Determination of the melting point of hard spheres from direct coexistence simulation methods

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(Received 17 December 2007; accepted 3 March 2008; published online 16 April 2008)

We consider the computation of the coexistence pressure of the liquid-solid transition of a system of hard spheres from direct simulation of the inhomogeneous system formed from liquid and solid phases separated by an interface. Monte Carlo simulations of the interfacial system are performed in three different ensembles. In a first approach, a series of simulations is carried out in the isothermal-isobaric ensemble, where the solid is allowed to relax to its equilibrium crystalline structure, thus avoiding the appearance of artificial stress in the system. Here, the total volume of the system fluctuates due to changes in the three dimensions of the simulation box. In a second approach, we consider simulations of the inhomogeneous system in an isothermal-isobaric ensemble where the normal pressure, as well as the area of the (planar) fluid-solid interface, are kept constant. Now, the total volume of the system fluctuates due to changes in the longitudinal dimension of the simulation box. In both approaches, the coexistence pressure is estimated by monitoring the evolution of the density along several simulations carried out at different pressures. Both routes are seen to provide consistent values of the fluid-solid coexistence pressure, $p=11.54(4)k_BT/\sigma^3$, which indicates that the error introduced by the use of the standard constant-pressure ensemble for this particular problem is small, provided the systems are sufficiently large. An additional simulation of the interfacial system is conducted in a canonical ensemble where the dimensions of the simulation box are allowed to change subject to the constraint that the total volume is kept fixed. In this approach, the coexistence pressure corresponds to the normal component of the pressure tensor, which can be computed as an appropriate ensemble average in a single simulation. This route yields a value of $p=11.54(4)k_BT/\sigma^3$. We conclude that the results obtained for the coexistence pressure from direct simulations of the liquid and solid phases in coexistence using different ensembles are mutually consistent and are in excellent agreement with the values obtained from free energy calculations. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2901172]

I. INTRODUCTION

The accurate location of first-order phase transitions from computer simulation requires the use of special numerical techniques.[1] One of the most widely used approaches involves the computation of the free energy of each phase, from which the location of the transition follows from the numerical solution of the equilibrium conditions of equality of temperature, pressure and chemical potential.[1] The free energy at any thermodynamic condition is generally evaluated from a numerical integration of some first-order derivative of the free energy along a reversible path that links the system under consideration with a reference state for which the free energy is known. For fluid phases, one typically considers the ideal gas phase as reference state, whereas for the solid phase, the reference system is taken to be an ideal Einstein crystal with the same structure as the solid of interest.[2] Once a single point on the coexistence curve has been determined, the rest of that curve can be calculated by numerical integration of the Clausius–Clapeyron equation.[3]

Though the free energy route to the location of phase transitions involving the solid phase proves to be quite accurate, the calculation of a single coexistence point typically requires many simulations, so a more straightforward approach would therefore be highly desirable. It was with this idea in mind that Ladd and Woodcock devised in the late 70s the direct coexistence method, in which the liquid-solid coexistence properties are estimated from the simulation of the two phases in coexistence.[4–6] Though the first applications of the method were not very successful, probably due to the small system sizes and short lengths of the simulations considered at the time, the method is now becoming increasingly popular. Some recent applications include the study of fluid-solid coexistence in simple fluids,[7–12] metals,[13–16] silicon,[17] ionic systems,[18] hard dumbells,[19] nitromethane,[20] and water.[21–29] These works share the approach to the calculation of the melting properties from the direct simulation of the inhomogeneous fluid-solid system, using either Monte Carlo (MC) or molecular dynamics (MD) schemes. Both simulation techniques are equally valid, although MD is the technique of choice if one is interested in dynamical properties, such as crystal-growth rate just to mention an example.

