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THE GROUND STATE OF SOLID He^3 AND THE EXCHANGE INTERACTIONS BETWEEN NUCLEAR SPINS OF He^3

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Abstract

Of the published theories of solid He^3*, that of Saunders has been shown to give an a priori prediction of the exchange interaction in fairly good agreement with the experimental results. In this paper, we improve that theory in three ways: (1) by using the correct* He^3-He^3 *pair wave function, which is quite different from that used by Saunders; (2) by computing explicitly the single-particle projection of the many-body wave function, rather than replacing it with a Gaussian of equal curvature at the lattice site; and (3) by calculating the exchange integral J by numerical integration from the detailed wave function of (2), rather than by the use of a Gaussian. These changes do not make the agreement with observation significantly better, but, since the underlying theory has no very firm basis, these calculations should be regarded as an example of what is still required to calculate J if one has a good theory of the solid. As for properties other than the exchange interaction, in the case of the bcc phase we have calculated the Debye temperature as* $\theta = 26.0(V/20)^{-2.265}$*, to be compared with the experimental* $\theta_{exp} = 28.5(V/20)^{-2.50}$.

1. Introduction

SINCE both solid He^3 and He^4 have served as the subject of thorough intensive experimental work, it is of interest to compare the results with theoretical predictions; the more so because several of the experiments yield results peculiar to a quantum solid. A good theory of the solid would predict, among others, the following quantities:

(a) the lattice structure of the solid;

(b) the cohesive energy $\langle E \rangle$ of the solid, at least at 0°K, as a function of the molar volume V;

(c) for He^3, the exchange interaction between nuclear spins, as a function of V;

(d) the zero-point energy, i.e. the Debye temperature θ as a function of V.

Unfortunately, there exists no theory capable of predicting the cohesive energy to within a factor 2, and hence all the other desirable predictions are presumably similarly unavailable. This situation is in marked contrast with that for the other rare gas solids. For those, as well as for helium, we start with the same many-body Hamiltonian [1]:

$$\mathscr{H} = \sum_i T_i + \sum_{i>j} V(r_{ij}) \tag{1}$$

where T_i is the kinetic energy of the atom i, r_{ij} is the distance between atoms i and j, and $V(r)$ is the pair potential, which is usually taken of Lennard-Jones form:

$$V(r) = 4\ \varepsilon\ [(\sigma/r)^{12} - (\sigma/r)^{6}] \tag{2}$$

The minimum $-\varepsilon$ of the potential thus occurs at $r = \sigma(2)^{1/6}$. The potential depends only on the electronic configuration of the atoms and is therefore the same for both isotopes of helium: $\sigma = 2.556$ A and $(\varepsilon/k) = 10.22$°K.

The attractive term of this potential is the Van der Waals force; one could calculate the coefficient of this r^{-6} term, knowing the energy and the wave functions of the ground state and excited electronic levels of the individual atom. The mathematical form of the repulsive term has no theoretical justification and is somewhat arbitrary. The above-mentioned numerical values of ε and σ are calculated from measurements of the second virial coefficient. For helium, various investigators have sought theoretical expressions of the pair potential [2] which usually fit equation (2) fairly well at large distances but deviate from it at small distances and around the minimum.

If one neglects the kinetic energy of the ground state compared with the potential energy, which would be possible were the atomic mass m very large, the classical approximation to the ground state energy of a crystal of atoms interacting pairwise with the potential of equation (2) is:

$$E_{00} = \sum_{i>j} V(r_{ij}) \tag{3}$$

where the sum is taken over the lattice of assumed symmetry and lattice parameter. If the atomic mass is not infinite, then the next approximation involves the minimization of the total energy: the potential from equation (3), and the kinetic from the zero-point vibration of the atoms in the resulting (locally harmonic) potential wells.

In any case, having found the cohesive energy $<E>$ per atom as a function of V, the actual crystal symmetry and lattice spacing at 0°K for a given applied pressure P are those which correspond to the minimum value of the enthalpy H:

$$H = <E> + P\ V/A$$

the pressure P being given by:

$$P = -A\ d/dV <E>$$

A being the Avogadro number.

