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Density-functional theory of solid-to-solid isostructural transitions

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Abstract. We apply density-functional theory to study the expanded-FCC-to-condensed-FCC transition of a system of hard, spherical particles with a short-ranged attractive interaction, predicted recently by the simulations of Bolhuis and Frenkel. Our approach is based on a non-perturbative treatment of the repulsive hard-core part of the potential, using the modified weighted density approximation (MWDA), and a mean-field approximation for the attractive part. We confirm by means of this simple theoretical treatment the existence of an isostructural solid-to-solid transition which terminates at a critical point, in quantitative agreement with the simulation data. We obtain, within this approximation, classical critical exponents for the continuous transition.

1. Introduction

One of the most important and best known phase transitions is the freezing of a fluid into a regular crystalline lattice accompanied by a spontaneous breaking of the continuous translational symmetry. Although many empirical facts have accumulated during the last century, it is only since the last decades that microscopic aspects of freezing have been studied [1].

The best way to get a direct theoretical insight into the molecular freezing mechanism is to consider very simple models which exhibit freezing and melting. The most simple system is that of hard spheres, i.e. a classical many-particle system whose interaction is governed solely by an excluded spherical volume around each particle. Since the Boltzmann factor of hard spheres is independent of temperature, their phase diagram depends only on their number density ρ . Computer-simulation studies show that there is a first-order freezing transition from a fluid with density $\rho_f\sigma^3 = 0.94$ to an FCC-crystalline solid with density $\rho_s\sigma^3 = 1.04$, σ being the hard-sphere diameter. The hard-sphere system is entirely governed by entropy, hence freezing turns out to be dominated by packing effects. Computer simulations have also revealed that other classical systems characterized by a spherically symmetric pair potential $v(r)$ exhibit freezing. The current view is that freezing is induced by the repulsive core of the interaction while details of the transition (such as the structure of the crystalline lattice and the exact location of the melting line) are triggered by energy, i.e. by the softness of the core and by the attractive part of $v(r)$. For soft interactions (e.g. inverse-power-law and repulsive Yukawa potentials) a BCC solid is thermodynamically stable and solid-to-solid transitions from an FCC to a BCC structure are possible [2]. Based on computer simulations, Bolhuis and Frenkel [3] recently reported another *isostructural*

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solid-to-solid transition for hard spheres with a very short-ranged attractive interaction. In the temperature–pressure diagram these transitions form a first-order line between two FCC crystals with different lattice constants which terminates at a critical point of two solid phases.

In constructing microscopic theories of freezing based on classical statistical mechanics considerable progress was made using *density-functional methods*, which are based on the fluid state and view freezing as a condensation of fluid density modes. Different approximations of the free-energy density functional have been proposed, for a review see [4]. As a non-trivial reference system, hard-sphere freezing is obtained without any parameter fitting, and quantitative agreement between theory and simulation is achieved. Among the best approximations are the non-perturbative weighted-density approximation [5] (WDA), and a modified weighted-density approximation [6] (MWDA), by Ashcroft and co-workers. Frequently the treatment of more complicated potentials $v(r)$ is done via thermodynamic perturbation theory around a hard-sphere reference system. This approach has been successfully applied to a Lennard-Jones interaction [7, 8].

In this paper we present a density-functional theory for the isostructural solid-to-solid transition discovered by Bolhuis and Frenkel [3], for systems composed of particles which interact by means of a hard-sphere plus a short-range attractive square-well potential. A theoretical study of similar systems by Tejero *et al* has also recently been published [9], but the pair potential in this case was taken to be of a double Yukawa form which, for different choices of the Yukawa parameters, can model long-range potentials (such as Lennard-Jones [10]) as well as short-range ones. We use hard spheres as a reference system treating them with the MWDA. The attractive part of the potential is approximated by a simple mean-field approach. Within this theory we confirm the isostructural solid-to-solid transition quantitatively. Taking the capability of the theory for granted, we predict the location of the point at which the solid–solid coexistence disappears altogether, because it is always preempted by the melting transition. Within our theory we find that the critical exponents are classical. Our theory has the further advantage of being relatively simple, and numerically less involved than a direct simulation. We remark that it is the first density-functional theory which predicts isostructural solid-to-solid transitions in simple systems. There have been density-functional studies on sticky hard spheres which however did not focus on solid-to-solid transitions [11] and on solid-to-solid transitions in Yukawa systems [12] where, however, a change in the crystalline structure occurs.

