Structure Formation in Binary Dipolar Monolayers

Ph.D. theses

Imre Varga

Department of Theoretical Physics
University of Debrecen
Debrecen
2007

Prepared at
the Department of Theoretical Physics
of the University of Debrecen

Supervisor
Dr. Kun Ferenc

Introduction

Structure formation by self-assembly in many particle systems has been the subject of intensive scientific research during the past decades. In a large variety of systems, due to their thermal motion and interaction the particles aggregate and build-up clusters with a broad spectrum of structural properties. Diffusion driven aggregation of particles has been extensively studied in the 80's and 90's and by today this problem is well understood. However, structure formation when the interaction of the particles has a dominant role in the process has been much less investigated. A special type of attraction driven self-assembly occurs in electro- and magnetorheological fluids (also called smart 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. Since the presence of aggregates also changes the rheological and optical properties of the colloid, which can easily be controlled by external fields, rheological fluids have many technological applications. 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, furthermore, open up possibilities to study the statistical physics of low dimensional systems such as the phenomena of two-dimensional melting and structural phase transitions.

Binary colloidal dispersions are obtained when two types of particles with different material properties, mass, size, charge, number, ... are suspended in a viscous liquid. Such colloids have recently been found to show interesting aggregation phenomena with novel structural and kinetic properties. The simplest realization of binary colloids is a 1:1 mixture of two components having positive and negative charges. 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].

During my Ph.D. studies I 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

[1] H. M. López-López et al., Soft Matter **2**, 1025 (2006).

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. 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. Depending on the composition of the system and on the driving frequency, several novel types of structure formation have 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[2].

The goal of my Ph.D. was to carry out a thorough experimental and theoretical investigation in order to understand self-assembly processes in binary dipolar monolayers, to identify the most important parameters of the system governing the pattern selection, to explore all possible structures and to study the statistical physics of this special two-dimensional system.

New scientific results

1. I 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. 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. My experimental method overcomes several difficulties of the techniques used in the literature, *i.e.*, there is no need for an external driving field, hence, electro-hydrodynamic effects are completely eliminated, there is no sliding friction with the substrate, the initial condition is well-controllable.

[2]W. D. Ristenpart, I. A. Aksay, and D. A. Saville, Phys. Rev. Lett. **90**, 128303 (2003).

Due to the large particle size the thermal motion is hindered so that 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 [R2, R4].

2. I introduced a model of binary dipolar monolayers which takes into account all the relevant interactions in the particle system. 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 obtained by computer simulations solving numerically the equation of motion of particles (molecular dynamics) without considering thermal noise. In order to study the stability of molecular crystals with respect to thermal fluctuations, I also developed a computer simulation program to solve the Langevin equation of the particles (Brownian dynamics) which explicitly captures the effect of thermal noise. Besides the computer simulation programs, I also worked out a computer program package for the evaluation of the experimental and simulation results [R1, R3, R6].

3. I pointed out that at low concentrations $\phi \leq 25\%$ BDMs undergo kinetic aggregation, which also represents an interesting special case of heteroaggregation phenomena of colloids. 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. The dynamic exponents of the average cluster size and cluster number are increasing functions of the concentration with an increasing difference so that Vicsek-Family scaling only holds in the dilute limit. Computer simulations are in a good quantitative agreement with the experimental findings. Additionally, I 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 [R1, R3, R5].

4. I 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. Even clusters have a higher reaction rate than the odd ones leading to even-odd oscillations of the concentration of clusters. I explained the phenomenon in terms of the morphology of clusters and their long-range anisotropic interaction. I showed that discrimination can be observed up to the crossover cluster size, and the higher relative dipole moment of the components leads to a more pronounced discrimination effect [R3, R5].

5. My experiments and computer simulations revealed that at higher concentrations $\phi > 25\%$ crystallization occurs, *i.e.*, particles of the two components form various types of planar crystal lattices. I 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 ϕ of the particles, and on the relative concentration ϕ_r and relative dipole moment μ_r of the two components triangular lattice, square lattice, and two-types of honeycomb lattices can be obtained. I determined analytically the parameter regimes of different lattice types and concluded that electro-hydrodynamic flow discussed in the literature does not play a crucial role in crystallization. The experiments and computer simulations are in a good agreement with my analytic predictions [R1, R2, R4].

6. I showed that in binary dipolar monolayers crystalline states analogous to colloidal molecular crystals observed in colloids interacting with a periodic array of traps, can emerge 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 both on their distance and relative orientation. I carried out a detailed analysis of trimer lattices and pointed out that the translational degrees of freedom lead to novel structures not observed with substrates. 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 [R6].

Publications

Refereed journals

R1 **I. Varga**, F. Kun, and K. F. Pál, *Structure formation in binary colloids*, Physical Review E **69**, 030501(R) (2004).

R2 **I. Varga**, H. Yamada, F. Kun, H.-G. Matuttis, and N. Ito, *Structure formation in a binary monolayer of dipolar particles*, Physical Review E **71**, 051405 (2005).

R3 N. Yoshioka, **I. Varga**, F. Kun, S. Yukawa, and N. Ito, *Attraction-limited cluster-cluster aggregation of Ising dipolar particles*, Physical Review E **72**, 061403 (2005).

R4 **I. Varga** and F. Kun, *Pattern formation in binary colloids*, Philosophical Magazine **86**, 2011 (2006).

R5 **I. Varga**, N. Yoshioka, F. Kun, S. Gang, and N. Ito, *Structure and kinetics of heteroaggregation in binary dipolar monolayers*, Journal of Statistical Mechanics: Theory and Experiment, P09015 (2007).

R6 **I. Varga**, F. Kun, S. Gang, and N. Ito, *Molecular Crystalline States in Binary Dipolar Monolayers*, Journal of Statistical Mechanics: Theory and Experiment, accepted (2007).

Talks and conference proceedings

T1 **I. Varga**, and F. Kun, *Aggregation of particles in a binary dipolar monolayer*, microCAD 2005 International Sciencific Conference, Miskolc, Hungary, March 10-11, 2005.

Posters

P1 **I. Varga**, F. Kun, and K. F. Pál, *Ordered structures in a binary monolayer of dipolar particles*, 1st Szeged International Workshop on Advances in Nanoscience, Szeged, Hungary, October 26-28, 2003.

P2 **I. Varga**, F. Kun, and K. F. Pál, *Structure formation in binary colloids*, 29th Conference of the Middle European Cooperation in Statistical Physics, Bratislava, Slovakia, March 28-April 1, 2004.

P3 **I. Varga**, and F. Kun, *Aggregation and crystallisation in binary colloids*,
3rd Graduate School on Condensed Matter Physics,
Debrecen, Hungary, September 6-11, 2004.

P4 **I. Varga**, and F. Kun, *Cluster discrimination in binary dipolar monolayers*,
30th Conference of the Middle European Cooperation in Statistical Physics, Cortona, Italy, April 3-6, 2005.

P5 **I. Varga**, and F. Kun, *Colloidal molecular crystals in dipolar monolayers*,
31st Conference of the Middle European Cooperation in Statistical Physics, Primosten, Croatia, April 23-26, 2006.