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Monte Carlo Simulation of Vacancies in Rare-Gas Crystals*

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The thermodynamics of vacancy formation in rare-gas crystals is studied by using Monte Carlo simulation of a many-body system. In the calculations, we assume a pairwise-additive Lennard-Jones potential and measure the change in Helmholtz free energy associated with reversibly adding a particle to a crystal containing a single vacancy. The addition is carried out by varying a coupling parameter joining one particle to the others in the crystal. Results for both 32- and 108-particle systems show that in a macroscopic (rare-gas) crystal near the triple point (1) the fraction of lattice sites vacant is about 1/3000, and (2) relaxation of particles neighboring a vacant site is less than 1% of an equilibrium interparticle spacing. These calculations are in excellent agreement with the earlier work of Glyde.

I. INTRODUCTION

During the past decade, a number of papers[1–8] have appeared concerning the thermodynamics of vacancy formation in crystals, especially in solid argon near the triple point. Besides the intrinsic interest of vacancies, a study of them gives information on diffusion in crystals, which depends upon the presence of vacancies, and on many-body forces. A comparison of the energy required to form a vacancy with the energy required to sublime an atom makes it possible to estimate the magnitude of many-body forces.

At high, near-melting temperatures where vacancies are most easily formed rare-gas crystals attain a mushy consistency which makes reliable density measurements difficult. The most obvious way to estimate the number of vacancies in a crystal is to compare the theoretical density deduced from the nearest-neighbor spacing with the measured bulk density.[6–8] This works only if more complicated defects such as cracks and dislocations are absent. As has been pointed out in review articles,[9,10] two very significant questions are still unanswered: (1) the fraction of vacancies in an otherwise perfect crystal at the melting point; and (2) the importance of many-body forces. The most recent work suggests that the number of vacancies at melting is, in rare-gas crystals, no more than 0.5%.

Previous calculations have relied on a cell-model approach (Einstein or Lennard-Jones–Devonshire).[5] Surprisingly, no approximate lattice-dynamic (Born–von Kármán) calculations for the vacancy problem have been reported. Since the results so far obtained vary considerably, we thought it well justified to carry out a different approach which correctly takes into account many-body correlations and anharmonicity. For this purpose we have used the Monte Carlo method,[11,12] which gives exact results for any classical system of particles interacting with a specified potential function. The primary disadvantages are: (1) only a few significant figures in the results, and (2) many hours of computer time used up.

To determine the number of vacancies in a crystal, a special crystal is simulated in the computer. In it a single particle is coupled to the others with a variable strength coupling parameter.[13] By measuring the work necessary to uncouple this special particle from the others in the crystal, we obtain directly the free energy of vacancy formation. By calculating free energy for the whole crystal as a function of the number of vacancies, we can then find the number of vacancies which gives the lowest free energy—this gives the fraction of vacancies at equilibrium in a macroscopic crystal. The small fraction of vacancies we actually find, less than 1 part in 5000, makes it possible to treat the vacancies as independent of each other. Measurement of the relaxation of particles near a vacancy showed the mean displacement to be so small, less than a percent of the nearest-neighbor spacing, that it could not be accurately determined. Earlier, Glyde[5] reported that the high-temperature relaxation of the neighboring particles was away from the site of the vacancy and of this same order of magnitude. The insignificant lattice relaxation makes it practical to carry out the calculation with the small systems which are manageable using the Monte Carlo method. Results from systems of 32 and 108 particles, using corrected lattice-energy sums to simulate an infinite system, agreed with each other.

