LETTER TO THE EDITOR

Solid to solid isostructural transitions: the case of attractive Yukawa potentials

Zs T Németh† and C N Likos‡

† Department of Physics, University of Veszprém, PO Box 158, H-8201 Veszprém, Hungary
‡ Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-34014 Grignano (TS), Italy

Abstract. We present a density functional study of the expanded fcc to condensed-fcc transition of a system of hard spheres with an additional short-range attractive Yukawa potential. The approach rests on a separation of the interaction into a hard-sphere reference part, treated nonperturbatively by means of the modified weighted-density approximation, and a mean-field treatment of the attractive Yukawa tail, in analogy with earlier work on the short-range square-well potential. The method confirms the existence of an fcc–fcc isostructural transition terminating at a critical point, and yields results for the critical temperature that are in very good agreement with simulations.

While liquid–gas transitions of classical, spherically symmetric particle systems are well understood topics of equilibrium statistical physics and solid–solid phase transitions between solids possessing *different* crystal symmetries have also been extensively studied, *isostructural* transitions between solids of the *same* crystal symmetry have only recently been given special consideration. The motivation for the study of such transitions has been given by the recent computer simulations of Bolhuis *et al* [1, 2]. These Monte Carlo simulations predicted a novel type of isostructural fcc–fcc solid transition for systems characterized by a hard sphere and with a very short-ranged attractive interaction.

The solid–solid coexistence curve for such systems (in the temperature–pressure plane) terminates at a critical point and depends strongly on the range of the interparticle attraction. The discovery of Bolhuis *et al* presented us with a new symmetry for the phase diagrams of simple systems: for sufficiently long-ranged attractive potentials (larger than aproximately one-third of the diameter σ of the hard spheres) it shows one solid and two fluid phases; for very short-range attractions (shorter than about 7% of σ for square-well potentials) there are one fluid and two solid phases, while in the intermediate cases it consists only of a single fluid and a single crystal phase.

While conducting computer simulations in the early eighties Young and Alder found another type of fcc–fcc transition [3]. The system studied in those simulations was hard spheres (HS) with an attractive square-well potential of range δ equal to one-half of the HS diameter σ ($\delta/\sigma = 0.5$). The phase transition was induced in the crystal lattice by the second nearest neighbours, whose distance from the central particle is $\sqrt{2}$ times that of the nearest neighbours. For an appropriate potential range, when only the first and second neighbours interact with each other in a strongly localized solid (such as in the case of $\delta/\sigma = 0.5$), and the potential is steep enough, a solid–solid isostructural transition may indeed occur. However, because there is no real potential steep enough at this distance to

stabilize the solid in a more condensed state by means of the second-neighbour attraction, this transition was considered to be an artefact of the steepness of the square-well potential [2, 3]. If the range of the square-well potential is even longer, allowing particles in the third, fourth, etc, shells to interact, we may observe a whole spectrum of thermodynamicaly stable isostructural solids with different densities coexisting with each other [4]. However, this is again merely an artefact due to the unrealistic steepness of the square-well potential-tail; for smooth potentials, this transition does not occur.

On the other hand, short-ranged square-well potentials are not too unrealistic for colloidal systems; for such potentials, the fcc–fcc transition observed in the simulations of Bolhuis and Frenkel is caused mainly by the potential energy gain due to the direct interaction between *first* neighbours in the condensed fcc-solid. Unlike the Young–Alder transition, this new solid–solid isostructural transition persists even if the sharp square-well potential is substituted by a smoother one like a Yukawa tail [2], i.e. it appears to be *insensitive* to the particluar form of the attractive potential, provided of course that it is sufficiently short-ranged.

Considerable theoretical progress has already been made in the understanding of these computer simulation results. On the basis of the very illustrative uncorrelated cell-model [1, 2] the qualitative features of the phase diagram can be readily understood. Daanoun *et al* [5] have presented a van der Waals theory for solids to manifest the symmetry of the fluid and solid coexistence regions of the system and Tejero *et al* [6, 7] have studied this systems by means of a variational method based on the Gibbs–Bogoliubov inequality. Finally, succesful density-functional treatments of the problem have recently been proposed for the HS plus square-well interaction [8–10]. The strong physical motivation of this work is to test whether the insensitivity of the phase diagram to the steepness of the attractive potential mentioned above is reproduced by the simple mean-field density-functional approach presented earlier for the square-well interaction [8]. In other words, we ask the question: does the simple mean-field approximation which gives satisfactory results for the short-range square-well potential continue to produce phase diagrams in reasonable agreement with simulation if the attraction is replaced by a smooth Yukawa form? As we show below, the answer is in the affirmative, and in fact the results for the Yukawa interaction are in some respects even better than those for the square-well.

