

## LETTER TO THE EDITOR

**Isostructural solid–solid transitions in square-shoulder systems**A R Denton<sup>†§</sup> and H Löwen<sup>†‡</sup><sup>†</sup> Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany<sup>‡</sup> Institut für Theoretische Physik II, Universität Düsseldorf, D-40225 Düsseldorf, Germany

Received 7 October 1996

**Abstract.** Applying a practical density-functional-based perturbation theory, we examine the phase behaviour of a model system interacting via a hard core plus a square-shoulder repulsion. For sufficiently narrow shoulders, the theory predicts coexistence between expanded and condensed isostructural (fcc) crystals, in quantitative agreement with available simulation data. In contrast to the attractive square-well system, atomic localization is found to *increase* with increasing temperature.

Recent computer simulations [1, 2] and theoretical studies [3–8] of systems interacting via extremely short-range pair potentials have produced convincing evidence for a first-order isostructural phase transition between expanded and condensed solids, the corresponding phase diagram exhibiting three-phase coexistence between a single fluid phase and the two solids. Possible physical manifestations of such systems are uncharged colloidal particles mixed with non-adsorbing polymer, and charge-stabilized colloidal suspensions, whose macro-ions interact via electrostatic and van der Waals forces [9].

In this letter we employ a combination of density-functional (DF) theory [10] and thermodynamic perturbation theory to study the phase behaviour of a model system interacting via a hard core of diameter  $\sigma$  and a repulsive square shoulder of width  $\delta$  and height  $\epsilon$ . Since  $\epsilon$  scales with temperature, the system is completely characterized by the single parameter  $\delta/\sigma$ . Our goal is to examine the influence of short-range repulsion on the stability of the solid–solid transition and on the temperature dependence of atomic localization at high density. Compared with the closely related attractive square-well system of equal interaction range, the solid–solid critical point is predicted to shift towards higher densities and lower temperatures. Furthermore, the atoms are found to become increasingly localized about their lattice sites as the temperature is raised.

The relevant theoretical quantity is the Helmholtz free-energy functional  $F[\rho]$ , a functional of the spatially varying one-particle density  $\rho(\mathbf{r})$ . For pair potentials including a steeply repulsive core interaction, thermodynamic perturbation theory [11, 12] accurately approximates  $F[\rho]$  by decomposing the full pair potential  $\phi(r)$  into a repulsive short-range reference potential  $\phi_0(r)$  and a relatively weak long-range perturbation  $\phi_p(r)$ . In our case,  $\phi_0(r)$  is the hard-sphere (HS) pair potential and  $\phi_p(r)$  is a step function of height  $\epsilon$  and range  $\sigma + \delta$ .

To first order in the perturbation,

$$F[\rho] \simeq F_{HS}[\rho] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}') g_{HS}(\mathbf{r}, \mathbf{r}') \phi_p(|\mathbf{r} - \mathbf{r}'|) \quad (1)$$

§ E-mail: a.denton@kfa-juelich.de.

where  $g_{HS}(\mathbf{r}, \mathbf{r}')$  is the pair distribution function of the HS solid. The HS solid free energy  $F_{HS}[\rho]$  separates naturally into an (exactly known) ideal-gas term and an excess term  $F_{ex}[\rho]$ . For the latter, we use the modified weighted-density approximation (MWDA) [13]:

$$F_{ex}^{MWDA}[\rho]/N = f_{HS}(\hat{\rho}) \quad (2)$$

where  $f_{HS}(\hat{\rho})$  is the excess free energy per particle of the *uniform* HS fluid evaluated at a weighted density

$$\hat{\rho} \equiv \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}')w(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}) \quad (3)$$

defined as a *weighted* average of the physical density with respect to a weight function  $w(r)$ , which in turn is specified by the requirement

$$\left( \frac{\delta^2 F_{ex}^{MWDA}[\rho]}{\delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}')} \right)_{\rho(\mathbf{r}) \rightarrow \hat{\rho}} = -k_B T c_{HS}^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho) \quad (4)$$

where  $c_{HS}^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho)$  is the two-particle Ornstein–Zernike direct correlation function. The fluid-state input functions  $f_{HS}$  and  $c_{HS}^{(2)}$  we take from the analytic solution of the Percus–Yevick equation for hard spheres [11].