In Sec. II we derive an expression for the number of vacancies in terms of energies directly measureable by Monte Carlo and the excess entropy. In Sec. III the

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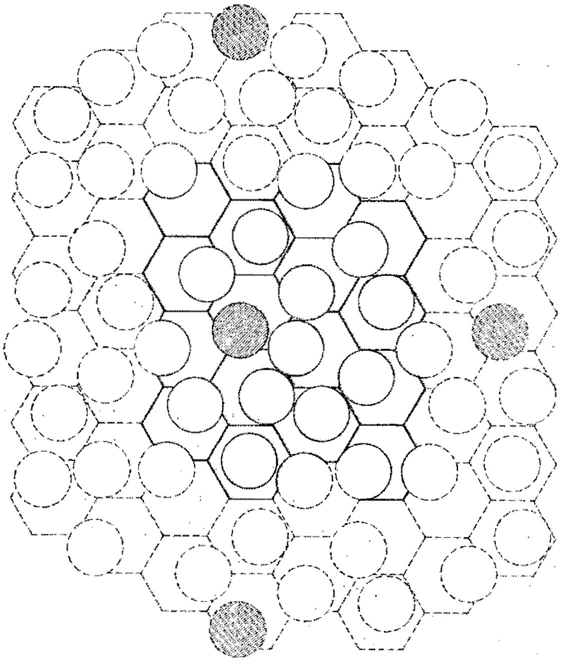

FIG. 1. Two-dimensional analog of the single-occupancy system. The system is outlined with heavy lines. The center of each of the 16 particles is restricted to lie within its cell. The shaded particle, ω, interacts with the others through the coupling parameter λ. In the Monte Carlo calculations periodic boundary conditions were used, so that each particle interacts with the $N-1$ particles or periodic images closest to it (the images are indicated by broken lines).

Monte Carlo calculations at two different temperatures are described; the results are applied to argon at 60° and 80°K and are extended to krypton at 83° and 110°K, using corresponding states for the measured energies. The last section is reserved for a comparison of our results with those of others.

II. THEORY

To calculate the relative stability of two competing phases or to find the equilibrium concentrations of two reacting species, one must calculate that free energy, either Gibbs or Helmholtz, which is minimized at equilibrium. A calculation of the change in free energy caused by uncoupling one particle from a crystal makes it possible to calculate the equilibrium number of empty sites.

Since free energy is not a dynamical variable depending explicitly on particle coordinates and velocities, one must consider a reversible process joining the two states whose free energies are to be compared. The two possibilities for each position in a crystal lattice are occupied (normal) and unoccupied (vacancy). The natural process (for a computing machine!) linking two states is the uncoupling of a particular particle from the rest of the lattice by using a variable coupling parameter λ which can be continuously reduced from 1 (fully coupled) to 0 (uncoupled). To make sure that the uncoupled particle is not free to roam throughout the crystal it is convenient to restrict each particle to the region of space closer to its lattice site than to any other. As will be discussed in detail later, it was found to be rare indeed that in the solid a fully coupled particle would leave the region of space close to its lattice site. The natural choice for these confining cells is a Wigner–Seitz cell. If the cell size is large with respect to the mean displacement of a fully-coupled particle, then the actual choice of the cell will not affect the calculated fraction of vacancies. However, the actual choice of the cell size will affect the energy of the *coupled* particle, especially for small values of the coupling parameter, and thus will affect *interim* results.

Consider then a periodic array of singly occupied cells arranged in a face-centered lattice. A two-dimensional analog is shown in Fig. 1. Since in the solid phase the root-mean-squared displacement is always small with respect to the lattice spacing, the introduction of the cells is only a convenience not affecting the results.

For the *perfect* lattice we define the "single-occupancy" configurational integral Q_{SO},

$$Q_{\mathrm{SO}}\equiv\int_{\Delta}\cdots\int_{\Delta}\exp\left(-\frac{\Phi}{kT}\right)d\mathbf{r}^{N}\equiv\exp\left(-\frac{A_{\mathrm{SO}}}{kT}\right)\equiv q^{N},\tag{1}$$

where the Δ's indicate that each particle remains in its own cell during the integration over the particle coordinates $\mathbf{r}^{N}$, and where A_{SO} is the configurational Helmholtz free energy for the (hypothetical) perfect crystal. To express the fact that Helmholtz free energy is extensive, $A_{\mathrm{SO}}\propto N$, we introduce the intensive variable q, independent of N (for N large enough), and dependent on the number density N/V and the temperature T.

