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Structure in confined colloid suspensions

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ABSTRACT

The study of confined condensed matter is motivated by the observation that when the range of molecular interaction and the length scale associated with position correlation in a system are similar to the length scale of confinement, that system can support structures and have transport properties that differ from those found in the bulk. This Letter is a selective overview of information that has been obtained about the nature of phase transitions from studies of confined quasi-two-dimensional colloid suspensions, with attention paid to the roles of the colloid–colloid interaction and the extent of deviation from an idealized geometry of confinement, e.g. whether and/or how phase transitions in quasi-one-dimensional and quasi-two-dimensional systems differ from those in a two-dimensional system or a three-dimensional system.

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1. Introduction

The study of confined condensed matter is motivated by the observation that when the range of molecular interaction and the length scale associated with position correlation in a system are similar to the length scale of confinement, that system can support structures and have transport properties that differ from those found in the bulk. The domains of stability of these structures and transitions between them depend on the commensurability of the several length scales, and the structures themselves influence the transport properties of the system. Understanding the interplay of the several length scales is a challenge to both the theory of equilibrium states and the theory of transport. Further motivation for the study of confined condensed matter follows from the observation that there are many real world physical and biological phenomena and processes that depend on the properties of such systems, examples of which are structural changes in adsorbed monolayers, liquids in porous media, and membranes and transport of molecules and ions through zeolites and membrane channels.

Of the possible choices, why select confined colloid systems for study? The short answer to this question has two parts. First, by virtue of the McMillan–Mayer theory [1], the equilibrium properties of a confined colloid suspension of particles undergoing Brownian motion are isomorphous with those of a confined molecular system in which the potential of mean force between colloid particles in the suspension replaces the direct interaction between molecules. The density, temperature and composition dependences of the colloid–colloid potential of mean force play roles in defining particular equilibrium states of the system. Second, the

development of digital video microscopy [2] has revolutionized the experimental study of confined colloid suspensions, thereby opening up for examination questions that, for technical reasons, cannot presently be addressed in a confined molecular system. Prominent amongst these questions is the dependence of the nature of phase transitions on system dimensionality and interactions. Digital video microscopy also permits tracking of individual particles, hence direct observation of the time evolution of colloid motion. Unlike the equilibrium properties, the transport properties of a colloid suspension differ from those of a molecular system because particle motions are coupled by both direct colloid–colloid interaction and by solvent induced hydrodynamic interaction.

This Letter is a selective overview of information about the nature of phase transitions in confined quasi-two-dimensional (q2D) colloid suspensions, with attention paid to the roles of the colloid–colloid interaction and the extent of deviation from an idealized geometry of confinement, e.g. whether and/or how phase transitions in quasi-one-dimensional (q1D) and q2D systems differ from those in a two-dimensional (2D) system or a three-dimensional (3D) system. Attention will be restricted to one-component suspensions of spherical particles.

2. Quasi-one-dimensional systems

We consider a suspension of colloid spheres in some small molecule solvent. The spatial distribution of the spheres depends on the dimensionality of the confining space, the fraction of space occupied and the sphere–sphere interaction.

The packing structure supported in a one dimensional (1D) suspension is not very interesting since the close packed configuration is a linear array of spheres (rods) and there can be no transition from a disordered phase to a phase with long range order at

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nonzero temperature if the sphere–sphere interaction has finite range [3]. In a q1D planar ribbon channel with width less than two particle diameters, so hard spheres cannot pass one another, a close packed array has zigzag geometry. Increasing the planar channel ribbon width to several sphere diameters generates a system with between q1D and q2D character. In such a system, at any nonzero temperature, fluctuations destroy all possible order not imposed by the explicit symmetry breaking associated with the boundary conditions. If the walls that define a q1D ribbon channel are smooth, they break continuous rotational symmetry but support rotations by $\pm\pi$, permit nonzero even order bond orientation order, and permit density modulation along the normal to the channel axis [4]. The length scale for the density modulation depends on the particle packing fraction, and the number of strata (lines of particles parallel to the channel walls) is dependent on the ribbon width. If the walls that define a q1D ribbon channel are regularly corrugated, or have some other defined structure, the confined system can be ordered [5].

The q1D structures found in the limiting cases of very short-range and very long-range sphere–sphere interaction have interesting similarities and differences. Consider, first, hard sphere systems confined by smooth walls. If the ribbon channel holds an integer number of close packed strata (a commensurate configuration), the system forms a perfect 2D triangular lattice [6]. Nevertheless, this solid cannot support a shear stress, and it can flow along the channel like a liquid. If the ribbon channel can hold somewhat more than an integer number of close packed strata, say $n + \delta$, $n = 1, 2, \dots$; $0 < \delta < 1$, there is a linear buckling instability in the direction perpendicular to the channel axis, and the system breaks into many triangle shaped close packed hexagonal regions that are displaced in the direction parallel to the channel axis [6]; the scale length of the local ordered regions is the channel width. In general, long wavelength fluctuations in the particle positions destabilize long-range order. If the channel width and hard sphere diameter are commensurate, the amplitude of fluctuation is suppressed and only long-range order is destabilized. If the channel width and hard sphere diameter are incommensurate, the fluctuations destabilize local order. Viewed overall, as shown by both experiment [7,8] and computer simulation [6,9], a finite length q1D ribbon channel will support apparent crystalline order

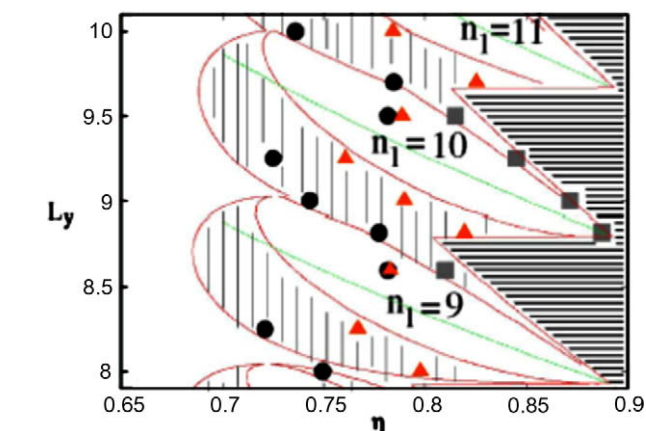


Fig. 1. From Ref. [6]. Part of the phase diagram (for the region with 8–10 strata) of hard discs confined in a ribbon channel. In this figure the one-phase regions are clear, the two-phase coexistence regions are vertically striped and the forbidden regions are horizontally striped. The symbols \circ , \square and \triangle represent data obtained from simulations. On the lines labeled $n_l = 9, 10, 11$ the width of the ribbon is commensurate with the hard disc diameter. Densities smaller than corresponding to any particular point marked \circ are modulated liquid, and densities greater than corresponding to any particular point marked \triangle are solid. The continuous curves are the phase boundaries predicted by a mean field theory analysis of the system.

at high packing density and, for fixed density, many discontinuous transitions involving changes in the number of strata parallel to the confining walls as the wall separation increases. A “phase diagram” for ribbon widths from 8 to 10 sphere diameters, obtained from simulation data, is displayed in Fig. 1, and sample experimental data are displayed in Fig. 2.

At a specified packing fraction, the structure supported in a confined system of hard spheres is determined by the commensurability of the wall spacing and sphere diameter. Colloids that interact via long-range screened Coulomb repulsion (Yukawa potential) [10] or long-range magnetic dipole–dipole repulsion [4,11] also form ordered structures in a ribbon channel. In these cases, the

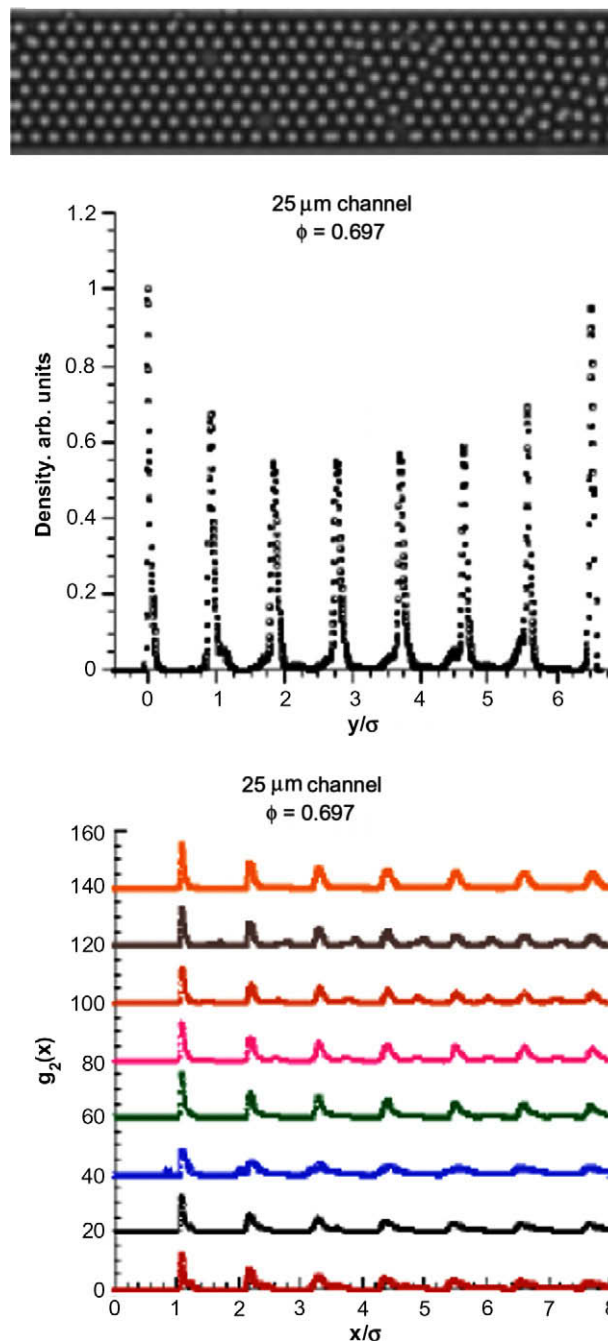


Fig. 2. From Ref. [8]. Top: Image of a 25 μm ribbon channel filled with 3.01 μm near hard spheres at a packing fraction 0.697. Middle: The density distribution of the colloid particles normal to the ribbon channel axis. Bottom: The pair correlation functions of the colloid particles along the individual strata in the ribbon channel.