Hartree calculations [3] have been published for the noble gas crystals. These calculations compute the local potential near a lattice point, due to all other atoms, by integration over the atomic wave functions concentrated near the other lattice points. Given this (spherically-averaged) potential, the atomic wave function near the reference lattice point was calculated by numerical integration. This technique is equivalent to a true variational calculation over the set of *spherical* wave functions which contain no correlations between atoms and thus provides the lowest energy possible using such wave functions. The results are shown in Table 1. The energy calculated in this approximation for crystalline helium is very high compared with the measured value (see Appendix A); it is thus clear that the non-spherical nature of the atomic wave functions and the correlation of the atomic vibrations must be considered in any valid calculation of the ground state of solid helium.

TABLE 1

For different noble gas crystals, the second column gives the measured cohesive energy. The data for Xe, Kr, Ar and Ne are taken from reference 4. For He^3 and He^4 the experimental value of cohesive energy was found as explained in Appendix A, the values from reference 3 being in error. The third and fourth columns give the results of Hartree calculations made by L.H. Nosanow and G.L. Shaw [3], for cohesive and kinetic energies. One may note that solid He^4 has been found in face-centered-cubic form (β phase) only at very high pressure and temperature [5].

		Hartree Calculations	
	Experimental cohesive energy (cal/mole)	Calculated cohesive energy (cal/mole)	Calculated kinetic energy (cal/mole)
Xe	−3830 ± 50	−3830	+65
Kr	−2590 ± 50	−2630	+73
Ar	−1850 ± 12	−1859	+97
Ne	−450 ± 10	−431	+85
He^4 (fcc, $a \sim 3.7$ A)		+13.9	
He^4 (hcp, $a \sim 3.67$ A)	−12.2		
He^3 (bcc, $a \sim 3.8$ A)	−1.2	+34.5	+71.8

A different approach was taken by Saunders [1] (henceforth referred to as EMS). His calculation gives for the energy of the ground state of solid He^3 of minimum density $E_0 \sim 11$ cal/mole, which is not so close to the experimental value that one would have any confidence, *a priori*, in the exchange energy calculated from the wave functions which give such a poor value for the total energy. In fact even the sign of that energy seems wrong although the experimental cohesive energy of solid He^3 given in Table 1 may well be inaccurate, as explained in Appendix A. It was surprising, therefore, to find that recent measurements [6,7,8] of the exchange interaction in both body-centered-cubic (α) and hexagonal-close-packed (β) He^3 agreed fairly well with the results of EMS's theory. Figure 1 gives, versus the molar volume V in solid He^3, predictions of EMS concerning the exchange interaction $J/2\pi$, in units of frequency, together with the exchange interaction deduced from nuclear-magnetic-resonance measurements of references 6 and 7. The exchange interaction between nearest neighbors is defined as $\hbar J\, \mathbf{I}\cdot\mathbf{I}'$.

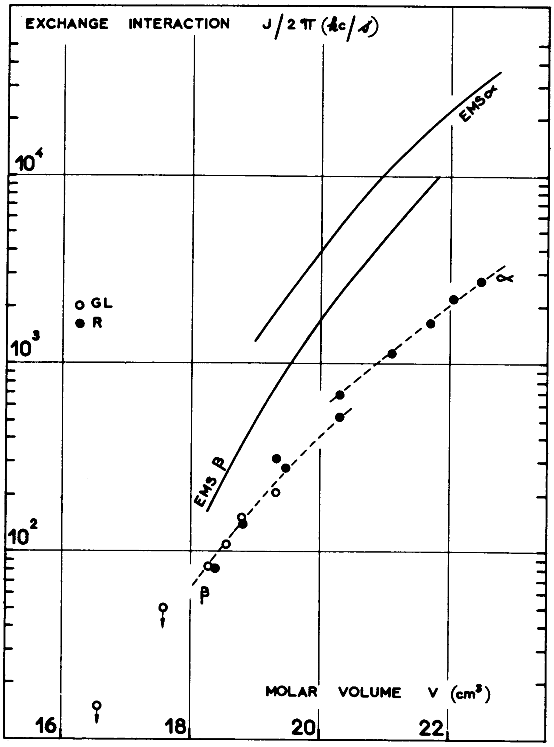

FIGURE 1

The exchange interaction $J/2\pi$, in kilocycles per second, versus the molar volume V in solid He^3, in α and β phases. The solid lines are predictions from Saunders' theory (see reference 7 for details of numerical calculations). The circles give values of the exchange interaction deduced from measurements of nuclear resonance linewidth (open circles: measurements of reference 7; solid circles: measurements of reference 6).

