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Optimum vacancy concentration in a crystal

Sunil P. Singh, Charanbir Kaur, and Shankar P. Das*
School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India

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The importance of the presence of a small fraction of vacancies in a crystal structure is demonstrated from considerations of thermodynamic stability. We include in the density functional theory the effects due to the distortion of the lattice structure surrounding the vacancy and show that the free energy is less when vacancies are present. Near freezing point, our theoretical model obtains the equilibrium vacancy fraction in the hard sphere crystal to be $\sim 10^{-5}$ and it decreases with increase of the density.

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I. INTRODUCTION

A characteristic property of the crystal state is imperfection in the lattice structure [1]. Among the several types of defects that occur in a crystal, we consider here the situation in which a small fraction of the lattice sites remain vacant. The presence of these point defects constitutes an intrinsic feature for the thermodynamic stability of the crystal. Density functional theory (DFT) [2–5] has been used to study the thermodynamics of the crystal state in a variational approach. Here the free energy of the system is treated as a functional of the density function. Beyond the freezing point, the inhomogeneous density function $n(\mathbf{r})$ for the crystalline state corresponds to the minimum value of the free energy for the system. A crucial input in these theories is the choice of the density function. $n(\mathbf{r})$ is often parametrized [6] as a summation over Gaussian profiles centered around different lattice points in the crystal. The inverse square of the width of the Gaussian profile, denoted by α [henceforth called the width parameter (WP)], represents the degree of inhomogeneity of the structure considered. Thus the liquid or the homogeneous density state corresponds to $\alpha \rightarrow 0$ while the inhomogeneous crystal state corresponds to a large α representing strongly peaked Gaussian density profiles. There have been several theoretical attempts [7–9] in the past to justify the small vacancy concentrations in the crystal close to freezing point. However, incorporating such a subtle effect in a theoretical model constructed from a proper statistical mechanical approach has remained a challenge. In the present paper we propose a model for an imperfect crystal in which the distortion created by a vacancy in the surrounding density profile is described through a modification of the inhomogeneous density function $n(\mathbf{r})$, defined in the classical density functional theory of simple liquids [2–5]. The modified density function is now used for the minimization of the free energy. The thermodynamic functions for the solid state with strongly inhomogeneous density profile are obtained using the modified weighted density functional approximation (MWDA) [10]. Here the inhomogeneous liquid is mapped into an effective liquid whose density is computed from the MWDA equations and the free energy is then obtained using standard formulas for the liquid state. The optimum value of the defect concentration obtained here is of $O(10^{-5})$ at freezing, which is close to the experimental and simulation results.

II. THE MODEL

The formulation of the density functional theory presented here involves two major steps, namely, (a) the proper parametrization of the density function describing the equilibrium crystalline state and (b) computation of the free energy as a functional of the density.

A. The density function

The first step in constructing the DFT model is the choice of a suitable inhomogeneous density function $n(\mathbf{r})$ for representing the crystal state with vacancies. The inhomogeneous density function $n(\mathbf{r})$ for an imperfect crystal is constructed so as to include the effect of vacancies on the surroundings as follows. The sites around each vacancy are labeled as *affected sites* (AS's) due to the neighboring void. Thus the total number of AS's is zN_D, assuming that the vacancies are few enough so that no AS is common to two or more vacancy sites. All other $N-zN_D$ occupied sites on the lattice are treated as *normal sites* (NS's). The density function $n(\mathbf{r})$ is obtained as a sum of the contributions from two types of Gaussian profiles with WP's α_D (AS's) and α (NS's),

$$n(\mathbf{r}) = \sum_{\mu=1}^{N-zN_D} \phi_\alpha(|\mathbf{r}-\mathbf{R}_\mu|) + \sum_{i=1}^{N_D}\sum_{\gamma=1}^{z} \phi_{\alpha_D}(|\mathbf{r}-\mathbf{R}^i_\gamma|), \qquad (1)$$

