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Interfacial properties in lattice gases: A density functional approach

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The lattice analog of classical density functional theory is used to present a unified description of both bulk phase transitions of the order-disorder type in three-dimensional lattice gases and the detailed interfacial properties under conditions of two-phase coexistence. Good quantitative agreement of the calculated phase diagram with Monte Carlo simulations is achieved. For planar interfaces with different orientations we compute the interfacial tension. Moreover, we investigate in detail the structure and the free energy of steps and interpret our result as indication of a roughening transition.

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I. INTRODUCTION

Interfacial properties in systems that undergo first-order phase transitions represent a topic of active research in various branches of statistical physics and materials science. Recent developments in experimental surface probes [1], like surface diffraction, scanning tunneling microscopy [2], or perturbed angular correlation spectroscopy [3], substantially increased our knowledge of the microscopic structure of surfaces and interfaces. Of particular interest are thermally driven surface phase transitions. For example, it has become possible to observe in detail the phenomenon of surface roughening on atomic scales [4], the corresponding structure of atomic steps [5], and the evolution of disorder on the surface [3–5]. Theories in this area [6–10] mostly start from a simplified picture of a simple cubic lattice consisting of occupied and vacant cells, where occupied cells are regarded as elementary building units of the crystal. One introduces an attractive interaction between neighboring occupied cells to account for the cohesive energy of the crystal. In a certain temperature range this leads to a two-phase equilibrium between a dense ("crystal") and a dilute ("vapor") phase. Equivalent formulations are in terms of the ferromagnetic Ising model or the binary alloy problem. Such theories then imply a description of the statistics of interfacial configurations. Much work, both analytic and numerical, employs the solid-on-solid (SOS) approximation [9], with the important conclusion [10] that the roughening transition is of the Kosterlitz-Thouless type [11].

In view of the above-mentioned advances in experimental techniques, allowing the observation of microscopic surface structures in different kinds of materials, it seems necessary to develop theories starting from more realistic models of interatomic interactions. One step in this direction has been taken recently by Schmid and Binder [12]. Using Monte Carlo simulation they established a roughening transition in a lattice gas model with interaction parameters adapted to the (Fe-Al) system. In our present work we propose an analytic approach in terms of the lattice version of density-functional theory [13]. Within this theory, order-disorder transitions in lattice gases are regarded as the discrete analog of the well-known freezing theory for continuous fluids [14]. Starting from a specific interaction model we demonstrate that both the bulk transition from a disordered, "fluid" state to an ordered, "crystalline" superstructure and the detailed interfacial properties of the two phases at coexistence can be investigated on the same footing. Specifically, by varying the temperature while maintaining the two-phase equilibrium, our calculations allow us to distinguish two different regimes. At low temperatures ($T<T_R$) there exist well-defined steps in the interface, whereas at high temperatures ($T>T_R$) the profile of steps is washed out completely and the step free energy $f^{(s)}$ decreases with increasing size L of the system in the lateral direction (parallel to the interface). This suggests that our theory reproduces essential aspects of a roughening transition at the temperature T_R. It is to be noted, however, that density-functional theory is basically of the mean-field type and therefore cannot account for long-range fluctuations associated with interfacial roughening. These fluctuations are characterized by a correlation length ξ depending exponentially on temperature for temperatures $T\leq T_R$ and reflect themselves in a corresponding temperature dependence of the step free energy $f^{(s)}\propto\xi^{-1}$ [9]. However, the main difference of density-functional theory (DFT) in comparison with the simple mean-field approximation (MFA) is that it involves renormalized temperature- and concentration-dependent effective interactions, which are determined by the Ornstein-Zernike direct correlation function of the disordered state. In this way, an essential part of interparticle correlations is taken into account. Therefore, the DFT is expected to allow more reliable estimates of structural and thermodynamic properties of interfaces than the MFA.

