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Computer Modeling of Binary Dipolar Monolayers

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Abstract

We investigated the structural and dynamic properties of so-called binary dipolar monolayers (BDM). BDMs are planar colloidal systems containing two sorts of particles which have a permanent or induced dipole moment. The direction of the dipole moment of the particles is fixed to be perpendicular to the plane of motion and has opposite orientation for the two components. The goal of our work was to carry out a thorough investigation by computer simulation in order to understand self-assembly processes in BDMs.

Keywords: computer simulation, structure formation, dipolar particles

1. Introduction

Interesting structure formation processes can be observed in electro- or magnetorheological fluids, which are composed of particles suspended in an electromagnetically passive viscous liquid. The particles either have a permanent dipole moment or attain an induced moment due to polarization when subjected to an external electric or magnetic field. In rheological fluids the long range anisotropic interaction and the inherent frustration of the dipolar particle system result in a large variety of interesting phenomena from cluster-cluster aggregation to the formation of crystalline lattices with various types of symmetry. Dipolar monolayers are obtained when the motion of particles is restricted to the two-dimensional plane. Such two-dimensional systems provide a deep insight into the dynamics of pattern formation and to the structure of aggregates.

Colloidal crystallization has been investigated not only on homogenous substrate, but also on periodic 2D substrate. Novel colloidal structures have been found both numerically and experimentally. In these systems colloidal particles are trapped in each potential minima, which is generated by interference patterns

of laser beams. The trapped particles can be regarded as bounded entities with only rotational degrees of freedom. This molecular crystalline states display long range positional and orientational order, depending on the structure of substrates and the number of particles in a potential minima [1].

Binary colloidal dispersions are obtained when two types of particles with different material properties, mass, size, charge, number, ... are suspended in a viscous liquid. Binary colloids are involved in a large variety of natural phenomena and have potential industrial applications, which calls for a thorough experimental and theoretical investigation.

We studied the behavior of binary dipolar monolayers (BMD), which are two dimensional systems of dipolar particles. The direction of the dipole moment of the particles is fixed to be perpendicular to the plane of motion and the two component of the system have oppositely oriented dipole moments. The first experimental realization of BDMs was presented recently by sedimenting two types of particles in a liquid and subjecting the system to an AC electric field perpendicular to the bottom plate of the container. The particles attained an induced dipole moment which had opposite orientation (up and down) in a certain frequency range of the driving field. Depending on the composition of the system and on the driving frequency, several novel types of structure formation have been reported [2].

2. Computer model

We introduced a model of binary dipolar monolayers which takes into account all the relevant interactions in the particle system [3]. In the computer model spherical particles are considered which have a point-like dipole moment in the middle. The system of N particles consists of N_+ and N_- particles of dipole moment μ_+ pointing upward (+), and dipole moment μ_- pointing downward (−), respectively, in a square shaped simulation box with side length L (fig. 1). The partial concentrations of the components ϕ_+ and ϕ_- are defined as the coverage $\phi_\pm = N_\pm R^2\pi/L^2$, whose ratio provides the relative concentration $\phi_r = \phi_-/\phi_+ = N_-/N_+$. The total particle concentration ϕ is defined analogously $\phi = \phi_+ + \phi_- = (N_+R^2\pi + N_-R^2\pi)/L^2$. For simplicity, in the computer simulations we fix μ_+ and vary the ratio $\mu_r = \mu_-/\mu_+$, *i.e.* the relative dipole moment. Similarly, we fix N and vary the simulation box size L with respect the concentration ϕ.

The particles move in two dimensions under the action of the dipole-dipole force with dipole moments fixed to be perpendicular to the plane of motion.

