

Equilibrium Concentration of Point Defects in Crystalline ^4He at 0 K

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Received September 24, 1993; final April 22, 1994

We calculate the concentrations of vacancies and interstitials in the ground state of a Bose solid which models ^4He . Because ground-state boson wave functions are nodeless, their probability densities correspond to classical Boltzmann factors, and properties of Bose solids, such as the concentration of vacancies and interstitials, can be calculated using classical statistical mechanics. We model the ground-state wave function of ^4He with the product (Jastrow) form that corresponds to a classical $1/r^b$ pair potential, and use a quasiharmonic approximation to calculate the concentrations of vacancies and interstitials in an fcc lattice with this potential. We find that the fractional concentration of vacancies at the melting point is 1.60×10^{-5} for $1/r^9$ and 6.36×10^{-6} for $1/r^6$, while the interstitial fractional concentrations are 1.32×10^{-3} and 1.08×10^{-5} , respectively; the defect concentrations decrease by 7–16 orders of magnitude when the crystal density increases by 50%. At the same density, and with the same $1/r^9$ potential, the concentration of vacancies in an hcp lattice is essentially the same as in an fcc lattice, but the interstitial concentration is much lower, apparently because the fcc lattice contains a more favorable split-interstitial site than does hcp. Therefore, our fcc vacancy results should be directly relevant for (hcp) ^4He , providing what we think is a lower bound on the vacancy concentration, while the interstitial concentration in ^4He is probably much lower than our results.

KEY WORDS: Vacancies; interstitials; solid helium.

1. INTRODUCTION

Helium has long been one of the most intriguing elements to physical scientists, for reasons ranging from its inert chemical nature to its abundance in stars and rarity on earth. For condensed-matter physicists, helium stands out as the one element that remains a liquid when cooled at low pressure to

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0 K, due to its small mass and weak interaction potential. These combine to give helium enough zero-point quantum motion to prevent solidification; the large quantum effects have many other consequences for the liquid, including superfluidity and its associated striking phenomena.

Quantum effects are also responsible for the possibility that an equilibrium helium crystal can contain point defects at 0 K, which cannot occur in a classical solid. Point defects, particularly vacancies, have been studied in solid ^4He for many years. Much of the work has been motivated by the speculation that while a perfect crystal cannot Bose-condense,^(1,2) the presence of vacancies in solid ^4He could allow Bose condensation, giving the solid superfluid-like properties.⁽³⁻⁵⁾ There have been theoretical estimates of the 0 K vacancy concentration (i.e., the fraction of crystal sites which are vacant) ranging from essentially zero⁽⁶⁾ to 10^{-4} ,⁽⁷⁾ and many experimental searches for vacancies and superfluid properties (recently reviewed by Meisel⁽⁸⁾), which have placed an upper limit on the vacancy concentration of about 10^{-4} . However, both the experimental and theoretical knowledge about 0 K vacancies in solid ^4He is sketchy, and we have seen very little work on interstitials and other point defects.

There is compelling reason to believe that solid ^4He has an appreciable concentration of point defects at its 0 K melting point, as can be seen from the following argument. The ground-state wave function of N bosons is nodeless, and we can therefore choose its phase so that the square of the wave function (i.e., the probability density) is positive for all positions of the N atoms. An everywhere positive probability density can formally be written as $\exp(-\Phi/k_B T)$, a classical Boltzmann distribution, which means that the ground-state Bose crystal is equivalent to a classical crystal with potential energy Φ at a positive temperature T ,⁽⁹⁾ and in fact when the 0 K ^4He solid is at its 0 K melting pressure, the corresponding classical crystal is at its melting temperature. Classical solids at their melting temperatures generally have appreciable concentrations of vacancies and interstitials, so unless the potential Φ corresponding to the ^4He ground state is exceptional, we can also expect solid ^4He to contain appreciable defect concentrations at its 0 K melting point.⁽⁴⁾

In this paper, we invoke the correspondence between the ground-state boson wave function and the classical potential to calculate the vacancy and interstitial concentrations in a tractable model for ^4He using classical statistical mechanics. We choose the well-known Jastrow product form for the ^4He wave function, which on the one hand exactly represents a legitimate boson model with a closed-form interaction [Eq. (11) below], and on the other hand simultaneously corresponds to a classical pairwise additive potential. Although Jastrow wave functions give very good energies in Monte Carlo calculations of liquid helium, for solid helium the

total energy is “unreasonably high”⁽¹⁰⁾ unless the wave function is combined with, e.g., single-particle wave functions which localize the atoms at the lattice sites. Hansen and Pollock speculate that this is related to the fact⁽¹⁰⁾ that the vibrational amplitude at melting, as measured by the Lindemann ratio, is much higher when localizing wave functions are used rather than a pure Jastrow form; the high Lindemann ratio has been confirmed by later simulations that also give reasonable energies,^(11,12) but it has apparently never been experimentally measured for helium. Still, the localizing functions are unsatisfactory, since they remove the exchange and translational symmetry of the wave function⁽¹³⁾ and also complicate the calculation, so we do not use them in this paper. We also note that many-body terms could be combined with the Jastrow wave function to give a better description of the quantum solid. However, these terms have been found to make a difference of only a few percent in Monte Carlo calculations⁽¹⁰⁾ of the pressure and energy of solid helium. Since their use would considerably lengthen our calculations, and their effect on defect concentrations is probably small, we do not include them.

