**TOPICAL REVIEW**

# Colloidal soft matter under external control

**H Löwen**

Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1,
D-40225 Düsseldorf, Germany

**Abstract**
The physics of soft-matter systems controlled by external fields is reviewed
and previewed. Particular emphasis is placed on statistical properties of well-
characterized colloidal dispersions in different confining situations, in laser-
optical, magnetic and electric fields as well as under shear. These are very active
research areas where different complementary methods such as experiments,
computer simulations and theory have been applied in parallel. Recently
discovered novel phase transitions, generated and triggered by an external field,
are described and the perspectives in this field for the next decade are discussed.

## 1. Introduction

By definition, soft-matter systems cover at least one structural length scale in the mesoscopic
regime between a micrometre and a nanometre. By this relatively broad definition, quite
different classes of materials such as colloidal dispersions, polymers, membranes and
biological macromolecules are included. These systems are 'soft' as they react much
more sensitively to mechanical perturbations (such as shear) as compared to pure molecular
materials.

Research activities in the field of soft matter are interdisciplinary and have exhibited rapid
growth and strong diversification. There are many reasons for this. First, soft-matter systems
are essential in many technical applications ranging from paints to lubricants and drilling
fluids [1, 2]. Second, soft-matter systems are omnipresent in medical and pharmaceutical
applications such as colloidal carrier fluids for drug delivery [3, 4]. Furthermore, soft-matter
systems play a key role in biological problems such as recognition of DNA [5, 6], transport
through cell membranes [7] and protein crystallization [8–11]. Using new preparation methods,
by a combination of supramolecular constituents one is able to compose 'intelligent' materials
with novel properties [12, 13]. Last but not least, the 1991 physics Nobel prize awarded to
P G de Gennes for statistical theories of soft matter [14] has given rise to flourishing fundamental
research in the field of soft matter. The framework of statistical physics allows for quantitative
predictions of soft-matter properties which can be verified directly in experiments and can be
exploited for a systematic search for new material characteristics.

In this topical review we focus on one important part of this broad and interdisciplinary
subject, namely on the *physics of colloidal dispersions*. The latter are solutions of mesoscopic
solid particles with a stable (i.e., non-fluctuating) shape embedded in a molecular fluid solvent.

This class of materials includes nevertheless a broad range of different systems, such as aqueous suspensions of polystyrene or latex spheres or rods as well as dusty plasmas. Among the various soft-matter systems, colloidal dispersions play a particular role as they can be both prepared and characterized in a controlled way. The effective interaction between the colloidal particles can be tailored by changing, e.g., the salt concentration in the solvent [15]. Moreover, colloidal suspensions can be regarded as a prototype of soft matter as they represent in a certain sense the simplest complex fluids (note that the term 'complex' does not necessarily imply 'complicated'): the length-scale separation between the molecular solvent and the mesoscopic particles is almost complete. This is a unique situation. Spherical particles without any additional structure on the mesoscopic length scale possess the simplest and highest possible symmetry. This directly implies that a simple theoretical modelling of a single particle without many fitting parameters is possible. Interesting questions concern collective many-body effects induced by cooperation of many particles. A striking advantage of colloidal dispersions lies in the fact that these questions can be studied simultaneously by using three different complementary methods, namely *experiment, computer simulation* and *theory*. This can be demonstrated using three examples:

(i) the *bulk freezing transition* of sterically stabilized colloidal suspensions or binary mixtures thereof, for which light-scattering experiments [16,17], Monte Carlo simulations [18] and the classical density functional theory of freezing [19, 20] were developed at the same time and proved mutually stimulating;

(ii) the *kinetic glass transition* where colloidal systems have played a pioneering role in establishing an experimental test of mode-coupling theory [21];

(iii) more recently, experimental studies of *crystal nucleation* have been performed [22, 23] which have been compared to classical nucleation theory [24, 25] and computer simulations using the transition-path sampling method [26].

A profound theoretical understanding also provides an insight into the general basic principles and mechanisms of phase transformations; in this way colloids play a prominent role as *model systems* for condensed matter in general. Although bulk phase transitions of colloidal soft matter have become well understood, important questions in confining geometries and additional external fields are still open. The motivation to study the influence of external fields has two main sources. First, by definition, soft matter reacts sensitively to external perturbations and manipulations. The occurrence of stable colloidal bulk samples is the exception rather than the rule, i.e., one has to protect the sample carefully against tumbling and other perturbations which already requires an experimental effort. In reality, e.g., in industrial applications, colloidal matter is generically exposed to external perturbations. The sensitivity of colloidal soft matter to external fields has been exploited empirically in many different technical applications but it is fair to say that the systematic scientific understanding is still immature. Based on statistical mechanics, such a systematic approach could provide both qualitative and quantitative predictions. The second reason is that qualitatively novel effects can be induced. One example is the shear-banding instability, i.e., the spontaneous formation of sheets with different microstructures in linear shear flow. Further examples will be described in more detail below.

In contrast to molecular condensed matter systems, working with colloids provides the fascinating possibility to control and tailor the external perturbation and study their influence on scales of length and time which are typically associated with the particle structure. The typical relaxation time of the colloidal particles is of the order of milliseconds which is orders of magnitude larger than molecular relaxation times. Likewise, the relevant length scale for the colloidal structure lies in the mesoscopic rather than molecular range. This implies that

real-space and real-time experiments become feasible, whereas this cannot be achieved for atomic and molecular systems due to their fast relaxation (except maybe for the very special phenomenon of critical slowing down near a critical point). Thus, a direct comparison with coarse-grained computer simulations and theories opens up new perspectives and promises new fundamental insights as well as qualitatively novel effects. The final goal is to systematically control properties of colloidal matter using external fields.

