Solid-Fluid Coexistence for Inverse-Power Potentials

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We report Monte Carlo studies of solid-fluid coexistence for the soft-sphere potential: $\phi(r) = \varepsilon(\sigma/r)^n$. Applying a recently developed integration method that proceeds along a coexistence line, we determined coexistence for essentially a continuum of softness $s \equiv 1/n$ from $s = 0$ (hard spheres) to ca. $s = 0.25$. For $s < 0.16$, we estimate that fcc is the stable crystal, and that bcc is stable for softer potentials; however, this result is not conclusive. We find substantial disagreement with early coexistence data for $n = 12$, 9, 6; and 4, while confirming more recent studies for $n = 12$ and 6.

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The thermodynamic equilibrium between two solid phases or between a solid and a fluid is a common phenomenon which has nevertheless eluded a general, quantitative description. The past fifteen years have been a time of great activity in the development of theoretical treatments for inhomogeneous fluids in general, and for these "freezing" transitions in particular [1]. Work has necessarily focused on a few model substances, with particular attention paid to the inverse-power potential, which defines a system of classical "soft spheres." This model captures the role of molecular repulsion in freezing, and it is characterized by the pairwise-additive, spherically symmetric intermolecular potential: $\phi(r) = \varepsilon(\sigma/r)^n$, where ε, σ, and n are model parameters and r is the molecular separation. The soft-sphere model has several appealing features. Its thermodynamic behavior exhibits scaling properties which result from the dependence of the potential on the single group $\varepsilon\sigma^n$; thus the entire phase diagram (for a system of given n) can be extracted from a single coexistence datum. Moreover, the qualitative features of the phase diagram can be modified substantially by adjusting n. For large n, the potential becomes increasingly hard and short ranged (approaching the hard-sphere potential as $n \to \infty$), and freezing is into a close-packed structure, usually assumed to be fcc; the bcc structure is unstable with respect to shear. As n diminishes toward unity, the interactions become increasingly soft and long ranged, and the bcc phase becomes mechanically stable (at $n = 7$). For the classical one-component plasma (OCP) ($n = 1$), bcc represents the only crystalline phase because it is the structure of both lowest energy (at zero temperature) and greatest entropy. At intermediate n, fcc represents the lowest-energy structure, while bcc retains the higher entropy. Thus, as the temperature is raised from zero, there exists in these cases the possibility of a fcc-bcc polymorphic transition which precedes the transition to the fluid. This behavior is seen in the alkali metals and in iron.

Advancement of theories of freezing has been facilitated by model "experimental" data made available by molecular simulation [2,3]. These phase-coexistence data are not easily obtained. Computational limits on the system size preclude the physical approach to evaluating coexistence, in which both phases are placed in contact in the same simulation volume; the interface—if it can form at all—overwhelms the bulk behavior. In practice, homogeneous phases must be simulated, and coexistence established by satisfying the well-known requirements of thermodynamic phase equilibrium. Two problems arise: First, the conditions of coexistence can be found this way only by performing a search which requires many simulations at "uninteresting" state conditions (i.e., away from coexistence). Second, the chemical potentials needed to establish coexistence can be notoriously difficult to evaluate. Insertion-based methods (including Gibbs ensemble Monte Carlo [4]) are difficult to reconcile with the nature of the crystalline phase (even considering defects [5]), and are generally unreliable for dense systems. Thermodynamic integration has therefore arisen as the method of choice for evaluating solid-phase chemical potentials. It is reliable and it fits well with the coexistence search process. However, even this approach is not trouble-free, and much effort has been devoted to devising reliable integration pathways to implement it. A typical report describes great efforts that, in the end, yield a few precious coexistence points or possibly a single isotherm. Nonetheless, the utility of the data so obtained certainly has justified the efforts. Monte Carlo calculations performed for the soft-sphere potential with $n = 1$ [6], 4, 6, 9 [7], 12 [8–10], and ∞ [11,12] have confirmed much of the qualitative behavior described above. There is, however, substantial disagreement between early simulation data and the results of two ($n = 12$ [13] and 6 [14]) more recent studies that adopt better integration pathways. Discussion follows below.

The recently introduced Gibbs-Duhem integration method [15] represents what is arguably the most efficient combination of the search and the integration procedures needed to determine phase equilibrium by molecular simulation. Integration advances *along the coexistence line,* so each simulation yields a phase equilibrium point. The method has been used to evaluate vapor-liquid coexistence in pure substances [15] and mixtures [16], and solid-fluid coexistence in a model for C_{60} [17].

