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On fluid-solid direct coexistence simulations: The pseudo-hard sphere model

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We investigate methodological issues concerning the direct coexistence method, an increasingly popular approach to evaluate the solid-fluid coexistence by means of computer simulations. The first issue is the impact of the simulation ensemble on the results. We compare the NpT ensemble (easy to use but approximate) with the Np_zT ensemble (rigorous but more difficult to handle). Our work shows that both ensembles yield similar results for large systems (>5000 particles). Another issue, which is usually disregarded, is the stochastic character of a direct coexistence simulation. Here, we assess the impact of stochasticity in the determination of the coexistence point. We demonstrate that the error generated by stochasticity is much larger than that caused by the use of the NpT ensemble, and can be minimized by simply increasing the system size. To perform this study we use the pseudo hard-sphere model recently proposed by Jover *et al.* [J. Chem. Phys. **137**, 144505 (2012)], and obtain a coexistence pressure of $p^* = 11.65(1)$, quite similar to that of hard spheres (only about 0.6% higher). Therefore, we conclude that this model can be reliably used to investigate the physics of hard spheres in phenomena like crystal nucleation. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4823499>]

I. INTRODUCTION

One of the first questions addressed by numerical simulations has been the possible existence of a fluid-solid transition for hard spheres¹ (HS). The existence of the transition was definitely established by Ree and Hoover² after performing free-energy calculations. Since then, the fluid-solid transition has been determined for a number of systems, typically by imposing the condition of equal chemical potential for both phases at equilibrium. Recently, we have shown that free-energy calculations for solids can be easily performed with open source programs such as GROMACS or LAMMPS.^{3–7} Thus, the free-energy route to determine the location of the fluid-solid coexistence has been, and still is, quite useful.

In 1977, Ladd and Woodcock^{8,9} proposed an alternative approach, often referred to as direct coexistence method. They proposed the simulation of two different phases within the same simulation box in order to find the conditions at which the system is at coexistence. Direct coexistence simulations were not particularly popular in the 1980s and 1990s but have experienced a great upsurge in the last 15 years. In fact, it has been shown that direct coexistence simulations, where a solid is in contact with a liquid phase in the simulation box, can be quite useful in determining the equilibrium conditions for a number of systems, such as hard spheres,^{10–13} Lennard-Jones¹⁴ (LJ), systems where quantum effects are included either on the electronic structure^{15–17} or in the motion of the nuclei^{18–20} and molecular models such as water.^{21–29} Fluid-solid equilibrium obtained from direct coexistence sim-

ulations should be identical to that obtained from free-energy calculations.³⁰ Thus, direct coexistence simulations are an interesting alternative to free-energy calculations. The main advantage of the direct coexistence simulations is their simplicity, whereas their main disadvantage is that very long runs may be needed if the dynamics of the solid-fluid interface is slow.

Although the direct coexistence method is becoming quite popular there are some methodological issues that are not completely settled yet. The first one is related to the stochastic character of the method. Typically, the initial configuration consists of a solid slab in contact with a liquid one (of approximately the same width). The liquid-solid interface is then equilibrated and from the time evolution of the total energy, or any other parameter sensitive to the growth of the crystal phase, one can determine whether the system freezes or melts. Usually, a single run is performed for a series of pressures (or temperatures) and the coexistence pressure (or temperature) is evaluated as an average between the highest pressure at which the system melts and the lowest at which it freezes. However, things are more complex than this. It is well known that at conditions where the solid is the thermodynamically stable phase the growth rate of a crystal in simulations is a stochastic quantity which may differ significantly between two runs.^{29,31,32} Furthermore, when the system is close to the coexistence point one may obtain complete freezing or melting by slightly changing the initial configuration (either in position and/or in momenta space).³² Therefore, for finite-size systems close to coexistence the probability of freezing is not given by a step function with values 1 and 0 as it would be the case for an infinitely large system but the step function is rather smeared out. The consequence is that when close to the

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thermodynamic coexistence point, the runs have a stochastic character making it interesting to evaluate to what extent such stochasticity may affect the determination of the coexistence point. The second issue regards the choice of a simulation ensemble. Two ensembles are commonly used in direct coexistence conditions: Np_zT and NpT . In the Np_zT the pressure change is applied only in the direction perpendicular to the interface (labelled as z axis). In the NpT ensemble the three simulation box sides are allowed to fluctuate independently. Some concerns about the validity of this second ensemble have been recently raised.³³ Strictly speaking, the Np_zT is the correct ensemble for this kind of simulations. However, for reasons that shall be discussed below, the use of the Np_zT ensemble is a bit more cumbersome. Moreover, as far as we are aware, the error introduced by the use of the NpT ensemble (instead of the rigorous Np_zT ensemble) has not been comprehensively studied yet. In this paper, we address these two issues concerning the direct coexistence simulations, namely, its stochastic character and the relevance of the chosen ensemble on the resulting coexistence point.