structures are determined by the strength of the long-range part of the repulsion and not the particle diameter. For example, Monte Carlo simulations of configurations with minimum energy at $T = 0$ show that a system with colloids that interact with a Yukawa potential ($V_0 \exp(-\kappa r)/r$, with screening length $1/\kappa$) and are confined to a q1D channel by a harmonic potential perpendicular to the channel axis undergoes successive transformations from a configuration with one ordered chain to two ordered chains, then to three ordered chains, then to four ordered chains, etc., as the particle density increases [10] (see Fig. 3). The one-to-two chain transition is continuous and all other transitions involving more chains are first order. At nonzero temperature, the thermal excitation of the particles is anisotropic, with larger amplitude motion parallel to than perpendicular to the channel walls. At sufficiently high temperature, there occur transitions between the ordered chain structures. The simple Lindemann criterion for melting asserts that a solid melts when the average amplitude of displacement of a particle from its lattice site is of order 10% of the lattice spacing. Using that criterion to define melting at any specified particle density, when the screening length in the Yukawa interaction is very large, the ordered system melts to a liquid and the apparent melting temperature as a function of particle density has minima at those densities at which the $T = 0$ transitions between structures occur (Fig. 4). The melting temperature decreases as the screening length in the Yukawa interaction decreases. When the screening length in the Yukawa interaction is small, the system melts first in the unconfined direction whilst it remains ordered in the confined direction, forming what is sometimes called a locked floating solid. The melting process occurs first in the chains adjacent to the confining wall.

Both experimental studies and Brownian dynamics simulations of particles that interact via long-range magnetic dipole–dipole repulsion and are confined in ribbon channels have been reported [4,10,11]. The equilibrium packing structures exhibit layering parallel to the channel walls with periodic changes in widths of the strata in the interior of the channel as the channel width changes; the latter are associated with changes in the defect concentration (deviations from sixfold nearest neighbor packing) in the center of the channel as the channel width changes (Fig. 5). In the large ribbon width limit, the bond orientation correlation function for the interior strata is indistinguishable from that in 2D, but as the channel width is decreased the q1D system becomes more disordered than the unbounded 2D system and supports oscillations

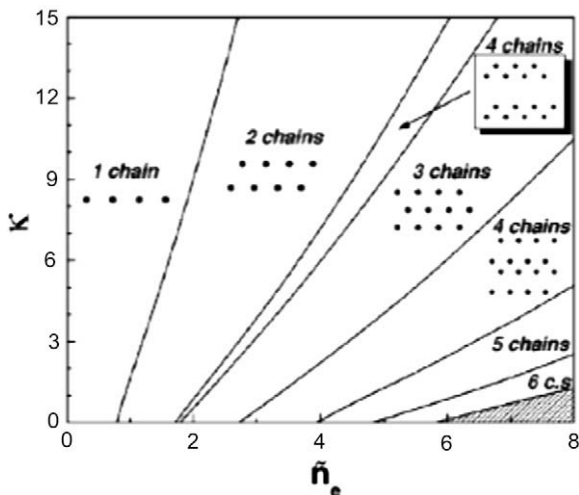


Fig. 3. From Ref. [10]. Phase diagram for colloid particles, confined to a ribbon channel, that interact with a Yukawa potential; κ is the inverse shielding length and \bar{n}_e is the density.

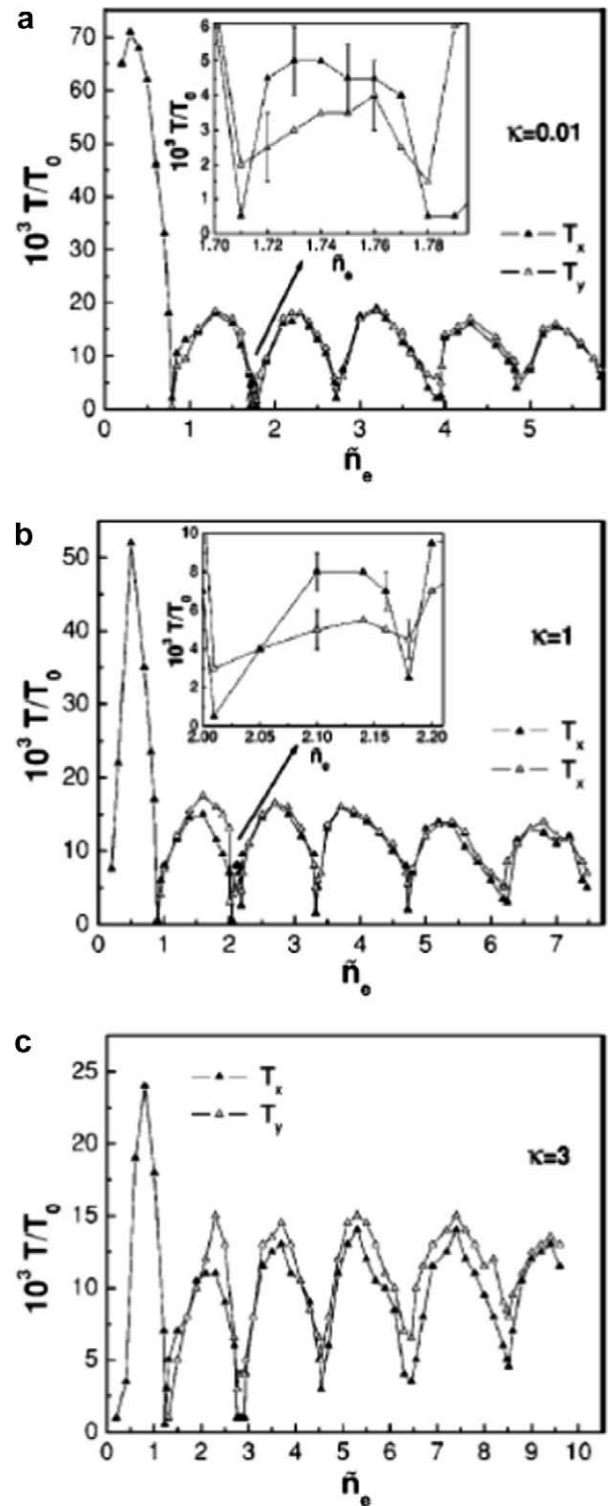


Fig. 4. From Ref. [10]. The melting temperature of an assembly of colloid particles, confined to a ribbon channel, that interact with a Yukawa potential, as a function of density.

in the defect concentration. The oscillatory changes in defect concentration are like order-to-disorder transitions.

The modulation of the density distribution perpendicular to the axis of the ribbon channel in each of the colloid systems described is the common signature of repulsion between the particles. While commensurability of the channel width to particle diameter ratio plays an important role in determining the structures available

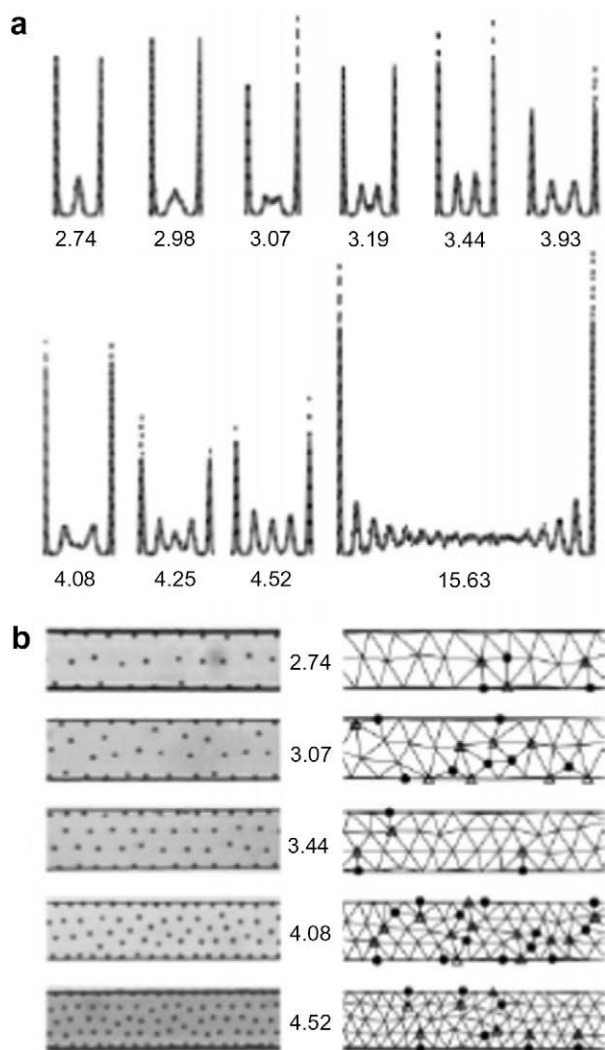


Fig. 5. From Ref. [4]. Top: Density distribution of colloid particles that interact with magnetic dipole repulsion normal to the ribbon channel axis, for several dimensionless channel widths $w = L/(\sqrt{3}/2\rho)^{1/2}$ and dimensionless field $\Gamma = \mu_0 M^2/4\pi k_B TR^3$, with μ_0 the magnetic permeability of free space, M the magnetic dipole moment and $R = (\sqrt{3}/2\rho)^{1/2}$ the average particle spacing. Bottom: Image of the particle distributions and associated Delaunay triangulations. Open triangles denote seven-coordinated particles and circles denote five-coordinated particles. The dimensionless field strength for these experiments was $\Gamma = 12$.

to hard spheres, it is not well defined when the interaction has long-range.