This paper thus addresses three objectives. The first is to argue that in principle the ground state of the ${}^4\text{He}$ crystal must contain a nonvanishing concentration of point defects, most importantly vacancies. The second is to advocate the general formalism of classical statistical mechanics as an access route to quantitative study of those point defects. The third is to use the boson model generated by the Jastrow wave function to illustrate the second objective, and to provide a first rough estimate of the expected zero-point defect concentrations as a possibly helpful guide for experiment.

2. CLASSICAL THERMODYNAMICS OF POINT DEFECTS

As we mention above, there is a well-known⁽⁹⁾ correspondence between the ground state of a Bose crystal and an equivalent classical crystal, arising because the ground-state wave function Ψ is nodeless. This means that if we choose the phase appropriately, we can make Ψ real everywhere, allowing us to write

$$\Psi^2(\mathbf{R}) = \exp \left[- \frac{\Phi(\mathbf{R})}{k_B T} \right] \quad (1)$$

where \mathbf{R} represents the collective atom coordinate; fixing the arbitrary temperature T fixes the potential Φ . Just as $\Psi^2(\mathbf{R})$ is the probability of finding the configuration \mathbf{R} in the quantum Bose crystal, $\exp[-\Phi(\mathbf{R})/k_B T]$ is the probability of finding this configuration in the corresponding classical crystal with potential energy $\Phi(\mathbf{R})$. We can exploit this correspondence to

use classical statistical mechanics to calculate certain properties, such as the concentration of point defects, of the ground state of a Bose crystal with a known wave function.

In classical thermodynamics, equilibrium at constant volume and temperature corresponds to the minimum Helmholtz free energy $F = U - TS$. We can write the Helmholtz free energy for a crystal of N atoms and n noninteracting vacancies as⁽¹⁴⁾

$$F = F^* + nf - TS_c \quad (2)$$

where F^* is the free energy of a perfect crystal of N atoms with the same volume as the vacancy-containing crystal, $S_c = k_B \ln[(N+n)/(n!N!)]$ is the configurational entropy due to the placement of the n vacancies in the lattice, and f is the nonconfigurational part of the free energy cost of creating a single vacancy. The equilibrium number of vacancies can be found by setting $\partial F/\partial n|_{T,\nu} = 0$; for $n \ll N$ but still macroscopically large [as we must have in order to use Eq. (2)], using Stirling's approximation, we find that⁽¹⁴⁾

$$n = N \exp(-f/k_B T) \quad (3)$$

Other contributions to the configurational entropy can also be included as circumstances warrant. For instance, if the relaxation of the atoms around the vacancy site results in a state with lower symmetry (e.g., in an fcc lattice, if the 12 nearest neighbors of the vacancy rearrange into a configuration where two opposite atoms have moved symmetrically toward the vacancy) so that there are A possible orientations around each vacancy ($A = 6$ in the example), the configurational entropy has an additional term $k_B \ln(A^n)$, and so

$$n = AN \exp(-f/k_B T) \quad (4)$$

The quantity f has an interesting interpretation in the quantum regime. In the classical regime, f is the nonconfigurational part of the free energy difference between a crystal with a single vacancy and a perfect crystal. Since the configurational part of the free energy difference is $-k_B T \ln(N+1)$,

$$f = F[1 \text{ vacancy}] - F[\text{perfect}] + k_B T \ln[(N+1)] \quad (5)$$

where the free energies F now include the configurational parts, and since $F = k_B T \ln Z$,

$$\frac{n}{N} = \frac{A}{N+1} \frac{Z_N[1 \text{ vacancy}]}{Z_N[\text{perfect}]} \quad (6)$$

Here $Z_N[\text{configuration}]$ is the N -atom partition function for the given configuration; i.e., the portion of the total N -atom partition function corresponding to a lattice with a single vacancy or a perfect lattice. In the quantum language,

$$Z_N[\text{configuration}] = \int' \Psi^2(\mathbf{R}) d^{3N}\mathbf{R} \quad (7)$$

where the integral is restricted to the portion of \mathbf{R} space that fits the particular configuration. That is, the quantum wave function Ψ has some amplitude for configurations having different numbers of vacancies, and if the vacancies do not interact, their concentration is related to the ratio of the total probability amplitude for the zero- and one-vacancy configurations at the same total volume. Since it would be very difficult to include all possible numbers of vacancies in the quantum wave function, it is not clear to us in general how to calculate the vacancy concentration directly from Eqs. (6) and (7). In fact, the usual practice is to normalize the wave function so that the integral in Eq. (7) is identically 1 for the perfect crystal, and not to include the possibility of vacancies at all, even though the ground-state wave function for ${}^4\text{He}$ should contain vacancies. This practice is not compatible with the above calculation.