To perform this study, we use the pseudo-hard sphere model potential recently proposed in Ref. 34 that we will name the Imperial-Pseudo-Hard-Sphere (IPHS) model. In the IPHS potential particles interact via a continuous spherical potential (of Mie form where the typical powers of the LJ potential 12/6 are replaced by 50/49). Jover *et al.*³⁴ showed that this model at the reduced temperature 1.5 reproduces quite well the structure, thermodynamics and dynamics of the hard sphere potential. Thus the model can be regarded as the continuous counterpart of the popular hard sphere model. Moreover, since the potential is continuous it can be simulated using standard open source MD programs such as DLPOLY, LAMMPS, or GROMACS, which are much faster than most bespoke Monte Carlo codes. This makes this potential particularly convenient to tackle the two methodological issues addressed above, particularly so for the study of the stochastic character of direct coexistence, which requires one to perform a large number of simulations.

In addition, we determine the fluid-solid equilibrium for the IPHS model. The reduced coexistence pressure (at reduced temperature 1.5) is 11.65(1), which differs only by about 0.6% from the HS value (11.55–11.58).^{4,12,13,35–37} Thus, the potential also reproduces rather nicely the fluid-solid equilibrium of hard spheres. The potential proposed in

Ref. 34 could be also very useful to study nucleation (instead of using event driven dynamics for the HS model) since it reproduces the thermodynamics and the dynamics of the HS model.

II. NUMERICAL DETAILS

A continuous version of the hard sphere model has been recently proposed.³⁴ In this model the discontinuous hard sphere interaction is replaced by the expression:

$$\begin{cases} 50 \left(\frac{50}{49}\right)^{49} \epsilon \left[\left(\frac{\sigma}{r}\right)^{50} - \left(\frac{\sigma}{r}\right)^{49} \right] + \epsilon; & r < \left(\frac{50}{49}\right) \sigma \\ 0; & r \geq \left(\frac{50}{49}\right) \sigma \end{cases} \quad (1)$$

In order to simulate this model (IPHS) via molecular dynamics we will use the GROMACS package.³⁸ In what follows, all units will be given in reduced units: $T^* = k_B T / \epsilon$, $\rho^* = (N/V)\sigma^3$, $p^* = p\sigma^3/(k_B T)$ and $L^* = L/\sigma$ where σ is the particle's diameter and ϵ the energy unit. Time is given in $\sqrt{\sigma^2 m / (k_B T)}$ units. Reduced units are not included in GROMACS.³⁸ However, one can use the parameters of the LJ potential proposed for Ar (i.e., $\sigma = 3.405 \text{ \AA}$, $\epsilon/k_B = 119.87 \text{ K}$, $m = 6.69 \times 10^{-26} \text{ kg}$), and then convert the output of GROMACS from real to reduced units. Since the latest version of GROMACS can read potentials in tabular form the IPHS model can be easily simulated with this package.

We study the system both in the NpT and Np_zT ensembles using a velocity-Verlet integrator with a time step of 2 fs (this corresponds to a time step in reduced units of about $\delta t^* = 0.001$), with a Parrinello-Rahman barostat³⁹ and a velocity-rescale thermostat.⁴⁰ The temperature is always set to $T^* = 1.5$ (corresponding to 179.8 K when using the LJ parameters of Ar) and pressure within a range of $p^* = 11.3$ and 11.9 (corresponding to 7100–7500 bars). Notice that it is important to set the temperature to $T^* = 1.5$, since only at this reduced temperature the properties of the IPHS and HS models are similar.

