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Liquid-to-hexatic phase transition in a quasi-two-dimensional colloid system

Xinliang Xu and Stuart A. Rice
Departments of Physics and Chemistry and The James Frank Institute, The University of Chicago, Chicago, Illinois 60637, USA

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We report an analysis of the thickness dependence of the liquid-to-hexatic phase transition in a quasi-two-dimensional hard-sphere colloid system as the confining wall separation changes from 1 to 1.6 hard-sphere diameters. In our theoretical evaluation, we study the bifurcation of solutions to the integral equation for the pair correlation function. Our study predicts that at small wall separation the liquid-to-hexatic phase transition is continuous and that it occurs at lower density than the liquid-to-crystal phase transition density, in agreement with the predictions for a strictly two-dimensional system obtained from the Kosterlitz-Thouless-Halperin-Nelson-Young theory. At larger wall separation (larger than about 1.4 hard-sphere diameters), the liquid-to-hexatic phase transition density is predicted to occur at higher density than the liquid-to-crystal phase transition.

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I. INTRODUCTION

It is known that thermal fluctuations destroy the long-range positional order of a two-dimensional (2D) system. However, the system can still be highly ordered locally and form a 2D solid with quasi-long-range positional order and long-range orientation order. One of the consequences of the loss of the long-range positional order in the 2D solid is that the character of the freezing transition is fundamentally different from that in three dimensions. The theory developed by Kosterlitz, Thouless, Halperin, Nelson, and Young (KTHNY) [1–5] suggests that the 2D melting transition is a two-stage process, via an intermediate hexatic phase with quasi-long-range orientation order and short-range positional order. In the most widely accepted version of the theory both of these transitions are continuous. Verification of the KTHNY theory predictions has been difficult, as all experimental realizations are at best quasi-two-dimensional (Q2D) and the fluctuations inherent to a 2D system require the use of a very large number of particles in a computer simulation. Nevertheless, experimental studies of a variety of systems [6,7] have established the most important of the KTHNY predictions, the existence of a hexatic phase, while there remain some uncertainties concerning the order of the solid-to-hexatic and hexatic-to-liquid phase transitions and the details of the density dependences of the various lattice defect concentrations as a function of system density. Unlike the 3D melting transition, the character of the 2D transition displays a dependence on the particle-particle interaction. The best available evidence indicates that for a very long-ranged particle-particle potential, e.g., between magnetic dipoles, all of the KTHNY predictions are valid [6], whereas for a very short-range particle-particle interaction, e.g., between hard discs, the order of the liquid-to-hexatic transition is uncertain. The best available computer simulation of the 2D hard disc system, by Mak [8], indicates that this transition is either continuous (as predicted by KTHNY theory) or weakly first order, and that the density domain in which the hexatic phase is stable is very small. When the particle-particle interaction is more complex, e.g., a combined hard-core repulsion and weak very short-range attraction, the liquid-to-hexatic and hexatic-to-solid transitions can be first order [9].

There is another fascinating characteristic of a Q2D system, namely, the lattice to which it freezes changes symmetry as the thickness to which the system is confined is changed. Experimental studies of colloid dispersions confined between two glass plates [10–12] show that on increasing the confining wall separation the following sequence of crystalline structures is observed:

$$1\blacktriangle \rightarrow 2\blacksquare \rightarrow 2\blacktriangle \rightarrow 3\blacksquare \rightarrow \ldots .$$

The symbol ▲ denotes a layer with hexagonal lattice symmetry and ■ a layer with square lattice symmetry, and the integers in front of these symbols refer to the number of layers of particles between the confining walls. Computer simulations, by Schmidt and Lowen [13], generate a phase diagram that replicates these observations. These simulations do not address the question of whether, as a function of wall separation, a hexatic phase intervenes between the solid and liquid phases.

In this paper we present a theoretical analysis of the dependence on wall separation and density of the liquid-to-hexatic phase transition in a Q2D hard sphere colloid system, based on the bifurcation of solutions of the second equation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. We find that a continuous liquid-to-hexatic phase transition barely preempts a first-order liquid to solid transition for confining wall separations from 1 particle diameter to about 1.4 particle diameters; for larger wall separation a first-order liquid-to-solid transition occurs before the liquid-to-hexatic transition. The domain of stability of the hexatic phase in the 2D limiting case is in good agreement with the simulation data reported by Mak.

