

Point Defects in Hard-Sphere Crystals[†]

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Received: February 28, 2001; In Final Form: May 4, 2001

We report numerical calculations of the concentration of interstitials in hard-sphere crystals. We find that in a three-dimensional fcc hard-sphere crystal at the melting point, the concentration of interstitials is $2.7(4) \times 10^{-8}$. This is some 3 orders of magnitude lower than the concentration of vacancies. A simple, analytical estimate yields a value that is in fair agreement with the numerical results.

I. Introduction

Any crystal in equilibrium will contain defects, such as vacancies, interstitials, and dislocations. Of these, the point defects are the most common. Some 30 years ago, Bennett and Alder¹ estimated the equilibrium concentration of vacancies in a hard-sphere crystal and found that close to the melting point, this concentration could be quite high (typically, one vacancy per 4000 lattice sites). At present, the question of the concentration (and transport) of point defects in (colloidal) hard-sphere crystals takes on a renewed—and now quite practical—significance. Apart from the theoretical interest in hard sphere crystals as a model system, crystals from colloidal particles, having lattice sizes comparable to the wavelength of light, are being prepared and studied because of their potentially interesting photonic properties. Clearly, the presence of even a small number of defects can have a pronounced effect on the nature of photonic states in such materials. Moreover, as the accuracy of free energy calculations increases, it is no longer permissible to ignore the contribution of vacancies to the total free energy. The aim of the present paper is to review briefly the statistical mechanical description of a crystal with point defects. This problem is not completely trivial, as the concept of a vacancy or interstitial is inextricably linked to that of lattice sites, and lattice sites lose their meaning in a disordered state. So we should first address the question of whether it is permissible to count states with a different number of lattice sites as distinct. The answer is, of course, that this is only permissible if these different states can be assigned to distinct volumes in phase space. This is possible if we impose that every particle in a crystal is confined to its Wigner–Seitz cell. In three-dimensional crystals, this constraint on the positions of all particles has little effect on the free energy (in contrast, in a liquid, it is not at all permissible). In a two-dimensional crystal, the constraint is more problematic, at least in the thermodynamic limit. However, for large but finite two-dimensional systems, the single-occupancy cell constraint is also quite reasonable. Below, we describe two alternative (but equivalent) routes to arrive at the free energy of a crystal with vacancies. In one case, we use the grand canonical ensemble. This would seem to be the most obvious ensemble to use when describing a system with a fluctuating number of particles. Yet the analysis is complicated by the fact that not only the number of particles, but also the number of lattice sites, may fluctuate. In the second analysis, we consider

an isothermal–isobaric system. The latter approach is simpler and, apart from a minor correction, is equivalent to the one followed by Bennett and Alder.¹ We then describe our numerical approach to compute the concentration of interstitials in a hard-sphere crystal. We compare our numerical results with a simple theoretical estimate.

II. Free Energy of Vacancies

A. Grand Canonical Route. When considering the statistical mechanics of a crystal with vacancies, it is convenient to consider first a system with a fixed number of lattice sites, M , contained in a volume V . If this crystal is in contact with a particle-reservoir at chemical potential μ , then the number of vacancies in the crystal may fluctuate. In principle, the crystal could also contain interstitials, but for the time being, we shall ignore this possibility. It is then easy to write down the expression for the grand potential of the crystal Ξ'

$$\Xi'_M = \sum_{n=0}^M \exp[(M-n)\beta\mu] Q_{M-n}(V, T) \quad (1)$$

where $\beta \equiv 1/k_B T$. Note that this is not the true grand potential because we should also allow for fluctuations in the number of lattice sites. We denote the free energy of a crystal with no vacancies by $F^{(0)} = -kT \ln Q_M$. In practice, the equilibrium concentration of vacancies in a crystal is very low. We shall therefore make the approximation that vacancies do not interact. This assumption is not as reasonable as it seems, as the interaction of vacancies through the stress field is quite long-ranged. The assumption that vacancies are ideal makes it easier to compute the canonical partition function of a crystal with n vacancies

$$Q_{M-n}(V, T) \approx \frac{M!}{n!(M-n)!} Q^{(n)}(V, T) = \frac{M!}{n!(M-n)!} \exp(-\beta F^{(n)}) \quad (2)$$

where we have used the notation $F^{(n)}$ to denote the free energy of a crystal with n vacancies at given positions. As the vacancies are assumed to be noninteracting, it is clear that we can write

$$F^{(n)} = F^{(0)} - nf_1 = Mf_0 - nf_1 \quad (3)$$

where f_0 is the free energy per particle in the defect-free crystal

[†] Part of the special issue “Bruce Berne Festschrift”.