Let us consider, therefore, an interparticle potential consisting of a repulsive hard-sphere part and a short-ranged attractive Yukawa tail:

$$v(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon\left(\dfrac{\sigma}{r}\right)\exp\{-\kappa\sigma(r/\sigma - 1)\} & r > \sigma \end{cases} \tag{1}$$

where σ is the hard core diameter, ε is the well depth ($\varepsilon > 0$), and $(\kappa\sigma)^{-1}$ is a measure for the range of the attraction. This potential can be written in a natural form as $v(r) = v_0(r) + \phi(r)$ where

$$v_0(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \tag{2}$$

is the HS repulsion and

$$\phi(r) = \begin{cases} 0 & r < \sigma \\ -\varepsilon\left(\dfrac{\sigma}{r}\right)\exp\{-\kappa\sigma(r/\sigma - 1)\} & r > \sigma \end{cases} \tag{3}$$

is the Yukawa attraction.

Our method for calculating the Helmholtz free energy of the fluid and solid phases of such a system has been described elsewhere [8]. Here we briefly summarize the main points of our approach and refer the reader to [8] for details. Choosing the HS as the reference interaction, we first approximate the Helmholtz free energy of the system by the standard first-order perturbation theory expression [13]:

$$F[\rho(r)] = F_0[\rho(r)] + \frac{1}{2} \int \int \rho^{(2)}(v_0; r, r') \phi(|r - r'|) \, dr \, dr'. \tag{4}$$

In equation (4) above F and F_0 denote the Helmoltz free energies of the full and reference systems respectively, both being *unique functionals* of the, generally position-dependent, one-particle density $\rho(r)$. Moreover, $\rho^{(2)}(v_0; r, r')$ stands for the two-particle density of the *reference* system, itself a unique functional of the one-particle density. When the latter is a position-independent constant, as is the case for uniform (homogeneous) fluids, the functionals reduce to functions of the usual number density $\rho = N/V$ of a system of N particles enclosed in a prescribed volume V.

The two-particle density is usually written in the form

$$\rho^{(2)}(v_0; r, r') = \rho(r)\rho(r')g_0(r, r') \tag{5}$$

which defines the pair distribution function g_0 of the reference system. As the next step of our approximation, we ignore the correlations in both phases, i.e. we replace the pair distribution function g_0 by a step function:

$$g_0(r, r') = \begin{cases} 0 & |r - r'| < \sigma \\ 1 & |r - r'| > \sigma. \end{cases} \tag{6}$$

Our final approximate expression for the Helmoltz free energy therefore reads:

$$F[\rho(r)] = F_0[\rho(r)] + \frac{1}{2} \int \rho(r)\rho(r')\phi(|r - r'|) \, dr \, dr'. \tag{7}$$

For the uniform fluid (homogeneous phase) we adopt the very accurate Carnahan–Starling equation of state [14] for the excess free energy of the reference system and thus we obtain for the free energy density of a homogeneous system of number density ρ the following expression:

$$\frac{\beta F_{liq}(\rho)\sigma^3}{V} \equiv f_{liq}(\rho)$$

$$= \rho\sigma^3(\ln(\rho\sigma^3) - 1) + \frac{6\eta^2(4 - 3\eta)}{\pi(1 - \eta)^2} - \frac{2\pi(\rho\sigma^3)^2}{t}\left(\frac{1 + \xi}{\xi^2}\right) + 3\rho\sigma^3 \ln(\Lambda/\sigma) \tag{8}$$

where $\eta = \pi\rho\sigma^3/6$ is the packing fraction, $t = k_B T/\varepsilon$ is the reduced temperature, $\xi \equiv \kappa\sigma$, and Λ is the thermal de Broglie wavelength.