3. Two-dimensional systems

All real world nominally 2D systems are necessarily q2D systems. Yet the analysis of the data from experimental studies of q2D systems relies heavily on the predicted properties of 2D systems, so we must start with an overview of the latter.

It has been known for many years that, because of large amplitude thermal motions, at nonzero temperature, a 2D system does not support long-range translation (crystalline) order [12]. In the solid phase, the short-range translation order is very similar to crystalline order, but instead of having constant amplitude, the envelope of the position correlation function decays algebraically as a function of increasing particle separation, i.e. displays quasi-long-range order. However, a 2D system does support a different kind of true long-range order, bond orientation order. In the 2D

ordered state, the envelope of the bond orientation correlation function does not decay with increasing particle separation.

The study of 2D phase transitions has been greatly enriched by examination of the hard square [13] and hard hexagon [14] lattice gases. In the former, an occupied site in a square lattice prohibits occupation of the four nearest neighbor sites and in the latter, an occupied site in a triangular lattice prohibits occupation of the six nearest neighbor sites. In both cases, there is a continuous transition from the disordered state to an ordered state at a critical packing fraction, specifically 0.74 for hard squares and 0.83 for hard hexagons. Similarly, hard squares that can move continuously but only parallel to the x and y axes exhibit a continuous freezing transition at a packing fraction of 0.79 [15]. Hu and Mak [16] have argued that the phase transitions in the hard square and hard hexagon lattice gases are also percolation transitions at which there suddenly appears a continuous path of contacts from one side of a system to the other. We will return to this interpretation below.

Squares and hexagons match the fundamental symmetries of the square and triangular lattices, respectively; they can be packed so as to completely fill the 2D space. Pentagons and heptagons cannot be packed so as to completely fill the 2D space since they do not have symmetries that match any regular lattice. Simulation studies by Frenkel and coworkers [17] lead to the conclusion that in these cases there is a first order transition from a disordered phase to a rotator phase with the particle centers on a triangular lattice and random orientation of the pentagons (heptagons), and at higher density, a first order transition to a striped phase with oriented pentagons (heptagons).

Systems with strong magnetic dipole–dipole repulsion or only lightly screened Coulomb repulsion have properties that do not depend on the size of the particles. In a sense, they can be considered to completely fill the 2D space. If this analogy is useful, the phase transitions in such systems will have features that resemble those found in the hard square and hard hexagon systems more than those in the hard pentagon system.

The most widely accepted description of 2D phase transitions is that developed by Kosterlitz, Thouless, Halpern, Nelson and Young (KTHNY) [18]. This theory does not make direct reference to the structure in the system or the nature of the particle–particle interaction. Rather, it describes the 2D solid as a deformable elastic medium, with inclusion of the two classes of point topological defects with smallest excitation energy to mediate structural changes, and it relates the melting process to the mechanical instability of the 2D solid, not to equality of chemical potentials of the solid and liquid. The structure of the system and the nature of the particle–particle interaction are implicit in the calculation of the elastic constants and of the properties of the point topological defects. Although the theory allows for other possibilities, it is commonly taken to predict that a 2D system that supports only one ordered solid phase melts via sequential continuous phase transitions. The first transition is from the solid to a hexatic phase in which the envelope of the position correlation function decays exponentially, and the envelope of the bond orientation correlation function decays algebraically. The hexatic phase is, fundamentally, an anisotropic liquid. The solid-to-hexatic transition is driven by the dissociation of bound dislocation pairs in the solid. The second transition transforms the hexatic phase to the liquid phase in which the envelopes of both the position and bond orientation correlation functions decay exponentially; it is driven by the dissociation of individual dislocations to form disclinations.

Because the amplitudes of the fluctuations in a 2D system are very large, the elastic constants are altered from the bare values characteristic of the nonfluctuating uniform solid; KTHNY compute the change in the elastic constants from a renormalization analysis. The onset of instability of the solid is determined by a ratio of

renormalized elastic constants and the core energy of a dislocation.

When, at some temperature and density, $K = \frac{4a_0^2}{k_B T} \frac{\mu(\mu + \lambda)}{2\mu + \lambda} = 16\pi$, with μ and λ elastic constants and a_0 the lattice constant, there is a continuous transition to the hexatic phase, provided that the dislocation core energy is greater than $2.84k_B T$. At a higher temperature (and/or lower density), the dislocations, which consist of bound pairs of disclinations, unbind, leading to a transition from the hexatic phase to a liquid phase. The prediction of the existence of a hexatic phase intermediate between the 2D liquid and ordered solid phases is the most important contribution of KTHNY theory; it defines a qualitative difference between phase equilibrium in 2D and 3D systems. The other theoretical predictions, namely of the nature of the liquid-to-hexatic and hexatic-to-ordered solid transitions, and of the rates of decay of the envelopes of the bond orientation and position correlation functions in the different phases, are less central to characterizing the differences between 2D and 3D matter.

As noted above, the KTHNY theory buries the role of the particle interactions in the values of the elastic constants. In 3D, although there is no theorem that establishes that it must be so, the nature of the melting transition is found, via experiments, to be independent of the intermolecular potential; all known crystalline materials melt via a first order transition. The situation appears to be different in 2D, as illustrated by a density functional analysis reported by Pomirchi, Ryzhov and Tareyeva [19], who studied 2D melting in a system with square well interaction as a function of the width of the square well. They determine the density of the continuous transition of the solid-to-hexatic phase at a specified temperature using the KTHNY criterion for the instability of the 2D solid, with values of the elastic constants calculated from density functional theory. They also find the density of the first order solid-to-liquid transition using a variational calculation of the free energy of the solid. This theory predicts that when the square well has zero width, i.e. in the hard disc limit, the melting transition is first order and that there is no hexatic phase between the solid and liquid phases. When the square well width is increased from zero, the first order solid-to-liquid transition is initially replaced by a continuous transition, presumably to a hexatic phase, then with growth of the square well width replaced again by a first order transition and, when the attractive well becomes large enough that it includes second neighbor particles, the melting occurs via two continuous transitions. In Section 4 we will describe a different version of density functional theory that predicts that in a hard disc system, the continuous transition from the liquid to the hexatic phase just preempts the first order liquid-to-solid transition.

We close this section with some further observations concerning the hard disc system. Just as is the case for hard pentagons and heptagons, hard discs cannot be packed so as to completely fill the 2D space. Because of large amplitude fluctuations and very slow approach to equilibrium in 2D, the determination of the nature of the 2D freezing transition is very sensitive to the size of the simulation sample. The results of the most recent large-scale simulations of a dense 2D hard disc system (4×10^6 discs), reported by Mak [20], imply that the melting process consists of a continuous transition from the ordered 2D solid to the hexatic phase at a packing fraction close to 0.723, and either a very weak first order or a continuous transition from the hexatic to the fluid phase at a packing fraction close to 0.699. These conclusions are consistent with results of a study of the convergence of the virial expansion for the density as a function of the fugacity [21] that implies that the hard disc liquid-to-solid transition is continuous, and with the results of a study of the elastic moduli [22] that suggest that the KTHNY continuous transition from the hard disc solid to a hexatic phase just barely preempts the solid-to-liquid first order transition.

If the percolation transition can be identified with a geometric criterion for a phase transition, as has been suggested for the hard square and hard hexagon lattice gases [16], can one find a geometric criterion for the phase transitions in the hard disc system? Kozak et al. [23] have conjectured that in a 2D system of hard discs, the packing fraction at which the continuous transition from the ordered solid to the hexatic phase occurs, and that at which the very weak first order or continuous transition from the hexatic to the fluid phase occurs, can be correlated with the packing fractions of patterned networks (tessellations) of disc positions. They identify three tessellations that have less than close packed density, span 2D space, and have percolated continuity of disc-disc contact. One has a packing fraction of 0.729, very slightly larger than the estimated packing fraction at the ordered solid-to-hexatic transition, namely 0.723, and the other two have packing fractions of ~ 0.680 , slightly smaller than that identified as the upper end of the stability range of the liquid phase, 0.699. The region $0.680 < \rho^* = N\sigma^2/A < 0.729$ is identified with the hexatic domain. The end points of this region can be placed in correspondence with tessellations for which the defining unit structures are regular polygons, but not the hexatic domain, in which there are randomly dispersed clusters which need not be regular polygons. Kozak et al. suggest that the densities at which the percolated tessellations span the 2D space be regarded as special points along the density axis, since the symmetries and packing fractions of the tessellations at higher and lower density are different. They also suggest that the possibility of forming different symmetry tessellations with sensibly the same packing fraction is a geometric analogue of a bifurcation condition that divides the configuration space into qualitatively different domains. At the smaller of the special densities, the system chooses between changing from a disordered state to a partially ordered state or one of two ordered states. That is, viewing the space of possible disc configurations as a function of density, there is a density below which only disordered configurations are stable. Kozak et al. do not assert that such a correlation implies the actual occurrence of those tessellations, rather that each of the densities at which the solid-to-hexatic and hexatic-to-liquid transitions occur is a signature of the existence of a near-by tessellation that completely spans the 2D space. They also show that it is possible to construct a continuous many particle transformation from the dense fluid to the crystalline phase, and from the crystalline phase to the dense fluid, with both transformations mediated by the same intermediate configuration. The putative relationship between percolated tessellations of the plane and phase transitions and the ideas underlying the KTHNY theory is consistent with the calculated values of the bond orientation function.

