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Possibilities of phase separation in colloidal suspensions

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Abstract

Different physical mechanisms leading to phase separation in colloidal fluids are reviewed. Phase separation into two fluid phases can be induced by (a) the long-ranged van der Waals attraction between the colloidal spheres, (b) counterion overscreening, (c) added polymer (d) depletion effects of the solvent, (e) a solvent phase transition. If a strong short-range attraction between the colloidal spheres is present, phase separation occurs into two isostructural *solid* colloidal phases.

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1. Introduction

Phase separation from a homogeneous fluid phase into a gas-like and a liquid-like homogeneous phase possessing two different densities is most commonly known for classical fluids whose pairwise interaction has an attractive part. The most prominent example is a three-dimensional Lennard-Jones system. Its phase diagram exhibits a fcc-solid, a liquid and gas phase [1], see Fig. 1. Above the critical temperature T_c , only one fluid phase is stable. If the system is rapidly cooled down into the coexistence region below T_c , the system starts to decompose into the two stable gaseous and liquid phases until two macroscopic large regions of liquid and gas phases are built up.

A typical interparticle potential $V(r)$ for a stable fluid contains a strong repulsion for short distances r whereas for larger distances both attractive and repulsive forces are conceivable. There is a widespread belief in the literature that an arbitrary attraction for long interparticle distances necessarily leads to liquid–gas phase separation. However, one may easily find counterexamples against this hypothesis. What is true is that liquid–gas separation occurs provided the *range* of the attraction is long enough. For different concrete interparticle pair potentials, Coussaert and Baus [2] have recently investigated the stability of a liquid using a van der Waals theory. Their study strongly supports

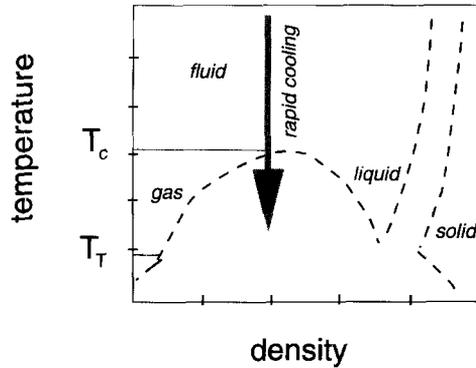


Fig. 1. Phase diagram in the density–temperature plane for a typical fluid with an attractive interparticle potential (e.g. Lennard-Jones interaction). If the range of the attraction is long enough, three different phases (gas, liquid, solid) can be formed and there is a critical temperature T_c and a triple temperature T_T . Rapid cooling (arrow) from the one-fluid-phase region into the density gap of the two-phase region induces decomposition into the two stable phases.

the view that liquid–gas phase separation only occurs for long-range attractions. On the other hand, the stability of a liquid is quite *independent of the amplitude* of the attraction since this quantity simply scales out with temperature.

Let us discuss a simple example: If the interparticle potential $V(r)$ consists of a hard-sphere repulsion and an attractive part proportional to $-1/r^n$, then it is the exponent n that decides the possibility of phase separation. Coussaert and Baus [2] found that liquid–gas phase separation occurs for $n \lesssim 7.6$. Then there is a certain region in the density–temperature plane where a liquid phase is thermodynamically stable, see Fig. 2(a). On the other hand, there is no stable liquid phase for $n \gtrsim 7.6$ and the phase diagram looks qualitatively as shown in Fig. 2(b). For $n \simeq 7.6$ there is an interesting limiting situation where the critical temperature coincides with the triple temperature. This means that, in the density–temperature plane, the endline of fluid densities exhibits a saddle point for $T = T_c \equiv T_T$.