The rest of the paper is organized as follows. In section 2 we describe the method and approximations used to study the problem. In section 3 we present the results, compare them with simulation data [3], and discuss the features of the obtained phase diagrams. Finally, in section 4 we propose ways to improve upon the theory presented in the paper, and conclude.

2. Theory

Following Bolhuis and Frenkel [3], we consider a system of spherical particles with a hard-sphere repulsive core and a short-range attraction, the latter being modelled by a square-well potential. Thus, the interparticle potential is taken to have the form

$$v(r) = \begin{cases} \infty & 0 \leq r < \sigma \\ -\varepsilon & \sigma \leq r < \sigma + \delta \\ 0 & r \geq \sigma + \delta. \end{cases} \quad (1)$$

In (1), σ is the hard-sphere diameter, δ is the width of the attractive potential, and $-\varepsilon$ is its depth ($\varepsilon > 0$). Our goal is to investigate the phase diagram of a system with an interaction given by (1) for the case of a short-range attraction, for which Bolhuis and Frenkel [3] have discovered the existence of an isostructural FCC-to-FCC transition at low temperatures. The strategy we follow is to separate the interaction (1) into a hard-sphere repulsion and an attractive part, and treat the former by means of density-functional theory (DFT), and the latter in the mean-field approximation (MFA). The most natural partition of the interaction (1) is to write

$$v(r) = v_0(r) + \phi(r) \quad (2)$$

where

$$v_0(r) = \begin{cases} \infty & 0 \leq r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (3)$$

is the hard-sphere (HS) interaction, and

$$\phi(r) = \begin{cases} 0 & 0 \leq r < \sigma \\ -\varepsilon & \sigma \leq r < \sigma + \delta \\ 0 & r \geq \sigma + \delta \end{cases} \quad (4)$$

is the attractive part. Our starting point is the Gibbs–Bogoliubov inequality [13], which states that the Helmholtz free energy F of a system characterized by the interparticle interaction v can be related to that of a reference system having interaction v_0 by

$$F \leq F_0 + \langle v - v_0 \rangle_0. \quad (5)$$

In equation (5), F_0 is the Helmholtz free energy of the reference system, and $\langle \mathcal{O} \rangle_0$ denotes the thermodynamic average of the quantity \mathcal{O} in the Hamiltonian of the *reference* system. Choosing the HS interaction as the reference Hamiltonian, and applying equation (5) for a uniform (homogeneous) fluid, we obtain

$$F(\rho_1) \leq F_0(\rho_1) + \frac{1}{2} N \rho_1 \int g_0(r; \rho_1) \phi(r) dr \quad (6)$$

where N is the number of particles in the specified volume V , $\rho_1 = N/V$ is the number density, and $g_0(r; \rho_1)$ is the radial distribution function [13] of the reference (HS) system. On the other hand, a crystalline solid is characterized by a *strongly non-uniform* one-particle density, $\rho(\mathbf{r})$. According to the basic theorem of density-functional theory [14], the Helmholtz free energy of a non-uniform (inhomogeneous) system is a *unique functional* of the one-particle density, $F = F[\rho(\mathbf{r})]$. Applying the Gibbs–Bogoliubov inequality to this case, we obtain

$$F[\rho(\mathbf{r})] \leq F_0[\rho(\mathbf{r})] + \frac{1}{2} \int g_0^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho(\mathbf{r})]) \rho(\mathbf{r}) \rho(\mathbf{r}') \phi(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} d\mathbf{r}' \quad (7)$$

where $g_0^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho(\mathbf{r})])$ is the pair distribution function of the solid, which is also a unique functional of the one-particle density [14]. We can also write $g_0 = h_0 + 1$, for both uniform and non-uniform phases, introducing the pair correlation function h_0 .

