Precise Simulation of Freezing Transitions

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ABSTRACT

Despite recent advances, precise simulation of freezing transitions remains a challenging task. In this work, a simulation method for fluid-solid transitions, based on a modification of the constrained cell model of Hoover and Ree, is developed. In the constrained cell model, each particle is confined within its own Wigner-Seitz cell. The constrained cell model is a limiting case of a more general or modified cell model which is constructed by adding an external field that controls the relative stability of the two phases. Constant-pressure simulations of the modified cell model indicate that the transition from the fluid to the solid is continuous at low and moderate pressures and discontinuous at higher pressures. The fluid-solid transition of model systems can been determined either by analyzing the field-induced phase transition of the corresponding modified cell model or via thermodynamic integration based on the same model.

Keywords: fluid-solid transitions, monte carlo, finite-size scaling, critical points

Despite recent advances, precise simulation of freezing transitions remains a challenging task. One of the simplest methods to calculate fluid-solid coexistence is thermodynamic integration. In their original work associated with the freezing transition of hard-spheres, Hoover and Ree [1], [2] modeled the solid phase as a constrained system in which each particle is confined to move in its own Wigner-Seitz cell. Hoover and Ree found that the pressure-density isotherm contains a kink or cusp at a density which is approximately 64% of the density at close packing and associated this anomaly with the mechanical stability point of the solid phase. At densities that are higher than the kink density, the solid phase can survive for substantial time intervals without the confinement imposed by the walls of the Wigner-Seitz cells. In contrast, at lower densities the solid cannot survive without the presence of the cell walls and it thus melts to a disordered, fluid-like phase.

The constrained cell model is a limiting case of a generalized or modified cell model which is constructed by adding a homogenous external field that controls the relative stability of the two phases. High values of the external field variable force configurations with one particle per Wigner-Seitz cell and thus favor the solid phase. Normal (unconstrained) behavior is recovered in the limit of vanishing field. The modified cell model can be used to link the fluid with the solid phase on a constant-pressure (or density) path by progressively increasing the strength of the field. Recently, Nayhouse *et al.* [3]–[7] used this model in the analysis of fluid-solid transitions. In the present work, the fluid-solid transition of a system of Lennard Jones particles at a reduced temperature of 2 is analyzed and its entire phase diagram is determined. The simulations are implemented at constant pressure using tempering [8], [9] and histogram reweighting [10], [11] techniques.

Consider a system of N particles of diameter σ that interact according to a pairwise additive potential, ϕ, which is of the Lennard-Jones form, i.e.,

$$\phi(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right] \quad , \tag{1}$$

where r is the distance between two particles and $\epsilon > 0$ is the depth of the potential. The potential energy of a configuration of a system of N particles in a periodic simulation box of volume $V = L^3$, is evaluated by calculating all pair terms for distances $r \leq L/2$ and adding a tail correction for $r > L/2$. In the isothermal-isobaric ensemble, the number of particles N, the pressure p, and the temperature T [or the inverse temperature $\beta = 1/(k_B T)$, where k_B is Boltzmann's constant], are fixed. The system volume, V, and the number density, $\rho = N/V$, both fluctuate about mean values, $\langle V\rangle$ and $\langle\rho\rangle = N/\langle V\rangle$, respectively. Appropriate reduced variables are defined as: $T^* = k_B T/\epsilon$ (reduced temperature), $p^* = \beta p\sigma^3 = p\sigma^3/k_B T$ (reduced pressure), $\langle\rho^*\rangle = \langle\rho\rangle\sigma^3$ (average reduced density), and $\langle v^*\rangle = \langle v\rangle/\sigma^3 = \langle V\rangle/\left(N\sigma^3\right) = 1/\langle\rho^*\rangle$ (average reduced volume per particle). The Monte Carlo moves comprise particle displacements and volume changes that are accepted with standard Metropolis acceptance criteria. For the fluid (i.e., the unconstrained) phase there is no cell occupancy constraint and the N particles are thus free to move throughout the entire simulation volume, V.

