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Isostructural solid-solid transition of (colloidal) simple fluids

C. F. Tejero,[1] A. Daanoun,[2] H. N. W. Lekkerkerker,[3] and M. Baus[2]
[1] *Facultad de Ciencias Físicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain*
[2] *Faculté des Sciences, Code Postal 231, Université Libre de Bruxelles, B-1050 Brussels, Belgium*
[3] *Van't Hoff Laboratorium voor Fysische en Colloidchemie, Universiteit Utrecht, Postbus 80051, 3508TB Utrecht, The Netherlands*

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A variational approach based on the Gibbs-Bogoliubov inequality is used in order to evaluate the free energy of simple fluids described by a double-Yukawa pair potential. A hard-sphere reference fluid is used to describe the fluid phases, and an Einstein reference crystal to describe the solid phases. Apart from the usual type of phase diagram, typical of atomic simple fluids with long-ranged attractions, we find two types of phase diagrams, specific to colloidal systems with intermediate and short-ranged attractions. One of the latter phase diagrams exhibits an isostructural solid-solid transition, which has not yet been observed experimentally.

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I. INTRODUCTION

Simple fluids [1] are systems of identical particles whose interactions can be adequately described in terms of a spherically symmetric pair potential $V(r)$ of the generic form

$$V(r) = \epsilon\phi\left(\frac{r}{\sigma}\right), \tag{1.1}$$

where ϵ measures the strength of the interaction and σ is a measure of the diameter of the particles, r being their center-to-center distance. Although triplet forces may occur in even the simplest atomic system (such as argon) [2], most of them can be adequately described in terms of the pair forces generated by (1.1) with simple forms of $\phi(x)$, such as the well-known Lennard-Jones (LJ) form

$$\phi_{\rm LJ}(x) = 4\left(\frac{1}{x^{12}} - \frac{1}{x^6}\right), \tag{1.2}$$

where $x = r/\sigma$. Many molecular and ionic systems can be given a similar simple fluid description [1,2]. More surprisingly, a vast amount of evidence has been gathered in recent years that, at the other extreme, very complex supramolecular systems (such as carefully prepared colloidal dispersions) [3] can often be described well in terms of a simple fluid of spherically symmetric colloidal particles interacting via a solvent-mediated effective pair potential of the form (1.1) [4]. This is true only as far as the equilibrium properties of these complex systems are concerned (so that the hydrodynamic interactions between the colloidal particles set up by the motion of the solvent can be neglected) [3] and we will thus henceforth restrict ourselves to these *equilibrium* properties. The major difference between the simple fluid description of atomic and colloidal systems stems then from the very different values of the scales, ϵ and σ, and the form of $\phi(x)$ in (1.1). Since ϵ and σ can be absorbed in the scales of the temperature (T), the density (ρ), and the pressure (p) by using the following reduced thermodynamic variables:

$$t = k_BT/\epsilon, \;\; \bar\rho = \rho\sigma^3, \;\; \bar p = p\sigma^3/\epsilon, \tag{1.3}$$

where t is the reduced temperature (k_B being Boltzmann's constant), $\bar\rho$ the reduced number density, and $\bar p$ the reduced pressure, the remaining difference, when using these reduced variables, will stem only from the form of the reduced pair potential $\phi(x)$ versus the reduced distance x. Whereas in the atomic systems the form of $\phi(x)$ barely changes, this is no longer true in the colloidal systems where, by some clever chemical engineering, one can produce a much larger variety of forms [3]. This then raises the question of how the equilibrium phase behavior of a simple fluid changes when one systematically changes the form of the potential function $\phi(x)$. From the above it will be clear that most of these forms will lie outside the range accessible to atomic systems but could be investigated experimentally by studying suitably prepared colloidal dispersions [3,4]. In general one expects the phase behavior of colloidal systems [3] to be similar to that of other simple fluids [1]. For instance, in most monodisperse charge-stabilized colloidal dispersions $\phi(x)$ is purely repulsive and well approximated by a Yukawa form, viz., $\phi(x) \sim e^{-\lambda x}/x$, of variable range $1/\lambda$. Under these circumstances the colloidal particles have been shown to undergo an order-disorder transition between a fluidlike configuration (F) and a solidlike configuration (S) [5]. Depending on the range (λ) the resulting (colloidal) crystalline configuration will have a body centered cubic (bcc) or a face centered cubic (fcc) structure with in between a structural bcc-fcc transition [5–8]. This is qualitatively similar to the phase behavior of soft spheres [1], viz., $\phi(x) = 1/x^n$. In the case of sterically stabilized colloidal dispersions [3] one can even set up an experimental system where the colloidal particles mimic a system of hard spheres with an order(S)–disorder(F) transition which fits quantitatively to the freezing of hard spheres into a compact lattice [4]. When nonadsorbing polymer is added to a sterically stabilized dispersion, the resulting $\phi(x)$ will have both a repulsive (due to volume exclusion) and an attractive (due to polymer depletion) component as for the atomic simple fluids [3,4,9]. Although these attractions have a very different origin, the resulting potential can be qualitatively similar to that of an atomic system. One major difference between the colloidal and the atomic simple fluid, which can have an important effect on the phase diagram, stems from the fact that, while in atomic systems the range of the attractions is always larger than or comparable to the range of the repulsions, this is no longer the case in colloidal systems where the range of the attractions can be controlled by varying the size (i.e., radius of gyration) of the added polymer [3]. The prevailing situation here is that the range of the attractions is shorter than the range of the repulsions. This leads to new physical phenomena not encountered for the atomic simple fluids. An already well-documented effect concerns the disappearance of the high-density fluid phase or "liquid" phase of the colloidal particles when the range of the attractions shrinks to below one-third of the diameter of the colloidal particles [3,9]. Recently, it was shown on the basis of computer simulations [10] that for attractions with a range roughly one order of magnitude smaller a novel phenomenon, namely, an isostructural solid-solid transition, should appear in the ordered phase of the colloidal particles. This phenomenon has not yet been seen experimentally but has been confirmed by a series of theoretical calculations [11,12] which systematically explored the changes occurring in the phase diagram of a simple fluid when varying the range of the attractions relative to the range of the repulsions. It is our purpose here to provide more details about one of these calculations [11].

