Thermal vacancies in close-packing solids

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Abstract – We derive an approximate expression for the equilibrium concentration of thermal monovacancies in solids which allows for a transparent interpretation of the vacancy volume and the energetic/entropic part in the corresponding Gibbs energy of vacancy formation $\Delta G_v$. For the close-packing crystals of the hard-sphere and Lennard-Jones model systems, very good agreement with simulation data is found. Application to metals through the embedded-atom method (EAM) reveals a strong sensitivity of the variation of $\Delta G_v$ with temperature to details of the EAM potential. Our result allows for an approximate, but direct measurement of crystal free energies and vacancy concentration in colloidal model systems using laser tweezers.

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Introduction. – Point defects, in particular vacancies, are the simplest deviation from an ideal crystal with perfect translational symmetry. At finite temperature, the thermal motion of the atoms in a crystal necessarily creates vacancies and causes a finite equilibrium concentration $n_{v,eq}$ of these. Thus, $n_{v,eq}$ is a very basic property of a crystalline material (with significance for other properties, most notably self-diffusion), nevertheless the magnitude and temperature dependence of $n_{v,eq}$ have been debated for nearly a century [1] without reaching a clear consensus. It is customary to express the equilibrium vacancy concentration as $n_{v,eq} = \exp(-\beta \Delta G_v)$ with $\Delta G_v$ being the Gibbs energy of vacancy formation and $\beta = 1/(k_B T)$ is the inverse temperature. In the materials science community, $\Delta G_v$ is usually further analyzed in terms of its entropic and enthalpic part where the entropic part is the more difficult one: here, the effects of lattice vibrations distorted by vacancies and anharmonicity enter. For metals, even approximate calculations of the entropic part using quantum density functional theory are a case for supercomputers and beset with uncertainties [2,3]. On the other hand, coming from classical statistical physics one would assume that the particles forming the crystal interact with classical potentials. Then the problem of vacancies and other point defects can be tackled using methods from statistical mechanics. Quantitative results have been obtained mainly by Monte Carlo simulations, and here with a focus on hard spheres (HS) [4–6]. A deeper understanding of these results is nevertheless missing. The equally important Lennard-Jones (LJ) model system has received less attention from the simulation side [7].

In this paper, we approach the problem from the theoretical side using an expansion of the crystal partition function developed by Stillinger and coworkers [8,9] (which falls into the realm of cell cluster theories). The expansion parameter is the number $n$ of particles which are free to move in an otherwise frozen matrix of particles at their ideal lattice positions. For the lowest-order term in this series ($n = 1$) we find a simple formula for $\Delta G_v$ in terms of the equation of state and some three-dimensional configuration integrals which are easy to calculate (see eq. (8) below). The agreement with simulation data in case of the two model systems HS and LJ is very good and provides us with an interpretation on the different origin of a finite vacancy concentration in solids with purely repulsive interactions between atoms (such as HS) and in solids with attractive interactions (such as LJ). We proceed by examining Ni as an example for a metal with a likewise face-centered cubic (fcc) crystal structure using the method of embedded-atom potentials (EAM). It turns out that EAM potentials in the physical spirit close to the original work [10] give a temperature behavior of the vacancy concentration close to the LJ solid and in line with the rare simulation results, whereas potentials that are used as mere fitting devices show a very different behavior.

Theory. – Here we present a compact derivation of our central result, eq. (8) below, to make clear the in-
volved approximation and physical terms. Consider the canonical partition function \( Q = Q(N,V,T) \) for \( N \) atoms interacting with a classical potential \( \phi(1,\ldots,N) \) of many-body nature, depending on the individual atom positions \( r_1,\ldots,r_N \):

\[
Q = \frac{1}{N!\Lambda^N} \int \prod_i \, dr_i \cdots \int \prod_i \, dr_N \exp(-\beta \phi(1,\ldots,N)). \tag{1}
\]

