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

C N Likos, Zs T Németh† and H Löwen

Sektion Physik der Ludwig-Maximilians Universität München, Theresienstraße 37, D-80333 München, Germany

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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

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

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

$$v(r) = v_0(r) + \phi(r) \tag{2}$$

where

$$v_0(r) = \begin{cases} \infty & 0 \leqslant r < \sigma \\ 0 & r \geqslant \sigma \end{cases} \tag{3}$$

is the hard-sphere (HS) interaction, and

$$\phi(r) = \begin{cases} 0 & 0 \leqslant r < \sigma \\ -\varepsilon & \sigma \leqslant r < \sigma + \delta \\ 0 & r \geqslant \sigma + \delta \end{cases} \tag{4}$$

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

$$F \leqslant F_0 + \langle v - v_0 \rangle_0. \tag{5}$$

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) f

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

$$F(\rho_l) \approx F_0(\rho_l) + \frac{1}{2}N\rho_l \int \phi(r)\,\mathrm{d}\boldsymbol{r} + \frac{1}{2}N\rho_l \int h_0(r;\rho_l)\phi(r)\,\mathrm{d}\boldsymbol{r} \tag{8}$$

for the homogeneous phase, and

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

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

$$F(\rho_l) = F_0(\rho_l) + \frac{1}{2}N\rho_l \int \phi(r)\,\mathrm{d}\boldsymbol{r} \tag{10}$$

for the liquid, and

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

where $\{\boldsymbol{R}\}$ is the set of lattice vectors of the given Bravais lattice. The limit $\alpha \to 0$ 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 ρ_K the Fourier components of $\rho(\boldsymbol{r})$, and by $\mu_K \equiv \rho_K/\rho_s$ the dimensionless Fourier components, the parametrization (13) immediately implies

$$\mu_K = \mathrm{e}^{-K^2/4\alpha} \tag{14}$$

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

$$\frac{\beta F_0^{\mathrm{id}}}{N} = \frac{1}{N}\int \rho(\boldsymbol{r})\Big[\ln(\rho(\boldsymbol{r})\sigma^3) - 1\Big]\,\mathrm{d}\boldsymbol{r} + 3\ln(\Lambda/\sigma). \tag{15}$$

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.

$$\beta F_0^{\mathrm{ex}}[\rho(\boldsymbol{r})] = N f_1(\hat{\rho}). \tag{16}$$

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

$$\hat{\rho}(\rho_s, \alpha) = \rho_s\Big[1 - \frac{1}{3\cdot 2^3\pi^3}\sum \mathrm{e}^{-K^2/2\alpha}c_0^{(2)}(\boldsymbol{K};\hat{\rho})\Big] \tag{17}$$

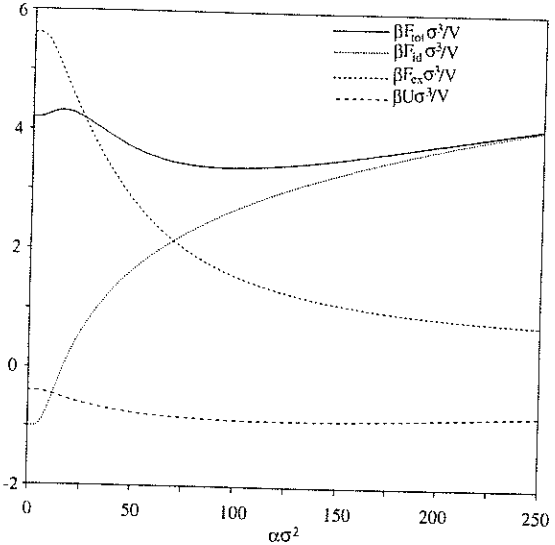
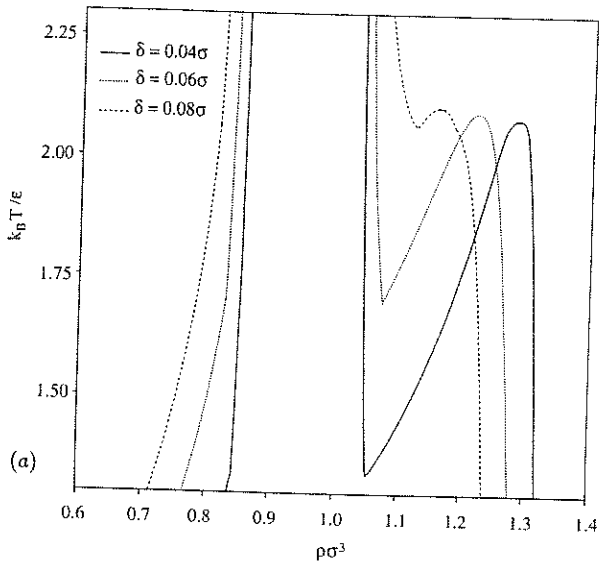
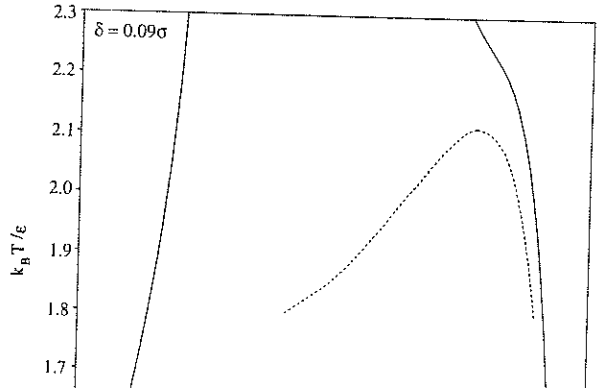
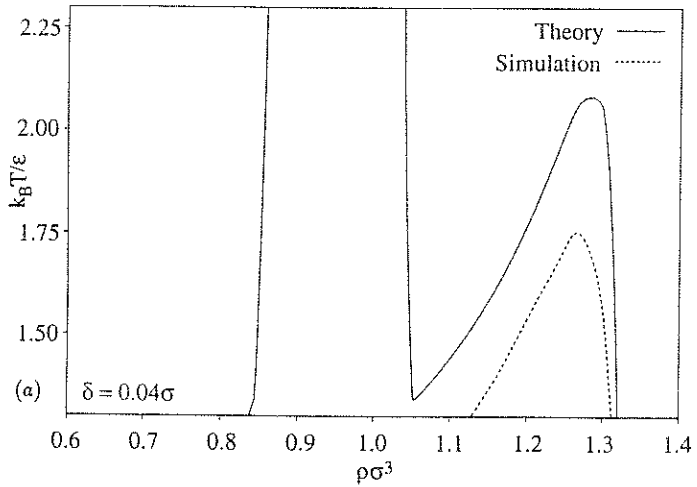