III. METHODOLOGY

A. Preparation of the initial configuration

First of all, we prepare an initial configuration consisting of a half-liquid/half-solid simulation box (Fig. 1) as follows: we first equilibrate half-box in the fcc-solid phase, then melt it and equilibrate it in the liquid phase. Next, we “glue” the two

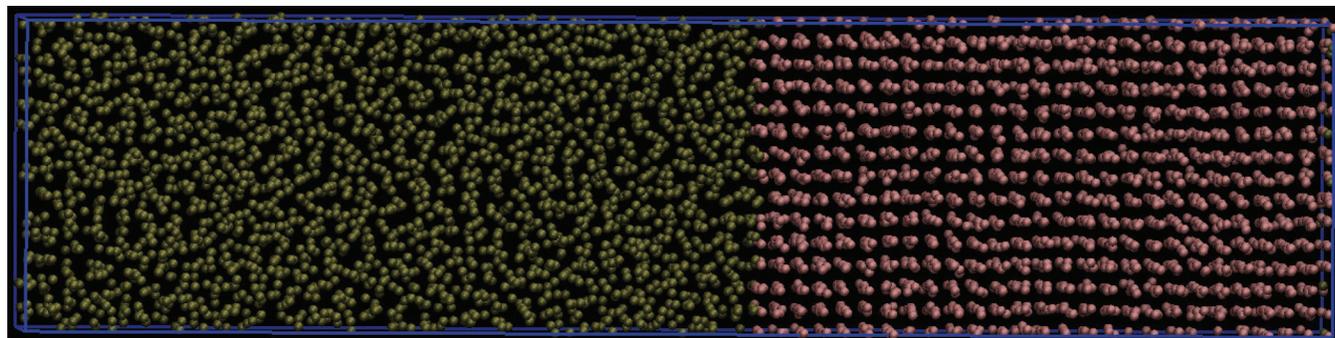


FIG. 1. Side view of an initial configuration containing 2548 liquid-like and 2548 fcc solid-like particles.

phases avoiding any overlapping particle. Finally, we equilibrate the liquid-solid interface for a short time (in our case, about 40 ps) making sure that the solid phase does not melt (keeping it frozen with an *ad hoc* GROMACS command).

B. Np_zT and NpT ensemble

A new configuration has to be prepared for each pressure of interest when the Np_zT ensemble is used, because the simulation box edges L_x and L_y have to be consistent with the equilibrium density of the solid at p_z . Otherwise the solid will present internal stress. We have shown in previous work that a stressed solid has a higher free energy than a non-stressed one.⁵ As a consequence, if L_x and L_y are not properly chosen, an incorrect (high) coexistence pressure will be obtained. The need of preparing a configuration for each state point can make the methodology rather cumbersome.

By contrast, if simulations are performed in the NpT ensemble it is enough to use a single configuration as an input for all pressures, given that L_x and L_y are allowed to relax to a value for which the solid is not stressed. However, direct coexistence simulations in the NpT ensemble are not strictly correct.³³ In what follows, we compare results obtained with both Np_zT and NpT ensembles.

C. Coexistence pressure and stochasticity

A configuration such as the one represented in Fig. 1 should freeze at a pressure above that of coexistence and melt at a pressure below the coexistence pressure. This is strictly true in the thermodynamic limit. However, a finite-size system at a pressure close to coexistence may stochastically freeze or melt with a given probability.³² To quantify this effect we run 100 trajectories starting from the same initial configuration at each pressure (different trajectories corresponding to a different set of initial momenta). Runs were performed until the entire system became either liquid or solid. The time required to achieve the complete melting/freezing was stochastic and depended crucially on the system size (varying from ~ 150 reduced time units for the smallest system to ~ 7000 for the largest one). Next, we evaluated the melting probability $P(p^*)$ and plotted it as a function of pressure. $P(p^*)$ goes from 1 at low pressures to 0 at high pressures and has a sigmoidal shape, similar to that observed for the density profile of a vapour liquid-interface.^{41–43} For this reason $P(p^*)$ can be fitted to

$$P(p^*) = \frac{1}{2} - \frac{1}{2} \tanh[(p^* - p_c^*)/d], \quad (2)$$

where p_c^* is the coexistence pressure, defined as the pressure for which the probability of melting is 0.5. d is a parameter related to the 10–90 sharpness of the probability profile. $\delta_{10-90} = 2.178d$ represents the width of the interval of reduced pressures where the probability of melting goes from 0.1 to 0.9. In that pressure interval the outcome of the simulations is stochastic. Therefore δ_{10-90} sets a lower limit for the uncertainty of the coexistence pressure when only one trajectory is performed for every selected pressure (which is the

way coexistence is usually determined by means of direct coexistence simulations).