Here, \( \Lambda \) is the thermal de Broglie wavelength. We consider a face-centered cubic (fcc) reference lattice with \( M \geq N \) lattice sites at positions \( s_k \), \( k = 1,\ldots,M \) spanning the volume \( V \). To decompose the full configuration space \( \Omega \), we denote by \( p(i) \) a mapping of a particle indexed by \( i = 1,\ldots,N \) to the lattice site \( p(i) \) such that \( p(i) \neq p(j) \) for \( i \neq j \). For any set of particle coordinates \( R = \{r_1,\ldots,r_N\} \) we may minimize the quantity \( \sum_{i=1}^N (r_i - s_{p(i)})^2 \) with respect to the possible mappings \( p \) and call the minimal \( p \) an association of \( R \) with \( p \). For a particular \( p \), the domain of all \( R \) associated with it forms \( \Omega_p \) and thus \( \Omega = \sum_p \Omega_p \). Obviously, there are \( N! \) mappings \( p \) onto the same set of lattice sites, differing only in the order of lattice sites, each of these giving the same contribution to \( Q \). Let \( l \) number only the mappings onto distinct lattice sites, \( p \equiv p_l \). Then,

\[
Q = \frac{1}{\Lambda^N} \sum_l \int \cdots \int_{\Omega_{p_l}} \prod_i \, dr_i \cdots dr_N \exp(-\beta \phi(1,\ldots,N)). \tag{2}
\]

Following ref. [8], one may write \( Q \) in terms of configuration integrals \( Z^i_{1}, Z^i_{1j}, \ldots \) which describe the correlated motion of one, two, \ldots particles in a background matrix of \( N-1, N-2, \ldots \) particles fixed at their associated lattice sites. These configuration integrals are defined as

\[
Z^i_{1} = \int \prod_i \, dr_i \exp(-\beta \phi(1,\ldots,N)) \quad \text{with} \quad r_j = s_j \quad (j \neq i),
\]

\[
Z^i_{1j} = \int \prod_i \, dr_i \int \prod_j \, dr_j \exp(-\beta \phi(1,\ldots,N)) \quad \text{with} \quad r_k = s_k \quad (k \neq i, j),
\]

\[
\vdots \tag{3}
\]

The integration domains fulfill \( \omega^j_{ij}, \omega^j_{ij}, \ldots \in \Omega_{p_l} \), and they depend on the indices of the free particles \( i, j \) and also on the mapping \( p_l \) determining at which lattice sites the other particles are fixed. The partition function is now expressed as the product

\[
Q = \frac{1}{\Lambda^N} \sum_l \prod_i Z^i_{1} \prod_{i<j} Z^i_{1j} Z^j_{1i} \cdots \tag{4}
\]

In the full product formula, the configuration integrals \( Z^i_{1j} \) all cancel save for the \( N \)-particle configuration integral \( Z^i_{1j} \) which makes the last equation an identity [8]. The individual factors contain the effect of the (correlated) motion of one, two, \ldots particles in the crystal.

For a practical application to crystals of particles with a steeply repulsive core and considering only configuration integrals for a few free particles, the integration domain \( \omega^i_{ij} \) is the volume of the Wigner-Seitz cell of particle \( i \) around its associated lattice site (see fig. 1). As an example, if particle \( i \) is next to a vacant site the integration domain \( \omega^i_{ij} \) should not extend to the Wigner-Seitz cell associated with the vacant site, since particle coordinates inside this vacancy Wigner-Seitz cell would change the association of the particle to an association with the vacancy Wigner-Seitz cell. For the integration domains including more than one particle we have \( \omega^i_{ij} =\omega^j_{ij} \otimes \omega^j_{ij} \cdots \). Although contributions of two free particles occupying the same Wigner-Seitz cell are thus neglected, these contributions are exponentially small due to a strong repulsive potential from their fixed neighbors.