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and $-f_1$ is the change in free energy of a crystal due to the creation of a single vacancy at a specific lattice point. (The choice of the minus sign in the definition will later turn out to be convenient.)

Combining eqs 1–3, we obtain

$$\begin{aligned}\Xi'_M &= \sum_{n=0}^M \frac{M!}{n!(M-n)!} \exp[(M-n)\beta\mu] \exp[-\beta(Mf_0 - nf_1)] \\ &\equiv Q_M \exp(M\beta\mu) [1 + \exp(-\beta[\mu - f_1])]^M\end{aligned}\quad (4)$$

Usually, $\exp[-\beta(\mu - f_1)]$ is much less than unity. This allows us to write

$$\Xi'_M = Q_M \exp(M\beta\mu) \exp[M \exp(-\beta[\mu - f_1])]\quad (5)$$

Using

$$\langle M - n \rangle = \frac{\partial \ln \Xi'}{\partial \beta\mu}$$

the average number of vacancies follows as

$$\langle n \rangle = M \exp[-\beta(\mu - f_1)]\quad (6)$$

Now, we should take into account the fact that the number of lattice sites itself is not actually fixed but will adjust to the number of vacancies. The total grand partition function is therefore a sum over all states with different number of lattice sites $M' = M + \Delta M$. In practice, $\Delta M \ll M$. We can then write

$$\Xi = \sum_{\Delta M=-\infty}^{\infty} \Xi'_{M+\Delta M}$$

Note that Ξ' depends on both $M + \Delta M$ and μ . We now choose the reference number of lattice sites such that in that particular case μ is equal to the chemical potential of the perfect lattice. That is

$$F^{(0)} + P^{(0)}V = M\mu$$

We also introduce a rather strange quantity, namely, the “grand canonical” partition function of a perfect lattice with a fixed number of particles (M): $\Xi_M^{(0)} \equiv Q_M \exp(M\beta\mu)$. Of course, $\Xi_M^{(0)}$ is not a true grand canonical partition function, as the number of particles in this system is fixed. The grand canonical partition function then becomes

$$\begin{aligned}\Xi &= \sum_{\Delta M=-\infty}^{\infty} \exp[-\beta F^{(0)}(M + \Delta M)] \exp[(M + \Delta M)\beta\mu] \times \\ &\quad \exp[(M + \Delta M) \exp(-\beta[\mu - f_1])]\end{aligned}\quad (7)$$

We assume (as usual) that in the thermodynamic limit, Ξ is dominated by the largest term in the sum. Hence, we have to determine the point where the derivative of Ξ with respect to M vanishes. To this end, we perform a Taylor expansion of the exponent in eq 7 in powers of ΔM . Note that for a perfect—defect free—lattice

$$\frac{\partial F^{(0)}}{\partial M} = \frac{\partial F^{(0)}}{\partial N} = \mu\quad (8)$$

and

$$\frac{\partial^2 F^{(0)}}{\partial M^2} = \frac{\partial \mu}{\partial N} = \frac{1}{N} \frac{\partial P}{\partial \rho}\quad (9)$$

Moreover

$$f_1(M + \Delta M) = f_1(M) + \frac{1}{V} \frac{\partial f_1}{\partial \rho} \Delta M + \mathcal{O}(\Delta M^2)\quad (10)$$

By combining eq 8–10, we obtain

$$\begin{aligned}\exp[-\beta(\mu - f_1[M + \Delta M])] &= \\ \exp\{-\beta[\mu - f_1(M)]\} &\left[1 + \frac{\beta}{V} \frac{\partial f_1}{\partial \rho} \Delta M + \mathcal{O}(\Delta M^2)\right]\end{aligned}\quad (11)$$

Note that $f_1 = F^{(0)} - F^{(1)}$. Hence

$$\frac{\beta}{V} \frac{\partial f_1}{\partial \rho} = \frac{\beta}{V} \frac{\partial f_1}{\partial V} \frac{\partial V}{\partial \rho} = \beta \frac{V}{N} (P^{(0)} - P^{(1)}) \equiv \beta \Delta P^{0,1}/\rho\quad (12)$$

where $\Delta P^{0,1}$ is the difference in the pressure of two crystals with M lattice sites, one with zero vacancies and the other with one vacancy (both in a fixed volume V and a temperature T). As a consequence

$$\begin{aligned}(M + \Delta M) \exp[-\beta(\mu - f_1[M + \Delta M])] &\approx \\ M \exp\{-\beta[\mu - f_1(M)]\} &\left\{1 + \frac{\Delta M}{M} + (\beta \Delta P^{0,1}/\rho) \Delta M\right\}\end{aligned}\quad (13)$$