$$\vec{F}_{ij}^{dd} = \frac{3\mu_i\mu_j}{r_{ij}^4}\vec{n}_{ij} \tag{2.1}$$

Under such conditions the dipole-dipole force is isotropic (central), it always falls in the plane of motion parallel to the line $\vec{n}_{ij}$ connecting the two particles. The carrier liquid only exerts a friction force (Stokes drag)

$$\vec{F}_i^{hyd} = -\alpha\frac{d\vec{r}_i}{dt} \tag{2.2}$$

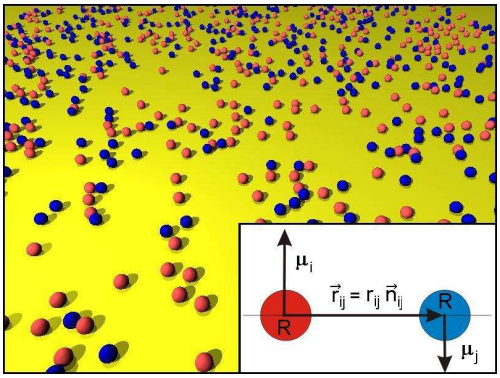

Figure 1: An initial configuration of the simulation with $N = 1000$ particles. The two components are indicated by the different colors. The inset explains the notation used in the model description.

on the particles, where $d\vec{r}_i/dt$ denotes the velocity of particle i. The drag coefficient α depends on the radius R of the particles and on the viscosity η of the liquid $\alpha = 6R\pi\eta$. The finite size of the particles is captured by introducing a repulsive contact force between the touching particles in the form of the Hertz contact law

$$\vec{F}_{ij}^{pp} = -k_{pp}((2R) - r_{ij})^{\frac{3}{2}}\vec{n}_{ij} = -k_{pp}\vec{f}_{ij}^{dd}, \tag{2.3}$$

where k_{pp} is a material dependent constant. The particle system is supposed to be fully dissipative, hence, the equations of motion of the particles simplifies to a first order differential equation system

$$\frac{d\vec{r}_i}{dt} = \frac{1}{\alpha_i}\sum_j \vec{F}_{ij}^{dd} - \frac{k_{pp}}{\alpha_i}\sum_{r_ij<2R} \vec{f}_{ij}^{pp}, \quad i = 1, \ldots, N. \tag{2.4}$$

2.1. Molecular dynamics simulations

Since thermal motion does not play an important role, the time evolution of the model system is obtained by computer simulation solving numerically the equations of motion of particles. Its basic idea is the discretization of the time and the approximation of the solution function with its truncated Taylor series

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \frac{d\vec{r}_i}{dt}\Big|_t \Delta t + \frac{1}{2!}\frac{d^2\vec{r}_i}{dt^2}\Big|_t \Delta t^2 + \frac{1}{3!}\frac{d^3\vec{r}_i}{dt^3}\Big|_t \Delta t^3 + O(\Delta t^4), \tag{2.5}$$

where Δt denotes the time step used in the integration of the equation of motion. We used 4th order Runge-Kutta method [7]. In order to achieve desired accuracy in the solution with minimum computational effort we used adaptive stepsize control, which means frequent changes in the stepsize on the grounds of the Cash-Karp

method [7]. This estimate is accurate to fifth order, one order higher than the original Runge-Kutta steps.

In order to ensure the disorder of the initial configuration, first point-like particles are placed in the simulation box randomly and independently. Then the particles are gradually blown-up, i.e. the particle radius is gradually increased such that after each increment, a molecular dynamics simulation is performed taking into account the repulsive force arising between overlapping particles and the friction force. As a result of the simulation all the particles can find equilibrium, overlap-free position. This procedure is repeated until the particle radius R reaches the desired value. Disorder is solely introduced by the randomness of the initial configuration, no random forces are taken into account. In order to reduce the surface effects in the simulation, we used periodic boundary conditions, assuming that the simulation box is part of a larger system. For simplicity, the minimum image convention was used such that the system was surrounded by its eight identical copies, which also implies that the dipole-dipole interaction was truncated at a cutoff distance $r_c = L/2$.

2.2. Brownian dynamics simulations

In certain parameter regimes of BDMs thermal noise can have a substantial roll in the time evolution of the system which cannot be captured by the simulation techniques presented in Chapter 2.1. In order to study the effect of thermal noise on the structure formation of binary dipolar monolayers (BDM) we carried out Brownian dynamics simulations by solving the Langevin equation

$$m_i \ddot{\vec{r}}_i = \vec{F}_i + \vec{\zeta}, \tag{2.6}$$

where $\vec{F}_i$ denotes the systematic force on particle i exerted by the other dipoles and by the contacting particles (see Chapter 2), and $\vec{\zeta}$ is the stochastic force arising due to the finite temperature of the carrier liquid. Particle positions $\vec{r}_i$ are obtained using the Euler scheme