After introducing our model and our basic approximations, we first calculate part of the phase diagram that is relevant to our discussion, and also the order parameter in the bulk bcc phase (Sec. II). Section III is devoted to the profiles and the thermodynamics of planar interfaces of different orientations. Most of the DFT calculations up to that stage are tested against Monte Carlo simula-

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tions. Our further objectives are the structure and the energetics of steps on a (001) interface, the relationship of such properties to interfacial roughening, and an approach to the anisotropic interfacial energy, which is the basis for the Wulff construction (Sec. IV). A short summary of our main results is added in the last section.

II. MODEL OF INTERACTIONS AND BULK PROPERTIES

Let us begin with the definition of our model. Particles on a simple-cubic lattice of sites l and spacing a are subject to pairwise interactions $V(l-l')$ extending up to third neighbors. Interaction constants $V(l)\equiv V_m$ for the mth neighbor ($m\le 3$) are assumed to be $V_1=V>0$, $V_2=-0.3V$, and $V_3=-V$. Note that a local hard-core repulsion is additionally taken into account through the exclusion of multiple occupation of sites. With these assumptions the dependence of the pair potential on distance roughly follows a realistic interatomic potential with attractive and short-range repulsive parts; see Fig. 1(a). Obviously, for particle concentrations near $\bar{n}=0.25$ our system will favor a bcc structure with a cubic unit cell of size $2a$. To describe the corresponding transition we introduce two sublattices A and B, as indicated in Fig. 1(b), such that the A sites form the bcc structure. The corresponding average occupation numbers $\langle n^A\rangle$ and $\langle n^B\rangle$ are regarded as order parameters in our problem.

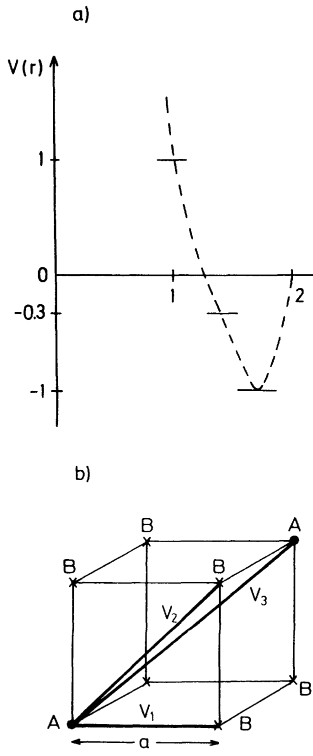

FIG. 1. Illustration of interaction model (a) and sublattice structure (b).

In order to obtain order-parameter equations, we shall employ the density-functional formalism for lattices. The starting point is the thermodynamic potential $\Omega\{\langle n_l\rangle\}$ as a function of the average occupation numbers $\langle n_l\rangle$ for arbitrary sites l,

$$\Omega\{\langle n_l\rangle\}=F_{\rm id}+F_{\rm exc}-\mu\sum_l\langle n_l\rangle \ , \qquad (1)$$

with

$$F_{\rm id}=k_BT\sum_l[\langle n_l\rangle\ln\langle n_l\rangle+(1-\langle n_l\rangle)\ln(1-\langle n_l\rangle)] \qquad (2)$$

representing the noninteracting lattice gas free energy. The excess free energy is approximated by [14,15]

$$F_{\rm exc}\simeq-\frac{k_BT}{2}\sum_{l,l'}c(l-l',\bar{n})(\langle n_l\rangle-\bar{n})(\langle n_{l'}\rangle-\bar{n}) \ . \qquad (3)$$

Here $c(l,\bar{n})$ denotes the direct correlation function of a homogeneous (disordered) reference state with average occupation $\bar{n}$. From the structure of Eq. (3) it is clear that $c(l,\bar{n})$ plays the role of an effective interaction. To calculate this quantity we follow our previous work [13] and use the lattice version of the Ornstein-Zernike equation together with the mean-spherical approximation. Let us remark here that simple mean-field theory corresponds to the approximation $c(l,\bar{n})\simeq-\beta V(l)$ for $l\neq 0$ and $c(0,\bar{n})=0$, with $\beta=(k_BT)^{-1}$.

