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## Unusual phase behaviour from peculiar pair potentials: A density-functional-perturbation study

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**Abstract** Applying a density-functional-based perturbation theory, we examine the phase behaviour of model colloidal systems characterized by hard core and additional piecewise-constant repulsive or attractive interactions. For sufficiently narrow square-shoulder repulsions, the theory predicts coexistence between expanded and condensed isostructural (f.c.c.) crystals, in quantitative agreement with available simulation data. A square-well attraction of

equal width results in a solid–solid critical point at lower density and higher temperature and a significantly wider coexistence region. Adding a constant long-ranged attraction leads to a novel phase diagram exhibiting a *quadruple* point, where two fluid phases and two solid phases coexist simultaneously.

**Key words** Colloids – phase behaviour – density – functional theory

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, or charge-stabilized colloidal suspensions, whose macroions interact via electrostatic and van der Waals forces [9].

Here we employ a combination of density-functional (DF) theory and thermodynamic perturbation theory to study the phase behaviour of model systems characterized by short- and long-range piecewise-constant interactions. Our goal is to isolate the influence of specific features of the pair potential on the stability of solid–solid transitions and to explore the intriguing possibility of *four*-phase (vapour–liquid–solid–solid) coexistence. We focus in particular on pair potentials composed of a hard core of

diameter  $\sigma$  plus a repulsive square-shoulder or attractive square-well of width  $\delta$  and magnitude  $\epsilon$ . Since  $\epsilon$  scales with temperature, these systems are completely characterized by the parameter  $\delta/\sigma$ . We further consider the influence of long-range attraction, in the simplest conceivable way, by adding to the square-well a “van der Waals” tail, i.e. a constant attraction of infinite range, but infinitesimal strength  $-a\epsilon\sigma^3/V$ , where  $V$  is the volume. This introduces an additional dimensionless parameter  $a$ , which gauges the strength of the attraction.

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 with a steeply repulsive short-range interaction, thermodynamic perturbation theory [10, 11] accurately approximates  $F[\rho]$  by decomposing the full pair potential  $\phi(r)$  into a repulsive short-range reference potential  $\phi_o(r)$  and relatively weak long-range perturbation  $\phi_p(r)$ . In our case,  $\phi_o(r)$  is the hard-sphere (HS) pair potential and  $\phi_p(r)$  is a step function of amplitude  $\epsilon$  and range  $\sigma + \delta$ .

To first order in the perturbation,

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

where  $g_{\text{HS}}(\mathbf{r}, \mathbf{r}')$  is the pair distribution function of the HS solid. The HS solid free energy  $F_{\text{HS}}[\rho]$  separates naturally into an (exactly known) ideal-gas term and an excess term  $F_{\text{ex}}[\rho]$ . For the latter, we use the modified weighted-density approximation (MWDA) [12]:

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

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

$$\hat{\rho} \equiv \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}), \quad (2')$$

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

$$\left( \frac{\delta^2 F_{\text{ex}}^{\text{MWDA}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right)_{\rho(\mathbf{r})=\rho} = -k_B T c_{\text{HS}}^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho), \quad (3)$$

$c_{\text{HS}}^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho)$  being the two-particle Ornstein–Zernike direct correlation function. The fluid-state input functions  $f_{\text{HS}}$  and  $c_{\text{HS}}^{(2)}$  we take from the analytic solution of the Percus–Yevick equation for hard spheres [10].

Following Likos et al. [4], we approximate  $g_{\text{HS}}(\mathbf{r}, \mathbf{r}')$  by a unit step function, thus properly excluding self-correlation but otherwise neglecting pair correlations. This mean-field approximation is expected to be quite reasonable in the high density solid, where two-particle correlations are determined largely by the highly non-uniform one-particle density. It is also supported by Monte Carlo simulations of the HS crystal [13] and by DF theory calculations for the Lennard–Jones system [14]. At the solid densities of interest here, the density distribution is parametrized to reasonable accuracy by the isotropic Gaussian ansatz,

$$\rho(\mathbf{r}) = \left( \frac{\alpha}{\pi} \right)^{3/2} \sum_{\mathbf{R}} e^{-\alpha|\mathbf{r} - \mathbf{R}|^2}, \quad (4)$$

the sum running over lattice sites  $\mathbf{R}$  of an f.c.c. crystal. Minimization of the functional  $F[\rho]$  with respect to the single variational parameter  $\alpha$  determines the free energy of the solid.

