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Equation of state of the hard-disc solid

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We present a study of the equation of state of the hard-disc solid, including the freezing transition. The study is based on a weighted-density approximation scheme for the free-energy density functional of hard discs. Using a standard procedure to construct such a functional in terms of a suitably chosen weighting function, augmented to include a cubic (rather than quadratic) approximation for the density dependence of the latter, we obtain the equation of state of the solid and use it to locate the densities where solid and fluid coexist. The equation of state is compared with constant-pressure Monte Carlo simulation data obtained by us and reasonable agreement is found. Also the location of the freezing transition is compared with available estimates based on extensive simulations performed by other groups. Although our mean-field-type theory does not take proper account of fluctuations and defects (which are believed to be important to determine the nature of this transition) are not treated at all, its prediction for the transition densities are quantitatively correct; however, the density gap at the (first-order) transition is overestimated. In addition, we observe that our results for the location of the transition crucially depend on how accurately the weighting function models the direct correlation function of the uniform fluid: As this description becomes better, the agreement with simulations improves. [S0163-1829(97)02329-1]

I. INTRODUCTION

Two-dimensional systems have attracted considerable interest in the last few decades.[1] Two issues are of particular importance: the effect of the low dimensionality on melting, and the phase behavior and nature of phase transitions in adsorbates physisorbed on substrates, which can exhibit competition between commensurate and incommensurate phases.[2]

These topics have been tackled using a number of different theoretical tools. Classical density-functional theory turns out to provide a useful framework since it gives a unified description of fluid and solid phases.[3] Thus far, however, effort has been mainly concentrated on the development of accurate free energy density functionals for three-dimensional models, most notably hard spheres, and relatively successful approximations have been constructed.[4–8] These approximations give very accurate results for the melting properties of hard spheres. When combined with ideas borrowed from perturbation theory for fluids,[9] these approximations provide an accurate theoretical device with which one can predict thermodynamic and structural properties of model systems of molecules interacting through both repulsive and attractive interactions.[10–12]

In perturbation theory the thermodynamic potential of a realistic molecular system is expressed in terms of the thermodynamic and correlation functions of a reference system.[9] The importance of the hard-sphere fluid as a useful model in perturbation theories largely stems from this fact. Knowledge about correlations of the reference system is a basic requirement of the theory. Unfortunately the implementation of the perturbative program in the context of solids is not as direct as one might think, due to lack of knowledge about correlations in nonuniform phases. Recently an accurate and easy-to-implement perturbation theory for classical three-dimensional solids has been developed.[11,12] The theory has been shown to provide accurate results for a variety of model systems, ranging from Lennard-Jones to very short-range attractive interaction potentials, intended to mimic real systems (e.g., colloidal suspensions). The basic ingredients of the theory are a new theoretical procedure to approximate the two-body correlation function, together with one of the available density-functional approximations for the hard-sphere solid equation of state and density distribution.

Similar progress for two-dimensional solids is still lacking, due in part to the fact that the natural reference system in two dimensions, the hard-disc model, has not been studied with so much detail.[4,13] The nature of the melting transition in two-dimensional systems of particles interacting via short-range potentials, and hard discs in particular, has been studied by computer simulation, but it still remains a debated subject.[14–18] On top of that, there is no adequate theoretical framework providing information on the thermodynamics and correlations of the hard-disc solid. This is a severe limitation for the successful implementation of the perturbative program in two-dimensional systems. For example, a structured substrate generates a certain amount of order in the adsorbed film, even if the latter is fluid; the precise nature of the ensuing correlations is unknown, and the situation worsens if the film becomes solid. This poses some difficulties in the development of any theoretical scheme aimed at a quantitative understanding of film phase behavior.

A few years ago Mederos *et al.*[19] attempted to generalize the zeroth-order weighted-density approximation, developed by Tarazona[4] to describe the freezing transition in systems of hard spheres and discs, to the study of hard discs in the presence of a substrate. Despite the power of the density-functional predictions as regards the qualitative description of the complex adsorption phase diagram, the theory had some limitations. In particular, the description of the properties of the hard-disc solid were rather poor. Obviously, any attempt at an adequate implementation of perturbation theory for realistic systems demands a more accurate description of the hard-disc solid. The present paper presents a systematic study of how the full (second-order) weighted-density approximation of Tarazona[5] can be extended successfully for hard discs. Recently, Takamiya and Nakanishi[20] made a first attempt along these lines with a view to understanding the structure of a fluid in the environment of a triatomic molecule. However, the hard-disc solid was not studied by Takamiya and Nakanishi.

In this paper we show that the explicit second-order scheme of Tarazona cannot be implemented as directly as in the hard-sphere case, and that the particular nature of hard discs requires going beyond the second-order virial approximation for the weighted density suggested by Takamiya and Nakanishi. The resulting equation of state for the solid is in relatively good agreement with the computer-simulation results obtained by us, and the location of the freezing transition is quite reasonable as compared with the results of the most recent computer work.

The paper is organized as follows. Section II is devoted to a brief presentation of the density functional theory and its ingredients, and we discuss how the weighting function is constructed. In Sec. III we give some details on the approximations used to describe the solid phase, and Sec. IV provides some information pertaining to the constant-pressure Monte Carlo simulations used to obtain the equation of state. Section V presents the results and finally in Sec. VI we present some conclusions.