For a cubic simulation box of volume $V = L^3$ that contains N particles, the constrained cell model is defined by dividing the volume, V, into N Wigner-Seitz cells, each of volume V/N, representative of the solid

phase under consideration. In this work, it is assumed that the stable solid form of the Lennard-Jones model is of the face-centered cubic (fcc) type. Thus, the cells are rhombic dodecahedra and $N = 4n^3$ $(n = 2, 3, \ldots)$. Each cell contains a single particle and Monte Carlo moves that violate the single occupancy constraint are rejected by the acceptance criteria.

The fluid- and solid-phase isotherms at $T^* = 2$ for $N = 256$ Lennard-Jones particles, obtained from the simulations, are shown in Fig. 1. There is a region of pressures, $5 \lesssim p^* \lesssim 6$, for which the volume distribution of the solid phase has a bimodal structure, see inset of Fig. 1, for instance. The shape of the volume distribution resembles that of a system undergoing some type of phase transition. The pressure–density isotherm of the solid phase exhibits an inflection point at pressure $p^* \cong 5.64$, which corresponds to a density $\rho \cong 0.7\rho_0$, where $\rho_0\sigma^3 = \sqrt{2}$ is the value of the reduced density at close packing. The inflection point is associated with the limit of mechanical stability of the solid. A solid phase at densities $\rho < 0.7\rho_0$, cannot survive without the confinement imposed by the walls of the Wigner-Seitz cells and it thus melts to a disordered, fluid-like phase.

In freezing transition studies via thermodynamic integration techniques, the free energy of both phases is calculated for a range of states from the low-density, ideal gas region to the high-density, close packed limit. In order to reduce the number of states that must be simulated, Hoover and Ree proposed a modified cell model [1], [2] by adding an external field of variable strength. High-field values favor single occupancy configurations (i.e., one particle per Wigner-Seitz cell) and thus stabilize the solid phase. Normal (unconstrained) system behavior is restored in the limit of vanishing field. Hoover and Ree thought that the modified cell model could be used to link the fluid with the solid phase thus reducing the number of simulated states in thermodynamic integration studies of freezing transitions. In their early work associated with hard-sphere freezing [1], [2], Hoover and Ree investigated the low-density behavior of this modified cell model through cluster expansion techniques. Recently, the modified cell model was reformulated in the isothermal-isobaric ensemble by Nayhouse *et al.* [3]–[7] and was used to analyze fluid-solid transitions of model systems.

Consider arbitrary distributions of the N particles into the N Wigner-Seitz cells. The occupation status (i.e., number of particles) of cell j ($j = 1, 2, \ldots, N$), can be described with the variable s_j which can only take two values: -1 if cell j contains one particle and zero otherwise. The occupation status of a specific configuration of the N particles (i.e., the number of singly occupied cells) can be expressed in terms of the variable $|M|$, where $M = \sum_j s_j$. Consider an external field variable, B say, and suppose that the interaction of this

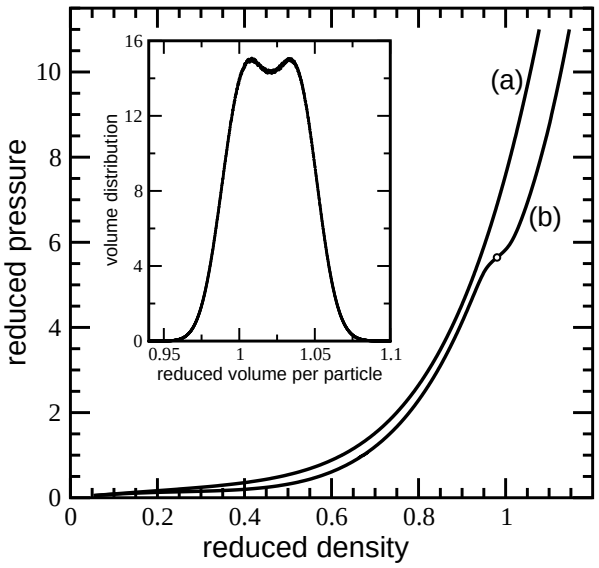

Figure 1: Reduced pressure, p^*, vs average reduced density, $\langle\rho^*\rangle$, for $N = 256$ Lennard-Jones particles at $T^* = 2$. (a): fluid; (b): constrained cell model. The inset shows the distribution of the reduced volume for the constrained cell model at $p^* = 5.644$. The state shown in the inset corresponds to the open circle, ($\circ$), on curve (b) in the main figure.