It is apparent that EMS has predicted the trend of the exchange interaction with density and even its absolute magnitude, with no adjustable parameters in his theory; and he has done this to an accuracy of a factor 2 to 10, i.e. he has calculated $\ln(\hbar J/|<E>|) \approx -11$ to an accuracy 10%. This is all the more remarkable because none of the results were available to EMS before his theory was published. Since EMS's theory was so good in calculating J, we studied it carefully with a view to improving it where possible. The rest of this paper is a critique of this theory and a presentation of some calculations we made in attempting to further EMS's stated program. Even when the theory is supplanted by a better one, our calculations of J may still be of some use in indicating a transparent method of calculation of certain consequences of the theory.

2. Review of Saunders' Theory

A reference to this theory is essential to an understanding of the present paper. EMS starts from the Hamiltonian given by equation (1), assumes that the exchange interaction is weak and takes into account correlations by looking for an approximate wave function of the following form:

$$\Psi = A \Pi_i \Phi_i(\mathbf{r}_i) \Pi_{i>j} \chi_{ij}(r_{ij}) \tag{4}$$

A is the permutation operator for Fermi statistics, in the case of He^3.

$$r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$$

Strictly speaking, the wave function Ψ should include functions of spin coordinates, though one may drop those for the moment, as long as one assumes the exchange interaction is weak. Using the Pluvinage method, EMS shows one can treat the r_{ij} as independent variables, on the same footing as the $\mathbf{r}_j$, dividing the Hamiltonian $\mathscr{H}$ into three parts:

$$\mathscr{H} = \mathscr{H}_0^1 + \mathscr{H}_0^2 + \mathscr{H}' \tag{5}$$

$$\mathscr{H}_0^1 = \Sigma_i (-\hbar^2/2m)\ \nabla_i^2 \tag{6}$$

$$\mathscr{H}_0^2 = (\hbar^2/m\sigma^2)\ \Sigma_{i>j} \left\{ -(\sigma/r_{ij})^2 \frac{\partial}{\partial r_{ij}} r_{ij}^2 \frac{\partial}{\partial r_{ij}} + (B/4\varepsilon) V(r_{ij}) \right\} \tag{7}$$

where $B \equiv 4m\sigma^2\varepsilon/\hbar^2$ (for He^3 $B = 16.60$; for He^4 $B = 22.2$). Provided $\mathscr{H}'$ (which is an operator containing both the r_{ij} and the $\mathbf{r}_i$) can be considered as a small perturbation, which is one of EMS's assumptions eventually to be justified afterwards, it is easy to find the functions $\Phi_i(\mathbf{r}_i)$ and $\chi_{ij}(r_{ij})$. The first, given by the Hamiltonian $\mathscr{H}_0{}^1$, are obviously standing waves. The second are given by the Hamiltonian $\mathscr{H}_0{}^2$:

$$\left\{ -(\sigma/r_{ij})^2 \frac{\partial}{\partial r_{ij}} r_{ij}^2 \frac{\partial}{\partial r_{ij}} + (B/4\varepsilon) V(r_{ij}) \right\} \chi_{ij}(r_{ij}) = (m\sigma^2/\hbar^2) E_{ij}(r_{ij}) \tag{8}$$

The function $\chi_{ij}(r_{ij})$, which can just as well be written $\chi(r_{ij})$, represents the correlations between particles i and j; an obvious limit condition for the solution of equation (8) is then:

$$\lim_{r\to\infty} \chi(r) = 1 \tag{9}$$

Were it not for this unusual limit condition, equation (8) would be the Schrodinger equation for the relative motion of two particles of mass m interacting with the potential (2). Evidently condition (9) can be fulfilled only if

$$E_{ij} = 0$$

Assuming the He^3 are well enough localized for a lattice site to be ascribed to every atom, EMS then shows that the single-particle probability density for atom i can be written as:

$$\gamma(i) = (\text{const})\ \pi_{k\neq i}\ \chi^2(u_{ik}) \tag{10}$$

u_{ik} being the distance from the lattice site k to atom i. Around the lattice site i, the single-particle density can be expanded as:

$$\gamma(i) = (\text{const}) \left\{1 - \frac{1}{2\sigma^2} \mathbf{r}_i \, G \, \mathbf{r}_i + \ldots\right\} \tag{10'}$$