This topical review is organized as follows. In section 2, we define the degree of complexity in different situations and for different systems in order to classify the difficulty of problems. In section 3, we describe interfaces and colloids in different confining situations. Then, in sections 4–7, we summarize recent progress achieved as regards phase transitions of colloidal dispersions in laser-optical, magnetic, electric and shear fields. New perspectives for the next decade are finally presented in section 8, and we conclude in section 9.

## 2. Complexity scale of systems and problems

Defining complexity is somewhat arbitrary; nevertheless we shall try to put the whole physics into a general classification scheme. One first has simply to distinguish between the complexity of the colloidal sample itself ('complexity of the system') and the complexity of the circumstances under which the colloidal sample is investigated ('complexity of the problem'). Schematically one may thus draw $x$- and $y$-axes which indicate these two different kinds of complexity; see figure 1. The simplest situation is a system composed of equally sized spherical particles in equilibrium corresponding to a one-component classical system with a radially symmetric (effective) pair potential $V(r)$ in the absence of any external field. Its total potential energy reads

$$U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{i<j}^{N} V(|\vec{r}_i - \vec{r}_j|) \tag{1}$$

where $\vec{r}_i$, $(i = 1, \ldots, N)$ are the three-dimensional position vectors of $N$ particles pointing towards the centres of the spheres. Typical examples for the pair potential $V(r)$ are hard-sphere interactions for sterically stabilized suspensions and Debye–Hückel screened Coulomb (or Yukawa) potentials for charge-stabilized suspensions [16].

The next level of *problem complexity* is to study the same system in an external potential. This means that an external energy

$$U_{\text{ext}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{i=1}^{N} V_{\text{ext}}(\vec{r}_i) \tag{2}$$

is added to the potential energy (1), $V_{\text{ext}}(\vec{r})$ representing the external potential, coupling to the particle centres.

Equilibrium statistics in the canonical ensemble is then obtained via the canonical partition function
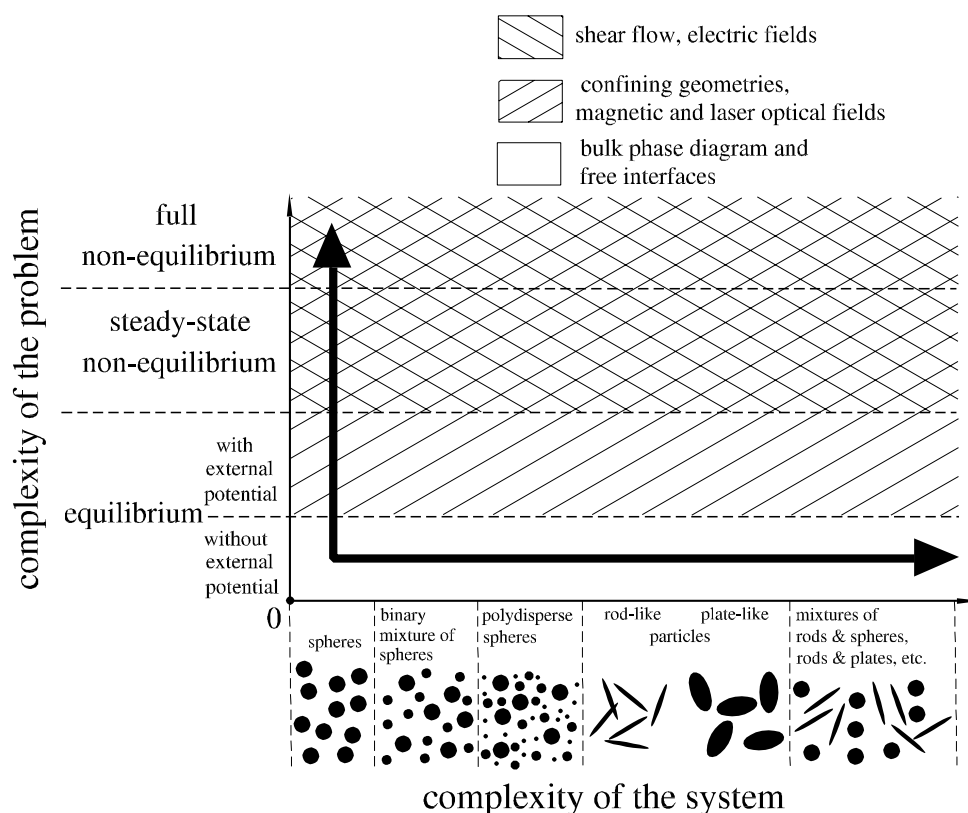
$$Z = \frac{1}{\Lambda^{3N} N!} \int d^3 r_1 \cdots \int d^3 r_N \, \exp\left[-U_{\text{total}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)/k_B T\right] \tag{3}$$

with

$$U_{\text{total}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) + U_{\text{ext}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{4}$$

where $\Lambda$ is the thermal wavelength and $k_B T$ the thermal energy [27]. The Helmholtz free energy $F$, whose non-analyticities in the thermodynamic limit indicate phase transitions, is obtained via

$$F = -k_B T \ln Z. \tag{5}$$

**Figure 1.** Schematic diagram of complexity: the *x*-axis shows the complexity of the system, the *y*-axis the complexity of the problem. The two arrows indicate possible research directions. The problems associated with different kinds of external field are also indicated.

