \pi_1 < 0$, the two fluids 1 and 2 are fully miscible and no distinct patterns are observed. For a sufficiently small $\Delta > 0$, binary fluid is immiscible and the average domain size $R$ grows with time according to the power law $R(t) \sim t^\beta$.

For low-volume fractions, growth takes place via the diffusive coalescence of droplets. In two dimensions two time exponents $\beta$ are obtained depending on which computational method is used (14). Two-dimensional lattice-gas automata, molecular
dynamics, and Langevin dynamics simulations reveal $\beta = 1/2$ but lattice-Boltzmann studies suggest that $\beta = 1/3$. It thus appears that the value of $\beta$ depends on the internal thermal fluctuations (13). If they are present $\beta = 1/2$, if not then $\beta = 1/3$. If the hydrodynamic effects are relevant and the average domain size is greater than the intrinsic hydrodynamic length $R_H$ [13, 14], the exponent is $\beta = 2/3$. The two phases separate completely out after a while (see Fig. 2a).

Otherwise, for a large $\Delta$ value, the binary fluid separates out quickly at first into stable droplets with various length scales, thus creating an emulsion-like substance with strongly varying physical properties, such as the viscosity (see Fig. 2b).

The dual character of the solvent (DPD) particle interacting with other DPD and colloidal particles comes from the different spatiotemporal models, which represent both kinds of particle ensembles. The DPD fluid is mesoscopic in character, while the colloidal particles represent a soft-sphere fluid usually applied for simulating microscopic ensembles. The problem lies in the matching of these two models, i.e., in defining the particular colloid/solvent interactions. Assuming that they are represented by the DPD forces and the colloidal particles interact only via the L-J potentials, we find that the colloidal particles will aggregate for a sufficiently deep L-J well $\varepsilon$. The fractal aggregates of internal hexagonal structure (see Fig. 3) are created. The results we obtained from simulation, shown in Fig. 3, are very similar to those obtained in the Skjeltrop experiment (20).

However, such kinds of interactions will not produce the micellar ordered structures created by real surfactant micelles.
[see, for example, (2, 3, 6, 7)], due to the repulsive DPD forces and the central character of CP–CP interactions. For example, the copolymers produce spherical micelles with compact, insoluble cores surrounded by a polymer brush, which interacts in a very complex way with the solvent. As shown in (21), the micelles can also have rod-like structures and can produce worm-like crystal arrays (22). Therefore, we have decided to use the L-J potential to describe the interaction between CP and DP particles. Thus we can model the attractive bonding forces between solvent and colloidal particles. Because both CP–CP and CP–DP interactions are represented by the same formula, we can easily control their mutual relations by varying the depths of their L-J potential wells \(\varepsilon\).

In the following sections we show that by introducing conservative L-J interactions between the colloid particles and solvent DPD particles, we can simulate the spontaneous creation of micelles and their aggregation in 2D crystal arrays.

### 3. Simple Ordering in a Discrete Particle Liquid

Unlike the MD simulations in which the particles represent atoms with a known size subject to experimentally determined forces, the DPD beads do not correspond to real atoms or molecules. They represent a “lump of fluid” of unknown size. The problem of matching the spatiotemporal scale of DPD fluid and its properties defined by scaling factors of DPD interactions to the real substances remains unresolved. In general, two approaches are used. The first one consists of mapping the interactions onto macroscopic parameters of fluid, e.g., viscosity, compressibility, diffusion coefficient, by using kinetic theory equations or, as is presented in (19), onto Flory–Huggins theory in the case of a polymer mixture. As shown in (15, 19), under some conditions, this approximation yields realistic results. But it does not resolve the problem of matching the spatiotemporal scales of DPD simulation to the actual physical scales. This is the principal reason that in the majority of DPD simulations presented in the literature (10, 13, 14, 18) dimensionless units are used, and the bead mass, radius of interactions, and also time step are set to unity.

The second approach, which should resolve the spatiotemporal problem of DPD simulation and improve the crude approximations of scaling factors of DPD interactions, consists of application of the MD technique to simulation of DPD clusters. However, such a cross-scaling, bottoms-up approach is still in the stage of infancy, although serious theoretical investigations have been conducted (11, 12).

In our simulations we used the first approach, by matching the scaling factors of DPD interactions to the macroscopic properties of fluid as shown in (15) in which the continuum limit equations are obtained from kinetic theory (11).

