Phase transitions in colloidal suspensions and star polymer solutions

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Abstract. Possibilities of fluid–solid and solid–solid phase transformations in colloidal suspensions and star polymer solutions are reviewed. We start from given interparticle pair potentials and predict the corresponding phase diagrams using computer simulations and density functional theory. When possible, the results are compared with experimental data. In particular, we discuss a cascade of freezing transitions for confined colloids and re-entrant melting and anisotropic solid phases for star polymer solutions.

In this paper we review recent work concerning unexpected phase behaviour for peculiar pair potentials which are realized for colloidal suspensions and star polymer solutions. We first discuss sterically stabilized colloids between two parallel glass plates modelled by hard spheres confined between two hard walls. A rich phase diagram including different layering transitions is obtained. Then we investigate the phase behaviour of a very soft potential diverging logarithmically with distance r at the origin. This potential is realized for star polymers in the scaling regime. The theoretical tools used to calculate the phase behaviour are computer simulations, liquid integral equations and solid-cell models.

The model that we discuss for freezing in slit pores consists of hard spheres of diameter σ confined between two parallel plates of distance H. The thermostatistical properties in equilibrium depend solely on two parameters, namely the reduced density $\rho_H = N\sigma^3/(AH)$ (where N is the number of spheres and A the system area) and the reduced plate separation $h = H/\sigma - 1$. Clearly one can continuously interpolate between two and three spatial dimensions by tuning the plate separation: for $H = \sigma$, our model reduces to that of two-dimensional hard discs, while for $H \to \infty$, the three-dimensional bulk case is recovered.

The equilibrium phase diagram as obtained by Monte Carlo computer simulation in the ρ_H–h plane [1, 2] is shown in figure 1 for moderate plate separations h. The phase behaviour is very rich and much more complicated than in the bulk. Cascades of different solid–solid transitions are found. For low densities the stable phase is an inhomogeneous fluid. All possible stable solid phases are also realized as close-packed configurations [3, 4] for a certain plate separation. Accordingly one finds stable layered structures involving intersecting triangular lattices (1△, 2△) and intersecting square lattices (2☐). Also a buckled phase (b) and a phase with a rhombic elementary cell (the rhombic phase (r)) are stable. All transitions are first order.

Similar phases were found in experiments on highly salted charged colloids between glass plates [5–7]. Here even higher reduced plate separations were studied. There is compelling
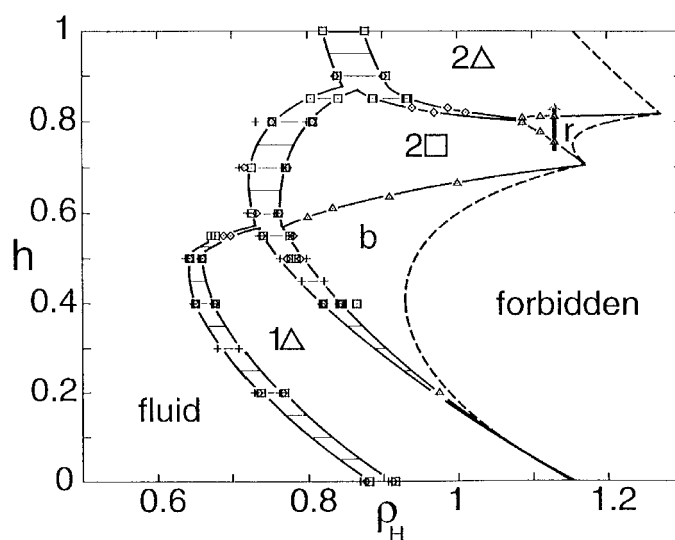
Figure 1. The phase diagram for hard spheres of reduced density ρ_H between parallel plates with effective reduced separation h. Symbols indicate different system sizes: $N = 192$ (+); $N = 384, 512$ (◇); $N = 576$ (△); $N = 1024, 1156$ (□). Six phases occur (fluid, 1△, b, 2□, r and 2△). The close-packing density is marked by a dashed line. Solid lines are guides to the eye. Thin horizontal lines represent two-phase coexistence. From references [1,2].

evidence that a prism phase consisting of alternating prisms built up from spheres is the close-packed configuration in certain domains of h [7]. Still a full quantitative mapping of the experimental data onto the theoretical phase digram of figure 1 has to be performed.

Let us comment on further related aspects of the model.

(a) First, it would be nice to perform a full theoretical calculation for the phase diagram of hard spheres between hard plates. It has already been shown that a solid-cell theory combined with a simple fluid-state free energy gives the same topology of phase behaviour [1,2]. It would be interesting to do a density functional calculation, e.g. with Rosenfeld's functional which possesses the correct geometry excluding configurations of overlapping spheres [8].

(b) Second, one should investigate different confining shapes. Intriguing examples are circular and polyhedral boundaries in two dimensions. Studies have been made for confined hard discs [9] and for magnetic colloids in several geometries [10].