The Gibbs–Bogoliubov inequality is used in most cases in a variational sense: on the right-hand side, one or more variational parameters are introduced, and these are varied until an optimal upper bound for the sought-for Helmholtz free energy is obtained. A usual variational parameter is the diameter of the reference HS interaction, for example. However, we do not have this freedom here, since the partition of the potential is determined by the potential parameters uniquely (equations (2)–(4)). Thus, as a first approximation, we treat the Gibbs–Bogoliubov inequality as an *equality*, i.e. we introduce the approximations

$$F(\rho_1) \approx F_0(\rho_1) + \frac{1}{2}N\rho_1 \int \phi(r) dr + \frac{1}{2}N\rho_1 \int h_0(r; \rho_1)\phi(r) dr \quad (8)$$

for the homogeneous phase, and

$$F[\rho(\mathbf{r})] \approx F_0[\rho(\mathbf{r})] + \frac{1}{2} \int \rho(\mathbf{r})\rho(\mathbf{r}')\phi(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} d\mathbf{r}' \\ + \frac{1}{2} \int h_0^{(2)}(\mathbf{r}, \mathbf{r}'; [\rho(\mathbf{r})])\rho(\mathbf{r})\rho(\mathbf{r}')\phi(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} d\mathbf{r}' \quad (9)$$

for the inhomogeneous one. The last term in equations (8) and (9) describes the effect on the internal energy from the correlations that arise due to HS repulsions alone. As a last approximation, (which greatly simplifies the implementation of the theory), we treat the attractive part in the mean-field approximation, i.e. we completely ignore this last term for both the liquid and the solid. Thus, our final approximation reads

$$F(\rho_1) = F_0(\rho_1) + \frac{1}{2}N\rho_1 \int \phi(r) dr \quad (10)$$

for the liquid, and

$$F[\rho(\mathbf{r})] = F_0[\rho(\mathbf{r})] + \frac{1}{2} \int \rho(\mathbf{r})\rho(\mathbf{r}')\phi(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} d\mathbf{r}' \quad (11)$$

for the solid. An alternative derivation of equations (8) and (9) is given in the appendix [15].

For the liquid phase, the excess free energy per particle of the HS reference system is given very accurately by the Carnahan–Starling equation of state [16]. To this, we have to add the ideal-gas term, and the MFA term, to obtain

$$\frac{\beta F(\rho_1)}{N} = \ln(\rho_1\sigma^3) - 1 + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} - \frac{2\pi\epsilon\rho_1\sigma^3}{3k_B T} \left[(1 + \delta/\sigma)^3 - 1 \right] + 3 \ln(\Lambda/\sigma) \quad (12)$$

where T is the temperature, $\eta = \pi\rho_1\sigma^3/6$ is the packing fraction of the HS liquid, and Λ is the thermal de Broglie wavelength. (The last term in (12), being identical at a given temperature for both liquid and solid phases, does not affect the comparisons between those, and will be henceforth ignored.)

For the solid having average density $\rho_s = N/V$, we shall adopt a usual (and accurate) parametrization for the one-particle density $\rho(\mathbf{r})$, and model this quantity as a sum of isotropic Gaussians centred around lattice sites, i.e.

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\{\mathbf{R}\}} \exp\{-\alpha(\mathbf{r} - \mathbf{R})^2\} \quad (13)$$

where $\{\mathbf{R}\}$ is the set of lattice vectors of the given Bravais lattice. The limit $\alpha \rightarrow 0$ corresponds to completely delocalized Gaussians, and it will be taken to correspond to the uniform liquid, whereas the Gaussians become more and more localized as α grows. Denoting by $\rho_{\mathbf{K}}$ the Fourier components of $\rho(\mathbf{r})$, and by $\mu_{\mathbf{K}} \equiv \rho_{\mathbf{K}}/\rho_s$ the dimensionless Fourier components, the parametrization (13) immediately implies

$$\mu_{\mathbf{K}} = e^{-K^2/4\alpha} \quad (14)$$

where $\{\mathbf{K}\}$ is the set of reciprocal lattice vectors (RLVs) of the given lattice, and $K \equiv |\mathbf{K}|$. The ideal part of the free energy of the solid is known exactly, and it is given by the expression

$$\frac{\beta F_0^{\text{id}}}{N} = \frac{1}{N} \int \rho(\mathbf{r}) \left[\ln(\rho(\mathbf{r})\sigma^3) - 1 \right] d\mathbf{r} + 3 \ln(\Lambda/\sigma). \quad (15)$$