For the calculation of the free energy of the crystalline solid (inhomogeneous phase) we first adopt the Gaussian parametrization of the one-particle density having the *prescribed* fcc periodicity, namely

$$\rho(r) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_R \exp\{-\alpha(r - R)^2\} \tag{9}$$

where $\{R\}$ is the set of fcc lattice vectors, and α is the localization parameter, with the Gaussians becoming sharper as α grows. Separating the reference free energy into its ideal and excess contributions,

$$F_0[\rho(r)] = \int \rho(r)\big[\ln(\rho(r)\Lambda^3) - 1\big]\,\mathrm{d}r + F_{ex}[\rho(r)] \tag{10}$$

we can evaluate the excess part by invoking the modified weighted density approximation (MWDA) [11] which is known to give accurate results for the hard-sphere interaction. The MWDA is based on a thermodynamic mapping of a solid of average density ρ and localization α into a liquid at a *weighted density* $\hat{\rho}(\rho, \alpha)$. The final expression for the weighted density is given in the original MWDA paper [11]. Here, we simply point out that the necessary input in order to perform such a mapping consists of the free energy per particle of the uniform liquid, $\tilde{f}_0(\hat{\rho})$ and its direct correlation function (DCF) $c^{(2)}(r; \hat{\rho})$. For these two quantities of the HS fluid (which are related to each other by the compressibility sum rule) we have two choices: we can adopt either the simpler Percus–Yevick (PY) expression for the DCF [12] and the associated compressibility equation of state [11], or the more accurate Verlet–Weis (VW) parametrization for the DCF [15, 16] which is by construction consistent with the Carnahan–Starling equation of state [14].

We have performed the MWDA mapping using both alternative inputs. The advantage of the PY input is that, since the DCF is short-range and has a polynomial form, and the one-particle density was assumed to be described by a sum of Gaussians, the MWDA iteration can be performed in reciprocal space for modest values of α ($\alpha\sigma^2 < 100$) and we can then switch to real space for high values of the localization (see [9] for details). The real space calculation is faster than the original reciprocal space one [11] by orders of magnitude, and also it allows us to examine solids of very high packing fractions (even very near to the close-packing limit, $\rho_{CP}\sigma^3 = \sqrt{2}$) and thus to consider values of ξ up to 100. On the other hand, the VW DCF possesses a 'tail' outside the hard core, and analytic expressions for this function are mere fits to the 'real' function which cannot be used as approximations for $c^{(2)}(r)$ for hard spheres [16]. Thus, when we use the VW input, we are forced to perform the mapping in reciprocal space; but as α grows, we have to keep more and more reciprocal lattice vectors (RLV) in order to guarantee the convergence of the MWDA RLV sums. We have kept up to 1850 RLV shells in our calculation, sufficient to guarantee convergence up to solid densities $\rho\sigma^3 = 1.36$. This restriction allows us to examine values of ξ only up to 40 with the VW input. We did not attempt to consider even higher values, since the calculation would then become extremely demanding in time, without offering any essentially new information.

The solid free energy is obtained as the minimum of the sum of ideal, excess and internal energy terms with respect to α, and we obtain for this quantity the final expression:

$$\frac{\beta F_{sol}(\rho)\sigma^3}{V} \equiv f_{sol}(\rho)$$
$$= \min_{\alpha}\left\{\rho\sigma^3\left[\frac{1}{N}\int \rho(r)\big[\ln(\rho(r)\sigma^3) - 1\big]\,\mathrm{d}r + \frac{f_0(\hat{\rho}\sigma^3)}{\hat{\rho}\sigma^3}\right.\right.$$
$$\left.\left.+\frac{1}{2N}\int\int \rho(r)\rho(r')[\beta\phi(|r - r'|)]\,\mathrm{d}r\,\mathrm{d}r'\right]\right\} + 3\rho\sigma^3\ln(\Lambda/\sigma) \tag{11}$$