We assume that the vacancy concentration is small, \( n_v = 1 - N/M \ll 1 \), such that vacancies do not interact with each other. For the moment, we truncate the product (4) after the first term. The sum over \( l \) (distribution of \( N \) particles onto \( M \) sites) results in a factor \( (M/N)^N \) and we find

\[
Q \approx \frac{1}{\Lambda^N} \left( \frac{M}{N} \right)^N (Z_v)^{N-(M-N)} \sum_{g_i} g_i \prod_{i} (Z_{sv,i})^{g_i(M-N)}. \tag{5}
\]

Here, \( g_i \) denotes the number of atoms in shell \( i \) around a fixed lattice site (e.g., \( g_1 = 12, g_2 = 6, \ldots \) in the isotropic HS/LJ systems with fcc structure). We assume a finite range of the interaction potential (up to shell \( n_m \)) and therefore we have for the \( M - N \) vacancies a number of \( (M-N)g_i \) of atoms which feel the vacancy at the shell \( i \) apart. The single-particle configuration integral for these

Fig. 1: (Color online) Schematic lattice in two dimensions with one vacancy. We assume a cut-off Lennard-Jones interaction potential. Shown are examples for the single-particle integral domains \( \omega^i \) around lattice sites \( s_i \), given by the hexagonal Wigner-Seitz cell surrounding the site \( s_i \). The grey scale (exaggerated) indicates the local potential \( -\beta \Phi \) due to all the other, fixed particles. The integral over \( \exp(-\beta \Phi) \) within the Wigner-Seitz cell gives the single-particle integral \( Z_{sv,1} \) for the cell next to the vacancy, \( Z_{sv,2} \) for the cell in second-shell distance to the vacancy and \( Z_s \) for the cell in the upper right corner). Different colors mark different shells around the vacant position up to fifth-shell neighborhood.
particles is given by $Z_{sv,i}$. All remaining particles are not influenced by the vacancies and contribute to the single-particle integral $Z_s$. See also fig. 1 for a visualization.

In the thermodynamic limit ($N, M \to \infty$, while keeping constant the particle number density $\rho = N/N$), one can use Stirling’s approximation, $\ln N! = N \ln N - N$, to write eq. (5) in the following form:

$$\frac{\beta F}{N} = -\frac{\ln Q}{N} = -\frac{Z_s}{\Lambda^3} - \frac{n_v}{1 - n_v} \sum_k g_k \ln \left( \frac{Z_{sv,i}}{Z_s} \right) + \frac{n_v}{1 - n_v} \ln n_v + \ln(1 - n_v),$$

where $F$ is the free energy. The equilibrium vacancy concentration is found by minimizing the free energy per particle with respect to $n_v$ under the assumption $n_v \ll 1$. This amounts to keeping only terms in the free-energy derivative which are independent or logarithmic in $n_v$.

$$n_{v, eq} \approx \exp \left( \frac{Z'_s}{Z_s} \rho \right) \prod_i \left( \frac{Z_{sv,i}}{Z_s} \right)^{g_i}_s.$$  

A prime denotes a derivative with respect to $\rho$. Here we have used ($\rho_M$ is the density of lattice sites) $\partial Z_s/\partial \rho_M = (\partial Z_s/\partial \rho_M)(\partial \rho_M/\partial \rho) = (\partial Z_s/\partial \rho_M)/(\rho/(1 - n_v)^2) \approx Z'_s \rho$.

Furthermore, $\beta F \approx -N \ln Z_s$ for small $n_{v, eq}$. Using the thermodynamic relation for the pressure $p = (F/N)/\rho^2$ and the definition $n_{v, eq} = \exp(-\beta \Delta G_v)$ we find the following central result of our work for the Gibbs energy for vacancy formation:

$$\Delta G_v = \frac{p}{\rho} - \beta^{-1} \sum_i g_i \ln \left( \frac{Z_{sv,i}}{Z_s} \right).$$  

The first term is just given by the crystal equation of state and ensures that $n_{v, eq}$ goes rapidly to zero for crystals under high pressure. Using the thermodynamic decomposition $\Delta G_v = p v_v + E_v - T \Delta S_v$, one sees that the “vacancy volume” $v_v$ is just given by $1/\rho$. $E_v$ and $-T \Delta S_v$ are the energetic and entropic part and are contained in the second term in eq. (8) (which we call the vacancy integral term in the following).