As usual, the theoretical determination of the phase diagrams proceeds via an accurate estimate of the free energy of the different phases involved. In [11] we based these estimates on the Gibbs-Bogoliubov inequality (see [1,12] and Sec. II below). For the systems described in Sec. III the corresponding reference systems which enter this inequality will be discussed in detail in Secs. IV and V. The construction of the resulting phase diagrams is given in Sec. VI while the final Sec. VII gathers our conclusions.

II. VARIATIONAL PROCEDURE AND GIBBS-BOGOLIUBOV INEQUALITY

We consider a system of N particles enclosed in a volume V at the equilibrium temperature T. Assume that we write the Hamiltonian describing the interactions between these particles as

$$H(\lambda) = H_0 + \lambda \Delta H \quad (0 \leq \lambda \leq 1), \tag{2.1}$$

where $H_0 \equiv H(\lambda = 0)$ is the Hamiltonian of a reference system and $H_1 \equiv H(\lambda = 1) = H_0 + \Delta H$ the Hamiltonian of the system we want to study, λ being a charging parameter. The Helmholtz free energy (at the given N, V, T values) corresponding to (2.1) is defined by

$$e^{-\beta F(\lambda)} = \int d\Gamma \, e^{-\beta H(\lambda)}, \tag{2.2}$$

where $\beta = 1/k_B T$ and the right-hand side of (2.2) is a shorthand notation for the canonical partition function defined over the phase space Γ of the Hamiltonian (2.1). The Gibbs-Bogoliubov (GB) inequality states then that

$$\Delta F \;\equiv\; F(\lambda = 1) - F(\lambda = 0) \;\leq\; \langle \Delta H \rangle_{\lambda=0}, \tag{2.3}$$

where $\langle \rangle_\lambda$ denotes the canonical average corresponding to (2.2). Indeed, from (2.2) and (2.1) we have $\partial_\lambda F(\lambda) = \langle \Delta H \rangle_\lambda$ with $\partial_\lambda = \partial / \partial \lambda$ and hence $\Delta F = \int_0^1 d\lambda \, \langle \Delta H \rangle_\lambda$, which we rewrite as

$$\begin{aligned} \Delta F &= \int_0^1 d\lambda \left[\langle \Delta H \rangle_{\lambda=0} + \int_0^\lambda d\lambda' \, \partial_{\lambda'} \langle \Delta H \rangle_{\lambda'} \right] \\ &= \langle \Delta H \rangle_{\lambda=0} - \beta \int_0^1 d\lambda \\ &\quad \times \int_0^\lambda d\lambda' \left\langle (\Delta H - \langle \Delta H \rangle_{\lambda'})^2 \right\rangle_{\lambda'}, \end{aligned} \tag{2.4}$$

which implies (2.3).

The way in which we will use the GB inequality is as follows. Let $F(N,V,T)$ be the Helmholtz free energy of the system of interest and $F_0(N,V,T)$ that of the reference system and assume that H_1 and H_0 differ only because the pair potentials $V(r)$ and $V_0(r)$ differ. Then we can rewrite (2.3) as

$$\begin{aligned} F(N,V,T) &\leq \tilde{F}(N,V,T) \\ &\equiv F_0(N,V,T) + \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \, \rho_0(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad \times [V(r_{12}) - V_0(r_{12})], \end{aligned} \tag{2.5}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and $\rho_0(\mathbf{r}_1, \mathbf{r}_2)$ denotes the pair-density of the reference system. In any case, the best estimate for F we can obtain from (2.5) is by minimizing the upper bound $\tilde{F}$; hence

$$F(N,V,T) = \min \tilde{F}(N,V,T), \tag{2.6}$$

where the minimization refers to the free parameters of the reference system. To implement the variational procedure based on (2.6) we have hence to look for a reference system which is at the same time simple enough to allow for an easy evaluation of $\tilde{F}$ and realistic enough so that the minimum of $\tilde{F}$ provides an accurate estimate of F.

III. CHOICE OF A PAIR POTENTIAL FOR THE SYSTEM

Before considering the choice of the reference system we have first to specify the system itself. As already stated in Sec. I, we will consider a simple fluid with a pair potential of the general form (1.1) but as we are interested not only in atomic simple fluids (such as argon) but also in the simple fluid description of colloidal dispersions with depletion forces, we will have to allow for large variations in the form of $\phi(x)$ of (1.1). One form of $\phi(x)$ which satisfies this requirement and at the same time leads to easy-to-compute expressions for (2.6) is the following so-called double-Yukawa (DY) form:

$$\phi(x) = \frac{c}{x}\left(e^{-a(x-1)} - e^{-b(x-1)}\right), \quad a > b, \tag{3.1}$$

where a, b, c are positive parameters. By construction we have $\phi(x = 1) = 0$, $\phi(x < 1) > 0$, and $\phi(x > 1) < 0$, while $\phi(x)$ has a minimum for $x = x_0 > 1$ such that

$$\phi'(x_0) = 0, \quad \frac{1 + a x_0}{1 + b x_0} = e^{(a-b)(x_0 - 1)}. \tag{3.2}$$

The value of $\phi(x)$ at this minimum will set the scale for the temperature. Keeping ϵ of (1.1) as this scale we will hence fix c of (3.1) to be such as to satisfy

$$\phi(x_0) = -1, \quad \frac{1}{c} = \frac{1}{x_0}\left(e^{-b(x_0-1)} - e^{-a(x_0-1)}\right), \tag{3.3}$$

which can be used to eliminate c from (3.1), leaving us with a two-parameter potential. Instead of the original parameters, a and b, it is physically more interesting to use as parameters the position of the minimum, x_0, and a second parameter δ characterizing the range of the attractive part of $\phi(x)$. To obtain an estimate of this range we put $\delta = (x_1 - x_0)/x_0 > 0$, where x_1 $(x_1 > x_0)$ is the value of x for which $\phi(x)$ has dropped to 1% of its value, -1, at the minimum:

$$\phi(x_1) = -0.01, \quad \frac{1}{c} = \frac{0.01}{x_1}\left(e^{-b(x_1-1)} - e^{-a(x_1-1)}\right). \tag{3.4}$$

