Colloidal suspensions driven by external fields

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Abstract. Colloidal suspensions have been proven to play a pivotal role of model systems in order to understand the principles of equilibrium phase transitions such as freezing and fluid-fluid demixing. One of the main reasons for that is that real space studies are possible thanks to the mesoscopic length scale of the particle size. The same model character of colloidal suspensions holds in non-equilibrium situations as e.g. represented by an external driving field (such as shear, gravity, an electric and/or magnetic field). In this paper some current examples of non-equilibrium transitions are reviewed where recent progress has been made by theory and computer simulation. In particular, we discuss the competition between phase separation and lane formation in driven colloidal mixtures, crystal nucleation in charged suspensions under shear and chain formation of two-dimensional superparamagnetic suspensions induced by an external magnetic field.

INTRODUCTION

Suspensions of mesoscopic colloidal particles are excellent realizations of classical statistical models since their interactions are tunable. One further advantage of colloidal suspensions lies in the fact that the particle configurations can be watched in real-space, e.g. by using confocal microscopy, which enables a direct comparison between experiments and theory. While in the past two decades most of the investigations of colloidal dispersions were done in the bulk either under equilibrium conditions or regarding the kinetic glass transition in order to explore the thermodynamics, structure and bulk phase behaviour, more recent studies exploit the fascinating possibility to expose colloids to external driving fields [1, 2] and to study thus non-equilibrium dynamics in a controlled way. One of the most intriguing possibilities is to fix and move the colloidal particles by using optical tweezers. In nonequilibrium situations, however, the dynamics of the colloids will enter explicitly. Hence a theoretical description is more difficult as long as the long ranged hydrodynamic interactions induced by the solvent flow will play a significant role.

In this paper we review some progress in the area of colloidal suspensions driven by external fields. In particular, three examples are discussed in detail, all of which have to do with certain aspects of slow dynamics in such complex fluids. It is known that binary mixtures of colloidal suspensions when driven by a constant external field (such as gravity or an electric field) can exhibit formation of particle lanes provided the driving forces acting on the two different particles species differ. These lanes can be intuitively understood by watching pedestrian motion in pedestrian zones [3] and are also mesoscopic analogs to the so-called two-stream instability in plasmas [4]. Here we study the competition between lane formation in a fluid-fluid phase-separating mixture and study the effect of anisotropic coarsening which is a slow dynamical process. The second topic concerns the presence of a shear field. It is known that typically a colloidal solid is melted by shear. But if the shear rate is reduced such shear-molten fluids can recrystallize into a solid. The question is how crystal nucleation rates are affected by shear. Since nucleation is a rare event, this intuitively has to do with slow dynamics. Finally we study the chain formation in anisotropically interacting magnetic colloidal spheres exposed to an external magnetic field. If the attraction between the particles is strong enough they form chains and the chains form aggregates. The dynamics towards the aggregates is very slow and the question is whether the aggregates finally crystallize into a lattice [5] or whether a liquid-chain phase is stable [6, 7, 8].

COMPETITION BETWEEN LANE FORMATION AND PHASE SEPARATION IN DRIVEN COLOIDAL MIXTURES

Spinodal decomposition of a phase-separating binary fluid mixture is a well-studied dynamical coarsening

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A set of different snapshots are presented in Figure 1 for different times. The starting configuration at \( t = 0 \) (see Fig. 1 a) is a completely mixed configuration as equilibrium for \( \Delta = 0 \) and \( F = 0 \). One clearly sees an anisotropic coarsening due to the external drive. Two extreme limit can be understood in more detail: first, if the driving field is much smaller than the fluid-fluid equilibrium line tension \( \gamma \), then the traditional isotropic phase separation will dominate at small times. At an interface the external field will then lead to a Rayleigh-Taylor instability leading to finger formation inside the phase separated region. This is presumably what has been seen in experiments of sedimenting colloidal-polymer mixtures [11] and was checked for pure interfacial situations [21]. On the other hand, if the driving force is much larger than \( \gamma \), the system directly relaxes into the laminar state.