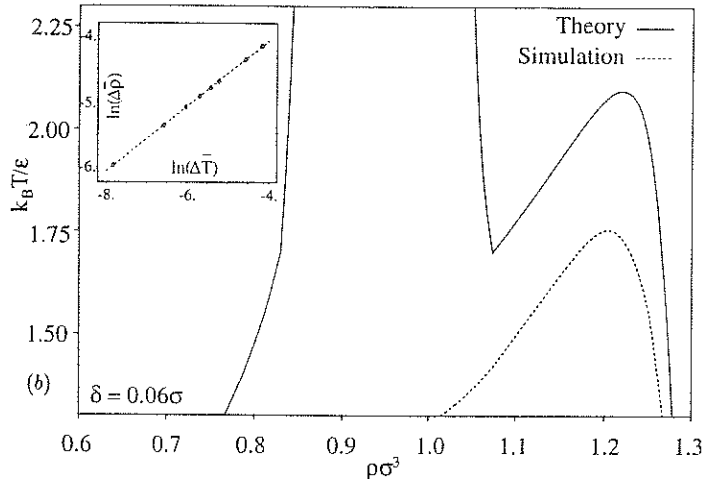
Figure 1. Ideal free energy F_{id}, excess free energy F_{ex}, MFA internal energy U at temperature $k_BT/\varepsilon = 1.0$, and total free energy F_{tot} per unit volume V of an FCC solid against the localization parameter $\alpha\sigma^2$. The values of the parameters are here $\rho_s\sigma^3 = 1.00$ 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_0^{id}, F_0^{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 localizati


δ = 0.04σ
δ = 0.06σ
δ = 0.08σ
2.25
2.00
1.75
1.50
$k_B T/\epsilon$
(a)
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
$\rho\sigma^3$


δ = 0.09σ
2.3
2.2
2.1
2.0
1.9
1.8
1.7
$k_B T/\epsilon$


Theory
Simulation
2.25
2.00
1.75
1.50
k_BT/ϵ
(a)
$\delta = 0.04\sigma$
0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4
$\rho\sigma^3$


Theory
Simulation
2.25
2.00
1.75
1.50
k_BT/ϵ
(b)
$\delta = 0.06\sigma$
$\ln(\Delta\bar{p})$
$\ln(\Delta\bar{T})$
-4.
-5.
-6.
-8.
-6.
-4.
0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3
$\rho\sigma^3$

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 slopes of the coexistence

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

We now choose a one-parameter integration path:

$$v_\alpha \equiv v(\boldsymbol{r}, \boldsymbol{r}', \alpha) = v_0(\boldsymbol{r}, \boldsymbol{r}') + \alpha(v(\boldsymbol{r}, \boldsymbol{r}') - v_0(\boldsymbol{r}, \boldsymbol{r}')) \tag{A2}$$

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

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

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

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

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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