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Thermodynamic stability of periodic and quasiperiodic crystals within a van der Waals approximation

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We investigate the relation between the thermodynamic stability of periodic and quasiperiodic crystals and the characteristics of the interaction potential within a simple van der Waals approximation to the free energy of a one-component two-dimensional system. We find that thermodynamically stable quasiperiodic crystals can be found only when the interaction potential has at least two negative minima separated by a positive maximum. [S1063-651X(98)00904-0]

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I. INTRODUCTION

At present the existence and nature of quasiperiodic crystals (quasicrystals) is already well documented [1]. The question of whether these quasicrystals are thermodynamically stable or metastable structures, however, has received conflicting answers [2]. The difficulty of this problem is related to the fact that most of the existing quasicrystals are metallic alloys and hence involve several atomic species between which complex effective potentials or pseudopotentials are operating. In principle, such a quasiperiodic structure can be stabilized by either entropic or energetic effects or by an interplay between both. In the case of entropic stabilization the alloy aspect is probably the dominant feature, whereas for energetic stabilization the particular features of the (intermetallic) potentials will dominate. In order to simplify the problem we focus our attention here mainly on the energetic stabilization mechanism. Although experimentally less realistic, this simplification allows us to consider single-component systems and hereby avoid the complications due to the alloy aspect. One-component quasicrystals have not been observed yet, but their possible existence is a question worth investigating for its own sake [3]. Even for one-component systems the problem is not simple because the question of thermodynamic stability requires one to compute the Gibbs free energy for all the competing structures and this for many temperatures and pressures. To simplify the problem further we will evaluate these free energies here within the van der Waals approximation of [4,5]. Such a mean-field approximation is bound to introduce large quantitative errors, but could well be sufficient to indicate those qualitative features of the interparticle potential that will favor the occurrence of a quasiperiodic structure in the system's phase diagram. Indeed, on all previous occasions this approximation has yielded qualitatively correct predictions when compared to more sophisticated theories [4,5]. Even so, the lack of periodicity of the quasicrystalline structures requires the evaluation of slowly convergent sextuple lattice sums. In order to avoid also this more technical problem we will consider here only two-dimensional quasicrystals for which the lattice sums are more easily evaluated. Whereas two-dimensional quasicrystals have been observed [6], we think that conclusions similar to those reached here for the two-dimensional systems can be obtained also in three dimensions, but at the expense of more elaborate calculations.

This paper is organized as follows. In Sec. II we summarize the van der Waals approximation already put forth elsewhere [4] and generalize it to quasiperiodic structures. In Sec. III we describe the periodic and quasiperiodic structures to be considered here. Section IV contains our choice for the interaction potential. The phase diagrams obtained in this way are discussed in Sec. V. Section VI contains our conclusions.

II. VAN DER WAALS THEORY

The basic ingredients of the van der Waals (vdW) theory are well known [4]. A simple fluid of spherical particules interacting through a pair potential $V(r)$ is considered:

$$V(r)=V_{HS}(r)+V_A(r), \tag{2.1}$$

with $V(r)$ consisting of a hard-sphere (HS) repulsion between HSs of diameter σ,

$$V_{HS}(r)=\begin{cases}\infty, & r<\sigma\\ 0, & r\geqslant\sigma,\end{cases} \tag{2.2}$$

and an attraction (A) of amplitude $\epsilon>0$ described by

$$V_A(r)=\begin{cases}0, & x<1\\ -\epsilon\phi(x), & x\geqslant 1,\end{cases} \tag{2.3}$$

where r is the distance between the pair of particles, $x=r/\sigma$, and the dimensionless function $\phi(x)$ will be specified further in Sec. IV. The thermodynamic properties of a system of N such particles enclosed in a volume V at the equilibrium temperature T can then be described by the Helmholtz free energy $F=F(N,V,T)$. Within the present vdW theory the latter is written [4]

$$F(N,V,T)=F_{HS}(N,V,T)+F_A^{ex}(N,V,T) \tag{2.4}$$

as the sum of the Helmholtz free energy (F_{HS}) of a system of HSs and the excess free energy (F_A^{ex}) due to the attractions. For F_{HS} a simple free-volume approximation is adopted whereby the HSs behave as an ideal gas in a reduced volume, αV, the "free" volume (the vdW covolume corresponds then to the "excluded volume" $V-\alpha V$); hence