In Table 1 we present the simulation parameters used in our 2D simulations. We assume that \(r_c\), \(\Delta t\), and \(M = M_{\text{CP}} = M_{\text{DP}}\) are equal to unity. The value of \(\varpi\), the scaling factor for conservative DPD forces, which is responsible for the compressibility of the DPD fluid, is chosen such that the DPD particle system exhibits liquid ordering on the mesoscale; i.e., its RDF is characteristic of the liquid phase. As is suggested in (19), the value of \(\varpi\) was computed assuming that the DPD fluid has a compressibility characteristic of water. The energy unit \((e_{\text{Unit}})\) is set artificially as a reference point for scaling both the L-J CP–CP and CP–DP interactions. It is equal to the \(\varepsilon\) parameter of the L-J force, for which the maximum value of the attractive part of the L-J force is equal to the respective absolute value of the DPD conservative force.

As discussed in the previous section, the solvent molecules are usually several orders of magnitude smaller than the colloidal particles. The problems with simulating an ensemble consisting of particles of such different sizes result from the different time scales on which the both types of particles evolve. By approximating the solvent by using DPD particles of the same size as the colloidal particles, we have met the requirements of both scales. Therefore, the \(\sigma\) parameters in L-J CP–CP and CP–DP interactions, which define the particle sizes, have the same values. The particle density \(n\) is such that the number of particles in cutoff radius \(r_c\) is about 20, as is usually assumed in standard 2D MD and DPD simulations (13, 14, 23–25). The same concerns \(r_c/\lambda\) and \(r_c/\sigma\) ratios, which are set at 2.5 (26). That is the reason for setting the cutoff radius equal to unity; \(\sigma\) is set to 0.4 (in dimensionless units).

The mass variation, physical property, and variations in density effects can be simulated by using different masses of DPD and colloid particles and/or different particle sizes for the

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**TABLE 1**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (in dimensionless units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire particle system</td>
<td></td>
</tr>
<tr>
<td>(r_c)</td>
<td>unit of length 1</td>
</tr>
<tr>
<td>(\Delta t)</td>
<td>unit of time 1</td>
</tr>
<tr>
<td>(M = M_{\text{CP}} = M_{\text{DP}})</td>
<td>unit of mass 1</td>
</tr>
<tr>
<td>(n)</td>
<td>particle density 6.37</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>average distance between neighboring particles 0.4</td>
</tr>
<tr>
<td>(\varepsilon_{\text{Unit}})</td>
<td>system size in (r_c) units 28–84</td>
</tr>
<tr>
<td>(T_0)</td>
<td>units of energy 4.75 \times 10^{-5}</td>
</tr>
<tr>
<td>(\Omega = \gamma r_0/2v_0^2(u^4/(kT/M)^{1/2}))</td>
<td>system thermal velocity 10,100</td>
</tr>
<tr>
<td>(\pi)</td>
<td>scaling factor for conservative forces 3.8 \times 10^{-3}</td>
</tr>
<tr>
<td>CP–CP interactions</td>
<td></td>
</tr>
<tr>
<td>(\varepsilon_{\text{CP–CP}})</td>
<td>L-J well depth 0.2–1.6(e_{\text{Unit}})</td>
</tr>
<tr>
<td>(\sigma_{\text{CP–CP}})</td>
<td>L-J parameter 0.4</td>
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<tr>
<td>CP–DP interactions</td>
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<tr>
<td>(\varepsilon_{\text{CP–DP}})</td>
<td>L-J well depth 0.1–1.6(e_{\text{Unit}})</td>
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<tr>
<td>(\sigma_{\text{CP–DP}})</td>
<td>L-J parameter 0.4</td>
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</tbody>
</table>
solvent and colloid. From a computational point of view the first approach is easier. In our simulations the masses and sizes for both types of particles were are set at unity and density variations arise only from the pressure fluctuations.

We define the value $\Omega = \gamma r_c/v^T$, which along with dimensionless parameters $\mu$ and $\lambda$ (see Table 1) fixes the dynamical regimes of the particle model (26). The ratio $r_c/v^T$ represents the time taken by a particle covering a distance $r_c$ at the thermal velocity $v^T$, while $\gamma^{-1}$ is the time associated with friction. Thus, the $\Omega$ value represents for the kinematic viscosity of DPD particle system (26). The scaling factor for the dissipative component of the DPD force, defined by the dimensionless $\Omega$ parameter, is set at 10 or 100. For $\Omega$ values greater than 100 the integration scheme becomes numerically unstable but $\Omega = 10$ yields reasonably fast relaxation for medium temperatures between $0.1 \varepsilon_{\text{Unit}}$ and $\varepsilon_{\text{Unit}}$.

The system size depends on the total number of particles $M$. Due to the long simulation times required to obtain ordered structures for some simulation conditions, we use a small number of particles $M = 5000$ and $M = 45,000$ in long runs, typically $N = 10^6$ time steps. The $\delta$ coefficient in the Brownian component of the DPD collision operator (Eq. [4]) can be computed with the formula (13, 14, 26)

$$\delta_{kl}^2 = 2 \cdot \gamma_{kl} k_B T M_{kl}. \quad [9]$$

We assume that initially the CPs and DPs are perfectly mixed and the temperature of the system is isothermal at $T_0$.