II. THEORETICAL BACKGROUND

As noted in the Introduction, our analysis of the dependence on wall separation and density of the liquid-to-hexatic phase transition in a Q2D hard sphere colloid system is based on the bifurcation of solutions of the second equation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. To implement that approach we use the leading terms of an exact representation of the triplet correlation function (see below). At this point, it is appropriate to set down a few words about these components of our analysis.

All modern theories of freezing start from an exact equation for the singlet density distribution, $\rho(1)$, as a function of position in space. This equation, derived independently by Arinshtein and by Stillinger and Buff [14], has the form

$$\ln \frac{\rho(1)}{z} = \sum_{k=1}^{\infty} \frac{1}{k!} \int S_{k+1}(1, \ldots, k+1) \prod_{i=2}^{k+1} \rho(i) d\{i\}, \quad (2.1)$$

where $S_{k+1}(1,\ldots,k+1)$ is the sum of all irreducible Mayer diagrams of order $k+1$, z is the fugacity of the system, and $d\{i\}$ denotes integration over the coordinates of particle i. The right-hand side of Eq. (2.1) is the generating functional for the set of n-particle direct correlation functions. In 1947 Mayer published a remarkable paper entitled "Integral equations between distribution functions of molecules" [15]. In this paper he reports a number of exact relationships between distribution functions at different fugacities, say z_α and z_β, and an interpretation of the solutions of the integral equations under the conditions of phase equilibrium. Among the many relations derived in that paper is

$$\frac{\rho}{z} = \sum_{m \geqslant 0} \frac{\rho^m}{m!} \int g_m(\rho, T, \{m\}) \prod_{j=1}^{m} f_{ij} d\{m\},$$

$$f_{ij} = \exp[-u_{ij}/k_B T] - 1. \quad (2.2)$$

In Eq. (2.2) $g_m(\rho,T,\{m\})$ are the m-particle correlation functions and u_{ij} is the pair interaction. Equation (2.2) is a variant of Eq. (2.1). Mayer showed that Eq. (2.2) and its generalization to nonfluid systems possess unique solutions in the one-phase regions supported by the system, and that the equations have solutions for all values of z except those, z_γ, at which phase changes occur. The equations do not describe the two-phase region since specification of the fugacity of a system does not specify the amounts of the two phases in equilibrium. The unique values of z_γ for which phase transitions occur are obtained from the eigenvalues of an equation involving a kernel that is related to the correlation function. In general, the distribution functions of the system are different in different phases, and do not approach one another as z_α or z_β approaches z_γ, the fugacity at the phase transition; when $z_\alpha = z_\gamma$ or $z_\beta = z_\gamma$ the solutions to the integral equation change character. The location of the phase transition can, therefore, be determined by finding where the solution to the nonlinear integral equation (2.1) for the distribution function, or a surrogate derived from it, changes character, i.e., bifurcates with a discontinuity in the density. Of course, the accuracy of this procedure is compromised by any approximations that reduce the accuracy of Eq. (2.1) or Eq. (2.2), but the principle on which the procedure is based is equivalent to the use of equality of chemical potentials and grand potentials to locate the phase transition. Some examples of the use of this procedure can be found in Refs. [16–18].

In the analysis that is presented below we find it necessary to use the three-particle correlation function. Relatively little is known of the detailed behavior of that function because the available experimental information is extremely limited and its calculation is very difficult. We use a representation of the triplet correlation function formalized by Meeron [19] and Salpeter [20],

$$g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = g_2(\mathbf{r}_1,\mathbf{r}_2) g_2(\mathbf{r}_1,\mathbf{r}_3) g_2(\mathbf{r}_2,\mathbf{r}_3) \times \exp\left(\sum_{n=1}^{\infty} \rho^n \delta_{n+3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \right), \quad (2.3)$$

where the coefficients of the density expansion $\delta_{n+3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ are $3n$-dimensional integrals. Specifically, $(\sum_{n=1}^{\infty} \rho^n \delta_{n+3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3))$ is the sum of all simple connected Mayer diagrams with three labeled unweighted root points, one or more unlabeled density-weighted field points, three or more f bonds [see Eq. (2.2) for the definition of f], no articulation points, and no direct bonds connecting the root points, such that the diagram does not become disconnected if the root points are removed. Rice and co-workers have shown that retention of the terms $\delta_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ and $\delta_5(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ gives a good, but not perfect, description of $g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$, and an accurate description of both $g_2(\mathbf{r}_1,\mathbf{r}_2)$ and the equation of state for several pair potential functions [21–27]. Evaluations of the first two terms, $\delta_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ and $\delta_5(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$, for a 2D hard-disk system have been reported elsewhere.