IV. RESULTS

A. NpT versus Np_zT ensemble

As an initial test we have computed the equation of state of the IPHS model in the fluid phase from our runs using GROMACS and compared to the results reported previously for the same model.³⁴ Our results were obtained with a fluid sample of 1372 particles, using MD NpT runs, with isotropic scaling of the simulation box. The comparison is shown in Fig. 2. As it can be seen the agreement between the results of this work and those reported previously is excellent. The pressure reported by GROMACS obtained from the virial theorem is fully consistent with the pressure imposed in the NpT runs. We have also determined the equation of state for the IPHS using our bespoke Monte Carlo program for a sample of about 1000 molecules. Results are also shown in Fig. 2. Once again the agreement with the results from GROMACS and with those reported previously by Jover *et al.*³⁴ is excellent. This gave us confidence that our implementation of the IPHS in GROMACS was correct.

Now we shall focus on the direct coexistence runs. Figure 3 shows the probability of melting as a function of pressure computed with simulations in the NpT and Np_zT ensembles for several system sizes. Each data point has been obtained averaging over 100 trajectories. The dashed lines are fits to Eq. (2). The coexistence pressure p_c^* is determined from the value at which the probability is 0.5 (see Table I). When simulating a small system (e.g., 768 particles) the two ensembles give a different coexistence pressure: $p_c^* = 11.557$ for Np_zT , and $p_c^* = 11.635$ for NpT . The difference is small but clearly detectable. The correct coexistence pressure for this system size is that obtained from Np_zT simulations, so the error introduced using the NpT ensemble is about 0.6%. This has already been pointed out by Frenkel.³³

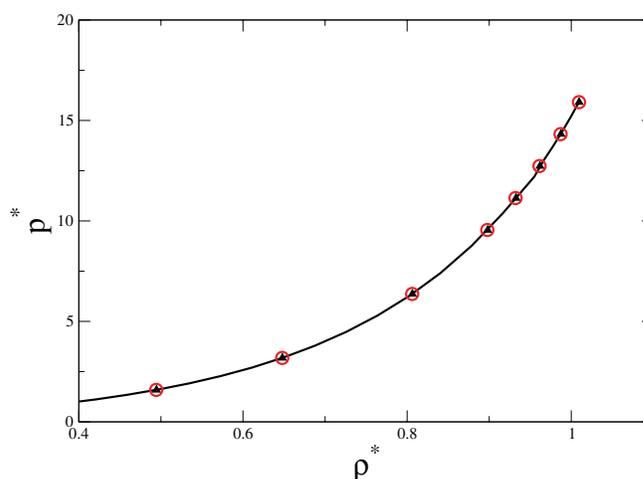


FIG. 2. Equation of state of the IPHS model in the fluid phase as obtained in this work from GROMACS (filled triangles), from a bespoke Monte Carlo program (open circles), and as obtained previously by Jover *et al.*³⁴ (solid line). The reduced pressure is defined as $p^* = p\sigma^3/(k_B T)$. The reduced number density is defined as $\rho^* = (N/V)\sigma^3$.

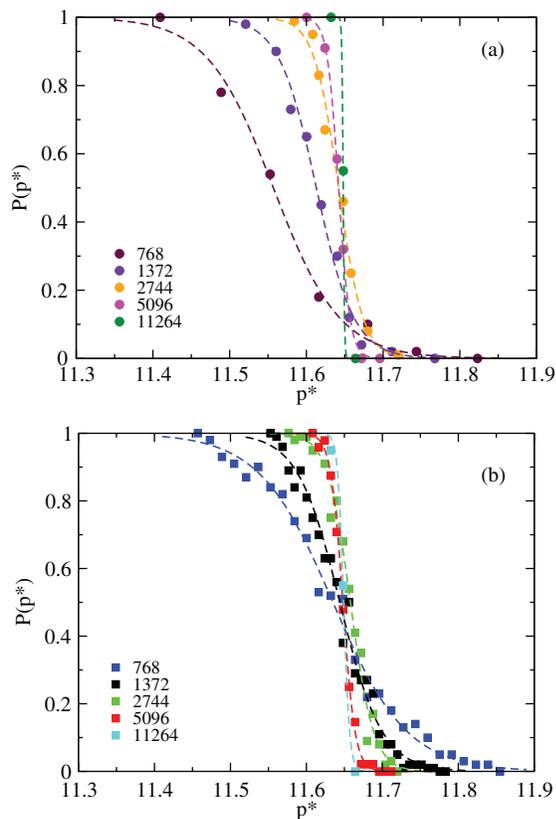


FIG. 3. Probability of melting for several hard sphere-like system sizes. (a) Results in the $Np_z T$ ensemble (top). (b) Results in the $Np T$ ensemble (bottom).