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The interface between a hard-sphere crystal and its melt under coexistence conditions has been the subject of a number of simulation studies.[9–11] The most extensive of these works is due to Davidchack and Laird,[11] who examined the structure and dynamics of the fcc (111) and (100) crystal-liquid interfaces for systems of about 10 000 hard spheres using constant-energy MD simulation. As the overall volume of the system is kept constant in the course of their simulations, possible stress in the bulk solid was eliminated by trial adjustment of the dimensions of the simulation cell. They report a value of $11.55(5)k_BT/\sigma^3$ for the liquid-solid coexistence pressure, where σ is the diameter of the hard spheres. This value is consistent with more recent estimates based on free-energy calculations[1,30–33] and lower than the value of $11.70(18)k_BT/\sigma^3$ reported by Hoover and Ree.[34]

In principle, the direct simulation of systems with a liquid-solid interface can be conducted in different ensembles. In this work, we examine different routes to the evaluation of the liquid-solid coexistence pressure as obtained from direct simulation of the two phases in coexistence using different ensembles. All simulations are implemented according to standard Metropolis MC algorithms and are undertaken in the following ensembles: (1) Constant-pressure ensemble in which the volume fluctuates as a result of changes in the three dimensions of the simulation box; this corresponds to the standard NpT ensemble, where N is the number of particles, p is the pressure, and T is the temperature. (2) Constant-pressure ensemble in which the volume fluctuates as a result of changes in the longitudinal dimension (perpendicular to the planar interface) of the simulation box with fixed transverse dimension. This corresponds to the Np_NAT ensemble, where p_N is the input (normal) pressure, and A is the area of the interface. (3) Variable-shape constant-volume (VSNVT) ensemble in which the longitudinal and transverse dimensions of the simulation box are allowed to fluctuate subject to the constraint of fixed overall volume. Note that, while in the VSNVT ensemble the coexistence properties can be obtained as an ensemble average over a simulation of the interface at equilibrium, in the NpT and Np_NAT ensembles it is not possible to have an interface at equilibrium (since the exact value of the coexistence pressure, with all the significant digits, is not known *a priori*, it is not possible to perform a NpT or Np_NAT simulation at the exact conditions of coexistence). In the constant-pressure approaches, the coexistence properties will be determined by performing simulations at different conditions and observing the growth or the melting of the crystal.

The direct simulation of the liquid-solid coexistence in each of the above (or possibly other) ensembles has advantages and disadvantages. The microcanonical ensemble, where the total energy is kept constant, has been the natural choice in a number of MD studies of the liquid-solid coexistence properties. Under these conditions, the transfer of heat poses a limit to the rate at which equilibrium is achieved. On the other hand, coupling the system to a thermostat leads to crystallization rates much higher than those found experimentally:[35] this is an advantage for the computation of the melting point, but not for the calculation of dynamical properties. Also, the solid is likely to be under stress when the simulation is carried out under standard constant-volume conditions, as the crystalline structure is not allowed to relax to equilibrium in the direction parallel to the interface. This is expected to yield inaccurate estimates of the melting point.[36] This problem can be alleviated by undertaking constant-pressure (or more appropriately, constant-stress) simulations. This method has the additional advantage that fluctuations in the volume will generally allow for larger changes in the relative amounts of liquid and solid in the system, this resulting in higher equilibration rates. However, the use of the standard constant-pressure method is not strictly valid for the simulation of systems with interfaces, as the pressure is a tensor property in this case, with different values of the normal and transverse (relative to the interface for planar interfaces) components of the pressure tensor. The normal component will be equal to the equilibrium pressure throughout the system; though this is also the case for the tangential pressure in the bulk phases, the latter component will be different from the bulk pressure in the interfacial region. As long as this region remains small compared to the longitudinal dimension of the system, one may anticipate that the anisotropy of the pressure tensor will be small so the standard constant-pressure scheme will be approximately valid. This (small) inconsistency can be removed by the consideration of a constant-pressure scheme in which the volume of the system is changed by varying the longitudinal dimension of the simulation box while keeping the transverse (interfacial) area constant. This procedure, however, cannot relax possible imbalanced bulk strain in the transverse direction in the crystal phase. Alternatively, one may consider the simulation of the fluid-solid interface in a canonical ensemble where the shape of the simulation box is allowed to change subject to the constraint that the total volume (as well as the number of particles and temperature) is kept fixed.[32,37,38] As the longitudinal and transverse dimensions of the simulation cell are allowed to change, the solid is expected to relax to equilibrium without building up bulk stress, as it would be the case in a standard constant-volume simulation.

