

## Prediction of an Expanded-to-Condensed Transition in Colloidal Crystals

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Monte Carlo simulations show that a system of hard, spherical particles with a short-ranged attractive interaction, can undergo a first-order transition from a dense to a more expanded solid phase with the same structure. This phase transition is analogous to the liquid-vapor transition in systems with longer-ranged attractive forces. In particular, the solid-solid transition terminates in a critical point. We argue that this phase transition should be experimentally observable in certain types of colloidal crystals.

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Since the work of van der Waals, we know that there is no essential distinction between a liquid and a vapor: above the critical temperature  $T_c$ , a vapor can be compressed continuously all the way to the freezing point. But below  $T_c$ , a first-order phase transition separates the dilute fluid (vapor) from the dense fluid (liquid). Yet, although the van der Waals theory becomes exact in the limit of weak, long-ranged intermolecular interactions [1], there is no fundamental reason why the liquid-vapor transition should occur in every atomic or molecular substance, nor is there any rule that forbids the existence of more than one fluid-fluid transition. Whether a given compound will have a liquid phase, depends sensitively on the range of the intermolecular potential: as this range is decreased, the critical temperature approaches the triple-point temperature, and when  $T_c$  drops below the latter, only a single stable fluid phase remains. This phenomenon is well known in mixtures of spherical colloidal particles and nonadsorbing polymer, where the range of the attractive part of the effective colloid-colloid interaction can be varied by changing the size of the polymer [2-4]. Experiment, theory, and simulation all suggest that when the width of the attractive well becomes less than approximately one-third of the diameter of the colloidal spheres, the colloidal "liquid" phase disappears. In fact, there is numerical evidence that in a molecular compound ( $C_{60}$ ), the range of the intermolecular attraction may be sufficiently short to suppress the liquid-vapor transition [5].

In this Letter, we consider what happens in colloidal systems with a very short-ranged attraction, where the liquid-vapor transition is absent. Below we show that these systems may exhibit a novel type of solid-solid transition that is in many ways reminiscent of the liquid-vapor transition: in particular, (1) the transition takes place between two phases that have the *same* structure, (2) the line of (first-order) solid-solid transitions ends in a critical point, and (3) the transition depends strongly on the range of the intermolecular attraction. In what follows, we use the so-called square-well model to describe the colloid-colloid interaction. In this model, the

intermolecular potential is of the following form:

$$\begin{aligned} v(r) &= \infty, & 0 \leq r < \sigma, \\ &= -\epsilon, & \sigma \leq r < \sigma + \delta, \\ &= 0, & r \geq \sigma + \delta, \end{aligned} \quad (1)$$

where  $\sigma$  denotes the diameter of the colloidal particle,  $\epsilon$  the depth of the attractive well, and  $\delta$  its width. This model, although simple, should provide an adequate description of a wide class of uncharged colloidal particles with short-ranged attraction.

Before presenting our simulation results, we first present an intuitive argument why the square-well model system might be expected to exhibit an isostructural solid-solid transition. To this end, we compare two situations: one is the expanded solid close to melting, the other is the dense solid near close packing. To a first approximation, we can describe the solid by a simple "uncorrelated" cell model [6,7] in which it is assumed that every particle moves independently in the "cell" formed by its neighbors. We denote the radius of this cell by  $a$ . For sufficiently short-ranged potentials, the solid can be expanded to a density where  $a$  is much larger than  $\delta$ , the width of the attractive well. In that case, a given particle can have at most three neighbors within the range of its attractive well, although the average number will be far less. In contrast, once the density of the solid is so high that  $a < \delta$ , then every particle interacts with all its nearest neighbors simultaneously. This leads to a fairly abrupt lowering of the potential energy of the system. At low temperatures, this decrease of the energy on compression will outweigh the loss of entropy that is caused by the decrease of the free volume, the Helmholtz free energy will exhibit an inflection point, and a first-order transition to a "collapsed" solid will result. In fact, we can analytically compute the phase behavior of this cell model where every particle moves in a dodecahedral cell formed by its neighbors [8]. These calculations indicate that, for sufficiently short-ranged attractions, a first-order solid-solid transition should take place. The cell model predicts a very simple relation between  $\delta$ , the

range of the attractive well, and the critical density of the solid-solid transition:

$$\rho_c/\rho_0 = \left(\frac{\delta}{\sigma} + 1\right)^{-3}, \quad (2)$$

where  $\rho_0$  denotes the density of the solid at regular close packing. Below, we shall compare this prediction with our simulation results.

