

## Revisiting the Frenkel-Ladd method to compute the free energy of solids: The Einstein molecule approach

Carlos Vega<sup>a)</sup> and Eva G. Noya

*Departamento de Química-Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain*

(Received 27 July 2007; accepted 5 September 2007; published online 18 October 2007)

In this paper a new method to evaluate the free energy of solids is proposed. The method can be regarded as a variant of the method proposed by Frenkel and Ladd [J. Chem. Phys. **81**, 3188 (1984)]. The main equations of the method can be derived in a simple way. The method can be easily implemented within a Monte Carlo program. We have applied the method to determine the free energy of hard spheres in the solid phase for several system sizes. The obtained free energies agree within the numerical uncertainty with those obtained by Polson *et al.* [J. Chem. Phys. **112**, 5339 (2000)]. The fluid-solid equilibria has been determined for several system sizes and compared to the values published previously by Wilding and Bruce [Phys. Rev. Lett. **85**, 5138 (2000)] using the phase switch methodology. It is shown that both the free energies and the coexistence pressures present a strong size dependence and that the results obtained from free energy calculations agree with those obtained using the phase switch method, which constitutes a cross-check of both methodologies. From the results of this work we estimate the coexistence pressure of the fluid-solid transition of hard spheres in the thermodynamic limit to be  $p^* = 11.54(4)$ , which is slightly lower than the classical value of Hoover and Ree ( $p^* = 11.70$ ) [J. Chem. Phys. **49**, 3609 (1968)]. Taking into account the strong size dependence of the free energy of the solid phase, we propose to introduce finite size corrections, which allow us to estimate approximately the free energy of the solid phase in the thermodynamic limit from the known value of the free energy of the solid phase with  $N$  molecules. We have also determined the free energy of a Lennard-Jones solid by using both the methodology of this work and the finite size correction. It is shown how a relatively good estimate of the free energy of the system in the thermodynamic limit is obtained even from the free energy of a relatively small system. © 2007 American Institute of Physics. [DOI: 10.1063/1.2790426]

### I. INTRODUCTION

One of the first findings of computer simulation was the discovery of a fluid-solid transition for a system of hard spheres.<sup>1</sup> It took some time to accept it, and it was definitively proven after the work of Hoover and Ree,<sup>2</sup> in which the location of the transition was determined beyond any doubt and, even more recently, when it was experimentally found for colloidal systems.<sup>3</sup> Certainly the study of phase transitions has always been a hot topic within the area of computer simulation. However, fluid-fluid phase transitions (liquid immiscibility, vapor-liquid) have received by far more attention than fluid-solid equilibria.<sup>4</sup> The appearance of the Gibbs ensemble<sup>5,6</sup> in the late 1980s provoked an explosion of papers dealing with vapor-liquid equilibria. The method, however, cannot be applied, in principle, to the determination of the fluid-solid equilibria. Special methods are needed to determine the fluid-solid equilibria, some of which have been proposed quite recently.<sup>7-9</sup> Without pretending to review all the literature on this problem, let us just mention the main methods that have been used so far to study the fluid-solid equilibria. The most commonly used approach performs free energy calculations for the fluid and for the

solid phases and determines the fluid-solid equilibrium by imposing the conditions of equal pressure, temperature, and chemical potential. Usually the chemical potential of the liquid is obtained via thermodynamic integration. Different methods are used to determine the chemical potential of the solid. In their pioneering work Hoover and Ree used the so-called cell occupancy method.<sup>2</sup> In this method each molecule is restricted to its Wigner-Seitz cell, and the solid is expanded up to low densities.<sup>2</sup> One of the problems of this method is the appearance of a phase transition in the integration path (from the solid to the gas). In the year 1984, Frenkel and Ladd proposed an alternative method, the Einstein crystal method.<sup>10</sup> In this method, that has become the standard method for determining free energies of solids, the change in free energy from the real crystal to an ideal Einstein crystal (in which there are no intermolecular interactions and each molecule vibrates around its lattice point via an harmonic potential) is computed. Since the free energy of the reference ideal Einstein crystal is known analytically, it is possible to compute the absolute free energy of the solid. This method was soon extended to complex systems, and in this way the phase diagram of many atomic and molecular systems was computed.<sup>11-25</sup> In the year 2000 Polson *et al.* revisited the method proposed by Frenkel and Ladd.<sup>26</sup> They

<sup>a)</sup>Electronic mail: cvega@quim.ucm.es

showed that the formulas proposed in the original paper were not fully correct and that the true energy of a crystal is lower by  $(2/N)\ln(N)$  than that of the original 1984 paper.<sup>10</sup>

A completely different approach to the problem of the fluid-solid equilibrium has been adopted by Bruce *et al.* who, in 1997,<sup>27–29</sup> proposed the phase switch Monte Carlo method. This method was first applied to the study of the free energy difference between fcc and hcp structures of hard spheres.<sup>27,28</sup> Three years later, Wilding and Bruce<sup>30</sup> and Wilding<sup>31</sup> showed that the method could be applied to obtain fluid-solid equilibrium, and the fluid-solid equilibria of hard spheres was determined for different system sizes. Quite recently Errington<sup>32</sup> and McNeil-Watson and Wilding<sup>33</sup> independently illustrated how the method can also be applied to Lennard-Jones (LJ) particles. In our view, the phase switch Monte Carlo is somehow the “Gibbs ensemble method” for fluid-solid equilibria because, as in the Gibbs ensemble method, phase equilibria are computed without free energy calculations. When deriving the phase switch method, Wilding and Bruce<sup>30</sup> and Wilding<sup>31</sup> pointed out that in a solid phase the number of permutations of the molecules may have not been accounted properly in previous free energy calculations.

In this paper a new method will be proposed to determine the free energy of a solid. The method can be regarded as a small modification of the Frenkel-Ladd method,<sup>10</sup> and, in fact, we shall denote it as the Einstein molecule (instead of the Einstein crystal). The derivation is quite simple and benefits from some of the ideas first introduced by Wilding and Bruce.<sup>30</sup> The methodology can be easily implemented within a Monte Carlo program. It will be shown how the free energies obtained from this new method are fully consistent with those obtained by Polson *et al.*,<sup>26</sup> not only for the thermodynamic limit (i.e.,  $N$  infinitely large) but also for finite sizes. In the new derivation it is obvious that the counting of configurations is performed properly. Also it will be shown how the fluid-solid equilibria obtained for  $N=32, 108, 256$  using the phase switch Monte Carlo method, the Einstein crystal method of Polson *et al.*,<sup>26</sup> and the Einstein crystal molecule methodology proposed here are fully consistent, giving the same results within statistical uncertainty. The equilibrium pressure of hard spheres for the fluid-solid equilibrium presents a strong size dependence. It will be shown that it is possible to correct, although in an approximate way, the system size dependence of the free energies of the solid, introducing some finite size corrections.

## II. METHOD

Let us consider first a simple system consisting on three hard disks (hard rods) confined to move within a segment of length  $L$ . The partition function of this system (after integrating over the momenta) is given by

$$Q = \frac{1}{3!\Lambda^3} \int_0^L \int_0^L \int_0^L e^{-\beta U'(x_1, x_2, x_3)} dx_1 dx_2 dx_3, \quad (1)$$

where  $\Lambda$  is the thermal de Broglie wavelength. The confinement is equivalent to have two hard walls located at a distance  $\sigma/2$  to the left of the point  $x=0$  and to the right of  $x$

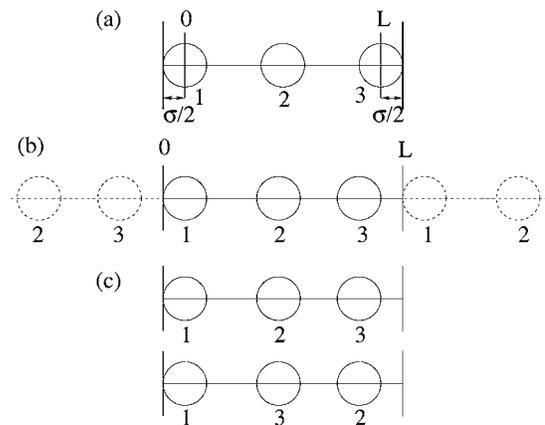


FIG. 1. (a) Three particles confined to move in the region  $(0, L)$ . For simplicity we consider the one-dimensional case (hard disks or, more properly, hard rods). (b) Three particles confined to move in the region  $(0, L)$  with periodic boundary conditions. (c) Possible permutations keeping the position of particle 1 fixed.