The purpose of this work is to assess the applicability and efficiency of direct simulations undertaken in different ensembles, where either the pressure, the normal pressure, or the volume are kept constant, for the prediction of the melting pressure. A comparison of the results will allow us to assess the error introduced when the simulation of the interfacial system is performed under constant-pressure conditions. Though the results reported here are limited to the liquid-solid coexistence of hard spheres, we believe that our conclusions are completely general and should be of application to a wider class of more complex systems.

II. METHOD

The first step to implement the direct coexistence method is to build a liquid-solid interface. For that purpose, we generated a fcc lattice with $6\times6\times18$ unit cells (2592 atoms) at a density close to the expected coexistence value of the hard-sphere solid. This box was replicated and expanded along the z direction so as to obtain a density close to the

expected coexistence density of the liquid. These two boxes were joined together along the xy face. The whole liquid-solid system will therefore include a total of 5184 hard spheres. According to this procedure, this initial configuration is free of overlaps. The liquid side of the system was first allowed to equilibrate while keeping the particles of the solid region fixed at their lattice sites. We observe that after a short simulation of about 40 000 MC cycles (1 cycle is defined here as N attempts to displace the particles) the initial crystalline structure of the liquid side is lost. Next, a short simulation is carried out but now allowing the crystalline structure of the solid region to relax while keeping the particles in the liquid side fixed. This initial stage was undertaken at constant overall volume. We consider periodic boundary conditions in all directions, which results in the stabilization of two planar (100) solid-liquid interfaces perpendicular to the z direction. Note that the specific type of atomic plane at the surface is expected to be relevant for the study of interfacial or dynamical properties but not for the determination of the coexistence properties. The simulation box was orthorhombic with linear dimensions of approximately $L_x=L_y\approx 9.5\sigma$, and $L_z\approx 59\sigma$. According to Davidchack and Laird,[11] the width of the liquid-solid interface is about 7–8 σ, so our choice of L_z should ensure bulk behavior in the solid and liquid regions far from the interfaces.

A first set of MC simulations was carried out in the standard NpT ensemble. Owing to the cubic symmetry of the solid fcc structure, we made use of a tetragonal scaling of the simulation box to sample volume fluctuations. This involves a coupled change of the transverse box dimensions L_x and L_y that changes the area of the interface (so that the cubic symmetry of the solid is preserved) accompanied by an independent attempt to change L_z. The maximum particle displacement was adjusted so as to ensure an acceptance ratio of about 40% of the attempted translational moves. As for the trial volume moves, we found that an efficient sampling of the configurational space was achieved using maximum box-length changes of $\Delta L_x/\sigma=\Delta L_y/\sigma=10^{-4}$, and $\Delta L_z/\sigma=2\times 10^{-3}$. This choice ensures an acceptance ratio of about 30% of the attempted volume moves. If the input pressure is above the coexistence pressure, the fluid will tend to crystallize, with an accompanying increase of the overall density of the system. By contrast, if the input pressure is below the melting point, the solid will tend to melt and the total density of the system will decrease. Monitoring the evolution of the total density along trajectories at different pressures will therefore allow us to bracket the coexistence pressure.

As mentioned earlier, the standard constant-pressure procedure discussed above is not strictly correct for the simulation of inhomogeneous systems characterized by an anisotropic pressure tensor. We have also considered simulations of the liquid-solid interfacial system in the Np_NAT ensemble. Here, p_N is the input (normal) pressure, which is coupled to variations of L_z. The cross section of the simulation, and therefore the interfacial area A, remains constant in the course of the simulations. In order to guarantee a strain-free bulk solid during the simulation, L_x and L_y were chosen at each value of the normal pressure p_N to fit the appropriate equilibrium value of the lattice parameter as given from the analytical equation of state of Hall.[39] Note that this was not necessary for the simulations carried out in the NpT ensemble, as the possible lateral stress is removed from the system due to the fluctuations in the transverse dimensions of the simulation box. As far as the computation of the coexistence pressure is concerned, we considered the same bracketing procedure as the one used in the NpT series.