Of course, cell-model calculations only provide a hint that there may be an isostructural solid-solid transition. The real test comes from direct Monte Carlo simulations of the square-well solid. In order to compute the phase diagram, we first must determine the dependence of the Helmholtz free energy of the solid on density and temperature. As the free energy of the solid cannot be measured directly in a Monte Carlo simulation, we use thermodynamic integration to relate the free energy of the square-well solid to that of a hard-sphere solid at the same density [9]:

$$\begin{aligned} F(\rho, \epsilon^*) &= F_{\text{HS}}(\rho) + \int d\epsilon^* \left(\frac{\partial F}{\partial \epsilon^*}\right) \\ &= F_{\text{HS}} + \int d\epsilon^* \frac{\langle E \rangle_{\epsilon^*}}{\epsilon^*}, \end{aligned} \quad (3)$$

where  $\epsilon^*$  is the reduced well depth  $\epsilon/k_B T$  and  $\langle E \rangle$ , the average internal energy of the system, a quantity that can be measured in a Monte Carlo simulation. The free energy of the hard-sphere solid is well known and is accurately represented by an analytical form proposed by Hall [10]. The presence of a first-order phase transition is signaled by the fact that the Helmholtz free energy becomes a nonconvex function of the volume. The densities of the coexisting phases can then be determined by a standard double-tangent construction.

In order to map out the phase diagram of the square-well solid for a wide range of densities, temperatures, and widths of the attractive well, several thousand independent simulations were required. To keep the computational costs within bounds, we chose to simulate a relatively small system consisting of 108 spheres. With such a small system size, finite-size effects are expected, in particular in the vicinity of a critical point. However, away from critical points finite-size effects should be so small that they will not affect the conclusions that we draw below. All our simulations were performed on a face-centered cubic (fcc) solid, because this is the stable solid structure both for the hard-sphere and the square-well model [11]. In what follows, we use reduced units, such that  $\epsilon/k_B$  is the unit of temperature, and  $\sigma$ , the hard-core diameter of the particles, is the unit of length. The simulation box was chosen to be cubic and periodic boundaries were applied. The densities ranged from  $\rho = 0.9$  which is below the hard-sphere melting point to  $\rho = 1.414$  which is almost at close packing ( $\rho_0 = \sqrt{2}$ ). The temperature of the system was varied in the range

$0 \leq 1/T \leq 2$ , in steps of 0.1.

For every value of the well width  $\delta$ , we performed some 1000 MC simulations of 20 000 cycles each. Simulations were performed for  $\delta = 0.001, 0.002, 0.003, 0.004, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05$ , and 0.06. In order to perform the double-tangent construction on the Helmholtz free energy, all simulation data were fitted to an analytical function of  $\rho$ ,  $\delta$ , and  $T$  [8]. Analysis of the fitted free energies showed that an isostructural solid-solid transition does indeed occur. Figure 1 shows the computed solid-solid coexistence curves in the  $\rho, T$  plane. The density gap between the dense and expanded fcc solids is wide at low temperatures, but shrinks to zero when the solid-solid critical point is approached. The coexistence curves are asymmetric, especially in the limit  $\delta \rightarrow 0$ . Because of the analogy with liquid-vapor coexistence, one might think that the solid-solid critical point should be of the 3D-Ising universality class, although the behavior in the limit  $\delta \rightarrow 0$  could be different. In this limit, the reduced critical temperature  $T_c$  goes to a finite limiting value of approximately 1.7. We stress that this limiting critical temperature is a property of the hard-sphere solid at close packing and it is tempting to speculate that, in this limit, the critical properties may be computed analytically.