In Fig. 4 we show the temporal changes in temperature, pressure, and average number of particles in the cutoff radius for a

![Fig. 4](image-url)

**Fig. 4.** Temporal changes in thermodynamic properties of the CP–DP binary particle system (in dimensionless units): (a) temperature of solvent particles; (b) thermodynamic temperature of colloid particles; (c) average partial pressures in solvent (DP) and colloid (CP) particle systems; (d) average number of particles within the cutoff radius. The assumed temperature $T_0 = 0.1 \varepsilon_{\text{Unit}}$ and pressure $P = 0.006$. 
CP–DP binary particle fluid. The system consists of 40,000 DPs and 5000 CPs. As shown in Figs. 4a and 4b, the temperature fluctuations for the colloidal particles are greater than those for the dissipative particles, because there are fewer CPs than DPs and there is a lack of dissipative components in CP–CP and CP–DP interactions. Due to the clustering of the colloidal particles, the temperature $T_{Th}$ of the system, computed as the average kinetic energy of the particle systems, should decrease. However, because the number of dissipative particles is usually a few times greater than the number of colloidal particles, $T_{Th}$ stabilizes very close to $T_0$ within a relatively short time. Thus, dissipative particles can stabilize the temperature of the entire system. As shown in Fig. 4c, the partial pressure $P_{Th}$ of the DPD fluid computed from the virial theorem [see, e.g., (24)] is also approximated accurately by the continuum limit equation

$$P_{k\neq l} = \frac{n \cdot \pi_k \langle r \rangle}{2D}, \quad [10]$$

where $\langle r \rangle = \frac{1}{2} r_c$ and $D = 2$ for a two-dimensional system ($D = \text{dimension of the system}$).

In Fig. 5 we present two snapshots from the DPD simulation for both the low (Fig. 5a) and high (Fig. 5b) kinematic viscosities ($\Omega = 10$ and $\Omega = 100$, respectively). As discussed above, for both cases the viscosity is locally variable depending on the local concentrations of the two species and their gradients. We note that physical properties, such as viscosity, have many scales, as reflected in Fig. 5. In Fig. 6 we show a zoomed-in snapshot...
FIG. 6. Zoomed-in fragment of a snapshot from the same simulation as shown in Fig. 5a but for $N = 40,000$ time steps. Colloidal particles are in white and dissipative particles are cast in dark gray.

from the first simulation at an earlier instant and in Fig. 7 is the temporal evolution of the colloidal array enclosed in the white rectangle in Fig. 5a. As shown in Fig. 6, the spherical micelles appear initially. They consist of a single CP particle surrounded by a few DP particles. They aggregate in clusters and create rod-like micelles, which build up worm-like arrays. After some time the character of the aggregation process changes and, as shown in Figs. 5 and 7, larger and larger worm-like structures are agglomerated from the smaller ones.

This change is reflected in Fig. 4d by the sudden jump in the slope of logarithmic increase in the average number of particles within the cutoff radius. We compare this figure with Fig. 8, where the temporal change in the average number of CPs in rod-like micelles is plotted against the number of time steps. From these two plots we may conclude that the aggregation of large worm-like structures overtakes the process of creation of rod-like micelles after about $7.0 \times 10^4$ time steps. As shown in Fig. 8, the speed of worm-like structure aggregation is approximately the same at the low and high viscosities of DPD fluid. However, the time needed to produce rod-like micelles from spherical ones is much longer than for more viscous DPD fluid.

All the simulation results presented here were obtained at $\pi = 3.8 \times 10^{-3}$. For 50% greater values of $\pi$, and thus a greater partial pressure in DPD fluid, the aggregation process becomes faster and then slows due to “freezing” of DPD fluid (15). The temperature used in the simulation $T_0 = 0.1 \varepsilon_{\text{int}}$ is optimal. For a lower $T_0$ the process of micelle aggregation slows down and for higher $T_0$ the micelle structures melt.

Depending on the $\chi = \varepsilon_{\text{CP-CP}}/\varepsilon_{\text{CP-DP}}$ ratio and $\{\varepsilon_{\text{CP-CP}}, \varepsilon_{\text{CP-DP}}\}$ values, we can obtain various colloidal array forms made of different micelles. The simplest form of micelle and colloidal array observed for a broad spectrum of $\chi = \varepsilon_{\text{CP-CP}}/\varepsilon_{\text{CP-DP}}$ values (from $5:2$ up to $1:5$) is shown in Figs. 9a, 9b, 9c, and Fig. 10a.
The micelles consisting of one CP surrounded by eight DPs create hexagonal arrays. Similar spherical micelles with surfactant brush are created by copolymers in solvent (2), whose rheological properties (21) are used in lubricating oils, which have a strong temperature dependence on viscosity. We note the striking similarity in the patterns shown in Figs. 9a and 9b, the hexagonal arrays produced in 2D crystallization of latex particles in thin latex film (3), and the metastable colloidal crystals drifting in colloid fluid (4) found in laboratory experiments.