$=L$  [see Fig. 1(a)]. The potential energy of the system  $U'$  is given as a sum over pair of molecules of the pair potential  $u'$ ,

$$U'(x_1, x_2, x_3) = u'(x_1, x_2) + u'(x_1, x_3) + u'(x_2, x_3). \quad (2)$$

This equation can be written in a more convenient way by defining new variables,

$$\begin{aligned} x_1 &\rightarrow x_1, \\ x_2 &\rightarrow x'_2 = x_2 - x_1, \\ x_3 &\rightarrow x'_3 = x_3 - x_1. \end{aligned} \quad (3)$$

Using these new variables the partition function can be expressed,

$$\begin{aligned} Q &= \frac{1}{3!\Lambda^3} \int_0^L dx_1 \int_{-x_1}^{L-x_1} \int_{-x_1}^{L-x_1} e^{-\beta[u'(x'_2)+u'(x'_3)+u'(x'_3-x'_2)]} dx'_2 dx'_3 \\ &= \frac{1}{3!\Lambda^3} \int_0^L dx_1 \kappa. \end{aligned} \quad (4)$$

In the last step we named  $\kappa$  the integral over  $x'_2$  and  $x'_3$ . It can be seen that this integral  $\kappa$  depends explicitly on the variable  $x_1$  through the limits of the integral. The system is nonhomogeneous due to the presence of the walls in the boundaries and, therefore, the value of the integral will depend on the position of particle 1.

Let us consider now the same three hard disks system, but where the hard walls that constrain the particles to move within  $(0, L)$  are replaced by periodic boundary conditions (pbcs) [see Fig. 1(b)]. The partition function of this system is similar to the partition function of the system with hard walls in the boundaries,

$$Q = \frac{1}{3!\Lambda^3} \int_0^L \int_0^L \int_0^L e^{-\beta U(x_1, x_2, x_3)} dx_1 dx_2 dx_3. \quad (5)$$

However, the use of pbc implies the adoption of the minimum image convention, i.e., the distance between two particles will be the distance between the closest images. This means that the pair potential between particles is now  $u$ ,

and not  $u'$  (the potential in a system without periodical boundary conditions). According to this  $u$  is given by the following expression:

$$u(x'_2) = u'(x'_{2,\min}),$$

$$x'_{2,\min} = x'_2 - L \times \text{anint}\left(\frac{x'_2}{L}\right),$$
(6)

where the anint function provides the nearest integer. Therefore the configurational integral of the system with pbc can be written as

$$Q = \frac{1}{3!\Lambda^3} \int_0^L dx_1 \int_0^L \int_0^L e^{-\beta[u(x'_2)+u(x'_3)+u(x'_3-x'_2)]} dx'_2 dx'_3$$

$$= \frac{1}{3!\Lambda^3} \int_0^L dx_1 \kappa'. \quad (7)$$

Notice that the use of pbc means that the variables  $x'_2, \dots, x'_N$  are still between 0 and  $L$  (in fact, molecules 2 and 3 can always be found at a distance between 0 and  $L$  from molecule 1). In this case  $\kappa'$  does not depend on the variable  $x_1$ . As a consequence of imposing pbc, the dependence on the location of particle 1 has been removed. Therefore, the partition function will adopt the form

$$Q = \frac{1}{3!\Lambda^3} L \kappa'. \quad (8)$$

Once the position of particle 1 has been fixed, there are two possible permutations of particles 2 and 3 [see Fig. 1(c)], and, therefore, the integral  $\kappa'$  can be split in two terms,

$$\kappa' = \int_0^L \int_0^{x'_2} e^{-\beta[u(x'_2)+u(x'_3)+u(x'_3-x'_2)]} dx'_2 dx'_3$$

$$+ \int_0^L \int_0^{x'_3} e^{-\beta[u(x'_2)+u(x'_3)+u(x'_3-x'_2)]} dx'_2 dx'_3 = 2\kappa''.$$
(9)

Hence, the partition function will be

$$Q = \frac{1}{3!\Lambda^3} L 2\kappa''. \quad (10)$$

This expression can be easily extended to the general case of a system with  $N$  particles. The configurational space  $(x'_2, \dots, x'_N)$  can be divided in  $(N-1)!$  fragments as, for example,  $x'_2 < x'_3 < \dots < x'_N$ .

$$Q = \frac{1}{N!\Lambda^N} L (N-1)! \kappa''. \quad (11)$$

The extension to the three-dimensional space is also straightforward,

$$Q = \frac{1}{N!\Lambda^{3N}} V (N-1)! \kappa'', \quad (12)$$

where now  $\kappa''$  is an integral over the  $(N-1)$  position vectors of particles  $(2, \dots, N)$ . In Eq. (12) one should consider the  $(N-1)!$  possible permutations between molecules  $2, 3, \dots, N$

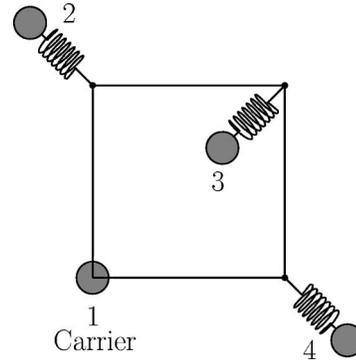


FIG. 2. Schematic representation of the Einstein molecule, in which particle 1 is fixed and acts as the carrier of the lattice. The movement of all the remaining particles is given relative to the position of particle 1.

once that the molecule 1 is fixed at the origin. The remaining  $N$  permutations (those due to molecule 1) are already taken into account by the factor  $V$  (i.e., when the molecule 1 that acts as origin moves in a system under periodical boundary conditions, the  $N$  remaining permutations are generated).<sup>30,31</sup> It would be incorrect to use simultaneously in Eq. (12) the terms  $V$  and  $N!$  in the numerator since then the permutations of molecule 1 would be counted twice.

Note that the integral  $\kappa''$  is for a given fixed position of particle 1 and for a given permutation of the remaining particles.

$$Q = \frac{V}{N\Lambda^{3N}} \kappa'' = \frac{V}{N\Lambda^3} \frac{\kappa''}{\Lambda^{3(N-1)}}. \quad (13)$$

Equations (12) and (13) are valid for any pair potential. It is clear that the problem of evaluating the free energy of a solid is just that of computing  $\kappa''$ .