In the bulk, phase coexistence is obtained by equating temperature, pressure and chemical potential in the two coexisting phases.

The *system complexity* is enhanced in a binary or multicomponent (polydisperse) mixture of spherical particles. In this case, one has to sum (integrate) over all particle species in the canonical trace (3). Even more complexity arises from orientational degrees of freedom as described by a unit vector. Then the thermodynamical trace involves an additional integration over the solid angle. This is essential for cylindrically symmetric (rod-like or plate-like) particle shapes. One may then consider mixtures of spheres and rods or plates and rods etc to enhance the complexity further. An even higher degree of complexity arises from additional internal degrees of freedom, as present in flexible particle shapes. One important and very popular direction of colloidal research is represented by the arrow in figure 1 parallel to the *x*-axis: this concerns equilibrium properties such as bulk phase transitions, in more and more complex systems.

On the other hand, *problem complexity* is enhanced by turning from equilibrium properties to non-equilibrium problems. This is demonstrated best by considering explicitly time-dependent trajectories $\vec{r}_i(t)$, $i = 1, \ldots, N$, of $N$ colloidal particles which are stochastically 'kicked' by the solvent molecules. In a field-free case, a time average yields equilibrium statistics, but an external field pushes the system into non-equilibrium. In a general situation

with neglected hydrodynamic interactions, the particle trajectories are obeying Langevin equations

$$\xi \frac{d\vec{r}_i}{dt} = -\vec{\nabla}_{\vec{r}_i} \sum_{j \neq i} V(|\vec{r}_i - \vec{r}_j|) + \vec{F}_i^{(R)}(t) + \vec{F}_{\text{ext}}^{(i)}(t). \tag{6}$$

Here $\xi = k_B T/D_0$ is a damping constant which is related to the short-time diffusion coefficient of the particles

$$D_0 = \lim_{t \to 0} \frac{\langle [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle}{6t} \tag{7}$$

via the fluctuation-dissipation theorem. Hydrodynamic interactions can be incorporated by a position-dependent diffusion tensor [16]. On the right-hand side of equation (6), there are different forces acting on the colloidal particles: first there is the force attributed to interparticle interactions; then there are random forces $\vec{F}_i^{(R)}$ describing the kicks of the solvent molecules acting on the $i$th colloidal particle. These kicks are Gaussian random numbers with zero mean, $\overline{\vec{F}_i^{(R)}} = 0$, and variance

$$\overline{(\vec{F}_i^{(R)})_\alpha(t)(\vec{F}_j^{(R)})_\beta(t')} = 2k_B T \xi \delta_{\alpha\beta} \delta_{ij} \delta(t - t'). \tag{8}$$

The subscripts $\alpha$ and $\beta$ stand for the Cartesian components, $\delta_{ij}$ means the Kronecker symbol and $\delta(t)$ is Dirac's function. If the external force $\vec{F}_{\text{ext}}^{(i)}(t)$ vanishes or can be derived from a time-independent external potential:

$$\vec{F}_{\text{ext}}^{(i)} = -\vec{\nabla}_{\vec{r}_i} V_{\text{ext}}(\vec{r}_i) \tag{9}$$

then a time average over the colloidal trajectories gives the same Boltzmann statistics as in equation (3), corresponding to an equilibrium situation. In general, the presence of external forces implies a non-equilibrium situation. The simplest non-equilibrium problem is that where a steady state of the system exists for large times. This means that there is a generalized time-independent current such that appropriate time and/or ensemble averages exist. In this case, a free-energy description breaks down in general. Phase transitions between different steady-state situations are still possible, but the traditional concepts of equating temperature, pressure and chemical potentials in two coexisting phases no longer apply. Only in exceptional cases can a transformation within a free-energy picture be found. Such a special case are monodisperse colloidal dispersions in space-independent but time-dependent external fields [28, 29] where

$$\vec{F}_{\text{ext}}^{(i)}(t) = \vec{f}(t) \tag{10}$$

with an $i$-independent function $\vec{f}(t)$. Prominent examples for steady-state situations are a constant shear flow or a constant or alternating electric field. It is clear that the Brownian dynamics of the particles will directly affect the nature of the steady state, while equilibrium statistical properties are independent of this dynamics.

The highest problem complexity is realized for fully non-equilibrium situations with explicit time-dependent processes. Again, there are many examples: relaxation from a metastable state into the equilibrium state, system response upon cessation of external fields, switching on electric fields, moving system boundaries etc. An explicit example for turning on a field is a harmonic optical tweezer potential at the origin:

$$\vec{F}_{\text{ext}}^{(i)}(t) = \begin{cases} 0 & \text{for } t < 0 \\ -\kappa \vec{r}_i(t) & \text{otherwise} \end{cases} \tag{11}$$

where $\kappa > 0$ governs the localization strength of the tweezer.

Clearly, due to the increasing complexity, the number of publications decreases rapidly with the distance from the origin in the schematic diagram shown in figure 1. Another interesting research route is indicated by the arrow in figure 1 parallel to the $y$-axis. This is a complementary (and less followed) route than that for increasing system complexity. The strategy here is to systematically increase the non-equilibrium nature of a sample whose equilibrium properties are well understood. This route has a high potential for yielding fundamental insights as well as novel applications.