where $\phi_\alpha(r)=(\alpha/\pi)^{3/2}e^{-\alpha r^2}$. In Eq. (1) above, (a) $\mathbf{R}^i$ denotes the position of the ith vacancy; (b) $\mathbf{R}^i_\gamma$ denote the coordinates of the z AS's with $\gamma=1,\ldots,z$ around each ith vacancy; and (c) $\mathbf{R}_\mu$ denotes the position of the μth NS. For the vacant site, no Gaussian profile is attributed. Also, $\alpha \neq \alpha_D$, i.e., the density profiles centered around an AS are different from those around a NS. We assume here (in making a single choice for α_D) that this difference in mass localization occurs symmetrically around the vacancy, and only up to the first coordination shell. For a fcc crystal, the number of AS's around a vacancy is thus $z=12$. The numbers of AS's z_i^A, NS's z_i^N, and vacancies z_i^D in the different coordination shells around an AS in a fcc lattice are shown in Table I.

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*Electronic address: shankar@mail.jnu.ac.in

TABLE I. The number of AS's z_i^A, NS's z_i^N, and vacancies z_i^D in the different coordination shells around an AS in a fcc lattice. $z_i = z_i^A + z_i^N + z_i^D$ is the total number of lattice sites in the corresponding shell of the fcc structure.

Shell no.	z_i^A	z_i^N	z_i^D	z_i
1	4	7	1	12
2	2	4	0	6
3	4	20	0	24
4	1	11	0	12

B. The free energy functional

We consider a canonical ensemble of N particles occupying the N_{pc} lattice sites of a face centered cubic (fcc) crystal in a volume V. Here, $N_{pc}=N+N_D$, such that the number N_D of sites are unoccupied and represent vacancies in the lattice. The parameter $\mathcal{A}=N/N_{pc}$ denotes the fraction of occupied sites in the crystal. The free energy is expressed as a functional of the inhomogeneous density function $n(\mathbf{r})$. It consists of the ideal gas contribution F_{id} and the interaction part F_{int}, i.e., $F=F_{\text{id}}+F_{\text{int}}$. The particle density and vacancy density are, respectively, denoted by $n_0=N/V$ and $n_D=N_D/V$. The ideal gas part for a crystal lattice with any of the N sites occupied out of N_{pc} total sites is obtained as

$$\beta F_{\text{id}} = \ln\left(\frac{N!N_D!}{(N+N_D)!}\right) + \int d\mathbf{r}\, n(\mathbf{r})\{\ln[\Lambda^3 n(\mathbf{r})] - 1\} \quad (2)$$

where Λ is the thermal wavelength appearing due to the momentum variable integration in the partition function. It is assumed that the vacancies are uniformly distributed in the system, occurring only as monovacancies, and that all the possible arrangements with a given number of vacancies are equally probable [1]. The first term in Eq. (2) can be expressed in terms of the fraction $\mathcal{A}$ as $N_{pc}[\mathcal{A}\ln\mathcal{A}+(1-\mathcal{A})\ln(1-\mathcal{A})]$ by using Sterling's approximation. The second term on the right-hand side (RHS) of Eq. (2) is a contribution from the particles being treated as an ideal gas. The partition function of an ideal gas of N particles is $Z_N=[V/(\Lambda^3 N!)]^N$ and the free energy $-\beta F=\ln Z_N$ is obtained as $N\ln n - N$. The second term is a simple generalization of the ideal gas part of the free energy for a nonuniform density, i.e., $n\rightarrow n(x)$, and can be obtained in a statistical mechanical formalism using the cell approach [11]. In the limit of large α and α_D, i.e., for strongly localized density profiles in the crystal, the density can be approximated in terms of Gaussians centered around a single site. This reduces the ideal gas part of the free energy given in Eq. (2) to

$$\beta f_{\text{id}}[n] = \frac{n_{pc}}{n_0}[\mathcal{A}\ln\mathcal{A} + (1-\mathcal{A})\ln(1-\mathcal{A})] + \left[\frac{3}{2}\ln\left(\frac{\alpha}{\pi}\right) - \frac{5}{2}\right] + \frac{3}{2}z\frac{n_D}{n_0}\ln\left(\frac{\alpha_d}{\alpha}\right), \quad (3)$$

where f_{id} denotes F_{id}/N, the ideal free energy per particle, and z is the number of affected sites around a vacancy.