We are now ready to examine freezing in a Q2D system. We consider a one-component system of particles interacting through pair forces. The second equation of the BBGKY hierarchy [26], relating the pair correlation function to the triplet correlation function in a homogeneous system, is

$$\nabla_1 g_2(\mathbf{r}_1,\mathbf{r}_2) = -\beta \nabla_1 v(\mathbf{r}_1,\mathbf{r}_2) g_2(\mathbf{r}_1,\mathbf{r}_2) - \beta\rho \int \nabla_1 u(\mathbf{r}_1,\mathbf{r}_3) g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) d\mathbf{r}_3. \quad (2.4)$$

As applied to our system we take the diameter of the hard disks to be $\sigma=1$, and use the customary notation $\beta = (k_B T)^{-1}$. The hexatic phase, as suggested by the KTHNY theory, can be described as homogeneous (liquid) but anisotropic. Equation (2.4) supports solutions with isotropic pair correlation function when the system density is less than the transition density, ρ_{Hex}; for densities greater than ρ_{Hex} but less than the liquid density at the freezing point, ρ_L, the pair correlation function is anisotropic. In the hexatic phase, the anisotropic pair correlation function is conveniently represented in the form (see Fig. 1 for definition of the angles)

$$g_2(\mathbf{r}_1,\mathbf{r}_2) = g(r_{12}) + \int d\mathbf{k}\, \phi(k) \cos(6\theta) \exp(i\mathbf{k}\cdot\mathbf{r}_{12}). \quad (2.5)$$

Very little is known about the detailed form of $\phi(k)$. From earlier studies [28], we assume that $\phi(k)$ is a function centered at $k_0 = \frac{4\pi}{r_0}$ that decays to 0 at about $k_0/2$ away from k_0, where $r_0 = (\frac{2}{\sqrt{3}\rho})^{1/2}$ is the separation between nearest neighbors. Then $\int d\mathbf{k}\, \phi(k) \cos(6\theta) \exp(i\mathbf{k}\cdot\mathbf{r}_{12})$ is peaked around $r_{12} = r_0$ and decays quickly to 0 as the separation r_{12} increases

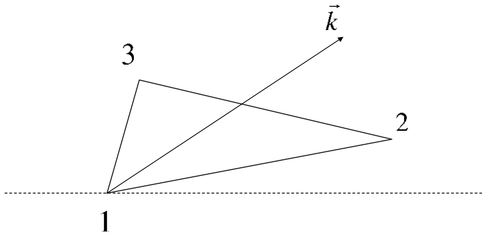

FIG. 1. Definition of angles used in this paper: θ is the angle between the reference axis (dashed line) and the vector $\vec{k}$. θ_{12}, θ_{13}, and θ_{23} are the angles between the reference axis and $\vec{r}_{12}$, $\vec{r}_{13}$, $\vec{r}_{23}$, respectively. α is the angle between $\vec{r}_{12}$ and $\vec{r}_{13}$. θ' is the angle between $\vec{k}$ and $\vec{r}_{12}$.

or decreases. We have found that the results described later in this paper are little changed (less than 10%) if it is assumed that $\phi(k)$ of the form $\cos[\pi(k-k_0)/k_0]$, or a Gaussian function centered at k_0 with standard deviation $k_0/4$, or a $\cos^2$ function centered at k_0. Substitution of Eqs. (2.3) and (2.5) into Eq. (2.4) yields

$$\nabla_1 \ln\left[1+\frac{\int d\mathbf{k}\,\phi(k)\cos(6\theta)\exp(i\mathbf{k}\cdot\mathbf{r}_{12})}{g(r_{12})}\right] = -\beta\rho\int d\mathbf{r}_3 \nabla_1 u(\mathbf{r}_1,\mathbf{r}_3)g(r_{13})\exp\left(\sum_{n=1}^{\infty}\rho^n\delta_{n+3}\right) \times \int d\mathbf{k}\,\phi(k)\cos(6\theta)\exp(i\mathbf{k}\cdot\mathbf{r}_{23}). \tag{2.6}$$

where we have assumed that $\int d\mathbf{k}\,\phi(k)\cos(6\theta)\exp(i\mathbf{k}\cdot\mathbf{r}_{12})=0$ at $r_{12}=1$. For hard disks, Eq. (2.6) takes the form