## 3. Colloidal interfaces and colloids in confining geometry

The understanding of the bulk phase diagram including freezing in one-component systems and fluid–fluid coexistence in binary mixtures has advanced a lot during the last decade. Once the bulk phase transitions are identified, the next natural question concerns *free interfaces* between two coexisting phases in equilibrium. The basic quantity which controls the thermodynamics of interfaces is the interfacial tension defined as

$$\gamma = \partial F / \partial A \tag{12}$$

where $A$ is the area of the interface and volume, temperature and particle number are kept fixed. For colloidal systems, the interfacial tension is much smaller than that of molecular samples. This is easily seen via the following argument. The dimension of $\gamma$ is energy per area. For entropically governed colloidal systems, $k_B T$ is the appropriate energy scale and a typical interparticle spacing $a$ (e.g. the first peak in the pair correlation function or the lattice constant of a colloidal crystal) is the appropriate length scale. Hence a typical value for $\gamma$ is

$$\gamma \approx k_B T / a^2. \tag{13}$$

For atomic and molecular solids, on the other hand, the energy scale is larger as it is governed by a chemical bond in many cases. Even more importantly, the length scale is microscopic. Putting these two facts together, one realizes that the interfacial tension is up to eight orders of magnitude smaller than that characterizing a molecular system. Hence the interfaces between two different colloidal phases are much more vulnerable to external mechanical perturbations.

The simplest example is a free fluid–fluid interface. This requires a bulk phase behaviour with stable fluid–fluid coexistence. Realizations could be charged colloids with high salt concentration and strong van der Waals attraction [30] or mixtures of neutral colloids and/or polymers which show a stable fluid mixing–demixing transition [31–33]. Direct measurements of the interfacial tension between two fluid phases were recently made by de Hoog and Lekkerkerker [34]. Density functional studies for model colloid–polymer mixtures have also led to an almost complete theoretical understanding of the surface tension [35, 36].

A further example is the free solid–fluid interface which occurs for any colloidal interaction with a strongly repulsive core. In this case, the surface tension depends additionally on the crystal orientation. For hard spheres, the corresponding solid–fluid surface tension has recently been calculated by computer simulation [37] to be close to $0.6 k_B T / a^2$ where $a$ is the lattice constant of the solid. Indeed, one sees that the simple estimate of equation (13) is nicely reproduced. The actual value depends slightly on the orientation of the interface.

Another kind of interface is obtained near a fixed external wall representing system boundaries. This can be modelled by the action of an external potential on the colloidal particles. Typical examples are planar hard walls:

$$V_{\text{ext}}(\vec{r}) = \begin{cases} \infty & \text{for } z < 0 \\ 0 & \text{otherwise} \end{cases} \tag{14}$$

where $z$ is the coordinate perpendicular to the wall and the location of the wall is at the origin $z = 0$. If a system approaches phase coexistence, the metastable phase shows up on top of the wall as a wetting phase [38, 39]. For complete wetting, the thickness of the wetting layer diverges if coexistence is achieved. For polymer–colloid mixtures, recent density functional studies have shown that an unusual first-order layering transition may occur corresponding to incomplete wetting [36]. This 'entropic wetting' has never been found in molecular systems such as rare gases and seems to be generic to entropically governed colloidal mixtures.

The behaviour becomes even richer if the external potential exhibits an explicit $x$- and/or $y$-dependence resulting in substrate patterns offered to a colloidal fluid. These can be wedge-like geometries [40] or two-dimensional periodic patterns obtained by 'gluing' colloidal spheres on a flat plate [41–45]. Both can act as templates to nucleate and stabilize stable crystalline sheets on top of the substrate [42]. In most cases, these sheets inherit their structure directly from the substrate. Thus it becomes possible to even produce phases which are unstable as bulk phases [46].

Colloidal suspensions are systems where wetting and heterogeneous nucleation phenomena can be seen excellently in real space and real time. In addition to confocal microscopy which works also in the bulk, there are surface-sensitive methods particularly designed for studying colloidal particles near surfaces and walls [47, 48]. By total-internal-reflection microscopy as first proposed by Prieve [47] one can probe the distance distribution of single colloidal particles near a wall and thus extract the wall–colloid interaction $V_{ext}(z)$ directly. This powerful technique yields precise information about the van der Waals forces [47] as well as depletion forces and interactions between charged particles and charged plates [49–51].

Even more confined situations are realized by a slit geometry of two parallel glass plates. One may continuously interpolate between two and three spatial dimensions by changing the plate distance. One important feature of colloids is that the two-dimensional limit can in fact be realized for strongly charged walls which confine the colloidal motion practically completely to the mid-plane. Using real-space methods such as video-microscopy [52–56], the positions of the colloidal particles can be observed directly. These experiments were particularly important for studies of two-dimensional melting which was predicted theoretically to proceed possibly via a hexatic phase with long-range orientational order [57]. As expected, for narrow slits of finite width, the additional degree of freedom along the $z$-coordinate also produces different structures as compared to the pure two-dimensional bulk case. For sterically stabilized colloids between hard walls the full phase diagram was calculated from theory and computer simulation for relatively narrow slits [58, 59] revealing stable buckling, rhombic and staggered square and triangle phases. For larger plate separations even more 'exotic' phases such as prisms were found [60].