Inserting the Taylor expansion in the expression for Ξ , we obtain

$$\begin{aligned}\Xi &= \exp[-\beta F^{(0)}(M) + M\beta\mu] \Sigma_{\Delta M} \times \\ &\quad \exp\left\{M \exp[-\beta(\mu - f_1(M))] \times \right. \\ &\quad \left. \left[1 + \frac{\Delta M}{M} + (\beta \Delta P^{0,1}/\rho) \Delta M\right] - \frac{\beta}{2} \frac{1}{M} \frac{\partial P}{\partial \rho} (\Delta M)^2\right\}\end{aligned}\quad (14)$$

It may seem inconsistent that we expand to second order in ΔM in the last term of eq 14 but only to first order in the preceding terms. However, as we show below, we actually expand—consistently—to second order in the vacancy concentration.

We define the fractional change in the number of lattice sites, y , as

$$y \equiv \frac{\Delta M}{M}\quad (15)$$

Similarly, we define the vacancy concentration x as

$$x = \frac{\langle n \rangle}{M} = \exp[-\beta(\mu - f_1)]\quad (16)$$

Finding the maximum in the exponent is then equivalent to maximizing

$$-\frac{\beta M}{2} \left(\frac{\partial P}{\partial \rho}\right) y^2 + Mx(0)[1 + y(1 + \beta V \Delta P^{0,1})]\quad (17)$$

where $x(0)$ is the value of x for $\Delta M = 0$ and ρ_s is the density of the ideal reference lattice. The maximum value is at

$$y = x(0) \frac{(1 + \beta V \Delta P^{0,1})}{\beta \left(\frac{\partial P}{\partial \rho}\right)}\quad (18)$$

and the maximum of the grand canonical potential is

$$\Xi \approx \exp(-\beta F^{(0)}(M) + M\beta\mu) \times \exp\left(Mx(0) + \frac{M}{2} \frac{x^2(0)(1 + \beta V \Delta P^{0,1})^2}{\beta \left(\frac{\partial P}{\partial \rho}\right)}\right) \quad (19)$$

Hence, the presence of vacancies increases the grand potential (as it should) and it changes (increases) the number of lattice sites. However, if the terms of order $\mathcal{O}(x^2(0))$ are ignored, the vacancy concentration is still given by eq 6.

The next question is how vacancies affect the melting curve. Now our definition of the reference system (i.e., the perfect lattice with the same μ) turns out to be convenient. Note that the grand canonical partition function is related to the pressure by

$$\beta PV = \ln \Xi = \beta P^{(0)}V + Mx(0) + \mathcal{O}(x(0)^2) \quad (20)$$

Ignoring terms quadratic in the vacancy concentration, we find that the effect of allowing for vacancies is to increase the pressure of the solid by an amount

$$\Delta P \approx x(0)\rho_s kT \quad (21)$$

Let us assume that the liquid was in equilibrium with the perfect crystal at pressure P and chemical potential μ . Then it is easy to verify that the shift in the coexistence pressure due to the presence of vacancies is

$$\delta P_{\text{coex}} = \frac{-x(0)kT}{\rho_l^{-1} - \rho_s^{-1}} \quad (22)$$

and the corresponding shift in the chemical potential at coexistence is

$$\delta \mu_{\text{coex}} = \frac{\delta \mu_{\text{coex}}}{\rho_l} \quad (23)$$

Direct calculations of the vacancy concentration in a hard-sphere crystal at melting¹ indicate that $x(0) \approx 2.6 \times 10^{-4}$. Hence, the increase in the coexistence pressure due to vacancies is $\delta P_{\text{coex}} \approx -2.57 \times 10^{-3} kT/\sigma^3$ (where σ is the particle diameter). The corresponding shift in the chemical potential at coexistence is $\delta \mu_{\text{coex}} = -2.74 \times 10^{-3} kT$. Note that this shift is very significant when compared to the accuracy of absolute free-energy calculations of the crystalline solid.²