II. THEORY

A. Density-functional formalism

In density-functional theory the free energy of an inhomogeneous system is written as a functional $F[\rho]$ of the one-particle density, $\rho(\mathbf{r})$, such that the equilibrium state is given by the functional minimum with respect to variations of $\rho(\mathbf{r})$.[3] The functional is constructed using information on correlations in the uniform phase. Of particular importance to our subsequent discussion is the two-particle direct correlation function $c(\mathbf{r},\mathbf{r}')$, related to the second derivative of the free energy by

$$c(\mathbf{r},\mathbf{r}') = -\beta \frac{\delta^2 \Delta F[\rho]}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}. \tag{1}$$

Here $\beta = 1/k_B T$, and $\Delta F[\rho]$ is the excess free energy over the ideal gas, so that the total free energy is

$$F[\rho] = F_{\rm id}[\rho] + \Delta F[\rho], \tag{2}$$

and $F_{\rm id}[\rho]$ is the (exact) ideal gas free energy,

$$F_{\rm id}[\rho] = \beta^{-1} \int d\mathbf{r}\rho(\mathbf{r})\{\ln[\Lambda^2\rho(\mathbf{r})] - 1\}, \tag{3}$$

where Λ is the de Broglie wavelength. The excess free energy is not known exactly and consequently it has to be approximated. One crucial point is that an accurate description of highly nonuniform systems (like solids) requires going beyond the usual local-density approximation. Various schemes have been proposed to take into account correlations in nonuniform systems approximately; these are reviewed in Ref. 3. One of the most successful approaches is the weighted-density approximation (WDA) of Tarazona,[4,5] which approximates ΔF in terms of a local-density-like expression but uses an averaged (or weighted) density $\overline{\rho(\mathbf{r})}$:

$$\Delta F[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\Delta\Psi(\overline{\rho(\mathbf{r})}). \tag{4}$$

In Eq. (4), $\Delta\Psi(\rho)$ is the excess free energy per particle of a uniform system of density ρ. The weighted density is calculated as a spatial average of the one-particle density,

$$\overline{\rho(\mathbf{r})} = \int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}'-\mathbf{r}|;\overline{\rho(\mathbf{r})}), \tag{5}$$

where $w(r;\rho)$ is a weighting function. The weighting function is chosen such that the free-energy functional recovers the correct direct correlation function in the uniform limit. The two basic ingredients of the WDA functional for a given model system are then $\Delta\Psi(\rho)$ and $c(r;\rho)$ for the corresponding uniform system, which are supposed to be known. For hard spheres one can use the quasiexact Carnahan-Starling equation of state together with the (closed) Percus-Yevick expression for the direct correlation function.

The above scheme has provided very successful approximations for the thermodynamic and structural properties of systems of hard spheres in the presence of various types of external potentials.[21] When the external potential is zero, the theory predicts a spatially self-structured phase which is identified as the hard-sphere solid, studied from the sixties by computer simulation.[22,23] In fact, good agreement between the various versions and extensions of WDA theory and simulation has been found as regards the location of the transition, the equation of state, and the Lindemann parameter.[3]

The construction of WDA theories relies heavily on the availability of accurate closed expressions for the free energy and correlation function of the uniform system. Undoubtedly the availability of the Percus-Yevick approximation for $c(r;\rho)$ and the Carnahan-Starling quasiempirical expression for $\Delta\Psi(\rho)$ has permitted the implementation of the WDA ideas into quantitatively successful functionals. However, the situation is not so satisfactory in the case of hard discs: There is no such thing as a Carnahan-Starling expression, and the Percus-Yevick theory does not provide a closed-form formula. Naturally this is an upsetting complication, but not an impediment, since at least one can obtain the necessary thermodynamic and structural ingredients numerically.

B. Properties of the hard-disc fluid

A number of theories have been proposed to account for the thermodynamic properties of the hard-disc fluid.[24] Except for scaled-particle theory (which is known to be inaccurate at high density), all these approaches are based on particular resummations of the virial series. The standard procedure is based on the fact that knowledge of the first few virial coefficients (either analytically or by simulation) permits the construction of accurate Padé approximants for the compressibility factor $Z(\rho)$,

$$Z(\rho)=\frac{1+\Sigma_{n=0}^{N}a_n\eta^n}{(1-\eta)^2}, \tag{6}$$

where $\eta=\pi\rho\sigma^2/4$ is the packing function and σ is the hard-disc diameter. The free energy per molecule $\Delta\Psi(\rho)$ follows from Eq. (6) by integration.[9] Theories for the structure of a fluid of hard discs in terms of the direct correlation function are much more scarce. This function cannot be obtained accurately by simulation. One obvious choice is the Percus-Yevick approximation to the Orstein-Zernike equation: Even though the resulting equation cannot be solved in closed form, it is possible to obtain the solution numerically without much computational effort. A critical issue is that of thermodynamic consistency. Since there are two independent relations between the thermodynamics and the structure functions, consistency should be imposed on the theory by demanding that the two relations be satisfied at the same time. This is an essentially unsolved problem. In the theory of Baus and Colot[25] (BC), the direct correlation function is constructed from a rescaled low-density expression, and it is made to be consistent with a Padé approximant for the compressibility factor through the compressibility equation. The virial equation is satisfied only at second order in density, and so thermodynamic consistency is not complete (it must be mentioned that, for hard spheres, the Carnahan-Starling equation of state and the Percus-Yevick direct correlation function also suffer from a similar shortcoming). However, since the expression for $c(r;\rho)$ provided by BC comes in closed analytic form, in the following we will take it as our reference direct correlation function, together with their Padé approximant for the compressibility factor $Z(\rho)$ and its associated free energy. Despite the incomplete thermodynamic consistency, the BC compressibility factor $Z(\rho)$ provides fairly accurate results at high fluid densities.[25]

C. Weighting function

In this section we show how to construct a weighting function for the WDA free-energy functional of hard discs. Differentiating ΔF twice with respect to $\rho(\mathbf{r})$ and taking the uniform limit $\rho(\mathbf{r})\rightarrow\rho$ leads to

$$\begin{aligned} c(r;\rho)=&-2\beta\Delta\Psi'(\rho)w(r;\rho)-\rho\beta\Delta\Psi''(\rho)\\ &\times\int d\mathbf{t}w(|\mathbf{r}-\mathbf{t}|;\rho)w(t;\rho)-2\rho\beta\Delta\Psi'(\rho)\\ &\times\int d\mathbf{t}w(|\mathbf{r}-\mathbf{t}|;\rho)\frac{\partial w(t;\rho)}{\partial\rho}. \end{aligned} \tag{7}$$