A completely confined situation is a finite system where no appropriate thermodynamic limit can be taken. Again such systems can be excellently realized by colloidal suspensions; even the number of particles can be controlled. An interesting example is colloids confined in an effective two-dimensional circular cavity [61, 62] or in a three-dimensional spherical cavity [63]. Phase behaviour in a finite system is not strictly defined as there is no thermodynamic limit but one can use structural and dynamical diagnostics to locate a phase boundary approximately. It was found in computer simulations and experiments that the dynamical correlations are drastically influenced by the confinement and the phase behaviour is significantly shifted with respect to the bulk phase behaviour. Even novel re-entrant transitions due to the finite system size were discovered [62].

In a ring-shaped channel, the dynamics of colloids was investigated [64]. This corresponds to single-file diffusion. For long times a subdiffusive motion where the mean square displacement scales with the square root of time was predicted theoretically [65, 66], which

was indeed confirmed experimentally [64]. Single-file diffusion also occurs in microporous solids such as zeolites but the advantage of colloids is that their dynamics can be monitored and controlled in real space (rather than in reciprocal space) and real time (rather than in frequency space).

## 4. Colloids in laser-optical fields

Laser-optical fields couple to different dielectric constants of the colloids and the solvent due to the radiation pressure difference [67, 68]. Hence the local electric field strength is a measure for an external potential acting on the colloidal spheres. Using this idea one can tailor an external potential and superimpose it on a colloidal bulk solution. Typically, the oscillation frequency of the laser beam is much larger than an inverse timescale relevant for colloidal motion. Hence, to a good approximation, the time-averaged intensity provides a static external field such that we are facing an equilibrium situation of colloids in a static external field. By index matching the solvent appropriately, one has the further fascinating possibility of influencing selectively just one component in a colloidal mixture. The idea of applying laser-optical fields in order to achieve tailored external potentials has many different applications. In the following we shall discuss some of them.

A very broad-ranging idea is to use optical fields to trap single particles or—in other words—to 'nail' a particle at a given fixed position. This set-up has become known as an 'optical tweezer'; for a review see [69, 70]. The external forces exerted on the trapped colloidal particle can be measured [71] and calculated theoretically [72]. In the simplest approximation the optical trap constitutes a harmonic external potential (centred without loss of generality at the origin):

$$V_{ext}(\vec{r}) = \frac{1}{2}\kappa \vec{r}^{\,2} \tag{15}$$

where $\kappa$ controls the strength of the trap. Optical tweezers establish direct access to measuring the diffusive motion of colloids in bulk and in restricting geometries [73, 74]. One may even use two optical tweezers at the same time to get direct insight into the interaction forces between the colloidal particles [75, 76] and to reveal the hydrodynamic interactions between the particles by cross-correlating their relative motion [77, 78].

The second idea is to impose a spatially oscillating external potential on a bulk colloidal suspension by means of crossed laser beams. The particles experience a periodic external potential

$$V_{ext}(\vec{r}) = V_0 \cos(kz) \tag{16}$$

where $V_0$ is the amplitude and $k$ is the modulation wave vector which is typically of the order of the inverse particle spacing. The freezing transition in a such a periodically modulated external potential (the so-called laser-induced freezing) is different from the bulk freezing. In a two-dimensional system, a large value of $V_0$ confines the colloidal positions in the wedges of the external potential. Still these one-dimensional arrays containing colloidal particles are strongly coupled; hence the freezing behaviour is expected to be intermediate between the one-dimensional and two-dimensional cases. This is a very rich situation where experiments [79–83], computer simulations [84, 85] and theory such as density functional theory of freezing [86, 87] and phenomenological elastic theory [88–90] have been developed simultaneously. An interesting re-entrant melting transition for increasing $V_0/k_B T$ has been found [87, 88] and novel hexatic-type intermediate phases have been predicted [88].

A very interesting technique uses several crossed laser beams to set up an external potential for the colloids that is periodic in two directions. Such an experiment has recently been

realized by Bechinger *et al* [91]. Several patterns such as square and triangular lattices can be superimposed on a two-dimensional colloidal system. If the strength of the laser-optical field is very high, then the colloidal particles are practically all trapped in the minima of the external potential. Interestingly, this limit thus constitutes a statistical lattice model for the colloidal degrees of freedom. Depending on the internal colloidal degrees of freedom per lattice site, an Ising or Potts model can be realized. By changing the laser intensity, one can hence cross over from discrete statistical models (such as the Ising or Potts model) to a continuous model. It would be very interesting to investigate the nature of the freezing transition in such an underlying patterned external potential.

The set-up for laser-induced freezing can also be used to study single-file diffusion along one single optical channel. The advantage over microporous solids is that the model channel is perfectly smooth and can be tuned by the external field. These and related set-ups possess a high potential for future studies and applications.

## 5. Colloids in magnetic fields

A magnetic field couples to the magnetic susceptibility of the colloidal material or its difference with respect to that of the solvent. This fact has been exploited in different applications. One typical set-up is as follows [92]. The colloidal particles are superparamagnetic and are suspended in a liquid drop pending from a glass plate. Due to gravity the particles sediment in the drop and are thus hanging at the liquid–air interface of the droplet. The external magnetic field is perpendicular to the interface. As the curvature of the liquid droplet is macroscopic, the interface is to a very good approximation planar. Hence this set-up establishes an almost perfect realization of a two-dimensional liquid floating on the air–liquid interface [93]. Fluctuations perpendicular to the interface are suppressed by the surface tension free energy. In fact, these systems are much better realizations of two-dimensional fluids than suspensions confined between two parallel glass plates, as in the latter case there are always out-of-plane fluctuations.