variable with cell j is Bs_j. If $b = \beta B$, the isothermal-isobaric partition function Δ, for N particles at temperature T, and pressure p, is

$$\Delta(N, p, T, b) = \sum_i \exp\left[-\beta E_i - \beta p V_i - b M_i\right] \quad , \quad (2)$$

where index i enumerates the states and E_i, V_i, and $|M_i|$, are the energy, volume, and number of singly occupied cells in state i. The unconstrained system corresponds to $b = 0$, whereas the constrained cell model of Hoover and Ree is recovered in the limit in which $b \to \infty$. In Monte Carlo simulations of a system of N particles at p, T, and b, the elementary updates comprise particle displacements and volume changes that are accepted with standard Metropolis acceptance criteria. For particle displacements, the acceptance probability must account for changes in the variable M when the center of a particle moves out of its current cell and enters a neighboring one. In this case, the acceptance probability from state i to j, α_{ij}, is given by

$$\alpha_{ij} = \min\left[1, \exp\left(-\beta\Delta E - b\Delta M\right)\right] \quad , \quad (3)$$

where $\Delta E = E_j - E_i$ and $\Delta M = M_j - M_i$.

The behavior of the modified cell model at $T^* = 2$ and at pressures $p^* \gtrsim 5$ was investigated via tempering techniques [8], [9]. The effect of the external field b, at constant pressure for $N = 256$ Lennard-Jones particles is shown in Fig. 2. Specifically, the variation of

the field variable, b, in terms of the average fraction of singly occupied Wigner-Seitz cells, $-\langle M\rangle/N$, is plotted in Fig. 2 for five isobars at pressures $p^* = 5$, 6, 7, 8, and 9. At high-field values, only single occupancy (i.e., $|M| = N$) configurations survive and the system is in the solid phase. As in the case of hard spheres [3], [4], the behavior of the five isobars shown in Fig. 2 resembles that of a system undergoing a phase transition. As b is reduced at fixed pressure from high values ($b \sim 4$) towards zero, the transformation of the solid to the fluid phase is continuous at low and intermediate pressures, see, e.g., isobar $p^* = 5$ in Fig. 2. At higher pressures, $p^* \gtrsim 6$, the shape of the isobars is similar to that of a system undergoing a first-order phase transition. The simulations indicate that there is a range of values of the field b, for which the distribution of volume V, and of the number of singly occupied cells $|M|$, both consist of two maxima (peaks) separated by a minimum. The inset of Fig. 2 shows the shape of the volume distribution for $b = 0.218$ and $p^* = 9$. For the state shown in the inset of Fig. 2, the average fraction of singly occupied cells is 90%. The specific value of b ($b = 0.218$) was found through histogram reweighting [10], [11]. Fig. 2 thus indicates that at high pressures, $p^* \gtrsim 6$, the transformation of the high-b, ordered, solid-like phase to the low-b, disordered, fluid-like phase occurs via a first-order phase transition. Furthermore, as the pressure increases, the order-disorder transition occurs at lower field values.