However, we can calculate f in the classical regime, starting with a quasiharmonic approximation (by quasiharmonic, we mean that the vibrational free energy depends on the density of the solid,⁽¹⁴⁾ whereas in a true harmonic approximation it would not) and appending anharmonic corrections from classical simulation if necessary. In this approach, the free energy consists of two parts: the internal nonvibrational potential energy \mathcal{V} , and the vibrational free energy of the $3N - 3$ normal modes in the crystal.⁽¹⁴⁾ Taking these normal modes to be classical harmonic oscillators with frequencies ω_j , and hence free energies $k_B T \ln(\hbar\omega_j/k_B T)$,⁽¹⁵⁾ we obtain

$$f = \mathcal{V}^v - \mathcal{V}^* + \sum_j j_B T \ln(\hbar\omega_j^v/k_B T) - \sum_j k_B T \ln(\hbar\omega_j^*/k_B T) \quad (8)$$

where the v superscript denotes a lattice with N atoms and one vacancy, and the $*$ denotes a perfect lattice of N atoms.

Similar expressions can also be derived for interstitials. The configurational entropy is $S_c = k_B \ln[N_S!/(n!(N_S - n)!)]$, where $N_S = A(N - n)$ is the number of sites for interstitials, including the possibility of different orientations in the site count. With this configurational entropy, Eq. (4) holds for interstitials, as does Eq. (8), substituting the superscript i for v , to denote a lattice with N atoms, one of which is an interstitial.

3. CALCULATION OF DEFECT CONCENTRATIONS

As we see from the previous section, we can calculate the concentrations of vacancies and interstitials in a ground-state Bose crystal if we know its wave function, which gives us the equivalent classical potential $\Phi(\mathbf{R})$, and if we can calculate the classical nonvibrational potential energy \mathcal{V} and normal mode frequencies ω_j for perfect and single-defect-containing N -atom crystals in this potential. Ideally, we would perform the calculation on an accurate model of a macroscopic helium crystal at various densities. However, in practice this is not possible, because the exact ground-state wave function of solid helium is not known, and because the computations required to find the normal modes and lattice energy for the relaxed (to mechanical equilibrium) defect-containing crystals limit the periodic cell size to something far smaller than macroscopic. To make the calculation feasible, we introduce several simplifications.

To approximate the ground-state wave function of helium, we choose the convenient and often-used Jastrow wave function mentioned in Section 1:

$$\Psi(\mathbf{R}) = \exp \left[-\frac{1}{2} \sum_{\langle ij \rangle} v(r_{ij}) \right] \quad (9)$$

which corresponds to the classical pairwise additive potential

$$\Phi(\mathbf{R}) = k_B T \sum_{\langle ij \rangle} v(r_{ij}) \quad (10)$$

It can be shown that this wave function is the exact ground state for the Schrödinger equation with potential energy

$$\begin{aligned} V(\mathbf{R}) = & \frac{\hbar^2}{m} \sum_{\langle ij \rangle} \left[v'(r_{ij})^2 - v''(r_{ij}) - \frac{2}{r_{ij}} v'(r_{ij}) \right] \\ & + \frac{\hbar^2}{m} \sum_{\langle ijk \rangle} [v'(r_{ij}) v'(r_{ik}) \cos \theta_{jik} + (\text{cyclic in } ijk)] \quad (11) \end{aligned}$$

where θ_{jik} is the angle between \mathbf{r}_{ij} and \mathbf{r}_{ik} . In our calculations, we use the pseudopotential

$$v(r) = (\sigma/r)^b \quad (12)$$

This pseudopotential is often used for helium,^(10,11) although pseudopotentials giving better variational energies have certainly been found,⁽¹⁶⁾ because of the computational advantages shown below. We choose σ so

that the density of the classical crystal at its melting point, as found by Hoover *et al.*,⁽¹⁷⁾ matches the 0 K density of ${}^4\text{He}$ at its melting point (e.g., $\sigma = 1.16$ for $b = 6$ and 0.990 for $b = 9$ in units of the ${}^4\text{He}$ melting-point lattice spacing). The quantum potential energy whose ground state is this particular Jastrow wave function has the pair potential $(\hbar^2/m)[b^2\sigma^{2b}/r^{2b+2} - b(b-1)\sigma^b/r^{b+2}]$; like the real helium interaction, this pair potential is strongly repulsive as $r \rightarrow 0$ and attractive as $r \rightarrow \infty$.

Given an approximate wave function, to calculate the defect concentrations we need the nonvibrational potential energy (i.e., the sum over all pairs of atoms of the classical pair potential) of perfect and single-defect-containing lattices of N atoms in the equivalent classical regime. This is calculated at mechanical equilibrium, which we reach in the defect-containing lattices by minimizing the total lattice energy (the perfect lattice is already in a state of mechanical equilibrium); this is the most time-consuming part of our calculation, because it requires repeated summing over all pairs of atoms. We use periodic boundary conditions and sum over the nearest image of each pair of atoms in the periodic cell, and we report results for cells as large as 216 atoms.

We also need the vibrational frequencies of the normal modes in the perfect and defect-containing lattices. In the quasiharmonic approximation, each component of the displacement from the equilibrium position of an atom obeys⁽¹⁸⁾

$$\ddot{u}_i = -\sum_j k_{ij}u_j \quad (13)$$

where the Hessian matrix is⁽¹⁸⁾

$$k_{ij} = \frac{1}{m} \frac{\partial^2 \Phi}{\partial u_i \partial u_j} \quad (14)$$

m is the mass of an atom, and the dots indicate time derivatives. Assuming that the atoms vibrate with amplitudes u_i^0 and a common frequency ω , we find that Eq. (13) implies that⁽¹⁸⁾

$$\omega^2 u_i^0 = \sum_j k_{ij} u_j^0 \quad (15)$$

i.e., the squared normal mode frequencies ω^2 are the eigenvalues of the Hessian matrix for the lattice. The second derivatives of Φ for our choice of wave function are trivial to calculate analytically, so once the mechanical equilibrium configuration has been found for a lattice, the Hessian matrix is easily computed and diagonalized.