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \frac{D}{k_B T}\vec{F}_i(t)\Delta t + \Delta\vec{r}_i^G, \tag{2.7}$$

where each component $\Delta r_{i\alpha}^G$ of $\Delta\vec{r}_i^G$ is sampled from a Gaussian distribution, with the density function

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(x-m)^2}{2\sigma^2}}. \tag{2.8}$$

The mean of the components $\Delta r_{i\alpha}^G$ is zero (m=0), while their variance is $2D\Delta t$. D is the diffusion coefficient of a particle, which is calculated from the solvent viscosity η and the size R of the particles according to the Stokes-Einstein relation $D = (k_B T)/(6\pi\eta R)$, where k_B and T are the Boltzmann constant and temperature, respectively. The unit of length in the system is the particle diameter d and the unit of time τ is defined as $\tau = d^2/D$. We measure the temperature in units of the

binding energy $E_3(\mu_r)$ of trimers at the given μ_r used, *i.e.* $T^* = k_BT/E_3(\mu_r)$ is the dimensionless temperature. In the simulations the time step Δt should be at least two orders of magnitude smaller than the characteristic time scale τ. We set $\Delta t = 0.01\tau$ from which the temperature range accessible at a given parameter set of the model can be determined. (For further details of the simulation technique see [6].)

3. Quantitative evaluation of experiments

We have constructed an experimental technique which provides a straightforward and controllable realization of binary dipolar monolayers. In the experimental setup, macroscopic particles are constructed by attaching metal particles of cylinder shape to swimmers. The metal particles are magnetized along their axis so that they have a permanent magnetic moment. The swimmers are cork discs which have two major roles in the setup: on the one hand they ensure the confinement of the composite particles to the air-water interface (floating) reducing also the friction force, on the other hand they prevent flipping constraining the dipole moments to be perpendicular to the plane of motion. The two components of the system are realized by the two opposite orientation of the dipole moments of the particles. This experimental method overcomes several difficulties of the other techniques used in the literature [2]. Besides its simplicity, an important advantage of our experimental techniques is that the time evolution of the particle system is easily accessible by direct optical observations.

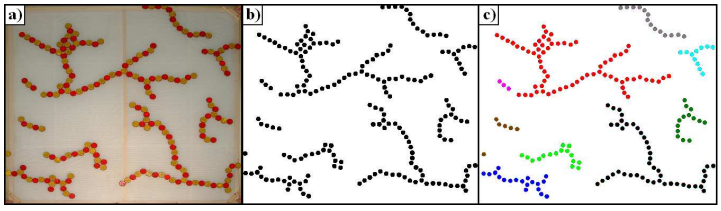

Figure 2: The steps of identifying clusters on experimental snapshots.

The process of aggregation was recorded by a digital video camera until a frozen state was attained in which no further changes occurred. For further analysis, snapshots were extracted from the movies at regular times (see fig. 2/a). In order to give a quantitative characterization of the dynamics of structure formation, and of the geometrical structure of growing aggregates, the coordinates of single particles have to be determined from the digital images by means of image processing. Starting from the colored snapshots of the system, we generated black-and-white pictures, in which black dots indicate particles on the white background (see fig. 2/b). The black-and-white images were further processed by a computer program

which determines the coordinates of the center of black discs. Based on the coordinates, the program identifies particle clusters and determines all the characteristic quantities of their structure. For cluster searching (fig. 2/c) we implemented the Hoshen-Kopelman algorithm.

4. Structural and dynamic properties of BDMs

To prove that our model gives a satisfactory description of the BDMs we compared the experimental and theoretical behavior of the system in a board range of the relevant parameters.

4.1. Aggregation

From a random initial configuration single particles start to move and aggregate. At low concentration anisotropic chain-like clusters join together at their ends forming longer chains. The length of alternating chains is limited. When the chain length becomes comparable to the average chain distance aggregation can occur not only at chain ends but also at internal particles. During the time evolution of the system cluster-cluster aggregation can be observed, resulting in chains and branching structures of alternating particles. It can be seen also on the snapshots of experiment and simulation on figure 3.

In order to characterize the structure of growing aggregates we calculated the radius of gyration for each cluster in the snapshots and averaged over clusters of the same size. We observed that in all cases that the cluster size as a function of the radius of gyration shows power law behavior, where the exponent is different for small and large cluster sizes. Since small clusters have chain-like morphology, while the large ones are branched, the fractal dimension of large clusters has a significantly higher value.