4. One layer quasi-two-dimensional systems

How accurately do the predictions concerning phase transitions in a 2D system describe those in a one-layer q2D system? The answer to this question draws on a mixture of results from real experiments and computer simulations.

There are several colloid systems that have pair interactions reasonably close to, but somewhat deviant from, the idealized hard-core repulsion. In a realizable suspension of uncharged colloid particles, one source of deviation of the interaction from the hard-core form arises from the nonzero dispersion of particle diameters. When the suspension is considered to be a one-component system of particles with an effective diameter, the averaging over the distribution of pair separations at contact generates an effective pair interaction with a repulsive part that is softer than the hard-core repulsion and an attractive well with a depth that depends on the width of the distribution of diameters [24]. In a

suspension of uncharged colloids with stabilizing polymer brushes, and in a suspension of charged colloids with salt concentration large enough to shield the Coulomb interaction with a screening length that is small compared to the colloid diameter, the repulsion between particles is softer than the hard-core repulsion. The same characterization applies to a suspension of microgel colloid particles with temperature tunable diameter [25], noting that in this case the steepness of the repulsion is also temperature dependent. Finally, for all realizable q2D systems account must be taken of the small amplitude out-of-plane motion. The most trivial consequence of the out-of-plane motion is the need to describe the colloid–colloid interaction with an effective diameter; more consequential changes in the system description will be necessary if the motion generates qualitative changes in the system behavior.

With these caveats in mind, the available experimental data for tightly confined q2D systems with near hard sphere interactions fall short of providing an unambiguous test of the KTHNY theory predictions.

Karnchanaphanurach et al. [26] studied sterically stabilized silica spheres confined between glass plates with a hydrophobic coating and separated by 1.03–1.14 particle diameters. They interpret their data to show a first order liquid-to-solid transition with an estimated coexistence region $0.684 < \rho^* < 0.704$, and without intervention of a hexatic phase. This conclusion is supported by fitting the shapes of the diffraction peaks computed from the observed positions of the particles (Fig. 6) and the rate of decay of the envelope of the pair correlation function. Because the spacing of the densities studied is rather coarse, the estimated locations of the end points of the coexistence region are likely uncertain by ± 0.01 – 0.02 . We note that the end points of this coexistence region

are close to the transition densities estimated from Mak's simulations [20], but the interpretation of the nature of the transitions is different. That said, residual polydispersity of the spheres and out-of-plane motion could hide a small density region where the hexatic phase is stable.

Han et al. [25] studied microgel spheres, with temperature tunable diameter, confined between glass plates with a hydrophobic coating and separated by approximately 1.25 particle diameters. Their data clearly show the existence of a hexatic phase interpolated between the liquid and solid phases, thus verifying the most important prediction of the KTHNY theory. The liquid-to-hexatic and hexatic-to-solid transition densities are found to be, approximately, 0.69 and 0.70, but the data are insufficient to unambiguously determine the order of the transitions. It is important to note that in this system the shape of the repulsive interaction also changes with temperature (see Fig. 1a of Ref. [25]), which complicates the comparison with predictions for a hard sphere system.

Consider next a q2D suspension of colloids with embedded paramagnetic ions [27]. Application of an external magnetic field induces parallel magnetic dipoles in the colloids, the strengths of which are proportional to the applied field. It can be arranged that the dominant interaction between particles is the long-range magnetic dipole–dipole repulsion. This system is arguably the best real world realization of a 2D system for three reasons. First, in this case, the nonzero dispersion of the colloid diameters is unimportant. Second, the variation from particle to particle of the concentration of paramagnetic ions and, hence, of induced magnetic moments, appears to be small. Third, the colloids used are large and heavy, so out-of-plane motion is more limited than in other systems. For this q2D system the available experimental evidence

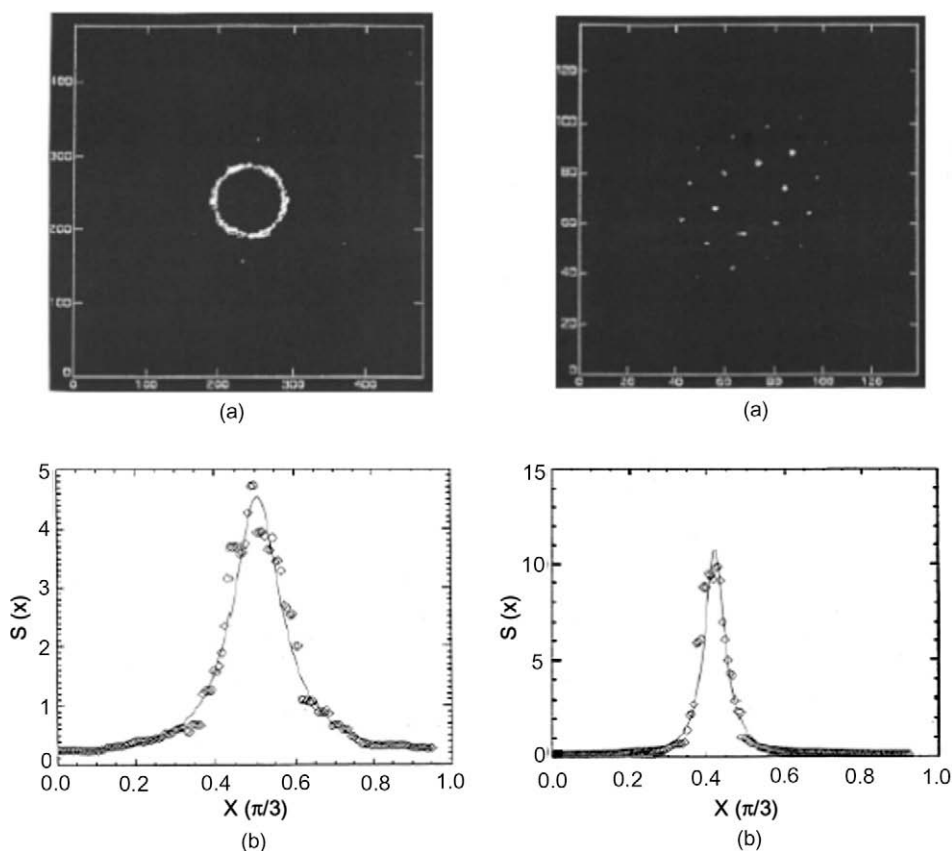


Fig. 6. From Ref. [26]. Left: Diffraction pattern and angular distribution of diffraction intensity for a sample with density $\rho^* = 0.684$. The solid line is a fit to the superposition of an isotropic background for the liquid phase and a Lorentzian for the solid phase. Right: Diffraction pattern and angular distribution of diffraction intensity for a sample with density $\rho^* = 0.704$. The solid line is a fit to a Lorentzian.

[27–30] supports all of the KTHNY predictions concerning the order of the liquid-to-hexatic transition and the decays of the envelopes of the position and bond orientation correlation functions.

Lin and Chen [31,32] have studied another q2D system with long-range colloid–colloid interaction, an assembly of charged polystyrene particles trapped in the water–decane interface. Because the amplitude of thermal capillary wave motion of this interface is very small, the centers of the particles are very tightly constrained to a nearly 2D configuration. The interaction in this system, including the shielding by counterions, falls off as r^{-3} . Consequently, phase transitions are observed at small densities, as shown in Fig. 7. The data establish the existence of a hexatic phase, but unlike the case with magnetic dipole–dipole repulsion, the liquid-to-hexatic transition is first order rather than continuous. The solid-to-hexatic phase transition is induced by generation of equal numbers of fivefold and sevenfold defects, as predicted by KTHNY theory, but the hexatic-to-liquid transition is accompanied by dramatic increases in the numbers of fourfold and eightfold defects, and a growing difference between the concentrations of fivefold and sevenfold defects, not accounted for by KTHNY theory.

