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 non-equilibrium 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 particles 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 molten 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 intimately 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 agregates 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 COLLOIDAL MIXTURES

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

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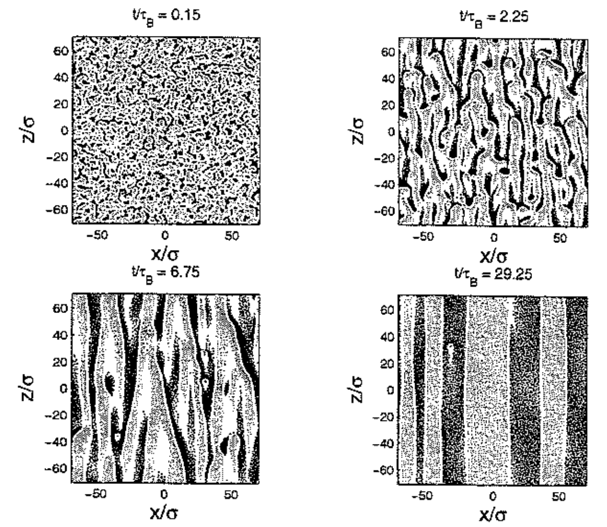

FIGURE 1. Simulation snapshots for a) $t = 0.15$, b) $t = 2.25\tau_B$, c) $t = 6.75\tau_B$, d) $t = 29.25\tau_B$. Simulation parameters are: $\kappa\sigma = 2.34$, $U_0 = 15$, $\frac{F\sigma}{k_BT} = 120$, $\rho\sigma^2 = 0.4$, $N_1 = N_2 = 4000$, $\Delta = 1.6$

process which slows down significantly until complete separation into two macroscopic portions of two fluids is reached [9]. Typically the structure grows with a power-law in time. When combined with another non-equilibrium situation, new pattern structures and growth laws do arise. One example is phase separation under shear [10], another situation occurs if the mixtures is driven by a constant external force which acts differently on the two different particle species. An experimental realization of such a situation is a sedimenting and phase-separating colloid-polymer mixture [11]. In the absence of phase separation, i.e. for a stable mixed fluid, it has been shown by computer simulation [12, 13, 14] and by theory [15] that - upon a critical force difference - the mixture spontaneously forms lanes containing only particles moving alike. The direction of the lanes is along the driving force direction.

Here we study the competition between phase separation and lane formation. We consider a two-dimensional model system interacting via a set of Yukawa pair potentials

The asymmetric binary colloidal mixture comprises $N_1 + N_2$ Brownian colloidal particles in an area S [12]. N_1 particles are of type 1, the other N_2 are of type 2 with partial number densities $\rho_1 = N_1/S$ and $\rho_2 = N_2/S$. In the following we set $\rho_1 = \rho_2 = \rho$. The colloidal suspension is held at fixed temperature T via the bath of microscopic solvent particles. Two colloidal particles are interacting via effective Yukawa potentials as follows:

$$\frac{V_{ij}(r)}{k_BT} = U_0\,\sigma_{ij}\frac{\exp(-\kappa(r-\sigma_{ij}))}{r}, \qquad (1)$$

where $(ij) = (11), (12), (22)$. Here r is the center-to-center separation, U_0 is the interaction strength measured in terms of the thermal energy k_BT and κ is the inverse screening length. The set of diameters, σ_{ij}, is nonadditive and given by

$$\sigma_{11} = \sigma_{22} = \sigma \qquad (2)$$

$$\sigma_{12} = \sigma(1+\Delta) \qquad (3)$$

where Δ is the dimensionless nonadditive parameter.

The dynamics of the colloids is completely overdamped Brownian motion. The friction constant is $\xi = 3\pi\eta\sigma$ with η denoting the shear viscosity of the solvent. The constant external force acting on the ith particle of species j, $\vec{F}_i^{(j)}$, has the same amplitude but an opposite direction for the both constituents of the binary mixture. It is $\vec{F}_i^{(1)} = F\vec{e}_y$ and $\vec{F}_i^{(2)} = -F\vec{e}_y$ where $\vec{e}_y$ is a unit vector along the y-direction of the system.