Using (3.1)–(3.4) we will eliminate (a, b) in favor of (x_0, x_1) and characterize $\phi(x)$ through the physically more transparent parameters x_0 and δ. The two-parameter family of potentials constructed in this way is very flexible and many particular potentials can be approximated by it. For instance, the well-known LJ potential of (1.2) can be approximated by using (3.1) with

$$a_{\mathrm{LJ}} = 14.3959, \qquad b_{\mathrm{LJ}} = 2.6978, \tag{3.5}$$

which correspond to

$$x_0^{\mathrm{LJ}} = 2^{1/6} \simeq 1.12, \qquad x_1^{\mathrm{LJ}} = 2.62. \tag{3.6}$$

For the discussion below we will concentrate mainly on the seven cases of Table I. The corresponding potentials are shown in Fig. 1. These potentials differ mainly by the range of the attractive part.

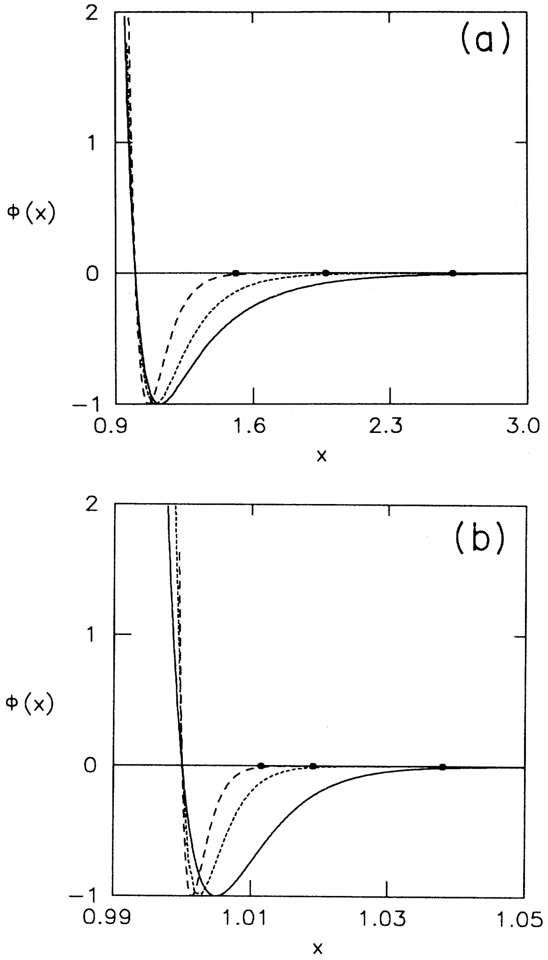

FIG. 1. The DY potential $\phi(x)$ of (3.1) versus x for (a) the three cases of Table I(a), $\delta = 1.34$ (full curve), $\delta = 0.79$ (dotted curve), and $\delta = 0.41$ (dashed curve); and (b) three of the four cases of Table I(b), $\delta = 3.28 \times 10^{-2}$ (full curve), $\delta = 1.65\times10^{-2}$ (dotted curve), and $\delta = 1.05\times10^{-2}$ (dashed curve). The full dot indicates, for each case, the position of x_1.

TABLE I. The parameters defining the potential (3.1) as obtained from Eqs. (3.2)–(3.4) for (a) three cases typical of atomic simple fluids, i.e., $\delta \simeq 1$ and (b) four cases typical of colloidal simple fluids, i.e., $\delta \simeq 10^{-2}$. Below we will label these different cases by their value of δ.

a	b	c	x_0	x_1	δ
		(a) Atomic			
14.4	2.7	2.1	1.12	2.62	1.34
14.4	5.2	3.1	1.10	1.97	0.79
14.4	14.0	104.1	1.07	1.51	0.41
		(b) Colloidal			
200	198.0	273.6	1.0050	1.038	0.0328
400	398.0	545.5	1.0025	1.019	0.0165
500	498.0	681.4	1.0020	1.015	0.0130
670	661.4	209.6	1.0015	1.012	0.0105

IV. VARIATIONAL DESCRIPTION OF THE FLUID PHASES

In the case of a disordered fluid phase we have for the pair density of (2.6)

$$\rho_0(\mathbf{r}_1,\mathbf{r}_2) = \rho^2 g_0(r_{12}), \tag{4.1}$$

where ρ is the number density ($\rho = N/V$) and $g_0(r_{12})$ the pair-correlation function of the reference system. For the reference fluid phase we will use a hard-sphere (HS) fluid, in which case $\int d\mathbf{r}\, g_{\rm HS}(r)V_{\rm HS}(r) \equiv 0$ and (2.6) becomes

$$\tilde{f}(\rho,T) = f_{\rm HS}(\rho,T) + 2\pi\rho \int_{\sigma_{\rm HS}}^{\infty} dr\, r^2\, g_{\rm HS}(r/\sigma_{\rm HS}, \eta_{\rm HS}) V(r), \tag{4.2}$$

where $\tilde{f}$ denotes the variational free energy per particle and $f_{\rm HS}$ that of the HS fluid, $\sigma_{\rm HS}$ is the HS diameter, and $\eta_{\rm HS} = \pi\rho\sigma_{\rm HS}^3/6$ the corresponding packing fraction.