The potential energy of the whole N-particle system is indicated by Φ in (1). Now consider a more general N-particle system in which one of the particles, Particle ω, is linked to the other $N-1$ particles in the system by a pair potential $\lambda\phi$ rather than ϕ. Then the potential energy Φ (assumed to be a sum of pair terms) and the configurational integral Q_{SO} become functions of the "coupling parameter" λ:

$$\Phi(\lambda)=\sum_{\substack{i=1\\ i\neq\omega\neq j}}^{N-1}\sum_{j=i+1}^{N}\phi(r_{ij})+\lambda\phi_{\omega};$$

$$\phi_{\omega}\equiv\sum_{i\neq\omega}\phi(r_{i\omega});$$

$$Q_{\mathrm{SO}}(\lambda)\equiv\int_{\Delta}\cdots\int_{\Delta}\exp\left[-\frac{\Phi(\lambda)}{kT}\right]d\mathbf{r}^{N}.\tag{2}$$

Particle ω is uncoupled by reducing λ from 1 to zero. The two limits are of particular interest; for λ equals 1, the system reduces to a perfect crystal, $Q_{\mathrm{SO}}(\lambda=1)\equiv Q_{\mathrm{SO}}\equiv q^{N}$; for λ equals zero, Particle ω is independent of the rest and contributes only a factor of Δ, the cell volume, to $Q_{\mathrm{SO}}(\lambda=0)$. The configurational integral for the $N-1$ remaining particles is $q^{N-1}q_{\mathrm{vac}}$. The dimensionless factor q_{vac} represents the effect of a single vacancy on the configurational integral.

If we consider a continuous reduction of λ linking the two states just described together, we can express the change in free energy for the process $A(\lambda=0)-A(\lambda=1)$ in terms of the ensemble average (indicated by $\langle\ \rangle$ brackets) of ϕ_ω:

$$\frac{A(0)}{kT}-\frac{A(1)}{kT}=\int_0^1\left[\frac{\partial \ln Q_{\mathrm{SO}}(\lambda)}{\partial\lambda}\right]_{N,V,T}d\lambda$$

$$\equiv\ln\left[\frac{q}{(\Delta q_{\mathrm{vac}})}\right]=-\int_0^1\left\langle\frac{\phi_\omega}{kT}\right\rangle_{\mathrm{Av}}d\lambda\equiv I. \quad (3)$$

We can determine the integral I by making Monte Carlo measurements of $\langle\phi_\omega\rangle$ for various values of λ.

In order to apply the results obtained from the uncoupling of one particle to a macroscopic crystal, we need an expression for the difference in free energy between a perfect N-particle crystal and an N-particle crystal with n vacancies. In the limit that $n\ll N$, so that the vacancies are independent, the configurational integral has the form

$$Q_N(n,V,T)=\left[q\left(\frac{N+n}{V}\right)\right]^N\left[q_{\mathrm{vac}}\left(\frac{N+n}{V}\right)\right]^n\binom{N+n}{N}. \quad (4)$$

In (4) we show explicitly the dependence of q and q_{vac} on density. Using the thermodynamic relation for the perfect crystal, $(\partial\ln q/\partial\ln V)_{N,T}=PV/NkT$, and ignoring terms of order $\exp(n^2/N)$, (4) takes on the form

$$Q_N(n,V,T)$$

$$=\left[q\left(\frac{N}{V}\right)\right]^N\left[\exp\left(-\frac{PV}{NkT}\right)\right]^n e^n\left[q_{\mathrm{vac}}\left(\frac{N}{V}\right)\right]^n\left(\frac{N}{n}\right)^n. \quad (5)$$

The choice of n that maximizes the configurational integral (and minimizes the Helmholtz free energy) is obtained by differentiating (5),

$$\frac{n}{N}=q\exp\left(-\frac{PV}{NkT}\right)\frac{\exp(-I)}{\Delta}=q_{\mathrm{vac}}\exp\left(-\frac{PV}{NkT}\right). \quad (6)$$

Equation (6) is the chief result of this section. It gives the equilibrium fraction of vacant lattice sites in terms of the integral I, which we can measure using Monte Carlo. This same result can also be obtained from the grand canonical ensemble for a system with a fixed number of cells of fixed size, but with a variable number of particles. We apply this relation to a system simulating a rare-gas solid in the following section.