$$F_{HS}(N,V,T)=F_{id}(N,\alpha V,T), \qquad (2.5)$$

with $F_{id}(N,V,T)=Nk_BT\{\ln\rho\Lambda^d-1\}$ the ideal gas Helmholtz free energy. Here $\rho=N/V$ is the number density, k_B is Boltzmann's constant, Λ is the thermal de Broglie wavelength, and d is the space dimensionality. For F_A^{ex} the standard mean-field approximation is adopted [4]:

$$F_A^{ex}(N,V,T)=\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2\rho(\mathbf{r}_1)V_A(r_{12})\rho(\mathbf{r}_2), \qquad (2.6)$$

where $\rho(\mathbf{r})$ is the one particle density and $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. When switching to the reduced free energy per particle $f=F/\epsilon N$, the reduced temperature $t=k_BT/\epsilon$, and the reduced density $\rho\sigma^d$ or packing fraction $\eta=\rho v_d$ (with v_d the volume of the hard d sphere), the above can be summarized as

$$f(\eta,t)=C(t)+t\ln\eta-t\ln\alpha(\eta)-e(\eta), \qquad (2.7)$$

where $C(t)=t\{\ln(\Lambda^d/v_d)-1\}$ is an immaterial constant, $t\ln\eta$ is the ideal gas contribution, $\ln\alpha(\eta)$ is the reduced excess entropy of the hard d spheres, and $-e(\eta)$ is the reduced excess energy resulting from the attractions (2.6). The basic vdW structure of Eq. (2.7) is assumed here to hold both for a disordered fluid (F) phase for which $\rho(\mathbf{r})\equiv\rho$ and for an ordered periodic or quasiperiodic structure for which $\rho(\mathbf{r})\equiv\Sigma_{j=1}^{N}\delta(\mathbf{r}-\mathbf{r}_j)$, with $\{\mathbf{r}_j\}$ characterizing the set of sites around which the particles are localized (see Sec. III). For a solid (S) the free-volume fraction $\alpha(\eta)$ of Eq. (2.7) will be approximated by its high-density cell-theory value [4]

$$\alpha_S(\eta)=\left[1-\left(\frac{\eta}{\eta_{cp}}\right)^{1/d}\right]^d, \qquad (2.8)$$

where η_{cp} is the value of η at close packing of the structure considered, whereas Eq. (2.6) gives rise to the following lattice sum for $e(\eta)$ of Eq. (2.7):

$$e_S(\eta)=\begin{cases}\dfrac{1}{2N}\displaystyle\sum_{i,j=1}^{N}\phi(x_{ij}) & \text{(aperiodic)}\\[2ex] \dfrac{1}{2}\displaystyle\sum_{j=1}^{N}\phi(x_j) & \text{(periodic)},\end{cases} \qquad (2.9)$$

where $r_{ij}=x_{ij}\sigma$ is the (d-dimensional) distance between site i and site j of the structure described by $\{\mathbf{r}_j\}$ and $\phi(x)$ was defined in Eq. (2.3). When the structure is periodic the double sum in Eq. (2.9) reduces to a single sum with $r_j=x_j\sigma$ being the (d-dimensional) distance of site j to an arbitrary site chosen as the origin. For the fluid (F) phase Eq. (2.6) yields instead

$$e_F(\eta)=4\rho v_2\int_1^\infty dx\; x\;\phi(x) \quad (d=2), \qquad (2.10)$$

where $v_2=(\pi/4)\,\sigma^2$. Finally, the free-volume fraction of the fluid phase $\alpha_F(\eta)$ is approximated by its low-density virial form, namely,

$$\alpha_F(\eta)=1-\frac{\eta}{\eta_0}, \qquad (2.11)$$

with the constant η_0 chosen so as to yield a maximum fluid density [$\eta<\eta_0$ and $\alpha(\eta)>0$] that interpolates between the exact low-density behavior $\alpha_F(\eta)=1-2^{d-1}\eta+O(\eta^2)$ and the physical upper limit at close packing [4],

