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STRUCTURE AND DYNAMICS OF BINARY DIPOLAR MONOLAYERS

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Abstract

We present an experimental and theoretical study of the structure and dynamics of binary dipolar monolayers. Varying the parameters of the system a large variety of interesting phenomena is obtained from kinetic aggregation to crystallization into various lattice types. We also show that in dipolar monolayers molecular crystalline states can be obtained without the application of an underlying periodic substrate.

I. Introduction

Binary colloidal dispersions are composed of two types of particles with different material properties, mass, size, charge, number, ... suspended in a viscous liquid. Such colloids have recently been found to show interesting aggregation phenomena with novel structural and kinetic properties [1]. Binary colloids are involved in a large variety of natural phenomena and have potential industrial applications from waste water treatment through mineral flotation to cell recovery, which calls for a thorough experimental and theoretical investigation [1].

Binary dipolar monolayers (BDMs) form a special type of binary colloids, *i.e.* they 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 have opposite orientation for the two components. Because of these features, BDMs are also called Ising dipolar systems. The first experimental realization of BDMs was presented only very 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 [2]. Depending on the composition of the system and on the driving frequency a large variety of novel structure formation has been reported. However, due to technical limitations these experiments could not provide a quantitative insight into the structure and dynamics of binary dipolar monolayers but initiated an intensive research in this field.

In this project we carried out a detailed investigation of the structure and dynamics of binary dipolar monolayers. Based on experiments, analytical calculations and computer simulations, we obtained a comprehensive understanding of structure formation in BDMs.

II. Experiments and Computer Simulations

For the purpose of a detailed quantitative study, we worked out an experimental technique which provides a straightforward and controllable realization of binary dipolar monolayers with particles of oppositely oriented dipole moments constrained to be perpendicular to the plane of motion [3]. In the experimental setup macroscopic particles are constructed by attaching metal particles of cylinder shape to swimmers. The metal particles are magnetized so that they have a permanent magnetic moment parallel to their axis. The swimmers are cork discs which have two major roles in the setup: (i) they ensure the confinement of the composite particles to the air-water interface (floating) reducing also the friction force, (ii) 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 which are set by hand when preparing the initial configuration. The system is characterized by the total concentration of particles ϕ, and the relative concentration ϕ_r, relative dipole moment μ_r, and polydispersity σ of the two components.

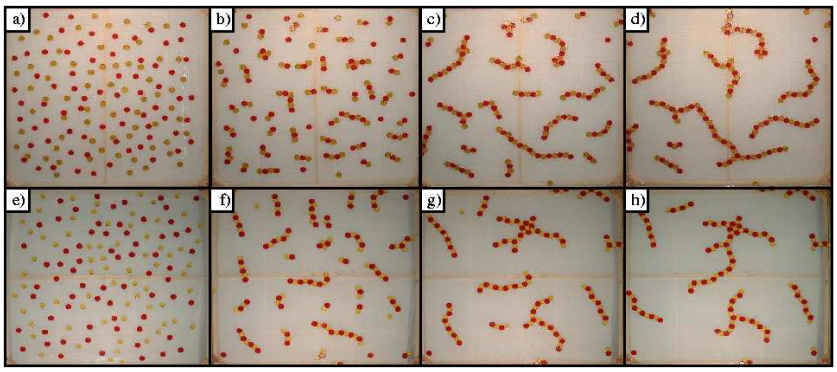

Figure 1: Examples for the aggregation of dipolar particles in two different experimental setups (a, b, c, d): $\mu_r = 1$, $\phi_r = 1$, $\phi = 7.5\%$, and $\sigma = 1$, (e, f, g, h): $\mu_r = 1$, $\phi_r = 1$, $\phi = 6\%$, and $\sigma = 1.5$.

Our experiments overcome several difficulties of the techniques used in the literature, *i.e.*, there is no need for an external driving field, hence, electrohydrodynamic effects are completely eliminated, there is no sliding friction with the substrate, furthermore, the initial condition is well-controllable. Due to the large particle size the thermal motion is hindered, the particles move along deterministic trajectories. The time evolution of the system is easily accessible by direct optical observations making possible a quantitative analysis of structure formation processes [3].