Using periodic boundary conditions introduces one extra complication into the calculation: the number of lattice sites is fixed, for a given periodic cell size, so that in practice the number of atoms used in the vacancy-(interstitial-) containing lattice is one less (more) than the number in the perfect lattice, whereas Eq. (8) calls for a fixed number of atoms in a fixed volume. With two changes, we can correct for the difference: first, we adjust the lattice spacing in the defect-containing lattice so that the number density is the same for the defect-containing and perfect lattices. Second, because the free energy for the perfect lattice can be regarded as distributed evenly among all the atoms (or normal modes, for the vibrational part), we scale the perfect-lattice free energy so that it corresponds to the same number of atoms (normal modes) as the defect-containing lattice, with the calculated free energy per atom (normal mode) of the perfect lattice. With these two changes, Eq. (8) becomes

$$\frac{f}{k_{\text{B}}T} = \frac{\mathcal{V}^v[a^v]}{k_{\text{B}}T} - \left(\frac{N-1}{N}\right) \frac{\mathcal{V}^*[a^*]}{k_{\text{B}}T} + \sum_{j=1}^{3N-6} \ln\left(\frac{\hbar\omega_j^v[a^v]}{k_{\text{B}}T}\right) - \left(\frac{N-2}{N-1}\right) \sum_{j=1}^{3N-3} \ln\left(\frac{\hbar\omega_j^*[a^*]}{k_{\text{B}}T}\right) \quad (16)$$

for vacancies, and

$$\frac{f}{k_{\text{B}}T} = \frac{\mathcal{V}^v[a^i]}{k_{\text{B}}T} - \left(\frac{N+1}{N}\right) \frac{\mathcal{V}^*[a^*]}{k_{\text{B}}T} + \sum_{j=1}^{3N} \ln\left(\frac{\hbar\omega_j^i[a^i]}{k_{\text{B}}T}\right) - \left(\frac{N}{N-1}\right) \sum_{j=1}^{3N-3} \ln\left(\frac{\hbar\omega_j^*[a^*]}{k_{\text{B}}T}\right) \quad (17)$$

for interstitials, where $a^v = ((N-1)/N)^{1/3} a^*$, $a^i = ((N+1)/N)^{1/3} a^*$, and a^* are the lattice spacings for the vacancy-containing, interstitial-containing, and perfect lattices, respectively, and N is the number of atoms in the perfect lattice.

We can now use Eqs. (16) and (17) in Eq. (4) to calculate the concentration of point defects in our Bose solid. However, the calculation would be too lengthy to carry out at many densities if it were not for the well-known⁽¹⁷⁾ scaling properties of the $1/r^b$ classical potential: if we scale all lengths by a factor c , the potential energy is scaled by a factor of $1/c^b$. This means that \mathcal{V} and the ω_j for a certain lattice spacing a_1 are related to the quantities for a different lattice spacing a_2 by

$$\mathcal{V}[a_1] = \left(\frac{a_2}{a_1}\right)^b \mathcal{V}[a_2] \\ \omega_j^2[a_1] = \left(\frac{a_2}{a_1}\right)^{b+2} \omega_j^2[a_2] \quad (18)$$

In other words, we only need to calculate the nonvibrational potential energy and the normal-mode frequencies of the perfect, vacancy-containing, and interstitial-containing lattices for one lattice spacing, and when we scale by appropriate factors, we will know the defect concentrations for all lattice spacings. Using a subscript 0 to refer to a quantity calculated at unit lattice spacing using the $1/r^b$ pair potential, we find the final expression for the single-defect free energy when the lattice spacing in the perfect lattice is a^* and the classical pair potential is $k_B T(\sigma/r)^b$:

$$\begin{aligned} \frac{f}{k_B T} = & \left(\frac{\sigma}{a^*}\right)^b \left[\left(\frac{N}{N-1}\right)^{b/3} \mathcal{V}_0^v - \left(\frac{N-1}{N}\right) \mathcal{V}_0^* \right] \\ & + \frac{1}{2} \sum_{j=1}^{3N-6} \ln \left[\left(\frac{N}{N-1}\right)^{(b+2)/3} (\omega_{0j}^v)^2 \right] \\ & - \frac{1}{2} \left(\frac{N-2}{N-1}\right) \sum_{j=1}^{3N-3} \ln [(\omega_{0j}^*)^2] \end{aligned} \quad (19)$$

for vacancies, and

$$\begin{aligned} \frac{f}{k_B T} = & \left(\frac{\sigma}{a^*}\right)^b \left[\left(\frac{N}{N+1}\right)^{b/3} \mathcal{V}_0^i - \left(\frac{N+1}{N}\right) \mathcal{V}_0^* \right] \\ & + \frac{1}{2} \sum_{j=1}^{3N} \ln \left[\left(\frac{N}{N+1}\right)^{(b+2)/3} (\omega_{0j}^i)^2 \right] \\ & - \frac{1}{2} \left(\frac{N}{N-1}\right) \sum_{j=1}^{3N-3} \ln [(\omega_{0j}^*)^2] \end{aligned} \quad (20)$$

for interstitials. Note that in the final expressions for the vibrational part of f , the factors of $\hbar/k_B T$ from Eq. (8) and the mass appearing in the Hessian matrix (14) cancel out because of the logarithms; all factors of σ and a also cancel out of the vibrational free energy. The first two cancellations would occur for *any* pair potential, because they only depend on there being the same number of normal-mode terms for the perfect and defect-containing crystals, but the last two depend on the scaling properties of the $1/r^b$ potentials.