Order-parameter equations are now obtained by setting $\langle n_l\rangle=\langle n^A\rangle$ or $\langle n^B\rangle$ for $l\in A$ or B, respectively, and minimizing Ω. Coexistence of the disordered phase and the bcc phase is in turn imposed by requiring $\Omega(\langle n^A\rangle,\langle n^B\rangle)=\Omega(\bar{n})$. Figure 2 shows the phase diagram obtained in this way in the range of densities $\bar{n}=(\langle n^A\rangle+3\langle n^B\rangle)/4<0.35$. Apart from the larger densities the transition is found to be strongly first order with a broad two-phase region. Data points in Fig. 2 are from Monte Carlo simulation. For later purposes (see Sec. III) we simulated here a two-phase situation in a box of size $L\times L\times L_z$ ($L_z>L$) with periodic boundary conditions. Initial conditions were chosen such that a perfectly

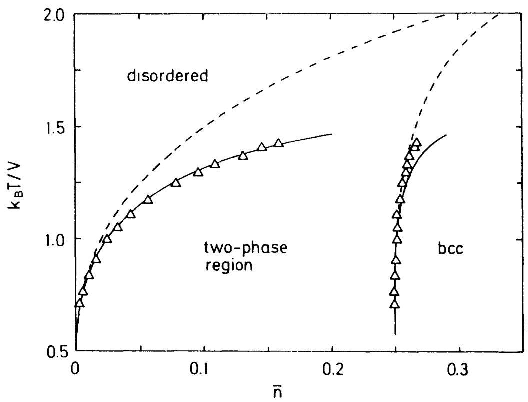

FIG. 2. Calculated part of the bulk phase diagram. The full curve refers to the density-functional approximation and the dashed curve to mean-field theory. Data points are from Monte Carlo simulation.

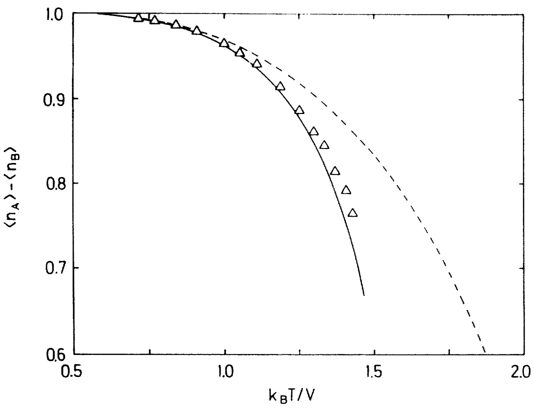

FIG. 3. Structural order parameter of the bcc phase at coexistence with the fluid phase as a function of temperature. Lines and data points as in Fig. 2.

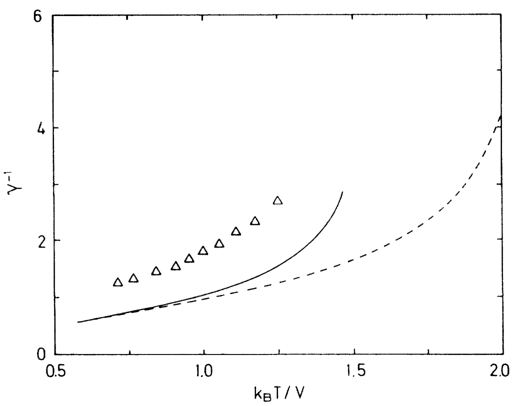

FIG. 4. Calculated temperature-dependent width γ^{-1} (in units of the lattice constant a) of (001)-interfacial profiles. Lines and data points as in Fig. 2.

ordered bcc structure and a disordered state are separated by a sharp, planar interface perpendicular to the z direction. After relaxation to equilibrium at a given temperature, we obtain the structure and the densities in the bulk phases as well as the interfacial structure. For the parameters in the $(\bar{n},T)$ plane, which we considered, a system size up to $L=24$, $L_z=56$ turned out to be sufficient [16].