where f_0 stands for the free energy density of the hard-sphere fluid. The phase boundaries are now located by performing the common-tangent construction on the $f_{liq}(\rho)$- and $f_{sol}(\rho)$-curves (equations (8) and (11)) with the last term in both being ignored as it does not affect the solutions of the common-tangent equations.
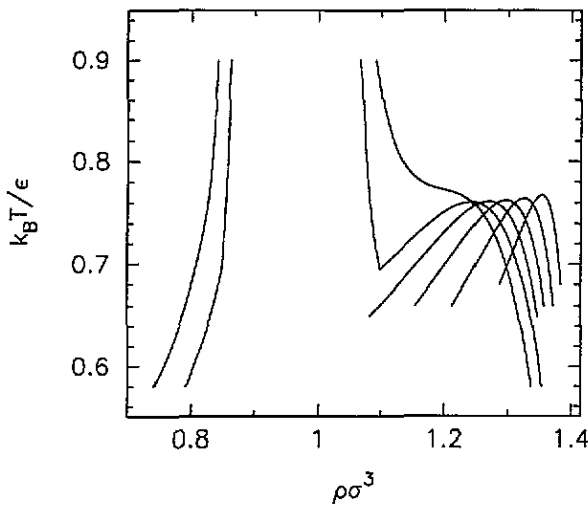
Figure 1. Phase diagrams of Yukawa systems obtained in the present approximation with PY input for the MWDA. From right to left $\xi = 100, 67, 50, 40, 33$ and 25. For the last value of ξ the fcc–fcc transition is just preempted by melting.
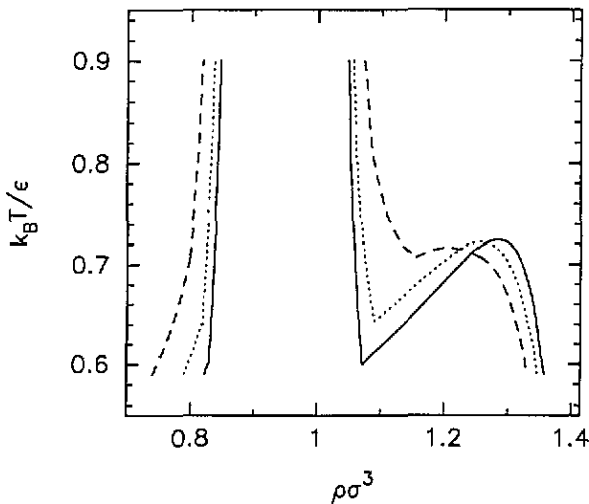

Figure 2. Phase diagrams of Yukawa systems obtained in the present approximation with VW input for the MWDA. Solid lines: $\xi = 40$; dotted lines: $\xi = 33$; dashed lines: $\xi = 25$. For the last value of ξ the fcc–fcc transition is still not preempted by melting.

The resulting phase diagrams from a PY input for $\xi = 25, 33, 40, 50, 67$ and 100 are presented in figure 1. As can be seen, the insensitivity of the isostructural transition to the precise form of the attractive potential is well reproduced by our theory. In basic agreement with the simulation results [2], the solid–solid transition is found to occur for values $\xi > 25$ only; for $\xi = 25$ and a longer range of the potential it is preempted by melting. The asymmetric solid–solid density gap is wide at low temperatures and shrinks to a point at criticality. As ξ increases, the solid–solid coexistence curves shift to the right, showing the same behaviour as the simulation results. The critical temperature is slightly

overestimated by about 2% for $\xi = 25$, by 3.3% for $\xi = 33$ and the results are worsening as the potential range decreases, but the difference between simulation and our simple theory is less than 10% even for $\xi = 100$ where it reaches its highest value.

The VW results for $\xi = 25$, 33 and 40 are shown in figure 2. Again, an fcc–fcc transition is predicted. This result shows a transition for $\xi = 25$ as well, which barely 'survives' the incipient melting transition. The approximation slightly underestimates the critical temperatures, by 3.3% for $\xi = 25$ and by 1.7% for $\xi = 33$ but is quite satisfactory otherwise.
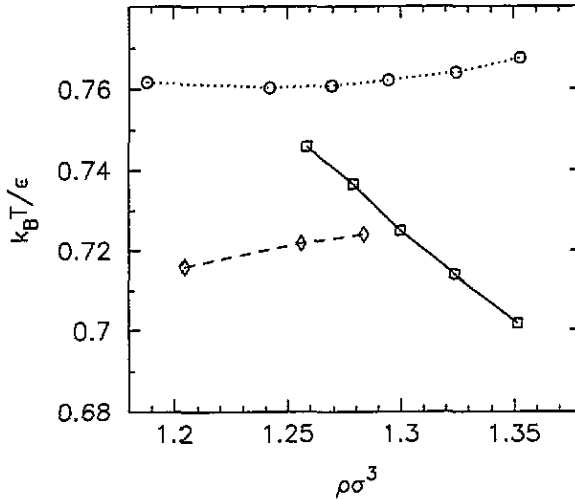

Figure 3. *A comparison of the critical parameters $(\rho_c \sigma^3, k_B T_c/\varepsilon)$ obtained from the present theory with the simulation results. Squares: simulation results [2]; from right to left, $\xi = 100, 67, 50, 40$ and 33. Circles: present work with PY-input for the MWDA. From right to left, $\xi = 100, 67, 50, 40, 33$ and 25, but for the last value the fcc–fcc transition is preempted. Diamonds: present work with VW input for the MWDA. From right to left, $\xi = 40, 33$ and 25. The lines are just guides to the eye.*