Pair distributions of the HS crystal have been studied by Monte Carlo simulation, from which useful parametrizations are available for the translational average of  $g_{HS}(\mathbf{r}, \mathbf{r}')$ . This information has been exploited in a simpler perturbation theory approach [8], which ignores the structure of the solid. In the DF approach, however,  $g_{HS}(\mathbf{r}, \mathbf{r}')$  itself is required. Following Likos *et al* [4], we approximate it by a unit step function:

$$g_{HS}(\mathbf{r}, \mathbf{r}') = \begin{cases} 0 & |\mathbf{r} - \mathbf{r}'| < \sigma \\ 1 & |\mathbf{r} - \mathbf{r}'| > \sigma \end{cases} \quad (5)$$

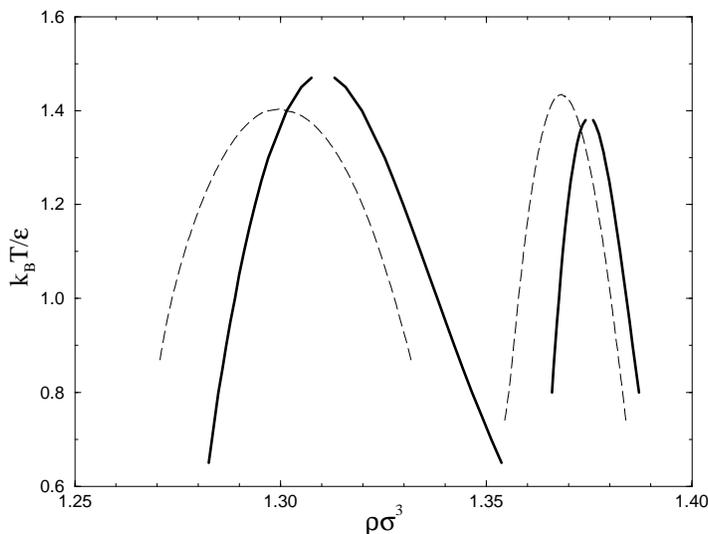
thus excluding self-correlation but otherwise neglecting pair correlations. This mean-field approximation is expected to be reasonable in the high-density solid, where two-particle correlations are determined largely by the highly non-uniform one-particle density, which is strongly peaked about the lattice sites. It is also supported by simulations of the HS crystal [14] and by DF theory calculations for the Lennard-Jones system [15]. At the very high solid densities of interest here, the density distribution may be parametrized by the isotropic Gaussian *ansatz*

$$\rho(\mathbf{r}) = \left( \frac{\alpha}{\pi} \right)^{3/2} \sum_{\mathbf{R}} e^{-\alpha|\mathbf{r} - \mathbf{R}|^2} \quad (6)$$

where the sum runs over the lattice sites  $\mathbf{R}$  of the close-packed fcc crystal. Minimization of the functional  $F[\rho]$  with respect to the single variational parameter  $\alpha$  determines the free energy of the solid.

For a given shoulder width, the solid free energy per volume is computed as a function of average reduced density  $\rho\sigma^3$  at fixed reduced temperature  $k_B T/\epsilon$ . Sufficiently short-range interactions ( $\delta \ll \sigma$ ) induce inflection in the curve of  $F/V$  versus  $\rho$  that results in solid–solid phase coexistence. The densities of coexisting phases are established by means of a Maxwell common-tangent (or equal-area) construction, ensuring equality of the chemical potentials and pressures in the expanded and condensed solids. Repetition of the procedure for a series of temperatures systematically maps out the solid–solid coexistence region in the  $T$ – $\rho$  plane.

