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Lattice-gas analog of density-functional theory: Application to ordering transitions

M. Nieswand
Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, Germany

A. Majhofer
Institute of Experimental Physics, Warsaw University, ulica Hoza 69, PL-00 681 Warsaw, Poland

W. Dieterich
Fakultät für Physik, Universität Konstanz, D-78434 Konstanz, Germany

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An alternative approach to ordering transitions in lattice gases is presented. Our approach can be regarded as the lattice analog of the well-known freezing theory for continuous fluids based on density functionals. Specifically, we discuss ordering in a three-dimensional model involving repulsive forces up to second neighbors and compare our results with Monte Carlo simulations. The utility of our method is demonstrated further by calculating the structure of a planar interface between coexisting ordered and disordered phases. It is pointed out that our theory is a good starting point for investigating problems of the interfacial kinetics.

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I. INTRODUCTION

The formulation of a molecular theory of the fluid-solid phase transition is a classic problem in statistical mechanics. An important step has been taken by Ramakrishnan and Yussouff [1], who constructed an order-parameter theory for the freezing transition, where the molecular forces enter only via the direct correlation function in the fluid state. This "freezing theory" has by now been generalized by a number of authors [2–4]. Reformulated in the language of density-functional theory [5], it has successfully been applied to several problems including phase diagrams of monatomic systems, the formation of colloidal crystals, or the structure of crystal-liquid interfaces [6].

Our present purpose is to demonstrate that the main ideas of freezing theory are also useful in the field of discrete lattice-gas systems. In that context it represents an alternative approach to ordering transitions in lattice gases, which are common in describing, for example, binary solid solutions [7], solid ionic conductors [8], or hydrogen in metals [9]. In a recent study we discussed the lattice-gas analog of density-functional theory [10]. Its application to ordering transitions in lattice gases appears to offer certain computational advantages in comparison with conventional lattice statistical methods [11–13], in particular, in cases of long-range interactions or in calculating interfacial profiles [14,15], although a detailed comparison of the different methods with respect to their quantitative accuracy remains to be done. Moreover, that theory may also pertain to certain problems of the crystal-fluid interface, such as growth processes or the roughening transition, which are often simulated by lattice models [16–18].

After a brief review of the general formalism in Sec. II, we analyze a specific model, where particles on a simple cubic lattice interact via repulsive nearest-neighbor ($V_{\rm NN}$) and next-nearest-neighbor ($V_{\rm NNN}$) potentials. In cases where the average occupation number of lattice sites is in the vicinity of $\bar{n}=\frac{1}{4}$, such a system undergoes a first-order transition from a disordered, "fluid" state to a bcc structure, as the temperature is lowered. In order to investigate some general aspects of that transition, we consider in Sec. III a three-parameter model for the direct correlation function and discuss the relation between the corresponding correlations in the "fluid" state and the bcc order parameters. Specific examples are considered in Sec. IV. There we present Monte Carlo simulation results in comparison with calculations of the pair-correlation function from the lattice version of the mean-spherical approximation (MSA). In Sec. V we show that the interfacial profile and the interfacial tension can be obtained in a rather straight-forward way within our formalism. We conclude our paper with some remarks about possible extensions of our method to problems of the interfacial kinetics.

II. FORMALISM

Consider a system of interacting particles distributed among the sites $\boldsymbol{l}$ of a regular lattice. The corresponding lattice-gas Hamiltonian is assumed to be of the form

$$H=\tfrac{1}{2}\sum_{l,l'}V(\boldsymbol{l}-\boldsymbol{l}')n_l n_{l'}+\sum_{l}(\varepsilon_l-\mu)n_l\ , \tag{1}$$

where $V(\boldsymbol{l}-\boldsymbol{l}')$ denotes the pair interaction, ε_l the local site energies, and μ the chemical potential. Lattice sites are either vacant or simply occupied; hence, the occupation numbers satisfy

$$n_l^2=n_l\ . \tag{2}$$

Our problem is to determine the grand-canonical average $\langle n_l \rangle_0$. A powerful tool in the analogous problem of computing the average density of inhomogeneous liquids is the density-functional method. As shown previously, that method can readily be adapted to lattice gases described by the Hamiltonian (1) [10]. For completeness, let us summarize briefly the main points of the formalism which we shall need in this paper.