A third series of simulations was performed in the VSNVT ensemble. Fluctuations in the transverse and longitudinal dimensions of the box were performed in a way similar to those considered in the NpT simulations, but with the additional constraint that the net result of the overall shape fluctuation should preserve the total volume. The VSNVT ensemble has already been used for other applications.[32,37,38] We should note that, in principle, simulations undertaken in this ensemble should result in a strain-free solid phase after equilibration. At variance with the constant-pressure series, the coexistence properties can now be computed from sampling equilibrium configurations of the liquid-solid inhomogeneous system in a single simulation. One may anticipate that the global system will only achieve equilibrium if the starting configuration is chosen close to the expected coexistence conditions. We computed the (integrated) normal (p_N) and tangential (p_T) components of the pressure tensor according to the mechanical route in the course of the VSNVT simulations. These components can be formally defined from their local components counterparts, which depend on z, as[40]

$$p_N=\frac{1}{V}\int d\mathbf{r}p_{zz}(\mathbf{r})=\frac{1}{L_z}\int dzp_{zz}(z), \tag{1}$$

$$p_T=\frac{1}{V}\int d\mathbf{r}\frac{[p_{xx}(\mathbf{r})+p_{yy}(\mathbf{r})]}{2}=\frac{1}{L_z}\int dz\frac{[p_{xx}(z)+p_{yy}(z)]}{2}. \tag{2}$$

For the present application, the pressure can be calculated from the running average of the pair virials of those molecular pairs with relative distances in the range σ to $\sigma+\Delta r$ in the limit $\Delta r\to 0$.[41,42] This is equivalent to the computation of the virial contribution of pair overlaps that would occur when an isotropic scaling transformation of the coordinates from $\mathbf{r}$ to $\mathbf{r}(1-\xi)^{1/3}$ is carried out,[41,42] where ξ is a small dimensionless parameter. This transformation involves a virtual decrease in the volume of the system from V to $V(1-\xi)$, where ξ and Δr can be seen to be related by[41]

$$\frac{\Delta r(\xi)}{\sigma}=\frac{1}{(1-\xi)^{1/3}}-1. \tag{3}$$

One can show[41] that the normal and tangential components of the pressure can be expressed as

$$\beta p_N=\rho+\frac{1}{V}\left\langle\sum_i\sum_{j<i}\frac{z_{ij}^2}{r_{ij}}\frac{H_{ij}}{\Delta r(\xi)}\right\rangle, \tag{4}$$

$$\beta p_T=\rho+\frac{1}{V}\left\langle\sum_i\sum_{j<i}\frac{x_{ij}^2+y_{ij}^2}{2r_{ij}}\frac{H_{ij}}{\Delta r(\xi)}\right\rangle, \tag{5}$$

where the limit $\Delta r(\xi)\to 0$ is implicitly assumed. Here, the angular brackets denote an ensemble average; $\rho=N/V$,

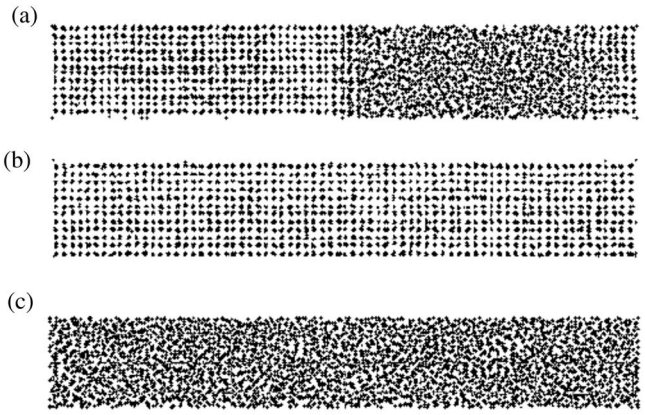

FIG. 1. (a) Starting configuration used in the series of direct simulations in the NpT ensemble. (b) and (c) are the final configurations at $p^*=11.70$ (above the melting point) and $p^*=11.45$ (below the melting point), respectively.

where N is the total number of particles; $\beta=1/(k_BT)$ is the inverse temperature; and H_{ij} is unity if particles i and j overlap after the coordinate transformation, and zero otherwise.