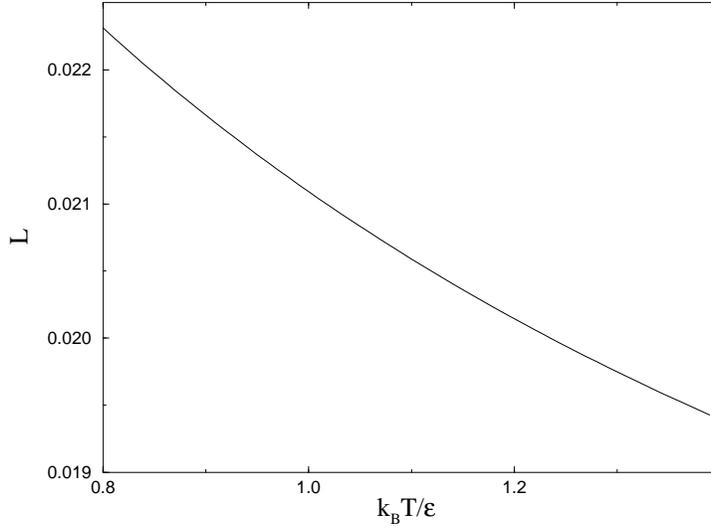
Predictions of the theory for isostructural solid–solid coexistence are presented in figure 1, together with recently available Monte Carlo simulation data [2] for comparison.



**Figure 1.** The phase diagram of temperature versus density (reduced units) for the square-shoulder system, exhibiting coexistence between two isostructural (fcc) solids. Solid curves are theoretical predictions, dashed curves the corresponding simulation data [2] for shoulder widths  $\delta/\sigma = 0.03$  (rightmost curves) and  $\delta/\sigma = 0.08$  (leftmost curves).

With increasing shoulder width, the solid–solid critical point shifts to lower densities and the coexistence region widens, while the critical temperature remains relatively constant. Evidently, the theory slightly overestimates the critical density, but otherwise is in excellent agreement with simulation. It is worth noting that the square-shoulder phase behaviour differs significantly from that of the inverted case of a square-well attraction. For a square well of width  $\delta/\sigma = 0.03$ , the same theory predicts a solid–solid critical point at lower density ( $\rho\sigma^3 \simeq 1.3$ ) and higher temperature ( $k_B T/\epsilon \simeq 2.4$ ), and a considerably wider coexistence region [16]. Furthermore, the square-shoulder transition remains stable over a wider range of  $\delta$ , as confirmed by simulation [2]. In passing, we mention that we have also examined the related case of a ‘square-barrier’ pair potential [16]. Separating the square shoulder from the hard core preserves the solid–solid transition, but shifts the critical point to significantly lower density and higher temperature. The combination of a square well and a square barrier is found to considerably enhance the stability of the transition. Furthermore, we have also investigated other forms of repulsion, such as a linear ramp and quadratic repulsions, but have found no evidence for solid–solid coexistence in these systems [16].

For the fluid phase, the uniform (constant- $\rho$ ) limit of equation (1) represents one conceivable approximation. In fact, we have explored this, taking for the HS fluid functions  $f_{HS}$  and  $g_{HS}(r)$  the essentially exact Carnahan–Starling and Verlet–Weis expressions [11], respectively. The result, however, in the relevant temperature range near the solid–solid critical point, is a severe overestimate of the free energy and a corresponding underestimate of the stability of the fluid phase. Further examination traces the problem to a failure of the perturbation theory for the fluid. While in the case of the solid the square-shoulder perturbation constitutes only a small fraction ( $<10\%$ ) of the reference free energy, for the fluid it makes a considerably larger contribution ( $>30\%$ ). Pending future calculations with a more accurate theory for the fluid phase, we refrain here from addressing the issue of fluid–solid coexistence and its implications for the stability of the solid–solid transition.



**Figure 2.** The Lindemann ratio  $L$  versus the reduced temperature  $k_B T / \epsilon$ , for shoulder width  $\delta/\sigma = 0.03$  and density  $\rho\sigma^3 = 1.36$ , illustrating the increasing atomic localization with increasing temperature for the square-shoulder system.