III. MONTE CARLO CALCULATIONS

The theory underlying Monte Carlo calculation of canonical ensemble averages (fixed N, V, and T) has been discussed by Wood and Parker.[12] To correlate the computer calculations with real crystals of argon and krypton, we use the Lennard-Jones potential

$$\phi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6], \quad (7)$$

with the potential parameters determined by Horton and Leech[14]:

$\epsilon/k=119$°K, $\sigma=3.40$ Å for argon,

$\epsilon/k=164$°K, $\sigma=3.64$ Å for krypton,

where k is Boltzmann's constant.

To assess the number dependence of the results, we initially carried out pairs of calculations for both 32 and 108 particles. We found that, when a long-range energy correction was included, the 32- and 108-particle results agreed within statistical accuracy. The energy correction to $\langle\phi_\omega\rangle_{\mathrm{Av}}$ is that portion of an infinite-crystal lattice sum (for a perfect crystal) which is missing in a 32- or 108-particle crystal.

The calculation proceeds in the usual way, with periodic boundary conditions and a starting configuration with each particle at the center of its cell. The density was selected from the x-ray determination of the lattice spacing at the selected temperature. A particle is selected randomly (for small coupling parameters we used a bias which had a 5–1 greater chance of selection for the nearest neighbors of particle ω) and a move is tried. Any move raising the energy of the system δE is accepted with probability $\exp(-\delta E/kT)$; a move lowering the energy is always accepted. Averages over such a series of configurations converge to a canonical distribution.[15] Since the exact shape of the cell to which each particle is confined is immaterial we used, instead of a Wigner–Seitz dodecahedron, the largest spherical cell consistent with nonoverlapping cells. The sphere radius was then half the nearest-neighbor spacing in the perfect lattice a. At the higher of the two temperatures, roughly 4°K below the triple point for argon, only about 1 move in 10 000 was rejected because of motion of a particle past its cell boundary. The vast majority of even this small fraction of moves would have been rejected on energy grounds.

We found that the energy $\langle\phi_\omega\rangle_{\mathrm{Av}}$ converges within 2% after 100 000 moves (about one-fourth of which are

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[14] G. K. Horton and J. W. Leech, Proc. Phys. Soc. (London) **82**, 816 (1963).

[15] In Refs. 11 and 12 it is pointed out that convergence is (formally) guaranteed if the Monte Carlo moves (i) allow all configurations to be sampled and (ii) satisfy the ratio condition that (probability of moving from state r to state s divided by the probability of moving from state s to state r) equals $\exp[(\Phi_r-\Phi_s)/kT]$. Our procedure of selecting moves in which some of the particles move much more often than others does not alter the ergodic property or any of the ratios but it does improve the *rate* of convergence.