The stochastic Langevin equations for the colloidal trajectories $\vec{r}_i^{(j)}(t)$ $(j = 1,2)$ (with $i = 1,...,N_1$ for $j = 1$ and $i = 1,...,N_2$ for $j = 2$) read as

$$\begin{aligned} \xi\frac{d\vec{r}_i^{(j)}}{dt} = & -\vec{\nabla}_{\vec{r}_i^{(j)}}[\textstyle\sum_{k=1}^{N_{j'}} V_{jj'}(|\,\vec{r}_i^{(j)} - \vec{r}_k^{(j')}\,|) \\ & + \textstyle\sum_{k=1,k\neq i}^{N_j} V_{jj}(|\,\vec{r}_i^{(j)} - \vec{r}_k^{(j)}\,|)] \\ & + \vec{F}_i^{(j)} + \vec{K}_i^{(j)}(t), \end{aligned} \qquad (4)$$

where j' is the complementary index to j ($j' = 1$ if $j = 2$ and $j' = 2$ if $j = 1$). The right-hand-side includes all forces acting onto the colloidal particles, namely the force resulting from inter-particle interactions, the external constant force, and the random forces $\vec{K}_i^{(j)}$ describing the collisions of the solvent molecules with the ith colloidal particle of species j. The latter are Gaussian random numbers with zero mean, $\overline{\vec{K}_i^{(j)}} = 0$, and variance

$$\overline{(\vec{K}_i^{(k)})_\alpha(t)(\vec{K}_j^{(n)})_\beta(t')} = 2k_BT\xi\delta_{\alpha\beta}\delta_{ij}\delta_{kn}\delta(t-t'). \quad (5)$$

The subscripts α and β stand for the two Cartesian components. Note that within this simple Langevin picture, hydrodynamic interactions are ignored.

We solve the Langevin 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 Δt was $0.0002\tau_B$, where $\tau_B = \xi\sigma^2/k_BT$ is a suitable Brownian timescale. We simulated typically 2×10^4 time steps which corresponds to a simulation time of $4\tau_B$.

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 equilibration 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 γ, 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 fomation inside the phase separated region. This is presumbaly what has been seen in experiments of sedimenting colloid-polymer mixtures [11] and was checked for pure interfacial situations [21]. On the other hand, if the driving force is much larger than γ, the system directly relaxes into the laning 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 sytems [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))

$$\frac{V(r)}{k_BT} = U_0\sigma\frac{\exp(-\kappa(r-\sigma))}{r}. \qquad (6)$$

The negative logarithm of the probability to find a solid-like cluster containing n solid-like particle 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 compare to data to classical nucleation theory.

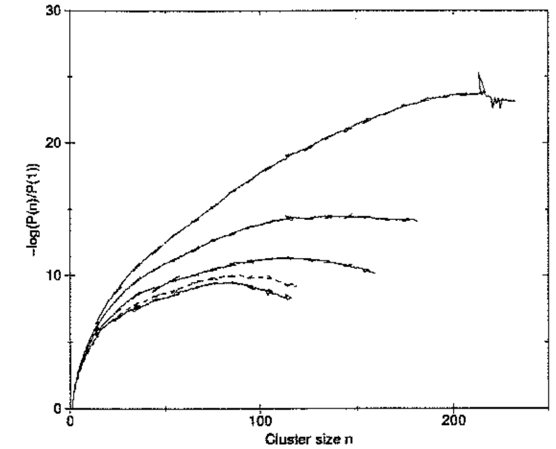

FIGURE 2. The negative logarithm of the probability $P(n)$ of finding a cluster which contains n solid particles, normalized to unity for $n = 1$. The solid curves correspond to Brownian dynamics simulations at different shear rates, the dashed line is the result for Monte Carlo simulations without shear. Simulations were performed for $\kappa\sigma = 5$, $U_0\sigma = 20$, pressure is $\frac{P\sigma^3}{k_BT} = 30$ and from top to bottom shear rates $\dot{\gamma}\tau_B = 0.04, 0.02, 0.01, 0$.