$$\eta_0=(2^{1-d}+\overline{\eta}_{cp})/2=\frac{1}{4}+\frac{\pi}{4\sqrt{3}}\simeq 0.7034 \quad (d=2), \qquad (2.12)$$

where $\overline{\eta}_{cp}$ represents the close-packing density of a close packed structure [whereas in Eq. (2.8) η_{cp} represents the close-packing density of the structure at hand, i.e., $\overline{\eta}_{cp}=\max\eta_{cp}$]. From Eq. (2.7) we can obtain the chemical potential μ and pressure p as

$$\overline{\mu}(\eta,t)=\frac{\partial}{\partial\eta}(\eta f(\eta,t)),$$

$$\overline{p}(\eta,t)=\eta^2\frac{\partial}{\partial\eta}(f(\eta,t)), \qquad (2.13)$$

where $\overline{\mu}=\mu/\epsilon$ and $\overline{p}=pv_d/\epsilon$ are the corresponding reduced quantities. To complete the thermodynamic description we can also obtain the reduced Gibbs free energy per particle $\overline{g}=G/N\epsilon$ by eliminating η in favor of $\overline{p}$. To this end the relation $\overline{p}=\overline{p}(\eta,t)$ is inverted as $\eta=\eta(\overline{p},t)$ and $\overline{g}(\overline{p},t)$ is obtained from $\overline{\mu}(\eta,t)$ as

$$\overline{g}(\overline{p},t)=\overline{\mu}(\eta(\overline{p},t),t). \qquad (2.14)$$

In this way the Helmholtz free energy $f(\eta,t)$ of Eq. (2.7), together with the pressure $\overline{p}(\eta,t)$ and the chemical potential $\overline{\mu}(\eta,t)$ of Eq. (2.13) and the Gibbs free energy $g(\overline{p},t)$ of Eq. (2.14), will provide a complete description of the phase behavior of a system of particles interacting via the potential (2.1)–(2.3) for both fluid phases [cf. Eqs. (2.10)–(2.12)] and (periodic or aperiodic) solid phases [cf. Eqs. (2.8) and (2.9)] in d dimensions (here $d=2$). The underlying approximation is the vdW approximation contained in Eq. (2.7) that ascribes all the excess entropy of the (F or S) structures to the repulsions, while the cohesion of these structures is ascribed to the excess energy provided by the attractions. Although a more subtle interference between the repulsions and attractions than that described here can occur in real systems, the physics contained within the vdW approximation is very basic and has never been in conflict with reality. Indeed, in all cases known to us the present vdW approximation has yielded qualitatively correct results [4,5]. It is in this spirit that we use it here to investigate how the particular features of the attractions [$\phi(x)$] influence the thermodynamic stability of the various periodic and quasiperiodic structures introduced in the following section.

III. PERIODIC AND QUASIPERIODIC STRUCTURES

The problem of thermodynamic stability is always one of relative stability. Indeed, out of two phases the phase with the lowest Gibbs free energy $g(\overline{p},t)$ is the thermodynamically favored phase at the given $\overline{p}$ and t. It is thus essential to clearly specify which phases have been allowed to compete. In what follows we will restrict ourselves to four different phases: the uniform fluid phase (either liquid or vapor) and three types of crystalline phases, a compact periodic structure, a noncompact periodic structure, and a quasiperiodic structure.

The periodic structures to be considered below consist of the triangular (S_t) lattice and the square (S_s) lattice. The compact structure is the triangular lattice ($\eta_{cp}^{S_t}\simeq 0.907$), whereas the square lattice is a more open structure ($\eta_{cp}^{S_s}=0.7854$).