Colloidal suspensions represent rather complex liquids due to the presence of the solvent and of co- and counterions and added polymer in the solution. Most discussions of gas–liquid phase separation of the colloidal spheres is done in the context of *effective* pair interactions between the spheres. The advantage with respect to ordinary simple liquids is that the interaction can be tailored e.g. by varying the salt concentration or the concentration of added polymer. The statement above immediately implies that an attraction in the effective interaction is not sufficient to drive a phase separation. The more difficult question concerns the range of this attraction. Depending on the range a liquid may or may not be stable. As discussed above, these two regimes are separated by an interesting situation where the triple point coincides with the critical point.

In this paper, I shall discuss whether and how phase separation is possible in colloidal suspensions. Gas–liquid as well as phase separation into two isostructural solid phases

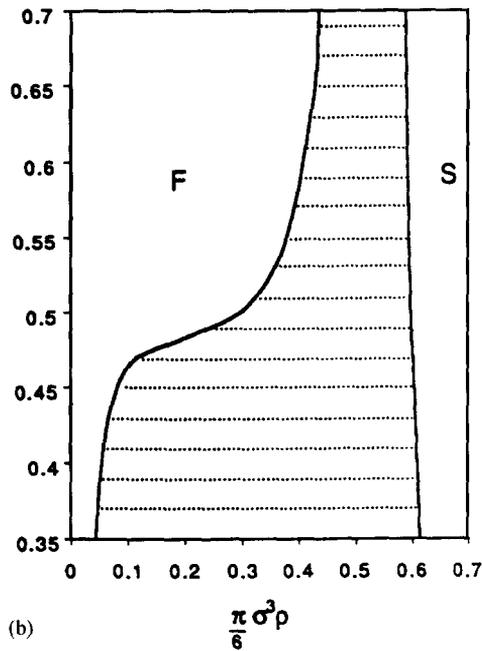
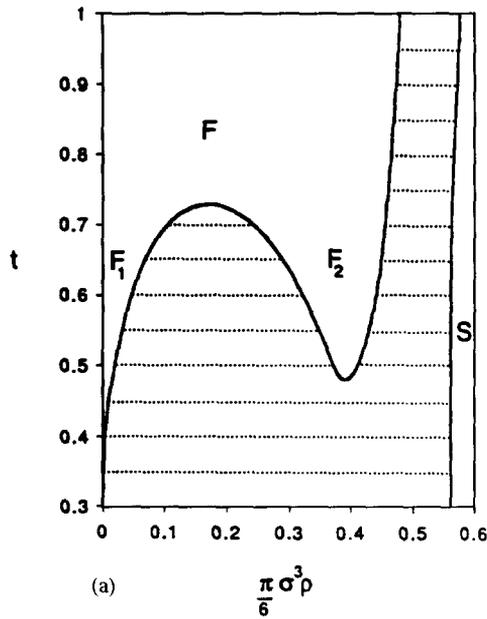


Fig. 2. Qualitative shape of the phase diagram: reduced temperature t versus reduced density $\pi\sigma^3\rho/6$ (from Ref. [62]). (a) Situation where a liquid (F_2) is stable with respect to the gas (F_1) and the solid (S). (b) Situation where always only a fluid (F) is stable.

is conceivable depending on the effective interaction between the colloidal spheres. Different physical mechanisms recently shown to lead to phase separation are reviewed.

2. Different mechanisms of fluid–fluid phase separation

2.1. Van der Waals attraction

If the solvent and the colloidal material have different polarizabilities, the effective interaction between two colloidal spheres necessarily involves the attractive van der Waals forces resulting in the interparticle potential

$$V_A(r) = -\frac{H}{6} \left[\frac{\sigma^2}{2(r^2 - \sigma^2)} + \frac{\sigma^2}{2r^2} + \ln \left(1 - \frac{\sigma^2}{r^2} \right) \right], \quad (1)$$

σ denoting the colloidal diameter and $H > 0$ the Hamaker constant. This attractive potential $V_A(r)$ is proportional to r^{-6} for large interparticle distances r and diverges as $1/(r - \sigma)$ near contact. Since the exponent $n = 6$ is smaller than 7.6, the long-range tail may induce liquid–gas phase separation. The theoretical investigation can be done within the framework of simple liquids. Explicit calculations were done by Victor and Hansen [3,4]. However, experimentally there have not yet been any unambiguous experiments verifying this kind of phase separation, although Victor and Hansen refer to a work of Kotera and coworkers [5] interpreted in terms of reversible coagulation in the secondary minimum of the DLVO potential. The reason seems to be that, in typical samples, one encounters conditions that are supercritical; for a more detailed discussion see [6].