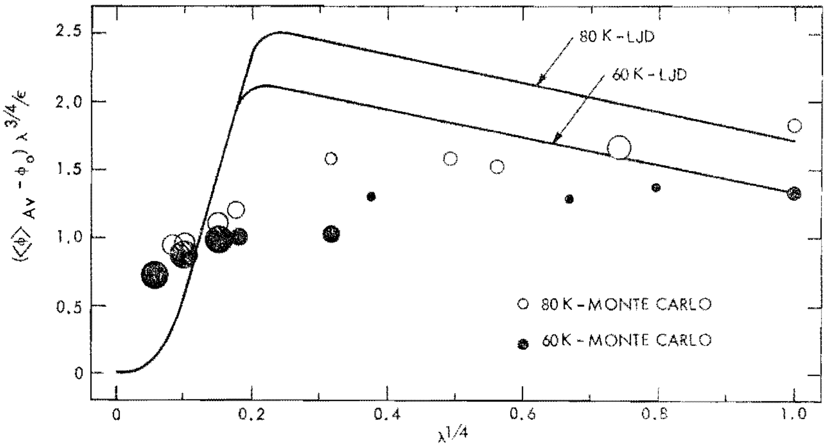

FIG. 2. The energy of Particle ω less its energy in a perfect lattice ϕ_O, multiplied by $\lambda^{3/4}/\epsilon$. This way of presenting the data is useful for determining I by numerical integration. The variation of the energy of Particle ω according to the Lennard-Jones–Devonshire theory for a spherical cell with radius equal to one-half the nearest-neighbor distance is also shown. The size of the symbols indicates the error limits.

accepted) as long as the coupling parameter is large enough (0.1 or more) so that the thermal coupling of Particle ω to the lattice is comparable to a nearest-neighbor interaction. For smaller coupling parameters the accuracy is reduced, but the integral I is insensitive to the small-λ values and could be determined with an over-all accuracy of 1 or 2%.

In Table I the average values of $\langle\phi_\omega\rangle_{Av}$ are listed (including the lattice correction). The rapid increase of $\langle\phi_\omega\rangle_{Av}$ as λ approaches zero complicates the numerical integration

$$I=-\int_0^1 \left\langle\frac{\phi_\omega}{kT}\right\rangle_{Av} d\lambda.$$

Since the average energy of a particle interacting with a fixed source of energy $\propto\lambda/r^{12}$ is of order $\lambda^{-3/4}$, we rewrote the integral as

$$I=-\left(\frac{\phi_O}{kT}\right)-4\int_0^1 \lambda^{3/4}\left\langle\frac{(\phi_\omega-\phi_O)}{kT}\right\rangle_{Av} d(\lambda^{1/4}), \quad (8)$$

where ϕ_O is the value which ϕ would have in a perfect lattice. The integrand is plotted in Fig. 2 for both temperatures. Since the Lennard-Jones–Devonshire model reproduces the energy of the fully coupled particle very well, we had hoped that that model would be useful in estimating I as well. The Lennard-Jones–Devonshire model is not useful, as Fig. 2 shows. The cell model results which are plotted assume that the energy of Particle ω less the energy for a fully coupled particle at the center of the cell is equal to *twice* the average value of the potential energy relative to the cell center, $\langle\phi-\phi_O\rangle$ which is calculated in this cell theory. Alternatively, one can equally well let the energy of Particle ω less the static lattice energy be just equal to $\langle\phi-\phi_O\rangle$. Neither choice yields results which are even close to the correct results for the fraction of vacancies, although the choice plotted does give $\langle\phi_\omega\rangle_{Av}$ accurately for the fully coupled system.

In Table II the Monte Carlo values found for energy, pressure, and the integral I are listed, and in Table III the number of vacancies found for argon and krypton are listed. The equation used for determining these is derived from (6), taking into account that the ratio of the cell volume actually used to the volume per particle

TABLE I. Values of $\langle\phi_\omega\rangle_{Av}$, the interaction energy of a solid-phase particle which is coupled to other particles with coupling parameter λ. All values have been corrected by adding on interactions which lie outside the finite periodic cell. The expected error in the quoted results is less than 1% for coupling parameters greater than 0.1, and approximately 10% for smaller coupling parameters.

