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Field-modulated structural transformation of planar binary dipolar hard spheres

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Abstract

Monte Carlo simulations are used to study the structural transformation of binary dipolar hard spherical particles. The particles are confined in a homogeneous plane and each dipole can orient out of the plane. Any two dipoles are parallel with each other when they belong to the same kind of particle, but antiparallel for the different kinds of particles. When the orientations of the dipoles rotate from being perpendicular to the plane to being parallel with the plane, various morphologies, such as the isotropic clusters, anisotropic clusters, an expanded block, long chains, and columns, emerge sequentially. We study the transformations between these structures by analyzing the orientation of the linking lines between the nearest neighbors, radius distribution functions and the average energies. In addition, numerical calculation of the energies of four ideal structures is carried out for the comprehension of these transformations.

1. Introduction

Dipolar interaction is widespread in colloidal suspensions such as ferrofluids, electrorheological and magnetorheological fluids [1–6]. These systems continue to attract attention from researchers for their special properties which originate from the anisotropy of the dipolar interaction. For example, the dipolar interaction makes colloids form chains and these chains will further self-assemble into networks which prevent the normal gas–liquid transition in dipolar fluids [7, 8]. Despite the lack of a gas–liquid transition, a special phase separation was presented by Tlusty and Safran [9], in which the components are the different kinds of chain defects. Apart from their significance in the fundamental research of statistical physics, dipolar fluids have extensive potential in industrial applications. The dipoles of colloids may be electric or magnetic in nature, and both types can interact with external fields. So dipolar fluids, because of their ability to vary their rheological and mechanical properties under the modulation of external fields, can be used to manufacture clutches, brakes, switches, etc [4, 6].

When the particles are confined in a plane (assumed the x–y plane) their dipoles can orient in three-dimensional space; this system is called a quasi-two-dimensional (Q2D) dipolar system [10] and has been studied through experiments [11–13] and computer simulations [14–18]. These studies focus on structure formation [11–13, 16, 17], phase separation [14, 15, 18], and dynamic properties [17, 18], respectively. External fields have a notable influence on the structure and properties of Q2D dipolar systems [12, 13]. The influence of a tilted field on a Q2D dipolar system has been studied by Weis [19]. Increasing the included angle between the field and the z-axis (the normal of the x–y plane), three structures emerge in the sequence of isotropic fluid, chains and columns. The systems in the above research [10–19] only contained one kind of dipolar particle. Recently, Ristenpart *et al* [20] have experimented with a planar structure of binary colloidal suspensions. Each colloidal particle possesses a dipole induced by an ac electric field which is perpendicular to the plane. In the high-frequency field, dipoles belonging to the different kinds of colloids are antiparallel with each other. Varga *et al* [21] studied the same system through molecular dynamics simulations and the simulation results agree well with the experiment [20]. In their work, the real dipoles are modeled by point-like dipoles with fixed moments embedded in the center of the particles. Another system composed of binary macroscopic dipolar particles has been studied through theoretical analysis and experiments [22, 23], and presented similar structures to the colloidal system [20].

In the simulations described in [14–19], there is only one kind of particle in the system. The dipoles of all particles

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are parallel with each other in such a system in a strong external field [19]. For a binary system [20], the dipoles belonging to the different kinds of particles are antiparallel with each other, so there are some novel structures relative to the system composed of one kind of particle. In previous studies [20–23] on the binary dipolar system, the dipoles of particles were perpendicular to the plane. Inspired by the work of Weis [19], which studied the influence of a tilted external field on the structure of Q2D single-type dipolar hard spheres, we will study in this work the influence of the orientation of an external field on the structure formation of a Q2D binary dipolar system. The paper is organized as follows. First we present the model and the simulation scheme. Then we study the structure of the binary mixture under a tilted field and give some simple theoretical explanations by analyzing the energies of four ideal structures. Finally, a brief summary and some concluding remarks are given.

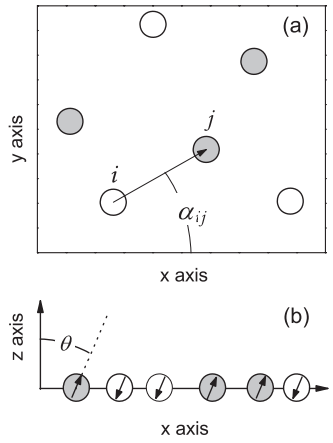

Figure 1. Schematic diagram of the system: (a) top view, (b) side view.