$$1+\cos(6\theta_{12})\frac{\int d\mathbf{k}\,\phi(k)\cos(6\theta')\exp(ikr_{12}\cos\theta')}{g(r_{12})} = \text{const}\exp(\rho g(1)\cos(6\theta_{12}))\int d\mathbf{k}\,k\phi(k)\cos(6\theta') \times\exp(-ikr_{12}\cos\theta')f(k,\theta',r_{12})), \tag{2.7}$$

where

$$f(k,\theta',r_{12}) = \int d\mathbf{r}_3 \exp\left(\sum_{n=1}^{\infty}\rho^n\delta_{n+3}(r_{12},r_{13},\alpha)\right) \times\exp(i\mathbf{k}\cdot\mathbf{r}_{13})\Theta(1-r_{13}),$$

$$\Theta(x)=\begin{cases}1, & x\geqslant 0,\\ 0, & x<0,\end{cases} \tag{2.8}$$

and α is the angle between vectors $\mathbf{r}_{12}$ and $\mathbf{r}_{13}$. To find the bifurcation point of Eq. (2.7) we first write $\phi(k)=\phi_0 h(k)$, where $h(k)$ is a scaled function that has unit value at $k=k_0$. Then Eq. (2.7) is of the form

$$1+a\phi_0\cos(6\theta_{12}) = \text{const}\exp[b\phi_0\cos(6\theta_{12})], \tag{2.9}$$

where a and b are parameters and ϕ_0 serves as the order parameter for the liquid-to-hexatic phase transition. If we integrate both sides of Eq. (2.9) over θ_{12} from 0 to 2π, we find

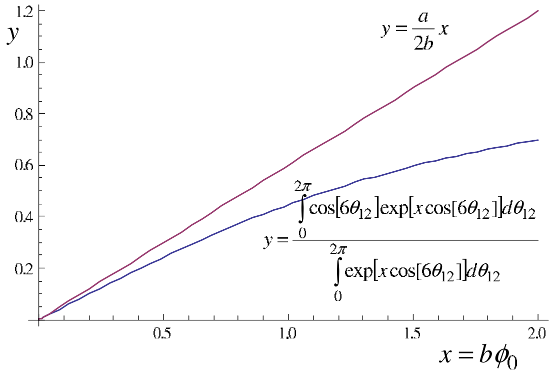

FIG. 2. (Color online) Location of the bifurcation point. The left-hand side of Eq. (2.12) is shown by the straight line, and the right-hand side of the same equation is shown by the curved line. As indicated by the graph, when $a/2b$, the slope of the straight line, is larger than 1/2, these two curves only intersect at the origin. And when $a/2b<1/2$, there will be a nontrivial solution that corresponds to the a hexatic phase.

$$2\pi = \text{const}\int_0^{2\pi}\exp[b\phi_0\cos(6\theta_{12})]d\theta_{12}. \tag{2.10}$$

We now multiply both sides with $\cos(6\theta_{12})$ and then integrate over θ_{12} from 0 to 2π to find

$$\pi a\phi_0 = \text{const}\int_0^{2\pi}\cos(6\theta_{12})\exp[b\phi_0\cos(6\theta_{12})]d\theta_{12}. \tag{2.11}$$

Then, dividing Eq. (2.11) by Eq. (2.10), we find

$$\frac{a}{2}\phi_0 = \frac{\int_0^{2\pi}\cos(6\theta_{12})\exp[b\phi_0\cos(6\theta_{12})]d\theta_{12}}{\int_0^{2\pi}\exp[b\phi_0\cos(6\theta_{12})]d\theta_{12}}. \tag{2.12}$$

In Fig. 2, we display the dependences of the left-hand side (straight line) and the right-hand side (curved line) of Eq. (2.12) on $x=b\phi_0$. It is clear that Eq. (2.12) has only one trivial solution ($x=0$) when $\frac{a}{2b}>\frac{1}{2}$, and has multiple solutions when $\frac{a}{2b}<\frac{1}{2}$. As the derivative of the right-hand side of Eq. (2.12) with respect to x decreases as x increases, we argue that the liquid-to-hexatic phase transition associated with this bifurcation point is continuous, and at the transition density ρ_{Hex} the bifurcation condition $\frac{a}{2b}=\frac{1}{2}$ is satisfied.