Let us now describe the Einstein molecule method which is the method proposed in this work. For that purpose we shall present first a new concept, namely, the ideal Einstein molecule. The ideal Einstein molecule consists of a reference atom 1, which is called the carrier, since this atom transports the lattice and the rest of the atoms of the system  $2, 3, \dots, N$  vibrate via a harmonic potential around their lattice positions (for a schematic representation, see Fig. 2). The location of the lattice positions is determined uniquely by the position of atom 1, the carrier. There is no pair potential between the atoms of the system (and hence the term ideal). The ideal Einstein molecule is just an ideal Einstein crystal where one of the atoms of the system, namely, atom 1, does not vibrate. Notice, however, that atom 1 is able to move and occupy any position in the simulation box. Let us now compute the free energy of the ideal Einstein molecule. All what is needed is to evaluate Eq. (12) for this particular case. In particular, since Eq. (12) is general, the only term that should be evaluated is  $\kappa''$ . Let us assume that the thermal de Broglie wavelength is given by a certain characteristic length denoted as  $\sigma$ . For this particular system, the ideal Einstein molecule  $\kappa''$  is computed as

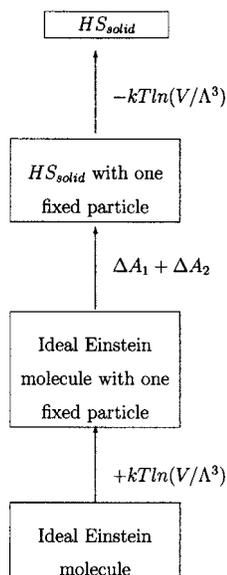
$$\kappa'' = \int e^{-\lambda_{\max}^* \sum_{i=2}^N (\mathbf{r}_i'^* - \mathbf{r}_{0,i}^*)^2} d\mathbf{r}_2'^* \dots d\mathbf{r}_N'^* = \left( \frac{\pi}{\lambda_{\max}^*} \right)^{3(N-1)/2}, \quad (14)$$

where  $\lambda_{\max}^* = \lambda_{\max}/(kT/\sigma^2)$ ,  $\mathbf{r}_i'^* = \mathbf{r}_i'/\sigma$  are the instantaneous positions of the particles, and  $\mathbf{r}_{0,i}^* = \mathbf{r}_{0,i}'/\sigma$  are the lattice positions of the crystal. Therefore, the Helmholtz free energy  $A_{\text{id-Eins-mol}}$  of the ideal Einstein molecule is given as

$$\begin{aligned} \frac{\beta A_{\text{id-Eins-mol}}}{N} &= -\frac{1}{N} \ln(Q) \\ &= \frac{1}{N} \ln\left(\frac{N\sigma^3}{V}\right) + \frac{3}{2} \left(1 - \frac{1}{N}\right) \ln\left(\frac{\lambda_{\max}^*}{\pi}\right). \end{aligned} \quad (15)$$

Note that this expression is identical to the expression obtained in Ref. 34 following a completely different route.

Let us now introduce a new concept. The ideal Einstein molecule with fixed molecule 1 is simply an ideal Einstein molecule where molecule 1 is fixed, and it is not allowed to move within the simulation box of volume  $V$ . The free energy of the ideal Einstein molecule with one fixed particle is just the free energy of the ideal Einstein molecule plus  $kT \ln(V/\Lambda^3)$  (the term  $V$  comes from the constraint on the position, whereas the term  $\Lambda^3$  comes from the constraint on the momentum). The method proposed in this work to compute the free energy of a solid is just a thermodynamic path from the ideal Einstein molecule, for which the free energy is known [Eq. (15)], to the solid of interest (for instance, a hard sphere solid, which will be denoted as  $\text{HS}_{\text{solid}}$ ). The three steps of the transformation are represented in the following scheme:



As it can be seen, the terms  $+kT \ln(V/\Lambda^3)$  and  $-kT \ln(V/\Lambda^3)$  that appear in the first and third steps cancel out. Therefore, the free energy of the hard sphere solid is computed by adding to the free energy of the ideal Einstein molecule, the free energy change between an ideal Einstein molecule with one particle fixed, and the HS solid with one particle fixed. This is done in two stages. In the first step, the harmonic springs are turned on gradually from the hard sphere solid and, hence, the energy of the system will be

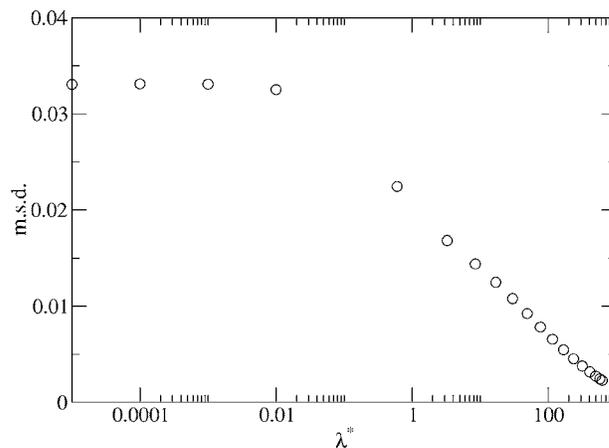


FIG. 3. Variation of the integrand of Eq. (17) [i.e., mean square displacement (msd)] as a function of  $\lambda^*$  for a hard-sphere solid with  $N=256$  particles at  $\rho^*=1.04086$ . Both the msd and  $\lambda^*$  are given in reduced units. Note that the integrand is well behaved even when  $\lambda^*$  tends to zero.

$$U(\lambda, \mathbf{r}'_2, \dots, \mathbf{r}'_n; \mathbf{r}_1)/(kT) = U_0(\mathbf{r}'_2, \dots, \mathbf{r}'_n; \mathbf{r}_1)/(kT) + \lambda^* \sum_{i=2}^N (\mathbf{r}_i'^* - \mathbf{r}_{0,i}^*)^2, \quad (16)$$

where  $U_0$  is the original potential (in this case, the hard sphere potential),  $\lambda^* = \lambda/(kT/\sigma^2)$  is the coupling parameter,  $\mathbf{r}_i'^*$  are the instantaneous positions of the molecules, and  $\mathbf{r}_{0,i}^*$  are the lattice positions of the crystal (in  $\sigma$  units, i.e.,  $\mathbf{r}_i'^* = \mathbf{r}_i'/\sigma$ ). Notice that  $U$  or  $U_0$  depend explicitly on  $\mathbf{r}'_2, \mathbf{r}'_3, \dots, \mathbf{r}'_N$  and parametrically on the position of the fixed particle 1. The free energy change in this first stage is computed as

$$\frac{\Delta A_2}{NkT} = \frac{1}{N} \int_{\lambda^*=\lambda_{\max}^*}^{\lambda^*=0} \left\langle \sum_{i=2}^N (\mathbf{r}_i'^* - \mathbf{r}_{0,i}^*)^2 \right\rangle d\lambda^*. \quad (17)$$

Notice that by construction  $\Delta A_2$  is always negative (i.e., the integrand is positive but the integration limits are from  $\lambda_{\max}^*$  to zero). In the second stage the free energy change between the system interacting via  $U(\lambda, \mathbf{r}'_2, \dots, \mathbf{r}'_n; \mathbf{r}_1)$  (with fixed molecule 1) and an ideal Einstein molecule with fixed molecule 1 is computed [i.e.,  $\Delta A_1/(NkT)$ ], which is simply given as

$$\frac{\Delta A_1}{Nk_B T} = -\frac{1}{N} \ln \left\langle \exp \left[ - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{u_0(r_{ij})}{k_B T} \right] \right\rangle, \quad (18)$$

where  $u_0(r_{ij})$  is, in this case, the hard sphere potential.

The reader may wonder if there is any singular behavior in Eq. (17) when  $\lambda$  approaches zero. The answer is that the integrand remains well behaved even when  $\lambda=0$  (see Fig. 3). The reason is that once atom 1 is fixed the translation of the system as a whole is suppressed. In the method of Frenkel and Ladd the translation of the system as a whole is avoided by fixing the center of mass of the system.<sup>10</sup> Here the translation is suppressed by fixing one of the particles of the system. Obviously both choices are possible and correct, and the free energy obtained by both routes must be the same. The derivation presented here for the case that one of the atoms of the system is fixed is particularly simple. The implemen-

TABLE I. Free energy for the hard-sphere solid at  $\rho^*=1.040\ 86$  using the Einstein molecule method and the Einstein crystal method as obtained in this work. For comparison the results reported by Polson *et al.* using the Einstein crystal method are also included (these values were taken from the fit given in Fig. 2 of Ref. 26, which is valid only for  $N>216$ ). Results obtained in this work with the Einstein molecule method for  $\rho^*=1.099\ 975$  and  $\rho^*=1.150\ 000$  are also presented. Finally, the free energies for the LJ system (truncated at  $2.7\sigma$ ) as a function of  $N$  and at a reduced density  $\rho^*=1.28$  and a reduced temperature  $T^*=T/(\epsilon/k)=2$  are also presented.