Once the magnetic field is applied, it induces a magnetic moment $M$ in the particles whose magnitude scales linearly with the magnetic field strength $B$ as

$$M = \chi B \tag{17}$$

where $\chi$ is an effective susceptibility. Hence the interparticle interaction between a colloidal pair confined to two dimensions is that of parallel dipoles. This interaction is repulsive and reads in detail as [92]

$$V(r) = \frac{\mu_0}{4\pi} \frac{M^2}{r^3}. \tag{18}$$

Consequently the strength of the interaction is completely controlled by the external field strength $B$ which makes it easy to change the interparticle coupling (equivalent to a temperature change). Being excellent realizations of two-dimensional systems, such samples have been used by Maret and co-workers to study the freezing transition. In fact, a full verification of the Kosterlitz–Thouless–Nelson–Halperin–Young scenario [57] was found, including an intermediate hexatic phase with long-ranged orientational correlations [94]. The transitions were also detected by dynamical diagnostics which are more sensitive than structural correlations [95]. Computer simulations of two-dimensional systems still suffer from significant finite-size corrections and long equilibration times.

A similar set-up of particles floating on a liquid meniscus was studied by Wen and co-workers [96]. A wealth of different crystalline two-dimensional structures were discovered ranging from triangular to oblique and rectangular lattices. For a binary mixture of colloidal particles even a two-dimensional quasicrystal with a fivefold symmetry was observed [96].

## 6. Colloids in electric fields

For charged colloidal suspensions consisting of mesoscopic polyions and microscopic counterions and coions [97], an external electric DC or AC field induces different effects as it couples to all charged particles. The counterion cloud around the polyions will react even at high field frequencies which will then in turn alter the effective interaction between the colloidal polyions due to the deformed electric double layer [98]. On the other hand, an electric field will also act on the polyions directly provided the frequency is small enough and induce a directed motion of them. Both effects will contribute to the total conductivity or the electrophoretic motion of the colloidal sample; for a review and compilation of literature see references [99].

It is fair to say that such electrokinetic effects are far from being understood completely on a microscopic basis. The traditional standard electrokinetic model for the mobility of a single (isolated) charged colloidal sphere in a homogeneous static electric field incorporates effects of the electric double layer, retardation induced by microions and electroviscous effects [100]. More recently this model has been generalized in different directions; see, e.g., [101, 102, 121]. The real challenge is to treat strongly interacting concentrated suspensions in a coherent way. Recent experiments have shown that there are novel effects for concentrated suspensions which are not predicted by the standard electrokinetic model [103–105]. For instance, surprisingly, the mobility was increasing with increasing particle concentration. One promising way to access such effects theoretically is to use mode-coupling schemes where recent progress has been achieved [106, 107]. As a complementary approach, there is a need to perform 'coarse-grained' computer simulations [108–112] to access electrokinetic effects from a more fundamental point of view.

Qualitative new effects induced by electric fields arise in a binary mixture of colloids carrying different charges. Then an AC electric field will accelerate the relative motion of two different particle species. This may lead to lane formation driven by an electric field. The latter is an intrinsic non-equilibrium phase transition and was first discovered in the context of pedestrian motion [113]. Typical computer simulation snapshots of a two-dimensional binary mixture exposed to an external shaking field are shown in figure 2 [114]. In detail, the results are for a binary symmetric Yukawa system. The interparticle interactions (including the cross-interaction) are the same for the two species but the particles couple differently to the electric field as described by an oscillatory external force

$$\vec{F}_{\text{ext}}^{(i)}(t) = \pm \vec{f}_0 \cos(\omega t) \tag{19}$$

where half of the particles get a plus and the other half a minus sign, $\vec{f}_0$ is the amplitude and $\omega$ is the frequency of the external field. While the configuration without external field is fluid-like as depicted in figure 2(a), a sufficiently strong amplitude yields 'lane formation'. The lanes are formed parallel to the direction of the field as can be seen in figure 2(b). It is important to note that colloidal suspensions can thus realize driven diffusive model systems which have been investigated theoretically for quite a while as they exhibit various interesting non-equilibrium phase transitions; for a review of these, see reference [115].

Much more complicated patterns are formed in charged suspensions in a very strong AC field. In experiments on charged particles confined between two plates with the electric field applied parallel to the plates, dynamical aggregates containing many colloidal particles were observed [116–118]. These are tilted bands with a characteristic angle with respect to the field direction. Such a zigzag-like pattern is called chevron structure. Its origin is the electrohydrodynamic flow induced by the electric field [117, 118].
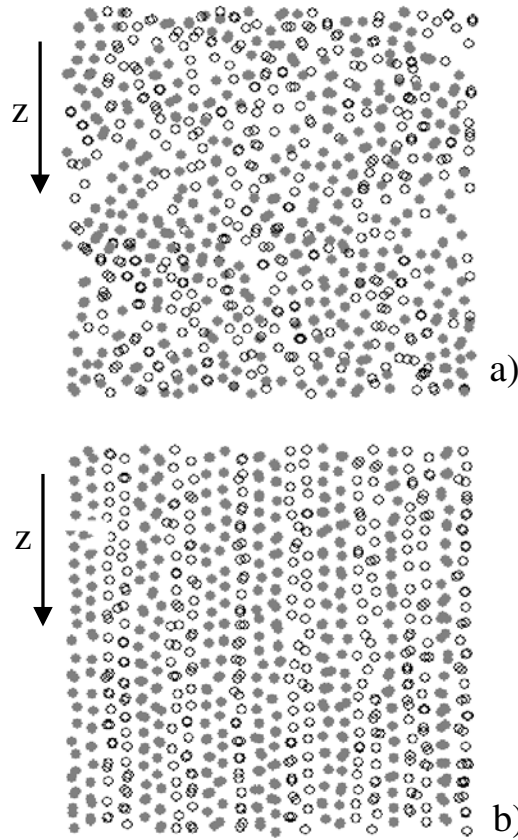
**Figure 2.** Computer simulation snapshots for a two-dimensional binary Yukawa fluid. The hollow and grey spheres represent the two particle species. The external field is along the $z$-direction, as indicated by the arrow. (a) The homogeneous fluid state without an external shaking field. (b) Structured lane formation induced by an external oscillating field coupling differently to the two particle species.