$(kT/\epsilon)=60/119$		$(kT/\epsilon)=80/119$	
λ	$\langle\phi_\omega\rangle_{Av}/kT$	λ	$\langle\phi_\omega\rangle_{Av}/kT$
0.00001	7840	0.00005	2320
0.0001	1720	0.0001	1430
0.0005	507	0.0005	470
0.001	323	0.001	292
0.01	30.8	0.01	49.9
0.02	15.3	0.06	−5.1
0.2	−24.85	0.1	−11.8
0.4	−27.91	0.3	−18.36
1.0	−30.73±0.03	1.0	−21.82±0.03

TABLE II. Monte Carlo values of the potential energy $\langle\phi\rangle_{Av}$, compressibility factor (PV/NkT), and integral I. The nearest-neighbor spacing in the perfect lattice is a. The Lennard-Jones potential parameters ϵ and σ are defined in Eq. (7). Predicted energies and compressibility factors according to the Lennard-Jones–Devonshire cell theory are also included in the Table.

(kT/ϵ)	60/119	80/119
(a/σ)	1.1215	1.1344
$(\langle\phi\rangle_{Av}/kT)_{MC}$	−15.37	−10.91
$(PV/NkT)_{MC}$	−0.42±0.08	−0.34±0.07
I_{MC}	24.1±0.2	15.8±0.2
$(\langle\phi\rangle/kT)_{LJD}$	−15.34	−10.96
$(PV/NkT)_{LJD}$	−0.26	+0.10

is $\pi\sqrt{2}/6$:

$$\frac{n}{N}=\frac{3\sqrt{2}e}{\pi}\exp\left(\frac{S^e}{Nk}-\frac{\frac{1}{2}\langle\phi_\omega(\lambda=1)\rangle_{\text{Av}}}{kT}-I\right)\exp\left(-\frac{PV}{NkT}\right). \tag{9}$$

The values for the excess entropy S^e (relative to a classical ideal gas at the same number density and temperature) were taken from experiment.[1,16] Since the entropies for argon and krypton deviate slightly from corresponding states as shown in Fig. 3, the predicted fraction of vacancies given in Table III is slightly different for the two. We also included in the table the predictions of the Lennard-Jones–Devonshire cell model for the excess entropy. The excess entropy is low[17] by a fairly uniform 0.3 Nk.

The best justification for the use of small-system Monte Carlo calculations comes from the *a posteriori* observation that the lattice relaxation is small (too small to determine its sign) near a vacancy and that the fraction of vacancies is small enough so that divacancies need not be considered. The estimated error arose primarily from the numerical integration. An error of 0.1 in I leads to a 10% error in n/N. We expect that the errors incurred in using the Lennard-Jones potential are not serious relative to the numerical error. The use of classical mechanics rather than quantum mechanics is also unimportant. Since the quantum Helmholtz free energy per particle exceeds the classical value by $(3/40)(h\nu_D/kT)^2kT$, where h is Planck's constant and ν_D is the Debye frequency, the effect of introducing quantum values for q would be to *decrease* the fraction of vacancies by 5%–10%. Thus our values should be expected to lie slightly above those for real crystals of argon and krypton.

TABLE III. Fraction of vacancies (n/N) found for crystals of argon and krypton using the experimental values for entropy and Monte Carlo values for internal energy, pressure, and the integral I. For comparison the entropies obtained from the Lennard-Jones–Devonshire cell model are also included. The estimated error in (n/N) is ±25%.

T (°K)	(n/N)	$(S^e/Nk)_{\text{expt1}}$	(S^e/Nk) LJD
Argon 60	0.0000027	−5.81	−6.13
Argon 80	0.00021	−5.24	−5.55
Krypton 83	0.0000025	−5.91	−6.13
Krypton 110	0.00019	−5.32	−5.55

IV. COMPARISON WITH EARLIER RESULTS

The results shown in Fig. 4 show that our estimates of the number of vacancies in rare-gas crystals lie below these found by most other investigators. In the experimental determinations of vacancy fraction, the danger is that the crystal specimens used contain defects other than vacancies. For this reason, Smith and Chapman[6] give their result for the vacancy fraction, based on comparing the actual and theoretical densities at the triple point as an upper bound, $(n/N)_{\text{SC}}<1/800$. Losee and Simons[8] predict a much higher vacancy fraction at the triple point, $(n/N)_{\text{LS}}=1/300$. They measure the distance between two markers in a krypton specimen as a function of temperature and compare this to the x-ray lattice spacing. In this exceedingly