2.2. Attraction by counterion overscreening

There is a controversial discussion in the literature on the question of whether equally charged spheres can attract themselves in their counterion solution. Based upon linear screening theory an attraction was claimed by different authors [7–9]. However, as was demonstrated by Overbeek [10] and later on by Rosenfeld [11], there is no such attraction within a correct treatment of linear screening theory. The resulting force is exactly the electrostatic part of the Derjaguin–Landau–Verwey–Overbeek potential [12,13] involving a Yukawa or screened Debye–Hückel interaction:

$$V_Y(r) = \frac{Z^2}{(1 + \kappa\sigma/2)^2 \epsilon r} \exp(-\kappa(r - 2\sigma)), \quad (2)$$

where Z is the macroion charge, ϵ the dielectric constant of the solvent and κ the Debye–Hückel screening constant. If nonlinear screening effects are included using the Poisson–Boltzmann approach [14], again there is no possibility of attraction between equally charged plates [15] and between equally charged spheres [16,17]. However, in the Poisson–Boltzmann theory, correlations between the counterions are neglected

completely. If they are included (full nonlinear screening) there may be a possibility of attraction between equally charged plates due to counterion overscreening; however the corresponding conditions are only met in suspensions containing divalent counterions of high concentration or highly asymmetric salts. These results are based on computer simulations [18–20], liquid integral equations [21] and density functional theory [22]. Still a full theory for two spheres (e.g. based on a reliable density functional for the inhomogeneous multi-component plasma) is needed to clear up the possibility of their attraction theoretically. If their effective attraction is strong enough, it may even drive liquid–gas phase separation.

Recently also a thermodynamic perturbation theory was proposed by Trigger et al. [23] which also predicts a possible attraction between charged spheres. The problem here is to justify the validity of the cumulant expansion where the macroion–counterion coupling is assumed to be small.

Approaching the problem from the experimental side, the situation is again puzzling. Recent claims by Tata et al. [24,25] for a vapor–liquid condensation in charged colloidal suspensions were criticized by Palberg and Würth [26]. The latter authors pointed out that one has to be very careful in checking the absence of any salt gradient in the sample. Another direct measurement of the effective interaction between two spheres was performed by Crocker and Grier [27]. At least for the parameters they explored there was no indication of any attraction. Kepler and Fraden [28], on the other hand, claim a possible attraction due to overscreening. One should bear in mind, however, that the experimental samples here are confined colloids between glass plates where the corresponding image charges can change the nature of screening considerably. Also, experimentally, it is difficult to distinguish between an attraction due to the van der Waals interaction and an attraction due to overscreening effects.

2.3. Effective attraction induced by added polymer

For stable colloidal suspensions whose interaction is governed solely by a repulsive potential, there may be phase separation if a nonadsorbing polymer is added to the solution. The first possibility of such a phase separation was pointed out 40 years ago by Asakura and Oosawa [29]; for a historical review see also [30]. Consider two big colloidal spheres near touching, see Fig. 3. Then there is a depletion zone of the added free polymer around these colloidal spheres. This implies that the osmotic pressure exerted onto the spheres by the excluded polymer is not balanced and gives rise to an effective attraction between the spheres [31,32]. This attraction then may cause phase separation. Recent extensive computer simulations on a mixture of colloidal particles and added polymer chains with steric interactions [33,34] confirm these attractions and a possible phase separation. Also the phase diagram of a colloid plus polymer system was experimentally completely investigated where a liquid–gas phase separation of the colloidal particles induced by the added polymer was found [35]. Both fluid–solid and gas–liquid–solid phase transitions have been clearly observed by Pusey and coworkers [36].