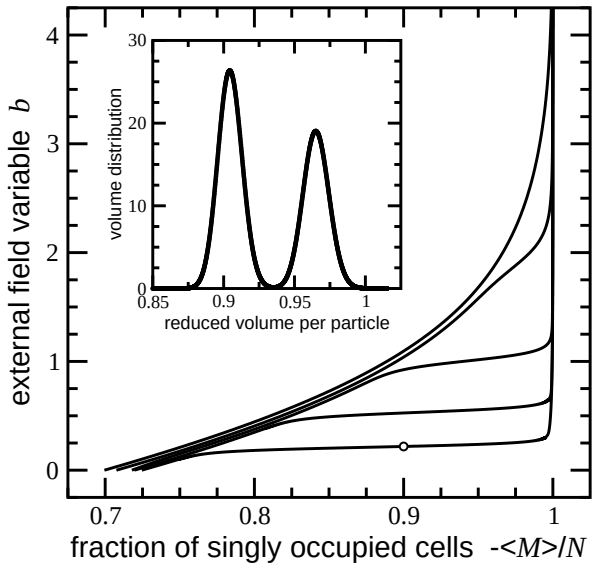

Figure 2: External field variable b, vs average fraction of singly occupied cells $-\langle M\rangle/N$, for $N = 256$ Lennard-Jones particles at $T^* = 2$. The curves from top to bottom correspond to reduced pressures $p^* = 5$, 6, 7, 8, and 9, respectively. The inset shows the volume distribution at $p^* = 9$ and $b = 0.218$. For this state, the average fraction of singly occupied cells is 90%. This state corresponds to the open circle, (○), on the $p^* = 9$ isobar of the main figure.

The field-induced order-disorder transition of the Lennard-Jones model at $T^* = 2$ has been studied via constant-pressure simulations and tempering techniques [8], [9]. The results for the coexisting densities of the ordered (solid-like) and the disordered (fluid-like) phase are shown in Fig. 3 together with the relevant portion of the p–ρ isotherms of the fluid and the solid phase of the Lennard-Jones model at $T^* = 2$. The coexisting densities of the ordered and the disordered phase lie in between respective isotherms of the solid and the fluid phase. As the pressure increases, the value of the field, b, at order-disorder coexistence decreases and as $b \to 0$, the densities of the ordered and the disordered phase approach those of the solid and fluid phase, respectively. The coexisting densities shown in Fig. 3, appear to be converging towards a terminal point in the neighborhood of the mechanical stability point of the p–ρ isotherm of the solid phase which is shown as a bullet, (•), in Fig. 3. The appearance of the field-induced phase transition of the modified cell model, shown in Figs. 2 and 3, is related to the mechanical stability of the solid. A mechanically stable solid phase that exists without the confinement imposed by the bounding surfaces of the Wigner-Seitz cells, will always be trans-

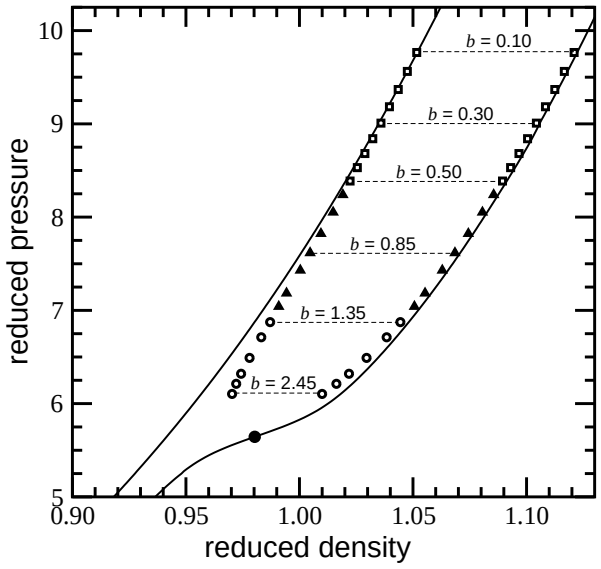

Figure 3: Phase diagram of the modified cell model for the Lennard-Jones system at $T^* = 2$ in the pressure-density plane. The solid lines correspond to the fluid and the constrained solid phases [i.e., curves (a) and (b) in Fig. 1]. The coexisting solid and fluid phases for finite values of b are shown as points and they correspond to system sizes, N, of (○): 2048, (▲): 1372, and (□): 864. The dashed horizontal lines are tie-lines and they are drawn for clarity. The point shown as bullet, (•), corresponds to the inflection point of the $T^* = 2$ isotherm of the constrained cell model.

formed discontinuously to a fluid phase.