2. Model and method

We consider the mixture of Q2D binary dipolar hard spherical particles. A schematic diagram of the system is illustrated in figure 1. The centers of the particles are confined in the x–y plane and the dipoles of the same (different) kind of particle are parallel (antiparallel) with each other. The x-axis is chosen along the direction of the in-plane component of the dipoles of one kind of particle, and θ is defined as the included angle between the z-axis and the dipoles of this kind of particle. Then the included angle between the z-axis and the dipoles of the other kind of particle is $\theta + \pi$. In the experiment [20], the external field is an ac electric field, so the strength and the direction of the induced dipoles vary periodically. The dipoles belonging to the different kinds of particles are antiparallel with each other due to the different polarizabilities of the particles. Because the period of oscillation of the electric field is very short for the particles moving in the x–y plane, the interaction between two induced dipoles is equivalent to the interaction between two point-like invariable dipoles located at the center of the particles [21]. The particles interact through the potential

$$U_{ij} = \begin{cases} \dfrac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - 3\dfrac{(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5}, & r_{ij} \geqslant \sigma, \\ \infty, & r_{ij} > \sigma, \end{cases} \tag{1}$$

where $\vec{\mu}_i$ is the dipole moment of the ith particle and $\vec{r}_{ij}$ denotes the displacement vector from particle i to particle j. σ is the diameter of the spheres and the two kinds of particles have the same diameter in our study.

In this work, the Monte Carlo (MC) simulations are performed in the canonical ensemble through the Metropolis algorithm. There are $N = 1024$ particles in a square box of length L with periodic boundary conditions, and the packing fraction $\rho = N\pi\sigma^2/(4L^2)$ is 0.2. Another packing fraction $\rho = 0.4$ is also used in our simulation. But there is no new structure relative to $\rho = 0.2$, so the result about $\rho = 0.4$ is not presented in this paper. Half of the particles have dipoles pointing in exactly the same direction $(\sin\theta,\ 0,\ \cos\theta)$, and the other half all point in exactly the opposite direction. The two kinds of particles have the same dipolar strength, and the reduced dipole moment $\mu^* = \mu/(k_{\mathrm{B}}T\sigma^3)^{1/2}$ is 2.75; here k_{B} is Boltzmann's constant and T is the absolute temperature. $\mu^* = 2.75$ is popularly adopted in simulations [10, 15, 17–19] and the interaction strength $2.75^2 k_{\mathrm{B}}T$ is realizable [20]. For every value of θ, the course of the simulations is divided into two parts. In the first part, 10^6 MC steps are executed to preheat the system. μ^* is 1.0 at the beginning and increases by $(2.75 - 1)/99$ every 10^4 steps. In the second part, another 10^6 MC steps are executed to collect data which are picked every 10^4 steps. All particles try to move in the x–y plane randomly once a MC step. Ewald summation [10, 24] is used to treat the long-range dipolar interaction. The relative parameters are chosen as in [25], such that the cutoff in real space is $L/2$, the cutoff in reciprocal space is $8 \times (2\pi/L)$ and so on. To facilitate the movement of the particles, we use the cluster move [26] in the simulations and the cluster is defined by the requirement: if $r_{ij} < 1.2\sigma$, then particles i and j belong to the same cluster.

When $\theta \neq 0$, there are nonzero x-components for the dipole moments. From equation (1), it can be found that there is no interaction between different directional components of the dipole moments, so we can consider the dipolar interactions between the z-components and between the x-components of any two particles separately. For the convenience of discussion, we define $U_{ij}^{\parallel}$ as the interaction between the x-components of two spheres and $U_{ij}^{\perp}$ as the interaction between the z-components. They read

$$U_{ij}^{\parallel} = \frac{\mu_i^x \cdot \mu_j^x}{r_{ij}^3} - 3\frac{(\mu_i^x \cdot x_{ij})(\mu_j^x \cdot x_{ij})}{r_{ij}^5}, \qquad U_{ij}^{\perp} = \frac{\mu_i^z \cdot \mu_j^z}{r_{ij}^3}, \tag{2}$$

where μ_i^x and μ_i^z are the x-component and z-component of the dipole $\vec{\mu}_i$ respectively, and x_{ij} is the x-component of $\vec{r}_{ij}$. When particles i and j are of the same (different) kind, $U_{ij}^{\parallel}$ and $U_{ij}^{\perp}$