(c) Third, similar layering transitions occur for charged systems, such as confined electrons [11] or plasma sheets [12].

We also note that one should investigate in more detail the stability of phases with long-range orientational order decaying algebraically for large distances. Apart from the well-known hexatic phase, also conceivable are 'tetratic' or 'duatic' phases, where fourfold and twofold symmetry, respectively, persists over large distances. Finally, rigorously establishing the close-packed structure for different h remains an unsolved mathematical problem. Only in the bulk cases has this been achieved [13], although there are more results [14] for finite hard-sphere systems in confinements differing from the two-plate situation considered here.

Let us now turn to star polymer solutions. A star polymer consists of f linear polymer chains that are attached to a common microscopic core [15]. The typical extension of such a star in a good solvent is governed by the so-called corona diameter σ, which measures the

spatial extension of the monomer density around a single star. In a concentrated solution with a finite star number density ρ, the stars are interacting. The interaction is repulsive due to the restriction of allowed configurations for the polymer chains from different centres. In a first approximation, the interaction is pairwise. An explicit form for the pair potential $V(r)$ (where r denotes the interparticle distance) was proposed recently: it consists of an ultrasoft part inside the coronae and falls off exponentially with core–core distance r outside the coronae of two stars. In detail,

$$V(r) = \begin{cases} \dfrac{5}{18} k_B T f^{3/2} \left[-\ln\left(\dfrac{r}{\sigma}\right) + \dfrac{1}{1+\sqrt{f}/2} \right] & \text{for } r \leqslant \sigma \\[3mm] \dfrac{5}{18} k_B T f^{3/2} \dfrac{\sigma}{1+\sqrt{f}/2} \dfrac{\exp(-\sqrt{f}(r-\sigma)/2\sigma)}{r} & \text{for } r > \sigma. \end{cases} \tag{1}$$

Here $k_B T$ is the thermal energy and f is the arm number of a single star. As the effective interaction is purely entropic, it simply scales with the thermal energy. There are many facts confirming that this pair potential (equation (1)) provides for a reasonable description of the effective interaction between the stars:

(i) The behaviour for very small r ($r \ll \sigma$) is consistent with scaling theory [16, 17].
(ii) Microscopic molecular dynamics computer simulations have been performed for several values of f and different numbers of monomers per chains [18]. They reproduce perfectly the overall shape of the effective interaction.
(iii) The scattering intensity for small-angle neutron scattering data could be well described by this pair potential without any fitting parameter for an 18-arm star [17, 19].

On the basis of Monte Carlo computer simulations for the pair potential (1), the phase diagram of star polymer solutions was calculated recently [20]. For the plane spanned by the reduced density $\eta = \pi \rho \sigma^3/6$ and the inverse arm number $1/f$, the results are displayed in figure 2. Remarkably, there is no freezing below a critical arm number $f_c \approx 34$. For $f > f_c$ there is freezing, with increasing density, into a bcc lattice, which then remelts upon further compression. This is in accordance with an earlier qualitative analysis of Witten *et al* [21]. For higher arm numbers, freezing into an fcc lattice occurs, since the potential is becoming steeper as f is increasing. For higher densities, however, there are less common solid structures:
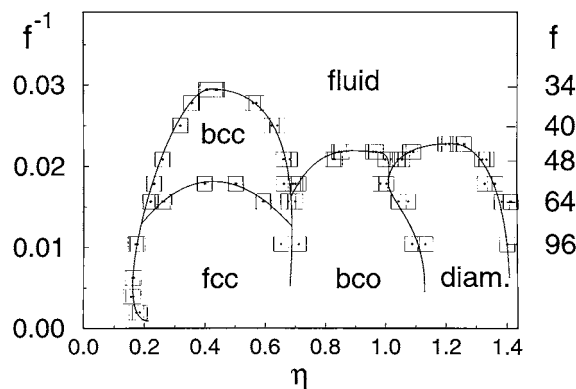

Figure 2. The phase diagram of star polymer solutions for different arm numbers f versus reduced density η. The squares are the results from computer simulation and mark coexistence conditions. The lines are a guide to the eye.

an anisotropic body-centred orthogonal phase as well as a diamond lattice become stable. This is the first time that such crystal structures have been determined to be stable for radially symmetric pair potentials. Obviously this is due to the ultrasoft core together with the crossover at distances comparable to the corona diameter of the stars [20]. A very peculiar behaviour occurs for intermediate arm number $f \approx 48$: increasing the density, the system first freezes, then remelts, then refreezes. Such behaviour has also been found experimentally in spherical diblock copolymer micelles by Gast and co-workers [22].