III. THE 2D HARD-DISK LIQUID-TO-HEXATIC PHASE TRANSITION

In a two-dimensional hard-disk system, for $r_{12}=r_0$ we have

$$a(\rho) = -2\pi\int_0^{\infty}kJ_6(kr_0)h(k)dk, \tag{3.1}$$

$$b(\rho) = \rho g(1) g(r_0) \int_0^\infty k h(k) dk \int_0^{2\pi} d\theta' \cos(6\theta') \times \exp(-ikr_0 \cos\theta') f(k,\theta',r_0), \tag{3.2}$$

where $J_n(x)$ is the Bessel function of the first kind of order n. The bifurcation condition is then just

$$-2\pi \int_0^\infty k J_6(kr_0) h(k) dk = \rho_{Hex} g(1) g(r_0) \int_0^\infty k h(k) dk \int_0^{2\pi} d\theta' \cos(6\theta') \times \exp(-ikr_0 \cos\theta') f(k,\theta',r_0). \tag{3.3}$$

where $f(k,\theta',r_0)$ is the sum of terms in powers of the density of which only the first few terms has been evaluated. To zero order in ρ, Eq. (2.3) reads

$$g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = g_2(\mathbf{r}_1,\mathbf{r}_2) g_2(\mathbf{r}_1,\mathbf{r}_3) g_2(\mathbf{r}_2,\mathbf{r}_3), \tag{3.4}$$

which is just the superposition approximation. And at this order we have

$$f(k,\theta',r_0) = \int d\mathbf{r}_3 \exp(i\mathbf{k}\cdot\mathbf{r}_{13}) \Theta(1-r_{13}) = -\frac{2\pi}{k} J_1(k). \tag{3.5}$$

Substitution of Eq. (3.5) into Eq. (3.3) gives

$$\int_0^\infty k J_6(kr_0) h(k) dk = -2\pi \rho_{Hex} g(1) g(r_0) \times \int_0^\infty J_1(k) J_6(kr_0) h(k) dk. \tag{3.6}$$

Information about the pair correlation function of a 2D hard-disk liquid at different densities is available in the literature [29,30].

As described before, $h(k)$ is a function centered at k_0 that drops to 0 at about $k_0/2$ distant from its center. With no further information concerning its shape, we adopt the simple ansatz

$$h(k) = \begin{cases} \cos[\pi(k-k_0)/k_0], & \text{if } |k-k_0| \le k_0/2, \\ 0, & \text{otherwise}. \end{cases} \tag{3.7}$$

After substitution of Eq. (3.7) into Eq. (3.6) we find the phase transition at

$$\rho_{Hex} = 0.723. \tag{3.8}$$

Of course, the superposition approximation is known to be inaccurate for densities close to the freezing point, and the calculations by Rice and co-workers, using the approximation to $g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ that includes the terms $\delta_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ and $\delta_5(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$, have been shown to yield much more accurate pair correlation functions and equations of state. Accordingly, we have also calculated the phase transition densities using the values of $\delta_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ and $\delta_5(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ obtained in earlier studies, and a Pade approximation to the term $\sum_{n=1}^\infty \rho^n \delta_{n+3}(r_{12},r_{13},\alpha)$. The predicted 2D hard-disk liquid-to-hexatic phase transition densities corresponding to each of these approximations are summarized in Table I. All of the predictions imply that the liquid-to-hexatic phase transition just barely preempts the liquid-to-crystal phase transition at about $\rho_{Hex} \approx 0.88$ (the multiorder parameter theory described in [31] predicts a first-order liquid-to-crystal phase transition with $\rho_L = 0.902$ and $\rho_S = 0.907$). The predicted liquid-to-hexatic phase transition density agrees with the result obtained from the computer simulation study by Mak.

TABLE I. The density of the 2D liquid-to-hexatic transition predicted at different levels of approximation for the triplet correlation function using the theory described in Sec. III.

	ρ_{Hex}
Superposition approximation	0.723
First-order approximation	0.889
Second-order approximation	0.884
Pade approximation	0.876

IV. THICKNESS DEPENDENCE OF THE Q2D LIQUID-TO-HEXATIC PHASE TRANSITION

We now examine the thickness dependence of the liquid-to-hexatic transition for hard spheres confined between two parallel walls with separation slightly larger than the particle diameter σ. We define the direction perpendicular to the plates to be z, and use x and y for coordinates in any plane parallel to the walls. In our previous study [32], we mapped the Q2D system onto the more familiar 2D system via a scaled-particle ansatz. Specifically, the pair correlation function at contact for the Q2D system with density ρ confined by two parallel walls with separation $H=(1+h)\sigma$, namely $g^{Q2D}(r_{12}=\sigma, z_1, z_2, \rho)$, was taken to be independent of z_1 and z_2, with its value being that of the pair correlation function at contact for the 2D system of particles with diameter σ^*, $g^{2D}(r_{12}=\sigma^*, \rho\sigma^{*2})$, where $\sigma^{*2}=\sigma^2(1-\frac{h^2}{6})$. This mapping, when used with the bifurcation analysis of the thickness dependence of the liquid-to-hexagonal solid phase boundary, yields good agreement with the computer simulation data of Schmidt and Lowen.