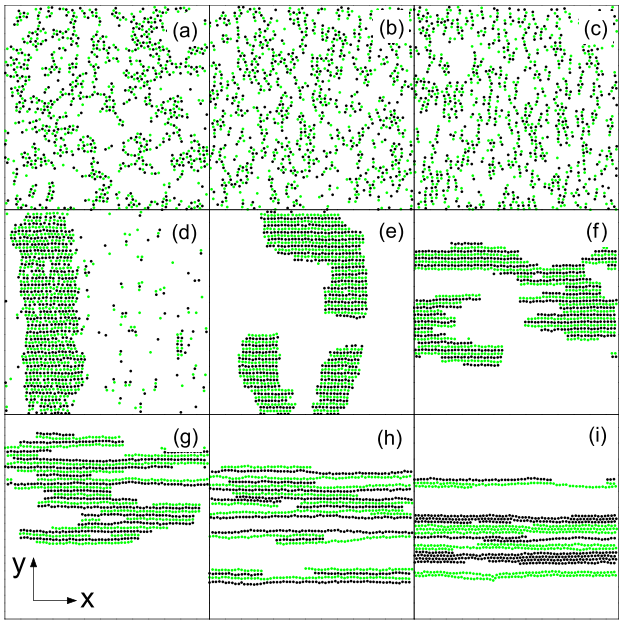

Figure 2. Snapshots of the configurations of 1024 Q2D binary dipolar spheres with the dipole moment $\mu^* = 2.75$ and the density $\rho = 0.2$. From (a) to (i), the value of included angle θ is 0°, 20°, 30°, 40°, 50°, 60°, 70°, 80°, and 90°, respectively.

(This figure is in colour only in the electronic version)

can be simplified to $U^{\parallel}_{ij,\,\mathrm{s}}$ ($U^{\parallel}_{ij,\,\mathrm{d}}$) and $U^{\perp}_{ij,\,\mathrm{s}}$ ($U^{\perp}_{ij,\,\mathrm{d}}$) as follows

$$U^{\parallel}_{ij,\,\mathrm{s}} = \frac{\mu^2}{r^3_{ij}} \sin^2\theta \left(1 - 3\cos^2\alpha_{ij}\right), \qquad U^{\perp}_{ij,\,\mathrm{s}} = \frac{\mu^2}{r^3_{ij}} \cos^2\theta,$$
$$U^{\parallel}_{ij,\,\mathrm{d}} = \frac{\mu^2}{r^3_{ij}} \sin^2\theta \left(3\cos^2\alpha_{ij} - 1\right), \qquad U^{\perp}_{ij,\,\mathrm{d}} = -\frac{\mu^2}{r^3_{ij}} \cos^2\theta, \tag{3}$$

where α_{ij} is the included angle between $\vec{r}_{ij}$ and the x-axis, and $\cos^2\alpha_{ij} = x^2_{ij}/r^2_{ij}$. It is clear that both $U^{\perp}_{ij,\,\mathrm{s}}$ and $U^{\perp}_{ij,\,\mathrm{d}}$ are isotropic, and the former is repulsive while the latter is attractive; but both $U^{\parallel}_{ij,\,\mathrm{s}}$ and $U^{\parallel}_{ij,\,\mathrm{d}}$ are anisotropic, and the former demands the same kind of particle to align along the x-axis while the latter demands different kinds of particles to align along the y-axis. $U^{\parallel}_{ij}$ is the origin of the structural anisotropy. To investigate the degree of this anisotropy, we define P as the average value of $|\cos\alpha_{ij}|$, and here particle i is the nearest neighbor of particle j. If all nearest neighbors align along the x-axis (y-axis), P will be 1 (0). For the isotropic structures, $P = \int_0^{2\pi} |\cos\alpha| \mathrm{d}\alpha/(2\pi) = 2/\pi \simeq 0.637$. We consider the nearest neighbors between the same kind of particle and between the different kinds of particles, respectively, and use P_{s} to represent P for the former and P_{d} for the latter.