System	$\rho^*$	$N$	$A/(NkT)$		
			Einstein molecule	Einstein crystal	Polson
HS	1.040 86	32	4.767(2)	4.767(2)	
HS	1.040 86	108	4.896(2)	4.895(2)	
HS	1.040 86	256	4.931(2)	4.931(2)	4.928
HS	1.040 86	500	4.944(1)	4.943(1)	4.943
HS	1.040 86	1372	4.954(1)	4.952(1)	4.953
HS	1.040 86	2048	4.955(1)	4.954(1)	4.955
HS	1.099 75	256	5.601(2)		
HS	1.099 75	500	5.615(2)		
HS	1.099 75	2048	5.627(1)		
HS	1.150 00	256	6.240(2)		
HS	1.150 00	2048	6.269(1)		
LJ	1.28	256	2.570(4)		
LJ	1.28	500	2.586(4)		
LJ	1.28	864	2.592(3)		
LJ	1.28	1372	2.594(3)		

tation of the methodology is also quite straightforward. Without loss of generality let us just describe the procedure for the hard sphere solid. In that case, a fcc HS solid is generated. Then the harmonic springs are turned on. Atom 1 remains always fixed and static on its initial lattice position. The rest of the atoms of the system move and the energy of the system is computed via Eq. (16). The integrand of Eq. (17) is computed. Notice that the lattice remains fixed along the simulation. When one of the particles of the system (say particle 2) moves, there is no need of moving the lattice as in the Frenkel-Ladd method where the center of mass is fixed. For this reason the implementation is particularly simple. The lattice remains static, all atoms of the system but atom 1 move, and atom 1 remains fixed at the initial lattice position. In the second stage  $\Delta A_1$  is computed in a similar way. In this case a Markov chain is generated for an ideal Einstein molecule with fixed atom 1, and the average of the Boltzmann factor of the solid of interest is computed from time to time.

In summary, the free energy of a solid is computed in this work as

$$A_{\text{HS}}/(NkT) = A_{\text{id-Eins-mol}}/(NkT) + \Delta A/(NkT), \quad (19)$$

where  $\Delta A$  is given by

$$\Delta A(N, \lambda_{\text{max}}^*)/(NkT) = \Delta A_1/(NkT) + \Delta A_2/(NkT). \quad (20)$$

### III. RESULTS

#### A. Free energies from the Einstein molecule approach

Let us start by analyzing the effect on the configurational properties of fixing one of the molecules of the system. We considered a fcc solid of hard spheres with  $N=108$  and  $\rho^*$

$=(N/V)\sigma^3=1.040\ 86$ .  $NVT$  Monte Carlo simulations were performed in the traditional way (all particles move) and in the new way (all particles but molecule 1 move). The radial distribution function was identical in both cases which clearly shows that fixing one of the molecules of the solid (say particle 1) does not affect the configurational properties.

Let us now present the results of the free energy calculations performed in this work. We considered a fcc close packed structure with a reduced number density  $\rho^*=(N/V)\sigma^3=1.040\ 86$ . For the smaller systems the maximum value of  $\lambda$  used in the calculations was  $\lambda_{\text{max}}^*=632.026$ , while for the two larger systems we used  $\lambda_{\text{max}}^*=1000$ . We also computed the free energy at two other number densities,  $\rho^*=1.099\ 975$  and  $\rho^*=1.150\ 000$ , in these cases considering three and two system sizes, respectively. At  $\rho^*=1.099\ 975$  we used  $\lambda_{\text{max}}^*=1774.927$  and at  $\rho^*=1.150\ 000$ , the maximum value of  $\lambda$  was set to  $\lambda_{\text{max}}^*=2500$ . The integral was evaluated using the Gauss-Legendre quadrature algorithm with between 15 and 20 different values of  $\lambda$  in the interval  $\lambda^*=0$  and  $\lambda_{\text{max}}^*$ . Typically the runs consisted of 50 000 cycles for equilibration followed by 400 000 cycles for obtaining averages, except for  $N=32$ , and 108, for which runs ten times longer were used.

The free energies as obtained in this work from the Einstein molecule methodology (where molecule 1 is fixed) are presented in Table I. At the smallest density we have also computed the free energy by using the traditional Einstein crystal methodology (where the center of mass of the system is fixed). For comparison, the results obtained by Polson *et al.* using the Einstein crystal methodology are also included in the table (they were taken from the empirical fit provided in Fig. 2 of their paper).<sup>26</sup> For the density  $\rho^*=1.040\ 86$  the

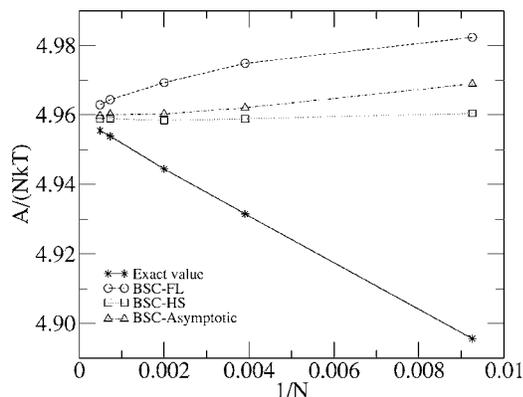


FIG. 4. Dependence of the free energy of the hard-sphere solid with the system size. The free energy corrected with FSC-FL, FSC-HS, and FSC-asymptotic [as given by Eq. (36)] corrections are also shown.

free energy, as calculated with the Einstein molecule approach, has been plotted in Fig. 4. The first thing to be noted is that free energies obtained from the three different sources agree within the statistical error. That gives us confidence on the new methodology proposed in this work. A more detailed view of the different terms contributing to the total free energy is presented in Table II. As it can be seen, the value of each individual term,  $\Delta A_1$ ,  $\Delta A_2$ , and  $A_{\text{ref}}$ , is different when the center of mass of the system is fixed or when molecule 1 is fixed. However, the total sum does not depend on the arbitrary choice of the reference coordinate (center of mass or atom 1). The results presented in Table I are independent of the methodology (and of the author!). At this stage we would like to stress that the free energy of a solid with  $N$  molecules in a certain solid structure and with a given Hamiltonian is unique and should not depend on the methodology used to determine it. Notice that for hard spheres the only parameter needed to describe the pair potential is the value of  $\sigma$ . However, for a LJ system it is not sufficient to give the values of  $\sigma$  and  $\epsilon$ . The distance at which the potential is truncated ( $r_c^* = r_c/\sigma$ ) should also be provided when describing the pair potential. According to this the free energy of a LJ fcc solid with  $N=256$  is not the same when  $r_c^* = 2.7$  and when  $r_c^* = 5$  because the potential is not identical in both cases.