The present Letter describes application of the Gibbs-Duhem integration technique to freezing in the soft-sphere model. The study is interesting in several respects. The integration path chosen here involves a mutation of the potential, rather than a traversing of thermodynamic state space. This approach makes it possible to obtain a detailed picture of the phase behavior along a continuum of values of n from the hard-sphere limit to about $n = 4$. In addition, it is demonstrated how the emergence of new phases (viz., the bcc crystal) can be accommodated by the technique. Surprisingly, the integration method remains reliable even as the transition becomes very weak, although it does show limits.

The method begins with a variation of the isothermal Gibbs-Duhem equation

$$d(\beta\mu) = \beta p v \, d\ln p + \lambda ds, \qquad (1)$$

where μ is the chemical potential, v is the molar volume, p is the pressure, and $\beta = 1/kT$, with k Boltzmann's constant and T the absolute temperature. The parameter $s \equiv 1/n$ describes the softness of the potential, and takes on values from zero (hard spheres) to unity (OCP); λ is defined by Eq. (1). Given two coexisting phases of soft spheres, Eq. (1)—written for each phase—may be used to derive the change in the saturation pressure dp required to maintain coexistence as the softness s is perturbed an amount ds

$$\left(\frac{\partial \ln p}{\partial s}\right)_{\mathrm{sat}} = -\frac{\lambda_1 - \lambda_2}{\beta p(v_1 - v_2)} \equiv f(s,p), \qquad (2)$$

where the subscripts indicate the two phases and the equation defines $f(s,p)$; this formula is a variant of the Clapeyron equation. In the Gibbs-Duhem method, Eq. (2) is integrated using predictor-corrector techniques as any first-order ordinary differential equation might be. The right-hand side is evaluated by isothermal-isobaric (NpT) Monte Carlo (or molecular dynamics) simulations conducted for each phase simultaneously; the simulated phases occupy their own volumes, and thus are not in direct contact. The parameter λ is given by the ensemble average $\lambda = -\beta\varepsilon s^{-2}\langle(\sigma/r)^{1/s}\ln(\sigma/r)\rangle$. The pressure is continually refined throughout the simulation as the averages of λ and v in each phase converge to their final values. Once complete, the process may be continued by incrementing s and repeating, thereby yielding the coexistence properties over a wide range of values of s. The hard-sphere coexistence datum provides a convenient starting point for this procedure [11]. Also, in this limit λ can be expressed in terms of the volumetric properties [18]: $\lambda_{\mathrm{HS}} = 3\gamma(\beta p v - 1)$, where γ is Euler's constant.

Using this method we determined solid-fluid coexistence properties of the soft-sphere potential for values of the softness parameter from zero to ca. 0.25, in steps of 0.01. Our results are displayed in Fig. 1. The NpT Monte Carlo simulations were conducted for two system sizes (solid, fluid): (108, 128) and (500, 432) (the small-system series was conducted in steps of 0.005). Standard cubic periodic boundary conditions were imposed on the solid, while truncated-octahedron periodic boundaries were used for the fluid phase; long-range interactions were handled in the usual manner [3]. Each simulation sampled 10 000 cycles beyond an initial relaxation period of 5000 cycles, where a cycle represents one attempted translation per particle and five attempted volume changes. Further details will be presented elsewhere [19].

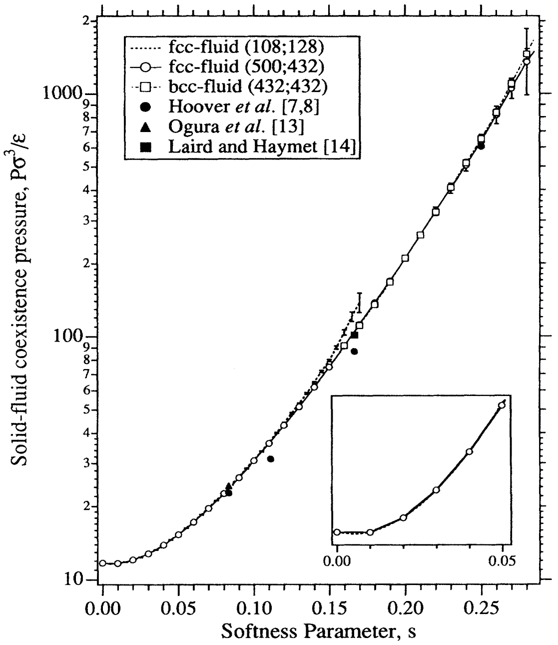

FIG. 1. Coexistence lines determined in this study. Confidence limits (67%) are indicated where they are larger than the plotting symbol. Numbers in the legend refer to the number of spheres used to simulate each phase (solid, fluid). The inset is an expansion of the region near $s = 0$.