Finally, consider a suspension of uncharged colloids, the surfaces of which are covered with short nonpolar polymer chains. If the colloids are suspended in water, incipient contact between the nonpolar polymer brushes will be attractive; then as the colloid–colloid separation decreases the loss of configurational entropy by the interpenetrating brushes leads to an effective soft repulsion. If the colloid–colloid separation is reduced still further, the interaction becomes strongly repulsive, nearly hard-core like. The attractive component (depth ε) has a range that is only a few percent of the particle diameter (see the insert in Fig. 8). We call this interaction the MR potential. In the 2D limit, as shown by simulation studies reported by Bladon and Frenkel [33], a colloid system with interaction of this generic type (a narrow square well potential) supports an isostructural solid I-to-solid II transition. In the vicinity of the critical temperature for this isostructural transition, fluctuations both induce formation of a hexatic phase and influence the nature of the phase transitions at lower densities. The simulation results show that a 2D system with an MR interaction can exhibit first order liquid-to-hexatic, hexatic-to-solid I, and solid I-to-solid II transitions. It is worth noting that the KTHNY theory can be extended to the case when the 2D system supports two ordered solid phases by assuming that the elastic free energy of the system includes a term descriptive of the strain arising from the change in density associated with an isostructural solid-to-solid transition [34]. With this assumption, the modified KTHNY theory can account for all of the essential results of the simulation studies

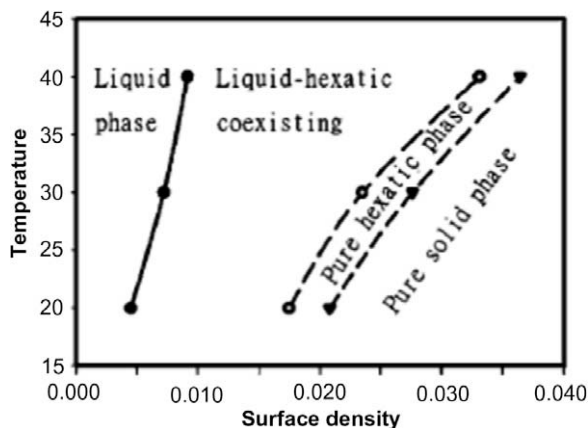


Fig. 7. From Ref. [32]. Phase diagram of a q2D assembly of charged colloid particles constrained to lie in the water–decane interface.

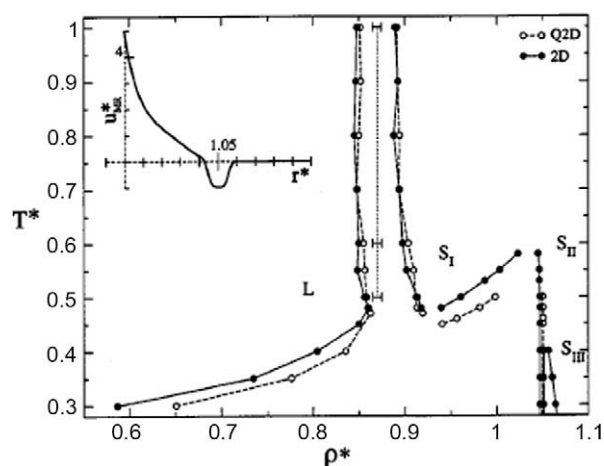


Fig. 8. From Ref. [35]. Phase boundaries for 2D and q2D suspensions of colloid particles that interact with an MR potential (see inset). L, S_I , S_{II} and S_{III} denote the stable liquid, solid I, solid II and solid III phases, respectively. The dotted line connects the density points for $T^* = 1.00, 0.60$ and 0.50 where the square-root Lorentzian characteristic of a hexatic becomes a better fit than a Lorentzian to the structure function. For both the 2D and q2D systems at all temperatures the density at which it occurs is $\rho^* = 0.87$.

of Bladon and Frenkel. However, the modified analysis does not provide *a priori* guidance as to when the elastic free energy should or should not contain such an extra contribution.

How, if at all, do phase transitions in a q2D system differ from those in a 2D system? The issue to be resolved is whether the small amplitude out-of-plane motion in a q2D system generates only quantitative corrections to the 2D phase diagram, or if it generates qualitative changes to that phase diagram. Frydell and Rice [35] have compared the phase diagrams of q2D and 2D systems composed of particles with an MR interaction (Fig. 8). Both systems undergo a first order solid I–solid II and solid II–solid III isostructural transitions induced by the attractive and repulsive components of the interaction, respectively. In q2D, although solid II has a puckered structure, the symmetry of that structure projected on a plane is the same as that of solid I.

Introduction of the out-of-plane motion shifts the low-density portion of the phase boundaries involving the solid II phase. The liquid–solid I coexistence line is nearly the same for the two systems. The solid II–solid III transition is shifted to lower temperature and to higher density in the q2D system. Calculation of the renormalized elastic constants reveals that in the q2D system the first order melting transition preempts the KTHNY transition for the reduced temperatures $T^* \equiv k_B T / \varepsilon = 1.00, 0.60$ (Fig. 9). The findings are similar for the 2D system: when $T^* = 0.60$ the KTHNY transition barely preempts the first order melting transition, and when $T^* = 1.00$ and 0.50 the first order melting transition preempts the KTHNY transition. The shift in the coexistence line is that expected from a simple physical argument, namely, at any selected density at which the liquid is stable, its entropy is increased by allowing out-of-plane motion. Similarly, allowing out-of-plane fluctuations of the solid I structure increases its entropy and thereby extends the density range over which it is stable. Eventually the density becomes so large that the puckered structure of solid II becomes stable. Clearly, the change from 2D to q2D confinement has nonnegligible effect on the nature of the phase transitions in the system studied.

Marcus and Rice [36] have reported the results of an experimental study of a q2D suspension of sterically stabilized polymethylmethacrylate spheres confined in a cell with wall separation about 1.2 particle diameters that are believed to have an MR-type interaction. Their results establish the existence of a hexatic phase

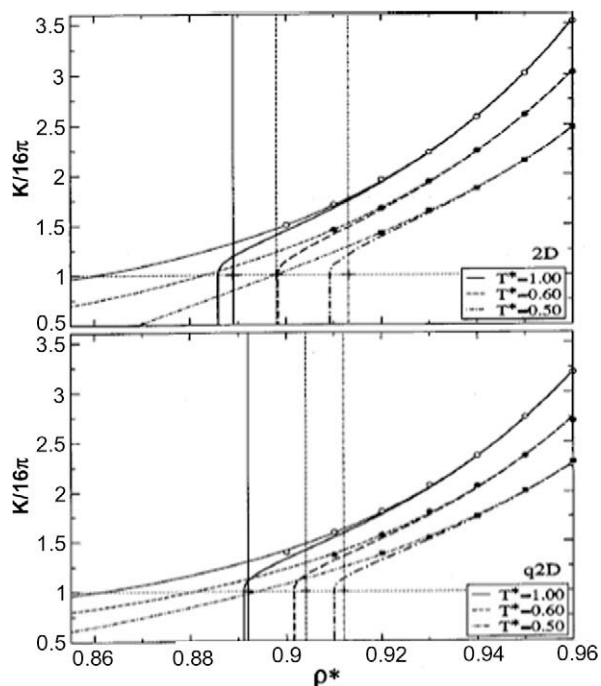


Fig. 9. From Ref. [35]. Renormalization of $K/16\pi$ (bold lines) at $T^* = 1.00, 0.60$ and 0.50 as a function of density for 2D and 2qD suspensions of colloid particles that interact with an MR potential. The data points are values of $K/16\pi$ obtained from simulation data, and the vertical lines denote the first order transition melting densities.

between the liquid and solid phases, and the occurrence of first order transitions between the liquid and hexatic phases and between the hexatic and solid phases, consistent with the general features of the Bladon–Frenkel and the Frydel–Rice simulations.

5. Transitions in multilayer q2D systems

We can generalize the class of q2D systems to include those confined to have a thickness of more than one but only a few sphere diameters. That kind of confinement will support new structures, different from both the 2D and 3D structures. Indeed, experimental studies of colloid suspensions confined between two plates [37–46], whether the interaction has short-range or long-range, show a cascade of ordered solid-to-ordered solid transitions.

For suspensions of particles with near hard sphere interaction, increasing the confining wall separation generates the following sequence of structures:

$$1\Delta \rightarrow 2\Box \rightarrow 2\Delta \rightarrow \Box \rightarrow \dots \quad (5.1)$$

The symbol Δ denotes a layer with hexagonal lattice symmetry and \Box a layer with square lattice symmetry. The integers in front of these symbols denote the number of layers of particles between the confining walls. A phase diagram derived from Monte Carlo simulations is displayed in Fig. 10. As written, the structural sequence $1\Delta \rightarrow 2\Box \rightarrow 2\Delta \rightarrow \Box \rightarrow \dots$ is incomplete in that it includes only lattices with hexagonal and square symmetries, and it implies that increasing the wall separation leads only to integer numbers of layers in the available space. However, when the wall separation is greater than that needed for the structure $n\Delta$ but smaller than that needed for the $(n+1)\Box$ structure, instability with respect to other structures can occur. Specifically, the layer of particles can buckle [47,48]. The buckling of a plane of particles is coupled to an in-plane

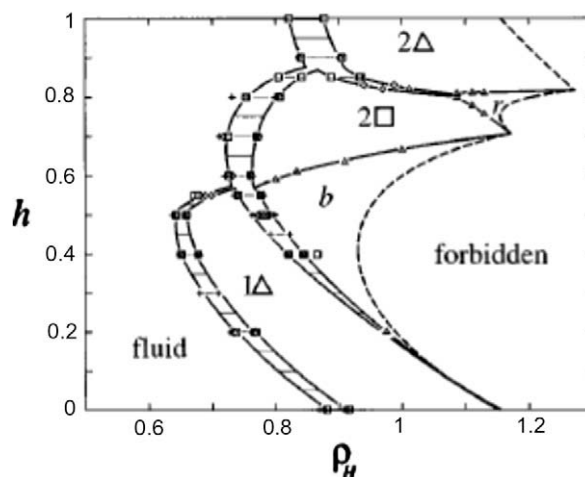


Fig. 10. From Ref. [47]. Phase diagram for hard spheres contained between smooth hard walls separated by $H = \sigma(1 + h)$.

order–disorder transition in which the lateral positions of particles that are localized at the same height are ordered. This ordering can take the form of linear or zigzag rows of particles. The symmetry of the emerging up and down phases for a single layer makes the buckled phase, B , an intermediate structure between the $n\Delta$ and $(n+1)\Box$ lattices. The stability region of B increases with the gap between the confining walls until B becomes unstable with respect to the formation of a crystal with an additional layer. The two transitions, $n\Delta \rightarrow nB \rightarrow (n+1)\Box$, are found to be first order.