In practice, the components of the pressure were evaluated for a grid of values of ξ (here, we consider $\xi=0.025$, 0.020, 0.015, 0.010, and 0.005) and the running averages were finally obtained from extrapolation to $\xi\to 0$. Besides the coexistence pressure, we have obtained the coexistence densities by averaging the density profile $\rho(z)$ over distances well removed from the interfaces, where each phase is expected to exhibit bulk behavior. The density of the solid can be alternatively calculated from the equilibrium values of the lattice parameters, which in turn can be expressed in terms of the running averages of the transverse dimensions of the simulation box.

III. RESULTS

We start by presenting the results obtained from simulations in the NpT ensemble. The starting configuration is depicted in Fig. 1(a), where one can observe that the fluid has already crystallized in the proximity of the solid after the preliminary equilibration stage. This behavior had already been observed in previous simulations,[9] but should not affect the calculations. One can choose to start with different relative amounts of liquid and solid, as long as the system accommodates bulk regions of each phase. The results obtained from a series of direct simulations in the NpT ensemble are shown in Fig. 2. This figure shows the evolution of the total density for different trajectories generated at different pressures. In what follows, we express the pressure and density in conventional reduced units, $p^*=\beta p\sigma^3$ and $\rho^*=\rho\sigma^3$, respectively. It can be seen that at $p^*\geqslant 11.55$, the density increases, which is an indication that the liquid is trying to freeze. After running sufficiently long, the density is seen to reach a plateau, with fluctuations around a solidlike value of $\rho^*\approx 1.04$. At this point the full liquid region has crystallized. This can also be checked by visual inspection of configurations of the system [see Fig. 1(b)]. By contrast, the density of the system at $p^*\leqslant 11.53$ decreases as the simulation proceeds, which indicates that the liquid phase is growing at the

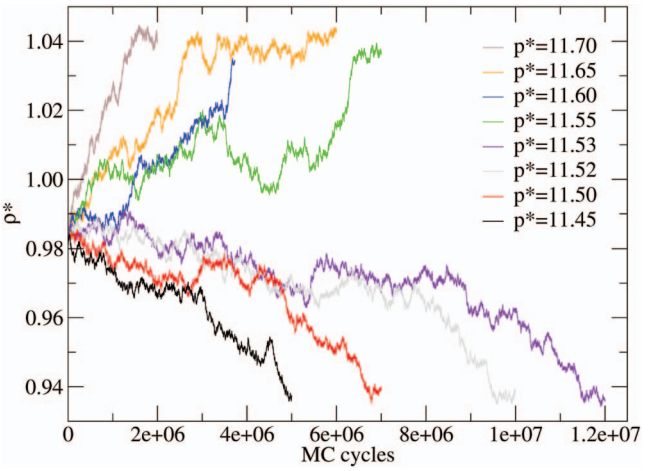

FIG. 2. (Color) Evolution of the total density along different MC trajectories as obtained from direct simulations in the NpT ensemble for inhomogeneous systems of hard spheres containing two liquid-solid interfaces at different pressures.

expense of the solid, i.e., the solid exhibits a tendency to melting. Once again, the density reaches a plateau with oscillations around an average liquidlike value of $\rho^*\approx 0.93$, which shows that the initial solid region has fully melted. As before, this is corroborated by looking at configurations of the system in this region [see Fig. 1(c)]. This series of simulations allows us to accurately determine an upper and a lower limit of the coexistence pressure that leads to an estimate of $p^*=11.54(2)$ for the melting point of hard spheres. According to the results included in Fig. 2, we infer that quite long simulations are needed to fully crystallize the fluid phase (for pressures above the melting point) or to fully melt the solid phase (for pressures below the melting point). Moreover, it can be observed that longer simulations are generally required for pressures close to the coexistence point. Indeed, at $p^*=11.53$ and $p^*=11.52$, the solid was observed to melt completely only after 10^7 MC cycles.

