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COMMENT

Comment on 'Density-functional theory of solid-to-solid isostructural transitions'

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Abstract. In a recent paper Likos *et al* apply the mean-field approximation to study the phase diagram of simple classical systems with extremely short-ranged attractive interactions. We show in this comment that the mean-field approximation gives rise to important quantitative and qualitative errors in this problem.

In a recent paper Likos *et al* [1] have presented a density-functional theory of the novel isostructural solid-to-solid transition in simple systems with extremely short-ranged attractive interactions [2]. Their theory is a standard first-order perturbation theory where the attractive contribution to the free energy has been further simplified by writing the reference system radial distribution function (rdf) as a step function. In summary, they write the following Helmholtz free energy expression:

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

for the liquid phase. N is the number of particles, ρ_l is the liquid density, $\varphi_p(r)$ is the attractive part of the potential, $F_0(\rho_l)$ is the free energy of the reference system which is in this case a uniform HS system whose free energy is accurately given by the Carnahan–Starling equation of state. For the solid phase they write

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

where the reference system is now a non-uniform HS system whose free energy is a density functional which Likos *et al* approximate by the Denton and Ashcroft modified weighted density approximation [3]. The theory in this form has been applied to study the solid-to-solid isostructural phase transition of the square well potential and, in particular, the phase diagram evolution with the attractive range δ.

First, we would like to start by pointing out that equations (1) and (2) implicitly contain *different* degrees of approximation. It has been shown that the mean-field approximation for the free energy of the solid phase, equation (2), is a reasonably accurate approximation [4]. However, its counterpart for the liquid phase, equation (1), clearly underestimates the attractive contribution to the free energy. Details have been given in [4]. Here we shall

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only give an intuitive argument. The perturbation contribution to the free energy is usually written as

$$U_p\left[\rho(\boldsymbol{r})\right] = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\rho_0^{(2)}(\boldsymbol{r},\boldsymbol{r}')\varphi_p(|\boldsymbol{r}-\boldsymbol{r}'|) \tag{3}$$

where $\rho_0^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ is, according to first-order perturbation theory, the pair distribution function of the reference system. This function is usually written in terms of $g_0(\boldsymbol{r},\boldsymbol{r}')$, the extension of the radial distribution function to the case of the inhomogeneous reference system, as

$$\rho_0^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \rho(\boldsymbol{r})\rho(\boldsymbol{r}')g_0(\boldsymbol{r},\boldsymbol{r}'). \tag{4}$$

Then the mean-field approximation consists in substituting g_0 by a step function. In the solid phase this is a reasonable approximation because most of the correlation structure of $\rho_0^{(2)}$ is already implicitly included in the peaks of $\rho(\boldsymbol{r})$. In the liquid phase, however, the mean-field approximation completely neglects any correlation effect. The final result is a clear underestimation of the attractive energy of the liquid phase as compared to the solid one. This has important effects on the results of Likos *et al.*

(1) They predict that the solid-to-solid phase transition disappears from the phase diagram (because it is pre-emptied by the melting transition) for $\delta > 0.085$ while the simulation result is $\delta > 0.06$. This discrepancy means an error of ≈41%. Its origin is, obviously, the underestimation of the attractive energy in the fluid phase.

(2) The mean-field approximation, (1) and (2), gives qualitatively incorrect results for the phase diagram when δ is further increased. In fact, for the Lennard-Jones potential it predicts a phase diagram *without* liquid–gas transition (because the coexisting liquid and gas are metastable states with respect to the sublimation transition) and, therefore, without critical and triple points. The reason is, again, the underestimation of the attractive energy in the liquid phase.

The above arguments will also allow us to make to Likos *et al* suggestions on how to improve their theory. They suggest as a straightforward improvement the inclusion of the correlation effects retaining the last term in their equations (8) and (9). This will obviously mean an improvement of the attractive energy estimation of the liquid phase. However, it is not straightforward to implement this idea for the solid phase because very little is known about $h_0^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ and any mapping of it into the uniform limit has to be carefully done (as we proposed some time ago [5, 4]); otherwise the attractive energy is overestimated in the solid phase because the correlation effects are taken into account many times. This can be easily understood if we consider the limit of zero temperature where $\rho_0^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ is exactly given by a sum of delta function (centred at *different* lattice sites) products. At the same time, the local solid density, $\rho(\boldsymbol{r})$, is given by a sum of delta functions centred at every lattice site. This shows, again, that the mean-field approximation is reasonably accurate in the solid phase and that most of the correlation structure of $\rho_0^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ (which is the function with physical meaning) is already included in the density product of equation (4).

The preceding discussion shows that the role of the last term in (9) Likos *et al* is completely different from its role in the case of the liquid phase, equation (8) in the same paper. In particular, it is now clear that, in contrast to what happens with the liquid–gas critical temperature, the inclusion of this term will not necessarily produce a better estimation of the solid–solid critical temperature. The solid–solid transition is the consequence of a delicate free energy balance. Therefore, the critical temperature is expected to change significantly if a different HS functional is used for the reference system. This is supported by our result [6] using our perturbation theory [5, 4] together with the Tarazona's free energy model for non-uniform HS systems [7], which significantly overestimates the solid–solid critical temperature (our result is $k_BT_c/\epsilon \approx 2.7$, to be compared with $k_BT_c/\epsilon \approx 2.1$ of Likos *et al* and the simulation result $k_BT_c/\epsilon \approx 1.7$ of Bolhuis and Frenkel). However, we obtain excellent results for the critical density (see figure 9 in [6]) and for the phase diagram evolution with the parameter δ. In particular, we obtain an error of only ≈1% in our prediction for the δ value where the solid–solid transition is preempted by the melting transition (to be compared with the ≈41% of Likos *et al*).

A final comment on the suggested non-perturbative approximation to deal with the full interaction. We have shown [6] that for the δ range where the solid–solid transition is present in the phase diagram the fluid free energy branch always shows the usual van der Waals loop corresponding to the liquid–gas condensation. This transition does not appear in the phase diagram because the corresponding gas and liquid states are metastable with respect to the sublimation transition. Then, the non-perturbative approximation for the full interaction (based on a thermodynamic mapping of the solid phase into a homogeneous phase at the same temperature but at an effective density) will fail, at least at low temperatures, because, as Likos *et al* explain for the case of systems with long-ranged attractive interactions, the free energy of the effective uniform system is not well defined in the region corresponding to condensation. Furthermore, this strategy (if possible) will provide a theory which will only apply to a limited range of δ values.

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