We start with the following function of the set of mean occupation numbers $\{\langle n_l \rangle\}$:

$$\Omega_\varepsilon(\{\langle n_l \rangle\})=\sum_l \varepsilon_l \langle n_l \rangle + F(\{\langle n_l \rangle\}) - \mu \sum_l \langle n_l \rangle \ . \tag{3}$$

This function is minimized by the equilibrium values $\langle n_l \rangle_0$, and its minimum is equal to the grand potential of the system. As usual [5], we decompose the intrinsic free energy

$$F(\{\langle n_l \}) = F_{\text{id}} + F_{\text{exc}}$$

into the ideal (noninteracting) lattice-gas free energy:

$$F_{\text{id}} = k_B T \sum_l [\langle n_l \rangle \ln\langle n_l \rangle + (1-\langle n_l \rangle)\ln(1-\langle n_l \rangle)] \ , \tag{4}$$

and the excess part F_{exc} due to interactions. Minimization of (3) then leads to the self-consistency condition for the mean occupation numbers:

$$\langle n_l \rangle = \{1+\exp[\beta(\varepsilon_l - \mu) - c_1(l,\{\langle n_l \rangle\})]\}^{-1} \ , \tag{5}$$

which has the form of Fermi's distribution function modified by the correlation potential

$$c^{(1)}(l,\{\langle n_l \rangle\}) = -\beta \frac{\partial F_{\text{exc}}}{\partial \langle n_l \rangle} \ . \tag{6}$$

In the last equations T denotes the temperature and $\beta=(k_B T)^{-1}$. In the following we confine ourselves to an approximation where the quantity $c^{(1)}$ is linearized with respect to the deviations $\langle n_l \rangle - \bar{n}$ from some homogeneous reference state of the system characterized by the mean occupation $\bar{n}$:

$$c^{(1)}(l,\{\langle n_l \rangle\}) \approx c^{(1)}(\bar{n}) + \sum_{l'} c^{(2)}(l-l',\bar{n})(\langle n_{l'} \rangle - \bar{n}) \ . \tag{7}$$

Quantitative tests presented in Ref. [10] lead us to conclude that (7) provides a sensible approximation for the purpose of this paper. The kernel

$$c^{(2)}(l-l',\bar{n}) \equiv c(l-l',\bar{n})$$

is equal to the direct correlation function of the reference state and can be related to the pair-correlation function $g(l-l')$ of the reference state via the lattice-gas analog of the Ornstein-Zernike-equation:

$$g(l-l')-1 = C(l-l') + \bar{n}\sum_{l''} C(l-l'')[g(l''-l')-1] \ , \tag{8}$$

with

$$C(l-l') = c(l-l') - \frac{\delta_{l,l'}}{1-\bar{n}} \tag{9}$$

and

$$g(l-l') = (1-\delta_{l,l'})\langle n_l n_{l'} \rangle / \bar{n}^2 \ . \tag{10}$$

In order to simplify our notation, we have dropped in the last equations the $\bar{n}$ dependence of the various correlation functions. Note that in contrast to conventional density-functional theory of continuous fluids, the functions $C(l-l')$ entering (8) and $c(l-l')$ defined by (7) differ by a local term $\delta_{l,l'}/(1-\bar{n})$. This difference is ultimately a consequence of the local hard-core repulsion between particles taken into account through the constraint (2) on our basic variables.

Given the pair interactions, the above scheme allows us to relate the average occupation numbers of an inhomogeneous lattice gas to the pair-correlation function of the corresponding homogeneous system. Our main concern in the following will be to develop the lattice-gas analog of the freezing theory of continuous liquids [2–6]. In other words, we wish to apply the present scheme to first-order lattice-gas phase transitions of the order-disorder type. Therefore, we consider a system with constant site energies $\varepsilon_l \equiv 0$. As the reference state we take the homogeneous disordered phase, whose mean occupation satisfies

$$\bar{n} = [1+\exp(-\beta\tilde{\mu})]^{-1} \ , \tag{11}$$

where

$$\tilde{\mu} = \mu + k_B T c^{(1)}(\bar{n}) \ . \tag{12}$$

A possible ordered phase is described by a nontrivial periodic solution of the structure equation (5), which now takes the form

$$\langle n_l \rangle = \left[1+\exp\left[-\beta\tilde{\mu} - \sum_{l'} c(l-l')(\langle n_{l'} \rangle - \bar{n})\right]\right]^{-1} \ . \tag{13}$$

Considering the solution of (13) with $\langle n_l \rangle \neq \text{const}$, which minimizes $\Omega \equiv \Omega_{\varepsilon=0}$, we have the following condition for two-phase coexistence:

$$\Delta\Omega = \Omega(\{\langle n_l \rangle\}) - \Omega(\bar{n}) = 0 \ . \tag{14}$$

The symmetry of the ordered phase depends on the symmetry of the underlying lattice and on the function $c(l)$, which is determined by the interaction potential $V(l)$.