B. NPT Route. Bennett and Alder¹ work with the Gibbs free energy rather than the Helmholtz free energy. Their expression for the vacancy concentration is based on the analysis of the effect of vacancies on the Gibbs free energy of a system of N particles at constant pressure and temperature. First, we define g^{vac} , the variation in the Gibbs free energy of a crystal of M particles due to the introduction of a single vacancy at a given lattice position

$$g^{\text{vac}} \equiv G_{M+1,1}(N, P, T) - G_{M,0}(N, P, T) \\ = F_{M+1,1}(V_{M+1,1}) - F_{M,0}(V_{M,0}) + P(V_{M+1,1} - V_{M,0}) \quad (24)$$

where the first subscript refers to the number of lattice sites in the system and the second subscript to the number of vacancies. In this equation, we distinguish M , the original number of lattice sites, and N , the number of particles, even though in the present

case $N = M$. Let us write f_1 (eq 37) as

$$-f_1 \equiv F_{M+1,1}(V_{M+1,0}) - F_{M+1,0}(V_{M+1,0})$$

Hence

$$g^{\text{vac}} = F_{M+1,1}(V_{M+1,1}) - F_{M+1,1}(V_{M+1,0}) + F_{M+1,1}(V_{M+1,0}) - \\ F_{M+1,0}(V_{M+1,0}) + F_{M+1,0}(V_{M+1,0}) - F_{M,0}(V_{M,0}) + \\ P(V_{M+1,1} - V_{M,0}) \quad (25)$$

The next step is to introduce a hypothetical defect free crystal with M lattice sites at the same pressure as that of the system with $M + 1$ lattice sites. The volume of this system is $V_{M,0} = \{M/(M + 1)\}V_{M+1,0}$. Similarly, the free energy of this hypothetical system is $F_{M,0} = \{M/(M + 1)\}F_{M+1,0}$. Note also that

$$F_{M+1,1}(V_{M+1,1}) - F_{M,0}(V_{M,0}) = -P\Delta v = -f_1 + f_0 \quad (26)$$

where $\Delta v \equiv v^{\text{vac}} - v^{\text{part}}$ is the difference in volume of a vacancy and a particle at constant pressure and a constant number of lattice sites. Moreover

$$P(V_{M+1,1} - V_{M,0}) = P(\Delta v + V/N) \quad (27)$$

Hence, the Gibbs free energy difference associated with the formation of a vacancy at a specific lattice site, $G_{M,1} - G_{M-1,0} \equiv g^{\text{vac}}$, is then

$$g^{\text{vac}} = P(V_{M+1,1} - V_{M,0}) - f_1 + (\Delta v + V/N)P + f_0 \\ = P(V_{M,1} - V_{M,0} + V_{M,0} - V_{M-1,0}) - f_1 + f_0 \\ = P(V/N) - f_1 + f_0 \\ = (P/\rho + f_0) - f_1 \\ = \mu_0 - f_1 \quad (28)$$

where we have defined $\mu_0 \equiv (P/\rho + f_0)$. Now we have to include the entropic contribution due to the distribution of n vacancies over M lattice sites. This total Gibbs free energy then becomes

$$G = G_0(N) + ng^{\text{vac}} + MkT \left(\frac{n}{M} \ln \frac{n}{M} + \left[1 - \frac{n}{M}\right] \ln \left[1 - \frac{n}{M}\right] \right) \quad (29)$$

$$\approx G_0(N) + ng^{\text{vac}} + nkT \ln \frac{n}{M} - nkT \quad (30)$$

If we minimize the Gibbs free energy with respect to n , we find

$$\langle n \rangle \approx M \exp(-\beta g^{\text{vac}})$$

where we have ignored a small correction due to the variation of $\ln M$ with n . If we insert this value in the expression for the total Gibbs free energy, we find

$$G = G_0(N) + \langle n \rangle g^{\text{vac}} - \langle n \rangle g^{\text{vac}} - \langle n \rangle kT = G_0 - \langle n \rangle kT$$

The total number of particles is $M - \langle n \rangle$. Hence, the Gibbs free energy per particle is

$$\mu = \frac{G_0 - \langle n \rangle kT}{N} = \mu_0 - \frac{\langle n \rangle kT}{N} \\ \approx \mu_0 - x_v kT \quad (31)$$

Thus, the change in chemical potential of the solid is

$$\Delta\mu = -x_v kT \quad (32)$$

from which it follows that the change in pressure of the solid at fixed chemical potential is equal to

$$\Delta P = x_v \rho_s kT \quad (33)$$

This is equivalent to eq 21 above. Hence the Bennett–Alder scheme is equivalent to the grand canonical scheme. (In ref 1, a slightly different expression is found, but this is due to a small error in the derivation in that paper.)