Now the WDA strategy consists of optimizing the weighting function so as to reproduce the correct direct correlation function in this limit. Taking $c(r;\rho)=c_{\rm BC}(r;\rho)$, $\Delta\Psi(\rho)=\Delta\Psi_{\rm BC}(\rho)$, and Fourier transforming the above expression, we obtain

$$\begin{aligned} c_{\rm BC}(q;\rho)=&-2\beta\Delta\Psi'_{\rm BC}(\rho)w(q;\rho)-\rho\beta\Delta\Psi''_{\rm BC}(\rho)\\ &\times[w(q;\rho)]^2-2\rho\beta\Delta\Psi'_{\rm BC}(\rho)w(q;\rho)\frac{\partial w(q;\rho)}{\partial\rho}. \end{aligned} \tag{8}$$

For each wave vector q, this is a differential equation in ρ, with $w(q;\rho)$ as the dependent variable, which is solved numerically. This approach was used by Curtin and Ashcroft[6] in their version of the WDA for hard spheres. Now the numerically exact weighting function in q space is transformed back to real space to give the weighting function which reproduces the ''correct'' (i.e., BC) direct correlation function. The latter can be used in Eq. (5) to compute the averaged density. However, this is not the approach we will follow since, from a practical point of view, the full density dependence of the weighting function is not easily handled in actual calculations; this is the reason why it is convenient to introduce a density parametrization, based on a truncated virial expansion for $w(r;\rho)$:

$$w(r;\rho)=w_0(r)+w_1(r)\rho+w_2(r)\rho^2+\cdots. \tag{9}$$

The coefficients $w_n(r)$ can be obtained order by order if Eq. (8) is expanded in powers of ρ. Using

$$c_{\rm BC}(q;\rho)=c_0(q)+c_1(q)\rho+c_2(q)\rho^2+\cdots \tag{10}$$

and

$$\beta\Delta\Psi_{\rm BC}(\rho)=f_1\rho+f_2\rho^2+f_3\rho^3+\cdots, \tag{11}$$

explicit formulas for the virial coefficients $w_n(q)$, with

$$w(q;\rho)=w_0(q)+w_1(q)\rho+w_2(q)\rho^2+\cdots, \tag{12}$$

are obtained in terms of $c_n(q)$ and f_n by identifying powers of ρ. The first three coefficients are

$$w_0(q)=-\frac{c_0(q)}{2f_1}, \tag{13}$$

$$w_1(q)=-\frac{c_1(q)+4f_2w_0(q)+2f_2[w_0(q)]^2}{2f_1[1+w_0(q)]}, \tag{14}$$

and

$$\begin{aligned} w_2(q)=&-\{c_2(q)+6f_3[1+w_0(q)]w_0(q)\\ &+4f_2[1+2w_0(q)]w_1(q)\\ &+2f_1[w_1(q)]^2\}/\{2f_1[1+2w_0(q)]\}. \end{aligned} \tag{15}$$

Transforming Eq. (12) back to real space provides the necessary coefficients $w_n(r)$.

In practice, Tarazona used the exact $w_0(r)$ and $w_1(r)$ coefficients in his theory for hard spheres and optimized $w_2(r)$ in such a way that the high-density behavior of the resulting $c(r;\rho)$ were in agreement with the Percus-Yevick result. This strategy yields direct correlation functions in reasonable agreement with the aimed-at Percus-Yevick function,[5] except at high density. A similar approach was followed by Takamiya and Nakanishi[20] (TN) to construct a corresponding functional in two dimensions, using the BC direct correlation function and equation of state as input. The first virial coefficient $w_0(r)$ follows directly by identifying the coefficient of the density-independent term in the virial expansion of Eq. (7) and using $c_0(r) = -\Theta(r-\sigma)$. We obtain

$$w_0(r) = \frac{1}{\pi\sigma^2}\Theta(\sigma - r). \tag{16}$$

An alternative method to find $w_0(r)$ is to use Eq. (13) with $f_1 = \pi\sigma^2/2$ and

$$c_0(q) = \int d\mathbf{r} c_0(r) e^{i\mathbf{q}\cdot\mathbf{r}} = -\frac{2\pi}{q} J_1(q\sigma), \tag{17}$$

and then apply inverse Fourier transform. TN used for $w_1(r)$ a parametrized form fitted to the exact function, which follows from Eq. (14). Finally, following Tarazona, TN optimized $w_2(r)$ using a simple parabolic form, truncated at $r = \sigma$:

$$w_2(r) = \begin{cases} a_0 + a_1 r + a_2 r^2, & r < \sigma, \\ 0, & r > \sigma. \end{cases} \tag{18}$$

However, the approximation for $c(r;\rho)$ obtained with this approach is rather poor, even at moderate densities. Figure 1 depicts the BC and TN direct correlation functions[26] at two different densities. We note the gross discrepancy in the whole interval in r. The TN parametrization worsens rapidly for increasing density (note that the densities considered in the figures are within the expected range where the transition to the solid phase should occur). The disagreement is particularly acute for $r > \sigma$; the nonvanishing tail in the TN direct correlation function is partly due to the truncation of the $w_2(r)$ coefficient at $r = \sigma$ which generates a noncompensated structure through the convolution equation (7).[27]

On the basis of the results presented in Fig. 1, we conclude that the TN parametrization is not suitable for our purposes: Since we are interested in describing the hard-disc solid, it is of paramount importance to use a weighting function which reproduces faithfully the direct correlation function in the entire density range up to the solid regime (i.e., $\rho \sim 1\sigma^{-2}$; we note that the close-packing density for discs is $\rho_{\mathrm{cp}} \approx 1.15\sigma^{-2}$). The TN approximation for $w_2(r)$ is not flexible enough, in that the absence of a tail for $r > \sigma$ prevents an adequate cancellation of the tail in $c(r;\rho)$.