For the excess free energy of the non-uniform system, we adopt the modified weighted density approximation (MWDA) of Denton and Ashcroft [6], which is known to give excellent results for HS systems, and which is computationally straightforward. Denoting by $f_1(\rho)$ the free energy per particle of the uniform system at density ρ , the MWDA approximates the excess free energy of the *non-uniform* system by that of a *uniform* system, but evaluated at a specified *weighted density* $\hat{\rho}$, i.e.

$$\beta F_0^{\text{ex}}[\rho(\mathbf{r})] = N f_1(\hat{\rho}). \quad (16)$$

The weighted density $\hat{\rho}$ is evaluated self-consistently as a weighted average over $\rho(\mathbf{r})$; in the Gaussian approximation, $\hat{\rho}$ is determined by solving the implicit equation

$$\hat{\rho}(\rho_s, \alpha) = \rho_s \left[1 - \frac{1}{2\beta f_1'(\hat{\rho})} \sum_{\mathbf{K} \neq 0} e^{-K^2/2\alpha} c_0^{(2)}(\mathbf{K}; \hat{\rho}) \right] \quad (17)$$

where $c_0^{(2)}$ stands for the direct correlation function (DCF) of the uniform liquid. We implement equations (16) and (17) to determine the excess free energy of the HS system for a given density ρ_s and localization. For the excess free energy per particle of the liquid, we adopt again the CS expression, and we use the associated Verlet–Weis [17] parametrization for the direct correlation function.

Finally, the MFA internal energy U of the FCC solid (the second term in the RHS of equation (11)) is most easily evaluated in Fourier space, where the double integral turns into a sum over the RLVs of the lattice, yielding the expression

$$\frac{\beta U}{N} = \frac{\rho_s \sigma^3}{2} \sum_{\mathbf{K}} e^{-K^2/2\alpha} \beta \tilde{\phi}(\mathbf{K}) \quad (18)$$

where

$$\tilde{\phi}(\mathbf{K}) = \frac{4\pi}{K\sigma^3} \int_0^\infty r \sin(Kr) \phi(r) dr. \quad (19)$$

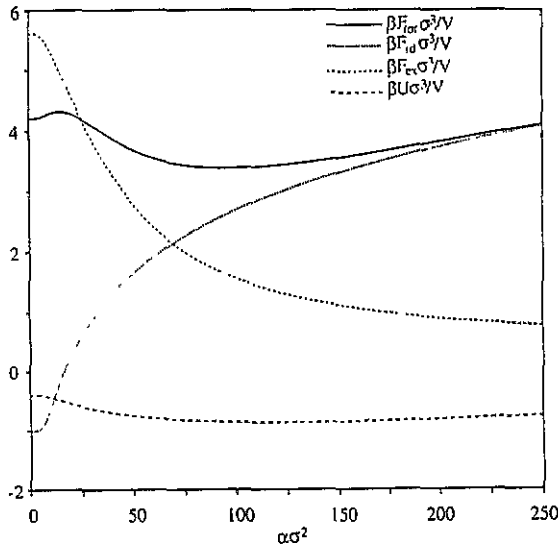


Figure 1. Ideal free energy F_{id} , excess free energy F_{ex} , MFA internal energy U at temperature $k_B T/\varepsilon = 1.0$, and total free energy F_{tot} per unit volume V of an FCC solid against the localization parameter $\alpha\sigma^2$. The values of the parameters are here $\rho_s\sigma^3 = 1.00$ for the average density, and $\delta = 0.06$ for the range of the attractive part of the potential. The competition between the three terms results in a minimum for the total free energy for a non-zero value of the localization parameter.