Parallel to the experiments, we introduced a model of binary dipolar monolayers which takes into account all the relevant interactions in the particle system [4, 5, 6]. In the model spherical particles are considered which have a point-like dipole moment in the middle. 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. The carrier liquid only exerts a Stokes drag on the particles. 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. Since thermal motion does not play a crucial role, the time evolution of the model system is followed by solving numerically the equation of motion of particles (molecular dynamics) without considering thermal noise. Starting from a random initial configuration, computer simulations provide deterministic particle

trajectories [4, 5, 6]. In order to study the stability of molecular crystals with respect to thermal fluctuations, we also developed a computer simulation program which explicitly solves the Langevin equation of the particles (Brownian dynamics) [8].

III. Results and Discussion

We pointed out that at low concentrations $\phi \leq 25\%$ BDMs undergo kinetic aggregation, which also presents an interesting special case of heteroaggregation phenomena of colloids. Figure 1 presents examples of the aggregation process of dipoles on the surface of water. Experiments revealed that the dipolar clusters are fractals which show a crossover from the universality class of self-avoiding random walks to the more compact branching morphologies of reaction limited cluster-cluster aggregation [7]. The crossover cluster size S_c decreases with the concentration as $S_c \sim \phi^{-1}$. The average cluster size and the number of clusters have a power law dependence on time. The dynamic exponents of the average cluster size and cluster number are increasing functions of the concentration and they are equal only in the dilute limit. Computer simulations are in a good quantitative agreement with the experimental findings [4, 5]. Additionally, we showed that in the absence of contact friction of the particles, the growing clusters are less compact characterized by a lower value of the fractal dimension [4, 5].

We showed experimentally and by means of computer simulations that in aggregation processes of BDMs cluster discrimination occurs, *i.e.*, clusters of an even and odd number of particles have a different time dependent behavior [5, 7]. Even clusters have a higher reaction rate than the odd ones leading to even-odd oscillations. We explained the phenomenon in terms of the morphology of clusters and their long-range anisotropic interaction. We showed that cluster discrimination can arise solely up to the crossover cluster size S_c and the higher relative dipole moment of the components leads to a more pronounced discrimination effect [5, 7].

Our experiments and computer simulations revealed that at higher concentrations $\phi > 25\%$ crystallization occurs, *i.e.*, particles of the two components from various types of planar crystal lattices. We showed analytically

that in a monodisperse particle system the outcome of structure formation is determined by three parameters: depending on the value of the total concentration ϕ of the particles, and on the relative concentration ϕ_r and relative dipole moment μ_r of the two components triangular lattice and square lattice, furthermore, two types of honeycomb lattices can be obtained. We determined analytically the parameter regimes of the lattice types and concluded that the electrohydrodynamic flow of the experiments of Ref. [2] prevented the observation of honeycomb lattices of low packing fraction. The experiments and computer simulations are in a good agreement with our analytic predictions [4, 6].