For computing the excess part of the free energy, we use the modified weighted density approximation [12] in the present calculation. In this approach the excess free energy depends upon the global average of the density rather than the local average density. This technique has been extensively used, especially for studying the first order phase transition in hard sphere systems. In this treatment, the excess part of the free energy functional of the inhomogeneous structure is approximated as the liquid state free energy of a homogeneous system with density $\hat{n}$ as $F_{\text{int}}=Nf_{\text{int}}(\hat{n})$, where f_{int} represents the excess free energy per particle of the homogeneous state. Here $\hat{n}$ is the average density of the solid normalized with weight function $w(r)$. $\hat{n}$ is specified by requiring that the second functional derivative of the MWDA excess free energy yields the correct direct correlation function $c(r)$ in the uniform density limit [12]. The weighted density $\hat{n}$ is obtained from the self-consistent solution of the integral equation for the equivalent liquid,

$$2f'_{\text{int}}(\hat{n})\hat{n} = -\frac{1}{\beta N}\int d\mathbf{r}_1 \int d\mathbf{r}_2 c(|\mathbf{r}_1-\mathbf{r}_2|;\hat{n})n(\mathbf{r}_1)n(\mathbf{r}_2) - n_0\hat{n}f''_{\text{int}}(\hat{n}), \quad (4)$$

where the prime on f_{int} denotes the derivative with respect to density. Equation (4) is solved iteratively to obtain $\hat{n}$. For a hard sphere system (of diameter σ) we choose the Percus-Yevick (PY) solution of $c(r)$ and the corresponding free energy function $f_{\text{int}}(\hat{\eta})$, where $\hat{\eta}=\pi\hat{n}\sigma^3/6$. For this purpose some simplification of the above equation in terms of the density function (1) is needed.

The nontrivial task in solving the integral equation (4) is the evaluation of the first term on the RHS involving the product of the density at two different points. Using the definition (1) for $n(\mathbf{r})$ this term reduces to the integral

$$\mathcal{I}(\hat{n},\alpha,\alpha_D) = -(\beta N)^{-1}[I_{NN}(\alpha,\alpha,\hat{n}) + I_{AN}(\alpha,\alpha_D,\hat{n}) + I_{AA}(\alpha_D,\alpha_D,\hat{n})], \quad (5)$$

where the integral $I_{NN}(\alpha,\alpha;\hat{n})$ represents the "interaction" or the product of the NS's in the two densities. Similarly, $I_{NA}(\alpha,\alpha_D;\hat{n})$ corresponds to the contribution involving the NS's and the AS's, while $I_{AA}(\alpha_D,\alpha_D,\hat{n})$ corresponds to that involving both the AS's. Through some trivial algebra these integrals are expressed in terms of the overlap integral

$$A_{\alpha_1,\alpha_2}(R) = \bar{\alpha}\int d\mathbf{r}_1 \int d\mathbf{r}_2 e^{-\alpha_1 r_1^2 - \alpha_2|\mathbf{r}_2-\mathbf{R}|^2} c(r_{12}) \quad (6)$$

where $\bar{\alpha}=(\alpha_1\alpha_2/\pi^2)^{3/2}$, $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$, and the R denotes the distance between the corresponding sites. We obtain

$$I_{NN}(\alpha,\alpha) = (N - z_T N_D)I_B + N_D\sum_{i=2}^{4} z_i I'_i, \quad (7)$$

where $z_T=\Sigma_{i=1}^4 z_i$. In writing Eq. (7) we are ignoring overlaps of the density profiles beyond the fourth shell around the origin. For the terms contributing to I_{NN} two kinds of possibilities occur as shown in the RHS of Eq. (7). The first term involving $I_B=\Sigma_R A_{\alpha,\alpha}(R)$ represents the contributions resulting from the product of two NS's, both of which are located

TABLE II. The number $\tilde{z}_{ji}^N$ of NS's in the ith cell around a NS that is located in the jth cell around the vacancy.