In Fig. 4 the $P(p^*)$ curve is compared for the two ensembles at three different system sizes (768, 2744, and 5096). Although differences are clearly visible for the smallest system, it is also clear that the curves become quite similar as one increases the system size.

In Fig. 5 we plot an estimate of the relative error in the coexistence pressure made by using the approximate $Np T$ instead of the rigorous $Np_z T$ ensemble. This is calculated as $100(p_c^*(Np T) - p_c^*(Np_z T))/p_c^*(Np T)$ (in green in Fig. 5). The relative error is quite small. It is smaller than 0.75% for the smallest system studied and it rapidly drops as the system

TABLE I. Coexistence pressure p_c^* (where $P(p_c^*) = 0.5$) computed with $Np_z T$ and $Np T$ ensembles for different system/box sizes. L_z^* is the long box edge. $L_y^* = L_x^*$. σ_{p^*} is the estimated error of the coexistence pressure and δ_{10-90} the 10–90 thickness of $P(p^*)$ (in reduced pressure units).

Method	Size	L_z^*	L_x^*	$\frac{L_z^*}{L_x^*}$	$p_c^* \pm \sigma_{p^*}$	δ_{10-90}
$Np_z T$	768	21.33	6.37	3.34	11.557 ± 0.005	0.189
$Np_z T$	1400	26.67	7.75	3.43	11.613 ± 0.001	0.108
$Np_z T$	2744	25.01	10.90	2.29	11.642 ± 0.004	0.070
$Np_z T$	5096	46.08	10.97	4.18	11.642 ± 0.004	0.032
$Np_z T$	11 264	74.41	12.53	5.94	11.648 ± 0.003	0.009
$Np T$	768	21.33	6.37	3.34	11.635 ± 0.005	0.213
$Np T$	1400	26.67	7.75	3.43	11.644 ± 0.005	0.123
$Np T$	2744	25.01	10.90	2.29	11.658 ± 0.005	0.066
$Np T$	5096	46.08	10.97	4.18	11.648 ± 0.004	0.035
$Np T$	11 264	74.41	12.53	5.94	11.649 ± 0.004	0.017

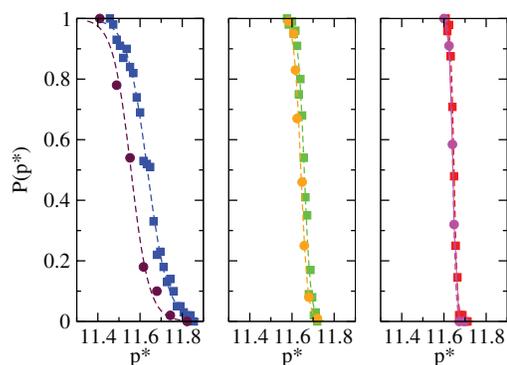


FIG. 4. Probability of melting for a system of 768 (left), 2744 (center), and 5096 (right) hard sphere-like particles simulated with $Np_z T$ (squares) or $Np T$ (circles) method.

size is increased, being virtually zero for the largest system. In the next section, we will demonstrate that the error in the coexistence pressure due to the use of the $Np T$ ensemble is much smaller than that caused by stochasticity.

As it can be seen in Fig. 3 and in Table I, the value of the coexistence pressure obtained from $Np_z T$ simulations increases slightly with the system size. It is well known^{12,44–48} that the coexistence pressure of hard spheres is subject to finite size effects. For hard spheres, periodic boundary conditions provide extra thermodynamic stability to the solid phase, and the coexistence pressure tends to increase as the system size increases. The same is found here for the IPHS model. However, for a system size of 2744 particles the coexistence pressure is already quite similar to that of a system with 11 264 particles. That means that system sizes of about 3000 particles provide a coexistence pressure not too far from the thermodynamic limit. On the other hand, coexistence pressures estimated with the $Np T$ ensemble do not change much with the system size (at least for the model considered in this work).