The justification for our using the DY form of (3.1) to describe the system's pair potential stems from the fact that its combination with the HS fluid as reference system for the fluid leads to an expression in (4.2) which involves the Laplace transform of $r g_{\rm HS}(r)$:

$$\int_0^\infty dy\, e^{-zy}\, y g_{\rm HS}(y;\eta_{\rm HS}) = z H(z;\eta_{\rm HS}),$$

which, within the Percus-Yevick (PY) approximation for the HS fluid, is known analytically [13]:

$$H(z,x) = \frac{L(z,x)}{12xL(z,x) + S(z,x)e^z}, \tag{4.3}$$

where

$$L(z,x) = (1 + x/2)z + (1 + 2x), \tag{4.4a}$$

$$S(z,x) = (1-x)^2 z^3 + 6x(1-x)z^2 + 18x^2 z - 12x(1+2x). \tag{4.4b}$$

Within the same PY approximation the HS free energy $f_{\rm HS}$ can be written

$$\beta f_{\rm HS}(\rho,T) = \ln(\rho\Lambda^3) - 1 + f_{\rm ex}^*(\eta_{\rm HS}), \tag{4.5}$$

where $\Lambda = h/\sqrt{2\pi m k_B T}$ denotes the thermal de Broglie wavelength for particles of mass m and

$$f_{\rm ex}^*(x) = \frac{3x(2-x)}{2(1-x)^2} - \ln(1-x) \tag{4.6}$$

is the (dimensionless) excess free energy. Introducing the dimensionless variables (1.3), we obtain the following variational free energy

$$\frac{1}{\epsilon}\tilde{f}(\eta,t;\lambda) = t\left(\ln\eta - \frac{3}{2}\ln t + C - 1\right) + t f_{\rm ex}^*(\eta\lambda^3) + 12c\eta\lambda^3\left[ae^a H(a\lambda,\eta\lambda^3) - be^b H(b\lambda,\eta\lambda^3)\right], \tag{4.7}$$

where $\eta_{\rm HS} = \eta\lambda^3$, i.e., $\eta = \pi\rho\sigma^3/6$, and $\lambda = \sigma_{\rm HS}/\sigma$, while $C = \ln(6\Lambda_0^3/\pi\sigma^3)$, with $\Lambda_0 = h/\sqrt{2\pi m\epsilon}$, is a constant. Equation (4.7) has to be minimized [for a given potential (a,b,c)] with respect to the variational parameter λ (such that $\eta_{\rm HS} = \eta\lambda^3 < 1$) for given values of the thermodynamic parameters (η,t). The way in which the minimum of (4.7) with respect to λ is formed is illustrated in Fig. 2. If $\lambda_{\rm min}(\eta,t)$ denotes the value of λ for which (4.7) attains its minimum the resulting estimate for the free energy obtained from the GB inequality (2.6) is

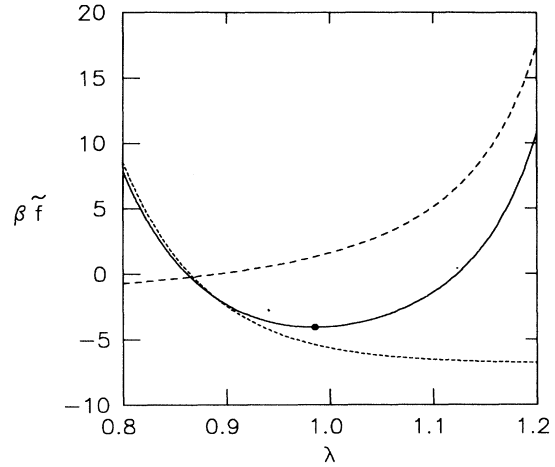

FIG. 2. The reduced variational free energy per particle, $\beta\tilde{f}$, of the fluid phase [see (4.7)] vs the variational parameter λ for the $\delta = 1.34$ case at $\bar{\rho} = 0.8$ and t=1 (full curve). The full dot indicates the position of $\lambda_{\rm min}$. Also shown are the hard-sphere reference free energy (dashed curve) and the perturbation term (dotted curve).

$$f(\eta,t) = \tilde{f}(\eta,t;\lambda_{\rm min}(\eta,t)). \tag{4.8}$$

The quality of this estimate depends (1) on the quality of the PY description (4.3)–(4.6) of the HS fluid and (2) on the quality of the HS fluid as a reference fluid for the fluid described by the DY pair potential (3.1). The quality of the PY approximation for the HS is very satisfactory (see, e.g., [1]) while the quality of the HS system as a reference fluid for the DY system was found in [14] to be equally satisfactory for the particular case of the LJ potential. Here we will use this variational description of the DY fluid for a whole family of potentials, all having the same strength as the LJ potential but with a different range (mostly shorter than for the LJ case) for the attractions. We found the present method to be very flexible, easy to implement, and fairly accurate. For instance, the critical temperature of the LJ system is reproduced to within 5% (cf. also [11]).

V. VARIATIONAL DESCRIPTION OF THE SOLID PHASES

Although the HS solid is presumably also a good reference system for the solid phases of the DY system, we will not use it here because no analytic expressions are available to describe the HS solid, even in the PY approximation. Instead, we will use as reference system an Einstein solid characterized by the following reference Hamiltonian:

$$H_0 = \sum_{j=1}^{N}\left(\frac{1}{2m}\mathbf{p}_j^2 + \frac{k}{2}(\mathbf{r}_j - \mathbf{r}_j^0)^2\right), \tag{5.1}$$

where $(\mathbf{p}_j, \mathbf{r}_j)$ denote the momentum and position of particle j of mass m bound harmonically to the site $\mathbf{r}_j^0$. For a solid phase of the DY system of a given structure we will use an Einstein solid of the same structure, fixing hereby $\{\mathbf{r}_j^0\}$, while the value of the spring constant k will be determined variationally. In order to implement the GB inequality (2.6) with (5.1) the reference free energy per particle $f_0(\alpha, T)$ is easily computed as

$$f_0(\alpha, T) = 3k_BT \ln\left(\frac{\Lambda}{\sigma}\sqrt{\frac{\alpha}{\pi}}\right), \tag{5.2}$$

where α is a dimensionless spring constant

$$\alpha = \frac{k\sigma^2}{2k_BT}, \tag{5.3}$$

and (2.6) becomes

$$\tilde{F}(N, \alpha, T) = 3Nk_BT \ln\left(\frac{\Lambda}{\sigma}\sqrt{\frac{\alpha}{\pi}}\right) + \frac{\epsilon}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} W(x_{ij}^0; \alpha)$$
$$-\frac{3}{2}Nk_BT. \tag{5.4}$$