G being a dimensionless diagonal three-by-three matrix, the elements of which are proportional to the second derivatives of $\gamma(i)$ at the origin. In the neighborhood of lattice site i, $\gamma(i)$ behaves as

$$\exp \left\{- \frac{1}{2\sigma^2} \mathbf{r}_i \, G \, \mathbf{r}_i\right\}$$

and EMS assumes that $\gamma(i)$, when properly normalized, is given in the whole space by:

$$\gamma(i) = \varphi_i^*(\mathbf{r}) \; \varphi_i(\mathbf{r}) = \sigma^3\{8\pi^3/||G||\}^{½} \exp \left\{- \frac{1}{2\sigma^2} \mathbf{r}_i \, G \, \mathbf{r}_i\right\} \tag{11}$$

where $||G||$ is the determinant of the matrix G, in our case the product of its diagonal elements. Equation (11) defines φ, which is assumed to be real. Making use of the probability density (11), EMS computes the total energy per atom for the ground state (cohesive energy):

$$<E> = 1/3 \int \varphi_i^* \, (\mathbf{r}) \left\{- (\hbar^2/4m) \; \nabla^2\right\} \; \varphi_i(\mathbf{r}) \; d^3 \, \mathbf{r} = (\hbar^2/24m\sigma^2) \; tr \; G \tag{12}$$

where tr G is the sum of the diagonal (only) elements of G.

The matrix elements of G are in fact very easy to calculate. For a given direction $\mathbf{r}_i$, equation (10′) can be written as:

$$\gamma(i) \sim (\text{const}) \; (1 - \delta^2 \, \mathbf{r}_i^2 + \ldots) \tag{13}$$

the vector $\mathbf{r}_i$ being taken with respect to the lattice site i. The single-particle density parameter δ^2 is given by:

$$\delta^2 = - \Sigma_{k \neq i} \; g(R_{ik}) \; \frac{1 - \cos^2 \theta_{ik}}{2} \tag{14}$$

where R_{ik} is the distance between lattice sites i and k, θ_{ik} is the angle between the vectors $\mathbf{r}_i$ and $\mathbf{R}_{ik}$, and the function $g(r)$ is related to the correlation function

$$g(r) = (\frac{1}{r} + \frac{1}{2} \frac{d}{dr}) \; (\frac{2}{\chi}) \; \frac{d\chi}{dr} = r^{-2} \; \frac{d}{dr} \; r^2 \; \frac{d}{dr} \ln \chi \tag{14'}$$

In the case of a cubic lattice, for all the shells of atoms surrounding a given atom i, the average value of $\cos^2\theta_{ik}$ is 1/3 and equation (14) becomes:

$$\delta^2 = - \frac{1}{3} \; \Sigma_{k \neq i} \; g(R_{ik}) \tag{15}$$

the matrix G being then just the constant $2\delta^2\sigma^2$. For the hcp lattice, equation (15) is not valid and the single-particle parameter δ^2 could be anisotropic. It turns out that $\gamma(i)$ departs from isotropy only by about 3% in the very neighborhood of the origin lattice site i and that equation (15) is then a very good approximation, even for the hcp lattice. Equation (12) then gives for both lattices:

$$<E> = (\hbar^2/4m)\ \delta^2 \tag{16}$$

The exchange interaction J is given by a procedure very like the Heitler-London model, which ascribes to a pair of He^3 atoms (1 and 2) located around two nearest-neighbor lattice sites (i and j) a wave function

$$\Psi_\eta = (1/\sqrt{2})\ \left\{\varphi_j(\mathbf{r}_1)\varphi_i(\mathbf{r}_2) + \eta\varphi_j(\mathbf{r}_2)\varphi_i(\mathbf{r}_1)\right\} \tag{17}$$

the individual orbitals $\varphi_i(\mathbf{r})$ being taken as:

$$\varphi_i(\mathbf{r}) = \text{const}\ \pi_{k\neq i}\ \chi(u_{ik}) \tag{18}$$

the constant in equation (18) being adjusted so that:

$$\int |\varphi_i(\mathbf{r})|^2\, d^3\mathbf{r} = 1 \tag{19}$$

and the parameter η being +1 or −1 when the pair is in singlet or in triplet spin state. EMS then finds for J the following expression:

$$\hbar J = 2E - 2\Delta <E> \tag{20}$$

where

$$E = \frac{1}{3}\int \varphi_j^*(\mathbf{r}_1)\varphi_i^*(\mathbf{r}_2)\ \left\{-\frac{\hbar^2}{2m}\ (\nabla_1^2 + \nabla_2^2)\right\}\ \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)\ d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \tag{21}$$

$$\Delta = 2\ \left\{\int \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})d^3\mathbf{r}\right\}^2 \tag{22}$$

provided the overlap of orbitals φ_i and φ_j is weak, i.e. the quantity Δ is small enough.

EMS makes again the same Gaussian assumption and replaces in these equations $\varphi_i(\mathbf{r})$ by $\gamma(i)^{1/2}$, using equation (11).

Finally, all the properties of the ground state of solid He^3 are contained in the knowledge of the correlation functions $\chi(r)$ and the remaining problem is to solve the following differential equation:

$$-(\sigma/r)^2\ \frac{d}{dr}\ r^2\frac{d\chi}{dr} + B\ \left\{(\sigma/r)^{12} - (\sigma/r)^6\right\}\ \chi = 0 \tag{23}$$

Thus far we have but sketched EMS' theory and his procedure. For a full discussion, see ref. 1.

3. Modifications to Saunders' Theory

I. The pair wave function

(a) Using the reduced variable $s \equiv (r/\sigma) \equiv q^{-1}$, equation (22) can be written:

$$-\frac{1}{s}\frac{d^2}{ds^2}(s\chi) + B\chi(s^{-12} - s^{-6}) = 0 \tag{23'}$$

Following EMS, let us call F_0 and (F_1/s) two independent solutions for that differential equation, with the following asymptotic expansions [9] when $s \to \infty$:

$$F_0 = -(B/12s^4) + (B^2/672s^8) + (B/90s^{10}) + \ldots + Cn/s^n + \ldots \tag{23a}$$

$$F_1 = 1 - (B/20s^4) + (B^2/1440s^8) + (B/110s^{10}) + \ldots + Dn/s^n \ldots \tag{23b}$$

$$C_n = \frac{B}{n(n-1)}(C_{n-10} - C_{n-4}) \qquad D_n = \frac{B}{n(n+1)}(D_{n-10} - D_{n-4})$$

The most general solution of equation (23) satisfying condition (9) is then:

$$\chi(s) = F_0 + (C_1/s)F_1 \tag{24}$$

On the grounds that the term $(C_1/s)F_1$ gives an outgoing flux at large distances, an unsatisfactory characteristic which cannot be permitted in Ψ'', EMS chooses $C_1 = 0$, which argument we believe to be in error. (In any case, a sufficient condition for zero outgoing flux is that C_1 be real.) A detailed analysis of equation (23') [9] shows that $F_0 \to -\infty$ for $s = (r/\sigma) \to 0$, which is indeed inadmissable. EMS arbitrarily cuts his correlation function to zero when $r \leqslant \sigma$. With such a correlation function we can compute [10] the density parameter δ^2, as explained in Section 2, for various lattice structures: α, β, and γ (face-centered cubic), then the cohesive energy, by means of equations (15) and (16). Figure 2 shows the results of these calculations. In Section 2, we explained how to compute the exchange interactions by means of EMS's theory, the results of which computation are summarized by the solid lines of Fig. 1.

(b) As was just suggested, we disagree with EMS's correlation function. Since the Lennard-Jones potential becomes infinite for small distances, we shall choose the coefficient C_1 of equation (24) by the condition that $\chi(0) = 0$. Numerical integration detailed in Appendix B provides us directly with this correlation function, for which C_1 turns out to be 2.369 [9]. That function, henceforth simply referred to as χ, is shown in Fig. 3, together with the function $F_0(s)$. It is seen that in using F_0 instead of χ, one greatly reduces the range of correlation and that χ has a maximum $\chi = 2.104$ for $s = (r/\sigma) = 1.64$. The meaning of this maximum is discussed in Appendix B; it is evidence of a trend to have a bound pair of atoms when the parameter B in equation (23) is increased. If the mass of He^4 were 1% greater, there would be a bound system for two atoms of He^4, assuming the accuracy of the potential of equation (2). The increased trend to make bound states between two He^4 atoms may account for the phase separation observed at low temperature in solid He^3-He^4 mixtures [12].