For lower values of $\chi$, the separate, stable, two-shell micelles appeared with a few DPs in the center surrounded by a shell consisting of six CPs formed in a perfect hexagon and several DPs in the external shell (see Fig. 10b). These micelles appear also for larger values of $\chi$ but die out very quickly. When $\chi$ is lower, they merge in groups of two or three but do not produce larger clusters. Similar micelles, but without the external shell, produce the arrays for $\chi = 8$ (see Figs. 9c, 10d). The rod-like structures, similar to a spherical structures, appear very often in colloidal suspensions (21) and in biological cells (27) (see Fig. 10e). The aqueous micellar solution of hexadecyltrimethylammonium bromide in the presence of potassium bromide (22) produces worm-like structures but the tetrametric protein streptavidin is bound to a partially biotinylated lipid monolayer (2), elongated 2D colloid arrays similar to these shown in Figs. 5, 9d, and 11.

4. SUMMARY

Our DPD simulations reveal clearly the bright prospects of the dissipative particle dynamics method as applied to simulating complex fluids and their sharply varying physical properties, such as viscosity, on the mesoscale. Some properties of complex fluids, such as micelle aggregation in ordered arrays in colloidal suspensions, can be obtained numerically by assuming a (12-6)
FIG. 9. Multiscale nature of snapshots taken from a simulation with 5000 particles (CPs = 1000, DPs = 4000) in $10^4$ time steps. Colloidal arrays obtained for different values of $\text{CP–CP}$ and $\text{CP–DP}$ in L-J interactions. (a) $\text{CP–CP}/\text{CP–DP} = 2 : 3$ ($\text{CP–CP} = 0.4\sigma_{\text{LJ}}$); (b) same as for (a) but CPs = 500; (c) $\text{CP–CP}/\text{CP–DP} = 5 : 1$ ($\text{CP–CP} = 1 \sigma_{\text{LJ}}$); (d) $\text{CP–CP}/\text{CP–DP} = 1 : 5$ ($\text{CP–DP} = 1 \sigma_{\text{LJ}}$); (e) $\text{CP–CP}/\text{CP–DP} = 8 : 0.5$ ($\text{CP–CP} = 1.6 \sigma_{\text{LJ}}$); (f) zoomed-in rectangle from (e). The local physical properties vary strongly spatially.
L-J model of interactions between colloid–colloid and colloid–solvent particles in the solvent DPD fluid. We show that the change in interaction coefficients results not only in the creation of various forms of colloidal arrays but also in the aggregation of different forms of micelles. The spherical and rod-like micelles obtained spontaneously in 2D DPD simulations and the forms of arrays they produce reveal many similarities to the colloidal structures observed in nature (2–5).

We may conjecture that the application of more realistic CP–CP and DP–DP potentials allows one to employ the particle model as a useful tool for the testing of new nanoscale materials. The L-J potential should be replaced in the future by an effective “depletion potential,” or by direct simulation of depletion forces assuming a much smaller diameter of solvent particles. Asymmetric colloid–solvent potential (e.g., three-body potentials) can be also used. It is justified, e.g., for polymer solvents. We can simulate polymer chains in the same way as is done in (19) joining monomers in polymer chains by using a harmonic spring-like potential. All these modifications are recommended for future investigations. We must bear in mind that the calculations will be more expensive from a computational point of view. For example, the application of the hard sphere with depletion adhesive potential or DLVO potentials [see review papers (1, 2)] requires much more computational power due to the considerable decrease in the Δt value. This drawback results from the very short range of CP–CP and CP–DP attractions and the steep repulsion between particles. Typical runs for $M = 5 \times 10^3$ particles simulated in $10^8$ time steps require 5 h of CPU time on a single SGI Origin 2000 R12000 processor.

No attempt was made here to perform simulations that might control the extent and type of anisotropy for the micelle structures. We regard this step as being premature. The influence of various types of interactions (other than L-J) on the micellar patterns created should be examined first.

The DPD-MD model can be used also to simulate the Turing pattern in reaction diffusion systems and interface dynamics described in (28). Our results on interface dynamics simulation...
in Rayleigh–Taylor mixing, using both pure MD technique and the DPD paradigm, were presented in (29–31).

Finally, we surmise that the spontaneous creation of micelles and micelle arrays in an initially premixed CP–DP 2D particle system confirms the elementary lesson of complexity articulated by Goldenfeld and Kadanoff (32) that “nature can produce complex structures even in simple situations, and can obey simple laws even in complex situations.”

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