A much simpler situation arises if the frequency of the AC electric field is very high. For colloids confined between glass plates, this results in an effective dipolar repulsion between the particles which has the same form as equation (18) except that the interaction strength is now governed by the amplitude of the electric field. Such a set-up was also used to study two-dimensional melting [119, 120].

## 7. Colloids under shear

A given velocity flow field of the solvent will dynamically couple to the colloids [122]. The sensitivity of colloidal dispersions to such shear flow fields is easily demonstrated by the magnitude of the shear modulus $G$ of a colloidal crystal, which measures the free-energy cost for shearing an elementary cell of the crystal. The dimension of the shear modulus is energy per volume. Following the same argument as given for the interfacial tension in equation (13), a typical value of the $G$ is

$$G \approx k_B T / a^3 \tag{20}$$

where $a$ is the crystal lattice constant. Consequently, the shear modulus of a colloidal crystal is up to twelve orders of magnitude larger than that of an atomic crystal, so stresses well beyond the elastic limit can be attained under laboratory conditions for colloidal samples.

In cells of different geometry, the effect of shear flow can be controlled and precisely measured using scattering or direct imaging methods. One can study both linear and oscillatory shear. These situations are steady-state non-equilibrium problems in the sense discussed in section 2. Particular focus has been placed on the change of bulk phase transitions with respect to shear.

One would expect that shear would favour the disordered (fluid) as compared to the colloidal crystal, i.e., shear flow would result in melting of the colloidal crystal. This was indeed found experimentally for linear shear flow nearly two decades ago [123–125]; for a review see e.g. [16]. But this is not the end of the story. Subsequently, precise measurements have shown a much richer scenario for the effects of shear flow on crystallization phenomena. In fact, even the inverse effect, namely shear-induced crystallization or shear-induced ordering, was observed for oscillatory shear; i.e. a sample which is disordered at equilibrium can still become completely ordered in an oscillatory shear flow [126–130]. The detailed processes leading to nucleation of shear-induced crystalline states are still unclear. There are also experimental findings which support the idea that shear flow selects between the crystal structures face-centred cubic and random hexagonal stacking [131, 132]. Hence, in this case, the shear rate is a control parameter of the system in addition to the more common ones like temperature, pressure or chemical potential. Furthermore, the crystal nucleation rate can be accelerated significantly by shear flow [123, 126, 129].

Also the shear-induced melting transition of colloidal crystals reveals interesting phenomena. It was found that two different non-equilibrium 'phases' with different microstructures can coexist. The systems split into 'bands' of crystalline and shear-melted regions. They shear at different rates. The phenomenon is called *shear banding* [133–135]. By increasing the shear rate, the molten band grows at the expense of the crystalline regions in formal analogy to phase coexistence in equilibrium systems. The shear-banding instability appears to be quite general as it occurs also in polymer [136–139], micellar [140] and surfactant [141, 142] systems. Again, the microscopic details of the shear-banding mechanism are still unclear. Shear thinning as well as particle shape transformations in the shear flow may play a key role.

Finally, the change of fluid–fluid transitions with respect to shear has been investigated. In detail, the shift of the critical point and the spinodal line induced by shear flow has been studied experimentally and theoretically [143].

As far as computer simulations are concerned, there are many non-equilibrium Brownian dynamics simulation studies of colloids, the latter being the appropriate dynamics for such systems; see, e.g., [144–148]. Most of them, however, neglect hydrodynamic interactions which are essential for dense colloidal suspensions. These interactions can be efficiently handled using more recently developed 'coarse-graining' techniques such as lattice Boltzmann methods [108–110], dissipative particle dynamics [111], Stokesian dynamics simulations [112] or an approach treating the colloid as a fluid particle in order to soften the hydrodynamic boundary conditions on the colloidal surfaces [149]. Such computer simulations will play a pioneering role in clarifying the microscopic processes underlying and driving shear-induced phase transitions.

Theoretical studies for colloids in shear flow are either based on simple phenomenological models [150] or on mode-coupling theories [151–155]. The former approach reduces to a Landau-type description of phase transitions in the equilibrium situation without shear. On the basis of such a simple phenomenological model, a re-entrant crystallization transition of a shear-melted solid was predicted for higher shear rates [150]. Mode-coupling theories operate

on a full microscopic level and require structural equilibrium correlations as input. Inspired by the success that mode-coupling theories had in the description of the dynamics of the glass transition, one might surmise that the latter will offer more insight into the microscopic processes of shear-induced phase transitions.