One final note on the computation is that we, like most researchers who have done calculations on ${}^4\text{He}$, use an fcc lattice, even though ${}^4\text{He}$ is hcp at the 0 K melting point. This practice is partially justified by the calculations of Hansen and Pollock,⁽¹⁰⁾ who find very similar values for the energy and other properties on hcp and fcc lattices in $1/r^5$ pseudopotentials with Gaussian localization functions. Furthermore, by performing lattice sums, it can be shown that with a classical $1/r^b$ pair potential, the fcc lattice

has a very slightly lower lattice potential energy than the hcp lattice when $b \geq 5$, suggesting that the fcc structure is slightly more stable with these potentials. However, Hansen and Pollock's simulated helium solid can apparently be induced to condense either into an fcc or hcp structure, depending on where the localization functions are centered, and we expect that without localization functions, in calculations with few atoms the periodic boundary conditions completely determine which crystal structure is more likely. We use an fcc structure mainly because the classical melting points⁽¹⁷⁾ (used to choose the appropriate σ to match the helium melting point density) have only been determined for fcc lattices, and only for $b = 4, 6, 9$, and 12 . So we find it convenient to limit ourselves to these values of b and to an fcc lattice, and then to compare the fcc results to those found in an hcp lattice at the same densities using the same potential.

4. RESULTS

As outlined in the previous section, the calculation of the defect concentration for a given number of atoms N in the perfect lattice and a given value of b proceeds with the following steps. First, we remove an atom from the perfect lattice with unit lattice spacing (or add an atom to it) and relax to a minimum in the summed $1/r^b$ pair potential. This step in the calculation requires some care, because a configuration may be a local minimum in many directions in configuration space and still be neither a global nor a local minimum. So, to guarantee we are at a local minimum (to a tolerance of 10^{-6} in energy), we first minimize using the conjugate gradient method,⁽¹⁹⁾ then we minimize along random directions for each particle until the energy no longer changes, change the random directions, and repeat until the energy does not change; and finally we minimize along the eigenvectors of the Hessian matrix, followed by random directions for each particle, until the energy no longer changes.

The next step is to calculate and diagonalize the Hessian matrices for the perfect and defect-containing lattices in their relaxed configurations. Then, we use the energies found in the minimization step and the Hessian matrix eigenvalues to calculate the free energies of Eqs. (19) and (20) as a function of density. The energy tolerance of 10^{-6} in the relaxation of the lattice corresponds to a fractional error of a few times 10^{-4} in the free energies.

We have calculated the single-vacancy and single-interstitial free energies for the $1/r^6$ and $1/r^9$ potentials of fcc lattices ranging from 27 to 216 atoms; the results are shown in Fig. 1. The defect concentrations can be computed from the free energies using Eq. (4). We find that there are three possible configurations for an interstitial at a given site [$A = 3$ in