To improve the fitting, we have to use a different parametrization. Let us consider the extended virial expansion (9). Various strategies are possible at this stage. It seems clear that the first two coefficients should be kept exact in order to reproduce both the limit $w(r;\rho=0)$ and the correct density dependence at low density. In the following we will consider parabolic (truncated at second order in density) and cubic (truncated at third order) parametrizations. In the latter case, the coefficients $w_2(r)$ and $w_3(r)$ can be optimized together; one could keep the exact $w_2(r)$, obtained from Eq. (15) and optimize $w_3(r)$, but this is not so flexible a parametrization and we have chosen to use the first strategy since it provides better results.

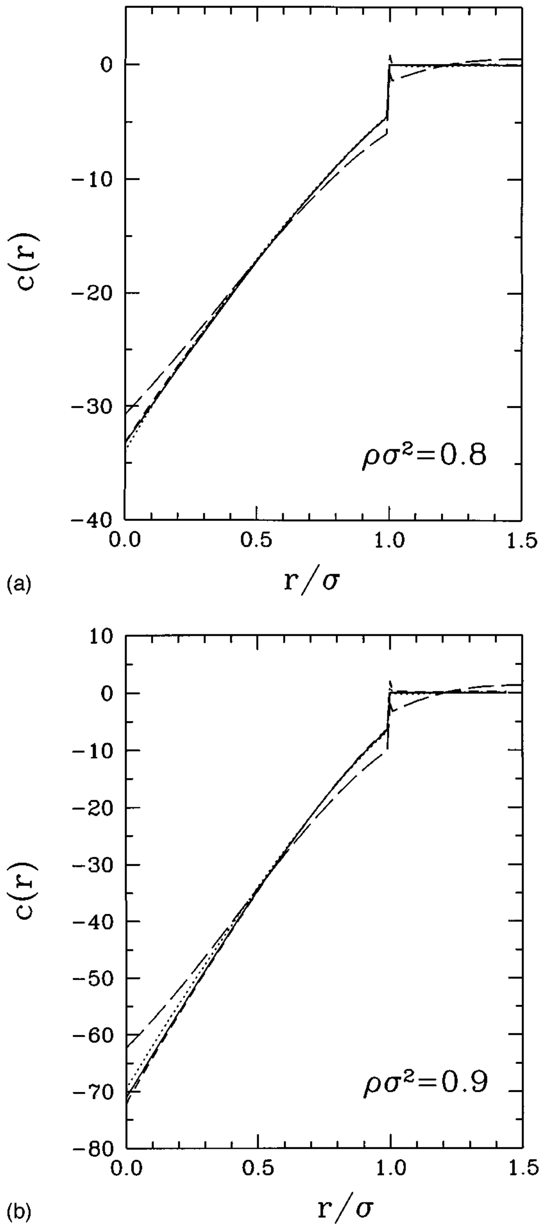

FIG. 1. Direct correlation function of the Baus-Colot theory (solid line) and the corresponding predictions from different weighted-density approximation theories using different forms of the weighting function and for two different densities. The long-dashed line corresponds to the Takamiya-Nakanishi approximation; the dotted line is our parabolic approximation, whereas the short-dashed line corresponds to our cubic approximation. (a) $\rho\sigma^2 = 0.8$, (b) $\rho\sigma^2 = 0.9$.

To optimize the coefficients we used parametrized virial coefficients containing a few variational parameters $w_2(r;\{\lambda_i\})$ and $w_3(r;\{\mu_i\})$ and minimized in the least-squares sense; i.e., we minimized the function

$$S_c(\{\lambda_i\},\{\mu_i\}) = \sum_{kl} W(r_k;\rho_l)[c_{\mathrm{BC}}(r_k;\rho_l) - c(r_k;\rho_l;\{\lambda_i\},\{\mu_i\})]^2, \tag{19}$$

where $W(r;\rho)$ is a weight function (to put more emphasis in particular regions of r and ρ during the minimization) and

$c(r_k;\rho_l;\{\lambda_i\},\{\mu_i\})$ is obtained from the functional, Eq. (7). Different parametrizations for w_2 and w_3 and different weight functions W were used, but the accuracy of the fit was not satisfactory. In particular, the resulting direct correlation function (not shown) does not follow the reference BC function for $r \geqslant \sigma$ very accurately. We believe the reason for these discrepancies is twofold: (i) the real-space (double) integrals (7) connecting the direct correlation function and the weighting function in real space are sensitive to the numerical approximations used to evaluate them, and (ii) the minimization is numerically difficult since the function S_c in Eq. (19) shows a shallow minimum with respect to the variational parameters.

An alternative strategy is to make direct use of the exact weighting function and perform an optimization with $w(r;\rho)$ instead of $c(r;\rho)$ as target function; since we have the exact weighting function in real space, obtained from Eq. (7), we can minimize

$$S_w(\{\hat{w}_i(r)\}) = \sum_l \{w_{\rm BC}(r;\rho_l) - [w_0(r) + w_1(r)\rho_l + \Delta w(\rho_l;\{\hat{w}_i(r)\})]\}^2, \tag{20}$$

where the exact first two virial coefficients $w_0(r)$ and $w_1(r)$ are retained and the minimization is performed at each value of r with respect to the variational parameters $\{\hat{w}_i(r)\}$, $i=2,3,\ldots,K+1$. The sum is extended over a density grid $\{\rho_l\}$, $l=0,2,\ldots,N$, with $\rho_l = lh$, $h=0.1$. The function Δw can be taken as a polynomial in ρ,

$$\Delta w(\rho;\{\hat{w}_i(r)\}) = \sum_{k=1}^{K} \hat{w}_{k+1}(r)\rho^{k+1}, \tag{21}$$