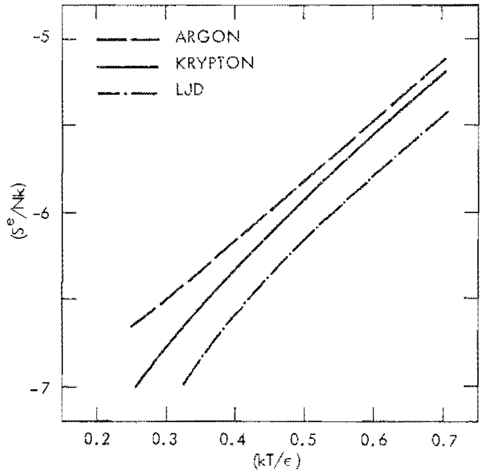

FIG. 3. Excess entropy (over a classical ideal gas at the same density and temperature) for argon, krypton, and the Lennard-Jones–Devonshire cell model. The curves for argon and krypton terminate at the triple point $kT/\epsilon \doteq 0.704$.

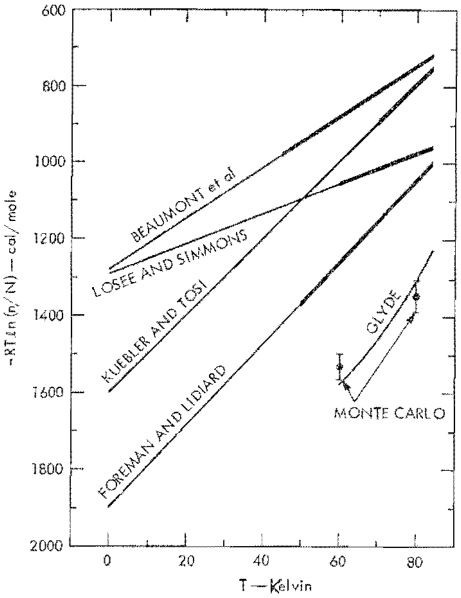

FIG. 4. The fraction of vacancies in argon as determined by various investigators. Our results, at 60° and 80°K, are the points shown. The straight lines, based on phenomenological ΔH's and ΔS's of vacancy formation, are terminated at the triple point.

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[16] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1449 (1961).

[17] E. G. D. Cohen, J. De Boer, and Z. W. Salsburg, Physica **23**, 389 (1957).

TABLE IV. Comparison of various estimates for the fraction of vacancies in argon at the triple point. The first three results given are based on comparing bulk and x-ray densities (Losee and Simmons' measurements were carried out on krypton; the results for argon were obtained using corresponding states). The next set of three results is based on extrapolating idealized low-temperature properties to high temperature, subtracting these from actual high-temperature results, and ascribing the difference to vacancies. The last two results, ours and Glyde's, come from calculations based on a Lennard-Jones pair potential appropriate to argon. Many investigators have supposed that $RT\ln(n/N)$ can be represented by a linear function of temperature. These expressions are also given below.

$(n/N)_{\text{triple point}}$	$RT\ln(n/N)$	Investigators
<0.0013	···	Smith and Chapman
0.0037	···	Van Witzenburg
0.0032	$2.0RT$—1290 cal	Losee and Simmons
0.0138	$3.4RT$—1280 cal	Beaumont *et al.*
0.0110	$5.1RT$—1600 cal	Kuebler and Tosi
0.0025	$5.4RT$—1900 cal	Foreman and Lidiard
0.00055	···	Glyde
0.0004	···	This work

difficult experiment the specimen is a grained rod of solid inert gas, not a single crystal, and it seems possible that this explains the large fraction of vacancies found by Losee and Simons. In all, we think that our results are consistent with the experiments so far carried out in that the experiments are expected to err on the side of too many vacancies.