It is natural to parametrize the ordered structure in terms of mean occupation numbers $\langle n_\alpha \rangle$ referring to suitably defined sublattices α and then to solve the corresponding order-parameter equations derived from (13). A specific example will be treated in subsequent sections.

III. ORDERING TRANSITION IN A THREE-DIMENSIONAL LATTICE GAS

Let us focus our attention on particles distributed on a three-dimensional simple cubic lattice of spacing a in the presence of repulsive two-body interactions extending up to second neighbors, and apply the scheme described in Sec. II to possible ordering transitions. We do not attempt here to explore the complete phase diagram, but confine ourselves to the special case where the average occupation of lattice sites is close to $\bar{n}=\frac{1}{4}$. There we expect that ordering takes place to a bcc structure with a cubic unit cell of size $2a$. The simplest set of $c(l)$ values compatible with this transition consists of $c(0)=c_0$; $c(l)=c_1,c_2$ when l connects, respectively, nearest or next-nearest neighbors, and $c(l)=0$, otherwise. In addition we assume $c_i<0$ $(i=0,1,2)$. The problem of relating $c(l)$ to interaction constants in the underlying lattice-gas Hamiltonian will be deferred to Sec. IV. According to Eq. (8), the pair-correlation function in the disordered state is now given as

$$g(l)=1+\int\frac{d^3k}{(2\pi)^3}e^{ikl}\tilde{C}(\mathbf{k})[1-\bar{n}\tilde{C}(\mathbf{k})]^{-1}\ , \tag{15}$$

where

$$\begin{aligned}\tilde{C}(\mathbf{k})=c_0&-(1-\bar{n})^{-1}\\&+2c_1(\cos ak_x+\cos ak_y+\cos ak_z)\\&+4c_2(\cos ak_x\cos ak_y+\cos ak_x\cos ak_z\\&\qquad+\cos ak_y\cos ak_z)\end{aligned} \tag{16}$$

and the integral in (15) is taken over the first Brillouin zone of the substrate lattice. To characterize the bcc state, we introduce order parameters $\langle n_\alpha\rangle$, where $\alpha=A$ refers to sites forming the bcc structure and $\alpha=B$ to the remaining sites of the underlying simple cubic lattice. Obviously, the average density of our "bcc crystal" is determined as $\bar{n}_{\text{bcc}}=(\langle n_A\rangle+3\langle n_B\rangle)/4$ and may differ from the density of the coexisting liquid $\bar{n}$. Putting $\eta_\alpha=\langle n_\alpha\rangle-\bar{n}$, the self-consistency condition (13) takes the form

$$\langle n_\alpha\rangle=[1+\exp\beta(\varepsilon_\alpha^{\text{corr}}-\bar{\mu})]^{-1}\ , \tag{17}$$

with $\beta\bar{\mu}$ chosen such that the density of the "fluid" is $\bar{n}=\frac{1}{4}$ [cf. Eq. (11)] and the correlation potential $\varepsilon_\alpha^{\text{corr}}$ is given by

$$-\beta\varepsilon_\alpha^{\text{corr}}=c_0\eta_\alpha+2(c_1+2c_2)\times\begin{cases}3\eta_B\ , & \alpha=A\\(\eta_A+2\eta_B)\ , & \alpha=B\ .\end{cases} \tag{18}$$

It turns out that the corresponding grand-potential function $\Omega(\langle n_A\rangle,\langle n_B\rangle)$ shows a double minimum structure for a range of parameters c_i. It is in turn possible to find c_i values such that these two minima, corresponding to the disordered and the ordered phase, become equal, i.e., they fulfill condition (14). Simultaneously, these parameters c_i should be consistent with the actual pair-correlation function in the fluid state at coexistence. This will be discussed further in Sec. IV, where we investigate an explicit interaction model.

Let us also remark that for a number of triples (c_0,c_1,c_2) fulfilling Eq. (14), we have found that the corresponding maximum values of the static structure factor

$$S(\mathbf{q})=1+\bar{n}\sum_l[g(l)-1]e^{i\mathbf{q}\cdot l} \tag{19}$$

fall in the narrow range $S(q_m)=8.3\pm0.2$. Here q_m denotes the position of the main peak of $S(q)$. This is to be compared with the "quasiuniversal" value $S(q_m)\simeq3$ observed in continuous liquids at coexistence with a bcc phase [19]. Clearly, this difference is due to an enhanced "preordering" caused by the underlying lattice.