Here $x_{ij}^0 = |\mathbf{r}_i^0 - \mathbf{r}_j^0|/\sigma$ and $W(x_{ij}^0; \alpha)$ represents a Gaussian averaged DY potential (3.1)

$$W(x_{ij}^0; \alpha) = \int d\mathbf{x}_i \int d\mathbf{x}_j\, \varphi_\alpha(\mathbf{x}_i)\phi(x_{ij})\varphi_\alpha(\mathbf{x}_j), \tag{5.5}$$

where $x_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$, $\mathbf{x}_i = \mathbf{r}_i/\sigma$, and $\varphi_\alpha(\mathbf{x}_i)$ denotes the normalized Gaussian density profile of particle i around the site $\mathbf{r}_i^0 = \sigma\mathbf{x}_i^0$ as induced by (5.1):

$$\varphi_\alpha(\mathbf{x}_i) = \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(\mathbf{x}_i - \mathbf{x}_i^0)^2}, \tag{5.6}$$

with α still given by (5.3). If henceforth we only consider perfect solids, i.e., crystals with all sites occupied, then all sites are equivalent and the double sum of (5.4) can be written as N times a simple sum over spherical shells a distance $x_j^0 \equiv x_{j1}^0$ from the lattice site x_1^0 taken as origin $(x_1^0 = 0)$. The variational free energy per particle is then given by

$$\frac{1}{\epsilon}\tilde{f}(\bar{\rho}, t; \alpha) = \frac{3}{2}t(\ln\alpha - \ln t - 1) + t(C - \ln(6\sqrt{\pi}))$$
$$+\frac{1}{2}\sum_j{}' W(x_j^0, \alpha), \tag{5.7}$$

where the prime indicates that the origin is excluded from the sum and we have introduced the dimensionless variables (1.3) and the constant C of (4.7). Equation (5.7) has to be minimized [for a given potential (a, b, c)] with respect to α $(0 < \alpha < \infty)$ for a lattice of given density $\bar{\rho} = \rho\sigma^3$ and temperature t. If $\alpha_{\min}(\bar{\rho}, t)$ is the value of α at the minimum, our estimate of the free energy per particle of the given lattice structure is given by (2.6) as

$$f(\bar{\rho}, t) = \tilde{f}(\bar{\rho}, t; \alpha_{\min}(\bar{\rho}, t)). \tag{5.8}$$

In Fig. 3 we show how the minimum of the variational free energy $\tilde{f}$ of (5.7) is formed.

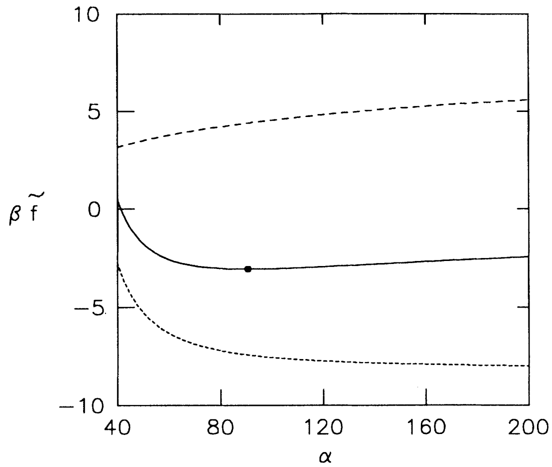

FIG. 3. The reduced variational free energy per particle, $\beta\tilde{f}$, of the (fcc) solid phase [see (5.7)] vs the variational parameter α for the $\delta = 1.34$ case at $\bar{\rho} = 0.8$ and $t = 1$ (full curve). The full dot indicates the position of $\alpha_{\min}$. Also shown are the Einstein-solid reference free energy (dashed curve) and the perturbation term (dotted curve).

For the DY potential (3.1) the expression (5.5) can be explicitly evaluated as

$$W(x; \alpha) = \frac{c}{x}\left[e^a\, E(a; \alpha; x) - e^b\, E(b; \alpha; x)\right], \tag{5.9}$$

where

$$E(y; \alpha; x) = \frac{1}{2}e^{y^2/2\alpha}\left[e^{-yx}\mathrm{erfc}\left(\frac{y - \alpha x}{\sqrt{2\alpha}}\right)\right.$$
$$\left. - e^{yx}\mathrm{erfc}\left(\frac{y + \alpha x}{\sqrt{2\alpha}}\right)\right] \tag{5.10}$$

and $\mathrm{erfc}(x) = (2/\sqrt{\pi})\int_x^\infty dt\, e^{-t^2}$. With the aid of (5.9) and (5.10), the lattice sum (5.7) can be evaluated numerically to any preassigned accuracy and the quality of the estimate given by (5.8) will depend then only on the quality of the Einstein solid as a reference system. From simulation work [15,8] and previous theoretical work [16] on different potentials it is known that the Einstein solid is a good reference system and we will hence use (5.8) here for the solid phases of the DY potential. The combination of the Einstein solid and HS fluid as reference systems also remains fairly accurate since we found [11] that it reproduces, for instance, the triple-point temperature of the LJ system to within 1%.

VI. PHASE TRANSITIONS OF DY SYSTEMS

The GB inequality (2.6) together with the HS fluid of Sec. IV and the Einstein solid of Sec. V as reference systems provide us with a convenient means to evaluate free energies of simple fluids. When the simple fluid is described by a DY potential (3.1) this method leads, moreover, to analytic expressions for the variational free energies of the fluid (4.7) and solid (5.7) phases which depend on only a single variational parameter and hence are easily minimized. This is essential when, as here, the final aim is to compute phase diagrams, which requires that the free energies be computed for many thermodynamic states and many phases. This is the more so when the physical questions are concerned with the changes which occur in the phase diagram when the potential is changed within a three-parameter family of expressions such as (3.1). As discussed already in Sec. III, the three parameters (a, b, c) of (3.1) will be reduced to two independent ones by requiring that all the potentials $\phi(x)$ have the same value, -1, at their minimum $x = x_0$, which leads to $c = c(a, b)$. This restriction is without physical consequences because changing the strength of the potential $\phi(x)$ would only amount to change the temperature scale, ϵ, of $V(r)$ in (1.1). A specification of the remaining two parameters (a, b) is equivalent to a specification of the two alternative parameters (x_0, x_1) introduced in Sec. III. The parameter of physical interest is $\delta = (x_1 - x_0)/x_0$, which is a measure of the range of the attractions relative to that of the repulsions. Some effects due to changes in x_0 can be observed but we have found these to be much weaker than the changes with respect to δ. We will thus simplify the discussion below by focusing our attention mainly on the changes induced by modifying δ. Similarly, we will restrict the variation of the thermodynamic states to those regions of the $(\bar{\rho}, t)$ plane which contain the characteristic points of the phase diagram, such as critical and triple points. Finally, besides the fluid phases, we have investigated only solid phases with a face centered cubic (fcc) structure and verified that in the regions studied the other cubic structures remained thermodynamically metastable (i.e., have a higher free energy) with respect to the fcc structure. We now study, within this restricted parameter space, the various phase transitions of the DY system.