There are several potential sources of error in the procedure. First is the stochastic error in v and λ, which gives rise to corresponding errors in $f(s,p)$, and eventually in the pressure p. We have estimated this error by analyzing the fluctuations in v and λ according to the method of Kolafa [20], and applying standard propagation-of-error rules to estimate the error in the pressure. The resulting error bars are indicated in Fig. 1. This source of error becomes more important as s increases and the transition becomes weaker [$f(s,p)$ becomes the ratio of increasingly small numbers]. The small-system calculations succumbed to the effect relatively early, as the accumulating error in the pressure led the fluid to crystallize at $s = 0.17$ (this could of course happen even if the pressure is not in error, and it is more likely to do so for a small system). Error due to the finite integration step was estimated by reapplying the integration formulas to half of the simulation data (thereby doubling the integration step size), with little observed effect on the large system (although halving the step size from 0.01 to 0.005 had a measurable influence on the small-system results). Errors related to stability—which concern whether errors in the pressure are amplified or attenuated by their effect on $f(s,p)$—can be significant if the integration path proceeds in the direction of a weaker transition [16], as is the case here. To gauge its effect, we performed a brief series of simulations along the fcc-fluid coexistence line, from $n = 12$ to $n = 9$; the $n = 12$ pressure was displaced by 8% before beginning the series. The resulting coexistence line proceeded along a course parallel to the original, indicating that small errors in p have an insignificant effect on $f(s,p)$ (for s in this range). A final source of error arises from the finite size of the simulated systems. Figure 1 indicates that this error is not significant for small values of s, but for large s (>0.16) we cannot gauge its extent without data for yet larger systems.

Emergence of a thermodynamically stable bcc phase can be detected by performing a series of simulations for bcc soft spheres, *following the (s,p) path defined by the fcc-fluid integration.* We apply a Wigner-Seitz single occupancy (SO) constraint [11] to ensure that the (mechanically unstable) bcc crystal does not melt. At every point along the path, the chemical potential in each phase α can be computed by introducing Eq. (2) into Eq. (1), and integrating the simulation data

$$\beta\mu_\alpha[s,p(s)] - \beta\mu_\alpha^{\mathrm{HS}} = \int_0^s \{(\beta p v)_\alpha f[\tilde{s}, p(\tilde{s})] + \lambda_\alpha\} d\tilde{s}\,.$$

The resulting values of μ for the fcc and fluid phases will, of course, be the same along their line of coexistence. We expect the SO bcc chemical potential to begin at a higher value, and to approach the fcc-fluid values as the integration proceeds. Eventually the curves should intersect, indicating three-phase coexistence. From this point on, freezing of the fluid into the fcc phase is superseded by freezing into the bcc, and fluid-fcc coexistence no longer occurs. The integration procedure can, in principle, be continued along both of the coexistence lines (bcc-fluid and fcc-fluid) that emerge from the triple point. The (metastable) fcc-fluid coexistence line can also be extended by continuing the integration procedure.

We evaluated the chemical potentials for the bcc and fcc phases in this manner, and we plot the result in Fig. 2. We computed this curve twice, performing two independent fcc-fluid series to $s = 0.30$, and two corresponding bcc series (to $s = 0.17$). The difference between the two fcc-fluid saturation pressures remained well within their estimated errors. The reproducibility of the chemical-potential difference is also very good for s in the range 0.0–0.13. However, beyond this point significant discrepancy is observed between the two values. This result is not entirely surprising, as $\mu_{\mathrm{fcc}} - \mu_{\mathrm{bcc}}$ here is the small difference between large (ca. 50) numbers. The shaky behavior exhibited in this range of softness reminds one of the difficulty encountered when a SO system is compressed through its density of stability [11]: a bcc crystal of soft spheres achieves mechanical stability [21] only beyond $s = 0.1305$.

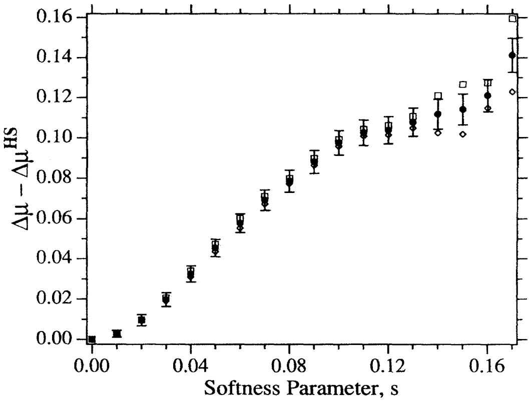

FIG. 2. Difference between the chemical potentials of the fcc and bcc phases as a function of the potential softness, relative to the difference for the hard-sphere system (i.e., $\Delta\mu \equiv \mu_{\mathrm{fcc}} - \mu_{\mathrm{bcc}}$). The open squares and diamonds are results from two independent integration series, and the filled circles are their arithmetic mean.