so that the (optimized) coefficients $\hat{w}_i(r)$, $i=2,3,\ldots,K+1$, give approximate (or resummed) higher-order virial coefficients for the weighting function (in the following the caret on w will be dropped, and so it is to be understood that w_i, $i \geqslant 2$, are the weighting function virial coefficients resulting from the least-squares fit). In principle one can include as many coefficients as desired but, as mentioned earlier, we have limited ourselves to the cases $K=1$ (parabolic approximation) and $K=2$ (cubic approximation). The method has the advantage that, by retaining the exact first two coefficients and, in particular, the zeroth-order coefficient, the discontinuity of

$$w_{\rm BC}(r;\rho) - w_0(r) - w_1(r)\rho \tag{22}$$

is largely suppressed. The reason is that, in a thermodynamically consistent theory (i.e., a theory with an equation of state and a direct correlation function compatible at the level of both the virial equation and the compressibility equation), the whole discontinuity of $w(r;\rho)$ at $r=\sigma$ is collected by $w_0(r)$ *only*; thus, $w_n(r)$, with $n=1,2,\ldots$, should be continuous functions at $r=\sigma$. Since the BC theory provides consistent expressions for $\beta\Delta\Psi(\rho)$ and $c(r;\rho)$ with respect to the compressibility equation, but is consistent only up to second order with respect to the virial equation, it is possible that the above procedure generates small discontinuities in the higher virial coefficients $w_n(r)$, $n>1$.

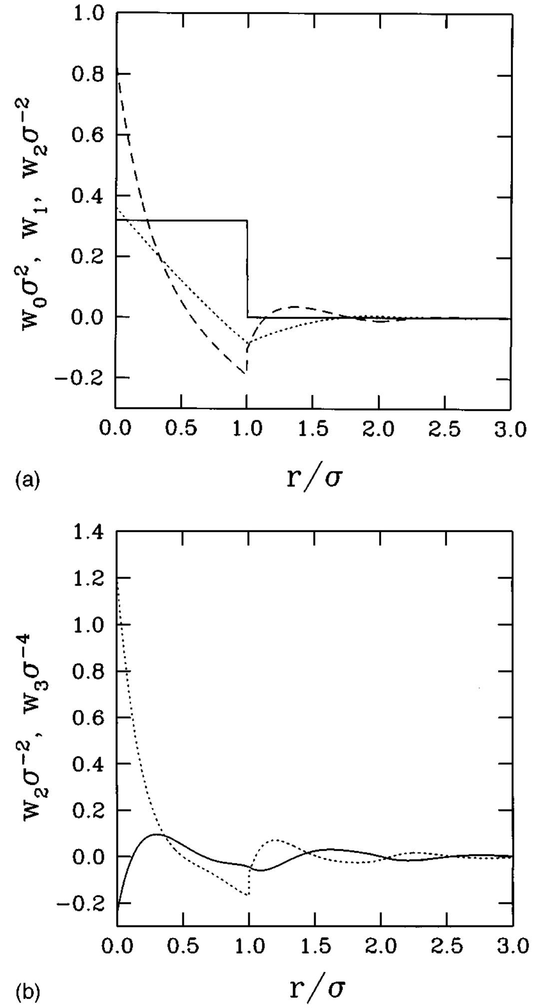

FIG. 2. (a) Weighting functions $w_0(r)$ (solid line), $w_1(r)$ (dotted line), and $w_2(r)$ (dashed line) used in our parabolic approximation for the weighting function. $w_0(r)$ and $w_1(r)$ are the exact functions appearing in the virial expansion of the weighting function, whereas $w_2(r)$ is the optimized function obtained from a least-squares fit to the Baus-Colot reference weighting function using the parabolic approximation. (b) Optimized weighting functions $w_2(r)$ (solid line) and $w_3(r)$ (dotted line), using the cubic approximation for the full weighting function.

Figure 2 shows the virial coefficients which result from the above procedure. In Fig. 2(a) the fitting was limited to only one function $w_2(r)$, corresponding to the parabolic approximation. In Fig. 2(b) we include two functions $w_2(r)$ and $w_3(r)$, corresponding to the cubic approximation. Note that in both cases we used the exact $w_0(r)$ and $w_1(r)$ virial coefficients [depicted in Fig. 2(a)]. As expected, the coefficients $w_2(r)$ and $w_3(r)$ show a small discontinuity, although from the figure this is not evident in the $w_2(r)$ corresponding to the cubic approximation.

Figure 1 also contains the direct correlation functions calculated from the above parabolic and cubic approximations. Note that in both cases the $r>\sigma$ tail is almost completely suppressed, but there is an important difference between the two approximations at small distances r, the cubic approximation giving a better agreement with the reference BC direct correlation function in this region. We may conclude that the parabolic approximation (9) is too simple to account for the rapid density variations of $c(r;\rho)$ in the density range of interest (viz., $\rho/\rho_{\text{cp}}\sim 0.78$, compared with 0.74 for hard spheres). The discrepancy at short distances of the parabolic approximation is, as will be shown later, crucial and affects the results for the solid properties quite substantially. Therefore, it is neccessary to go beyond the parabolic approximation and include an additional virial term in the weighting function.