The quasiperiodic (S_q) structure to be considered here is a two-dimensional dodecagonal quasicrystal that can be built from squares and triangles. Of course, many different quasiperiodic structures can be formulated or observed [1], but we think that the essential features of the energetic competition between periodic and quasiperiodic structures are well illustrated by the choice made here, which involves the same building blocks (triangles and squares) for both the periodic and quasiperiodic lattices. To this end we consider one of the quasilattices put forth in [7]. The points of the two-dimensional plane with Cartesian coordinates (x,y) will be represented by the complex numbers $z=x+iy$. The triangular lattice with unit lattice spacing corresponds then to the set of complex numbers

$$\Omega=\{n_1+n_2\omega\}, \tag{3.1}$$

where the n_i ($i=1,2$) are integers ($n_i=0,\pm 1,\pm 2,\dots$) and $\omega=\exp(2\pi i/3)=(-1+i\sqrt{3})/2$. Let $z_1=n_1+n_2\omega$ and $z_2=n'_1+n'_2\omega$ be two arbitrary points of Eq. (3.1) and consider the set of points

$$Q=\{z_1+z_2\zeta\}=\{n_1+n_2\omega+n'_1\zeta+n'_2\omega\zeta\}, \tag{3.2}$$

where $\zeta=\exp(\pi i/6)=(\sqrt{3}+i)/2$ and $\zeta\omega=\exp(5\pi i/6)=(-\sqrt{3}+i)/2$. The quasilattice ($S_q$) is then formed by those points $z=z_1+z_2\zeta$ of the set (3.2) that satisfy moreover the six conditions

$$\left\{(\mathrm{Re}z)\frac{\cos(\pi/12)}{\sin[(2n+1)\pi/12)]}+(\mathrm{Im}z)\frac{\cos(\pi/12)}{\cos[(2n+1)\pi/12]}\right\}^2\leqslant 1, \tag{3.3}$$

where $n=0,1,2,3,4,5$. The corresponding quasilattice is shown in Fig. 1. The density at close packing of this structure can be computed along the lines of [8]. This has to be done numerically and yields $\eta_{cp}^{S_q}\simeq 0.785$, a number very close to that of the square lattice ($\eta_{cp}^{S_s}\simeq 0.7854$).

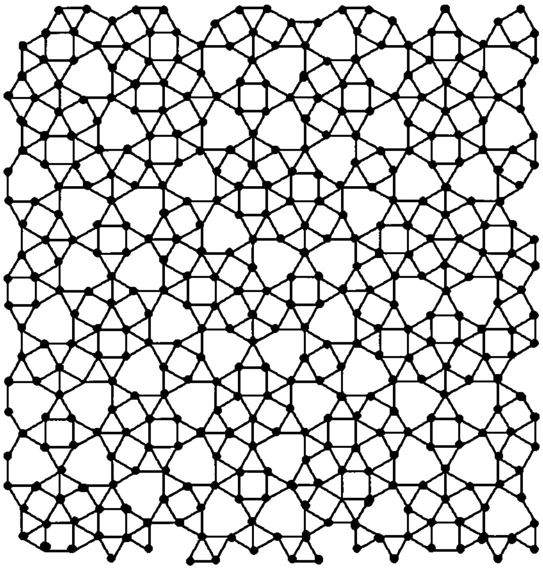

FIG. 1. Quasiperiodic planar lattice with dodecagonal symmetry as obtained from Eqs. (3.2) and (3.3). The dots represent the lattice sites, while the lines exhibit the lattice structure as consisting of a tiling with regular triangles, squares, and trigonal hexagons [7]. At close packing the density of this quasilattice is very close to that of the square lattice with the same lattice spacing.

IV. THE INTERACTION POTENTIAL

To proceed we still have to specify the potential function $\phi(x)$ of Eq. (2.3). To this end we will take advantage of the observation made in [9] that the stable lattice structure is very sensitive to the relative position of the maximum of $\phi(x)$ [or minimum of $V_A(r)$, cf. Eq. (2.3)] and the position of the nearest neighbors, as given for the various structures considered here in Table I.