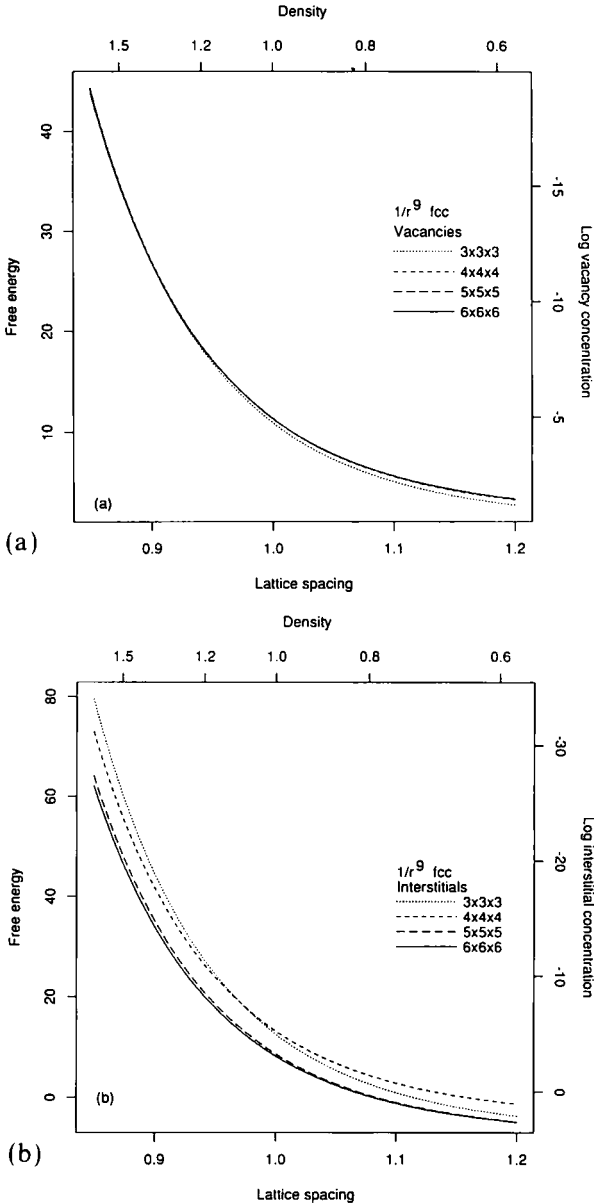


Fig. 1. Single-defect free energy $f/k_B T$ (left scale) and \log_{10} of defect number density (right scale) as a function of lattice spacing (bottom scale, in units of the lattice spacing at the melting point) and density (top scale, in units of the 0 K melting point density) in Jastrow wave function fcc Bose solids with $1/r^b$ pseudopotentials. We show results for $b = 9$, (a) vacancies and (b) interstitials, and $b = 6$, (c) vacancies and (d) interstitials, for periodic cells ranging in size from $3 \times 3 \times 3$ to $6 \times 6 \times 6$ atoms on the same plot.

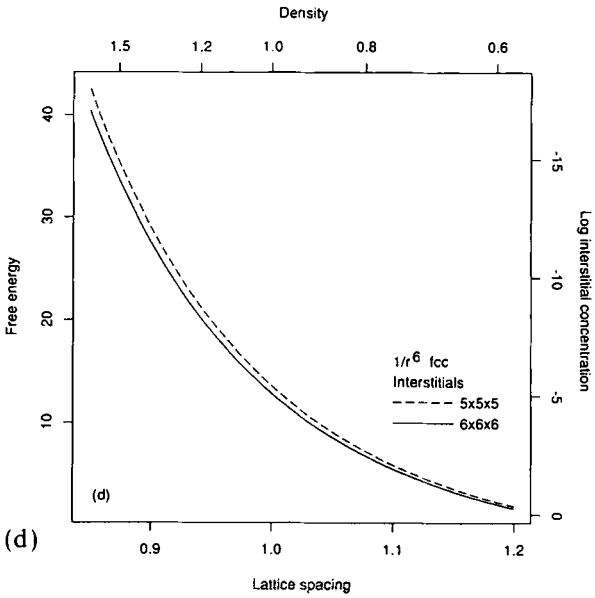
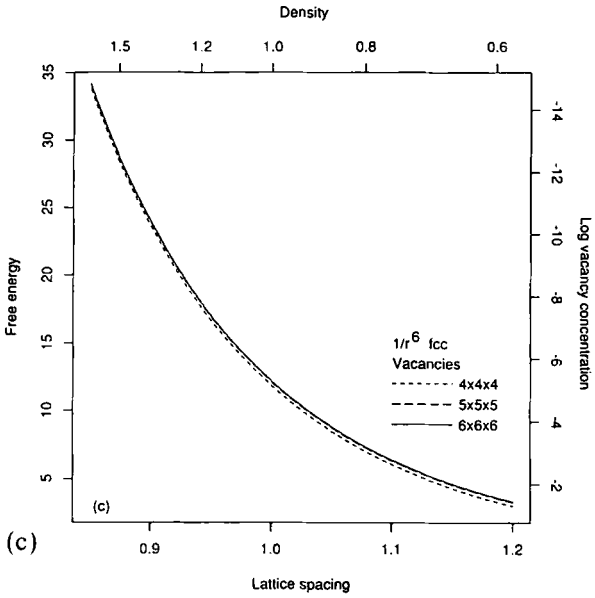


Fig. 1. (Continued)

Eq. (4)]: an interstitial atom always pairs with another atom to form a so-called “split interstitial,” and we find that a split interstitial at a given lattice site can be oriented in three equivalent directions, along any of the three lines joining two opposite squares in the nearest-neighbor polyhedron (see Fig. 2a), and that the nearest-neighbor polyhedron distorts around the pair. For vacancies, the relaxed configurations we find show a slight inward shift of the 12 nearest neighbors toward the vacant lattice site, retaining the symmetry of the lattice, so $A = 1$. Using these values of A , we find that the vacancy concentration at the melting point is 1.60×10^{-5} for $1/r^9$ and 6.36×10^{-6} for $1/r^6$, while the interstitial concentrations are 1.32×10^{-3} and 1.08×10^{-5} , respectively; the defect concentrations are 7–16 orders of magnitude smaller when the density is 50% higher (see Fig. 1).

We have also calculated the defect concentrations on a 216-atom hcp lattice with the $(\sigma/r)^9$ potential. Since we do not know the melting point of the hcp $1/r^9$ crystal, we use the same σ as in the fcc calculation, and present the results in Fig. 3 using the same units for a as in the fcc calculation. The

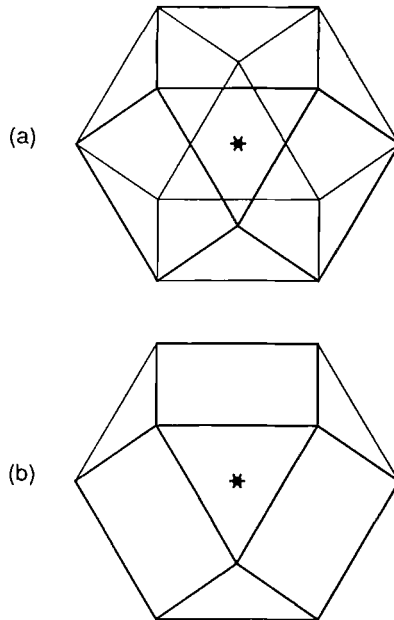


Fig. 2. (a) An fcc lattice site and the polyhedron formed by its 12 nearest neighbors. Note that each square face is opposite another square face, and each triangular face is opposite another triangular face. (b) The same view of the nearest-neighbor polyhedron for an hcp lattice, where now the square faces are opposite the triangular faces.