Evidently, results from the simulation, DFT, and MFA all agree for lower temperatures $k_BT \lesssim V$, but the MFA overestimates the width of the two-phase region at higher temperatures. The DFT, however, continues to show excellent agreement with the Monte Carlo data along the "liquidus" curve, whereas it overestimates the density of the bcc phase along the "solidus" curve in the range $k_BT \gtrsim 1.3V$. Also, the DFT yields good agreement of the bcc-order-parameter $\langle n^A \rangle - \langle n^B \rangle$ at coexistence with the corresponding Monte Carlo results, as seen in Fig. 3. This confirms the expected quantitative improvement of DFT predictions over the MFA.

III. PLANAR INTERFACES

Now we turn to a discussion of interfacial properties at the two-phase equilibrium. First let us consider a planar (001) interface perpendicular to the z axis of the underlying simple-cubic lattice. The average occupation $\langle n_k^\alpha \rangle$ of sublattices α ($\alpha = A,B$) will now depend on the coordinate across the interface: $l_z = ka$; $k = 0, \pm 1, \ldots$. These quantities are determined by minimizing Ω under the constraints that $\langle n_k^\alpha \rangle$ approach bulk values $\langle n^\alpha \rangle$ as $k \to +\infty$ and $\langle n_k^\alpha \rangle \to \bar{n}$ as $k \to -\infty$. Let us assume the variational ansatz

$$\langle n_k^\alpha \rangle - \bar{n} = (\langle n^\alpha \rangle - \bar{n})(1+\tanh\gamma k)/2 \; , \qquad (4)$$

where, for simplicity, the characteristic width γ^{-1} is taken independent of α. It should be noted that in the presence of an interface the B sites are no longer all equivalent. By numerical minimization of Ω we have confirmed that restriction to only two sublattices and the ansatz (4) are valid approximations. It turns out that γ^{-1} is a smoothly increasing function of temperature. This is shown in Fig. 4 together with MFA calculations and results from numerical simulation (see Sec. II), where the simulated interfacial profiles were fitted by Eq. (4). Although there is no quantitative agreement between the numerical data and the DFT curve, the latter again represents a notable improvement in comparison with the MFA.

For the rest of our discussion let us therefore rely on the DFT approach. The corresponding interfacial tension is given by $\sigma_{(001)} = [\Omega(\langle n_k^\alpha \rangle) - \Omega(\bar{n})]/A$, where A is the surface area. Results for $\sigma_{(001)}$ together with analogous results for other principal symmetry directions are plotted in Fig. 5. It is seen that the (011) interface with the closest packing has a lower interfacial tension than the (001) interface, whereas $\sigma_{(011)}$ and $\sigma_{(111)}$ are almost degenerate. By increasing the temperature, however, the

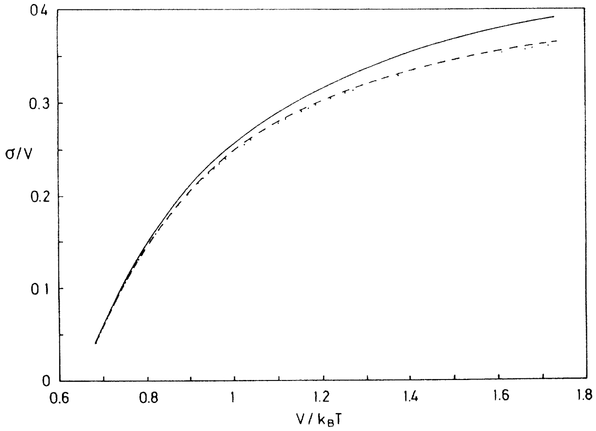

FIG. 5. Interfacial tension as a function of the inverse temperature for the principal symmetry directions: —— (001), — — — (011), · · · · (111).

orientation dependence of the interfacial tension becomes small and ultimately seems to disappear.

Let us remark here that analogous calculations for interfaces within the cluster variation method have been presented before [17]. The present method, however, seems more straightforward.