In order to easily locate the extrema of $\phi(x)$ we will write it as a sum of Gaussians

$$\phi(x)=\sum_n c_n\exp[-a_n^2(x-b_n)^2],\quad x=\frac{r}{\sigma}, \tag{4.1}$$

where the $c_n=\epsilon_n/\epsilon$ are relative amplitudes, while the constants a_n and b_n fix, respectively, the ‘‘range’’ and the ‘‘center’’ of the nth Gaussian ($n=1,2,\dots$). Of course, our choice of Gaussian potentials has no particular physical meaning and similar results can be obtained by using different mathematical forms. Note that most of the investigations below involve in fact only a single Gaussian [in which case we can set $c_1=1$ because the c_n in Eq. (4.1) are relative

TABLE I. Number of sites (n_j) at a given relative distance (x_j/x_1) from a central site for the periodic lattices considered here (S_t for the triangular, S_s for the square lattice). Note that the second-nearest-neighbor distance of the compact lattice (S_t) exceeds that of the noncompact lattice (S_s) by a factor $\sqrt{3/2}$.

x_j/x_1	$n_j^{S_t}$	$n_j^{S_s}$
1	6	4
$\sqrt{2}$	0	4
$\sqrt{3}$	6	0

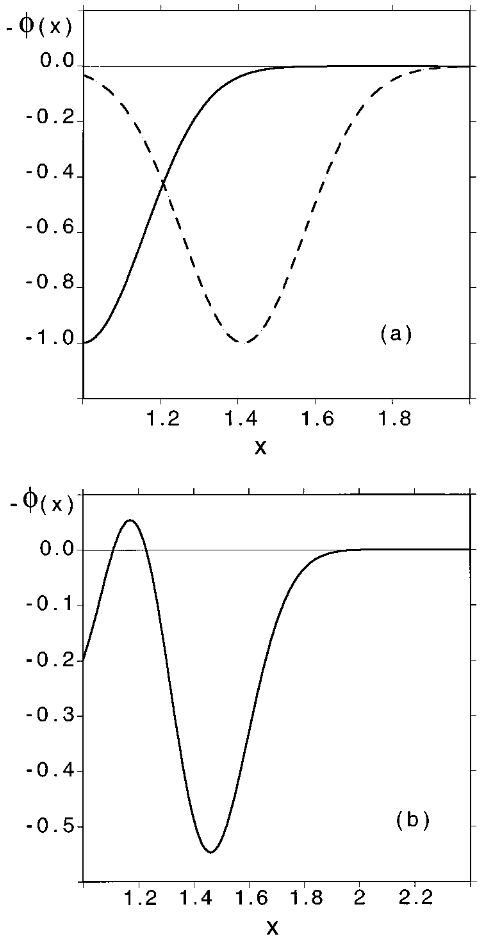

FIG. 2. Dimensionless attraction $V_A(r)/\epsilon \equiv -\phi(x)$, of Eq. (2.3) versus the dimensionless distance $x=r/\sigma$ in units of the hard-d-sphere diameter σ for the Gaussian potentials of Eq. (4.1). (a) A single Gaussian with $c_1=1$, $a_1=20$, and $b_1=1$ (full line) $\sqrt{2}$ (short-dashed line). The former potential favors the compact lattice (S_t), while the latter favors the noncompact lattice (S_s). (b) A triple Gaussian with $c_1=0.4$, $c_2=-0.5$, $c_3=0.7$, $a_1=a_2=a_3=20$, $b_1=1$, $b_2=1.2$, and $b_3=\sqrt{2}$. This potential mimics an oscillating (intermetallic) potential and favors the quasilattice.

amplitudes, the overall amplitude being set by ϵ of Eq. (2.3)] with the exception of the study of the quasicrystals for which a more general potential of the type (4.1) with $n=1,2,3$ will be used. The various types of potentials, within the general family (4.1), to be used below are shown in Fig. 2.

V. PHASE DIAGRAMS

We now consider, in order of increasing complexity, a series of particular cases of Eq. (4.1).