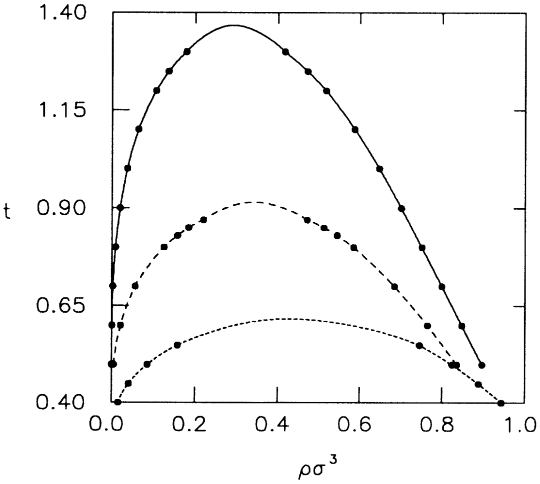

FIG. 4. The fluid-fluid coexistence curves in the t-$\bar{\rho}$ plane for the three potentials of Table I(a): $\delta = 1.34$ (full curve), $\delta = 0.79$ (dashed curve), and $\delta = 0.41$ (dotted curve). It is seen that the critical temperature decreases while the critical density increases when reducing δ.

A. The fluid-fluid transition

The free energy of a disordered translationally invariant fluid phase of a DY system can be computed as indicated in Sec. IV. The free energy $f = f(\eta, t)$ is a convex function of $1/\eta$ which for t below some critical value, t_c, develops a van der Waals loop separating the free energy of the fluid (F) into a low-density branch (F_1) and a high-density branch (F_2). Performing Maxwell's double tangent construction on such a loop one finds the low-density fluid phase F_1 and the high-density fluid phase F_2 which can coexist at the given temperature. Examples of F_1-F_2 coexistence curves obtained in this way are shown in Fig. 4. It is seen there that t_c increases with δ while the critical density $\bar{\rho}_c$ decreases. For atomic simple fluids the resulting F_1-F_2 phase transition corresponds to the gas (F_1)–liquid (F_2) transition while for the colloidal simple fluids it corresponds to the transition between two disordered phases of different density.

B. The isostructural solid-solid transition

When the free energy of a perfect crystal phase of a DY system is computed as indicated in Sec. V, a very similar behavior is found. The free energy of the solid phase (S) is again separated into a high-density branch (S_1) and a branch of lower density (S_2), corresponding hence to a more expanded solid, by a van der Waals loop. This occurs for temperatures below a critical temperature t'_c different from t_c. In particular, the changes with respect to δ are much weaker for t'_c than for t_c. The resulting S_1-S_2 transition thus ends always in a critical point (Fig. 5). This is possible because the present transition is isostructural and hence without symmetry breaking. In other words, the high-density (S_1) and low-density (S_2)

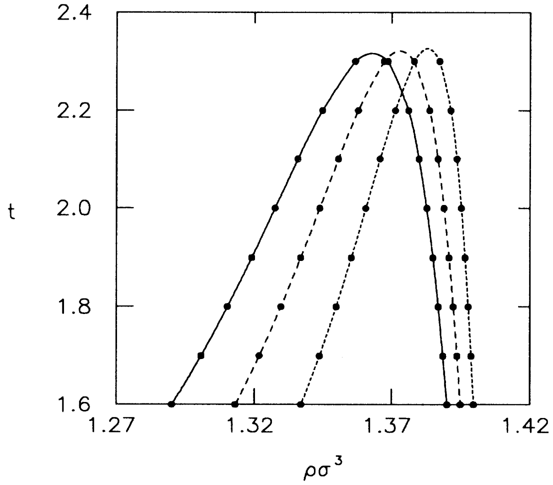

FIG. 5. The isostructural (fcc) solid-solid coexistence curves in the t-$\bar{\rho}$ plane for the three potentials of Table I(b): $\delta = 1.65\times10^{-2}$ (full curve), $\delta = 1.30\times10^{-2}$ (dashed curve), and $\delta = 1.05\times10^{-2}$ (dotted curve). It is seen that the critical density increases when reducing δ while the critical temperature remains almost constant.

solids have the same symmetry and differ only in their density. Similar results have been found in the computer simulations of Bolhuis and Frenkel [10] and in our related theoretical calculations [11,12]. This transition is different from a structural phase transition between two solids of different density and different structure, for which the symmetry breaking excludes the existence of a critical point. Notice that the word "solid" is used here in its usual sense for atomic simple fluids while for colloidal simple fluids it designs a periodic configuration of the colloidal particles. Such colloidal "crystals" have only very soft mechanical properties when compared to atomic solids. The above symmetry considerations, however, apply to both systems. Both types of systems could, in principle, exhibit both isostructural and structural phase transitions. We have made a limited number of searches for a face centered cubic (fcc) to body centered cubic (bcc) structural phase transition but found that, at least in the parameter space investigated here, the bcc structure is always metastable because it has a higher free energy than the fcc structure. Other structural transitions, such as to a hexagonal close packed structure, are still possible but these usually involve such small free-energy differences that it does not appear reasonable to investigate them within the present variational approach. Henceforth we will thus assume that there is only one stable structure for the DY solids which we take to be the fcc structure although, within the present approximation, it could be any of the compact structures.