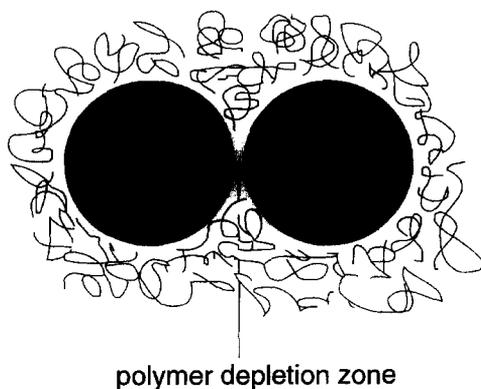


Fig. 3. Sketch of the depletion zone of added polymer in between two large colloidal spheres close to touching.

2.4. *Effective attraction between big spheres in a solvent of small spheres*

The same depletion effect occurs if the polymer is modelled as a spherical random coil that cannot penetrate into the colloidal particles. Equivalently one can discuss a two-component mixture of big colloidal hard spheres and small hard spheres with additive diameters. Most of the discussion was based on a study of liquid integral equations. The Percus–Yevick closure does not give rise to phase separation. Using the more correct Rogers–Young closure scheme, Biben and Hansen [37,38] found that the osmotic pressure by the small spheres exerted onto the big spheres yields phase separation of the big spheres provided the ratio of diameters is small enough. This result is of peculiar importance since it implies that a phase separation can be driven purely by entropy. The same result was found [39] in a more extended parameter space. The physical “depletion” picture is similar to that for an added polymer, see Fig. 4, and was elucidated by Lekkerkerker and Stroobants [40] who used a semi-phenomenological approach to model the relevant free energies in order to show that the depletion mechanism is really strong enough to drive phase separation. A third complementary approach was proposed by Rosenfeld [41,42] who used a renormalized density functional approach to get a very good equation of state for the hard-sphere mixture also yielding phase separation.

An important point, however, is that any approach cited above involves some approximations. The direct simulation of a strongly asymmetric hard-sphere mixture for similar packing fractions of the big and small spheres requires too much CPU time on present-day computers due to ergodicity problems. Therefore one may look for simpler models which can be solved exactly or by computer simulation. Indeed, two-dimensional hard-core lattice models were found whose analytical solution exhibits a similar kind of demixing [43,44]. Also a mixture of small and large hard cubes was investigated by computer simulation [45] which again shows phase separation.

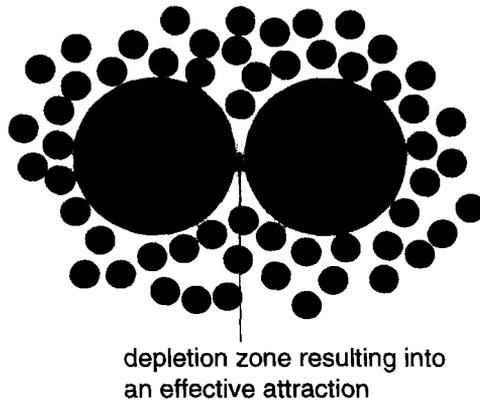


Fig. 4. Same as Fig. 3, but now for a mixture of large spheres and small spheres where the packing fractions of the large and small spheres are comparable.

Finally the problem was also attacked from the experimental side. The phase separation in hard-sphere mixtures was indeed detected in strongly asymmetric bimodal suspensions of sterically stabilized [46,47] or charge-stabilized [48,49] colloidal spheres. Hence, from theory, simulation and experiment, there seems to be a strong consensus that such a type of phase separation does occur. A final remark concerns the question of whether the phase separation is fluid–fluid or fluid–solid: initially Biben and Hansen [37,38] proposed a fluid–fluid scenario but recent experiments [47] show that the transition is in fact a fluid–solid transition. This was suggested on theoretical grounds in Ref. [40] and is also discussed in Ref. [46].