Although the splitting of $\Delta G_v$ into the equation of state and the vacancy integral term was derived here in the leading truncation of the Stillinger series, the results stays valid in higher truncations (with further corrections to the vacancy integral term) as long as the vacancies can be assumed to be non-interacting.

**Numerical results.** For HS, the free energy per particle in the approximation with one free particle is within 1% of available simulation results. The second term (two free particles) accounts for the remaining discrepancy [11]. This underlines the rapid convergence of the Stillinger series and assures us that the first term already contains the basic physics. Due to the short range of the HS potential, only the particles in the first shell around the vacancy contribute to the vacancy integral term ($n_m = 1$ in eq. (8)).

The corresponding results for $n_{v, eq}$ are shown in fig. 2 and show very good agreement with the simulation data above the liquid-solid coexistence density. The main contribution to $\Delta G_v$ stems from the equation-of-state term $p/\rho \geq 10 k_B T$, whereas the vacancy integral term contributes about $-1 k_B T$.

In the case of LJ, we have used a truncated and shifted version of potential, $U_{LJ}(r) = U_{LJ}(r) - U_{LJ}(r_c)$ for $r < r_c$ and 0 otherwise, with $U_{LJ} = 4 \epsilon \sigma^2[(\sigma/r)^{12} - (\sigma/r)^6]$ and $r_c$ is the cut-off range. The approximative crystal equation of state compares well with the parametrization of van der Hoef [12,13] below and around the triple temperature (see fig. 3(a)). For higher temperatures deviations are visible, but at the same time also the liquid-solid coexistence density shifts upwards such that the stable crystal is still well described. In fig. 3(b), we show $\Delta G_v$ along the sublimation line ($p = 0$, solid-gas coexistence) up to the triple point where it forks into the liquid-solid coexistence line and the line of zero pressure. Comparison is only possible to the sublimation line simulation data of ref. [7] where a vacancy has been placed in the middle of a rather small cubic simulation box of side length $3 a$ where $a$ is the side length of the fcc cubic unit cell (i.e., the simulation box contains 107 particles). This means that the cut-off $n_m$ on the maximal number of shells in eq. (8) has to be chosen such that the maximum shell radius $\approx 1.5 a$ (i.e., vacancies in the periodic images do not interact). This is the case for $n_m = 4$ with maximum shell radius $\sqrt{2} a$. Our data are consistent with the simulation data and furthermore show that the often-made assumption $\Delta S_v$ being $T$-independent holds only approximately. We also see that near the triple point $\Delta G_v$ is of the order of $10 k_B T$ as it was for HS near coexistence. The origin, however, is completely different: the pressure term in eq. (8) does not contribute but the vacancy integral term gives rise to “missing cohesive free energy". For $T = 0$, $\Delta G_v$ becomes the vacancy formation energy $E_v$ which for a system interacting with pair potentials is near the modulus of the cohesive energy $|E_{coh}|$ (it would be exactly equal if the atoms remain fixed at their
potential range through the maximum shell index (plane. We use the same long-range cut-off as in ref. [12] known. (c) Equilibrium vacancy concentration in the \((T,\rho)\) circles are simulation data from ref. [7], error bars are un-

ament through a sum of single-particle displacements in the ideal lattice sites around the vacancy). It is interesting to

ote that the effect of the collective particle displacements (to make \(E_v\) minimal) is contained in the vacancy integral term through a sum of single-particle displacements in the potential field of otherwise fixed atoms. Finally, fig. 3(c) shows \(n_{v,eq}\) for stable crystals in the \((T,\rho)\)-plane which is quickly calculated using eq. (8). At the triple point \(n_{v,eq} \approx 10^{-4}\) is maximal.