In this paper we use a slightly more sophisticated mapping of the Q2D system onto a 2D system. Consideration of the geometry of a pair of particles in the Q2D system suggests that the effective diameter for particles with different displacements from the midplane should approach the true particle diameter as r_{12} increases. To implement this observation we again assume that $g^{q2D}(r_{12}, z_1, z_2, \rho)$ is independent of z_1 and z_2. We define the effective pair separation by

$$R_{12}^{*2} = r_{12}^2 - \frac{\int_{-h\sigma/2}^{h\sigma/2} dz_1 \int_{-h\sigma/2}^{h\sigma/2} dz_2 (z_1 - z_2)^2}{(h\sigma)^2} = r_{12}^2 - \frac{\sigma^2 h^2}{6}. \tag{4.1}$$

Then the effective diameter for particles with separation r_{12} will be

$$\sigma^{*2}(r_{12}) = \sigma^2\left(1 - \frac{\sigma^2 h^2}{6r_{12}^2}\right). \quad (4.2)$$

With these assumptions, for a Q2D system Eq. (3.6) becomes

$$\int_0^\infty kJ_6(kR_0)h(k)dk = -2\pi\rho\sigma^*(1)g(\sigma^*(1),\rho\sigma^{*2}(1))g(R_0,\rho\sigma^{*2}(R_0)) \times \int_0^\infty J_1(k)J_6(kR_0)h(k)dk. \quad (4.3)$$

In the 2D limit $\rho_{Hex}\approx 0.9$ at the transition, so that $R_0 = (\frac{2}{\sqrt{3}\rho})^{1/2}\approx 1.1$, and it is a fairly good approximation to set $\sigma^*(R_0)\approx\sigma^*(1)$. Then the liquid-to-hexatic phase transition density, $\rho_{Hex}(h)$, satisfies the condition

$$\frac{\rho_{Hex}(0)}{\rho_{Hex}(h)} = 1 - \frac{h^2}{6}. \quad (4.4)$$

The adoption of Eq. (4.2) for the effective particle diameter slightly changes the thickness dependence of the liquid-to-crystal phase transition from that predicted using the definition $\sigma_{eff}/\sigma = 1-(h^2/6)$.

In the direct correlation function representation, the key functions we need to evaluate to determine the bifurcation point are

$$\sigma_0 = \rho_L\phi_0\int c_L(\mathbf{r})d\mathbf{r}, \quad (4.5)$$

$$\sigma_{\mathbf{G}} = \rho_S\int c_L(\mathbf{r})\exp(-i\mathbf{G}\cdot\mathbf{r})d\mathbf{r}. \quad (4.6)$$

The Ornstein-Zernike equation, in Fourier space, reads

$$1 - \rho c(k) = \frac{1}{1+\rho h(k)}, \quad (4.7)$$

where $c(r)$ is the direct correlation function and $h(r)=g(r)-1$. We note that σ_0 and $\sigma_{\vec{G}}$ contain information about both the short-range and long-range order of the system. While it is difficult to evaluate the thickness dependence of σ_0 and $\sigma_{\mathbf{G}}$, we argue that because the effective diameter $\sigma^*(r)$ decays very quickly to σ as r increases, it is reasonable to make the approximation that $\sigma_{\mathbf{G}}^{q2D}=\sigma_{\mathbf{G}}^{2D}$, $\sigma_0^{q2D}=\sigma_0^{2D}$. Thus we have $\rho_L(h)=\rho_L(0)$ and $\rho_S(h)=\rho_S(0)$.

Figure 3 shows the results we have obtained for the thickness dependence of the liquid-to-hexatic and liquid-to-crystal phase transitions. As expected, the results for the liquid-to-crystal transition differ slightly from our earlier results (Table II), both because of use of a different effective diameter mapping and the use of a seven-order parameter bifurcation analysis for the two-dimensional hard-disk freezing. The new liquid-solid phase boundary remains in good agreement with the simulation data of Schmidt and Lowen for small h. At larger h the deviation of the predicted phase boundary from that observed is a consequence of the deterioration of the accuracy of the effective diameter approximation.