2.5. Phase separation induced by a solvent phase transition

In standard samples of colloidal suspensions the solvent is far away from any phase transition. One can think, however, about many ways of reaching a solvent phase transition for experimentally accessible conditions. The most prominent examples are silica spheres embedded in a mixture of lutidine and water exhibiting a coexistence of a lutidine-rich and water-rich phase close to room temperature. This sample was extensively studied by Beysens and coworkers [50–52]. Indeed, near the critical point, aggregation and partitioning of the colloidal particles was found.

The physical mechanism of driving such a kind of phase separation strongly depends on whether the solvent phase transition is first or second order. For a *first-order* solvent phase transition, a general theoretical investigation was done by the author [53,54] based on a Ginzburg–Landau description of the solvent phase transition. If, near phase coexistence, the metastable phase wets the colloidal surfaces, there are certain regions of this metastable phase around each colloidal sphere which are separated by an interface from those regions where the stable phase is present, see Fig. 5(a). On the one hand, there is a gain in energy since the colloidal surface prefers the metastable phase, but

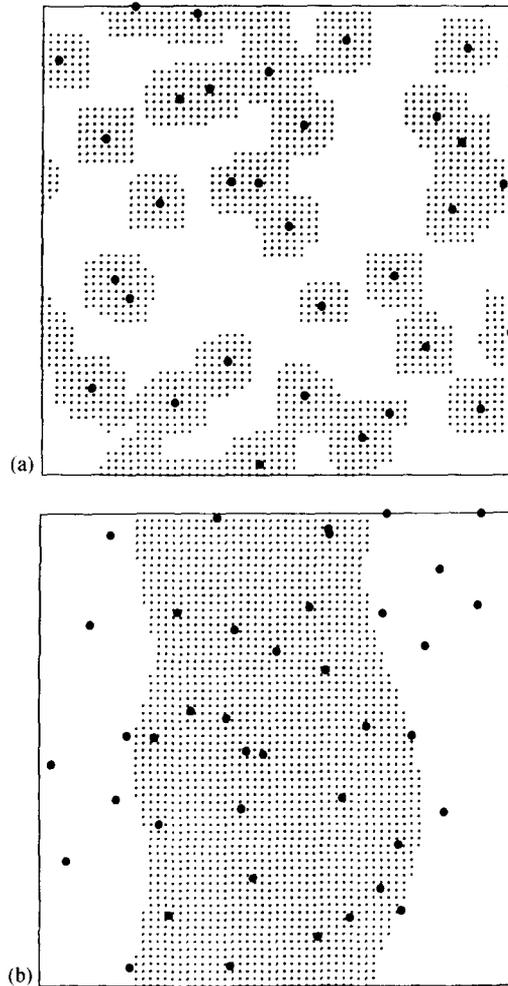


Fig. 5. Results for the interface between the metastable phase and the stable phase from computer simulation (from Ref. [53]): the colloid positions (black circles) are projected from a slab to the xy -plane of the simulation box. The dark pixels indicate that – on z -average – the metastable phase is present while a white region is filled with the stable phase. (a) Clustered situation. (b) Phase-separated situation. Here the colloid density is higher in the region filled with the metastable phase.