We have also estimated the melting point of hard spheres from MC simulations undertaken in the Np_NAT ensemble. Figure 3 shows the results obtained using this approach.

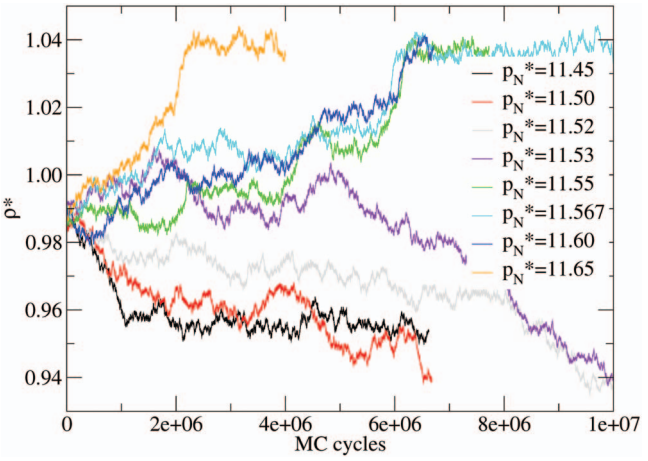

FIG. 3. (Color) Evolution of the total density along different MC trajectories as obtained from direct simulations in the Np_NAT ensemble for inhomogeneous systems of hard spheres containing two liquid-solid interfaces at different pressures.

From the evolution of the density at different pressures, we observe that the melting pressure as obtained from Np_NAT simulations is about $p^*=11.54(2)$, which is in excellent agreement with the value estimated from NpT simulations. These results indicate that the error introduced by the use of the NpT ensemble in the presence of the interface is small for systems with the dimensions considered here, the error being similar to the intrinsic uncertainty of the direct coexistence method. Further evidence will be given later. As observed in the NpT series, quite long Np_NAT simulations are required to drive the initial configuration to one phase or the other, with simulations of similar length in both implementations. Slightly shorter simulations seem to be needed in the former case, probably because the change in volume is due to fluctuations in the three directions of the simulation box, which results in higher destabilization rates of the initial configuration.

The results presented so far show that the NpT ensemble is a valid choice to estimate the coexistence properties of a fluid-solid transition. It has the advantage over the Np_NAT approach that the same starting configuration can be used for generating the different constant-pressure trajectories, as the fluctuations along the x and y directions will allow the solid phase to relax to its equilibrium structure. This is also a clear advantage over simulations performed under conditions that do not allow possible imbalanced stress in the solid phase to relax.

Our estimates of the coexistence pressure of the fluid-solid transition of hard spheres obtained from direct coexistence methods are found to be in excellent agreement with the values obtained from other methods. According to computations reported recently by two of us[33] using free-energy based methods, the melting transition for systems of hard spheres takes place at $p^*=11.54(4)$ in the thermodynamic limit. Similar values are obtained by Frenkel and Smit[1] ($p^*=11.567$), Wilding and Bruce[31] [$p^*=11.50(9)$], Speedy[30] [$p^*=11.55(11)$], and Fortini and Dijkstra[32] [$p^*=11.57(10)$]. We have also explored to what extent our reported values of the coexistence pressure are affected by finite-size effects. For the particular case of the liquid-solid transition in hard spheres it is known that for systems of finite size[31,33,43] the transition takes place at pressures below the value obtained in the thermodynamic limit. This effect, however, is only expected to be noticeable for systems of, approximately, less than 1000 particles; we should therefore anticipate that finite-size effects must be small for the sizes considered here. Nonetheless, we decided to check this point by determining the coexistence pressure using the Einstein molecule approach[33] for systems containing similar number of particles to the ones considered here. In particular, we have computed the Helmholtz free energy of a cubic fcc crystal consisting of $N=5324$ hard spheres at a density of $\rho^*=1.040\,86$, obtaining the value $F/(Nk_BT)=4.9575$, which is very close to its value in the thermodynamic limit.[2,33,34,44–47] From this value, and using the analytical equation of state of Kolafa *et al.*[48] for the fluid phase and that of Hall[39] for the solid phase, we find that the liquid-solid coexistence pressure is $p^*=11.54$ for $N=5324$, which is essentially equal to its value in the thermodynamic limit within the accuracy of our calculations. We therefore conclude that the size of the samples considered in our simulations was large enough, so that finite-size effects were negligible.