A. Hard-(d-) sphere transitions

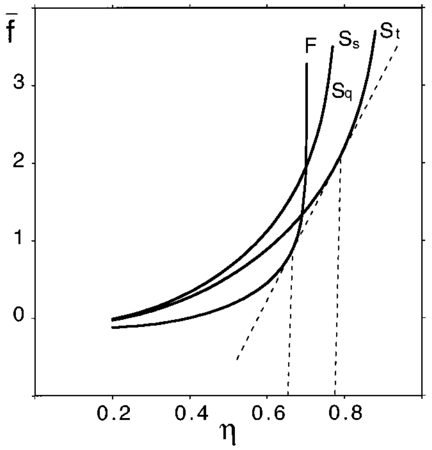

FIG. 3. Reduced free energy per unit volume ($\overline{f}=v_d\beta F/V$) versus the packing fraction ($\eta=\rho v_d$) of a hard-d-sphere system as obtained within the present vdW theory. The double-tangent construction, yielding the fluid (F) solid (S) coexistence densities, is indicated by the dashed lines. For $d=2$ the competing phases are the fluid (F), the quasilattice (S_q), the square lattice (S_s), and the triangular lattice (S_t). The resulting stable F-S transition is between an F phase ($\eta_F \simeq 0.66$) and the triangular lattice ($\eta_{S_t} \simeq 0.78$). Note that the free energies of the square and quasilattices cannot be distinguished on this scale.

When $\phi(x)\equiv 0$ the above vdW theory describes a system of hard d spheres. In such a system the only possible phase transition is an order-disorder transition between a disordered fluid phase and an ordered crystal structure. This transition is seen to be monitored by the free-volume entropy of Eqs. (2.8) and (2.11). From the equations of Sec. II it follows [4] that the stable crystal structure is the one with the highest close-packing density (see Fig. 3). This result is in agreement with the simulations of [10] and observations of [11]. The position of this transition in, say, the temperature-density plane is an important feature of a phase diagram because it provides a partition of this plane into two domains, one for the fluid and one for the solid phases. The present vdW theory, although very approximate, yields a fair estimate for the position of the HS-freezing transition of d spheres (see Fig. 3). Because the quasicrystalline structures are not compact structures they cannot be stabilized by the HS interaction alone, not in the present vdW theory but also not in the more sophisticated theories of [3,12,13].

B. Isostructural transitions

As is well known [4], the introduction of attractions between the HSs $\phi(x)\neq 0$ can lead to a transition between phases of the same structure, i.e., isostructural transitions, be it disordered or ordered structures. The interplay between the order-disorder transition and these isostructural transitions has been the subject of much recent work, in particular with respect to the isostructural solid-solid transition, which at present is still unobserved [14]. In order to convince ourselves that the systems governed by potentials of the type (4.1) behave in a similar way we first consider the case

$$\phi(x)=\exp[-a^2(x-1)^2], \quad x\geq 1, \tag{5.1}$$

where the parameter a fixes the range of attractions relative to the range (σ) of the HS repulsions. For long-ranged attractions (small a) the isostructural solid-solid transition is metastable, whereas for short-ranged attractions (large a) the isostructural fluid-fluid (or vapor-liquid) transition is metastable. There exists, moreover, a range of intermediate-a values for which both isostructural transitions are metastable