The dynamics of aggregation process can be characterized by the average cluster size and number of clusters as a function of time. They have power law behavior with concentration dependent exponents. We found that Vicsek-Family scaling only holds in the dilute limit [4].

4.2. Crystallization

At high enough concentrations the particle system rapidly attains a frozen structure. The extended structure is typically composed of islands having crystalline order. Starting from the random initial conditions particles of the two components form various types of planar crystal lattices. Triangular lattice, square lattice, and two-types of honeycomb lattices with hexagonal symmetry can be obtained. We showed analytically that in a mono-disperse particle system the outcome of structure formation is determined by three parameters: depending on the value of the total concentration of the particles, and on the relative concentration and relative dipole moment of the two components. We determined the parameter regimes of

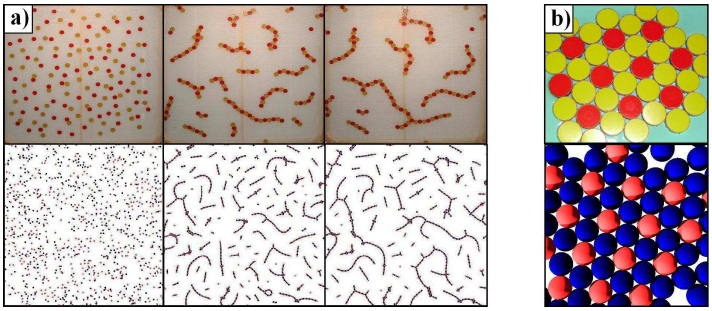

Figure 3: a) The time evolution of the system during cluster-cluster aggregation. b) An enlarged example of crystalline states: honeycomb structure. Experiments (upper row) and simulations (lower row) are in good agreement.

the occurrence of each structure. The experiments and computer simulations are in a good agreement with our analytic predictions [3].

4.2.1. Molecular crystals

We showed that in binary dipolar monolayers crystalline states can occur analogous to colloidal molecular crystals observed in colloids interacting with a periodic array of traps [1], but in this case without the application of an underlying substrate. The n-mers of BDMs are bounded configurations of particles with oppositely oriented permanent dipoles whose interaction depends on their distance, relative orientation and the relative dipole moment and the interaction has also repulsive and attractive regimes.

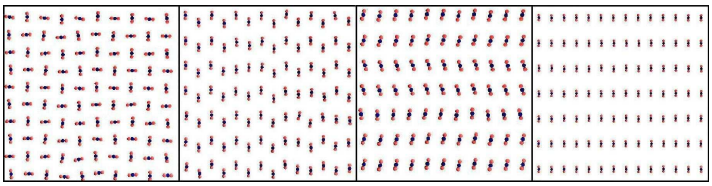

Figure 4: Molecular crystalline states of trimer systems with different positional and orientational order.

We explore the possible crystal structures of trimers by means of computer setting the initial particle positions based on our analyzes of the trimer potential. The placement of handmade trimers practically substitute the substrate in the initial state of the simulations. Lattice structures of a high degree of positional and orientational order were obtained by computer simulations relaxing the system by

solving the equation of motion of the particles without thermal noise (see fig. 4). The structure of these lattices depends on the two perpendicular lattice constants.

Brownian dynamics simulations revealed that the binary dipolar molecular crystals are instable states of the monolayer, namely at any non-zero temperature the crystalline order has a finite lifetime which is a decreasing function of both the temperature and the system size. At lower temperature the crystalline order dominates, while at the same time at the higher temperature the crystal structure is already lost, random walk of the trimers can be observed [5].

5. Summary

We constructed a dynamical computer model of binary dipolar monolayers. In order to describe the structure formation observed in the experiments we carried out both molecular dynamics simulations and Brownian dynamics simulations varying the parameters of the system in a board range. To compare the simulation results to the experimental findings we qualitatively evaluated the experiments by some means of image processing. Based on these we determined the relevant parameters of the system. We predicted and found the possible structures establishing the parameter regimes of their occurrence, finding good agreement between the experiments and our simulations. Several physical processes of the BMDs can be understandable and explainable by our results.

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