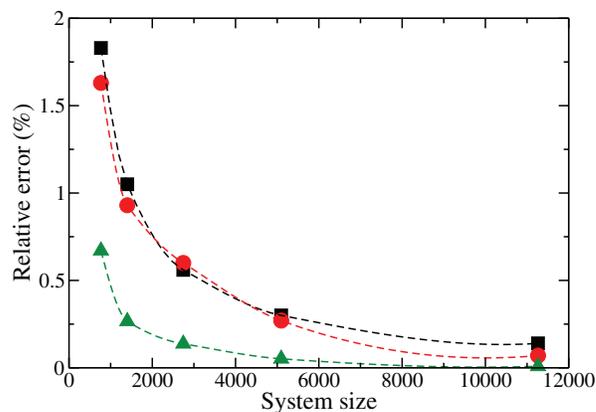


FIG. 5. System size dependence of the relative error in the coexistence pressure. Green triangles: error due to using the approximate $Np T$ ensemble instead of the rigorous $Np_z T$. Black squares: error due to the stochastic nature of the direct coexistence runs for the $Np T$ ensemble (this error refers to the case in which only one trajectory is performed for each selected pressure). Red dots: same as black squares but for the $Np_z T$ ensemble. Dashed lines are spline interpolations to the data as a visual aid.

B. Stochasticity

As shown in Fig. 3, the width of the pressure interval where the probability of melting is different from either one or zero shrinks significantly as the system size increases (this is quantified by δ_{10-90} in Table I). As previously discussed, by performing only one trajectory for every selected pressure (as is usually done) one cannot reduce the uncertainty of the coexistence pressure below the width of the stochastic interval, δ_{10-90} . Thus, the quantity $100 \times \delta_{10-90}/p_c^*$ gives an idea of the lowest relative error that can be achieved by running only one trajectory per pressure. In Fig. 5, $100 \times \delta_{10-90}/p_c^*$ is plotted for both ensembles considered (black squares correspond to NpT and red dots to Np_zT) and compared to the relative error made when using NpT instead of Np_zT ($100(p_c^*(NpT) - p_c^*(Np_zT))/p_c^*(NpT)$), in green in Fig. 5).

The relative error is similar for both ensembles and rapidly drops as the system size is increased. It is about 1.7% for the smallest system and lower than 0.5% for a system of 5000 particles. Although the curves in Fig. 5 have been computed for the IPHS model we hope they can provide a guide for the evaluation of phase equilibrium via direct coexistence in other systems.

It is evident from Fig. 5 that the relative error due to the stochasticity of the runs is much larger than that arising from the use of the approximate NpT ensemble. Therefore, when only a single trajectory is performed for each selected pressure, the advantage of using the rigorous but cumbersome Np_zT instead of the approximate but handy NpT ensemble is somewhat limited. It is also clear that the use of large systems is highly recommended when performing direct coexistence simulations as the 10–90 thickness and the influence of the chosen ensemble decreases considerably upon increasing the system size.

C. Pressure tensor

We have also analysed the value of the pressure tensor (as obtained by GROMACS using the virial theorem). When performing NpT simulations the pressure tensor is diagonal, and we found that the three components along the diagonal of the tensor are, to within statistical uncertainty, equal to the pressure p , as they should be.

When using Np_zT simulations the pressure tensor is also diagonal, but the values along the x and y axis were found to be slightly larger than along the z axis. For a system size of about 5000 particles we found p_x^* to be about 0.016 larger than p_z^* . The sign is consistent with the results reported by Laird *et al.*¹⁰ for a HS system (these authors also noticed that the anisotropy of the pressure tensor is even sensitive to the particular solid plane forming the interface with the liquid). In this work the fluid-solid interface was created along the 100 plane. The difference between p_x^* and p_z^* decreases as the value of L_z increases. This is a consequence of: (1) the thickness of the fluid-solid interface (where $p_x^*(z)$ is locally different from p_z^*) being hardly affected by the size of the system; (2) the fact that $p_x^*(z)$ becomes identical to p_z^* far from the interface. As a consequence of the latter, when L_z is sufficiently large relative to the size of the interfacial region,

one can expect that the value of p_x^* does not differ much from p_z^* as illustrated here.