The results of Table I show a strong size dependence in the value of the free energy of a fcc hard sphere solid. This is an intrinsic property of the fcc hard sphere solid (it remains to be analyzed if the  $N$  dependence is so strong for other systems), and, therefore, any method to evaluate free energy of solids presenting a weak  $N$  dependence for the fcc hard

spheres must be incorrect since it is an intrinsic property of the system. The free energies presented in Table I were fitted to the following expression:

$$\frac{\beta A}{N} = \frac{1}{N} \ln\left(\frac{N\sigma^3}{V}\right) + \frac{3}{2}\left(1 - \frac{1}{N}\right) \ln\left(\frac{\lambda_{\text{max}}^*}{\pi}\right) + d_1 + \frac{d_2}{N} + \frac{d_3}{N^2}. \quad (21)$$

The origin of this expression is as follows. The free energy of the fcc solid is obtained by adding to the free energy of the ideal Einstein molecule [as given by Eq. (15)] the term  $\Delta A$ . We found that  $\Delta A$  can be described quite well by the following expression:

$$\Delta A/(NkT) = d_1 + \frac{d_2}{N} + \frac{d_3}{N^2}. \quad (22)$$

When  $\Delta A/(NkT)$  as given by Eq. (22) is inserted in Eq. (21), then it is simple to show that the total free energy can be written (for a fixed density),

$$A/(NkT) = e_1 + \frac{e_2}{N} + \frac{e_3}{N^2}. \quad (23)$$

As it can be seen in Eq. (22),  $\Delta A$  tends to a finite value ( $d_1$ ) for large values of  $N$ . We found that Eq. (21) fits the free energies extraordinarily well [the fit is equally good using Eq. (23)]. By using the free energies calculated in this work using the Einstein molecule method (taking only the data for  $N \geq 256$ ) and the fit described by Eq. (21), we estimate that the free energy of the infinitely large system is  $A/(NkT) = 4.9590(2)$ , which is in very good agreement with the results given by Polson *et al.* [namely,  $A/(NkT) = 4.9589$ ],<sup>26</sup> by Chang and Sandler [ $A/(NkT) = 4.9591$ ],<sup>35</sup> and by Almaraz [ $A/(NkT) = 4.9589$ ].<sup>34</sup> Therefore, the value of the free energy of hard spheres in the thermodynamic limit for the density  $\rho^* = 1.04086$  seems to be firmly established.

For the second considered density,  $\rho^* = 1.099975$ , we obtained that the free energy in the thermodynamic limit is  $A/(NkT) = 5.631(1)$ , which again is in good agreement with the value reported by Frenkel and Ladd,  $A/(NkT) = 5.635$ .<sup>10</sup> Finally, at  $\rho^* = 1.150000$ , we estimate that the free energy in the thermodynamic limit is  $A/(NkT) = 6.273(2)$ .

Let us now illustrate how the Einstein molecule approach can also be applied to a LJ system. The only difference between the free energy calculation for the HS and for the LJ system is that, for the LJ system, the value of  $\Delta A_1$  is computed as

TABLE II. Value of the different terms that contribute to the free energy ( $\Delta A_1$ ,  $\Delta A_2$ , and  $A_{\text{ref}}$ ), either for the Einstein molecule or Einstein crystal methods.

N	$\lambda_{\text{max}}$	Einstein molecule				Einstein crystal			
		$\Delta A_1/(NkT)$	$\Delta A_2/(NkT)$	$A_{\text{ref}}/(NkT)$	$A_{\text{tot}}/(NkT)$	$\Delta A_1/(NkT)$	$\Delta A_2/(NkT)$	$A_{\text{ref}}/(NkT)$	$A_{\text{tot}}/(NkT)$
108	632.026	0.0172	-3.0046	7.8830	4.896	0.0175	-2.9400	7.8180	4.895
256	632.026	0.0174	-3.0116	7.9254	4.931	0.0175	-2.9797	7.8929	4.931
1372	1000.00	0.0018	-3.6862	8.6383	4.955	0.0018	-3.6802	8.6304	4.952
2048	1000.00	0.0018	-3.6866	8.6403	4.955	0.0015	-3.6819	8.6347	4.954

$$\frac{\Delta A_1}{Nk_B T} = -\frac{1}{N} \ln \left\langle \exp \left[ - \left( \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{U_{LJ}(r_{ij})}{k_B T} - \frac{U_{LJ, \text{lattice}}}{k_B T} \right) \right] \right\rangle + \frac{U_{LJ, \text{lattice}}}{Nk_B T}, \quad (24)$$

where  $U_{LJ, \text{lattice}}$  is the lattice energy of the LJ solid (the energy of the system when the molecules stand on their lattice positions). The brackets denote that the average is performed over configurations generated for the ideal Einstein molecule. We shall consider a LJ system with the potential truncated at  $2.7\sigma$  and with long range corrections [obtained by assuming  $g(r)=1$  beyond the cutoff]. Then we shall perform calculations for the state  $T^*=2.00$   $\rho^*=1.28$  for different system sizes, namely,  $N=256, 500, 864,$  and  $1372$ , and keeping the cutoff radius constant for all these sizes. The free energies obtained from the Einstein molecule approach are presented in Table I. Extrapolation to  $N$  infinity yields  $A/(NkT)=2.601$ . For the same state Barroso and Ferreira obtained  $A/(NkT)=2.596$  in the thermodynamic limit.<sup>36</sup> However, the value of Barroso and Ferreira cannot be directly compared to our value, since they changed the cutoff distance along with the system size, whereas our reported value is for a system where the cutoff distance was fixed to  $r_c=2.7\sigma$  for all the system sizes. In any case both values are relatively close. It is interesting to mention that when the free energies of this work are plotted as a function of  $1/N$ , the slopes obtained (for the larger values of  $N$ ) are about  $-7$  for HS with  $\rho^*=1.04086$ ,  $-7.8$  for HS with  $\rho^*=1.09975$ ,  $-8.7$  for HS with  $\rho^*=1.15000$ , and of about  $-7.7$  for the LJ system truncated at  $r_c=2.7\sigma$  and at  $\rho^*=1.28$ . Therefore the strong size dependence found for the free energy of HS at with  $\rho=1.04086$  seems also to exist for the LJ system and for the HS at a higher density. Note also that for HS the slope seems to increase slightly for the higher densities. In summary, the free energy of solid phases (for spherical potentials) presents a strong size dependent and this is an intrinsic feature of solids of finite size. It starts to be clear that free energy calculations with a weak size dependence are probably incorrect.

## B. Fluid-solid equilibria of hard spheres for systems of finite size

Now let us compute the phase equilibria for the hard sphere system. For that purpose  $NpT$  simulations have been performed for hard spheres with  $N=32, 108, 256,$  and  $500$ , for the fluid phase and for the fcc solid. The simulations of the fluid phase started at low pressures and the pressure was increased from one run to the next. The runs consisted of about 400 000 cycles (a trial move per particle plus a trial volume change) for the systems with 256, 500 molecules and ten times longer for the system with 32, and 108 molecules. The final configuration of a run was used as the input configuration for the next run. For the solid we started from a pressure around  $p^*=13$  and then performed several consecutive simulations decreasing the pressure. It was observed that for the smaller size,  $N=32$ , in the neighborhood of the phase transition, the system spontaneously visited configurations of the fluid and solid phases in a single simulation. Therefore,

TABLE III. Coefficients of the polynomial fit of  $(Z-1)/\rho$ , where the first and second coefficients have been taken as  $B_2$  and  $B_3$ , respectively.

$N$	108	256	500
$b_0 (=B_2)$	2.094 395	2.094 395	2.09 4395
$b_1 (=B_3)$	2.741 557	2.741 557	2.741 557
$b_2$	-3.745 924	-0.791 769	2.716 848
$b_3$	40.031 639	21.670 039	1.249 620
$b_4$	-80.734 920	-37.537 537	4.746 022
$b_5$	77.664 752	32.774 223	-4.645 178
$b_6$	-24.246 409	-6.815 284	5.273 870

in this particular case, to estimate the equation of state it was necessary to perform  $NVT$  simulations (that prevent the switching between the two phases) for the thermodynamic states near the phase transition (either above and below the transition), and the pressure was estimated from the virial theorem.<sup>37</sup> The results of the simulations for each system size were fitted to the following expressions for the solid and fluid phases:

$$Z/\rho = a_0 + a_1\rho + a_2\rho^2 \quad \text{for the solid}, \quad (25)$$

$$(Z-1)/\rho = \sum_{i=0}^n b_i\rho^i \quad \text{for the fluid}, \quad (26)$$

where  $Z=p/(\rho kT)$  is the compressibility factor,  $a_i$  and  $b_i$  are the adjustable parameters, and  $n$  is the number of terms in the polynomial. The coefficients of the fit are presented in Tables III and IV. The free energy of the fluid phase can be obtained easily as

$$A/(NkT) = A_{\text{ideal}}/(NkT) + \int_0^\rho \frac{(Z(\rho')-1)}{\rho'} d\rho', \quad (27)$$

$$A_{\text{ideal}}(N)/(NkT) = \ln(\rho\Lambda^3) - 1 + \ln(2\pi N)/(2N). \quad (28)$$

Without loss of generality we shall assume that the thermal de Broglie wavelength is given by  $\Lambda=\sigma^3$ . The last term in  $A_{\text{ideal}}$  is a logarithmic correction to the Stirling approximation. This term is especially important for the smaller system sizes ( $N=32, 108, 256$ ). Once the free energy is known, the chemical potential can be obtained simply as  $\mu/(kT) = G/(NkT) = A/(NkT) + Z$ .