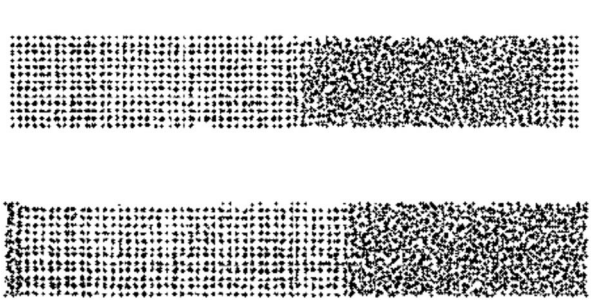

FIG. 4. Snapshots of the (a) starting and (b) final configurations used in the variable-shape constant-volume (VSNVT) simulation.

We now turn to present the results obtained from simulations performed in the VSNVT ensemble (see Fig. 4). The initial configuration was generated in a way similar to that considered in the NpT series. The simulation is divided into 20 blocks each consisting of 2.5×10^5 cycles, where one cycle amounts to N trial molecular displacements followed by one trial change of either the longitudinal or the transverse dimension of the simulation box (the other dimension is changed so as to keep the total volume constant). Block averages of the normal and tangential components of the pressure were computed from Eqs. (4) and (5). The system was found to reach equilibrium quite quickly, probably because the starting configuration was already close to the appropriate equilibrium conditions. The densities of the coexisting solid and fluid phases were obtained from the equilibrium density profile, the corresponding values being $\rho^*_{\mathrm{sol}}=1.0369(33)$ and $\rho^*_{\mathrm{liq}}=0.9375(14)$. The coexistence densities are in very good agreement with values obtained from free energy calculations: $\rho^*_{\mathrm{sol}}=1.0376$, $\rho^*_{\mathrm{liq}}=0.9391$ (Frenkel and Smit[1]); $\rho^*_{\mathrm{sol}}=1.0367(10)$, $\rho^*_{\mathrm{liq}}=0.9387(10)$ (Fortini and Dijkstra[32]); and $\rho^*_{\mathrm{sol}}=1.0372$, $\rho^*_{\mathrm{liq}}=0.9387$ (Vega and Noya[33]). These values are also consistent with the values $\rho^*_{\mathrm{sol}}=1.037$, $\rho^*_{\mathrm{liq}}=0.938$ reported by Davidchack and Laird[11] from constant-energy MD simulations of the liquid-solid system. As for the coexistence pressure, we find $p^*_N=p^*=11.54(4)$, which is fully consistent with the values reported from constant-pressure simulations and free energy calculations.

The value of the tangential pressure obtained from VSNVT simulations was found to be $p^*_T=11.53(5)$, which shows that the anisotropy of the pressure tensor is rather small for the present application. This gives additional evidence that the use of the NpT ensemble is fully justified here. It is to be noted that the anisotropy of the pressure tensor $\Delta p\equiv p_N-p_T$ is related to the surface stress S (see, for example, Ref. 11) by

$$S=\tfrac{1}{2}\int_0^{L_z}dz[p_N(z)-p_T(z)]=\tfrac{1}{2}L_z(p_N-p_T), \tag{6}$$

where $p_N(z)\equiv p_{zz}(z)$, and $p_T(z)=[p_{xx}(z)+p_{yy}(z)]/2$. The last equality in Eq. (6) follows from the definitions given in Eqs. (1) and (2); the factor 2 appearing in Eq. (6) accounts for the existence of two interfaces in the system. It is to be noted

that S reduces to the usual surface tension for fluid-fluid interfaces. Considering the value $\beta S\sigma^2=-0.17(6)$ reported by Davidchack and Laird for the surface stress of the (100) solid-liquid interface, one could predict a value $\Delta p^*=2S/L_z=-0.006(2)$ after using a typical value $(L_z/\sigma\approx 60)$ for the dimensions of the systems considered here. This is consistent with our resulting value of $\Delta p^*=0.01(6)$.