V. DISCUSSION AND CONCLUSIONS

In this work, we estimate the value of the coexistence pressure for the IPHS model (at the reduced temperature of 1.5) to be 11.65(1), comparable with the value of about 11.58 reported for hard spheres.^{13,35,36} Thus the difference in the coexistence pressure between these two potentials is rather small (i.e., of about 0.6%). Therefore, the similarities found by Jover *et al.*³⁴ between the IPHS model and HS model can also be extended to the coexistence pressure.

To determine the coexistence pressure, we have used the rigorous Np_zT and the approximate NpT ensemble. As previously suggested,³³ the results depend on the ensemble for small system sizes. However, the differences become negligible as the system size increases. We observe that around the coexistence pressure the probability that the system freezes or melts is stochastic in character. The width of the pressure interval where the runs are stochastic decreases as the system size increases.

The error in the coexistence pressure arising from the use of the approximate NpT ensemble is much lower than that from the stochasticity of the runs. The main advantage of the NpT with respect to the Np_zT is that once a fluid-solid interface has been prepared, it can be used as initial configuration for any pressure, since the barostat will adapt the dimension of the system in the direction parallel to the interface to avoid the appearance of stress. In the Np_zT ensemble an initial configuration must be prepared for each pressure considered and the procedure is somewhat cumbersome (the size of the simulation box in the direction of the interface must be chosen with care to correspond to the equilibrium density of the solid at the considered pressure). For the cubic solid (fcc) considered in this work, the density at a certain value of p_z determines the value of L_x and L_y that should be used in the simulations. Even though for cubic solids the implementation of Np_zT is rather straightforward, when dealing with molecular solids it can be cumbersome, since the unit cell often has low symmetry (i.e., triclinic, monoclinic, trigonal, etc.). In this case the parameters of the unit cell (i.e., a , b , c and α , β , and γ) should be determined in advance before starting the Np_zT runs. For molecular solids the use of the NpT ensemble with a Parrinello-Rahman barostat³⁹ allowing not only the relaxation of the length of the three sides but also the values of the angles formed by the sides of the simulation box (required when dealing with solids of triclinic, monoclinic, or trigonal symmetry) is particularly convenient. Once again the system size should be rather large, and the relative size of the interface with respect to L_z (being the z direction perpendicular to the fluid-solid interface) should be as small as possible. With this in mind the use of the NpT ensemble should provide reasonable results.

We also estimate the pressure tensor in both cases and observe that in the NpT ensemble, as one would expect, the three components along the diagonal are equal to the pressure. When simulating the IPHS model in the Np_zT ensemble, the values along the x and y axis are larger than the one along

z (when the interface is formed by the 100 plane). However, the difference between p_x^* and p_z^* decreased as the value of L_z increased.

It is worthwhile discussing the convenience of using NVT or NVE simulations in the direct-coexistence method. The two ensembles are equivalent when dealing with the vapour-liquid equilibrium, where the initial configuration with the vapour and liquid slab evolves to equilibrium. This allows one to determine the equilibrium vapour pressure (NVT) or the equilibrium vapour pressure and temperature (NVE). However, the use of NVT or NVE ensembles is not recommended when dealing with fluid-solid equilibrium. The reason is that the system evolves towards equilibrium reaching a certain equilibrium pressure. Since the volume is fixed, it is quite likely (unless the value of the equilibrium pressure is known in advance) that the parameters of the unit cell in the initial configuration do not correspond to the correct values at the equilibrium pressure. The solid will then be under stress, and the “equilibrium pressure” is not the coexistence pressure between an equilibrated solid and an equilibrated fluid, but rather between a “stressed” solid and a fluid. For this reason, the natural ensemble to adopt with fluid-solid equilibria and direct coexistence simulations is the Np_zT . However, as illustrated in this work, with some care (i.e., large systems) the NpT ensemble provides reasonable results.

In conclusion, when dealing with direct coexistence simulations, the use of large systems is strongly recommended as this minimises the error due to the use of the approximate, but handy, NpT ensemble and the error associated with the stochastic character of the runs. Of course it is always possible to perform a probability analysis as illustrated in our work when the goal is to obtain with extremely high accuracy the coexistence pressure, but then the calculations become much more expensive, from a computational point of view, than free-energy calculations.

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