For sufficiently large sizes the equation of state does not depend much on the system size. For this reason, we used accurate analytical expressions of the equations of state to describe the solid and fluid phases for the larger systems ( $N=1372$  and  $N=2048$ ). For the systems smaller than  $N=500$  the equations of state have been estimated from simu-

TABLE IV. Coefficients of the polynomial fit to the equation of state of the solid phase as a function of the system size.

$N$	108	256	500
$a_0$	133.931 604	83.700 810	104.222 694
$a_1$	-276.945 806	-178.152 913	-218.919 919
$a_2$	153.148 121	104.655 212	124.941 771

TABLE V. Coexistence pressure as a function of system size using the values of the free energy as obtained using the fit given by Polson *et al.*, using our own Einstein crystal method simulations with the Polson formula, and using the Einstein molecule method. For the smaller sizes ( $N \leq 500$ ), the equations of state for both the solid and the liquid have been obtained in this work, whereas for the larger sizes we have chosen to use analytical equations of state (Refs. 38 and 41). Notice the good agreement between this work and the results of Wilding (Ref. 30) and Errington (Ref. 32).

$N$	$p^*$				
	Polson	Einstein crystal	Einstein molecule	Wilding	Errington
32		9.69	9.69(8)	9.55	
108		11.01	11.02(5)	10.94	11.00(6)
256	11.22	11.25	11.26(5)	11.23(3)	11.25(1)
500	11.33	11.34	11.35(3)		11.34(1)
1372	11.48	11.48	11.50(3)		
2048	11.51	11.51	11.52(3)		

lations, as described before (some finite size effects are visible for these system sizes, specially for the smaller ones).

Two possible equations of state that describe with extraordinary accuracy the equation of state of hard spheres in the fluid phase are the one proposed by Kolafa and Malijevsky<sup>38</sup> and the one proposed by Speedy.<sup>39</sup> The Carnahan-Starling equation<sup>40</sup> is not sufficiently accurate to describe the liquid phase and it yields coexistence pressures about 0.10 higher than those obtained from the equation of state (EOS) of Kolafa and Malijevsky<sup>38</sup> or Speedy.<sup>39</sup>

As with regards to the solid phase, the free energy is calculated using the following expression:

$$A(\rho)/(NkT) = A(\rho_{\text{ref}})/(NkT) + \int_{\rho_{\text{ref}}}^{\rho} (Z/\rho') d\rho', \quad (29)$$

and the values of the Helmholtz free energy at the reference state ( $\rho = 1.04086$ ) are taken from Table I. For small systems (i.e., with less than 500 molecules) the equation of state is sensitive to the size of the system and, therefore, it will be estimated from the simulations performed in this work. For the two larger systems (i.e.,  $N = 1372$  and 2048) an analytical EOS will be used. Two examples of accurate EOS for the fcc solid are the equation of state proposed by Hall<sup>41</sup> and the equation of state of Speedy.<sup>42</sup>

In Table V the coexistence pressures are presented for all the system sizes. Our estimated uncertainties for the coexistence pressure are of about 0.03 for the larger system sizes, about 0.05 for the intermediate ones ( $N = 108, 256, 500$ ), and about 0.08 for the system with  $N = 32$  particles (taking into account all uncertainties associated with the calculations). As it can be seen in Table V, the coexistence pressure exhibits a strong size dependence. The coexistence pressure increases with  $N$ . The solid is quite stable for small system sizes. Assuming that this behavior can be extrapolated to other systems, one may expect that in the thermodynamic limit the fluid-solid equilibrium will be shifted in the direction of reducing the “territory” of the solid phase with respect to the transition found for a system of finite size.

Let us now consider the coexistence pressure of hard spheres in the thermodynamic limit. It may be estimated in two different ways. The first approach consists in evaluating the free energy of the solid phase in the thermodynamic limit

and then computing the fluid solid equilibrium by using analytical EOS for the fluid and solid phases. In the second approach the coexistence pressure is determined for several values of  $N$ , and the coexistence pressure in the thermodynamic limit is obtained by extrapolation. In Fig. 5 the coexistence pressure is plotted as a function of  $1/N$ . A linear behavior is found. By using the first approach we obtain  $p^* = 11.55(2)$  in the thermodynamic limit, whereas by extrapolating the coexistence pressure (for sizes  $N > 256$ ) we obtain  $p^* = 11.53(3)$ . Both results agree quite well. As a consequence we estimate that the coexistence pressure of hard spheres is  $p^* = 11.54(4)$ . This value is in agreement with the estimates of Frenkel and Smit<sup>43</sup> (11.567), of Wilding and Bruce<sup>30</sup> [11.50(9)], and of Speedy<sup>39</sup> [11.55(11)]. The effect on the coexistence pressure of using Kolafa or Speedy EOS for the fluid phase and/or Hall or Speedy for the solid phase is of about 0.02. Using the value  $p^* = 11.54(4)$ , we obtained that the coexistence densities are  $\rho_s^* = 1.0372$  for the solid and  $\rho_l^* = 0.9387$  for the fluid, values that are in very close agreement with those reported by Frenkel and Smit<sup>43</sup> ( $\rho_s^* = 1.0376$  and  $\rho_l^* = 0.9391$ ). Finally, the chemical potential at coexistence is  $\mu^* = 16.04$ , which is consistent with the value reported by Sweatman<sup>9</sup> ( $\mu^* = 15.99 - 16.08$ ).

### C. Finite size corrections

The strong size dependence found for the coexistence pressure means that the only reliable way of obtaining the

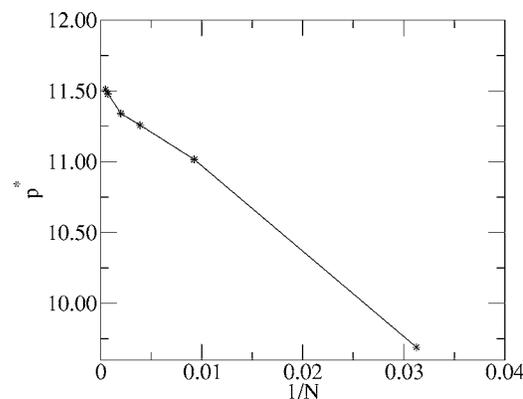


FIG. 5. Dependence of the coexistence pressure with the system size for the HS solid.

coexistence pressure in the thermodynamic limit is either determining the melting pressure for different system sizes and extrapolating to infinite size, or eventually determining the coexistence pressure for a sufficiently large system. For instance, from the results of this work it is clear that to estimate the coexistence pressure of hard spheres within 1% of the thermodynamic limit, systems of about 1000 molecules are needed. It should be recognized that determining coexistence pressure from free energy calculations is rather computationally expensive. For a certain fixed value of  $N$ , about 50 simulations are needed to estimate the coexistence (including equation of state and free energy calculations). Repeating that for different sizes (say, three values of  $N$ ) requires about 150 simulations. And all these simulations just to get the coexistence pressure in the thermodynamic limit. The problem may even be more severe for molecular systems, where three to four different solid structures may appear and the whole procedure must be repeated for each of the solid phases. All this discussion suggests that although free energy calculations provide, in principle, accurate values of the coexistence properties for a certain value of  $N$ , it would be of practical interest to introduce finite size corrections that allow us to estimate approximately the coexistence properties in the thermodynamic limit. We should admit that when performing simulations we are typically interested in the properties of the system in the thermodynamic limit (i.e., with  $N$  going to infinity and with no truncation of the potential). In many respects we simulate a finite system with a finite range of the potential as a method to estimate the properties of the system when becomes infinitely large and when the potential has not been truncated. The introduction of finite size corrections for the free energy of solids requires the introduction of approximations [something similar to the  $g(r)=1$  approximation used to correct for the introduction of the cutoff].