The total free energy of the FCC solid is the sum of the ideal, excess, and Mean-Field parts. For any given average solid density $\rho_s\sigma^3$, this sum has to be minimized with respect to the localization parameter α . In figure 1, we show the typical behaviour of F_{id} , F_{ex} , and U as functions of the localization parameter. An important point is that the very dense FCC solids which we have to consider in order to investigate the possibility of isostructural transitions are characterized by an extremely high value of the localization parameter. Typically, $\alpha_{min}\sigma^2$ is of the order of several thousands for $\rho_s\sigma^3 > 1.25$; (cf. $\alpha_{min}\sigma^2 \sim 100$ for freezing). This means that in order to achieve a minimum of the total free energy, the MWDA as well as the MFA calculations have to be carried out for very high α values, and in order to guarantee the convergence of the RLV sums for both of them (equations (17) and (18)), a large number of RLVs has to be included in the sums. We have included up to 1850 shells of RLVs in our calculations, a number which turns out to be sufficient to guarantee the convergence for the range of densities and temperatures considered here.

Having developed the approximations to obtain the Helmholtz free energy of the uniform and non-uniform phases for any value of the thermodynamic density, the coexistence parameters of the model are then determined by means of the well known common-tangent construction.

3. Results and discussion

We have considered the values $\delta/\sigma = 0.04, 0.06, 0.08$, and 0.09 . It will be shown that the first three are small enough for the phase diagram to display an FCC–FCC coexistence which is *not* preempted by the melting transition (i.e. the triple temperature for the liquid–FCC–FCC

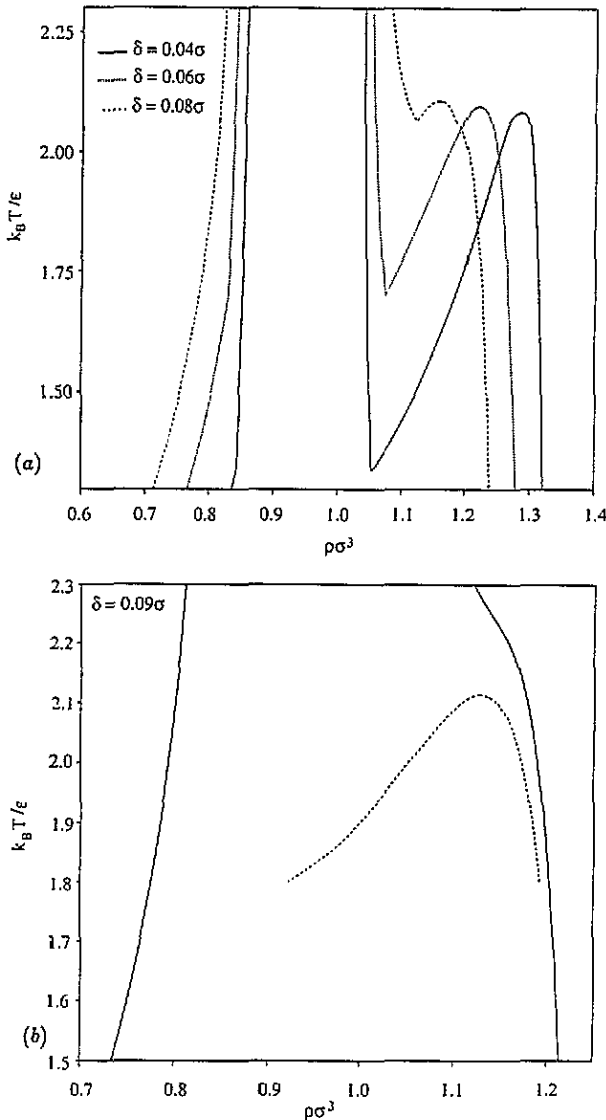


Figure 2. Theoretical predictions for the phase diagrams of square-well systems (a) for $\delta/\sigma = 0.04, 0.06,$ and $0.08,$ and (b) for $\delta/\sigma = 0.09.$ For the latter case, we also show the 'solid-solid coexistence curves' obtained by performing the common-tangent construction on the solid curves *alone* (the dashed lines). Clearly, the solid-solid transition is preempted by melting in this case, and thus it never materializes.

coexistence is lower than the critical temperature of the FCC-FCC coexistence), whereas in the latter case the opposite is true. We have not considered even smaller values of δ/σ (for which Bolhuis and Frenkel have carried out simulations [3]), since for these cases the coexisting solids are very dense, the localization parameter (especially at low temperatures) is *extremely high*, and therefore a very large number of RLVs must be included in the MWDA and MFA summations, thus making the calculation very expensive, without offering any new insights.

