HNUE JOURNAL OF SCIENCEDOI: 10.18173/2354-1059.2021-0043Natural Sciences 2021, Volume 66, Issue 3, pp. 20-28This paper is available online at http://stdb.hnue.edu.vn

TEMPLATE-SHAPE DEPENDENCE ASSEMBLY OF JANUS NANOPARTICLES AT WATER-OIL INTERFACE

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Abstract. In this work, we investigated the crystal formation of anisotropic nanoparticles, namely Janus particles, at the water-oil interface using the dissipative particle dynamics simulation method. By considering three different interface templates, including planar, droplet, and rod, we observe an increase of the disorder-order transition packing fraction with increasing the curvature radius of the templates. Furthermore, the nanoparticles in the planar template assemble into a hexagonal lattice, while for the two remaining templates they aggregate into colloidsome-like structures.

Keywords: pickering emulsions, water-oil interfaces, DPD simulations.

1. Introduction

A Pickering emulsion is an effect in which nano/micro-sized particles are stabilized at the interface between the two phases, e.g. water and oil [1]. Pickering emulsion has been extensively studied due to many potential applications, including crude oil separation [2-3], biofuel [4-5], drug delivery [6], and food preservation [7]. In order to extend these applications, investigation of the self-assembled structure of nanoparticles (NPs) at an interface via Pickering emulsion is essential.

In recent years, numerous experimental studies have attempted to describe the stability of the nanoparticle at the interface [8-11]. Shuting et al. [11] prepared Janus nanoparticles with tunable amphiphilicity for stabilizing droplets via assembly at oilwater interfaces. The authors showed that the stability of Pickering-emulsions is dependent on the adhesion energy at the water-oil interfaces. Using dissipative particle dynamics, Striolo et al. [12] investigated the structural and dynamical properties of various systems of nanoparticles assembled at the water/oil interface. Notably, with an increase of the surface packing fraction, a transition from a disorder to an order state is observed. Later, Striolo et al. [13] extended their work by considering ellipsoidal Janus nanoparticles. It was shown that for nanoparticles

Received June 30, 2021. Revised October 15, 2021. Accepted October 22, 2021.

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of a high aspect ratio, steric effects seem to cause an isotropic-to-nematic phase transition as the packing fraction increases.

It was known that oil-water interfaces have been widely used as a platform for selfassembly of amphiphilic nano- and micro-sized particles into hierarchical structures [14, 15]. The shape of oil-water interfaces depends on the minimization free energy ΔG , which is in the order $\Delta G_{plane} > \Delta G_{rod} > \Delta G_{sphere}$ [16]. Additives are normally used to control the shape of oil-water interfaces in experiments [16].

To our best knowledge, however, there is no report on the role of the oil-water interface shape on the resulting structure of nanoparticles. In addition, the concentration of Janus nanoparticles at spherical confinement in which the disorder-order transition occurs has not been studied. In this work, we examine a self-assembled behavior of Janus nanoparticles interacting with each other at the water-oil interface, using different interfaces to find the surface packing fraction so that when the system stabilizes, the nanoparticles are arranged in the order state or other close-packed structures. Our work could be helpful to prepare more complex nanostructures by simply tuning the geometry of water-oil interfaces. Moreover, the current model can be easily extended to two-component systems (colloidal alloys) that include two types of nanoparticles with different sizes or chemical behaviors. Such complex systems or low-coordination architectures, such as diamond, pyrochlore, and other sought-after lattices, possess a wide range of potential for photonics applications [17, 18].

2. Content

2.1. Models and computational methods

Dissipative particle dynamics (DPD) is a simulation method for particle dynamics [19]. The motion of particles is calculated by solving the equations of motion over a certain time span. The equations of motion describe how particles move under the influence of forces. In DPD, the motion of the particle is simulated at a constant temperature under a special thermostat. DPD uses a stochastic and momentum conserving thermostat, which distinguishes the method from Brownian or Molecular Dynamics.

Consider a set of interacting beads with uniform mass m. Let r_i be the position of bead i and v_i be its velocity. The change in the position and velocity over time is given by the equations of motion [19].

$$\frac{\partial \mathbf{r}_i}{\partial t} = \mathbf{v}_i \quad ; \quad \frac{\partial \mathbf{v}_i}{\partial t} = \mathbf{f}_i \tag{1}$$

Where f_i is the force on bead i due to interaction with the other beads. In general, this force can be written as:

$$\mathbf{f}_{i} = \sum_{i \neq j} \left(\mathbf{F}_{ij}^{C} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R} \right) + \mathbf{f}_{i}^{s} + \mathbf{f}_{i}^{A}$$
(2)

The term in brackets is the force due to the interaction of bead i with its neighbor, j, whether bonded or not. This term has three components: conservative (C), dissipative (D), and random (R) forces. The remaining terms are forces due to bonded interactions:

springs (S) and angles (A). A detailed description of the DPD formalism can be found in the literature [20].

We carried out the DPD simulations using Mesocite program [21], a molecular mechanics module for potential energy, geometry optimization, and classical dynamics calculations. Here, beads are used to present water, oil, and nanoparticles [12]. One bead describes five water molecules, while two beads represent oil molecules (decane) to ensure that the mass of the bead is about 90 atomic mass units (ca. 90 amu). Two oil beads are connected by a harmonic spring. To represent the Janus nanoparticles, we used two different beads: apolar (ap) beads and polar (p) beads. In principle, one can change the contact angle of nanoparticles at the oil-water interface by tuning the ratio between the number of apolar beads and the number of polar beads. For simplicity, we fix this ratio to be 0.5, or equivalently the contact angle of 900. Each spherical nanoparticle consisted of 192 beads, with a diameter of $15R_c$ where $R_c = 7.66$ nm is the cutoff radius. Following the work by Groot et. al. [22], we estimate the interaction parameters between the constituent beads using the compressible behavior of fluids. All necessary DPD interaction parameters are given in Table 1.