Our first finite size correction (FSC-liquid) applies to the liquid phase. It can be stated simply as

$$\frac{A_{\text{ideal}}(N \rightarrow \infty)}{NkT} \simeq \frac{A_{\text{ideal}}(N)}{NkT} - \frac{\ln(2\pi N)}{2N}. \quad (30)$$

This equation simply amounts to neglect the logarithmic correction to the free energy of a system of finite size. Actually this is quite oftenly used when computing the free energy of the liquid (i.e., the logarithmic correction is not included in the ideal term). Notice that the  $\ln(2\pi N)/(2N)$  is not negligible for systems with less than about 200 molecules.

We shall now present some simple prescriptions that may help us to estimate more accurately the free energy of the solid phase in the thermodynamic limit. These three prescriptions may just be considered as a first step, admitting that further work is needed on about how to introduce finite size corrections. The finite size corrections will correct for the size dependence of the free energy, without modifying the Hamiltonian when changing the size of the system. In this work we will keep the Hamiltonian when increasing the system size.

The first FSC for the free energy of the solid phase will be denoted as the Frenkel-Ladd FSC (FSC-FL).<sup>10</sup> It is given by

$$A_{\text{solid}}(N \rightarrow \infty)/(NkT) \simeq A_{\text{solid}}(N)/(NkT) + (2/N)\ln(N). \quad (31)$$

The Frenkel-Ladd treatment (which provides an incorrect description of the free energy of a system of  $N$  molecules) can be regarded as a primitive version of FSC. Although the Frenkel-Ladd formulas are strictly incorrect, they can be regarded as a primitive version of the finite size correction to the true free energy of the system (this last one given by the Polson *et al.* formalism<sup>26</sup> or alternatively by that proposed in this paper).

A second alternative formula for the finite size correction is

$$A_{\text{solid}}(N \rightarrow \infty)/(NkT) \simeq A_{\text{solid}}(N)/(NkT) + (7/N). \quad (32)$$

The origin of this formula is as follows. It has been previously discussed that when the free energy of the fcc solid is plotted as a function of  $1/N$  a slope close to  $-7$  is obtained for both the HS solid and for the LJ solid. Therefore, by adding  $7/N$  to the free energy of a system of finite size, a rough estimate of the free energy of the system is recovered. This empirical correction will be denoted as hard sphere finite size corrections (FSC-HS).

The third proposed FSC consists in taking the thermodynamic limit ( $N \rightarrow \infty$ ) of the expression used to calculate the free energy [Eq. (21)] and, for that reason, it will be named FSC asymptotic. As seen in Eq. (21), the free energy of the solid is obtained by adding the free energy of an ideal Einstein molecule plus the free energy change between this reference system and the system of interest [ $\Delta A/(NkT)$ ]. Based on this, we propose three alternative ways of defining the FSC asymptotic. In the first approach we will use simply the expression of the free energy of the ideal Einstein molecule in the thermodynamic limit (rather than its value for finite  $N$ ). The approximation resembles that proposed for the liquid before. Simply one takes the limit of  $N$  going to infinity in an analytical expression (that of the ideal Einstein crystal molecule). This approximation can be written as

$$A_{\text{solid}}(N \rightarrow \infty)/(NkT) \simeq \frac{3}{2} \ln\left(\frac{\lambda_{\text{max}}^*}{\pi}\right) + \Delta A(N, \lambda_{\text{max}}^*)/(NkT). \quad (33)$$

As it can be seen the first version of the FSC asymptotic amounts to replace the free energy of the ideal Einstein molecule of  $N$  molecules by its thermodynamic limit.

The second proposed variant of the FSC asymptotic consists on taking also the limit of the integral  $\Delta A(N, \lambda_{\text{max}}^*)/(NkT)$  when  $N$  tends to infinite. Assuming that  $\Delta A_1$  is almost independent of the system size,  $\Delta A(N, \lambda_{\text{max}}^*)/(NkT)$  shows the same dependence with  $N$  as the term  $\Delta A_2$ .  $\Delta A_2$  is the integral of a sum of  $(N-1)$  terms, divided by a factor  $N$  [see Eq. (17)]. Supposing that all the terms of the sum (i.e., the contribution to the mean square displacement of each particle) are equal,  $\Delta A_2$  can be approximated by

TABLE VI. Free energies of HS (three densities) and LJ as obtained in this work (true free energy) and when including finite size corrections (FSC), with the FSC-FL, FSC-HS, and FSC-asymptotic approximations [in the last column the first value corresponds to Eq. (33), the second to Eq. (35), and the third to Eq. (36)].

System	$\rho^*$	$N$	$A/(NkT)$			
			True free energy	FSC-FL	FSC-HS	FSC asymptotic
HS	1.040 86	32	4.767	4.984	4.986	5.014,4.920,4.967
HS	1.040 86	108	4.896	4.982	4.960	4.969,4.941,4.955
HS	1.040 86	256	4.931	4.975	4.959	4.962,4.950,4.956
HS	1.040 86	500	4.944	4.969	4.958	4.960,4.954,4.957
HS	1.040 86	1372	4.954	4.964	4.959	4.960,4.957,4.959
HS	1.040 86	2048	4.955	4.963	4.959	4.959,4.958,4.959
HS	1.040 86	$\infty$	4.959	4.959	4.959	4.959
HS	1.099 975	256	5.601	5.644	5.628	5.638,5.623,5.631
HS	1.099 975	500	5.615	5.640	5.629	5.634,5.626,5.630
HS	1.099 975	2048	5.627	5.635	5.631	5.632,5.630,5.631
HS	1.099 975	$\infty$	5.631	5.631	5.631	5.631
HS	1.150 000	256	6.240	6.283	6.267	6.276,6.264,6.270
HS	1.150 000	2048	6.269	6.276	6.272	6.274,6.272,6.273
HS	1.150 000	$\infty$	6.274	6.274	6.274	6.274
LJ	1.28	256	2.570	2.613	2.597	2.618,2.593,2.606
LJ	1.28	500	2.586	2.611	2.600	2.611,2.598,2.604
LJ	1.28	864	2.592	2.608	2.600	2.606,2.599,2.603
LJ	1.28	1372	2.594	2.605	2.599	2.603,2.598,2.601
LJ	1.28	$\infty$	2.601	2.601	2.601	2.601

$$\frac{\Delta A_2}{NkT} = \frac{N-1}{N} I = \left(1 - \frac{1}{N}\right) I, \quad (34)$$

where  $I$  is the contribution to the integral of one single arbitrary particle. In the limit of infinite size, only the term  $I$  remains, and the FSC asymptotic is given by the expression

$$A_{\text{solid}}(N \rightarrow \infty)/(NkT) \simeq \frac{3}{2} \ln\left(\frac{\lambda_{\text{max}}^*}{\pi}\right) + \frac{\Delta A(N, \lambda_{\text{max}}^*)/(NkT)}{(1 - 1/N)}. \quad (35)$$