In figure 2(a), we show the obtained phase diagrams (in the temperature-density plane)

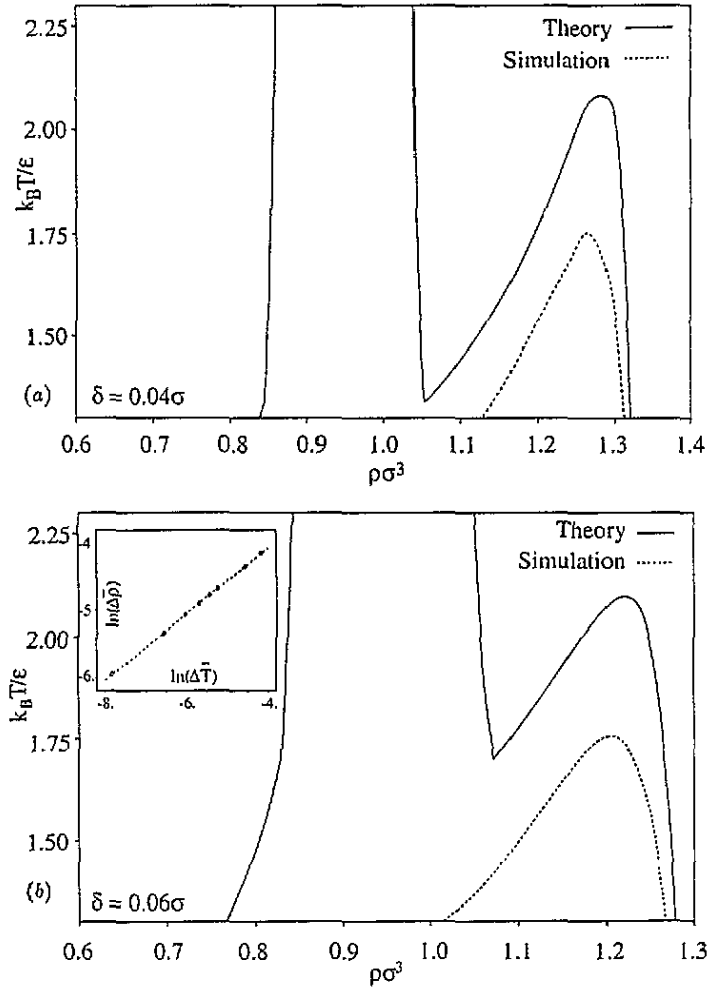


Figure 3. Theoretical (this work) against simulation [3] results for the coexistence curves. (a) $\delta/\sigma = 0.04$, and (b) $\delta/\sigma = 0.06$. Inset: log-log plot of the deviations of the density from ρ_c against the deviations of the temperature from T_c , for $\delta/\sigma = 0.06$. Here $\bar{\rho} \equiv \rho\sigma^3$, $\bar{T} \equiv k_B T/\epsilon$, $\Delta\bar{\rho} = \bar{\rho} - \bar{\rho}_c$, and $\Delta\bar{T} = \bar{T} - \bar{T}_c$. The data are fitted by a straight line having slope $0.49 \approx 1/2$ (the dashed line), indicating a value $\beta = 1/2$ for the critical exponent.

for the choices $\delta/\sigma = 0.04, 0.06$, and 0.08 . It can clearly be seen that an isostructural FCC-to-FCC transition does take place. The separation of the triple from the critical temperature becomes smaller with increasing δ , until it eventually disappears for $\delta/\sigma \gtrsim 0.08$. This estimate is obtained by considering that (a) for $\delta/\sigma = 0.08$ the two temperatures are already very close, and (b) for $\delta/\sigma = 0.09$ the FCC-to-FCC transition is readily preempted by the melting one, and the phase diagram consists of simply two phases, namely the uniform liquid and the FCC solid (see figure 2(b)). It must be emphasized that no liquid-gas transition has been found for these values of δ , within the framework of this approach. On the other hand, it is a well known fact that for long-range attractions (large δ) a coexistence between two uniform phases does occur. (Of course, in this case there is no solid-solid transition.) Thus, the phase diagram evolves from a picture with just one fluid phase and two isostructural coexisting FCC solids for small δ , to a single fluid and a single solid for intermediate δ to

the usual case of two fluid phases and one solid phase for large values of δ .