Shell no.	$\tilde{z}_{2i}^N$	$\tilde{z}_{3i}^N$	$\tilde{z}_{4i}^N$
1	8	10	11
2	5	5	6
3	20	21	20
4	12	10	11

in the bulk away from the vacancy. The origin of the second term involving I_i' is more subtle. The NS's close to the vacancy have AS's as well as NS's in their neighborhood. Let $\tilde{z}_{ij}^N$ denote the number of NS's in the jth shell around such a NS which itself is located at the ith shell from the vacancy. The contribution involving such NS's is given by $I_i'=\Sigma_{j=1}^{4}\tilde{z}_{ij}^N A_{\alpha,\alpha}(R_{ij})$. The coordination numbers z_i and the $\tilde{z}_{ij}^N$ for a fcc lattice are presented in Tables I and II, respectively. The distance of the nth shell from the origin is obtained in general as $R_n/a=\sqrt{n/2}$, for a fcc crystal lattice. The lattice constant is $a=(4/n_{pc})^{-1/3}$ where $n_{pc}=N_{pc}/V$. Similarly we obtain for the other two integrals in Eq. (5), $I^{AN}(\alpha,\alpha_D;\hat{n})=2\Sigma_R A_{\alpha,\alpha_D}(R)$ and $I^{AA}(\alpha_D,\alpha_D;\hat{n})=\Sigma_R A_{\alpha_D,\alpha_D}(R)$. Furthermore, the α values corresponding to crystals are large enough so that in the various integrals presented above, the contribution from sites beyond the second shell is negligible. The density of the equivalent liquid, i.e., $\hat{n}$, is obtained by iterating Eq. (4) for different values of α, α_D, and n_D. The integral equation for $\hat{n}$ is solved iteratively and the interaction part of the free energy is then obtained using the PY expression.

III. RESULTS

With the above formulation, we compute the total free energy per particle of the imperfect crystal $f=f_{\text{int}}(\hat{n})+f_{\text{id}}[n]$ corresponding to a given average number density n_0 of the particles. f_{id} denotes F_{id}/N, the ideal gas part of the free energy, and f_{int} is obtained from a solution of Eq. (4). In the usual DFT formulation without any vacancy the minimization is with respect to the single parameter α. In the present case the free energy is minimized with respect to all the parameters n_D, α_D, and α in the density function. In Fig. 1, the contour plot of the free energy surface corresponding to particle density $n_0^*=1.0$, is shown in the n_D-α_D plane. The corresponding α (the WP for the NS's), i.e., is equal to its value at the free energy minimum. The different closed contours enclose the minimum free energy point. From the optimum values corresponding to the minimum we find that $\alpha_D<\alpha$ in general, conforming with the expectation that the mass localization is less near the vacancy. The inset shows the minimum of $\Delta f_\alpha=f(\alpha)-f_{\text{min}}$ with respect to α while the α_D and n_D are fixed at their optimum values corresponding to the free energy minimum.

The often cited illustration for justifying the presence of vacancies in a crystal involves a simple model for the imperfect crystal in which the free energy is written as N_D times a vacancy formation free energy ϵ_v (say) plus the configurational entropy contribution. Using Stirling's approximation, the minimization of the free energy of the crystal with respect to the number of vacancies gives the equilibrium vacancy concentration $N_D/N=\exp(-\beta\epsilon_v)$ [1]. Thus with this model the value of ϵ_v is required to be able to obtain vacancy concentration. From this point of view, our model gives a first principle estimation (in terms of the basic interaction potential between the particles) of the vacancy concentration. To illustrate this, we compute the quantity $\Delta f_D\equiv\Delta F_{\text{int}}/N_D$, where ΔF_{int} is the difference between the interaction part of the free energy of the perfect crystal and the one with defects. For the perfect crystal $n(\mathbf{r})$ is parametrized in terms of only the single Gaussian profile with width α and $n_D=0$. The free energy $F(\alpha)$ is obtained by minimization with respect to the single parameter α. In order to obtain the energy cost in creating a vacancy in this perfect structure we compute at the same value of α the free energy for the imperfect crystal $\bar{F}(n_D,\alpha)$ minimized with respect to n_D. The difference in the per vacancy free energy, i.e., $\Delta f_D\equiv\Delta F/N_D$, is shown in Fig. 2 for different values of n_0. We also show here for comparison the above mentioned result expected from the simple lattice model, i.e., $-\ln(N_D/N)$. It should, however, be noted that our model does include the effect of the vacancies on the surrounding, which goes beyond the simple lattice model of independent vacancies. At higher densities the system becomes more compact and it requires more energy to take out any particle from interior site to the surface. Thus the defect density n_D decrease with the increase of n_0 as is shown in Fig. 3. The free energy of the solid state is compared with that of the corresponding liquid state. The excess free energy of liquid state is computed from the Carnahan-Starling equation of state. This comparison is shown in the inset of Fig. 3 indicating a freezing at $n_0^*=0.968$ beyond which the solid state is thermodynamically more stable [12].