As can be seen in Fig. 1, the critical temperature depends only weakly on  $\delta$ . In contrast, the solid-solid coexistence region shifts to lower densities as the well width is increased. This effect can easily be understood by noting that a dense square-well solid can be expanded at virtually no cost in potential energy, up to the point where the nearest-neighbor separation is  $1+\delta$ . It is only when the solid is expanded beyond this limit that the potential energy increases steeply and a transition to the expanded solid may occur. Hence, the larger  $\delta$ , the lower the density where the phase transition will take place. In fact,

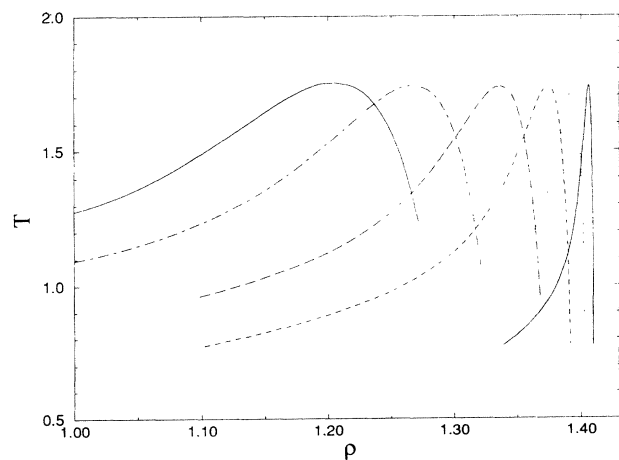


FIG. 1. Solid-solid coexistence curves of square-well systems in the  $T, \rho$  plane. From left to right:  $\delta = 0.06, 0.04, 0.02, 0.01, 0.005$ , and 0.002.

as can be seen in Fig. 2, the dependence of the critical density on  $\delta$  is described remarkably well by Eq. (2), that was based on the crude cell model mentioned above.

When  $\delta$  becomes large, the solid-solid transition will disappear because it will be preempted by the melting transition. We note that the melting behavior of a system of hard spheres with a narrow but finite attractive well, should be rather similar to that of a system of adhesive spheres, i.e., hard spheres with an infinitely narrow, but infinitely deep, square well. The melting line of this latter model was recently estimated by Tejero and Baus, using density-functional theory [12]. In fact, we cannot directly compare Fig. 1 with the melting curve of Ref. [12] because, for the adhesive-sphere model,  $\epsilon/k_B T$  is infinite. A comparison between square-well and adhesive-sphere models is best made by defining a temperaturelike parameter  $\tau$  [13] that is related to the second virial coefficient:

$$\tau = \frac{1}{4}(1 - B_2^{\text{AHS}}/B_2^{\text{HS}})^{-1} \equiv \frac{1}{4}(1 - B_2^{\text{SQW}}/B_2^{\text{HS}})^{-1}, \quad (4)$$

where  $B_2^{\text{HS}}$ ,  $B_2^{\text{AHS}}$ , and  $B_2^{\text{SQW}}$  denote the second virial coefficients of hard spheres, adhesive hard spheres, and square-well particles, respectively.

In Fig. 3, we have plotted the computed solid-solid coexistence curves in a  $\tau$ - $\rho$  diagram. The estimated solid-liquid coexistence curves of the adhesive-sphere system is indicated in the same figure. Figure 3 shows that for sufficiently low values of  $\tau$ , the solid-solid coexistence curve will cross the melting line. This implies that, at low temperatures, the expanded solid is no longer stable and the dense solid coexists with the fluid. This may explain the puzzling observation of Tejero and Baus [12] that the (expanded) adhesive-hard-sphere solid becomes mechanically unstable below  $\tau \approx 3$ . Figure 3 indicates that for