IV. STRUCTURE AND FREE ENERGIES OF STEPS

Our next aim is to investigate properties of steps on a (001) interface. Their orientation is taken along the y direction. To achieve this we assume a finite extension $2L$ of our system in the x direction, $l_x = ia$, $-L \le i \le L$, and impose shifted periodic boundary conditions,

$$\langle n^{\alpha}_{i-L,k} \rangle = \langle n^{\alpha}_{i+L,k+1} \rangle \ . \tag{5}$$

Together with the previous asymptotic conditions with respect to the k dependence, Eq. (5) is satisfied by the variational ansatz

$$\langle n^{\alpha}_{i,k} \rangle - \bar{n} = (\langle n^{\alpha} \rangle - \bar{n})(1 + \tanh\{\gamma[k - k_0(i)]\})/2 \ . \tag{6}$$

with

$$k_0(i) = \frac{1}{2}\left[1 + \frac{\tanh\delta i}{\tanh\delta L}\right] \ . \tag{7}$$

By these equations the point of inflection in the k-dependent interfacial profile depends on i in a manner describing a step centered at $i=0$, with a typical width δ^{-1} in the x direction. Substituting for γ, our previous result in the strictly planar case, we now minimize Ω with respect to δ. (Independent minimization of Ω with respect to both parameters γ and δ leads to essentially the same results.) The temperature-dependent width of a step, $\delta^{-1}(T,L)$ obtained in this way is plotted in Fig. 6 for different L. At lower temperatures, e.g., $k_B T \sim 0.5V$, we find narrow step profiles, $\delta^{-1} \ll L$. On increasing the temperature, δ^{-1} generally grows and initially is independent of L until it becomes comparable with L. Then, for even higher temperatures, it levels off to a value proportional to L. Indeed, in that range the quantity δL becomes independent of L, as seen from the inset in Fig. 6.

This behavior is interpreted as follows. The width δ^{-1} in our theory reflects some average over fluctuations in the location of the step, physically originating from thermally excited kinks. For low temperatures these fluctuations are small and steps are well defined. On the other hand, at high temperatures δ^{-1} ceases to be an intrinsic property of a step. Rather, the step profiles become totally washed out over the lateral size $2L$ of our system, reflecting strong local disorder at the interface. These findings suggest the association of these two temperature regimes with the flat and the rough state of the interface, with an estimated roughening temperature near $T_R \simeq 1.2V/k_B$. (The occurrence of a maximum and the subsequent drop in δ^{-1}, displayed in Fig. 6, may not be of physical relevance as it occurs in a temperature range where the increasing degree of disorder in the interface is already taken into account by a rapid growth of the width γ^{-1}; see Fig. 4.)

This interpretation is substantiated further by investigating the corresponding step free energy $f^{(s)}(T,L)$, which is the difference of the interfacial tension in the presence and without a step. As seen from Fig. 7, $f^{(s)}$ initially decreases with increasing T and is independent of L for $T < T_R$, whereas for $T > T_R$, $f^{(s)}$ is independent of T and becomes smaller as we increase L. As mentioned before, our theory, being of the mean-field type, is not able to recover the generic temperature dependence of $f^{(s)}$ near T_R as predicted by the Kosterlitz-Thouless theory [11]. However, it is interesting to note that for $T < T_R$ we find the approximate proportionality $f^{(s)}(T) \propto \delta(T)$. This is in fact expected from the exact relation $f^{(s)}(T) \propto \xi^{-1}(T)$ valid near T_R and the approximate relationship $\delta(T) \propto \xi^{-1}(T)$ [18].