In figure 3, we show again our results, but now we put on the same plots the simulation data of Bolhuis and Frenkel [3]. It can be seen that our mean-field approach has the usual characteristics of all mean-field theories: the critical temperature T_c is overestimated (by about 17%). However, the critical density ρ_c is rather insensitive to the approximation. Unfortunately, no simulation data are available for the triple temperature T_t , so a comparison cannot be made at present. Nevertheless, we expect that the triple temperature from our MFA is not too far from the true one, and in particular that the deviation for T_t is smaller than for the T_c . The reason is that at T_t the fluctuations, which are ignored in the MFA, and which are responsible for the overestimation of T_c , are much more strongly suppressed than at criticality. We have also calculated the critical exponent β defined by the scaling relation $(\rho - \rho_c) \sim (T - T_c)^\beta$ for T close to T_c , obtaining the classical exponent $\beta = 1/2$. (See figure 3(b), inset.)

Other than the expected overestimation of T_c , it can be seen from figures 2 and 3 that the theory reproduces all the qualitative and quantitative features of the simulations. A summary of the results is given in table 1, where also a comparison is made for the critical density with the simulations [3] and the predictions from the cell model [3]. Referring to figures 2, 3, and to the entries of table 1, the following remarks can be made.

(i) The critical temperature T_c is rather insensitive to the range of the interaction δ , and it shows a slight decrease as δ is lowered.

(ii) The shape of the FCC–FCC coexistence lines is asymmetric, and this asymmetry becomes stronger for smaller δ , i.e. as the right part of the coexistence curves approaches the close-packing limit. The theoretical curves also reproduce the ‘shifting’ of the coexistence curves to the right, as well as the ‘narrowing’ of the typical width of the curves as δ decreases.

(iii) The critical density ρ_c is very close to the simulation result, albeit also slightly overestimated by the theory. It is particularly interesting that the actual simulation result is for the cases considered here intermediate between the MFA value and the prediction of the cell model, $\rho_c \sigma^3 = \rho_0 \sigma^3 (1 + \delta/\sigma)^{-3}$, where $\rho_0 \sigma^3 = \sqrt{2}$ is the close-packing limit of the density.

(iv) Within the range of δ which we have examined, the dependence of the triple temperature as well as the critical temperature on δ is linear. In fact, if we define $\bar{T} \equiv k_B T/\varepsilon$, and $\bar{\delta} \equiv \delta/\sigma$, then the results shown in table 1 can be fitted by straight lines as follows:

$$\bar{T}_t = 18.2\bar{\delta} + 0.60867 \quad (20)$$

and

$$\bar{T}_c = 0.575\bar{\delta} + 2.06017. \quad (21)$$

From equations (20) and (21) above, we can readily obtain an estimate for the ‘critical’ value δ_* for which the triple temperature is equal to the critical temperature, and thus for $0 < \delta < \delta_*$ there is a solid–solid coexistence and a single fluid phase, whereas for $\delta > \delta_*$ the solid–solid coexistence is preempted by melting. In addition, for $\delta_* < \delta \lesssim \sigma/3$, there is only one fluid phase [3], and thus the phase diagram consists of just one fluid and one solid phase in this range. This value is predicted to be

$$\delta_*/\sigma = 0.08235 \quad (22)$$

within the framework of our theory. In reality, this value must be somewhat smaller since, as we argued above, the critical temperature is overestimated in our theory by an amount which is larger than that for the triple temperature.

Table 1. The triple temperature T_t , critical temperature T_c , and critical density ρ_c for the FCC-FCC transition predicted by this work, for different values of δ . For the last quantity, we also show the results from simulation, and the predictions of the cell model, for comparison.