A more detailed comparison of the critical parameters, which allows for a few additional remarks to be made, is shown in figure 3. Referring to this figure, we first point out that, as in the case of square-well (SQW) potentials [8, 9], the critical densities are always in good agreement with simulation, regardless of the type of approximation used (in our case always within 1% of the simulation result). Still in analogy with the SQW case, the theory with PY input predicts a higher value for the critical temperature (for given ξ) than the theory with VW input used in the MWDA mapping. Moreover, even the highest discrepancy for T_c for PY input in the Yukawa case ($\sim$10% for $\xi = 100$) is a lot smaller than the corresponding one for the SQW case (37%, see [9]). Unlike the SQW case, the VW-input theory now *underestimates* the critical temperature. Such behaviour seems surprising at first sight, since it is usually stated that a characteristic of mean-field-type theories is the overestimation of critical temperatures. However, we should keep in mind that the validity of this statement partly rests on the assumption that the reference part of the Hamiltonian can be treated *exactly*. In our case, on the other hand, the HS part of the solid free energy is still the result of an approximate calculation, namely the MWDA scheme, with the *additional approximation of a Gaussian density profile regardless of the values of the thermodynamic and interaction parameters* of the problem. Thus, the details of the interference of errors

from the reference and mean-field terms in the Helmholtz free energy can bring about the underestimation of the critical temperature observed here.

The feature in which the results from the present approach are in considerable disagreement with the qualitative behaviour from simulations is the evolution of the critical temperature with decreasing interaction range. Simulations show that T_c decreases as ξ grows and the theory predicts, wrongly, the opposite trend (see figure 3). A plausible explanation of this effect is that the mean-field approximation employed here is getting less accurate as the range of the potential decreases; thus, we have a systematic increase of the error in the critical temperature as ξ grows, and this leads to the inaccurate result mentioned above. However, we reiterate that the unavoidable inaccuracies in the treatment of the reference part also play an important role in the predictions of our simple theory on the critical parameters, and so it is not possible to isolate the factors that cause the various errors.

In our opinion, the most important result of this work is the fact that the simple mean-field approach is in agreement with the 'experimental' finding that the existence of an fcc–fcc transition induced by the first neighbours is quite insensitive to the steepness of the attractive potential; in view of this, it is now safe to assume that the same qualitative features in the phase diagram will be observed if instead of a Yukawa attraction we use, say, a power-law attraction $\phi(r) \sim -r^{-n}$, with n sufficiently large ($n \sim 100$). Moreover, even quantitatively, the mean-field approximation gives results that agree reasonably well with the simulation data. To improve the approach beyond mean-field, one can perform a full nonperturbative mapping of the solid phases into uniform ones, in a way analogous to that presented in [9] for square-well systems; indeed, the structural and thermodynamic functions of the hard-core Yukawa fluid are readily available in analytic form from the mean-spherical approximation (MSA) solution of the model, and this makes the proposed mapping fairly straightforward to implement.

References

[1] Bolhuis P and Frenkel D 1994 *Phys. Rev. Lett.* **72** 2211
[2] Bolhuis P, Hagen M and Frenkel D 1994 *Phys. Rev.* E **50** 4880
[3] Young D A and Alder D J 1980 *J. Chem. Phys.* **73** 2430
[4] Bolhuis P private comunication
[5] Daanoun A, Tejero C F and Baus M 1994 *Phys. Rev.* E **50** 2913
[6] Tejero C F, Daanoun A, Lekkerkerker H N W and Baus M 1994 *Phys. Rev. Lett.* **73** 752
[7] Tejero C F, Daanoun A, Lekkerkerker H N W and Baus M 1995 *Phys. Rev.* E **51** 558
[8] Likos C N, Németh Zs T and Löwen H 1994 *J. Phys.: Condens. Matter* **6** 10965
[9] Likos C N and Senatore G 1995 *J. Phys.: Condens. Matter* **7** 6797
[10] Rascón C, Navasqués G and Mederos L 1995 *Phys. Rev.* B **51** 14899
[11] Denton A R and Ashcroft N W 1989 *Phys. Rev.* A **39** 4701
[12] Hansen J P and MacDonald I R 1986 *Theory of Simple Liquids* 2nd edn (New York: Academic)
[13] Evans R 1979 *Adv. Phys.* **28** 143
[14] Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 635
[15] Verlet L and Weis J J 1972 *Phys. Rev.* A **45** 939
[16] Henderson D and Grundke E W 1975 *J. Chem. Phys.* **63** 601