All of these qualitative considerations are also valid for confined particles with softer repulsive interactions [49], and for confined particles with MR-type interactions [48,49], and they follow from the Landau theory of phase transitions, in which the thermodynamic potential is expanded about that for the flat state [50], and from an analysis based on free-volume theory [47]. Finally, for a system with colloid–colloid interactions of the MR type, the two-layer packing of particles in the square array has large interlayer lattice spacing, with the particles located at the minima of the attractive well. In this case the hexagonal to square lattice transition is first order. On the other hand, for a two layer system with hard core colloid–colloid interactions, there are two degenerate stable intermediate states, linear and zigzag rhombic phases, that are separated from the square lattice by strong first order transitions, and from the hexagonal lattice by either weak first order or by second order transitions [48,49].

A simple interpretation of the phase diagram as a function of wall separation for suspensions of near hard spheres follows from the observation that, because the equilibrium state in the limit of high pressure corresponds to maximum volume density, the successive transitions are driven by the competition between the free volume available to n square packed layers with smaller overall thickness than n hexagonal packed layers, and the free volume associated with more efficient packing within a hexagonal packed layer than in a square packed layer. Computer simulations and cell model calculations for the hard sphere system each generate a phase diagram that replicates the alternation of hexagonal and square lattice symmetry found [47], noting that neither theoretical approach addresses whether, as a function of wall separation, a hexatic phase intervenes between the solid and liquid phases.

For suspensions of particles with Coulomb interaction, immersed in uniformly distributed counterions and neglecting the discrete structure of the counterions, increasing the confining plate separation at $T = 0$ generates the following sequence of structures [51]:

$$\text{fluid} \rightarrow \Delta \rightarrow 2B \rightarrow 2\Box \rightarrow 2R \rightarrow 2\Delta \quad (5.2)$$

The symbol R denotes a phase with rhombic symmetry. At small density the colloid particles tend to stay in the potential minima generated by the counterion background, but at larger density the particle–particle repulsion dominates the particle background attraction, and the system supports a complex sequence of multi-layer ordered structures.

A Yukawa interaction can, by varying the screening length $1/\kappa$, be thought of as intermediate between the hard sphere and Coulomb interactions. The zero temperature phase diagram is rather complex (Fig. 11). For example, interpolating between the 2Δ and $3\Box$ phases, Oguz et al. [52] find the following transitions:

$$\begin{aligned} 2\Delta &\rightarrow 3\Box \\ 2\Delta &\rightarrow BWI \rightarrow 3\Box \\ 2\Delta &\rightarrow BWI \rightarrow 2P_\Delta \rightarrow 2P_W \rightarrow 3\Box \\ 2\Delta &\rightarrow BWI \rightarrow 2P_\Delta \rightarrow 2hcp(100) \rightarrow 2P_\Delta \rightarrow 2P_W \rightarrow 3\Box \\ 2\Delta &\rightarrow BWI \rightarrow 2P_\Delta \rightarrow 2hcp(like) \rightarrow 2hcp(100) \rightarrow 2P_\Delta \rightarrow 2P_W \rightarrow 3\Box \end{aligned} \quad (5.3)$$

The symbols BWI , P_Δ and P_W refer to a so-called Belgian waffle iron phase and prism phases with triangular and square bases, respectively. This cascade is qualitatively different from that separating the $2\Delta \rightarrow 3\Box$ transition in the hard sphere system.

None of the studies sketched above looked for the interpolation of a hexatic phase between the liquid and ordered solid phases as the wall separation of the confined suspension is increased from the 2D limit of zero. There is only one reported analysis of the dependence on wall separation and density of the liquid-to-hexatic, liquid-to- 1Δ and liquid-to- $2\Box$ transitions in a q2D colloid system. Xu and Rice [53] locate these transitions by the bifurcation of solutions of the first and second equations of the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy for the particle distribution functions in the system [54]. The theory, which makes no direct reference to either the elastic constants of the system or the concentrations and interactions between particular lattice imperfections, determines the wall separation dependence of the

density at which the pair correlation function of a q2D hard sphere system changes analytic form.

Consider, first, the 2D limit of the q2D hard sphere system. There are three key elements in the Xu–Rice analysis. First, to predict the liquid-to-hexatic transition one needs a representation of the two-particle distribution function of the anisotropic liquid that describes long-range bond orientation order. The diffraction pattern, hence the structure function, of a hexatic phase has peaks with a characteristic elongation into finite arcs. Xu and Rice use this property to represent the pair correlation function in the hexatic phase in the form

$$g_2(\mathbf{r}_1, \mathbf{r}_2) = g(r_{12}) + \int d\mathbf{k} \phi(k) \cos(6\theta) \exp(i\mathbf{k} \cdot \mathbf{r}_{12}), \quad (5.4)$$

in which $\phi(k)$ is a function centered at $k_0 = 4\pi/r_0$ that decays to 0 at about $k_0/2$, and r_0 is the separation between nearest neighbors. This choice for the representation of the pair correlation function is different from that proposed by Ryzhov and Tareyeva [55]. Second, to predict the liquid-to-ordered solid transition, they employ a representation of the nonuniform one-particle distribution function that reflects the particular lattice symmetry. Third, because the BBGKY hierarchy relates the n -particle distribution function to the $(n+1)$ -particle distribution function, a representation of the triplet correlation function is needed. Xu and Rice use a Padé approximant extension of the exact density expansion of the triplet correlation function truncated after the five-particle term [56]. This approximation has been shown to give a rather good but not perfect description of both the pair correlation function and the equation of state of simple liquids. With these approximations Xu and Rice find that the 2D hard disc system undergoes a continuous liquid-to-hexatic transition at lower density than the liquid-to-crystal transition (Fig. 12), in agreement with the KTHNY theory prediction, and unlike the prediction by Ryzhov and Tareyeva [55].

In the approach adopted by Xu and Rice, analysis of the wall separation dependence of the confined liquid-to-hexatic and liquid-to-ordered solid transitions requires knowledge of the wall separation dependence of the pair correlation function of the liquid. That information is not available, so Xu and Rice used an approximation that maps the q2D system onto a 2D system via a scaled-particle ansatz. Specifically, for wall separation $H = \sigma(1+h)$ they assumed that the effective diameter for particles

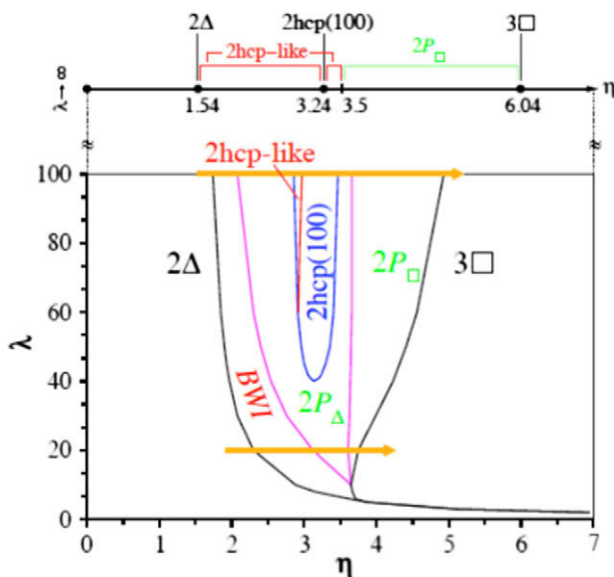


Fig. 11. From Ref. [52]. Zero temperature phase diagram of a suspension of particles with a Yukawa interaction confined between two hard walls separated by H ; $\lambda = \kappa H$ is the reduced screening and $\eta = NH^2/A$ is the reduced density. The line just above this phase diagram displays the limiting behavior when $\kappa \rightarrow \infty$ (the hard sphere limit).

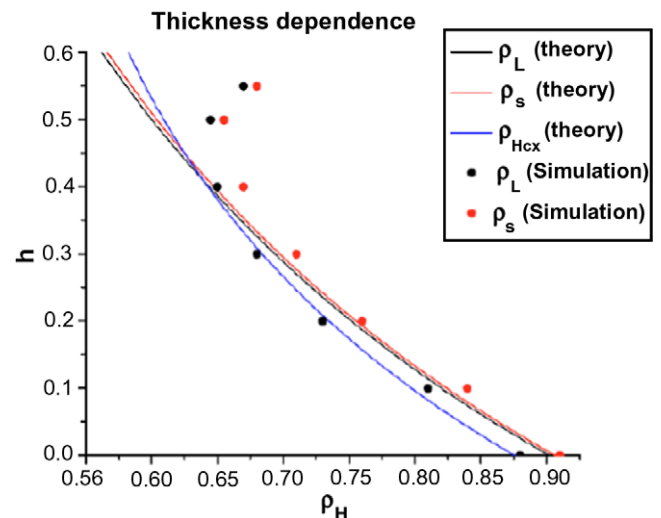


Fig. 12. From Ref. [53]. Thickness dependences of the liquid-to-crystal phase transition (black line and red line) and the liquid-to-hexatic phase transition (blue line). Simulation results for the liquid-to-crystal phase transition, by Schmidt and Lowen [47], are shown as points.