As an important by-product of the variational DF approach, we obtain also the Gaussian width parameter  $\alpha$ , containing information regarding atomic localization. A more physical measure is the Lindemann ratio  $L$ , defined as the ratio of root mean square atomic displacement to the nearest-neighbour distance. For the fcc crystal,  $L = \sqrt{(3/\alpha)}/a$ , where  $a = (4/\rho)^{1/3}$  is the lattice constant. Figure 2 illustrates the characteristic temperature dependence of  $L$  at fixed density, revealing an *increase* in atomic localization with increasing temperature. This clearly goes against usual intuition, according to which increasing temperature results in thermal disordering of atomic positions. It may be readily explained, however, by noting that at high densities the nearest-neighbour distance lies inside the range of the repulsive shoulder. As the temperature is lowered, or equivalently as the height of the shoulder is raised, the system can lower its internal energy if it responds by broadening the atomic density distribution, thus spreading more of the distribution outside the range of the energetically unfavourable shoulder.

Summarizing, we have demonstrated that a relatively simple density-functional perturbation theory predicts for repulsive square-shoulder interactions of sufficiently short range a first-order isostructural solid–solid transition ending in a critical point, in quantitative agreement with available simulation data. For this purely repulsive system, the theory further predicts an increase in atomic localization with increasing temperature. Whether or not the remarkable phase behaviour exhibited by this model system can be observed experimentally is not yet clear. The present study, however, may help to resolve the issue by guiding the parametrization of more realistic pair potentials that better model the interactions in real colloidal systems. Work along these lines is in progress.

We gratefully acknowledge Drs A M Bohle and C N Likos for helpful discussions and Dr P Bolhuis for kindly providing the simulation data for the square-shoulder system prior to publication.

## References

- [1] Bolhuis P and Frenkel D 1994 *Phys. Rev. Lett.* **72** 2211  
Bolhuis P and Frenkel D 1995 *Phys. Rev. E* **50** 4880
- [2] Bolhuis P and Frenkel D 1996 *J. Physique* at press
- [3] Tejero C F, Daanoun A, Lekkerkerker H N W and Baus M 1994 *Phys. Rev. Lett.* **73** 752
- [4] Likos C N, Németh Zs T and Löwen H 1994 *J. Phys.: Condens. Matter* **6** 10965
- [5] Németh Zs T and Likos C N 1995 *J. Phys.: Condens. Matter* **7** L537
- [6] Likos C N and Senatore G 1995 *J. Phys.: Condens. Matter* **7** 6797
- [7] Rascón C, Mederos L and Navascués G 1995 *J. Chem. Phys.* **103** 9795
- [8] Kincaid J M, Stell G and Goldmark E 1976 *J. Chem. Phys.* **65** 2172
- [9] Pusey P N 1991 *Liquids, Freezing and Glass Transition (Les Houches Session 51)* ed J-P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland) pp 763–942
- [10] Oxtoby D W 1990 *Liquids, Freezing and Glass Transition (Les Houches Session 51)* ed J-P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland) pp 145–91  
Evans R 1979 *Adv. Phys.* **28** 143  
Löwen H 1994 *Phys. Rep.* **237** 249  
Singh Y 1991 *Phys. Rep.* **207** 351
- [11] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* 2nd edn (London: Academic)
- [12] Weeks J D, Chandler D and Andersen H C 1971 *J. Chem. Phys.* **54** 5237  
Andersen H C, Chandler D and Weeks J D 1976 *Adv. Chem. Phys.* **34** 105
- [13] Denton A R and Ashcroft N W 1989 *Phys. Rev. A* **39** 4701
- [14] Weis J-J 1974 *Mol. Phys.* **28** 187  
Kincaid J M and Weis J-J 1977 *Mol. Phys.* **34** 931
- [15] Mederos L, Navascués G, Tarazona P and Chacón E 1993 *Phys. Rev. E* **47** 4284
- [16] Denton A R and Löwen H 1996 unpublished