Once the weighting function coefficients have been obtained there remains the problem of extracting the averaged density from Eq. (5), which defines it in implicit form:

$$\begin{aligned}\overline{\rho}(\mathbf{r})&=\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\overline{\rho}(\mathbf{r}))\\&=\overline{\rho_0}(\mathbf{r})+\overline{\rho_1}(\mathbf{r})\overline{\rho}(\mathbf{r})+\overline{\rho_2}(\mathbf{r})[\overline{\rho}(\mathbf{r})]^2\\&\quad+\overline{\rho_3}(\mathbf{r})[\overline{\rho}(\mathbf{r})]^3+\cdots,\end{aligned}\tag{23}$$

where the virial averaged densities $\overline{\rho_i}(\mathbf{r})$ are defined by

$$\overline{\rho_i}(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w_i(|\mathbf{r}'-\mathbf{r}|).\tag{24}$$

The value of the averaged density at some point $\mathbf{r}$, $\overline{\rho}(\mathbf{r})$, is given by the (possibly multiple) roots of the polynomial

$$\overline{\rho_0}+(\overline{\rho_1}-1)\overline{\rho}+\overline{\rho_2}(\overline{\rho})^2+\overline{\rho_3}(\overline{\rho})^3+\cdots=0.\tag{25}$$

Truncation of the polynomial at second order leads to a second-degree equation, with only one physically acceptable solution:

$$\overline{\rho}=\frac{2\overline{\rho_0}}{1-\overline{\rho_1}+\sqrt{(1-\overline{\rho_1})^2-4\overline{\rho_0}\,\overline{\rho_2}}}.\tag{26}$$

The cubic approximation leads to a cubic equation, whose acceptable solution can be found by using a simple Newton iterative scheme:

$$\overline{\rho}^{[k+1]}=\overline{\rho}^{[k]}-\frac{\overline{\rho_0}+(\overline{\rho_1}-1)\overline{\rho}^{[k]}+\overline{\rho_2}[\overline{\rho}^{[k]}]^2+\overline{\rho_3}[\overline{\rho}^{[k]}]^3}{\overline{\rho_1}-1+2\overline{\rho_2}[\overline{\rho}^{[k]}]+3\overline{\rho_3}[\overline{\rho}^{[k]}]^2},$$

$$k=0,1,2,\ldots,\tag{27}$$

and starting from the initial guess $\overline{\rho}^{[0]}$ provided by the quadratic approximation (26).

III. SOLID PHASE

Our treatment of the solid phase is based on a real-space representation for the density distribution $\rho(\mathbf{r})$ in terms of Gaussian peaks centered at the lattice sites $\{\mathbf{R}\}$ of a regular triangular lattice,

$$\rho(\mathbf{r})=\left(\frac{\alpha}{\pi}\right)\sum_{\mathbf{R}}e^{-\alpha(\mathbf{r}-\mathbf{R})^2},\tag{28}$$

where α is a variational parameter, related to the Gaussian width. This approximation, which closely follows that of previous studies of the hard-sphere crystal, ensures a normalization of one molecule per lattice site. For the fluid phase, $\alpha=0$.

The virial averaged densities $\overline{\rho_i}(\mathbf{r})$ are obtained as follows. Using Eqs. (24) and (28),

$$\begin{aligned}\overline{\rho_i}(\mathbf{r})&=\left(\frac{\alpha}{\pi}\right)\sum_{\mathbf{R}}\int d\mathbf{r}'e^{-\alpha(\mathbf{r}'-\mathbf{R})^2}w_i(|\mathbf{r}'-\mathbf{r}|)\\&=\left(\frac{\alpha}{\pi}\right)\sum_{\mathbf{R}}\int d\mathbf{r}'e^{-\alpha(\mathbf{r}'-(\mathbf{R}-\mathbf{r}))^2}w_i(r')\\&=\left(\frac{\alpha}{\pi}\right)\sum_{\mathbf{R}}\int_0^\infty dr'r'w_i(r')e^{-\alpha(r'^2+|\mathbf{R}-\mathbf{r}|^2)}\\&\quad\times\int_0^{2\pi}d\phi'e^{2\alpha r'|\mathbf{R}-\mathbf{r}|\cos\phi'}.\end{aligned}\tag{29}$$

Now, introducing the modified Bessel function of zeroth order, $I_0(x)$, with integral representation

$$I_0(x)=\frac{1}{2\pi}\int_0^{2\pi}d\phi e^{x\cos\phi},\tag{30}$$

we have

$$\begin{aligned}\overline{\rho_i}(\mathbf{r})&=2\alpha\sum_{\mathbf{R}}\int_0^\infty dr'r'w_i(r')e^{-\alpha(r'-|\mathbf{R}-\mathbf{r}|)^2}\\&\quad\times[e^{-2\alpha r'|\mathbf{R}-\mathbf{r}|}I_0(2\alpha r'|\mathbf{R}-\mathbf{r}|)].\end{aligned}\tag{31}$$

The function between square brackets behaves smoothly for values of its argument $x=2\alpha r'|\mathbf{R}-\mathbf{r}|$ in the whole interval $0\leqslant x<\infty$, though it decays slowly with x; it can be computed numerically with high accuracy using asymptotic expansions and power series. The integral over r' can be approximated by Gaussian quadrature in the intervals $0\leqslant r'\leqslant|\mathbf{R}-\mathbf{r}|$ and $|\mathbf{R}-\mathbf{r}|\leqslant r'<\infty$ separately.

The integrals involved in the free-energy calculations were also computed using quadratures. Using the form (28) for the (periodic) density distribution $\rho(\mathbf{r})$, we have

$$\begin{aligned}\beta F&=\int d\mathbf{r}\rho(\mathbf{r})\{\ln[\Lambda^2\rho(\mathbf{r})]-1+\beta\Delta\Psi(\overline{\rho}(\mathbf{r}))\}=\left(\frac{\alpha}{\pi}\right)\sum_{\mathbf{R}}\int d\mathbf{r}e^{-\alpha(\mathbf{r}-\mathbf{R})^2}\{\ln[\Lambda^2\rho(\mathbf{r})]-1+\beta\Delta\Psi(\overline{\rho}(\mathbf{r}))\}\\&=N\left(\frac{\alpha}{\pi}\right)\int_{\text{all space}}d\mathbf{r}e^{-\alpha r^2}\{\ln[\Lambda^2\rho(\mathbf{r})]-1+\beta\Delta\Psi(\overline{\rho}(\mathbf{r}))\}\\&=N\left(\frac{\alpha}{\pi}\right)\int_0^\infty dr re^{-\alpha r^2}\int_0^{2\pi}d\phi\{\ln[\Lambda^2\rho(r,\phi)]-1+\beta\Delta\Psi(\overline{\rho}(r,\phi))\}.\end{aligned}\tag{32}$$

Taking advantage of this factorization, the integrals over r and ϕ can be approximated numerically using different quadratures. This is convenient, since in the solid phase the r dependence of the integrand is very strong, whereas its angular dependence is much smoother. The angular integral was computed using a 12-point trapezoidal rule, whereas the integral over r was approximated using an especially constructed 6-point quadrature formula involving orthogonal polynomials in the interval $[0,\infty)$ with respect to the weight function $\exp(-\alpha r^2)$. The accuracy of these quadratures was checked independently against Monte Carlo integrations over the unit cell.