there are also two energy penalties to pay for such an arrangement on the other hand. First, there is a free energy penalty scaling both with the volume of the region occupied by the metastable phase and with the reduced distance from coexistence. The second free energy penalty stems from the surface free energy needed to create an interface between the stable and metastable phase which scales with the area of the intersecting region. Hence there is a tendency in forming large clusters of the metastable phase containing many colloidal particles since the surface free energy is reduced at the expense of the higher energy due to the direct colloidal repulsion. If each of these energies is taken into account properly, an approximative analytical treatment as well

as a computer simulation [53,54] predict phase separation of the colloidal particles. In such a phase-separated case, there is a region filled with the metastable phase and many colloidal particles and another region with the stable phase containing only few colloidal particles, see Fig. 5(b). In fact there are two possibilities to reach this phase separation. Either it starts from a situation involving only the stable phase or it starts from a clustered situation (Fig. 5(a)). The transition from the clustered to the phase-separated situation turns out to be the first order [53,54]. This implies that the mean number of colloidal particles per cluster discontinuously jumps from a finite number of infinity. This transition can also be viewed as a percolation transition with respect to the region filled up with the metastable phase.

On the other hand, for a *second-order* solvent phase transition, the critical fluctuations of the solvent can induce an effective attraction between two colloidal spheres. This has a quantum mechanical analogon in the Casimir effect [55] where the vacuum fluctuations of the electromagnetic field result in an effective attraction between two neutral parallel metal plates. Recently Burkhardt and Eisenriegler [56] (see also [57]) found that the critical fluctuations give rise to an attractive interparticle potential that decays proportional to $-\exp(-r/\xi)/r^\gamma$ for large interparticle distances r where the exponent γ is slightly larger than 1 and ξ is the correlation length in the near-critical solvent. Directly at criticality, we have $\xi = \infty$ which implies that phases separation is strongly expected near criticality.

As already mentioned, a series of interesting experiments have been performed by Beysens and coworkers on colloidal silica spheres with a solvent mixture consisting of water and lutidine [50,51]. In the vicinity of the lower consolute point of the solvent mixture the colloidal spheres aggregate since they cover themselves with a lutidine-rich layer. Hence it appears that this aggregation might be related to the phase separation for a first-order solvent phase transition. More recently, experiments on silica colloids in reentrant liquid mixtures of 3-methylpyridine plus water plus heavy water exhibit a similar flocculation near the solvent phase transition [58]. In the experiments one can also reach criticality probing the influence of critical fluctuations. It is still not completely clear whether and how these experimental facts are exactly related to the theoretical mechanisms near and far from criticality.

3. Phase separation into two isostructural solid phases

If the interparticle potential has a very short-range attraction there is no way for liquid–gas phase separation. In this extreme case, however, there is a possibility of a phase separation into two isostructural solid phases. A corresponding phase diagram in the density–temperature plane is depicted in Fig. 6. Young and Alder [59] were the first to discover such a solid-to-solid transition for hard spheres with an attractive square-well potential of range δ equal to one-half of the hard-sphere diameter σ . By computer simulation they found that it is energetically more favourable for the second nearest neighbours to shrink forming a crystal with higher density which can coexist

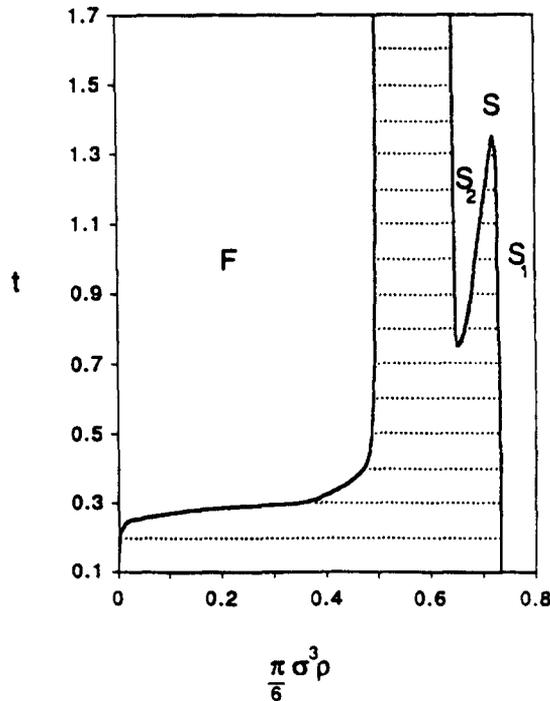


Fig. 6. Same as Fig. 2, but now for an interparticle potential with a short-range attraction. The phase diagram exhibits two isostructural solid phases (S_1 and S_2). The coexistence line terminates at a solid–solid critical point (from Ref. [62]).