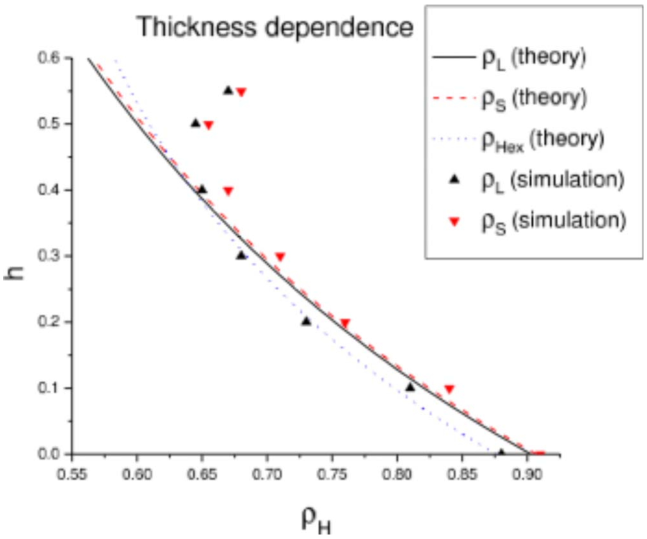

FIG. 3. (Color online) The thickness dependence of the liquid-to-crystal phase transition (black solid line and red dashed line) and the liquid-to-hexatic phase transition (blue dotted line). Earlier simulation results for the liquid-to-crystal phase transition, by Schmidt and Lowen [13], are shown as points.

V. CONCLUSIONS

Our analysis of the 2D liquid-to-hexatic transition differs considerably from that in the KTHNY theory. The latter is based on the use of a phenomenological Hamiltonian that represents the free energy of the system as that of an elastic continuum with additional contributions from the lowest energy lattice imperfections, namely dislocations and disclinations, and their interactions. Our approach, based on determining the density at which the pair correlation function of the system changes analytic form, makes no direct reference to either the elastic constants of the system or the concentrations and interactions between particular lattice imperfections. It does borrow from the KTHNY theory the concept that a hexatic phase might exist, as well as a characterization of the structure function of that phase. In our view, the ap-

TABLE II. Thickness dependence of the liquid-to-crystal phase transition. In this table, number density is defined as $\rho_H=\frac{N}{A(1+h)}$. ρ_{HL} and ρ_{HS} are the liquid density and the crystal density at the transition as calculated in our earlier study [32]; ρ'_{HL} and ρ'_{HS} are the densities obtained in this paper. The difference, as pointed out in the text, has two sources: the use of a multiorder parameter theory and a new effective diameter approximation.

h	ρ_{HL}	ρ_{HS}	ρ'_{HL}	ρ'_{HS}
0	0.931	0.934	0.902	0.907
0.1	0.848	0.851	0.820	0.825
0.2	0.781	0.784	0.752	0.756
0.3	0.727	0.729	0.694	0.698
0.4	0.683	0.685	0.644	0.648
0.5	0.648	0.650	0.601	0.605
0.6	0.619	0.621	0.564	0.567

proach presented in this paper has the advantage, albeit with the use of approximations, of simple extension to the treatment of Q2D systems, thereby addressing in a straightforward fashion the competition between the liquid-to-hexatic and liquid-to-solid transitions as a function of system thickness.