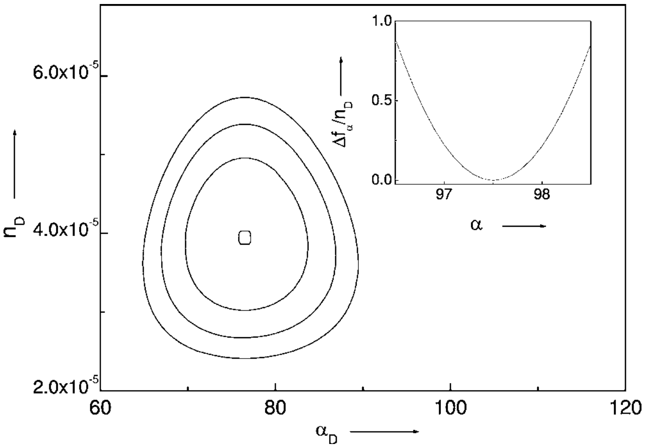

FIG. 1. Constant free energy contours at $n_0\sigma^3=1.0$ on the n_D (in units of σ^3) and α_D plane with fixed $\alpha=97.50$ (in units of σ^2) corresponding to the minimum. Inset shows variation of $\Delta f_\alpha/n_D$ (see text) vs α at $n_D=3.95\times10^{-5}$ and $\alpha_D=76.46$ corresponding to the minimum. Δf_α is expressed in units of β^{-1}.

It is straightforward to extend our approach to a binary system. Here a larger set of WP's (α) is needed to describe the two inhomogeneous density functions. In the case of ordered structures, the sites occupied by each component form

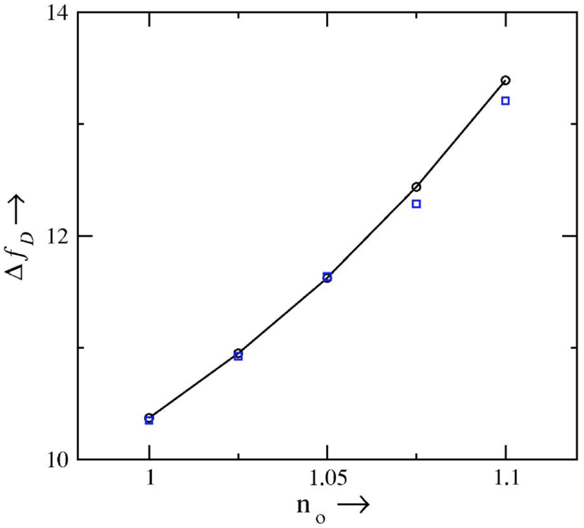

FIG. 2. (Color online) $\beta\Delta f_D$ (see text) vs n_0 (in units of σ^3) and the corresponding estimate $-\ln(N_D/N)$ (see text) for defect interaction energy from simple lattice model shown as squares. Δf_D is expressed in units of β^{-1}.