IV. MEAN-SPHERICAL APPROXIMATION AND MONTE CARLO SIMULATION

In Sec. III we examined some general features of the ordering transition regarding the c_i's as arbitrary negative parameters. Now we briefly discuss approximate analytical techniques to calculate the direct correlation function from the interaction model described above. A simple method is the mean-spherical approximation, which is well known in liquid structure theory [20] and which has also been applied to lattice-gas problems [21,22]. Setting the hard-core radius equal to the lattice constant, we have the closure relations

$$g(l)=0\ ,\quad |l|<a \tag{20}$$

and

$$c(l)=-\beta V(l)\ ,\quad |l|\geq a\ , \tag{21}$$

where (20) reduces to $g(0)=0$, implied already in our definition (10) of $g(l)$. Then the only unknown quantity we need to determine is $c(0)$. Let us now assume

$$V(l-l')=\begin{cases}V_{\text{NN}} & \text{for } l,l' \text{ nearest neighbors}\\V_{\text{NNN}} & \text{for } l,l' \text{ next-nearest neighbors}\\0 & \text{otherwise}\ .\end{cases} \tag{22}$$

With these assumptions, $c(0)$ is found by evaluating the Ornstein-Zernike relation (8), setting $l=0$, and substituting $c_1=-\beta V_{\text{NN}}$ and $c_2=-\beta V_{\text{NNN}}$ into (16). This leads to a special case of the three-parameter freezing theory discussed in Sec. III. Setting $R=V_{\text{NNN}}/V_{\text{NN}}=\frac{1}{2}$, we obtain parameters $c_i=c_i^{\text{MSA}}(T)$. Under the condition of two-phase coexistence, $T=T_c^{\text{MSA}}$, these are explicitly found as $c_0=-3.03$, $c_1=2c_2=-1.97$. The corresponding values $\langle n_A\rangle=0.629$ and $\langle n_B\rangle=0.133$ obtained from (14) imply a small discontinuity of the density at coexistence, $\bar{n}_{\text{bcc}}-\bar{n}\simeq7\times10^{-3}$. Simultaneously, we obtain the pair-correlation function $g(l)$, which is displayed in Fig. 1.

Next we compare these results with Monte Carlo simulations, where we use $L\times L\times L$ lattices up to a size $L=24a$ with periodic boundary conditions. For the moment we ignore the small density change at the transition and study the structure of homogeneous phases for fixed $\bar{n}=\frac{1}{4}$, or $\langle n_A\rangle+3\langle n_B\rangle=1$. On the high-temperature side of the transition, we start from random initial configurations and, after thermalization, obtain the pair-correlation function $g(l)$. Data points averaged over about 50 independent runs are shown in Fig. 1 for the

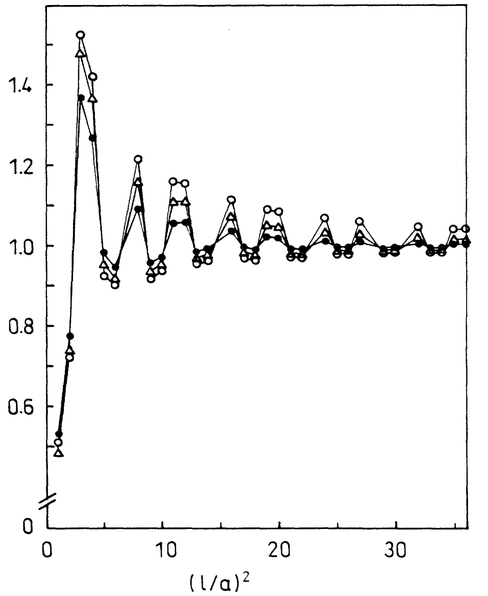

FIG. 1. Pair-correlation function of the disordered phase for $R=\frac{1}{2}$: open circles, results of Monte Carlo simulations for a lattice of size $L=24$ and $\beta V_{\mathrm{NN}}=1.7$ (near coexistence with the bcc structure); open triangles, MSA results for $\beta V_{\mathrm{NN}}=1.97$ (MSA coexistence); and solid circles, MSA results for $\beta V_{\mathrm{NN}}=1.7$.

case $R=\frac{1}{2}$ and $\beta V_{\mathrm{NN}}=1.7$, which is close to the estimated transition temperature (see below). Note that the peak structure in $g(l)$ reflects short-range order where the structure of the low-temperature bcc phase builds up locally. Obviously, a good quantitative representation of these data is achieved through the parameters $c_i=c_i^{\mathrm{MSA}}(T_c^{\mathrm{MSA}})$ given above, as seen from Fig. 1.