A previous analysis of the 2D liquid-to-hexatic transition based on determining the density at which the pair correlation function of the system changes analytic form, reported by Ryzhov and Tareyeva [33], differs from our analysis in several respects. First, they employ a somewhat different characterization of the hexatic phase. Whereas we describe the hexatic phase via the form of $\phi(k)$ in Eq. (2.5), they employ a real space description that sets $g_2(\mathbf{r}_1,\mathbf{r}_0)=g_2(|\mathbf{r}_1-\mathbf{r}_0|)[1+f(\mathbf{r}_1/\mathbf{r}_0)]$, with $g_2(|\mathbf{r}_1-\mathbf{r}_0|)$ the isotropic (liquid) part and $f(\mathbf{r}_1/\mathbf{r}_0)$ the anisotropic (bond orientation) part of the pair correlation function, and $\mathbf{r}_1$, $\mathbf{r}_0$ are the locations of near neighbor particles. Second, they exploit a microscopic representation of the elastic constants of the medium to calculate the solid-to-hexatic transition density, whereas we use the location of the bifurcation point at which the character of the pair distribution function changes from isotropic to anisotropic to identify the density of the liquid-to-hexatic transition. Both analyses involve approximations to the distribution functions that are plausible but not systematic. And, for the case under study, the 2D hard-disc system, Rhyzov and Tareyeva conclude that the solid-to-liquid transition is first order and that it preempts the liquid-to-hexatic transition; indeed, they assert that the hard-disc hexatic phase is absolutely unstable. In contrast, we predict that the liquid-to-hexatic transition in this system is continuous and just preempts the liquid-to-solid transition, in agreement with the simulation data reported by Mak. We suggest that the conclusion reached by Rhyzov and Tareyeva is compromised by the use of a hypernetted chain approximation for a key function, since the hypernetted chain approximation is known to be less accurate than the Percus-Yevick approximation for hard particle systems.

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[1] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **5**, L124 (1972).

[2] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).

[3] B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978).

[4] D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[5] A. P. Young, Phys. Rev. B **19**, 1855 (1979).

[6] K. Zahn, R. Lenke, and G. Maret, Phys. Rev. Lett. **82**, 2721 (1999).

[7] A. H. Marcus and S. A. Rice, Phys. Rev. Lett. **77**, 2577 (1996).

[8] C. H. Mak, Phys. Rev. E **73**, 065104(R) (2006).

[9] M. P. Allen, D. Frenkel, and W. Gignac, J. Chem. Phys. **78**, 4206 (1983).

[10] D. H. Van Winkle and C. A. Murray, Phys. Rev. A **34**, 562 (1986).

[11] C. A. Murray, W. O. Sprenger, and R. A. Wenk, Phys. Rev. B **42**, 688 (1990).

[12] C. A. Murray, *Bond-Orientational Order in Condensed Matter Systems*, edited by K. J. Strandburg (Springer, New York, 1992).

[13] M. Schmidt and H. Lowen, Phys. Rev. E **55**, 7228 (1997).

[14] E. A. Arinshtein, Dokl. Akad. Nauk SSSR **112**, 615 (1957); F. H. Stillinger and F. P. Buff, J. Chem. Phys. **37**, 1 (1962).

[15] J. E. Mayer, J. Chem. Phys. **15**, 187 (1947).

[16] B. Bagchi, C. Cerjan, and S. A. Rice, Phys. Rev. B **28**, 6411 (1983).

[17] B. Bagchi, C. Cerjan, and S. A. Rice, J. Chem. Phys. **79**, 5595 (1983).

[18] C. Cerjan, B. Bagchi, and S. A. Rice, J. Chem. Phys. **83**, 2376 (1985).

[19] E. Meeron, J. Chem. Phys. **27**, 1238 (1957).

[20] E. E. Salpeter, Ann. Phys. **5**, 183 (1958).

[21] G. Stell, Physica (Amsterdam) **29**, 517 (1963); in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frish and J. L. Lebowitz (Benjamin, New York, 1964), pp. 11–171.

[22] S. A. Rice and J. Lekner, J. Chem. Phys. **42**, 3559 (1965).

[23] D. A. Young and S. A. Rice, J. Chem. Phys. **46**, 539 (1967).

[24] W. J. McNeil, W. G. Madden, A. D. J. Haymet, and S. A. Rice, J. Chem. Phys. **78**, 388 (1983).

[25] A. D. J. Haymet, S. A. Rice, and W. G. Madden, J. Chem. Phys. **74**, 3033 (1981).

[26] J. P. Hansen and J. R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 1976), Chap. 2.

[27] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Wiley, New York, 1965), Chap. 2.

[28] Very little information about $\phi(k)$ is available. For some experiment indications, see J. D. Brock, *Bond-Orientational Order in Condensed Matter Systems*, edited by K. J. Strandburg (Springer, New York, 1992).

[29] F. H. Ree and W. G. Hoover, J. Chem. Phys. **40**, 939 (1963).

[30] D. Frydel and S. Y. Sheu (private communication).

[31] X. L. Xu, Ph.D. thesis, University of Chicago, 2007.

[32] X. L. Xu and S. A. Rice, Proc. R. Soc. London, Ser. A **464**, 65 (2008).

[33] V. N. Ryzhov and E. E. Tareyeva, Phys. Rev. B **51**, 8789 (1995).