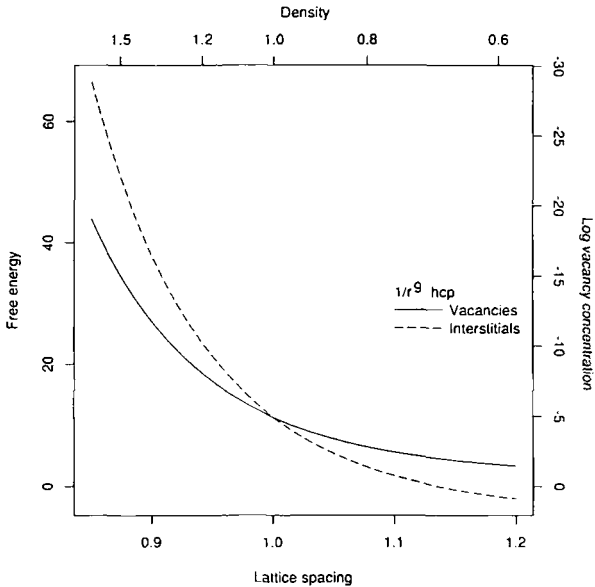


Fig. 3. The single-vacancy and single-interstitial free energies for a $6 \times 6 \times 6$ cell hcp lattice with a $1/r^9$ potential, and the vacancy concentration (the interstitial concentration is a factor of A higher than the right axis, but we have not been able to determine A). Comparing to Fig. 1, we see that the vacancy concentration is substantially the same as in an fcc lattice, while the interstitial concentration is much lower.

vacancy concentration is essentially the same, over the whole density range, as in an fcc lattice, which is not surprising, because of the similarity between the two lattices. For the interstitial, we found several very different (local energy minimum) configurations which were within one part in 10^6 in total lattice energy, so we cannot be certain that we have found the lowest-energy state for the interstitial-containing lattice. However, all configurations we found led to single-interstitial free energies $(3-4) k_B T$ higher than in an fcc lattice at the same density, apparently because an hcp lattice does not contain as convenient a place for an interstitial atom as does an fcc lattice (see Fig. 2b). Because of the difficulty in finding the lowest-energy state, we cannot determine A (and hence the interstitial concentration) for the hcp interstitial, but unless A is wildly different from the fcc value of 3, the interstitial concentration in an hcp lattice must be 1-2 orders of magnitude less than in fcc.

5. DISCUSSION

It might seem surprising that we can obtain meaningful results using such a small number ($N \leq 216$) of particles when the defect concentrations we calculate are much smaller than $1/N$. However, Fig. 1 does show a clear convergence with the size of the periodic cell, and the reason for the convergence becomes clear when we consider the sources of small- N errors. First, we use a nearest image cutoff for the potential, which means that the largest discarded terms in the potential energy are for pair distances that are about half the size of the periodic cell. For an $M \times M \times M$ periodic cell and a $1/r^b$ potential, we discard $\mathcal{O}(M^2)$ of these largest terms, while keeping $\mathcal{O}(M^3)$ terms at close to unit pair distance, so the error is $\mathcal{O}[(1/M)(2/M)^b]$. This is a few percent for $M=3$, but it rapidly decreases to about 10^{-4} at $M=5$ for $b=6$ and $M=4$ for $b=9$.

A second source of small- N error is that instead of having a single defect in a very large crystal, or many noninteracting defects, as the ideal calculation calls for, we have many periodic images of the defect which can interact through lattice-mediated elasticity. However, since the defects are separated by twice the nearest-image cutoff, and there are many more nearby discarded images than defects, this is a much smaller source of error than the nearest image cutoff.

Other sources of possible inaccuracies in our calculation are not directly related to the periodic cell size. First, the melting density for the $(\sigma/r)^b$ potentials⁽¹⁷⁾ has not been determined to arbitrary precision, which introduces some error in the choice of the σ that matches the melting point of helium to the melting point of the Jastrow wave function. Analyzing Eqs. (19) and (20), we see that the fractional error in the defect density n/N due to error in σ obeys

$$\frac{\Delta(n/N)}{(n/N)} \approx \frac{f_{\text{NV}}}{k_{\text{B}}T} \frac{\Delta\sigma}{\sigma} \quad (21)$$

where f_{NV} is the nonvibrational part of the single-defect free energy at the density of interest. As this is around $10k_{\text{B}}T$ at the melting point, a 1% error in σ makes a 10% error in n/N .

The quasiharmonic approximation used in this calculation is another possible source of inaccuracy. However, Hoover *et al.*⁽¹⁷⁾ find that the free energy calculated in this approximation agrees with their Monte Carlo results for $1/r^b$ potentials on perfect lattices up to the melting point, with approximately the same size error as the nearest image cutoff, and we expect this also to hold for defect-containing lattices. The difference between fcc and hcp lattices could also contribute to error in this calculation, since solid ${}^4\text{He}$ is hcp, and our calculation is done on an fcc lattice.