3. Results and discussion

The competition and cooperation between $U^{\parallel}_{ij}$ and $U^{\perp}_{ij}$ give this system complex morphologies. The structures of the system with different θ are illustrated in figure 2. When $\theta = 0$, the particles form many clusters through $U^{\perp}_{ij,\,\mathrm{d}}$, and the whole system is isotropic as $U^{\parallel}_{ij,\,\mathrm{s}} = U^{\parallel}_{ij,\,\mathrm{d}} = 0$. Increasing θ from 0° to 30°, the structure of the system changes from isotropic clusters to anisotropic clusters for the nonzero x-components of the dipole moments. The larger θ is, the more notable the anisotropy will be. When θ increases to 40°, almost all clusters aggregate to form a block which expands in the y-axis as shown in figure 2(d). In this block, the same kinds of particles link with each other to form short chains along the x-axis, and these short chains align side by side along the y-axis with alternative sorts. Increasing θ further, the chains composed of the same kinds of particles become longer and longer, and even a single chain can run through the system along the x-axis when $\theta \geqslant 70°$, as shown in figure 2(g). But, along the y-axis, still different chains link with each other. The chains composed of same kind of particle can partly align along the y-axis at $\theta = 80°$, and this kind of alignment forms obvious columns at $\theta = 90°$ as shown in figure 2(i). In the system of a single kind of dipole, two adjacent columns are separated by a space [19], but in this binary dipolar system different columns link with each other along the y-axis.

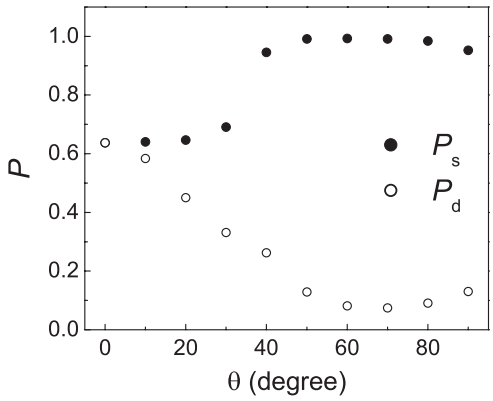

Figure 3. Average absolute value of the cosine of the included angle between the x-axis and the linking line of the nearest neighbors.

To find the detailed information about the structures, we calculate P and the radial distribution functions (RDF) $g(r) = (L^2/N)\langle\sum_{j\neq i}\delta(r - |\vec{r}_j - \vec{r}_i|)\rangle/(2\pi r)$ [27], where r is the distance. P is illustrated in figure 3 as the function of θ, and the RDF is illustrated in figure 4 with various θ. The RDF of the same kind of particle, $g_{\mathrm{s}}(r)$, is shown in the left panel and that of the different kinds of particles, $g_{\mathrm{d}}(r)$, in the right panel. At $\theta = 0$, the simulation results of P_{s} and P_{d} are both about 0.637, which accord well with the theoretical results and embody the isotropic character of the structures. At the same time, both g_{s} and g_{d} are flat and about 1.0 at large distance so there is no long-range order in this system. The minimum of g_{s}, which is about zero, appears at $r = \sigma$. The maxima of g_{s} and g_{d} appear at $r \approx 2\sigma$ and $r = \sigma$, respectively. These extrema embody the character of the clusters, in which different kinds of particles link with each other. Increasing θ from 0° to 30°, P_{d} rapidly decreases from 0.637 to 0.331, because the links between particles of different kinds are obviously along the y-axis. P_{s} shows a small increase because there are only a few links between particles of same kind along the x-axis. These links are also the reason why g_{s} is not zero at $r = \sigma$ when