Previous theoretical calculations have been of two kinds. The earlier ones of Beaumont *et al.*,[1] Foreman and Lidiard,[2] and Kuebler and Tosi[3] all relied on extrapolating a "perfect solid" property, either the entropy or the specific heat, from low temperature up to the triple point, and ascribing the differences found to the presence of vacancies. Since specific heat is a sensitive fluctuation quantity, a long extrapolation appears to us very risky. This was underlined by McGlashan[18] who managed to fit the observed specific heat curve for argon, all the way up to the triple point, with a simple potential and *no vacancies at all.*

The theoretical calculation coming closest to our results is Glyde's.[5] His fraction of vacancies (using *the same* potential function we used) agrees with ours within the statistical accuracy of our results. The temperature dependence we find for the fraction of vacancies appears to be slightly smaller than Glyde's.[19] Glyde assumes an Einstein model for the lattice containing a single vacancy, but includes relaxation corrections. This should be a vast improvement over any calculation based on low-temperature perturbation around a harmonic model, for at 80 kelvins the thermal part of the energy lies 10% below the harmonic prediction. The remarkable agreement with Glyde's calculation[19] is reassuring in view of the fact that he calculates six different contributions (assumed to be independent) to (n/N).

Most of the investigators so far mentioned define Gibbs free energy, enthalpy, and entropy for vacancy formation in a somewhat intuitive way. Although these quantities have no fundamental meaning and would be discarded when more accurate measurements reveal curvature (such as shown by Glyde's results) in a plot of $\ln(n/N)$ versus $1/T$, these phenomenological parameters are still of some interest and are shown in Table IV. The enthalpy of vacancy formation is the intercept of the plot in Fig. 3, while the entropy is the slope. It can be seen that the enthalpy for vacancy formation is reasonably close to the heat of sublimation for argon and krypton, at least according to our calculations. Losee and Simmons have pointed out that a large discrepancy between the two enthalpies would indicate strong many-body forces in the solid. It appears to us that at present ΔH is not well enough tied down to provide useful information on the magnitude of many-body forces in the crystal, except to say that they are not large.

We believe that our results are the most accurate ones based on the consequences of a given force law. Just how much error is introduced in our calculations by using a Lennard-Jones potential instead of solving the quantum-mechanical many-body problem exactly, none can say. The good agreement of the potential energies with those derived from experimental heats of sublimation (the discrepancy of about 40 cal/mole is about what one would expect from residual zero-point energy) suggests that the potential is useful in the range where we applied it. Since it is based on zero-degree data, the potential ought to be accurate throughout the solid phase for energy calculations. The bulk modulus for this potential, measured by Monte Carlo during the course of elastic-constant calculations,[20] agrees fairly well with the experimental values of Peterson *et al.*[4] We expect that the potential is also accurate for entropy since the discrepancy between experiment and Einstein model, 0.3 Nk, is in agreement with the calculated discrepancy between the Born–von Kármán entropy and the Einstein model, 0.25 Nk.[21]

In conclusion, we expect that the concentration of vacancies in the rare-gas solid is too small to have much impact on observable thermodynamic properties.

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[19] A more recent paper [H. R. Glyde and J. A. Venables, J. Phys. Chem. Solids **29**, 1093 (1968)] gives a smaller temperature dependence and a smaller estimate for (n/N) at the triple point, 0.0000755, along with the comment, "We expect (n/N) to be higher than this." Glyde and Venables' latest estimates do in fact lie somewhat below the lower uncertainty limit of our Monte Carlo calculations.

[20] D. R. Squire, A. C. Holt, and W. G. Hoover, "Elastic Constants for Argon. Theory and Monte Carlo Calculations," Physica (to be published).

[21] W. G. Hoover, J. Chem. Phys. **49**, 1981 (1968).