**CRYSTAL NUCLEATION UNDER SHEAR**

In the last years, remarkable progress has been made to calculate the free energy barrier for crystal nucleation via smart simulation methods using the umbrella sampling technique. In three spatial dimensions, results for the homogeneous crystal nucleation rate and the structure of the critical nucleus were obtained for Lennard-Jones systems [22], hard spheres [23] and Yukawa particles [24]. Under linear shear flow of a given shear-rate \( \dot{\gamma} \), the nucleation rate is expected to change drastically since usually a crystal is getting less stable with respect to a fluid phase (shear-thinning or shear-induced melting).

In a recent work [25], Brownian dynamics computer simulations of charged colloids as modelled by a Yukawa interaction without hydrodynamic interactions have been performed to address this problem. The pair potential reads as (see Eqn. (1))

\[
\frac{V(r)}{k_B T} = \frac{1}{2} U_0 \sigma \exp\left(-\kappa(r - \sigma)\right) \delta(r - \tilde{r}).
\]

The negative logarithm of the probability to find a solid-like cluster containing \( n \) solid-like particles normalized to unity for \( n = 1 \) is plotted versus \( n \) in Figure 2. It is tempting to interpret this data as a free energy even in the non-equilibrium steady-state situation setting the barrier height and the critical nucleus size. We have tested our Brownian dynamics data in the zero-shear limit against Monte-Carlo data and find good agreement, see again Fig. 2. For increasing shear rates \( \dot{\gamma} \), the barrier and the cluster size do increase. Further simulations will explore the structure of the critical nucleus and will contribute to data of classical nucleation theory.

**TWO-DIMENSIONAL MAGNETIC COLLOIDAL SUSPENSIONS IN AN EXTERNAL MAGNETIC FIELD**

Systems of colloidal particles at a liquid–gas interface controlled by magnetic interactions are valuable realizations of two-dimensional model systems to study the properties of their phase transitions and response to external fields. Here we consider two-dimensional macroscopic ensembles of paramagnetic particles, each carrying a magnetic moment \( \mathbf{m} \), under the influence of an arbitrary external magnetic field \( \mathbf{B} \).

The physical setup is schematically depicted in Fig. 3. The total potential energy of the system reads as:

\[
V_{\text{tot}} = \sum_{i,j} \left( u_0(n_{i,j}) + u_{\text{int}}(n_{i,j}, m_i, m_j) \right) - \sum_i B \cdot m_i.
\]

The subscript \( i,j \) stand for the two Cartesian components. Note that within this simple Landee picture, hydrodynamic interactions are ignored.

We solve the Landee equations of motion by Brownian dynamics simulations [16, 17, 18] using a finite time-step and the technique of Ermak [19, 20]. We use a square cell of length \( L \) with periodic boundary conditions. The typical size of the time-step \( \Delta t \) was 0.0002\( \sqrt{m_j} \), where \( T_j = \frac{E}{k_B T_j} \) is a suitable Brownian timescale. We simulated typically \( 2 \times 10^8 \) time steps which corresponds to a simulation time of 4\( \Delta t \).
is zero. The relative strength of the dipole interaction with respect to the thermal energy $k_B T$ is \( \lambda = \frac{m_1 m_2}{\Omega^2 k_B T} \approx 8 \).

Starting from a homogeneous disordered configuration, one clearly sees the formation of chain-like configurations. The results are obtained via molecular dynamics. Although this is not the proper dynamics of the colloids, it provides nevertheless qualitative insight into the dynamics of chain formation.

**CONCLUSIONS**

In conclusion, we have briefly described three different examples of slow dynamics in colloidal suspensions driven by an external field: i) phase separation kinetics under an external driving field, ii) crystalline nucleation under shear, and iii) chain formation in an external magnetic field. They all demonstrate that the formation of new complex structures such as phase-separating patterns and critical nuclei which initiate crystal birth are formed on time-scales which are considerably slower than the typical time scale characterizing single particle diffusion. The self-assembly of many particles leads to interesting structures on intermediate transient time-scales.

We think that colloidal suspensions in non-equilibrium will be valuable models to study further fundamental questions of slow dynamics. In particular, patterns formation in non-equilibrium and glass and gel formation in external fields are key areas in which progress can be expected in the near future.

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