As we have seen, at the same density and with the same potential, the concentration of vacancies in an hcp lattice with $b = 9$ is very close to the concentration in an fcc lattice. However, the concentration of interstitials is apparently much lower in the hcp lattice, due to the lack of good sites for split interstitials in the hcp lattice. So, we believe that the fcc vacancy calculations are directly relevant for helium, while the fcc interstitial calculations provide an upper bound on the concentration in helium.

Finally, we should also point out that Hoover *et al.*⁽²⁰⁾ have found that the equilibrium $1/r^b$ melting-point solid is actually bcc, not fcc, for $b \leq 6$; the bcc region of the phase diagram is quite small for $b = 6$,⁽²¹⁾ allowing a metastable fcc solid to exist at the melting point. However, for $b = 4$, the bcc region is much larger, which strongly disagrees with what is found in the ^4He phase diagram, and for that reason we have chosen not to consider $b < 6$ Jastrow wave functions. It is possible that an fcc solid with the equilibrium number of vacancies and interstitials would be more stable than a bcc solid for $b = 6$ at the melting point, since the defects lower the free energy, but we have not done the calculation necessary to check this.

Still, even with these sources of possible errors, this calculation does provide what we hope is a close lower bound on the concentration of vacancies in 0 K solid ^4He . We claim that it is a lower bound because, as we noted in Section 1, the Jastrow wave function for solid helium permits less atomic motion locally (in particular, there is less atomic motion in the neighborhood of a vacancy) than other wave functions which yield better energies in Monte Carlo calculations.⁽¹⁰⁾ Presumably a solid with less zero-point motion has fewer 0 K vacancies (certainly this is true in the extreme case of a classical solid with no zero-point motion, which can have no 0 K vacancies), so if the wave functions yielding better energies for helium are also more representative of its zero-point motion, the pure Jastrow solid would have fewer vacancies than real solid ^4He .

Our calculation also provides a motivation for more theoretical and experimental work on defects in solid ^4He . On the theoretical side, it would be instructive to calculate the defect concentrations in hcp helium instead of fcc, and to use a more realistic wave function for solid ^4He . The extension to hcp using the Jastrow wave function would only require calculation of the melting point for the $1/r^b$ hcp solids; using a more realistic wave function would require a much longer calculation, because the scaling properties of the $1/r^b$ potentials could no longer be exploited. We are not certain how the defect concentrations could best be found in the sort of Monte Carlo calculations that have yielded good energies for ^4He , but this should probably be explored.

The prediction of positive vacancy and interstitial concentrations in the ground state for our model indicates that it is Bose-condensed;^(2-5,8) the

same should be true for crystalline ${}^4\text{He}$, and it is therefore of some interest to calculate the condensed fraction in our model. It has been pointed out before^(1,22) that the presence of a condensate produces off-diagonal long-range order in the single-particle reduced density matrix

$$\rho_1(\mathbf{r}, \mathbf{r}') = C \int \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N \quad (22)$$

(C is related to the normalizing factor for the ground-state wave function Ψ). For a structurally perfect crystal, ρ_1 will vanish unless \mathbf{r} and \mathbf{r}' are localized near a common lattice site. However, the presence of point defects permits \mathbf{r} and \mathbf{r}' to drift away from one another to arbitrary relative positions in the crystal. Using the Jastrow wave function of Eq. (9), we can transform Eq. (22) into

$$\rho_1(\mathbf{r}, \mathbf{r}') = C \int \exp \left\{ -\frac{1}{2} \sum_{j=2}^N [v(r_{1j}) + v(r_{2j})] - \sum_{\langle ij \rangle} v(r_{ij}) \right\} d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N \quad (23)$$

where the second sum is over pairs of atoms, excluding atom 1. This last expression can be interpreted as the classical probability for configurations of two "half particles" embedded in a medium of $N-1$ "full particles," so a classical simulation could be used to investigate the density matrix and thereby estimate the condensate fraction in our model. Because the defect concentrations appear to be small, the condensate fraction is certainly also small, perhaps partially explaining the failure so far to observe a condensation phase transition or "supersolid" flow behavior in crystalline ${}^4\text{He}$.⁽⁸⁾

Of course, it is important to combine this theoretical work with further experiments. We would like to see a measurement of the vacancy and interstitial concentrations in solid ${}^4\text{He}$ as a function of density, independent of any possible Bose condensation. Unfortunately, it is apparently not clear at this point how to measure such small concentrations, and presumably the presence of both vacancies and interstitials would make independent measurements of either difficult. However, it might be possible to separate the vacancies and interstitials using an electric field. Since ${}^4\text{He}$ is a dielectric, its atoms are attracted to regions of strong electric field; i.e., interstitials are attracted to high-field regions, and vacancies are repelled from them. By contrast, as we see in Fig. 1, external pressure affects the two types of defects in the *same* way, so employing both types of crystal perturbations could in principle provide the concentrations independently.

ACKNOWLEDGMENTS

We thank Tom MacFarland for many helpful discussions and for pointing out several relevant references. We also thank Prof. Veit Elser for a discussion which led to the idea of the electric field experiments.

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