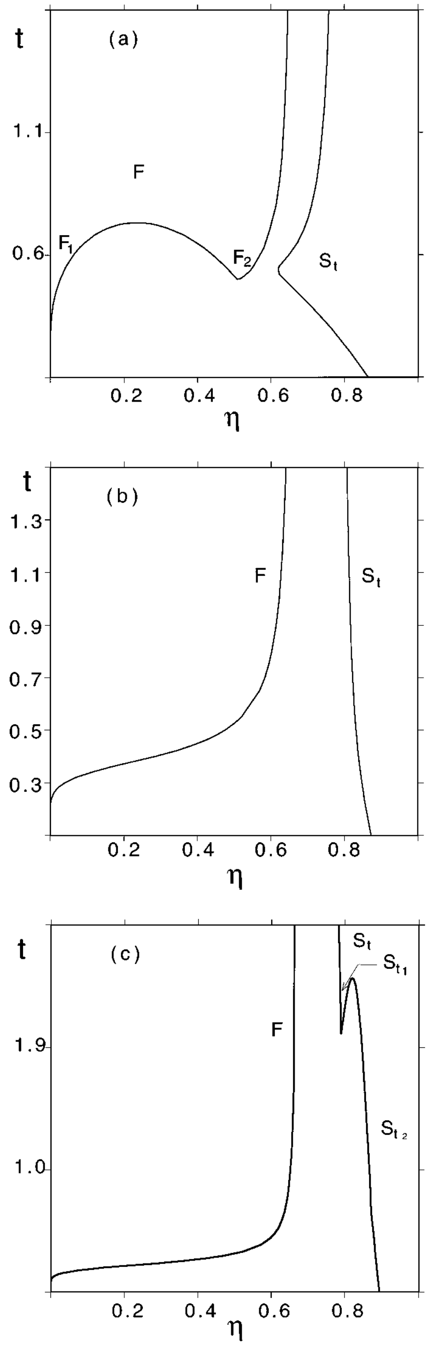

FIG. 4. Phase diagrams in the reduced-temperature ($t=k_BT/\epsilon$)–reduced-density ($\eta=\rho v_2$) plane for $d=2$ systems with a single-Gaussian attraction of the type (5.1). (a) For long-range attractions ($a\leqslant 3.38$) there is a stable isostructural transition between two disordered fluid phases (F_1 and F_2) in addition to the fluid-solid (S_t) transition. (b) For intermediate-range attractions ($3.38\leqslant a\leqslant 28$) the only stable transition is between the disordered fluid (F) and the ordered solid (S_t) phase. (c) For short-range attractions ($a\geqslant 28$) there is a stable isostructural transition between two ordered solid phases (S_{t_1} and S_{t_2}) in addition to the fluid-solid transition.

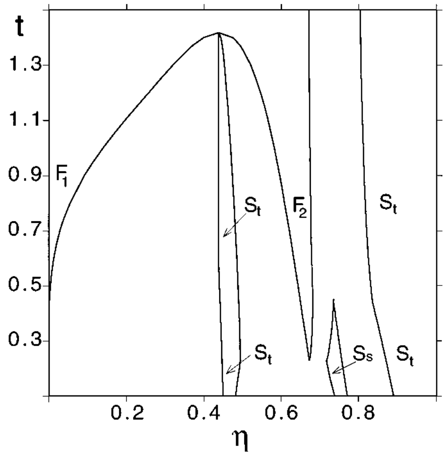

FIG. 5. Complete phase diagram in the temperature-density plane for a $d=2$ system with Gaussian attractions corresponding to Eq. (5.2) with $a=20$ and $x_0=\sqrt{2}$ (same notation as in Fig. 4). Note that there is a melting maximum in the low-density fluid–triangular lattice coexistence, while the square lattice is stable only at low temperatures and within a small density window.

and the phase diagram is reduced to an order-disorder transition. An example of the three types of phase diagram is given in Fig. 4 (see [4,5] for the $d=3$ case). Both the $d=2$ and $d=3$ systems, with either a Gaussian (5.1) or inverse power (see [4,5]) potential, thus behave in the same way. In particular, the thermodynamically stable solid phase is always the compact periodic structure.

C. Structural transitions

In order to stabilize the noncompact lattices and induce transitions between different structures, i.e., induce structural transitions, we now shift the center ($x=1$) of the Gaussian attraction (5.1) towards a new position $x=x_0$, with $x_0=x_2/x_1$ and x_n being the position of the nth nearest neighbor of the noncompact lattice (see Table I):

$$\phi(x)=\exp[-a^2(x-x_0)^2], \quad x\geqslant 1, \tag{5.2}$$

where $x_0=\sqrt{2}$ for $d=2$. Note that this is a simplified version of the argument put forth by Boyer in [9] for $d=3$. Indeed, the potential (5.2) is now more strongly binding at the position (x_2) of the second neighbor of the square lattice ($x_2/x_1=\sqrt{2}$) than at the position of the second neighbor of the triangular lattice ($x_2/x_1=\sqrt{3}$). The shift [see Fig. 2(a)] in the maximum of Eq. (5.2) as compared to Eq. (5.1) can have a profound influence on the system's phase diagram. At low temperatures, where the energetic considerations dominate, we now have structural phase transitions between the compact and noncompact crystal structures. We now also have a local maximum in the fluid-compact crystal melting line, a feature characteristic of short-ranged Gaussian potentials [15]. An example of such a phase diagram is shown in Fig. 5.