The existence of well-defined, individual steps at temperatures $T < T_R$ has been verified by additional calculations for interfaces containing two steps at a relative distance $2i_0$. An appropriate ansatz is Eq. (6), with $k_0(i)$ re-

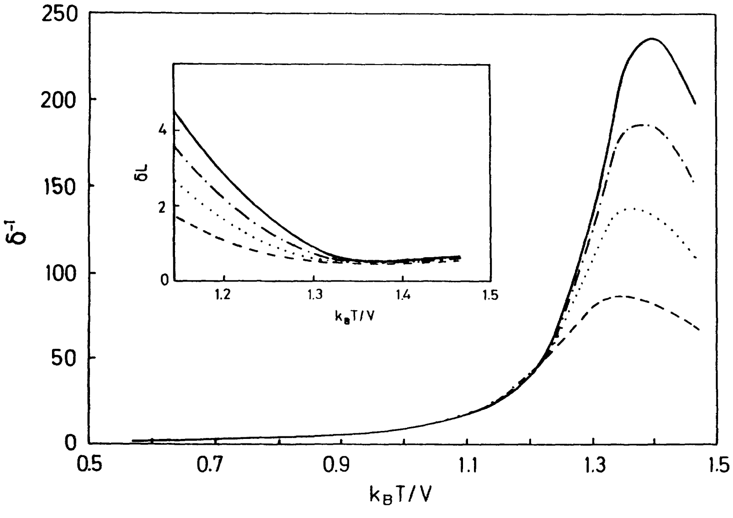

FIG. 6. Width δ^{-1} of the step profile versus temperature for different L: – – – $L=40$; · · · · $L=60$; –·–·–·$L=80$; ——$L=100$. The inset shows the product δL in the range $k_B T \ge V$.

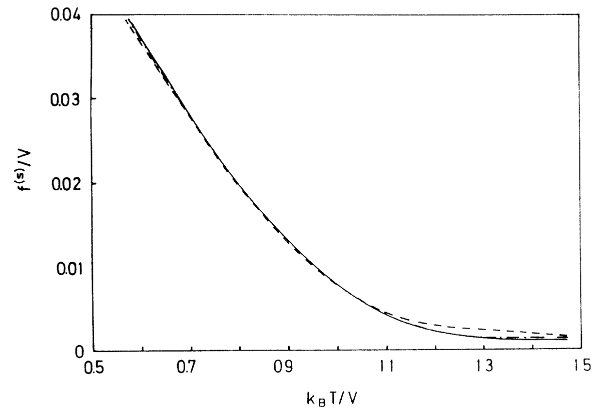

FIG. 7. Step free energy $f^{(s)}(T,L)$ versus temperature for different L: — — —$L=20$; —·—·—·$L=60$; ——$L=200$.

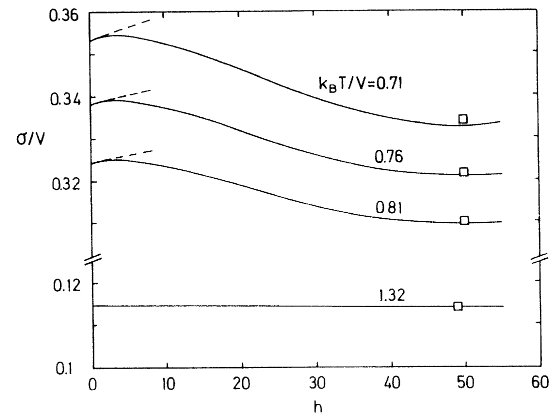

FIG. 9. Anisotropic interfacial tension σ versus h, where $\tan\theta = h/2L$, for different temperatures ($L=25$). The dashed lines indicate the initial slopes. The lowest curve corresponds to a temperature above our estimated roughening temperature. Data points (□) result from independent calculations for (011) interfaces.

placed by

$$k_0^{\pm}(i) = \frac{\tanh[\delta(i-i_0)] \pm \tanh[\delta(i+i_0)]}{\tanh[\delta(L-i_0)] + \tanh[\delta(L+i_0)]} + 1 \ , \qquad (8)$$

which satisfies boundary conditions $\langle n^{\alpha}_{i-L,k}\rangle = \langle n^{\alpha}_{i+L,k+2}\rangle$ in the case of the "+" sign, whereas $\langle n^{\alpha}_{i-L,k}\rangle \approx \langle n^{\alpha}_{i+L,k}\rangle$ in the case of the "−" sign, provided i_0 stays sufficiently below L. The corresponding free energies $f^{\pm}(i_0)$ at a temperature $k_BT = 0.58V$ are plotted in Fig. 8, showing that two steps repel each other in the overlap region.