C. The fluid-solid transition

The *total* free energy of the DY system will thus consist of a fluid branch F (consisting of two sub-branches F_1 and F_2 for $t \leq t_c$) and a solid branch S (consisting of two sub-branches S_1 and S_2 for $t \leq t'_c$). Since both the F branch and the S branch are convex functions of $1/\bar{\rho}$ it is always possible to perform a double tangent construction between these two branches. The corresponding F-S transition corresponds to the freezing-melting transition of the atomic systems or to the order-disorder transition of the colloidal dispersions. Since the two coexisting phases always have a different symmetry there can be no critical point, i.e., the transition remains first order throughout the whole density-temperature plane (Fig. 6). As such, the F-S transition will divide the density-temperature plane into a region occupied by the fluid phases and one occupied by the solid phases. When the above F_1-F_2 and S_1-S_2 transitions are situated in the "wrong" region of the density-temperature plane, they will be preempted by the F-S transition. The very position of this F-S transition thus plays a crucial role for the final outlook of the phase diagram of the DY systems.

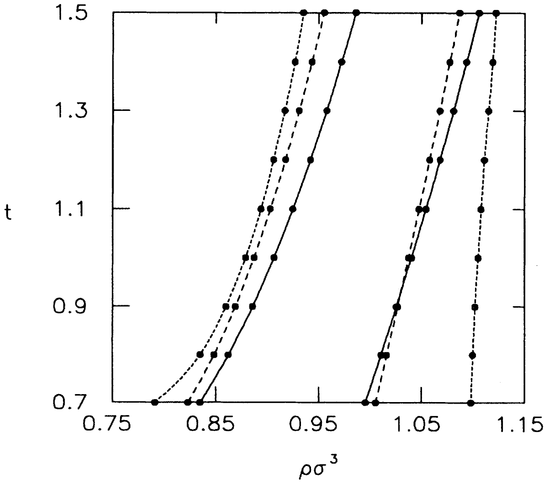

FIG. 6. The fluid–(fcc) solid coexistence curves in the t-$\bar{\rho}$ plane for the three potentials of Table I(a): $\delta = 1.34$ (full curve), $\delta = 0.79$ (dashed curve), and $\delta = 0.41$ (dotted curve). It is seen that reducing δ lowers the density of the fluid phase and increases the slope of the solid coexistence line.

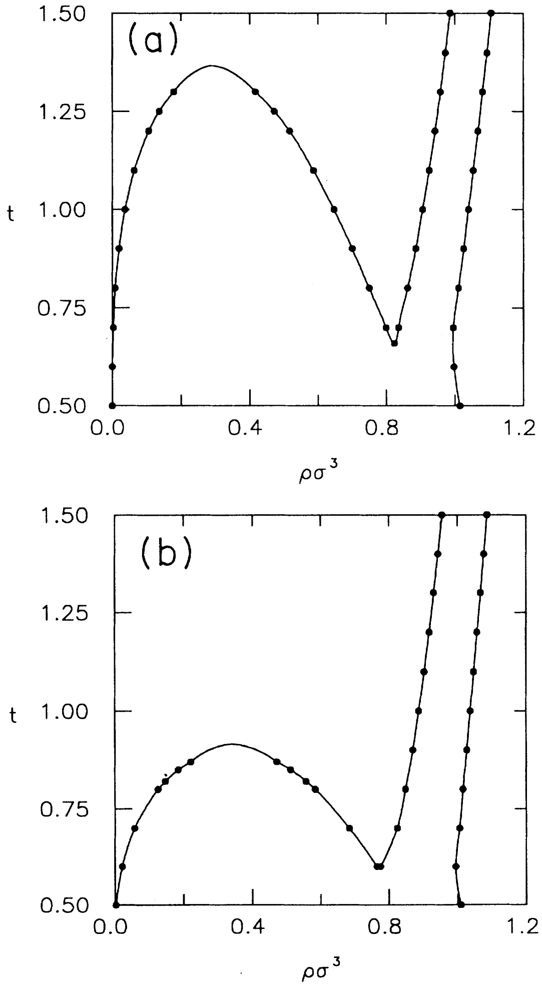

FIG. 7. The phase diagram in the t-$\bar{\rho}$ plane for (a) the $\delta = 1.34$ and (b) the $\delta = 0.79$ case. This phase diagram is typical for atomic simple fluids ($\delta \gtrsim 1$). It is seen that the major effect of reducing δ is to lower the F_1-F_2 critical point while the F_1-F_2-S triple point changes very little.

D. Phase diagrams

Knowing, for a given t value, the different free-energy branches and the location of the double tangents one can separate the stable from the metastable phase transitions by constructing the convex envelope of the total free energy. When changing moreover the value of t, the stable transitions will generate the phase diagram. In this way we have found three distinct types of phase diagram for the DY systems. As stated already above, all these diagrams must exhibit a S-F transition. In the first type of phase diagram the F_1-F_2 transition is stable while the S_1-S_2 transition is always metastable. The resulting phase diagram will hence exhibit a F_1-F_2 critical point and a F_1-F_2-S triple point. (Fig. 7). This is the situation which prevails for large δ values. It is also the situation which corresponds to (x_0, x_1) values typical of the atomic simple fluids (e.g., $\delta \geq 1$). In the second type of phase diagram both the F_1-F_2 and the S_1-S_2 transitions are always metastable with respect to the F-S transition. In such a diagram there are hence no critical or triple points (see Fig. 8). This situation prevails when the value of δ is roughly one order of magnitude smaller than the values characteristic of the atomic systems. The corresponding (x_0, x_1)-values are typical for many colloidal dispersions. Finally, in the third type of phase diagram, the F_1-F_2 transition is always metastable with respect to the F-S transition but the S_1-S_2 transition remains stable. In such a phase diagram there is hence a S_1-S_2 critical point and a F-S_1-S_2 triple point (Fig. 9). This is the situation which prevails for δ-values roughly one order of magnitude smaller than those of the previous case. Such small values of δ are outside the realm of the atomic systems but still quite realistic for the colloidal dispersions. Nev-