Finally, we have observed that both expressions give a free energy that deviates slightly from the thermodynamic limit. While the first proposed correction [Eq. (33)] underestimates the true free energy, the second one [Eq. (35)] overestimates it. Based on this observation we propose the third version of FSC asymptotic as the mean value of the two previous expressions,

$$\frac{A_{\text{solid}}(N \rightarrow \infty)}{NkT} = \frac{3}{2} \ln\left(\frac{\lambda_{\text{max}}^*}{\pi}\right) + \frac{1}{2} \left( \frac{\Delta A(N, \lambda_{\text{max}}^*)}{NkT} + \frac{\Delta A(N, \lambda_{\text{max}}^*)/(NkT)}{(1 - 1/N)} \right). \quad (36)$$

In Table VI the free energy of the fcc solid phase is presented for several values of  $N$  including all the proposed finite size corrections, namely, FSC-FL, FSC-HS, and the three variants of the FSC-asymptotic. Results are presented for the HS solid (for three densities) and for the LJ solid. The results for HS at  $\rho = 1.040\ 86$  have been plotted in Fig. 4. The FSC-FL yields, in general, free energies closer to the asymptotic limit than those of the finite size system. How-

ever, it tends to overestimate the free energy of the solid. The FSC-HS gives, in general, quite good predictions of the free energy in the thermodynamic limit, for either the HS and LJ solid. However, as seen before, the slope of the free energy against  $1/N$  shows a slight dependence on the density and, obviously, this means that the FSC-HS will not work as well for the higher density (see the results for  $\rho^* = 1.150\ 00$  in Table VI). In spite of this, the deviations are not too large and, in general, it is a quite good approximation. As with regards to the FSC asymptotic, the first variant [Eq. (33)] works very well for all the considered densities of the HS solid, but its predictions are not so good for the LJ solid. The same is true for the second variant of the FSC asymptotic [Eq. (35)], the only difference is that now the true free energy is underestimated, whereas with the first variant [Eq. (33)] the true free energy was overestimated. This observation took us to define the third variant of the FSC asymptotic [Eq. (36)], which corresponds just to take the mean of the other two proposed FSC asymptotic. This last approximation seems to work extremely well for all the densities and for both the HS and the LJ solid. Further work would be needed to understand why this correction provides so accurate results. We checked (results not shown) that also for the potential  $u(r) = \epsilon(\sigma/r)^{12}$  the FSC-HS yield quite good estimates of the free energy of the system in the thermodynamic limit. This can be checked easily by using the results reported by Polson *et al.* (see Fig. 1 of their paper).

In Table VII the coexistence pressures as obtained for  $N = 108, 256, \text{ and } 500$  (using simulation results of this work for the EOS in the fluid and solid phases for these sizes) and the finite size corrections are presented. As it can be seen the

TABLE VII. Comparison of the exact coexistence pressure as a function of the system size as calculated using the Einstein molecule method with the results of applying FSC corrections to the fluid [Eq. ((30))] and solid phases. The values in parentheses in the third column were obtained using the analytical EOS of Kolafa and Malijevsky for the liquid (instead of the EOS for the finite size system).

N	$p^*$			
	Exact value	FSC-FL	FSC-HS	FSC asymptotic
108	11.02	12.20 (11.80)	11.98	12.06,11.78,11.92
256	11.26	11.83 (11.73)	11.67	11.70,11.59,11.64
500	11.35	11.68 (11.67)	11.57	11.59,11.53,11.56
$\infty$	11.54	11.54	11.54	11.54

introduction of finite size corrections yields an improved estimate of the coexistence properties in the thermodynamic limit. In fact, the Frenkel-Ladd correction provides better estimates of the coexistence pressure in the thermodynamic limit than those obtained from the Polson *et al.* formula (this last formula provides the exact value of the coexistence pressure of the system of  $N$  molecules, but, unfortunately, the coexistence pressure is quite far away from the thermodynamic limit). Looking in retrospective the use of the Frenkel-Ladd formulas has been more appropriate in estimating the coexistence properties of systems in the thermodynamic limit than the true and correct Polson *et al.* formulas.<sup>26</sup> Maybe for this reason it took some time to conclude that they were not fully correct. The estimates of the coexistence pressure in the thermodynamic limit provided by including the FSC-HS correction are quite good even for small systems. The same applies when the FSC-asymptotic corrections are included.

#### IV. CONCLUSIONS

In this paper we have proposed a new method to estimate the free energy of a solid phase. The method is denoted as the Einstein molecule. The method can be regarded as a variant of the Frenkel-Ladd method. Instead of fixing the center of mass, as in the original Frenkel-Ladd methodology, one of the atoms of the system is fixed. The derivation of the main equations of the methodology and the implementation of the algorithm within a Monte Carlo program are quite simple. The free energies obtained from the new methodology are coincident with those reported previously by Polson *et al.*<sup>26</sup> The fluid-solid equilibria have been computed from the free energies of the fluid and solid phases. It is shown that both the free energies and the coexistence pressures (for the fluid-solid equilibria of hard spheres) present an important system size dependence. The predicted coexistence pressures obtained from free energy calculations are fully consistent with those obtained by Wilding and Bruce<sup>30</sup> and Wilding<sup>31</sup> from phase switch Monte Carlo simulations. Therefore both methods are appropriate methods to determine fluid-solid equilibria. The estimate of the coexistence pressure for hard spheres from this work is  $p^* = 11.54(4)$ , which is in good agreement with the estimates of Wilding and Bruce<sup>30</sup> [ $p^* = 11.50(9)$ ], of Frenkel and Smit<sup>43</sup> ( $p^* = 11.567$ ), and of Speedy<sup>39</sup> [ $p^* = 11.55(11)$ ]. It is now clear that the classical value of the coexistence pressure  $p^*$

= 11.70 given by Hoover and Ree<sup>2</sup> is somewhat high. Besides we have found that the accurate estimation of the coexistence pressure requires a good equation of state for both the fluid and solid phases. Probably for the solid an extremely accurate EOS is not as important, since, after all, the free energy calculations can be performed at a density close to the value at coexistence. However, for the liquid (for which the free energy is obtained by integrating the EOS from zero density), this is absolutely needed. In this respect, the Carnahan-Starling<sup>40</sup> equation of state is not good enough (in fact, it shifts incorrectly the coexistence pressure by about 0.10). The EOS of Kolafa and Malijevsky<sup>38</sup> or that of Speedy<sup>39</sup> is more appropriate.

In principle, the only correct way of determining the free energy of a solid in the thermodynamic limit is to repeat the calculations for several sizes and extrapolate to infinite size. However, this is computationally expensive. Therefore, we have proposed some finite size corrections, which are based on some approximations but that may yield reliable estimates of the properties of the system in the thermodynamic limit. Several FSC corrections have been considered in this paper. The first one is the Frenkel-Ladd expression<sup>10</sup> (that can be regarded as a logarithmic correction to the true free energy of the system, as given in the paper by Polson *et al.*<sup>26</sup>). The second one, the FSC-HS, amounts to add  $7/N$  to the free energy of the solid of  $N$  molecules. The addition of this term is motivated by the fact that for hard spheres this yields approximately the free energy of the system in the thermodynamic limit. The third variant, the FSC asymptotic, consists on taking the limit of  $N$  infinite in the expression used to calculate the free energy. Depending on how this limit is taken, we propose three different variants. For spherical potentials, one the variants of FSC asymptotic yields very good estimates of the free energy in the thermodynamic limit. It should be recognized that all the FSC corrections proposed here are approximate, but they may still be quite useful. Further work is needed to analyze in more details whether these corrections can or cannot be applied to system with orientational degrees of freedom or whether other approximations can be more appropriate.

We do hope that this paper, along with the work performed on the previous decade on fluid solid equilibria, stimulates further work in the area of coexistence between fluid and solid phases, that started 40 years ago with the work of Hoover and Ree. Probably the fluid-solid equilibria remind us that finite size effects can be really important even in computer simulations of simple systems, a lesson, well known at the beginning but somehow forgotten, probably due to the fact that the effects seem to be more important for solid phases than for the fluid ones.

#### ACKNOWLEDGMENTS

This work was funded by Grant No. FIS2007-66079-C02-01 of Dirección General de Investigación. 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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