Finally, we consider boundary conditions of the form

$$\langle n^{\alpha}_{i-L,k}\rangle = \langle n^{\alpha}_{i+L,k+h}\rangle \ , \qquad (9)$$

which generalizes Eq. (5) to interfaces inclined by an angle θ with respect to the (001) plane, where $\tan\theta = h/2L$. For the sake of simplicity, we merely modify our ansatz Eqs. (6) and (7) through the replacement $k_0(i) \rightarrow hk_0(i)$. For values of h in the range $1 \ll h < 2L$ we find δ to be of the order L^{-1} and the interfacial tension $\sigma(h)$ to decrease as h increases; see Fig. 9. The case $h=2L$ effectively corresponds to a (011) interface. In fact, our approximate curves are nearly consistent with the quantities $\sigma_{(011)}$ calculated before (cf. Fig. 5), as seen from the additional data points in Fig. 9. In the figure we also indicated the initial slope $[d\sigma(h)/dh]_0 = f^{(s)}(T)$. As expected, on approaching the roughening temperature from below, the $\sigma(h)$ curves tend to become essentially flat.

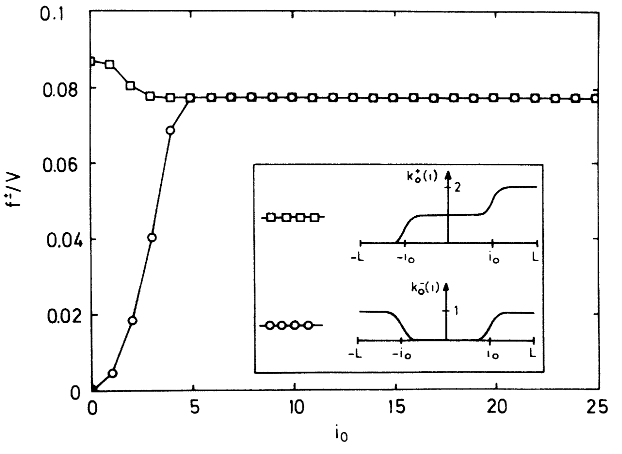

FIG. 8. Free energy $f^{\pm}(i_0)$ of a pair of steps with relative distance $2i_0$ at $k_BT=0.58V$, indicating a repulsive (□) and attractive (○) interaction for the two step geometries shown in the inset. Calculations were carried out for $L=40$. For the definition of $k_0^{\pm}(i)$ see Eq. (8).

V. SUMMARY AND CONCLUSIONS

To conclude, we have shown that with the help of the discrete lattice version of density-functional theory the bulk phase transition and static interfacial properties can be studied simultaneously for a fairly realistic interaction model. Our theory, originally based on concepts of liquid structure theory, may be regarded as a link between lattice statistical theories conventionally used to describe ordering transitions in bulk lattice gases [19] and simplified models, like the SOS models, which concentrate on interfacial configurations. As compared with the latter, our method provides a fairly realistic description of the bulk, where ordering occurs via a symmetry-breaking transition and where the ordered state contains defects in the form of vacancies (empty A sites) and interstitial atoms (occupied B sites). On the other hand, in comparison with standard cluster methods [17] it allows us to compute the structure of planar interfaces in a straightforward way. Furthermore, we demonstrated that our method also accounts for more detailed properties of interfaces. As an example, we investigated in some detail the properties of steps on a (001) interface. By analyzing the L-dependent width of steps and the step free energies, we identified two qualitatively different temperature regimes associated with the flat and the rough state of the interface. In conclusion, it appears that our approach represents an important step towards an improved understanding of the relationship between interfacial properties and molecular parameters.

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