IV. SIMULATION DETAILS

Phase transitions in purely two-dimensional systems have continued to prompt a large amount of interest in recent years. A basically unsolved problem concerns the nature of the freezing transition in systems of molecules interacting via short-range forces. Since the pioneering work by Alder and Wainwright,[22] several computer studies have been undertaken in an effort to unveil the character of the transition. However, different research groups, using different simulation techniques, have reported results which are at variance with each other. The basic problem is related to the large amplitude of transitional fluctuations and its dependence with the system size. Although there seems to be a consensus that the freezing transition in hard discs is weakly first order, there is some recent work supporting the second-order nature of the transition.[18] In the present work we do not intend to add any new contribution to that forum. Rather, we wish to concentrate on the solid phase with a view to obtaining accurate data for the equation of state and the mean-square molecular displacement. To our knowledge, there are no accurate simulations on the equation of state of the hard-disc solid which can be used to support our density-functional results.

Standard constant-pressure Monte Carlo simulations[28] were performed on systems of hard discs with a range of system sizes. The technique involves random displacements of the discs and global changes in area, to ensure thermal equilibrium at the specified constant external pressure. For a given value of the pressure, the simulations provide the equilibrium density and also structural properties like two-body distribution functions. The simulations for the fluid phase were performed on systems of 700 discs, spanning typically 2×10^5 steps per disc. Selected checks were performed on systems an order of magnitude larger, but no significant system size effects were observed. Typical errors involved in the density were of order $0.01\sigma^{-2}$.

In the solid phase simulations required considerably larger systems and longer runs than in the fluid. Typically our systems contained 10 864 discs. As observed by other groups, the evolving density took inordinate amounts of computer time to fluctuate about an average, constant value, and this was especially so close to the phase transition. The simulations also provided the root-mean-square displacements about the lattice sites, $\langle r^2\rangle$; from the latter the Gaussian width parameter α can be estimated as $\alpha=1/\langle r^2\rangle$. The mean-square displacement was observed to exhibit large fluctuations, leading to extremely long relaxation times. In our simulations we used special bookkeeping techniques such as link cells. Also, at high densities, an efficient constant-neighbor technique was used where, for a moving disc, overlaps were checked only with its nearest neighbors, the identity of the latter taken as fixed during the whole simulation (this method assumes no defects are created; the validity of this assumption was explicitly checked as the simulation proceeded). The length of the runs was typically 10^6 Monte Carlo steps per state point, with a few selected checks using longer runs. The errors in the density were estimated to be $\sim0.004\sigma^{-2}$ at low mean densities and $\sim0.002\sigma^{-2}$ at the highest densities.

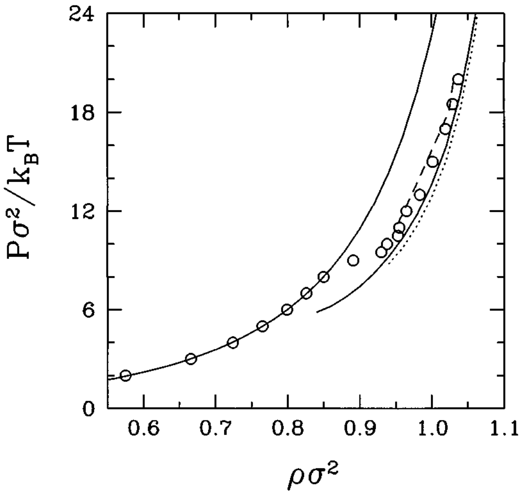

FIG. 3. Equation of state of the hard-disc system in the fluid and solid density ranges. Open circles correspond to our constant-pressure Monte Carlo simulations. The solid line is the equation of state obtained from the Baus-Colot theory (for the fluid phase) and our proposed cubic parametrization of the weighting function (for the solid phase). The dotted line corresponds to the quadratic parametrization, and the dashed line is the equation of state computed using the Takamiya-Nakanishi weighting function.

V. RESULTS

Figure 3 shows the equation of state, $P(\rho)$, of both the fluid and solid branches. In the case of the solid phase, we include the results obtained from the TN approximation and our quadratic and cubic approximations (note that all three approximations reduce to the BC theory in the uniform limit, i.e., in the fluid phase). Also shown are our computer simulation results. In the fluid phase the BC equation of state goes through the simulation points. The cubic theory is quite accurate and improves upon the results of the parabolic approximation. The TN equation of state, on the other hand, slightly overestimates the pressure and does not seem to show the correct curvature.

The results for the freezing transition, indicated in Fig. 3 by line segments, are summarized in Table I. Note the large discrepancy between the parabolic and cubic approximations, both in the location of the transition and in the density gap. The location predicted by the cubic approximation is much closer to the simulation results[15] of $\rho_l=0.887\sigma^{-2}$ and $\rho_s=0.904\sigma^{-2}$, but the density gap is still very much overestimated; i.e., the transition is predicted to be too strongly first

TABLE I. Results for the freezing transition of hard discs from the different weighted-density approximations considered in this paper and the computer simulations of Alder and Wainwright (Ref. 22), Hoover and Ree (Ref. 23), and Zollweg, Chester, and Leung (Ref. 15). ρ_l and ρ_s are the fluid and solid densities at coexistence, respectively; $\Delta\rho/\rho_l$ is the density gap at the transition, relative to the density of the fluid; L is the Lindemann parameter of the solid at the transition, defined by $L=(\rho_s\sqrt{3}/\alpha)^{1/2}$. TN, Takamiya-Nakanishi weighting function; *parabolic*, our parabolic approximation (see text); *cubic*, our cubic approximation (see text).