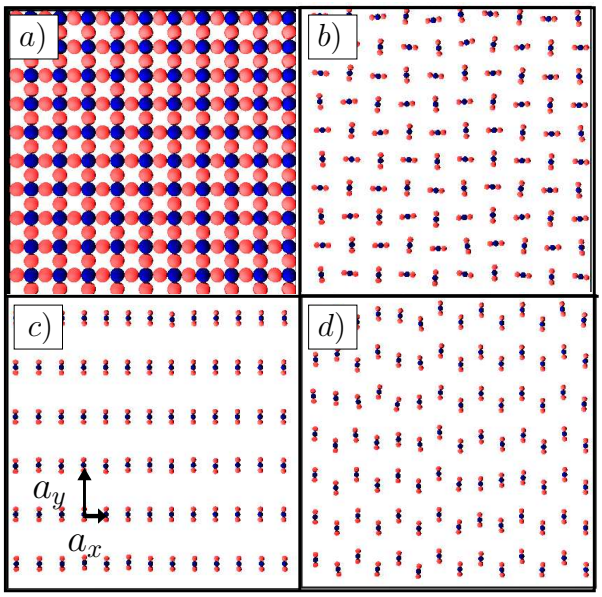

Figure 2: A bounded crystal of trimers with $\mu_r = 1$. (a) Molecular crystalline states of trimers obtained with $\mu_r = 1$ at different values of the lattice spacings in the horizontal a_x and vertical direction a_y: (b) $a_x = a_y = 5d$, (c) $a_x = 5d, a_y = 10d$, and (d) $a_x = 4d, a_y = 8d$. (Here d denotes the diameter of the particles.)

We showed that in binary dipolar monolayers (BDM) crystalline states analogous to colloidal molecular crystals observed in colloids interacting with a periodic array of traps [9, 10, 11, 12], can emerge without the application of an underlying substrate. The n-mers of BDMs are bounded

configurations of particles with oppositely oriented permanent dipoles. Our detailed analysis was restricted to trimers but structures composed of higher order n-mers can be studied analogously [8]. Computer simulations showed that in BDMs all lattice types can be recovered which have been obtained with substrates, furthermore, due to the translational degrees of freedom additional structures can arise. Examples of crystalline lattices of dipolar trimers can be seen in Fig. 2. Since no substrate is applied, binary dipolar molecular crystals (BDMCs) are purely based on the minimization of the interaction energy of repulsing n-mers which makes the system very sensitive to perturbations. Brownian dynamics simulations revealed that at any finite temperature BDMCs are instable states of the monolayer and have a finite lifetime t_c. The lifetime of the crystalline state proved to have a power law dependence on the temperature and on the system size, which cannot simply be understood in terms of an Arrhenius type law (see Fig. 3) [8].

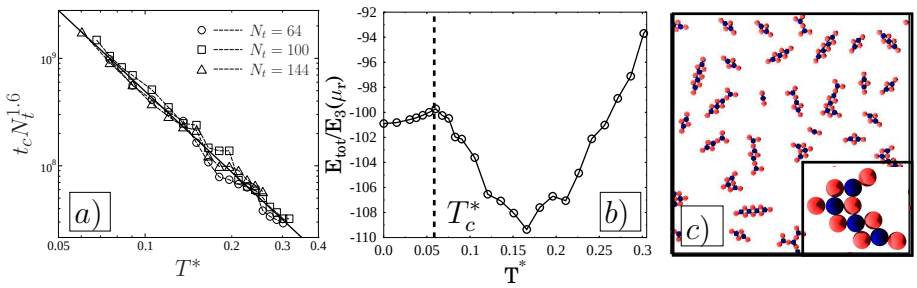

Figure 3: (a) Lifetime t_c of the crystalline state presented in Fig. 2(b) as a function of temperature T^* for different system sizes N_t at $\mu_r = 1$. Data collapse is obtained by rescaling t_c by the number of trimers N_t. The slope of the straight line is 2.5. (Note the log-log scale of the figure.) (b) Energy E_{tot} of the system of $N_t = 100$ trimers of Fig. 2(b) as a function of T^*. (c) Thermal noise driven aggregation of trimers. At high enough temperatures $T^* > T_c^*$, large clusters are formed with square packed structure. The inset shows a magnified view of a single cluster where the internal structure can be observed.

Colloidal molecular crystals interacting with periodic substrates show a two-step melting mechanism: when increasing the temperature first the

orientational order gets lost while the colloids are still confined, then the positional order disappears at a higher temperature when the particles get delocalized over the substrate [9, 10, 11, 12]. In BDMCs the absence of confining substrate has the consequence that such two-step melting cannot occur, orientational and positional order are strongly coupled and get lost at the same time [8].

Brownian dynamics simulations revealed that at finite temperatures the molecular crystalline structures are instable states of BDMs whose lifetime is a decreasing function of both the temperature and the system size. For trimers there exists a critical temperature T_c above which thermal noise driven aggregation occurs resulting in clusters of square lattice structure, analogously to the "freezing-by-heating" transition (see Fig. 3) [8, 13].

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