D. Quasiperiodic structural transitions

The above procedure of displacement of the "center of attraction" relative to the structure to be stabilized, although sufficient for stabilizing noncompact periodic structures, is unable to stabilize the quasiperiodic structure. This is because the entropic contributions to the free energy of the noncompact and quasiperiodic structures are almost identical, but the latter are still energetically unfavorable. We found, by trial and error, that in order to stabilize the quasicrystal phase one has to introduce a weak repulsion centered between the first and second nearest neighbors of the competing periodic structure. We thus take

$$\phi(x)=c_1\exp[-a^2(x-1)^2]+c_2\exp[-a^2(x-1.2)^2]+c_3\exp[-a^2(x-\sqrt{2})^2], \qquad (5.3)$$

with $c_1,c_3>0$ and $c_2<0$, in order to stabilize the quasicrystal relative to the triangular lattice. It is interesting to observe that the corresponding potential mimics, to some extent [see Fig. 2(b)], the oscillations present in the intermetallic pseudopotentials prevailing in the alloys for which quasicrystals have been found experimentally [16]. It is thus possible that for a one-component system, such as considered here, the thermodynamic stability of the quasicrystalline phase requires likewise a fine-tuning of the minima and maxima of the interaction potential relative to the positions of the first and second nearest neighbors of the competing periodic structure. To establish the thermodynamic stability of the quasicrystalline phase for Eq. (5.3) theoretically, however, is not an easy task even within this simple vdW theory. Indeed, because of the ''oscillations'' in the potential (5.3) [see Fig. 2(b)] the Helmholtz free energies of the different phases exhibit several ''loops'' that render the construction of double tangents and convex envelopes very tedious. In this respect it should be stressed here that several studies in the literature have been limited to studying situations where the quasicrystalline phase corresponds to a local minimum of the Helmholtz free energy. This, however, is not a sufficient condition for thermodynamic stability. Indeed, we have found many instances [also for potentials much simpler than Eq. (5.3)] where such local minima do exist but do not belong to the convex envelope to the Helmholtz free energies of all the phases involved. Under such circumstances the quasicrystal phase, although mechanically stable, is still thermodynamically metastable relative to the other phases. To establish unambiguously the thermodynamic stability of any phase we found that in the present case it is much more convenient to compare directly the Gibbs free energies $\overline{g}(p,t)$ of the different phases. A phase diagram obtained in this way for Eq. (5.3) is shown in Fig. 6.

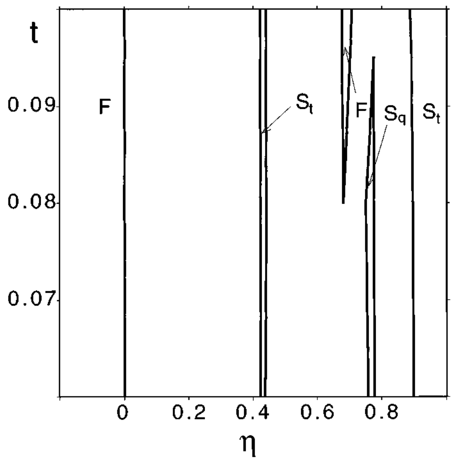

FIG. 6. Low-temperature region of the temperature (t) density (η) phase diagram of a $d=2$ system described by the potential of Fig. 2(b) (same notation as in Fig. 4). The quasilattice phase is stable only in a narrow density window.

VI. CONCLUSIONS

The thermodynamic stability of two-dimensional one-component periodic and quasiperiodic crystals has been investigated within the extended vdW theory of [4]. The use of such a simplified theory is justified here by the need to compute the Gibbs free energy in order to unambiguously locate the thermodynamically (as opposed to mechanically) stable phases. In particular, we find that quasiperiodic phases are stable only when the interaction potential has at least two negative minima separated by a positive maximum. It is found, moreover, that the minima and maxima of the interaction potential should be finely tuned with respect to the structure of the competing periodic crystals. This may explain why it is difficult to find stable quasicrystalline phases in one-component systems and why oscillating intermetallic pseudopotentials are required for stabilizing the quasicrystalline alloys.

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