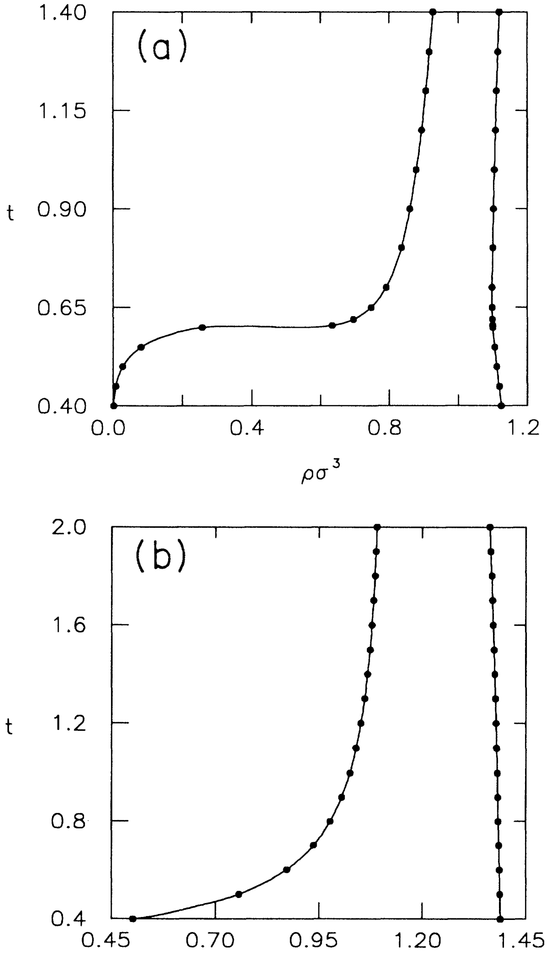

FIG. 8. The phase diagram in the t-$\bar{\rho}$ plane for (a) the $\delta = 0.41$ and (b) the $\delta = 3.28\times10^{-2}$ case. This phase diagram is typical for colloidal simple fluids with intermediate-range attractions ($\delta < 1$). The major effect of reducing δ is to lower the shoulder on the fluid side and to move the solid side of the F-S coexistence to higher densities.

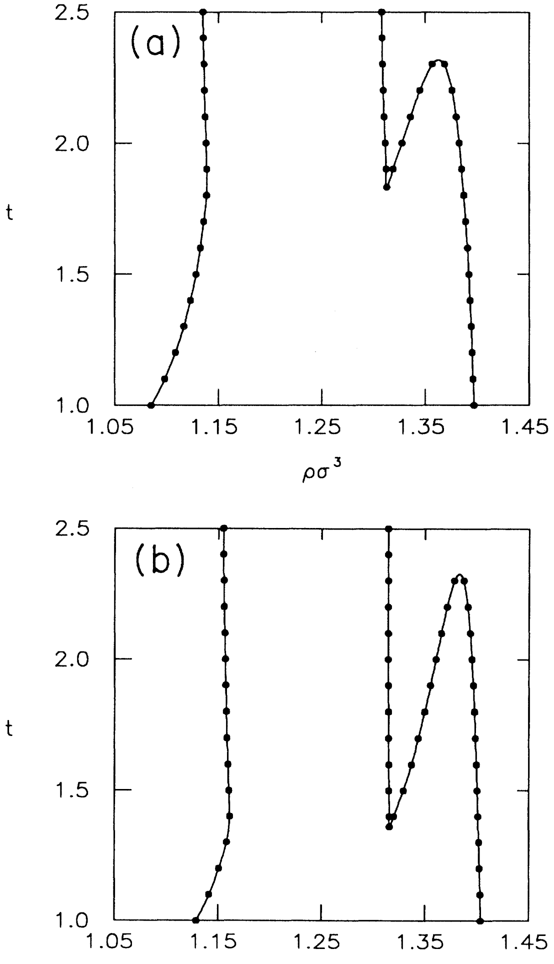

FIG. 9. The phase diagram in the t-$\bar{\rho}$ plane for (a) the $\delta = 1.65\times10^{-2}$ and (b) the $\delta = 1.05\times10^{-2}$ case. This phase diagram is typical for colloidal simple fluids with short-ranged attractions ($\delta \simeq 10^{-2}$). The major effect of reducing δ is seen to be the lowering of the F-S_1-S_2 triple-point temperature while the S_1-S_2 critical point changes very little.

ertheless, to the best of our knowledge, the corresponding S_1-S_2 transition has not yet been observed. In this respect it is important to realize that the latter transition is expected to occur in a density region where the experimental systems are easily caught into glassy configurations. Finally, it is interesting to note that when comparing the results of [9–12] it is seen that while some details do depend on the form chosen for $\phi(x)$ they all agree with respect to the location of the intermediate-δ range ($0.4 \gtrsim \delta \gtrsim 0.02$) separating the different types of phase diagram.

VII. CONCLUSIONS

We have used the double-Yukawa expression of Sec. III as a suitable means to study the effect of changes in the pair potential on the phase diagram of systems which can be described as simple fluids. In particular, we have envisaged both the ordinary atomic simple fluids and the simple fluid description of spherical colloidal particles dispersed in a host fluid to which nonadsorbing polymer, producing attractive depletion forces, has been added. The large number of free-energy estimates required to produce these phase diagrams have been obtained from a variational approach based on the Gibbs-Bogoliubov inequality of Sec. II. Combining the double-Yukawa potential with a hard-sphere reference fluid (Sec. IV) and an Einstein reference solid (Sec. V) produces analytic expressions for the variational free energies of the fluid and solid phases which are easily minimized. In this way we have found (Sec. VI) three distinct types of phase diagrams: one typical of the atomic simple fluids (Fig. 7) and two pertaining more specifically to the realm of colloidal simple fluids (Figs. 8 and 9). In particular, it was found that suitably prepared colloidal dispersions should exhibit a phase diagram with an isostructural solid-solid transition. These results are in agreement with other recent findings [10,12].

ACKNOWLEDGMENTS

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