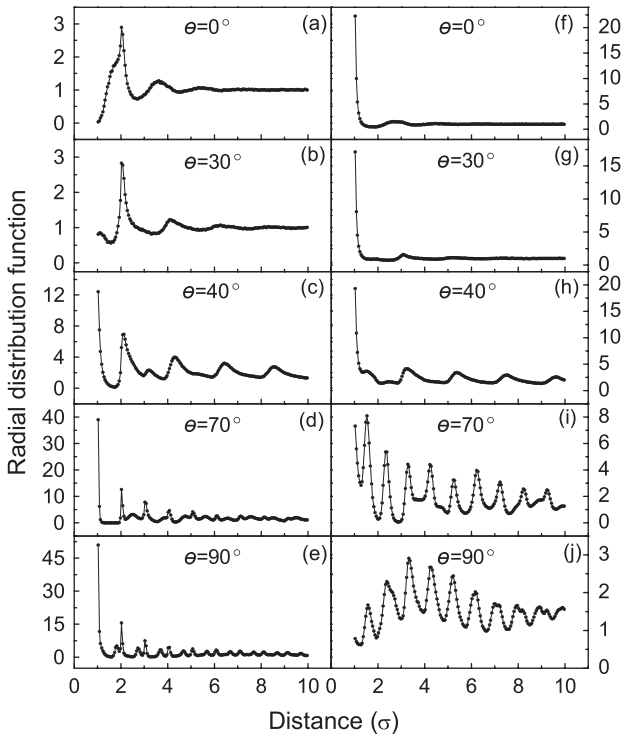

Figure 4. The left panels show the radial distribution functions of the same kinds of particles when the value of θ changes from (a) to (e). The right panels show the radial distribution functions of the different kinds of particles when the value of θ changes from (f) to (j).

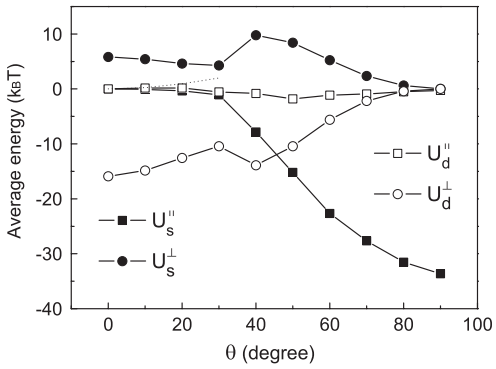

Figure 5. Average energy between two particles as the function of θ. The dotted line is the virtual $U_d^{\parallel}$.

$\theta = 30°$. When $\theta = 40°$, P_s increases a lot relative to $\theta = 30°$ and the value of g_s at $r = \sigma$ becomes a maximum. These two results are caused by the formation of short chains which are composed of the same kinds of particles and along the x-axis. The block composed of these short chains fluctuates g_s and g_d within the whole range of distance that we consider. Increasing θ from 40° to 90°, P_s reaches its maximum at $\theta = 50°$ and has a little decrease later for the formation of the columns, while P_d reaches its minimum at $\theta = 60°$ and has a little increase later for the same reason. When $\theta = 70°$, g_s and g_d fluctuate more frequently for the formation of long chains. When $\theta = 90°$, g_s has many regular peaks, which indicates that the same kinds of particles are arranged regularly in the columns. At the same time, the different kinds of particles can link with each other only at the borders of two adjacent columns, so g_d is small relative to $\theta = 70°$.

In figure 5, we plot the average energy $U_a^b = \langle U_{ij,a}^b \rangle$ versus θ for the investigation of the role played by the orientation of the applied field in the structural transformation; here $a \in \{s, d\}$ and $b \in \{\parallel, \perp\}$. We pick up these energies from the configurations obtained in the Monte Carlo simulations. The Ewald summation can be used to calculate the total energy of the system easily, but it is not feasible to calculate the energy between particles of same kind and that of different kinds, respectively, because the energy of the reciprocal space is not expressed as the summation of the pair interactions [25]. For this reason, here we substitute the Ewald summation by the simple truncation. The length of the truncation is $L/2 \simeq 31.7\sigma$ in our calculation, while 5σ is in fact enough for truncation in Q2D dipolar system [17, 28]. When $\theta \leqslant 30°$, $U_d^{\perp}$ is the dominant factor for the structure. Both $U_d^{\perp}$ and $U_d^{\parallel}$ are attractive, so they can cooperate with each other. $U_d^{\perp}$ links different kinds of particles and $U_d^{\parallel}$ makes these links anisotropic. The influence of $U_d^{\parallel}$ on the structural anisotropy is estimated through the following calculation. We substitute a nonzero θ into the isotropic configurations obtained in the previous simulations at $\theta = 0$ to pick up $U_d^{\parallel}$. This $U_d^{\parallel}$ is not the real one for the nonzero θ, and we call it the virtual $U_d^{\parallel}$ and illustrate it in figure 5 with the dotted line. When $\theta = 30°$, the virtual $U_d^{\parallel}$ is 2.53 k_BT higher than the real one, and this difference induces the transition from isotropic clusters to anisotropic clusters. $U_s^{\perp}$ is repulsive while average $U_s^{\parallel}$ is attractive. Because the former is much stronger than the latter when $\theta \leqslant 30°$, there are only a few links between particles of the same kind until $\theta = 30°$. When θ increases to 40°, $U_s^{\perp}$ has a obvious increase, while $U_s^{\parallel}$ and $U_d^{\perp}$ have an obvious decrease. The cooperation between $U_s^{\parallel}$ and $U_d^{\perp}$ can overcome $U_s^{\perp}$ to form the block. On increasing θ further, $U_s^{\parallel}$ becomes the dominant factor for the structure of the system, which results in the long chains along the x-axis.