We have chosen to work with the average of our two series, presented also in Fig. 2. The difference between the fcc and bcc chemical potentials as a function of s may be obtained from this curve by adding the corresponding difference for hard spheres. We determined the SO bcc hard-sphere chemical potential at the fcc-fluid coexistence pressure by integrating our own Monte Carlo data for the equation of state of the SO bcc crystal. The constant of integration was provided by a study of the hard-sphere, SO (spherical cell), bcc crystal conducted by Curtin and Runge [22]. Using Frenkel and Ladd's [12] datum for the fcc crystal, our result is $\mu_{\mathrm{fcc}}^{\mathrm{HS}} - \mu_{\mathrm{bcc}}^{\mathrm{HS}} = -0.12$. From Fig. 2, this value implies that the fcc-bcc-fluid "triple point" occurs at approximately $s = 0.16$. This result is sensitive to errors that could be introduced at many places in the procedure. Curtin and Runge, for example, apply an extrapolation which we estimate could give rise to an error of as much as -0.03 in $\mu_{\mathrm{bcc}}^{\mathrm{HS}}$. A change of this magnitude would cause the triple point to shift down to $s = 0.10$. However, as noted above, a (unconstrained) crystal of bcc soft spheres is mechanically unstable for this value of s.

Taking the fluid-fcc-bcc triple point as $s = 0.16$, we conducted a separate Gibbs-Duhem integration series for the bcc-fluid coexistence, and the result is indicated in Fig. 1. We find that the bcc-fluid and fcc-fluid coexistence lines remain essentially indistinguishable throughout the range of softness that we studied, and indeed the curves actually cross several times as the softness is increased. These crossings must be attributed to stochastic error, as it is unlikely that the fcc crystal would regain stability relative to bcc at freezing. The fcc-fluid series was halted at $s = 0.30$ upon melting of the crystal, although it is clear that by $s = 0.28$ the accumulated error had become unmanageable. We performed several other bcc-fluid series (not shown), taking the triple point to be $s = 0.15$ and 0.14, respectively, and another beginning with Laird and Haymet's [14] bcc-fluid coexistence datum for $s = 1/6$. All of these series produced bcc-fluid coexistence lines that begin and remain below the reported curve, and all were terminated at $s = 0.23$ to 0.25 because the crystal melted. We did not investigate fcc-bcc coexistence beyond the estimated triple point, as the extreme weakness of this transition would very likely render the integration method unusable.

Literature data are also displayed in Fig. 1. Early fcc-fluid coexistence calculations were performed by Hoover and co-workers [7,8] for $n = 12$, 9, 6, and 4, and agreement is seen with the result for $n = 12$ obtained by Hansen [9] at about the same time. These methods employed integration from either a low temperature state that is characterized by lattice dynamics or a low density state using the SO constraint. They agree also with the datum of Cape and Woodcock [10], who evaluated the $n = 12$ solid-fluid coexistence properties by direct simulation of both phases in the same volume. Ogura *et al.* [13] used a SO pathway to determine once more coexistence in the $n = 12$ model. Their calculations were more careful than Hoover *et al.* [8] in dealing with the "kink" seen in the SO isotherm, and their coexistence pressure differs significantly from that established by the previous workers. Laird and Haymet [14] very recently completed a study of the $n = 6$ potential, and they report the existence of a stable bcc phase. Their calculations employed a modification of the lattice-coupling integration scheme introduced by Frenkel and Ladd [12]. They too find a (metastable) fluid-fcc coexistence pressure that differs significantly from the results of Hoover, Gray, and Johnson [7].

Our calculations support the conclusions of Ogura *et al.* [13] and Laird and Haymet [14] regarding the fluid-fcc transition. We find that all of the early studies yielded saturation pressures that are too low, with the possible exception of the $n = 4$ datum of Hoover, Gray, and Johnson [7], which lies within our fcc-fluid error bars. We agree with Laird and Haymet that the bcc-fluid and the (metastable) fcc-fluid coexistence points are very narrowly separated at $n = 6$; our data lie slightly above theirs, but the difference cannot be considered significant. It is notable that the fcc-fluid and bcc-fluid saturation curves do not diverge appreciably as the softness is increased.

An unexpected result of our study is observed at the outset of the fcc-fluid series, and is highlighted by the inset in Fig. 1. We find here, near the hard-sphere limit of softness, a shallow minimum in the melting curve. Such an unexpected feature—not to mention the presentation of the entire coexistence line—would be extremely difficult to characterize using any established simulation method. Thus the Gibbs-Duhem integration technique promises to provide a rich set of simulation data with which to test new theories of phase coexistence, in general, and freezing, in particular.

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