with a crystal of a larger lattice constant that possesses a higher entropy. This transition, however, is basically triggered by the steepness of the square-well potential; it disappears for softer interactions.

For an even shorter-ranged interparticle potential, Bolhuis and Frenkel [60,61] have recently shown that an isostructural solid-to-solid transition can be induced by a coupling to the nearest neighbour particles. Solid–solid coexistence is possible if the range δ of the attractive square-well potential of the hard spheres is smaller than 0.07. This transition is persistent also for smoother potentials such as a double Yukawa potential.

From the underlying physics, this phase separation is by now well-understood. Already a very simple uncorrelated cell-model can qualitatively reproduce the results [60,61] and better quantitative agreement was achieved in using a van der Waals theory for solids [62], a variational method based on the Gibbs–Bogoliubov inequality [63,64] and classical density functional theory of freezing [65–68].

In two spatial dimensions, the freezing process is fundamentally different from that in three dimensions since the occurrence of an intermediate hexatic phase possessing long-range bond-orientational order is possible. A peculiar system which was studied recently by Bladon and Frenkel [69] consists of hard disks with a square-well attraction. In fact there is again a solid–solid critical point. In the neighbourhood of the critical point a hexatic phase was found.

Much less work has been spent on experiments on solid–solid phase separation. One may hope that colloidal suspensions can really mimic such a hard-core plus short-range attraction, e.g. due to the strong van der Waals attraction near contact. So in principle the solid–solid phase separation should be observable. Its experimental verification is highly probable but still lying ahead.

4. Future problems

This paper of course cannot comprehensively study all mechanisms of demixing. Since colloidal suspensions can be studied in many different complex situations, it might be expected that there are still further possibilities for phase separation, particularly for nonadditive binary and ternary mixtures, rod-like colloids [30], and polyelectrolytes [70].

Let us finish with a couple of arbitrarily chosen open questions. The first point concerns the violation of Gibbs' phase rule. Having the solid–solid phase separation in mind, it might be possible that for certain interparticle pair potentials in a one-component system a *quadruple point* occurs with four coexisting phases: gas, liquid and two isostructural solid phases. This would then immediately imply that Gibbs' phase rule is violated. In fact the DLVO potential is a possible candidate for such a situation. A detailed investigation is in progress.

Another interesting situation consists of a solvent near a first-order phase transition together with colloidal particles that are in a solid phase. One might surmise that the solvent-induced attraction again can give rise to a solid–solid demixing.

A third situation concerns a colloidal suspension confined between two parallel plates. The interaction with the plates can also induce phase separation with a rich scenario depending on details of the particle/solvent-plate interaction.

Last, the critical behaviour of the following two situations should be examined in more detail. First, the peculiar case where the critical point coincides with the triple point, as mentioned in the first section, has never been investigated as far as critical exponents and properties are concerned. Second, the exponents corresponding to the solid–solid critical point, as mentioned in the last section (see again Fig. 6), are not known. Within a density functional theory, it was shown that the exponents are classical [65]. This was highly expected since the density functional theory can be shown to be equivalent to a mean-field-like theory yielding classical exponents [1]. One might conjecture that the exponents are really classical due to the fact that certain critical modes are suppressed in the crystalline lattice. This may be quite similar to the classical critical point arising in phase diagrams of hydrogen in metals [71].

Acknowledgements

It is a pleasure to dedicate this paper to Prof. Rudolf Klein on the occasion of his sixtieth birthday.

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