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 assemblies of paramagnetic particles, each carrying a magnetic moment $\mathbf{m}_i$, 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:

$$V_{tot} = \sum_{i<j}\left[u_0(r_{ij}) + u_{dd}(\mathbf{r}_{ij}, \mathbf{m}_i, \mathbf{m}_j)\right] - \sum_i \mathbf{B}\cdot\mathbf{m}_i, \quad (7)$$

where $u_0(r)$ is a truncated and shifted Lenard-Jones potential which reads as

$$u_0(r) = \begin{cases} 4\varepsilon((\frac{\sigma_0}{r})^{12} - (\frac{\sigma_0}{r})^6) + \varepsilon & \text{for } r \leq \sqrt[6]{2}\sigma_0 \\ 0 & \text{else.} \end{cases} \qquad (8)$$

with length and energy scale σ_0 and ε and the dipole-dipole interaction is:

$$u_{dd}(\mathbf{r}, \mathbf{m}_i, \mathbf{m}_j) = -\frac{1}{r^3}\left[3(\hat{\mathbf{r}}\cdot\mathbf{m}_i)(\hat{\mathbf{r}}\cdot\mathbf{m}_j) - \mathbf{m}_i\cdot\mathbf{m}_j\right]. \quad (9)$$

Of particular interest are so-called *super-paramagnetic* particles [26] for which the magnetic moment completely aligns with the external field, if the latter is strong

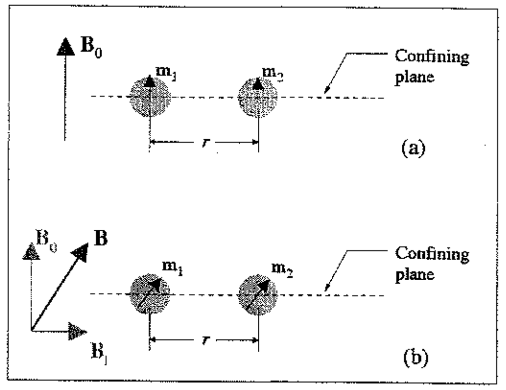

FIGURE 3. Sketch of two super-paramagnetic particles confined on a plane, under the influence of an external magnetic field **B**. In (a), the field is perpendicular to the plane and only the the isotropic part, $\sim r^{-3}$ of the interaction u_{dd} survives. In (b), there is an in-plane field component, rendering the interaction anisotropic, $u = u(\mathbf{r})$ in this case.

enough. In this case, we have $\mathbf{m}_i = \chi \mathbf{B}$, the last term in Eq. (7) becomes an irrelevant constant $N\chi B^2$ and the magnetic field plays the role of tuning the repulsions between the particles through its influence on the magnitude and orientation of the $\mathbf{m}_i$'s see Eq. (9) above.

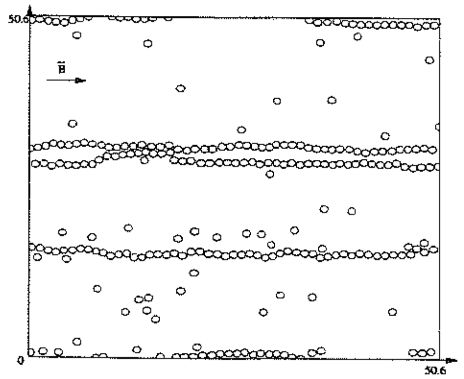

FIGURE 4. Chain formation in two dimensional dipolar colloids as obtained via a Molecular dynamics simulation. The starting configuration was homogeneous. The total simulation time was $35000t^*$ with $t^* = t\sqrt{\varepsilon}/\sigma/\sqrt{m}$ where m denotes the mass of the particles.

Novel experimental methods have shed new light on the statics and dynamics of two-dimensional systems of interacting magnetic colloids [26, 27, 28]. In the following we shall concentrate of the chain formation of two-dimensional super-paramagnetic colloids with an in-plane external magetic field where other preliminary computer simulations have already been published [29]. Snapshots of molecular dynamics simulations of $N = 256$ magnetic particles in an square box are presented in Figure 4. The parameters are number density $n^* = n\sigma_0^2 = 0.1$, the angle between the magnetic field and the plane is zero. The relative strength of the dipol interaction with respect to the thermal energy $k_B T$ is $\lambda = m^2/\sigma^3 kT = 8$.