a sublattice and hence the $n_s(\mathbf{r})$ has to be defined accordingly. For simplicity we consider here a disordered fcc structure, in which a given site is assumed to be occupied by atoms of both components with probabilities equal to the corresponding relative concentrations. The density profile including the vacancy is defined as a generalization of Eq. (1). Following Ref. [10] we use the definition $n_s(\mathbf{r})=x_s n(\mathbf{r})$, where n_s is the density for the species s and $n=n_1+n_2$. The self-consistent equations for the weighted densities for the individual components of the binary liquid are obtained following the scheme used for the simpler case [10] without defects. The expressions for the uniform liquid state excess free energy and the direct correlation function for the binary system are obtained from analytic solution [13] of the Percus-Yevick integral equation for hard sphere mixtures. In Fig. 4 we have plotted the packing fraction $\eta=(\pi/6)(n_1\sigma_1^3+n_2\sigma_2^3)$ of a binary crystal with the corresponding defect density. The qualitative nature of the dependence of n_D on the packing fraction is similar to that of a one-component system. The inset of this figure shows variation of n_D with the diameter ratio κ of the two species at fixed value of the concentration x and density n_0. As κ increases, the packing fraction increases because smaller particles are replaced by larger particles. Hence as in the one-component case the defect density decreases with increase in the packing fraction. For $\kappa \rightarrow 1$ the one-component result is recovered and is shown by the arrow in Fig. 4.

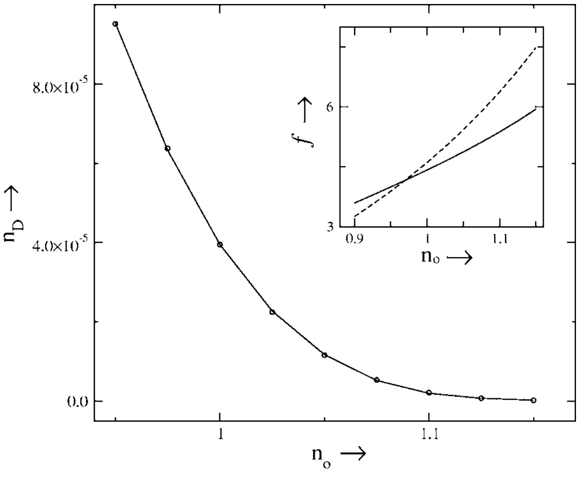

FIG. 3. Variation of defect concentration n_D with respect to n_0 (both in units of σ^3). Inset shows the variation of free energy of crystal (solid line) and liquid (dashed line) with density. Free energy is expressed in units of β^{-1}.

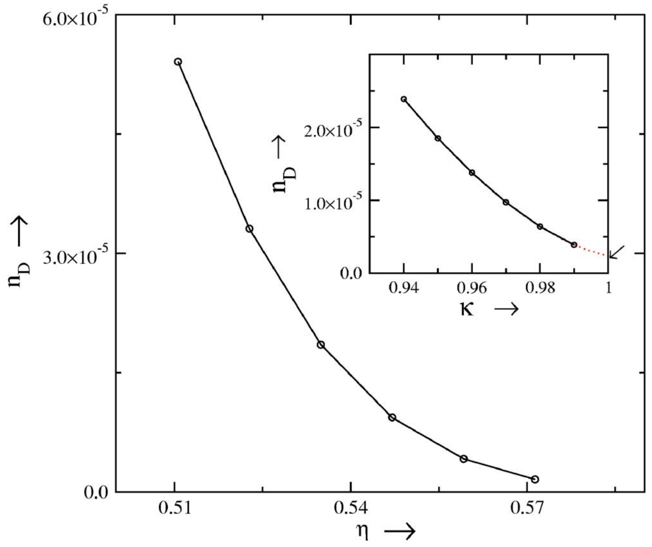

FIG. 4. (Color online) Variation of n_D (in units of σ_2^3) in binary system with n_0 (in units of σ_2^3) at fixed concentration $x=0.5$ and fixed value of diameter ratio $\kappa=0.95$. Inset shows variation n_D with κ at fixed density $n_0=1.1$ and relative concentration $x=0.5$. At this packing fraction, the value of n_D in the one-component limit is indicated with an arrow.