For low temperatures our simulations start out from an ideal bcc structure, where the B sublattice is initially empty. After thermalization, we obtain $\langle n_A \rangle$ as a function of temperature. Results for $L=12a$ are plotted in Fig. 2, where again we have used $R=\frac{1}{2}$. At $\beta V_{\mathrm{NN}}=1.78$, the values of the order parameter presented in the Figure are stable up to 10^3 Monte Carlo steps per particle (MCS). The value given for $\beta V_{\mathrm{NN}}=1.72$ corresponds to 10^3 MCS, where, however, we still observe a weak decay. On the other hand, for $\beta V_{\mathrm{NN}}=1.7$, the bcc structure is completely molten after about 10^2 MCS. Also, we observe that the stable points in Fig. 2 are insensitive to changes of the system size up to $L=24a$. Hence, we roughly estimate $V_{\mathrm{NN}}/k_B T_c \sim 1.73\pm0.05$ for the transition temperature T_c. Note that the temperature width of the two-phase region at $\bar{n}=\frac{1}{4}$ is expected to be less than our uncertainty in locating T_c from the data in Fig. 2. For the discontinuity $\langle n_A \rangle-\bar{n}$ of the order parameter at T_c, we estimate from Fig. 2 a value in the vicinity of 0.5 to 0.4. This is to be compared with the corresponding prediction within the MSA, which yields $\langle n_A \rangle-\bar{n}=0.384$ at T_c. Thus, it appears that the parameters $c_i=c_i^{\mathrm{MSA}}(T_c^{\mathrm{MSA}})$ are essentially consistent with simulation results both for the pair-correlation function presented in Fig. 1 and the discontinuity of the order parameter at T_c. We regard this as a satisfactory test of our freezing theory on lattices.

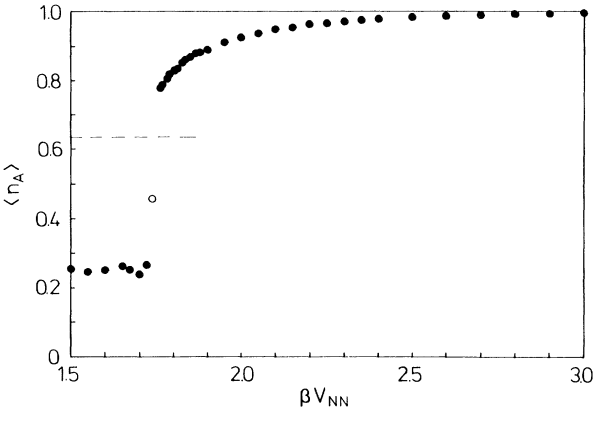

FIG. 2. Monte Carlo simulation results for the mean occupation number of the A sublattice as a function of βV_{NN} ($L=12a$). The error bars are smaller than the symbol size. The corresponding value given by the MSA at coexistence is indicated by the dashed line. For $\beta V_{\mathrm{NN}}=1.73$ (open circle), equilibration has not been reached until 10^3 MCS.

It turns out, however, that at a given temperature, the MSA substantially underestimates the correlations in the disordered state. This becomes apparent from Fig. 1, which also displays the pair correlation $g^{\mathrm{MSA}}(l)$ at $\beta V_{\mathrm{NN}}=1.7$. As a consequence, the MSA transition temperature turns out to be substantially lower, $V_{\mathrm{NN}}/k_B T_c^{\mathrm{MSA}}=1.97$. Nevertheless, the MSA does provide a useful qualitative description of the grand-potential function and the corresponding phase diagram in the vicinity of $\bar{n}=\frac{1}{4}$ (Fig. 3). We have also investigated the solution of the corresponding Percus-Yevick (PY) closure relation, which, however, gives an even lower transition temperature, $V_{\mathrm{NN}}/k_B T_c^{\mathrm{PY}}=2.1$.

So far, we have assumed $R=\frac{1}{2}$ in our calculations. By varying R, both the MSA and the PY approximations

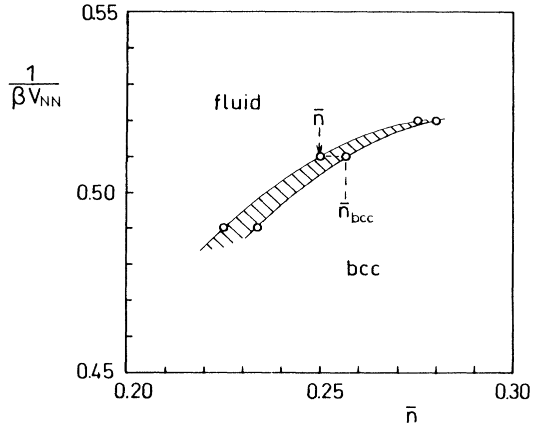

FIG. 3. Part of the phase diagram indicating the two-phase region near to $\bar{n}=\frac{1}{4}$, as computed within the MSA (see text).

predict an enhancement of T_c as R increases, e.g., $V_{\mathrm{NN}}/k_B T_c^{\mathrm{MSA}}=1.52$ for $R=0.75$.