Theory	$\rho_l\sigma^2$	$\rho_s\sigma^2$	$\Delta\rho/\rho_l$	L
TN	0.957	1.005	0.050	0.058
parabolic	0.907	0.984	0.085	0.095
cubic	0.843	0.907	0.076	0.148
Alder and Wainwright	0.880	0.912	0.036	-
Hoover and Ree	0.878	0.922	0.050	-
Zollweg *et al.*	0.887	0.904	0.019	-

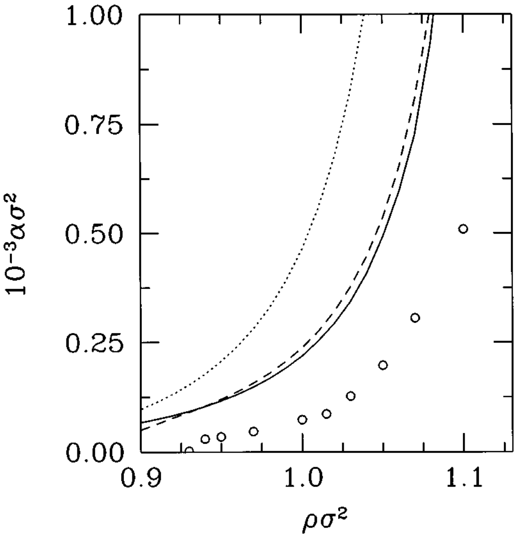

FIG. 4. Gaussian width parameter of the solid phase as a function of density. Solid line, cubic approximation; dashed line, parabolic approximation; dotted line, Takamiya-Nakanishi approximation; open circles, results from our Monte Carlo runs.

order. Even though the solid density is very accurate, the fluid density is ~5% lower than the simulation result. Of course we do not expect the density-functional approximation to give accurate predictions for the freezing transition, for the following reasons: (i) Fluctuation effects, not included in the mean-field-like density-functional theory, are very important in two dimensions, and (ii) the presence of defects, its dynamics, and mutual interaction might underlie the freezing mechanism in two dimensions, according to the Kosterlitz-Thouless-Halperin-Nelson-Young theory, and change qualitatively the freezing scenario from that of a simple first-order transition; these effects are not taken care of in our theory either. However, our theory should become more accurate as soon as the density is sufficiently high that the presence of defects and fluctuations is negligible and does not play any role.

As regards the behavior of the Gaussian width parameter, the results from the density-functional minimizations and the simulations are pictured in Fig. 4. We again stress the difficulty involved in estimating this parameter with good accuracy by simulation: Only at high density was it possible to obtain fully equilibrated values (fluctuating around a stable mean value); at low density our simulations are probably too short to produce stable mean values. Despite these considerations, it is clear from the figure that the density-functional results substantially overestimate the simulation data. This is to be expected since, as already discussed, fluctuations effects must have a large influence in the properties of the solid phase, especially close to the transition. Since the Gaussian width parameter is the inverse mean-square displacement, fluctuations tend to reduce the α parameter. A similar behavior, namely, the overestimation of the Gaussian width, is observed in the three-dimensional case; however, the effect is reduced in this case due to the higher dimensionality.

A standard way to combine the mean-square displacement to the mean distance between neighbors, a, is the Lindemann parameter $L=\langle r^2\rangle^{1/2}/a$. According to Toxvaerd,[29] diffusion in a (soft) repulsive solid sets in when $L\sim 0.18$; taking this (arbitrarily) as the critical point where the crystal melts,[30] we can compare it with our value for L at the transition, $L=0.148$ (Table I), and conclude that the density-functional theory at least provides a qualitatively correct Lindemann parameter at melting. Note that the results obtained with the TN and the parabolic approximation for the weighting function are significantly smaller (see Table I).

VI. SUMMARY AND CONCLUSIONS

In summary, we have presented an extension of the ideas of the weighted-density approximation for the free-energy density-functional of hard spheres to their two-dimensional counterpart, the hard-disc system. We have shown that it is crucial both to perform a careful optimization of the weighting function virial coefficients and to go beyond the quadratic approximation for the weighting function in order to accurately reproduce the direct correlation function in the uniform limit which is, together with the fluid equation of state, the basic ingredient of the theory. As comparison with our computer simulation results indicates, the improved theory shows much better agreement for the equation of state than the quadratic approximation. Also, even though the density-functional theory does not contain fluctuations (which makes any attempt to make a quantitatively meaningful comparison with simulation futile), it seems that the accurate implementation of the uniform direct correlation function into the functional is important to reproduce the location of the phase transition. Results of comparable accuracy have been obtained by Tejero and Cuesta[31] using a different density-functional approximation. This is to be contrasted with the three-dimensional case, where despite the quantitatively inaccurate behavior of the direct correlation function resulting from the parabolic approximation at high density, the weighted-density-approximation results for the location of the phase transition and equation of state are more accurate.

The present form of the functional can be used as a reference system for the study of a variety of problems, including the description of more realistic two-dimensional systems, e.g., Lennard-Jones molecules, and the behavior of films adsorbed on substrates of different symmetry and lattice parameter. In the latter case the difficulties involved in the accurate description of the freezing transition in two-dimensional systems disappear due to the presence of a substrate.

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[27] The exact $c(r;\rho)$ may have a nonvanishing tail for $r>1$. Note, however, that our reference direct correlation function, $c_{\mathrm{BC}}(r;\rho)$, is zero for $r>1$.

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