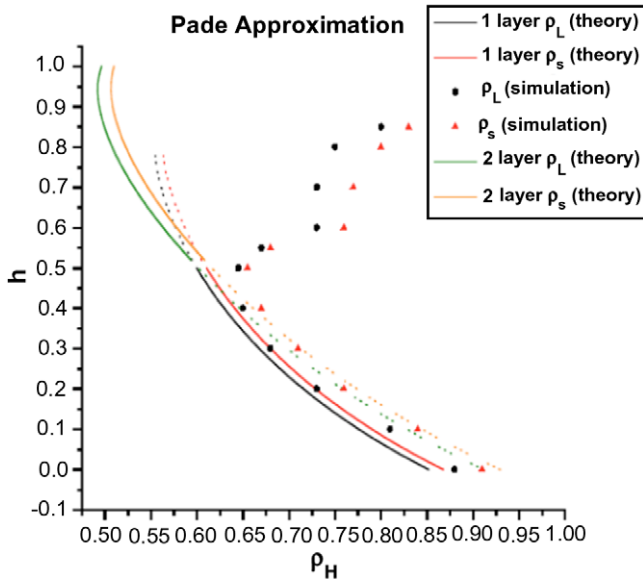


Fig. 13. From Ref. [53]. In the lower part of the figure the solid lines show the predicted liquid $\rightarrow 1\Delta$ phase boundaries as a function of h for $h < 0.5$ and the corresponding simulation data of Schmidt and Lowen [47]; the dotted lines show the predicted liquid $\rightarrow 2\Box$ phase boundaries. In the upper part of the figure the solid lines show the predicted liquid $\rightarrow 2\Box$ phase boundaries for $h > 0.5$; the dotted lines show the extensions of the predicted liquid $\rightarrow 1\Delta$ phase boundaries for $h < 0.5$.

with separation r is $\sigma_{\text{eff}}^2 = \sigma^2[1 - (\sigma^2 h^2 / 6r^2)]$. This approximation is best when $h \ll 1$, and becomes increasingly unsatisfactory as the system thickness increases. Xu and Rice find that for wall separations less than about 1.4σ , the liquid-to-hexatic transition density occurs at lower density than the liquid-to-crystal transition, with the reverse order of transitions predicted for wall separations greater than 1.4σ . Turning now to the liquid-to-solid transition, Xu and Rice find the agreement between the predicted shape of the q2D thickness dependence of the coexistence line between the hard sphere liquid and the 1Δ phase and that obtained from computer simulations to be rather good (see Fig. 12), as is the identification of the thickness at which the liquid prefers to freeze to the $2\Box$ phase (see Fig. 13), but the predicted shape of the q2D thickness dependence of the coexistence line between the hard disc liquid and the $2\Box$ phase is poor.

6. Structured fluctuations in q2D systems

The variation in crystal structure to which a q2D liquid freezes as the wall separation is increased can be used to examine whether structured fluctuations in the liquid serve as precursors to transitions to particular crystal lattices. The nucleation of crystallization has been studied for many years, but there remain ambiguities concerning the role of local ordered fluctuations in a liquid because of the lack of a direct connection between the definition of which structured fluctuations are important and a prescription for verifying such identifications. Sheu and Rice [57] have addressed this ambiguity for a q2D system by coupling an observable that can be used to identify local hetero-phase fluctuations in a liquid with an examination of the liquid $\rightarrow 1\Delta$ and liquid $\rightarrow 2\Box$ transitions. The observable they used is the aperture cross-correlation function of the liquid, $C(\mathbf{k}, \mathbf{q})$, which correlates the intensities of radiation, $I(\mathbf{k})$ and $I(\mathbf{q})$, scattered from a small volume measured at two distinct wave vectors \mathbf{k} and \mathbf{q} , with two detectors positioned such that \mathbf{k} is the difference between the incident radiation and scattered radiation wave vectors. $C(\mathbf{k}, \mathbf{q})$ is defined as the following grand canonical average over the particles contained in the illuminated volume:

$$C(\mathbf{q}, \mathbf{k}, t) = \frac{\langle I(\mathbf{q}, 0)I(\mathbf{k}, t) \rangle}{\langle I(\mathbf{q}) \rangle \langle I(\mathbf{k}) \rangle} \bigg|_{G_c} \quad (6.1)$$

$C(\mathbf{k}, \mathbf{q})$ is a measure of fluctuations that generate local order in the illuminated volume, specifically those that create configurations that satisfy the conditions for Bragg diffraction. Different choices of angle between the detectors can be used to monitor different locally ordered fluctuations, and measurements of the correlation between the intensities of the scattered radiation at two angles can be carried out at a single time or as a function of time.

Sheu and Rice have used $C(\mathbf{k}, \mathbf{q})$, calculated from molecular dynamics simulation data, to monitor locally ordered fluctuations in a q2D hard sphere fluid with thickness less than two sphere diameters. They find (see Figs. 14–17) that for wall separation H in the range $1\sigma \leq H \leq 1.57\sigma$ the liquid freezes into a single layer hexagonal solid and the locally ordered fluctuations exhibit only hexagonal symmetry that extends well into the liquid region. For $1.57\sigma \leq H \leq 1.75\sigma$ hexagonal fluctuations persist, and fluctuations with square ordered symmetry, that of the solid to which the liquid freezes, only emerge at densities $\sim 2\%$ below freezing. For $H = 1.8\sigma$ and 1.85σ , hexagonal ordered fluctuations are no longer found, and the square ordered fluctuations dominate the dense liquid region as the system freezes into a two layer square solid. For $H = 1.9\sigma$ and 1.95σ , where the liquid freezes into a two layer hexagonal solid, both square and hexagonal ordered fluctuations are observed. At lower densities, for these latter wall separations, the ordered fluctuations exhibit only square symmetry. Hexagonal symmetry ordered fluctuations appear at densities $\sim 7\%$ below freezing and become more dominant as the density is increased, but the square ordered fluctuations persist until the system is converted into the solid.

The results of these simulation studies show clearly that locally ordered fluctuations occur deep in the stable liquid domain of a

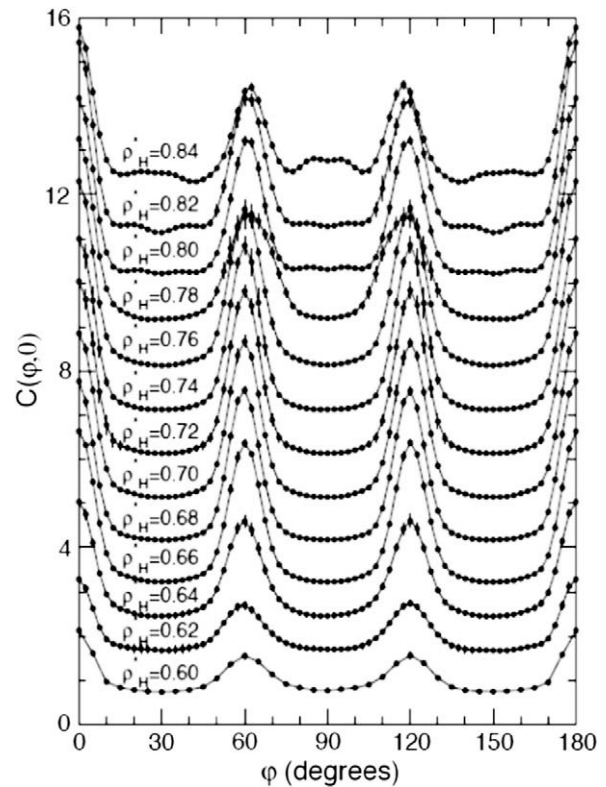


Fig. 14. From Ref. [57]. The zero time aperture cross-correlation function as a function of angle for various densities with wall separation 1.50 particle diameters. The fluid $\rightarrow 1\Delta$ and $1\Delta \rightarrow$ buckled phase transitions occur at $\rho_H^* = 0.62$ and 0.73 .

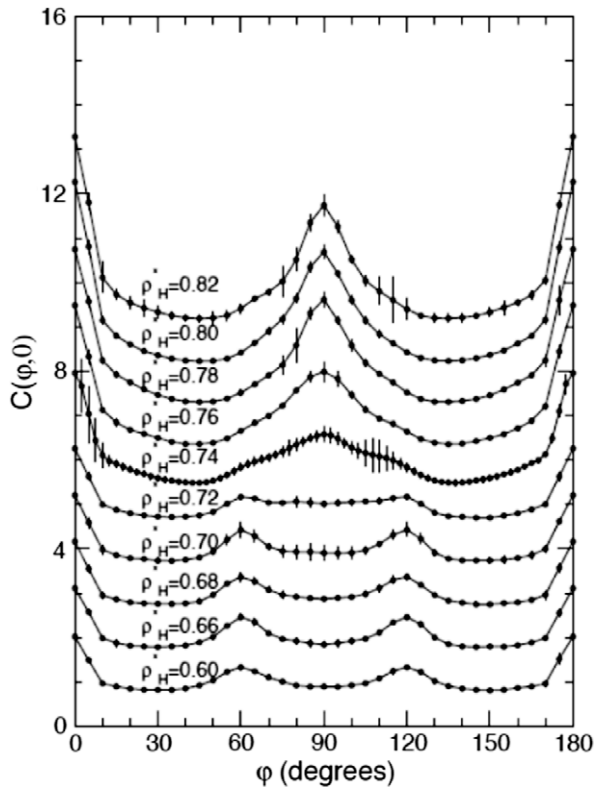


Fig. 15. From Ref. [57]. The zero time aperture cross-correlation function as a function of angle for various densities with wall separation 1.60 particle diameters. The fluid \rightarrow 2□ phase transition occurs at $\rho^* = 0.72$.