V. INTERFACIAL PROFILE

Another class of problems that is well adapted to density-functional theory is the calculation of interfacial profiles between a crystalline and a liquid state [2]. Previous work on spatially continuous systems is generally based on the assumption that the order parameters, in that case the Fourier amplitudes of the density with respect to reciprocal-lattice vectors, are slowly varying functions on passing through the interface. In our present context we are naturally dealing with a local representation. No assumption as to the width of the interface relative to interatomic distances is needed at this stage.

To be specific, we consider the ordering transition discussed in Sec. IV and examine the structure of a planar interface between both phases. For simplicity we assume a (0,0,1) interface perpendicular to the z axis of the cubic substrate lattice. Let us regard the substrate lattice to be built from lattice planes at positions $z_k=ka$, $k=0,\pm 1,\cdots$. In the vicinity of the interface, the B sites introduced in Sec. III are no longer all equivalent. Consider a B site in the kth plane and its two nearest-neighbor A sites. If the latter are in the same plane, the B site is called $B1$. Otherwise, we call it $B2$. The three sublattices A, $B1$, and $B2$, which have to be distinguished now, are enumerated by $\alpha=1$, 2, and 3, respectively, and their relative degeneracies γ_α are given by $\gamma_1=\gamma_2=1$, $\gamma_3=2$. Next, in order to parametrize the interfacial profile, we introduce sublattice occupation numbers $\langle n_\alpha(z_k)\rangle\equiv\langle n_{\alpha,k}\rangle$, which satisfy the limiting forms

$$\langle n_{\alpha,k}\rangle\rightarrow\begin{cases}\langle n_\alpha\rangle\ , & k\rightarrow-\infty\\ \bar{n}\ , & k\rightarrow+\infty\ .\end{cases} \tag{23}$$

As before, $\langle n_\alpha\rangle$ denotes the occupation of sublattice α in the bulk bcc phase and is given by $\langle n_1\rangle=\langle n_A\rangle$, $\langle n_2\rangle=\langle n_3\rangle=\langle n_B\rangle$. The proper generalization of the structure equation (17) now takes the form

$$\langle n_{\alpha,k}\rangle=\{1+\exp[\beta(\varepsilon_{\alpha,k}^{\mathrm{corr}}-\tilde{\mu})]\}^{-1}\ . \tag{24}$$

Here, $\varepsilon_{\alpha,k}^{\mathrm{corr}}$ is determined by

$$-\gamma_\alpha\beta\varepsilon_{\alpha,k}=\gamma_\alpha c_0\eta_{\alpha,k}+\sum_\beta(G_{\alpha,\beta}\eta_{\beta,k}+K_{\alpha,\beta}\Delta\eta_{\beta,k})\ , \tag{25}$$

where $\eta_{\alpha,k}=\langle n_{\alpha\alpha,k}\rangle-\bar{n}$,

$$\Delta\eta_{\alpha,k}=\eta_{\alpha,k+1}+\eta_{\alpha,k-1}-2\eta_{\alpha,k}\ ,$$

$$(G_{\alpha,\beta})=2(c_1+2c_2)\begin{bmatrix}0&2&1\\2&2&2\\1&2&0\end{bmatrix}\ , \tag{26}$$

and

$$(K_{\alpha,\beta})=\begin{bmatrix}0&4c_2&c_1\\4c_2&2c_1&4c_2\\c_1&4c_2&0\end{bmatrix}\ . \tag{27}$$

Equations (24) together with the boundary conditions (22) determine the order-parameter profiles across the interface as well as the k-dependent density $\bar{n}_k=\sum_\alpha\gamma_\alpha\langle n_{\alpha,k}\rangle/4$.

Before presenting numerical results, we first discuss a simple variational solution, based on the ansatz

$$\langle n_{\alpha,k}\rangle-\bar{n}=(\langle n_\alpha\rangle-\bar{n})f(z_k/\lambda)\ , \tag{28}$$

where $f(z)=(1+e^z)^{-1}$. λ is a variational parameter which determines the width of the interface and which for simplicity is taken independent of α. Expression (28) is substituted into the grand potential $\Omega(\langle n_{\alpha,k}\rangle)$. Minimization with respect to λ gives $\lambda=2.07a$ and order-parameter profiles represented by the solid lines in Fig. 4. There we have assumed the same values for the parameters $\bar{n}$ and c_i as given in Sec. III. It is seen that our model, which involves repulsive forces only, yields a smooth profile extending over about $4\lambda\sim 8$ atomic layers. This behavior is similar to results obtained by Haymet and Oxtoby [2] within a continuum freezing theory for a bcc crystal-melt interface and to predictions by the Tem-