It should be pointed out that the variation in volume due to the replacement of a particle by a vacancy can be computed either directly, in a constant-pressure simulation, or indirectly by measuring the change in pressure in a constant volume simulation. The two methods are related through the thermodynamic relation

$$\left(\frac{\partial V}{\partial P}\right)_{N,T} \left(\frac{\partial P}{\partial N}\right)_{V,T} \left(\frac{\partial N}{\partial V}\right)_{P,T} = -1 \quad (34)$$

Noting that the number of vacancies is $n = M - N$, we can see that the change in pressure with the number of vacancies for a fixed number of lattice sites is

$$-\left(\frac{\partial P}{\partial N}\right)_{V,T} = \left(\frac{\partial P}{\partial V}\right)_{N,T} \left(\frac{\partial V}{\partial N}\right)_{P,T} \quad (35)$$

In particular, the pressure change due to one vacancy (i.e., $\Delta P^{0,1}$, defined in eq 12) is

$$\Delta P^{0,1} = P_{M,0} - P_{M,1} = \Delta v \left(\frac{\partial P}{\partial V}\right)_{N,T} \quad (36)$$

III. Computational Scheme

A. Vacancies. Numerically, it is straightforward to compute the equilibrium vacancy concentration. As before, the central quantity that needs to be computed is $-f_1$, the change in free energy of a crystal due to the creation of a single vacancy at a specific lattice point. In fact, it is more convenient to consider $+f_1$, the change in free energy due to the removal of a vacancy at a specific lattice point. This quantity can be computed in several ways. For instance, we could use a particle-insertion method. We start with a crystal containing one single vacancy and attempt a trial insertion in the Wigner–Seitz cell surrounding that vacancy. Then f_1 is given by

$$f_1 = -kT \ln \left(\frac{V_{WS} \langle \exp(-\beta \Delta U) \rangle}{\Lambda^d} \right) \quad (37)$$

where V_{WS} is the volume of the Wigner–Seitz cell and ΔU is the change in potential energy associated with the insertion of a trial particle. For hard particles

$$f_1 = -kT \ln \left(\frac{V_{WS} P_{\text{acc}}(V_{WS})}{\Lambda^d} \right) \quad (38)$$

where $P_{\text{acc}}(V_{WS})$ is the probability that the trial insertion in the Wigner–Seitz cell will be accepted. As most of the Wigner–Seitz cell is not accessible, it is more efficient to attempt insertion in a subvolume (typically of the order of the cell volume in a lattice–gas model of the solid). However, then we also should consider the reverse move—the removal of a particle from a subvolume v of the Wigner–Seitz cell, in a crystal

without vacancies. The only thing we need to compute in this case is $P_{\text{rem}}(v)$, the probability that a particle happens to be inside this volume. The expression for f_1 is then

$$f_1 = -kT \ln \left(\frac{v P_{\text{acc}}(v)}{P_{\text{rem}}(v) \Lambda^d} \right) \quad (39)$$

Of course, in the final expression for the vacancy concentration, the factor Λ^d drops out (as it should) because it is canceled by the same term in the ideal part of the chemical potential.

B. Interstitials. As in the case of vacancies, the calculation of interstitials centers around the calculation of g_1 , the free energy associated with introducing an interstitial into the system (in the NPT ensemble). g_1 can be expressed as a sum of two parts: the free energy of introducing a point particle into the system ($g^{\text{ins}} = -kT \ln(1 - \eta)$, where η is the packing fraction) and the free energy of growing that particle to the same diameter ($\sigma_0 \equiv 1$) as those of the other particles (g^{grow}).

For the calculation of g^{grow} , we simulate an extended system consisting of a lattice of N particles with diameter $\sigma_0 = 1$ on (or near) lattice sites and one extra (interstitial) particle that has a diameter σ_1 that can vary freely. We interpret σ_1 as an additional coordinate, and, in this sense, the system that we are considering is an extended system. The partition sum for the extended system is

$$Q(N+1, P, T) = \int_0^1 d\sigma' Q(N+1, P, T, \sigma') \quad (40)$$

where $Q(N+1, P, T, \sigma')$ is the partition function for the isothermal–isobaric system with one interstitial particle with radius σ' . The probability of finding the interstitial particle with a specific radius $\sigma' = \sigma_1$ is

$$P(\sigma_1 | N+1, P, T) = \frac{\int_0^1 d\sigma' Q(N+1, P, T, \sigma') \delta(\sigma_1 - \sigma')}{Q(N, P, T)} = \frac{Q(N+1, P, T, \sigma_1)}{Q(N+1, P, T)} \quad (41)$$

and the Gibbs free energy $G(N+1, P, T, \sigma_1)$ of a system with an interstitial with diameter σ_1 is equal to

$$G(N+1, P, T, \sigma_1) = -k_B T \ln Q(N+1, P, T, \sigma_1) \quad (42)$$

Thus, the free energy difference between a system with a pointlike interstitial ($\sigma_1 = 0$) and a full-grown interstitial ($\sigma_1 = 1$) is

$$\begin{aligned} g^{\text{grow}} &= G(N+1, P, T, 1) - G(N+1, P, T, 0) \\ &= -kT \ln \frac{Q(N+1, P, T, 1)}{Q(N+1, P, T, 0)} \\ &= kT \ln \frac{P(0 | N+1, P, T)}{P(1 | N+1, P, T)} \end{aligned} \quad (43)$$