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) crystal 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 model systems to study further fundamental questions of slow dynamics. In particular, pattern 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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REFERENCES

1. Löwen, H., *J. Phys.: Condensed Matter* **13**, R415-R432 (2001).
2. Sullivan, M., Zhao, K., Harrison, C., Austin, R. H., Megens, M., Hollingsworth, A., Russel, W. B., Cheng, Z. D., Mason, T., and Chaikin, P. M., *J. Phys.: Condensed Matter* **15**, S11-S18 (2003).
3. Helbing, D., *Rev. Mod. Phys.* **73**, 1067-1142 (2001).
4. Anderson, D., Fedele, R., and Lisak, M., *American Journal of Physics* **69**, 1262-1266 (2001).
5. Yethiraj, A., and van Blaaderen, A., *Nature* **421**, 513-517 (2003).
6. Osipov, M. A., Teixeira, P. I. C., and Telo da Gama, M. M., *Phys. Rev. E* **54**, 2597-2609 (1996).
7. Groh, B., and Dietrich, S., *Phys. Rev. E* **63**, 021203 (1-11) (2001).
8. Weis, J. J., Tavares, J. M., and Telo da Gama, M. M., *J. Phys.: Condensed Matter* **14**, 9171-9186 (2002).
9. Onuki, A., *Phase Transition Dynamics*, Cambridge University Press, Cambridge, 2002.
10. Bray, A. J., *Philos. Trans. Roy. Soc. A* **361**, 781-792 (2003).
11. Aarts, D. G. A. L., van der Wiel, J. H., and Lekkerkerker, H. N. W., *J. Phys.: Condensed Matter* **15**, S245-S250 (2003).
12. Dzubiella, J., Hoffmann, G. P., and Löwen, H., *Phys. Rev. E* **65**, 021402 (1-6) (2002).
13. Dzubiella, J., and Löwen, H., *J. Phys.: Condensed Matter* **14**, 9383-9395 (2002).
14. Löwen, H., and Dzubiella, J., *Faraday Discussion* **123**, 99-105 (2003).
15. Chakrabarti, J., Dzubiella, J., and Löwen, H., *Europhys. Letters* **61**, 415-422 (2003).
16. Hoffmann, G. P., and Löwen, H., *Phys. Rev. E* **60**, 3009-3014 (1999).
17. Hoffmann, G. P., and Löwen, H., *J. Phys.: Condens. Matter* **12**, 7359-7370 (2000).
18. Löwen, H., Hansen, J. P., and Roux, J. N., *Phys. Rev. A* **44**, 1169-1181 (1991).
19. Allen, M. P., and Tildesley, D. J., *Computer Simulations of Liquids*, Clarendon Press, Oxford, 1989.
20. Ermak, D. L., *J. Chem. Phys* **62**, 4189-4196 (1975).
21. Wysocki, A., and Löwen, H., to be published.
22. ten Wolde, P. R., Montero-Ruiz, M., and Frenkel, D., *Phys. Rev. Lett.* **75**, 2714-2717 (1995).
23. Auer, S., and Frenkel, D., *Nature* **409**, 1020-1023 (2001).
24. Auer, S., and Frenkel, D., *J. Phys.: Condensed Matter* **14**, 7667-7680 (2002).
25. Auer, S., Blaak, R., Frenkel, D., and Löwen, H., to be published.
26. Zahn, K., Lenke, R., and Maret, G., *Phys. Rev. Lett.* **82**, 2721-2724 (1999).
27. Zahn, K., Méndez-Alcaraz, J. M., and Maret, G., *Phys. Rev. Lett.* **79**, 175-178 (1997).
28. Zahn, K., and Maret, G., *Phys. Rev. Lett.* **85**, 3656-3659 (2000).
29. Satoh, A., Chantrell, R. W., Kamiyama, S.-I., and Coverdale, G. N., *Journal of Colloid and Interface Science* **178**, 620-627 (1996).