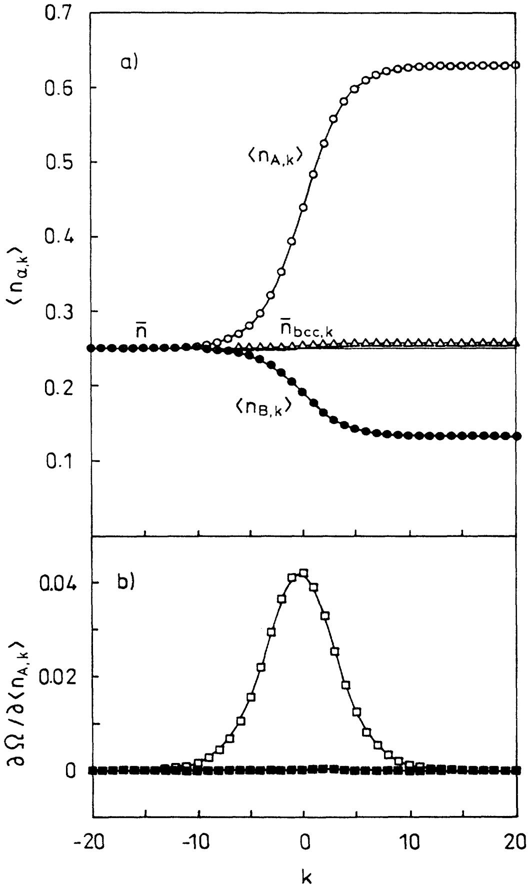

FIG. 4. Properties of the interface between coexisting fluid ($\bar{n}=\frac{1}{4}$) and bcc structure: (a) mean occupation numbers of different sublattices across the interface and (b) distribution of $\partial\Omega/\partial\langle n_{A,k}\rangle$ across the interface for the variational solution (open squares) and after numerical iteration (solid squares).

kin model [13].

Alternatively, we can solve numerically for $\langle n_{\alpha,k}\rangle$. This is achieved by an iterative procedure based on fictitious dynamical equations:

$$\langle n_{\alpha,k}(t+\Delta t)\rangle = \langle n_{\alpha,k}(t)\rangle + \Delta t \frac{\partial\Omega}{\partial\langle n_{\alpha,k}\rangle}\,, \tag{29}$$

with Δt chosen appropriately. Comparison of the numerical result with the variational solution in Fig. 4(a) shows that (28) gives an excellent description of the structure of the interface. The numerical solution leads to only minor differences in the characteristic widths of the different profiles $\langle n_{\alpha,k}\rangle$ and also to a small asymmetry in their z derivatives. The small error in our variational solution becomes more apparent, if we substitute it into the right-hand side of Eq. (29). This leads, for example, to the quantity $\partial\Omega/\partial\langle n_{A,k}\rangle$ plotted in Fig. 4(b). Upon subsequent numerical iteration, that quantity decays to almost zero after a few iteration steps.

Given the equilibrium shape of the interface, we can also calculate the interfacial tension

$$\sigma = [\Omega(\langle n_{\alpha,k}\rangle) - \Omega(\bar{n})]/N_{\parallel}\,, \tag{30}$$

where $N_{\parallel}$ denotes the number of bcc unit cells in the (x,y) plane. For the profile shown in Fig. 4(a) ($R=0.5$), we get $\beta\sigma \simeq 6\times 10^{-3}$, which is substantially smaller than the value obtained in Ref. [2] for crystal-melt interfaces. We interpret this difference as an effect due to the discrete lattice which leads to a higher degree of local ordering in the fluid phase. Since $\langle n_{\alpha,k}\rangle$ turns out to vary slowly with k on passing through the interface, it is reasonable to derive a continuum form of the present theory, which is done in the Appendix.

VI. CONCLUSIONS

In this paper we formulated the lattice-gas analog of the freezing theory for continuous classical liquids based on density functionals. Basically, this theory uses the static correlations in the disordered state as input and predicts the magnitude of the order parameters and other thermodynamic quantities associated with the crystalline state. In applying our discrete version of the freezing theory to ordering transitions in lattice gases, one should note that part of the hard-core effects are already taken into account by requiring that lattice sites be occupied at most by one particle. This should allow us to treat the explicit interactions, contained in the excess free energy F_{exc}, in a simpler way than is usually done in the corresponding continuum problem. Hence we confined ourselves to the linear approximation expressed in Eq. (7), which could be improved but appears sufficient in the present context. Generally, we expect that our method is particularly suited to lattice-gas problems involving longer-range interactions or spatial inhomogeneities. As an explicit example, we studied a system where particles on a simple cubic lattice interact via repulsive nearest-neighbor and next-nearest-neighbor forces. For average occupations in the vicinity of $\bar{n}=\frac{1}{4}$, this leads to a first-order transition from the disordered "fluid" state to a bcc structure. By comparison with Monte Carlo simulation, we showed that a simple parametrization of the direct correlation function, based on the mean-spherical approximation, accounts for both the pair-correlation function in the disordered state and the discontinuity of the order parameter at T_c. The transition temperature itself, however, is underestimated by the MSA.