	$k_B T_t / \varepsilon$	$k_B T_c / \varepsilon$	$(\rho_c \sigma^3)^a$	$(\rho_c \sigma^3)^b$	$(\rho_c \sigma^3)^c$
$\delta / \sigma = 0.04$	1.337	2.083	1.289	1.265	1.257
$\delta / \sigma = 0.06$	1.700	2.095	1.219	1.205	1.187
$\delta / \sigma = 0.08$	2.065	2.106	1.155	—	1.122

^a This work.

^b Simulation results (figure 2 in [3]).

^c Prediction of the cell model: $\rho_c \sigma^3 = \sqrt{2}(1 + \delta/\sigma)^{-3}$ (see [3]).

4. Conclusions

We have presented a simple density-functional theory of solid-to-solid isostructural transitions, which confirms the existence of the expanded-to-condensed FCC transition terminating at a critical point, and is in quantitative agreement with the predictions from the simulations. The existence of the transition is clearly due to the attractive part of the interaction, which is treated in the mean-field approximation in our theory. A straightforward improvement of the theory, which should improve the estimate of the critical temperature, would be, therefore, the inclusion of the correlation effects (the last terms in equations (8) and (9)) which we have ignored in this approach. Moreover, as a further improvement, we can treat *the full interaction* in a non-perturbative fashion, without any splitting into a hard-sphere and an attractive interaction. Indeed, most non-perturbative density-functional approaches are based on a *thermodynamic mapping of the solid phase into a homogeneous phase* at the same temperature, but having a 'coarse-grained' weighted density. The main problem in the implementation of such theories in systems with attractive, *long-range* potentials (e.g. Lennard-Jones) is that the fluid phase displays, below the liquid-gas critical temperature, a spontaneous separation into a dense liquid and a dilute gas, and in this region the thermodynamic functions of the fluid are not well defined. However, the systems with a *short-range* attraction are free of such difficulties, since a *single* fluid phase exists, and the mapping is, at least in principle, possible. We plan to return to these approaches in the *near future*.

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Appendix

Equations (8) and (9) of the main text can also be derived without reference to the Gibbs-Bogoliubov inequality. This follows directly from the fact that the equilibrium two-particle density of any system is related to the functional derivative of the excess Helmholtz free energy with respect to the interaction potential by [14]

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta F^{\text{ex}}[\rho(\mathbf{r})]}{\delta v(\mathbf{r}, \mathbf{r}')} \quad (\text{A1})$$

We now choose a one-parameter integration path:

$$v_\alpha \equiv v(\mathbf{r}, \mathbf{r}', \alpha) = v_0(\mathbf{r}, \mathbf{r}') + \alpha(v(\mathbf{r}, \mathbf{r}') - v_0(\mathbf{r}, \mathbf{r}')) \quad (\text{A2})$$

where v_0 is a reference potential (the hard-sphere interaction in our case), and the parameter α varies from zero to unity. With this choice, equation (A1) can be functionally integrated to give

$$F[\rho(\mathbf{r})] = F_0[\rho(\mathbf{r})] + \frac{1}{2} \int_0^1 d\alpha \int \int \rho^{(2)}(v_\alpha; \mathbf{r}, \mathbf{r}') (v(\mathbf{r}, \mathbf{r}') - v_0(\mathbf{r}, \mathbf{r}')) d\mathbf{r} d\mathbf{r}' \quad (\text{A3})$$

where $\rho^{(2)}(v_\alpha; \mathbf{r}, \mathbf{r}')$ is the two-body density corresponding to the interaction v_α . Clearly, the quantity $v(\mathbf{r}, \mathbf{r}') - v_0(\mathbf{r}, \mathbf{r}')$ in (A3) is just the attractive part $\phi(|\mathbf{r} - \mathbf{r}'|)$ of the potential. Now we make the following approximation: we replace the two-particle density $\rho^{(2)}(v_\alpha; \mathbf{r}, \mathbf{r}')$ by the distribution at the *reference* interaction:

$$\rho^{(2)}(v_\alpha; \mathbf{r}, \mathbf{r}') \approx \rho^{(2)}(v_0; \mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')(1 + h_0^{(2)}(\mathbf{r}, \mathbf{r}')). \quad (\text{A4})$$

Now the α integration in (A3) is trivial, and we obtain equation (9) of the main text for the non-uniform phase, and equation (8) for the uniform one.

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