Next we turn to metals. In this case, the embedded-atom method (EAM) is a semi-empirical, classical many-atom potential for computing the total potential energy [14] and it can be used straightforwardly in eq. (8). With regard to vacancies, many-body effects are necessary to include in the description of metals since for zero temperature \(E_v \approx 0.3|E_{coh}|\) for a number of metals (and not \(E_v \approx |E_{coh}|\) as for LJ) [14]. For the case of Ni, we examined three versions of the EAM potential: F85 from ref. [15], FBD86 from ref. [16], and M99 from ref. [17]. All of the potentials have been optimized with respect to a number of solid properties at \(T = 0\). F85 and FBD86 contain a separation into two parts, a repul-

sive pair potential due to host nuclei which mimics the repulsion between charge-screened nuclei, and an embed-

ding potential arising from the background electron den-

sity. For M99 however, such a physical interpretation is not intended, and a compound set of experimental and \(ab\ initio\) simulation results are used for optimizing the po-

tential parameters. In fig. 4(a) we show the variation of the Ni density with temperature at zero pressure (subli-

mation line). Experimental data are not known but the agreement with simulation data is very good for F85 and M99 [18]. In fig. 4(b) we compare \(\Delta G_v\) for the three poten-

tials. As a consistency check, at \(T = 0\) we recover the values for \(\Delta G_v = E_v\) calculated previously in [10,16,17] which confirms that \(E_v\) is accurately calculated by sum-

ning over single-particle displacements. However, the temperature dependence of \(\Delta G_v\) is completely different for the two types of potentials (F85/FBD86 vs. M99).

\(\Delta G_v(T)\) is monotonously decreasing with increasing \(T\) for F85/FBD86 with a slight increase of the slope for higher \(T\). This is similar to \(\Delta G_v(T)\) for LJ (see fig. 3(b)) and also consistent with EAM potential molecular sim-

ulation data for copper (also with an fcc lattice structure) [19]. On the other hand, \(\Delta G_v(T)\) for M99 has a local maximum for \(T \approx 500\) K. Furthermore, the vari-

ation of \(\Delta G_v\) with the maximum shell index \(n_m\) at a fixed temperature is also non-monotonic, in contrast to F85/FBD86 and the Lennard-Jones solid. These results reflect an essential difference in the parametrization es-

pecially of the pair part of the EAM potential. In F85 and FBD86, this pair part is purely repulsive and short-

ranged (up to the first [F85] and third shell [FBD86]). M99 assigns a good part of the attractive energy to the pair part and the pair part is significantly longer-ranged (cut off at the fifth shell) and contains oscillations. These oscillations account for both the non-monotonicity of \(\Delta G_v\) in temperature and \(n_m\). Thus, finite-temperature behav-

ior in observables is susceptible to the parametrizations of EAM potentials and should be considered from the beginning.
result by Stillinger et al. [8], specific for hard disks in the close-packed limit, the connection to the equation of state and missing cohesive free energy has not been made. For the more difficult case of metals we have shown that the temperature dependence of $\Delta G_v$ is significantly affected by details of the EAM potential parametrization. Therefore, we propose that $\Delta G_v(T)$ should be included in further EAM parametrizations. As a reference, $\Delta G_v(T)$ should be calculated in quantum density functional theory (qDFT) using eq. (8) with qDFT values for the potentials $\phi(1, \ldots, N)$ needed in the single-particle integrals $Z_v$ and $Z_{sv, i}$. Furthermore, the partition function, free energy and equilibrium vacancy concentration in this truncation could be measured directly in experiments with colloidal crystals if fixing of all but one particle on a lattice can be realized. This fixing appears to be possible employing laser tweezers [21,22]. The trajectory of the remaining free particle can be recorded and binned using video microscopy, thus directly accessing the integrands of the single-particle integrals $Z_v$ and $Z_{sv, i}$ [23].

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