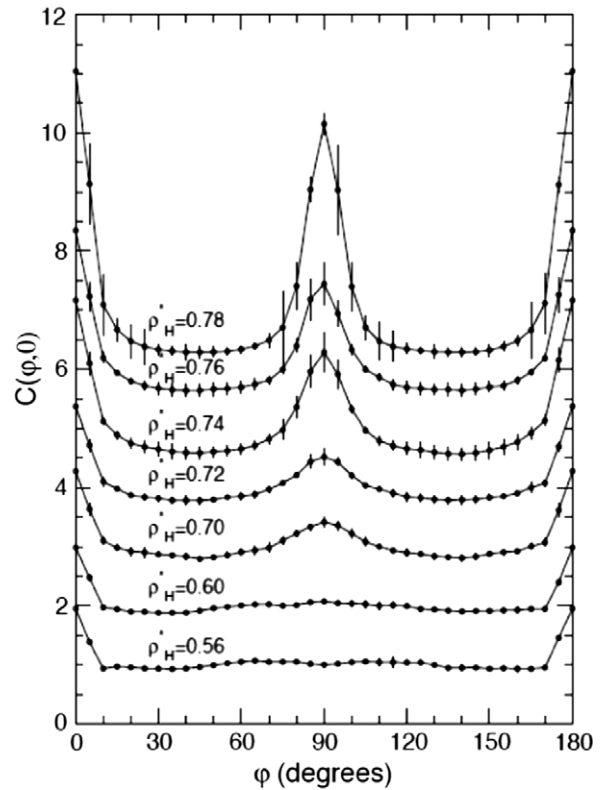


Fig. 16. From Ref. [57]. The zero time aperture cross-correlation function as a function of angle for various densities with wall separation 1.80 particle diameters. The fluid \rightarrow 2□ phase transition occurs at $\rho^* = 0.75$.

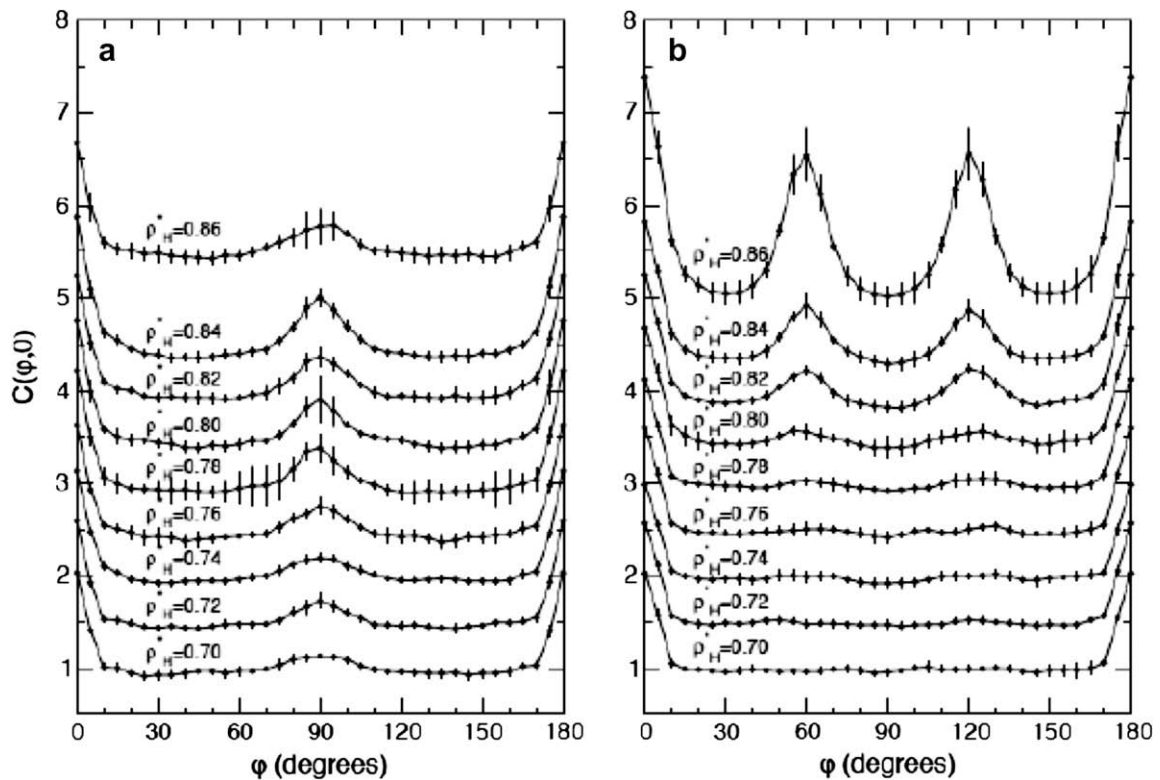


Fig. 17. From Ref. [57]. The zero time aperture cross-correlation function at the first two scattering rings as a function of angle for various densities with wall separation 1.90 particle diameters. The fluid \rightarrow 2Δ phase transition occurs at $\rho^* = 0.84$.

q2D confined colloid system. The particular order exhibited by these fluctuations is a function of both density and wall separation. At a specified wall separation and density, there is a precursor ordered local fluctuation in the q2D liquid that anticipates the character of the solid to which the liquid freezes, and the transformation from hexagonal to square packing in the solid–solid transition has a precursor in the ordered fluctuations in the liquid.

7. Perspectives

Although at first sight they appear to be arcane, studies of confined suspensions of spherical colloids have yielded a treasure trove of information. Arguably the most interesting of this information concerns the existence of a 2D phase, the hexatic phase, that interpolates between the fluid and ordered solid phases, and the unexpected dependence of the nature of 2D phase transitions on the character of the colloid–colloid interaction. These characteristics of 2D phase transitions define qualitative differences between the behavior of 2D and 3D matter. Other important information obtained concerning the properties of q2D systems delineates the subtle interplay between boundary conditions, the particle–particle interaction and the structures of ordered solids that a system supports. We have, at present, limited theoretical understanding of phase equilibrium in 2D and q2D systems. Simulations reproduce many of the experimental findings, and theoretical approaches that are variants of mean field theory provide clues with which to interpret the observations, but there is not yet a convincing physical picture that systematically captures and interprets all the observations. To improve our understanding of 2D and q2D phase transitions, we need to replace the instability representation of the phase transitions with an analysis that explicitly incorporates, without being externally imposed, the thermodynamic condition of equality of chemical potentials at the phase transitions, and which has an explicit dependence on the particle–particle interaction. This analysis must also incorporate the boundary conditions that define the system confinement in the representation of the various particle correlation functions.

Definitive studies of how the properties of a system change as the dimensionality changes from 2D to q2D to 3D have yet to be reported. Although not rigorously proven, for the 2D hard disc system the numerical evidence from studies of convergence of the virial series, simulation data, and bifurcation theory imply that there is a continuous liquid-to-hexatic phase transition. One test of the difference between 2D and q2D systems is the predicted interpolation of the hexatic phase between the liquid and ordered solid phases as the system thickness is increased from zero up to about 1.4 particle diameters. That prediction should be tested against experimental data.

Confined colloid suspensions can be used to examine multi-particle correlations that cannot yet be measured in molecular systems, such as the triplet correlation function and its dependence on particle interaction and alteration in mixtures. The two reported studies [58,59] show that our ideas concerning order in q2D liquids will likely require modification. Extensions of those studies to higher order correlation functions, and to changes associated with q2D \rightarrow 3D should be carried out.

This overview has focused on one-component suspensions of spherical colloid particles confined to spaces with very simple geometries. When the colloid particles have more complex shapes, when mixtures are examined, and when the geometry of the confining domain has curvature with scale length comparable to a particle diameter, the range of system properties is greatly expanded. And, because of the subtle interplay between boundary conditions, the particle–particle interaction and the structures of ordered sol-

ids that a system supports, there is opportunity to control the structure of the system and to create completely new structures. For example, there have been proposals for the design of self-assembling structures via design of the particle–particle interaction [60–64]. And, the potential use of confining domain shape to control structure is illustrated by simulation studies of the behavior of hard spheres confined in a smooth hard linear capillary [65,66]. If the capillary diameter is less than 2 hard sphere diameters the system supports only a fluid phase. When the capillary diameter is increased to 2.2 hard sphere diameters there is a discontinuous transition to a structure that consists of triads of spheres arranged in stacked planes that are perpendicular to the capillary axis. When the capillary diameter is increased further there are transitions to defected two-dimensional triangular lattices wrapped circumferentially within the capillary, with the number of wrapped shells determined by the capillary diameter. We can expect there to be many developments of these and other controllability schemes in future applications of confined colloid systems.

Acknowledgement

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