It is obvious that $P(\sigma | N+1, P, T, 1)$ can be very small for large values of σ_1 . To get an accurate histogram for $P(\sigma_1 | N+1, P, T, 1)$, we have to use a biased sampling scheme. We employ the method of umbrella-sampling/multicanonical sampling,^{5–7} where we associate a weight $\xi(\sigma)$ with σ , which we use while sampling over σ

$$P(\sigma | N+1, P, T, \{\xi\}) \propto P(\sigma | N+1, P, T) e^{\xi(\sigma)}$$

If we sample over this distribution, we get a histogram

$P(\{\sigma\}|N+1,P,T,\{\xi\})$, for which we can get the desired histogram $P(\{\sigma\}|N+1,P,T)$ by refolding the bias

$$P(\sigma|N+1,P,T) \propto P(\sigma|N+1,P,T,\{\xi\})e^{-\xi(\sigma)}$$

The weights $\xi(\sigma)$ are obtained by iteratively running the system and calculating (for the run $i + 1$, from the results of run i)

$$\xi_{i+1}(\sigma) = \xi_i(\sigma) - \ln P(\sigma|N,P,T,\{\xi_i(\sigma)\}) + C$$

where C is an arbitrary constant.⁷ This will make the histogram $P(\{\sigma\}|N+1,P,T,\{\xi\})$ converge to a flat distribution over the accessible range.

C. Interstitial-Type Discrimination. The fcc crystal has two types of possible places, or “holes”, in which interstitials can reside: one of octahedral shape and one of tetrahedral shape. There are four octahedral holes and eight tetrahedral holes in one fcc unit cell. To measure the relative concentrations of interstitials in these two types of holes, it turns out it is not possible to try to prepare the system in one hole and calculate g^{grow} because during the course of a simulation the interstitial makes many hops. These hops are caused by the interstitial taking the place of a lattice particle which then becomes the interstitial.

To measure the relative occupation probability of the different holes, we have to trace the interstitial. This is done by the following scheme: at the start of the simulation, every particle i except the original interstitial, is assigned to a lattice position \mathbf{R}_i . At fixed sampling intervals, the squared distance between the original interstitial and the nearest lattice sites ($\delta_{\text{int},i}^2 = (\mathbf{r}_{\text{int}} - \mathbf{R}_i)^2$) is compared with $\delta_i^2 = (\mathbf{r}_i - \mathbf{R}_i)^2$. If $\delta_{\text{int},i}^2 < \delta_i^2$, the interstitial and particle i exchange identity (i.e., the interstitial acquires a lattice position \mathbf{R}_i and particle i becomes the interstitial). Once we have identified the interstitial, it is straightforward to assign it to a tetrahedral or octahedral hole.

IV. Simulation Results

The free energy calculations were performed with $256 + 1$ particle systems ($4 \times 4 \times 4$ cubic fcc unit cells) at four different pressures. Different parts of the histogram $P(\{\sigma\}|N+1,P,T,\{\xi\})$ were calculated in parallel and subsequently combined. The calculation of the weights took about 20 iterations of 2×10^4 MC sweeps per CPU on 5 CPU's. Once the weights were known for one pressure, they could be used as starting points for the other pressures, accelerating the weight calculation considerably. Final calculations were done with approximately 20 iterations of 4×10^5 sweeps each (again on 5 CPU's). The final $P(\sigma|N,P,T)$ histograms for all four pressures are plotted in Figure 1.

For the calculation of μ at the different pressures, the results for the free energy of the perfect crystal² were used together with Hall's⁸ equation of state. The results are summarized in Figure 2 and Table 1. For one pressure ($P = 11.7$, the coexistence pressure), we calculated g_1 for a larger system ($N = 8 \times 8 \times 8 + 1 = 2048 + 1$) to check for finite-size effects: as can be seen from the results, these are negligible. Using the interstitial type discrimination algorithm described above, it was found that the (bigger) octahedral holes are far more likely to contain the interstitial than the tetrahedral holes (see Table 1).