Apart from the full experimental verification of the phase diagram, there is still the theoretical question of the relevance of triplet and other many-body interactions for higher densities. Recent calculations, based on scaling theory and computer simulation, have shown, however, that the triplet contributions are negligibly small [23]. We finally remark that the interaction depends sensitively on the solvent quality and on the nature of the polymer chains adsorbed onto the core. For a poor solvent close to the so-called Θ conditions, the potential has a completely different form [24]. If a polyelectrolyte such as gelatin is adsorbed instead of a neutral chain, again the effective interaction changes completely [25].

In conclusion, colloidal suspensions are ideal model systems for studying phase transformations. Since their effective interactions are tunable and their confinement is well controlled, a wealth of novel phase transitions can be observed. We also mention recent studies concerning the stability of one-component colloidal quasicrystals [26] and phase transitions in tobacco-mosaic-virus suspensions leading to liquid-crystalline phases [27]. It is remarkable that most of the progress in this field has been achieved through a fruitful collaboration between theory, computer simulations and experiment. Accepting this as established, we hope that the theoretical phase diagrams discussed in this paper can be verified (or disproved) for actual samples and that further interesting phases will be found which both enhance our fundamental understanding of mesoscopic matter and lead to new exciting applications.

References

[1] Schmidt M and Löwen H 1996 *Phys. Rev. Lett.* **76** 4552
[2] Schmidt M and Löwen H 1997 *Phys. Rev.* E **55** 7228
[3] Pansu B, Pieranski P and Pieranski P 1984 *J. Physique* **45** 331
[4] Pieranski P, Strzelecki L and Pansu B 1983 *Phys. Rev. Lett.* **50** 900
[5] Van Winkle D H and Murray C A 1986 *Phys. Rev.* A **34** 562
      Murray C A, Sprenger W O and Wenk R A 1990 *Phys. Rev.* B **42** 688
      Murray C A 1992 *Bond-Orientational Order in Condensed Matter Systems* ed K J Strandburg (New York: Springer)
[6] Weiss J, Oxtoby D W, Grier D G and Murray C A 1995 *J. Chem. Phys.* **103** 1180
[7] Neser S, Bechinger C, Leiderer P and Palberg T 1997 *Phys. Rev. Lett.* **79** 2348
[8] Rosenfeld Y, Schmidt M, Löwen H and Tarazona P 1996 *J. Phys.: Condens. Matter* **8** L577
      Rosenfeld Y, Schmidt M, Löwen H and Tarazona P 1997 *Phys. Rev.* E **55** 4245
[9] Németh Z T and Löwen H 1998 *J. Phys.: Condens. Matter* **10** 6189
      Németh Z T and Löwen H 1999 *Phys. Rev.* E **59** 6824
[10] Bubeck R, Neser S, Bechinger C and Leiderer P 1998 *Prog. Colloid Polym. Sci.* **110** 41
      Zahn K, Lenke R and Maret G 1999 *Phys. Rev. Lett.* **82** 2721
[11] Peeters F M 1997 *Two Dimensional Electron Systems* ed E Y Andrei (Amsterdam: Kluwer Academic) pp 17–32
      Peeters F M, Partoens B, Schweigert V A and Goldoni G 1997 *Physica* E **1** 219
[12] Mitchell T B, Bollinger J J, Dubin D H E, Huang X-P, Itano W M and Baughman R H 1998 *Science* **282** 1290
[13] See, e.g., Cipra B 1998 *Science* **281** 1267
[14] Wills J M 1998 *Math. Intelligencer* **20** 16
[15] For a review, see Grest G S, Fetters L J, Huang J S and Richter D 1996 *Adv. Chem. Phys.* **94** 67
[16] Witten T A and Pincus P A 1986 *Macromolecules* **19** 2509
[17] Likos C N, Löwen H, Watzlawek M, Abbas B, Jucknischke O, Allgaier J and Richter D 1998 *Phys. Rev. Lett.* **80** 4450

[18] Jusufi A, Watzlawek M and Löwen H 1999 *Macromolecules* **32** 4470
[19] Stellbrink J, Abbas B, Allgaier J, Monkenbusch M, Richter D, Likos C N, Löwen H and Watzlawek M 1998 *Prog. Colloid Interface Sci.* **110** 25
[20] Watzlawek M, Likos C N and Löwen H 1999 *Phys. Rev. Lett.* **82** 5289
[21] Witten T A, Pincus P A and Cates M E 1986 *Europhys. Lett.* **2** 137
[22] McConnell G A and Gast A P 1997 *Macromolecules* **30** 435
[23] von Ferber C, Jusufi A, Watzlawek M, Likos C N and Löwen H 2000 to be published
[24] Likos C N, Löwen H, Poppe A, Willner L, Roovers J, Cubitt B and Richter D 1998 *Phys. Rev. E* **58** 6299
[25] Likos C N, Vaynberg K A, Löwen H and Wagner N J 2000 to be published
[26] Denton A R and Löwen H 1998 *Phys. Rev. Lett.* **81** 469
[27] Graf H and Löwen H 1999 *Phys. Rev. E* **59** 1932