For the fluid phase, we use the uniform (constant  $\rho$ ) limit of Eq. (1) [11]:

$$f(\rho) \simeq f_{\text{HS}}(\rho) + 2\pi\rho \int_0^\infty dr r^2 g_{\text{HS}}(r) \phi_p(r), \quad (5)$$

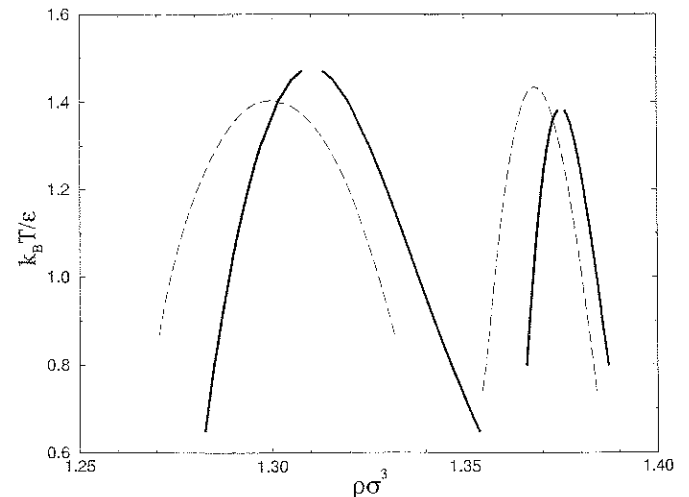
taking for the HS fluid functions  $f_{\text{HS}}$  and  $g_{\text{HS}}(r)$  the essentially exact Carnahan–Starling and Verlet–Weis expressions [10], respectively. The sole effect of the van der Waals tail is to add a structure-independent term proportional to  $(-a\rho^2/2)$  to the free energy per volume of both the fluid and the solid phases.

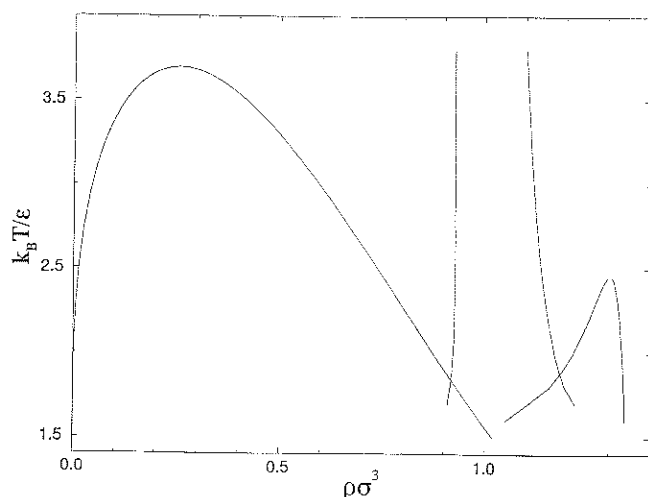
For a given pair potential, the fluid and solid free energies per volume are computed as a function of average reduced density  $\rho\sigma^3$  at fixed reduced temperature  $k_B T/\epsilon$ . Sufficiently short-range interactions ( $\delta \ll \sigma$ ) induce inflection in the curve of  $F/V$  vs.  $\rho$  that can result 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. Repetition of the procedure for a series of temperatures systematically maps out the phase diagram in the  $T - \rho$  plane.

Predictions of the theory for isostructural solid–solid coexistence in the square-shoulder system are presented in Fig. 1, together with recently available Monte Carlo simulation data [2]. 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 coexistence densities, but otherwise is in excellent agreement with simulation.