IV. CONCLUSIONS

We have estimated the coexistence pressure of the fluid-solid transition of hard spheres using direct coexistence methods, which involve simulations of systems containing a fluid and a solid phase separated by an interface. The MC simulations were carried out according to the prescriptions of several statistical ensembles. First, we performed simulations in two different constant-pressure ensembles, one in which the three dimensions of the simulation box are allowed to fluctuate (NpT), and a variant in which the area of the interface remains constant and the volume is sampled from fluctuations of the normal dimension of the box (Np_NAT). Rigorously, only the latter implementation is correct in the presence of an interface: in the NpT ensemble, one is imposing an isotropic input pressure to a system characterized by an anisotropic pressure tensor. The use of the NpT ensemble for the present application will only be justified as long as the anisotropy of the pressure tensor, Δp, turns out to be small. As Δp scales with the inverse of the longitudinal dimension of the simulation box, one should ensure that L_z is large enough. This will generally be the case for the geometries of the box used in direct simulation methods, where one is bound to use quite elongated boxes to avoid the mutual interaction of the two surfaces.

In both constant-pressure ensembles, the coexistence properties have been determined by performing simulations at different pressures and monitoring the evolution of the density along each trajectory (the density increases when the crystal grows and it decreases when the crystal melts). We find that both approaches lead to the same value of the coexistence pressure ($p^*=11.54$), which is fully consistent with the values obtained from free energy calculations. This indicates that the error introduced by the use of the NpT ensemble is quite small and seems to be within the accuracy of the direct simulation method. This makes us to believe that introducing a barostat for the investigation of the fluid-solid coexistence properties through direct coexistence simulations is a valid procedure (provided that the system is sufficiently large), and eliminates the possible risk of having the solid under stress (which may indeed occur when the volume and geometry of the simulation box remain constant).

Further evidence of the above conclusions was given from simulations performed in a variable-shape constant-volume ensemble. This scheme is expected to be particularly well suited to the direct simulation of two coexisting phases involving a crystalline solid, and allows the solid to relax to its equilibrium structure without introducing a barostat. Certainly, relaxation will be favored by considering volume-preserving changes of the simulation box consistent with the symmetry of the crystalline structure. The coexistence properties can be obtained by sampling from equilibrium configurations of the interfacial systems. The coexistence pressure corresponds to the normal pressure, for which we find a value $[p^*=11.54(4)]$ in full agreement with the estimates from the constant-pressure simulations given here as well as with results from constant-energy MD simulations[11] and free energy calculations.[1,30–33] The coexistence densities determined from VSNVT simulations, $\rho^*_{\mathrm{sol}}=1.0369(33)$, and $\rho^*_{\mathrm{liq}}=0.9375(14)$ are consistent with the values obtained from other techniques. For the systems considered here, we have explicitly computed the anisotropy of the pressure tensor and found that is rather small. This provides a stringent validation of the NpT methodology when applied to the study of the melting transition from direct simulations.

In summary, we have assessed the efficiency of direct simulation methods to the determination of the coexistence properties at the melting transition. These methods may provide an interesting route to test data obtained from free energy calculations. We have also shown that direct simulation methods can be implemented within different ensembles, the resulting data being indistinguishable within the estimated statistical errors. The value of $p^*=11.54$ at the melting transition of hard spheres seems to be now firmly established, and turns out to be slightly lower than the original value of 11.70 reported by Hoover and Ree.[34] Though the present investigation has been limited to systems of hard spheres, we may anticipate that most of our conclusions are expected to hold for other systems.

ACKNOWLEDGMENTS

Financial support for this work was provided by Project Nos. FIS2007-66079-C02-01 and FIS2007-66079-C02-02 of Dirección General de Investigación and Project No. S-0505/ESP/0229 from the Comunidad Autónoma de Madrid. Additional funding from the University of Huelva and Junta de Andalucía is also acknowledged. E.G.N. wishes to thank the Ministerio de Educación y Ciencia and the Universidad Complutense de Madrid for a Juan de la Cierva fellowship.

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