Table 1. Self-interaction parameters used in the DPD simulations (in k_BT/R_c units)

	water	oil	apolar	polar
water	131	198	178	110
oil		131	161	218
apolar			450	670
polar				450

In Figure 1, we show an example of the initial configuration of the simulated system. Water and oil demix, and nanoparticles whose apolar/polar beads are randomly initialized, adsorb at the water-oil interface. The interface may be like a spherical droplet or planar by choosing an appropriate parameter in Mesocite. Due to the constraint of periodic boundary conditions, all interfaces are inside the simulation box with a size of $V = L_x \times L_y \times L_z = 30 \times 40 \times 30 \times R_c^3$



Figure 1. Representative snapshot containing an immiscible mixture of water bead and oil bead Oil beads form a spherical droplet and Janus particles adsorb onto it

Template-shape dependence assembly of Janus anoparticles at water-oil interface

We performed each simulation for 106-time steps, which is equivalent to the realistic time of ca. 30 nanoseconds (ns). The other necessary parameters in the DPD simulations are given in Table 2.

Initial velocities	Random	
Temperature	298 K	
Time step	254 fs	
Dissipation strength	0.08854 amu/fs	
Dissipation radius	9.0 Å	

2.2. Results and discussion

The timescale in the DPD simulation is an important parameter to determine whether the system is in equilibration or not. Figure 2 shows the energy quantities such as potential, kinetic, non-bond energy as a function of time. The energies reach constant values after a timescale of 5s. Note that although such a timescale in DPD is much smaller than that of experiments (last minutes to hours) it is commonly used in the simulation of the fluid systems [23]. In addition, a relatively small difference in the potential energy and non-bond energy indicates that most the beads are in free Brownian motion [24].



Figure 2. Time-dependent energies for systems simulated

We consider three different shapes of the oil template, including the sphere, slab, and rod, with a constant surface area at $S = L_x \times L_z = 900R_c^2$, but changing the packing fraction of particles that is defined as $\eta = \frac{N \times \pi R^2}{S}$ where N is the number of Janus

particles, R is the radius of nanoparticles and S is the area of the oil template which is dependent on the radius of droplets. Here, R is kept fixed, while S and N are varied to tune η .

Figure 3 shows a top-view snapshot of the system for the case of the planar slab template obtained in the final stage of the simulation for N = 85 or equivalently η = 59.33%. The nanoparticles self-assembled into a two-dimensional hexagonal lattice. By subsequently increasing N in the range 75 - 90, we find a disorder- order transition η to ca. 59.33%, in good agreement with the experimental and simulation [12].



Figure 3. Top view snapshot of the hexagonal structure dense tightly for the number of nanoparticles of 85

Similarly, we change the number of particles on the droplet template while keeping the surface area of the droplet template to be the same as the slab template. Notably, for only $\eta = 35\%$ in the case of the droplet template, which is significantly smaller compared to that of the slab template, we observe a disorder-order transition. We interpret this as a result of a distinct difference in the curvature radius between the spherical droplet (Rdroplet / RC = 4.23) and planar (Rslab / RC = ∞).

In order to investigate the role of the curvature radius on the phase transition η , we consider a variety of different spherical templates. As shown in Figure 4, at a low packing fraction ($\eta = 30\%$), the nanoparticles diffuse freely on the droplet surface and therefore do not pack together to crystallize. Upon increasing the η to 35% leads to the formation of the crystal region. In particular, a further increase of η up to 40% deforms dramatically the droplet template, causing this to the non-spherical surface. This can be due to the presence of a large number of particles with strong pairwise interaction and shear effect applying on the oil droplet under hydrodynamic conditions. Note also that the curvature radius of the droplet template has a little effect on the structural transition packing fraction.



Figure 4. Packing of nanoparticles on the droplet surface at the different numbers of particles and different droplet ameters

For the rod-shaped template, we show in Figure 5 the crystallization process and find out the tightly packing fraction at which occurs the disorder-order transition to be 26%, which is quite smaller than that of the droplet-shape template (35%). It should be noted that for the droplet template, colloids self-assembled into a particular structure, like microcapsules. Dinsmore introduced such microcapsules as colloidsomes whose shells are composed of colloidal particles [25]. Colloidsomes offer significant flexibility concerning microcapsule functionality [26].



Figure 5. Packing of nanoparticles on the rod-shaped template at different packing fractions

3. Conclusions

In this work, we have investigated the disorder-order transition of Janus nanoparticles on some templates with different shapes using the means of the DPD simulations. We find that among the three templates used, the rod template possesses the smallest η , with a value of 26%, while the spherical template $\eta = 35\%$. The largest η value obtained in the planar template is 59.33%. Those results suggest that the geometry of templates plays an important role in the formation of crystallization of Janus nanoparticles at the water-oil interface. By visualizing the snapshots, we observe also the two-dimensional hexagonal lattice in the planar interface, but the colloidsome-like states [27] in the spherical and rod templates. Further work could be towards by evaporation of these templates to force the nanoparticles to pack together into more complex superstructures.

Acknowledgment. Kongxiong Xatyeng thanks the financial support from the Fundamental Research Program (2021) of the Institute of Physics, Vietnam Academy of Science and Technology.

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