Figure 2 displays our results for the full phase diagram of the square-well system with van der Waals tail. The long-range attraction proves to have only a minor effect

**Fig. 1** Phase diagram of temperature vs. density (reduced units) for the square-shoulder system, exhibiting coexistence between two isostructural (f.c.c.) solids. Solid curves are theoretical predictions, dashed curves the corresponding simulation data [2] for shoulder widths  $\delta/\sigma = 0.03$  (right-most curves) and  $\delta/\sigma = 0.08$  (left-most curves)





**Fig. 2** Phase diagram for the square-well system with constant long-range attractive tail, exhibiting a quadruple point. From left to right, curves represent vapour-liquid, liquid-solid, and solid-solid phase coexistence for the case of well width  $\delta/\sigma = 0.03$  and van der Waals parameter  $a = 40$

on solid-solid coexistence, which is seen to differ considerably from the square-shoulder case. For the same step width,  $\delta/\sigma = 0.03$ , the square-well critical point occurs at lower density and higher temperature and the coexistence region is significantly wider. Furthermore, the transition remains stable over a narrower range of  $\delta$  than for the square-shoulder system [2]. In the absence of long-range attraction, the theory predicts preemption by the liquid-solid transition for  $\delta/\sigma$  as small as 0.05–0.06. For such

short-range potentials, the vapour-liquid critical temperature falls well below the liquid-solid-solid triple point temperature, in which case only the liquid can coexist with the two isostructural solids. Inclusion of the van der Waals tail, however, raises the vapour-liquid critical point and the vapour-liquid-solid triple point. For a sufficiently strong attraction, as illustrated in Fig. 2, the two triple points can coincide, resulting in a *quadruple* point at which the two fluid phases coexist with the two solid phases.

Summarizing, using a relatively simple density-functional-perturbation theory, we have demonstrated that sufficiently short-range piecewise-constant interactions—whether attractive or repulsive—can result in unusual phase behaviour distinguished (at sufficiently low temperature) by a first-order isostructural solid-solid transition. Adding a weak constant long-range attraction to a square-well pair potential has little effect on the solid-solid transition, but strongly enhances the vapour-liquid transition. The resulting phase diagram exhibits *four* phases (vapour, liquid, expanded- and condensed-solids), which in this model can simultaneously coexist at a quadruple point. Whether or not the remarkable phase behaviour predicted for these model systems 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 (e.g., DLVO) that better model the interactions in real colloidal systems. Work along these lines is in progress.

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## References

- Bolhuis P, Frenkel D (1994) *Phys Rev Lett* 72:2211; (1995) *Phys Rev E* 50:4880
- Bolhuis P, Frenkel D (1996) *J Phys*, to appear
- Tejero CF, Daanoun A, Lekkerkerker HNW, Baus M (1994) *Phys Rev Lett* 73:752
- Likos CN, Németh ZS, Löwen H (1994) *J Phys Condens Matter* 6:10965
- Németh ZS, Likos CN (1995) *J Phys Condens Matter* 7:L537
- Likos CN, Senatore G (1995) *J Phys Condens Matter* 7:6797
- Rascón C, Mederos L, Navascués G (1995) *J Chem Phys* 103:9795
- Kincaid JM, Stell G, Goldmark E (1976) *J Chem Phys* 65:2172
- Pusey PN (1991) In: Hansen J-P, Levesque D, Zinn-Justin J (eds) *Liquids, Freezing and Glass Transition*. North-Holland, Amsterdam, pp 763–942
- Hansen JP, McDonald IR (1986) *Theory of Simple Liquids*, 2nd ed. Academic, London
- Weeks JD, Chandler D, Andersen HC (1971) *J Chem Phys* 54:5237; Andersen HC, Chandler D, Weeks JD (1976) *Adv Chem Phys* 34:105
- Denton AR, Ashcroft NW (1989) *Phys Rev A* 39:4701
- Weis J-J (1974) *Mol Phys* 28:187; Kincaid JM, Weis J-J (1977) *Mol Phys* 34:931
- Mederos L, Navascués G, Tarazona P, Chacón E (1993) *Phys Rev E* 47:4284