In an extension of this theory, one may consider situations away from thermodynamic equilibrium. If the density is the only variable obeying a local conservation law, one may use the spatially varying local chemical potentials $\mu_l = \partial\Omega/\partial\langle n_l\rangle$ as driving forces in constructing appropriate kinetic equations [23–25]. To illustrate how one might proceed, let us again assume a planar interface at equilibrium, as discussed in Sec. V. Now, after supercooling the system by a small amount ΔT, the ordered phase tends to grow and the interface is expected to move accordingly. Ignoring the small density change $\bar{n}_{\text{bcc}}-\bar{n}$, we expect that equations of motion for nonconserved order parameters $\langle n_{\alpha,k}\rangle$ of the form

$$\partial\langle n_{\alpha,k}\rangle/\partial t \propto \partial\Omega/\partial\langle n_{\alpha,k}\rangle$$

should hold. This suggests a dynamic interpretation of the recursive formula (28). In fact, solving (28) for the case $\Delta T\neq 0$ we find solutions of the form of stable interfacial profiles moving with a velocity $v\propto\Delta T$ for small ΔT. Further work, however, is needed to establish an appropriate description of the interfacial kinetics. This seems an interesting problem in view of recent experiments on the growth velocity of colloidal crystals [26].

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APPENDIX

We discuss here the continuum form of the theory of Sec. V, appropriate to slowly varying order-parameter profiles. This will enable us to give a simple expression for the interfacial tension, in analogy to Ginzburg-Landau theory.

Writing $z_k = ka \to z$, we regard $n_{\alpha,k}\to n_\alpha(z)$ as functions of the continuous variable z. The grand potential then becomes a functional of $n_\alpha(z)$ of the form

$$\beta[\Omega\{n_\alpha(z)\}-\Omega(\bar{n})] = N_{\parallel}\int dz\,[\omega_0(n_\alpha(z))+\omega_1(n'_\alpha(z))]\,, \tag{A1}$$

where $n'_\alpha(z)\equiv dn_\alpha(z)/dz$ and

$$\omega_1(n'_\alpha(z)) = \tfrac{1}{2}\sum_{\alpha,\beta} K_{\alpha,\beta}\, n'_\alpha(z)\, n'_\beta(z)\,. \tag{A2}$$

Here the matrix $K_{\alpha,\beta}$ is defined by Eq. (27). An expression for ω_0 is readily derived and need not be given explicitly. The interfacial profiles are now determined by the Euler-Lagrange equations

$$\frac{\partial \omega_0}{\partial n_\alpha} - \frac{d}{dz}\frac{\partial \omega_1}{\partial n'_\alpha} = 0 \ , \tag{A3}$$

subject to the appropriate boundary conditions [cf. Eq. (23)]. As usual, in the continuous form of the theory the quantity

$$-h = \omega_0 + \omega_1 - \sum_\alpha n'_\alpha \frac{\partial \omega_1}{\partial n'_\alpha} \tag{A4}$$

is locally conserved, $dh/dz \equiv 0$. By using the boundary conditions for $n_\alpha(z)$ as $z \to \pm\infty$, we conclude that $h=0$. Hence, we obtain the interfacial tension (5.8) in the simple form

$$\sigma = (\beta N_\parallel)^{-1} \sum_{\alpha,\beta} K_{\alpha,\beta} \int dz \, n'_\alpha(z) n'_\beta(z) \ , \tag{A5}$$

which is analogous to Ginzburg-Landau theory [27].

Finally, substituting our approximate variational solution

$$n_\alpha(z) = (\langle n_\alpha \rangle - \bar{n}) f(z/\lambda)$$

[see Eq. (28)], we obtain

$$\sigma = (6\beta N_\parallel)^{-1} \lambda \sum_{\alpha,\beta} K_{\alpha,\beta} (\langle n_\alpha \rangle - \bar{n})(\langle n_\beta \rangle - \bar{n}) \ . \tag{A6}$$

Using bulk order parameter $\langle n_\alpha \rangle$ as given in Sec. III, we obtain $\beta\sigma \simeq 7 \times 10^{-3}$, in good agreement with the numerical result of Sec. V.

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