IV. DISCUSSION

The density functional approach studied here considers whether the equilibrium state of a many-particle system will be the disordered liquid state or whether the system will prefer an ordered crystalline structure with inhomogeneous density distribution. The criterion for determining the preferred thermodynamic state is the minimization of the free energy, treated as a functional of the density function. The only input in the calculation of the free energy is the static (equilibrium) structure factor of the liquid. Thus using the basic interaction potential between the particles (which determines the corresponding input static structure factor for the liquid state) as the only starting point and using the thermodynamic extremum principle we are able to justify the crystalline state with the estimate of the defect concentration here. No *a priori* information about the solid state is needed. The present work is a suitable formulation of the DFT to include vacancies in the description of the crystal state. In earlier attempts at this problem using DFT, the modification of the density function is included in an averaged manner [7,8] or by simply taking the density profiles to be absent for the vacant sites [9]. More recent work treated it as a limiting case of an ideal crystal [8]. The value of the vacancy concentration was either found to be too high ($\sim 10^{-1}$ [7]) or found to be extremely low ($\sim 10^{-12}$ [9]) for the hard spheres. The interaction of the defect with its neighbors is missing in those works. If the number of AS's is zero, i.e., the crystal has only the NS's and the voids, then the present model is similar to that of Ref. [9]. Using a low-order perturbative expansion for the solid state free energy [2] around that of the liquid state, the defect concentration obtained is much less [9]. The imperfect crystal considered here is characterized by monovacancies only and no other defects or dislocations [14] are included in this treatment. The theory presented here is applied close to freezing. The higher-density states can be explored in our model by taking a larger number of affected shells around the vacant sites, and possibly a better approximation for the $c(r)$.

The vacancy concentration in solids has also been widely investigated through experiments and simulations. Losee and Simmons have calculated the vacancy concentration in krypton near the triple point by measuring the relative difference in the bulk volume and the volume measured in x-ray scattering experiments. This is equivalent to measuring the change in the linear dimension and lattice parameter of the specimen. The vacancy concentration thus obtained is of the order of the 10^{-3} [15]. Using the same technique Schwalbe has measured the defect concentration in argon solid at higher temperatures to be not more than 2.5×10^{-4} [16]. Vacancy formation in rare gas solids has also been studied using Monte Carlo methods. The relative concentration is estimated by calculating the change in the Helmholtz free energy due to reversibly adding a particle to a single vacancy crystal. In this way the vacancy concentrations obtained [17] near the triple point are $\sim 2.1\times 10^{-4}$ for argon and $\sim 1.9\times 10^{-4}$ for krypton. Subsequent computer simulations of the hard sphere crystal obtain a defect concentration of order of 10^{-5} [18–20]. Reiss and Schaaf [21] also found vacancies in the hard sphere crystal of the same order.

In our model, the relative vacancy concentration is determined by the interaction potential which determines the direct correlation function $c(r)$ used as an input here. The noble gas solids referred to above have a similar hard core potential as is considered in our theoretical model and hence the relative defect concentrations N_D/N for the two systems should be the same. However, as noted above for krypton and argon the defect concentrations at the triple point were found to be different. The difference in the observed defect concentrations mentioned above for the two systems was also found in subsequent simulation studies [17] as well. This arises from the different values of the excess entropy used in the corresponding calculation.

The present calculation can be straightforwardly extended to other crystal structures by constructing the corresponding description similar to that given in Tables I and II. However, the extension to ionic systems is more subtle. The density functional theories of freezing including the MWDA are in general known to work well for cases where there is appreciable volume change on freezing [22]. As the interaction becomes more slowly varying, this change decreases, and for Coulombic interaction there would be effectively no volume change [23]. The theoretical formulation for such systems will require extending the DFT to include the attractive part of the interaction. The appeal of the model presented here lies in producing a reasonably good estimate of the void concentration from simple calculations using an intuitive picture of the physical problem. This is an alternative to a direct but much more computer intensive method involving a full quantum-chemical calculation to estimate the void concentration [24]. We obtain an order of n_D that is closer to simulation and experimental results than was obtained in earlier models using a similar DFT approach.

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