V. Analytical Estimate of the Free Energy of Interstitials

As octahedral holes are the largest cavities in a fcc crystal, we limit our analysis to these. The number of octahedral holes

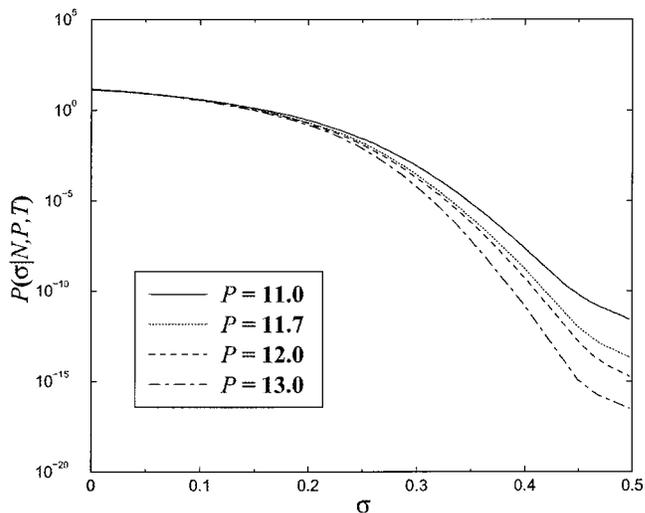


Figure 1. Normalized probability $P(\sigma|N,P,T)$ of finding an interstitial with radius $\sigma/2$ for hard-sphere crystals at (reduced) pressures 11, 11.7, 12, and 13.

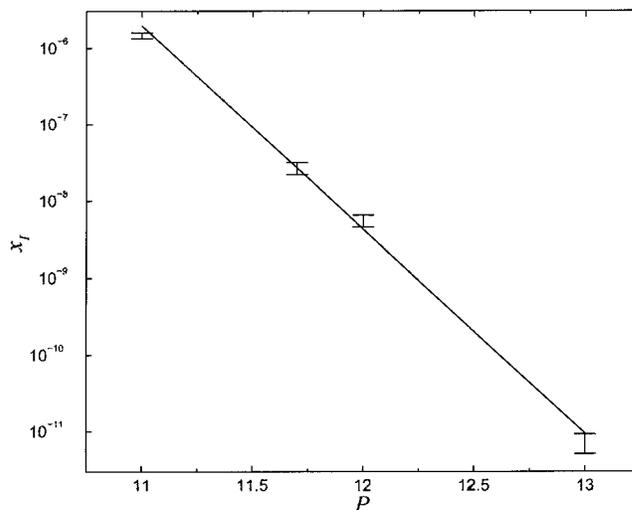


Figure 2. x_1 as a function of the reduced pressures P . The drawn line corresponds to a fit of the form $x_1 = \exp(-6.1P + 54)$.

in a fcc crystal is equal to the number of lattice sites, and the derivation of the expression for the concentration of interstitials is almost identical to the one for the vacancy concentration. Let us denote the change in free energy associated with the introduction of an interstitial at a specific octahedral site by f_1 . The concentration of interstitials is then

$$x_1 = \exp[-\beta(f_1 - \mu)] \quad (44)$$

In a static lattice, r_0 , the radius of such octahedral holes equals $(\sqrt{2}/2 - 0.5)a$, where a is the nearest-neighbor distance. For a hard-sphere crystal at melting, this radius equals $r_0 = 0.229 \sigma$. Clearly, to fit in an interstitial, the cavity has to be expanded. If we assume that the crystal is elastically isotropic (a fair approximation for a cubic crystal), then the work need to create a cavity of radius r equals³

$$W = 8\pi\mu r_0(r - r_0)^2 \quad (45)$$

where μ is the shear Lamé coefficient. How large should r be? Clearly, it should be at least 0.5σ ; otherwise, the interstitial would not fit into the lattice. But, in fact, it, should be larger, because the interstitial particle itself requires some free volume

TABLE 1: Simulation Results for the Properties of Interstitials in Hard-Sphere Crystals^a

P	N	η	μ	g_V/kT	x_I	h_{et}	C_{44}	$x_{I,analytical}$
11.0	256 + 1	0.536	16.5	29.9 (1)	1.5×10^{-6}	0.087(6)	41	1.1×10^{-6}
11.7	256 + 1	0.545	17.1	34.5 (2)	2.7×10^{-8}	0.032(2)	46	1.3×10^{-7}
11.7	2048 + 1	0.545	17.1	34.7 (2)	2.4×10^{-8}		46	1.3×10^{-7}
12.0	256 + 1	0.548	17.4	36.5 (2)	5.6×10^{-9}	0.079(9)	48	6.8×10^{-8}
13.0	256 + 1	0.559	18.4	44.1 (3)	7.2×10^{-12}	0.118(8)	57	3.2×10^{-9}