For a better understanding of the structural transformation, we calculate the energy between two neighboring chains. For ideal infinitely long chains, every particle in one chain feels the same interaction from the other chain, so we can use this interaction to express the energy between the two chains. In figure 6, we plot the energy between a single particle and a chain as the function of θ in four ideal structures. The chain is composed of 62 particles (the length of the container is about 63.4σ) and schematic diagrams of the structures are also shown in figure 6. In structure I, the chain is composed of particles of alternative sorts along the y-axis, and the single particle is linked with a particle of same kind in the chain along the x-axis. The energy between the single particle and the chain drops with the increase in θ and is zero at $\theta \approx 28°$, which qualitatively accords with the simulation result that a few anisotropic clusters can link with each other along the x-axis at $\theta = 30°$. In the remaining three structures, the chain is composed of particles of the same kind and in the x-direction. The single particle and the particles in the chain are of different kinds in structures II and III, and they are of the same kind in structure IV. The single particle links with the chain along

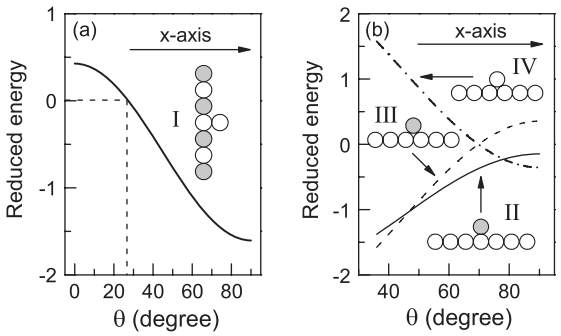

Figure 6. Reduced energy between a particle and a chain in four different structures as a function of θ.

the y-axis for all of the three structures, and the displacement between the single particle and its neighbor in the x-direction is 0 for structure II or 0.5σ for structures III and IV. For small θ, among these three structures, the energy of structure IV is highest, so a chain prefers to link with different chains in the y-direction. The energy of structure III is lower than that of structure II until $\theta = 47°$. This is the reason why P_d slowly decreases to its minimum until $\theta \approx 60°$ with the increase of θ, though the particles have already formed the block at $\theta = 40°$ which makes P_s increase rapidly. When $\theta \geqslant 79°$, structure IV is the one with the lowest energy among II, III and IV, so we can observe a few links between the chains of same kind at $\theta = 80°$ and the columns at $\theta = 90°$ as shown in figures 2(h) and (i).

4. Conclusion

In summary, we have studied the structural transformation of Q2D binary dipolar hard spheres confined in a plane. When the dipoles rotate from the direction perpendicular to the plane (z-axis) to that parallel with the plane (x-axis), five structures appear in the sequence as follows: isotropic clusters, anisotropic clusters, a block expanded in the y-direction, long chains along the x-axis, and columns along the x-axis. Through the analysis of the configurations obtained by the simulations, we obtained the RDF, P, and the average of energy, and these data show the detailed information about the structural transformations. Numerical calculations of the energies of four ideal structures give the results in good agreement with the simulation results. The order of the phase transitions between these structures has not been discussed in this paper, and it should be meaningful to investigate this issue via the finite size scaling analysis. Extended from the experiment [20] and the simulation [21], a tilted field introduces anisotropy to the system and enriches the structures in such a system. Binary hard spheres with opposite point dipoles can model the experimental system successfully [21], and from figure 3 of [20] it can be found that the strength of the dipolar interaction used in this work can be achieved experimentally. So it is believed that the structural transformations found in our simulations can be observed in real systems with tilted fields. Stronger dipolar interactions will be responsible for the formation of crystallized particles. So one possible way to progress from the present work is to study the transformation between different crystals induced by the rotation of the external field.

Acknowledgments

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