Of course, shear-induced phenomena and phase transitions also exist in molecular systems; for a recent review see [156]. The advantage of colloids is that scattering techniques and real-space imaging methods such as confocal microscopy [157–159] can be applied to the same sample in order to get full information about the change in the microstructure of the colloidal particles as well as the impact on the macroscopic shear-induced properties.

## 8. Perspectives

Perhaps the most obvious generalization which will be exploited in the next decade is that of combining different external fields in order to control many different colloidal properties at the same time. Let us just mention five examples:

(i) *Magnetic colloids in confining geometry*. Magnetic colloids can be studied in cavities and slit-like geometries. Finite-size effects in two-dimensional melting as well as wetting phenomena can thus be explored experimentally in a systematic way.

(ii) *Magnetic and laser-optical fields*. Two-dimensional magnetic colloids can be subjected to crossed magnetic and laser-optical fields. One interesting idea is to generate anisotropic interactions by means of a combination of fields and study the influence of such angle-dependent interactions between particles on the two-dimensional melting scenario.

(iii) *Magnetic and electric fields*. With this combination, unusual solid structures such as body-centred tetragonal crystals were found recently [160] and more fascinating phenomena can be expected.

(iv) *Magnetic fields and shear flow*. There are a wealth of magnetorheological effects such as non-equilibrium phase transformations including pattern formation [161–164] and chaining [165] in flow properties of magnetic colloids (or ferrofluids). We are just beginning to discover the richness of phenomena associated with such external influences.

(v) *Electric fields and shear flow*. As already mentioned, an external electric field can induce dipolar interactions between the particles. This leads to a controlled change in flow properties which are important in the development of electroviscous applications. The application of a shear flow produces a microstructure with a large dynamic yield stress. Phase separation and pattern formation, in particular shear banding, were recently found for such electrorheological fluids [162, 164, 166] and more effects are expected.

According to figure 1, further novel perspectives arise when considering fully time-dependent external fields beyond steady-state situations. One may turn on or switch off a constant or oscillatory field and study the relaxation into the different steady states. One example for the time evolution in the electric double layer upon applying an electric field was studied recently in reference [167]. Also a random time-dependent field could be studied. This requires much more theoretical 'microscopic' understanding but may also reveal unexpected novel dynamical behaviour.

Furthermore, the complexity of the system can be enhanced by studying rods, platelets and mixtures of these. The bulk phase diagram is already much richer than for spherical colloidal particles. One might expect even more complex non-equilibrium effects. Some groups have started activities in this direction but a full systematic understanding is still lying ahead.

More concretely, we re-emphasize that the physics of wetting phenomena can be understood in real space by using colloids. This will be exploited in the near future, in

particular for patterned substrates [39]. Another important area of research will focus on colloidal quasicrystals which have recently been seen in a mixture [96] and were theoretically predicted even in an effective one-component system [168].

Moreover, more refined theories of the hydrodynamic interactions are needed as the latter are relevant for equilibrium and non-equilibrium dynamics. A challenging completely microscopic approach should include the solvent molecules explicitly. A molecular dynamics simulation has been performed recently to predict the effective interaction between small charged colloids [169]. Such a calculation can be generalized to non-equilibrium situations to access for example the electrophoretic mobility. Such simulations are very demanding but provide an 'ab initio' approach to hydrodynamic interactions.

Finally there two further kinds of external field which are important for colloids. First, a *gravitational field* (which is omnipresent except for experiments performed in space shuttles) generates sedimentation dynamics and equilibrium sedimentation density profiles. By density matching the solvent to the colloidal mass, one can tune the relative strength of this interaction. For low gravity, the sedimentation density profile reveals the isothermal equation of state and indicates phase transitions directly [170]. While the equilibrium properties in a gravitational field are understood for hard-sphere colloids, charged colloids show an apparent mass smaller than the bare mass [170] which still poses a theoretical puzzle [171–173]. The sedimentation dynamics, on the other hand, exhibits a wealth of interesting non-equilibrium effects such as shock-like fronts [174], long-range velocity correlations [175], stratification [176] and modified crystal growth [177, 178]. A gravitational field can be combined with an electric field. An example is given in reference [179] where a new tangential force between a colloidal pair was discovered. Second, a sustained *chemical concentration gradient* (e.g. a salt gradient) pushes a colloidal dispersion out of equilibrium. A different phase behaviour induced by an imposed concentration gradient can occur [180].

## 9. Conclusions

To summarize, we have demonstrated that the interactions in colloidal suspensions can be easily tuned and tailored by external fields. In particular, a magnetic field can be used to control the amplitude of the repulsive interparticle interaction, laser-optical fields can establish tailored external potentials for the colloids and electric and shear flow fields drive the colloids into steady-state non-equilibrium states.

In conclusion, colloidal dispersions in external fields are excellent statistical model systems. This important fact has been accepted by the scientific community for bulk phase transitions such as freezing. But it is and will turn out to be true for interfacial phase transitions (such as wetting), for driven non-equilibrium systems (such as those exhibiting stratification and lane formation) and for realization of discrete lattice models produced by a strong confinement of continuous degrees of freedom via an external field.

Interesting questions and exciting new possibilities for controlling colloidal properties arise when combining these different fields or making them explicitly time dependent. In the next decade, a systematic understanding of all of these phenomena is expected via the complementary approaches of experiment, computer simulation and theory.

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