^a The values for the packing fraction η and the chemical potential μ were taken from refs 2 and 8. h_{et} is the fraction of interstitials found in tetrahedral holes. The values from the analytical estimate of section V are given as $x_{I,analytical}$, using C_{44} values interpolated from ref 4.

v_F . We should therefore minimize the sum of the free energy of a particle in a cavity of radius r and the elastic energy required to create such a cavity. Using $v_F = (4\pi/3)(r - \sigma/2)^3$, the expression for this free energy is

$$F(r) = -kT \ln[(4\pi/3)(r - \sigma/2)^3] + 8\pi\mu r_0(r - r_0)^2 \quad (46)$$

(In the above equation, we leave out the factor involving the de Broglie thermal wavelength, as it cancels anyway in the final result.) Differentiating eq 46 with respect to r yields the following equation for the equilibrium radius of the cavity:

$$-\frac{3kT(r - \sigma/2)^2}{(r - \sigma/2)^3} + 16\pi\mu r_0(r - r_0) = 0 \quad (47)$$

This yields the following equation for r :

$$r^2 - (\sigma/2 + r_0)r + \frac{\sigma r_0}{2} - \frac{3kT}{16\pi\mu r_0} = 0$$

and hence

$$r_I = \frac{\sigma/2 + r_0}{2} + \sqrt{\frac{(\sigma/2 + r_0)^2}{4} - \frac{\sigma r_0}{2} + \frac{3kT}{16\pi\mu r_0}} \quad (48)$$

Inserting eq 48 in eq 46, we obtain the expression for the total free energy of an interstitial at a specific lattice site

$$f_I = -kT \ln[(4\pi/3)(r_I - \sigma/2)^3] + 8\pi\mu r_0(r_I - r_0)^2 \quad (49)$$

If we use the parameters for a hard-sphere solid at melting ($\mu \approx C_{44} = 46^4$), we find that the predicted concentration of interstitials is approximately 1×10^{-7} . If the crudeness of the approximations involved in deriving this result is considered,

the agreement with the corresponding numerical estimate ($x_I \approx 3 \cdot 10^{-8}$) is gratifying. However, at higher densities, the agreement becomes worse, possibly because it is no longer justified to assume isotropic, linear, elastic behavior around an interstitial (see Table 1).

In summary, we have shown that the equilibrium concentration of interstitials in hard-sphere crystals is so low that most experiments will not be able to detect them. We find that interstitials are quite mobile. This implies that interstitials that are trapped during crystal growth should be able to diffuse rapidly to the crystal surface. This information is good news for experimentalists trying to grow photonic band gap materials. On the other hand, colloidal hard sphere crystals will have a high equilibrium concentration of vacancies. With the present accuracy of free-energy calculations, vacancies yield a detectable change in the free energies, but interstitials do not.

Acknowledgment. The work of the FOM Institute is part of the research program of FOM and was made possible through financial support by the Dutch Foundation for Scientific Research (NWO). D.F. gratefully acknowledges the fact that he first learned about computer simulation from the famous review in: Berne, B. J.; Harp, G. D. On the Calculation of Time Correlation Functions. *Adv. Chem. Phys.* **1970**, *17*, 63.

References and Notes

- (1) Bennett, C. H.; Alder, B. J. *J. Chem. Phys.* **1970**, *54*, 4796.
- (2) Polson, J. M.; Trizac, E.; Pronk, S.; Frenkel, D. *J. Chem. Phys.* **2000**, *112*, 5339.
- (3) Frenkel, J. *Kinetic Theory of Liquids*; Oxford University Press: New York, 1946.
- (4) Frenkel, D.; Ladd, A. J. C. *Phys. Rev. Lett.* **1987**, *59*, 1169.
- (5) Torrie, G. M.; Valleau, J. P. *J. Comp. Phys.* **1977**, *23*, 187.
- (6) Berg, B. A.; Neuhaus, T. *Phys. Rev. Lett.* **1991**, *68*, 9.
- (7) Smith, G. R.; Bruce, A. D. *Phys. Rev. E* **1996**, *53*, 6530.
- (8) Hall, K. R. *J. Chem. Phys.* **1970**, *57*, 2252.