The fluid-solid phase transition of the Lennard-Jones model at $T^* = 2$ can either be determined by analyzing the field-induced phase transition of the modified cell model in the high-p, zero-field limit, or via thermodynamic integration using the same model. Repetition of this process at different temperatures establishes the entire fluid-solid phase diagram. The results of this procedure for the Lennard-Jones model are shown in Fig. 4 together with the vapor-liquid phase diagram of the same model. Vapor-liquid coexistence was determined from constant-pressure simulations of the unconstrained system using tempering [8], [9] and histogram reweighting [10], [11]. As is evident from Fig. 4, the results of the present work are in excellent agreement with those of previous work [12]–[14].

The main advantage of the modified cell model in simulation studies of fluid-solid transitions is its simplicity. The extra effort (computational as well as programming) associated with the introduction of the external field variable into the ordinary isothermal-isobaric ensemble is minor. Unlike other methods that are based on complicated order parameters, the conjugate variable associated with the external field can be simply and transparently identified as the number of Wigner-Seitz cells containing a single particle. In the context of simulations of fluid-solid equilibria via thermodynamic integration, the modified cell model provides a path that connects the fluid with the solid phase, thus reducing the number of simulated states. Alternatively, the fluid-solid transition of the system of interest can be obtained by analyzing the field-induced phase transition of the corresponding modified cell model by standard flat-histogram techniques. These two alternative approaches of locating fluid-solid coexistence are equivalent, and the selection of one compared to the other depends on programming considerations. Future work comprises the determination of the phase diagrams of systems for which fluid-fluid demixing is metastable against freezing such as protein solutions and colloidal suspensions.

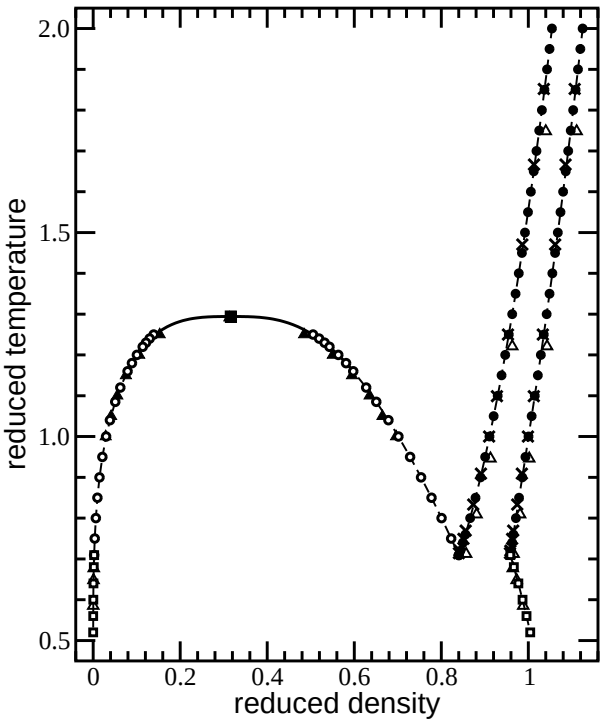

Figure 4: Phase diagram of the Lennard-Jones model in the temperature-density plane. All calculations have been performed for $N = 256$ particles. (●): liquid-solid coexistence; (○): vapor-liquid coexistence; (□): vapor-solid coexistence. The vapor-liquid critical point is shown as a filled square, (■). The solid line is a fit to scaling laws assuming Ising criticality. The triangles, (△), are the liquid-solid and vapor-solid coexistence data of Agrawal and Kofke [12]. The crosses, (×), are liquid-solid coexistence data obtained by McNeil-Watson and Wilding [13]. The filled triangles, (▲), are vapor-liquid coexistence data obtained by Chen *et al.* [14].

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