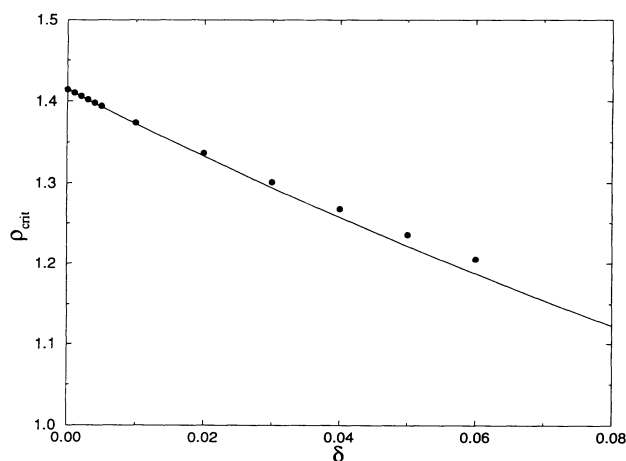


FIG. 2. Dependence of the computed solid-solid critical density of square-well systems, as a function of the well width  $\delta$ . The solid curve denotes the prediction of the uncorrelated cell model.

small values of  $\delta$  ( $\delta \leq 0.01$ ) the solid-solid transition occurs well before melting. We have, in fact, performed direct simulations of the melting transition for square well models [8] and found that only when  $\delta > 0.06$  the solid-solid transition is preempted by the melting transition.

It should be noted that isostructural solid-solid transitions are known to occur in dense Cs and Ce [14]. However, in this case the intermolecular potential is too long ranged to induce the mechanism described above and the transition is believed to be due to the *softness* of the intermolecular potential associated with a pressure-induced change in the electronic state of the metal ions. In fact, theoretical work of Stell and Hemmer [15] and simulations of Young and Alder [16] indicate that such softness may indeed result in solid-solid transition. We stress that the solid-solid transition reported in the present paper is different because it is not related to a pressure-induced change in the effective size of the particles.

An obvious question is whether the isostructural solid-solid phase transition due to short-ranged attraction, which we report here, can occur in real systems. We believe that such a transition can be observed in uncharged colloids with a short-ranged attraction. Such systems can be made, for instance, by adding nonadsorbing polymer to a suspension of hard-sphere colloids (for a review, see, e.g., Ref. [4]). The polymers induce an effective attractive force between the colloidal spheres. The range of this attraction is directly related to the radius of gyration of the polymer. Hence, a colloidal crystal to which a polymer has been added with radius of gyration less than 6% of the radius of the colloidal spheres, should exhibit the solid-solid phase behavior of the models discussed in this Letter.

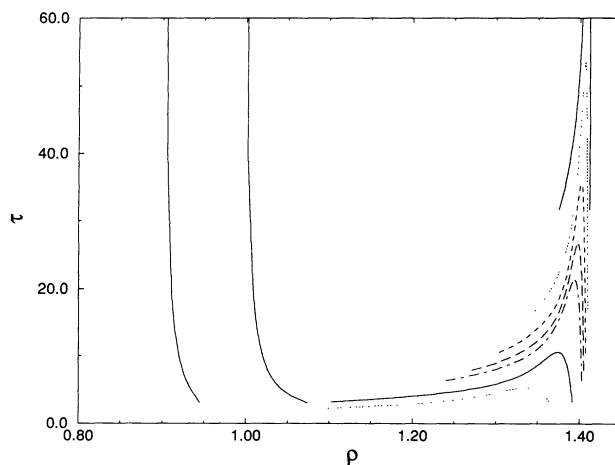


FIG. 3. Simulated phase diagrams in the  $\tau$ ,  $\rho$  plane (see text). The almost vertical curves near  $\rho=1$  indicated the estimated melting curve of adhesive hard spheres [12]. On the right are the computed solid-solid coexistence curves. From top to bottom:  $\delta = 0.001, 0.002, 0.003, 0.004, 0.005, 0.01, 0.02$ .

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