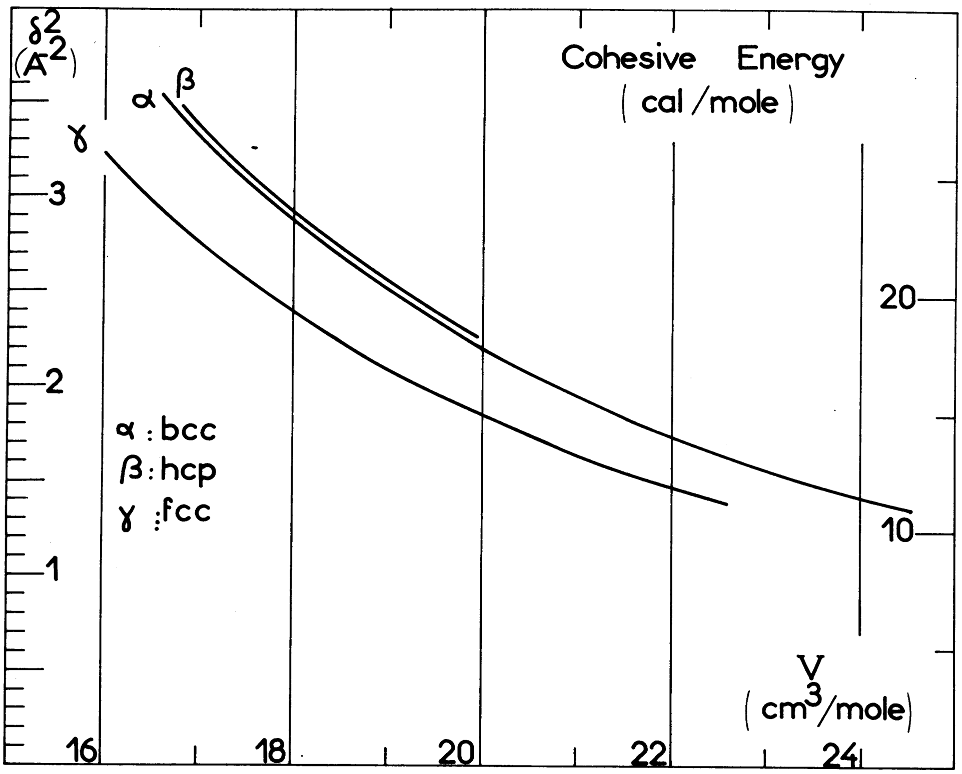

FIGURE 2

The single-particle density parameter δ^2 (left scale) versus molar volume V, for various lattice structures, obtained with Saunders' correlation function F_0. The maximum molar volume of solid He^3 [11] is $V \sim 24.8$ cm^3/mole. These curves are the results of numerical calculations detailed in reference 1 and in note 15 of reference 7. The cohesive energy can be read from the curves by the use of the right-hand scale.

2. *The single-particle density*

We have shown in Section 2 how EMS replaces the true single-particle density $\gamma(\mathbf{r}_i)$ given by equation (10) by the Gaussian having the same curvature at the origin. This might possibly give a reasonable approximation to the total energy, but the exchange interaction is very probably considerably altered by the arbitrary specification of the form of γ.

In order to eliminate unnecessary approximation, we have calculated γ directly from equation (10), by actual multiplication of the pair wave-functions $\chi(u_{ik})$. In Fig. 4, γ is shown along a line $\underline{a}$ joining nearest neighbors in the basal plane of the hcp lattice and also along a line $\underline{b}$ perpendicular to $\underline{a}$. In this figure, $\gamma(r_i)$ has been normalized so that $\gamma(0) = 1$. The method of numerical calculation is presented in Appendix C, since the values of γ are used also in the calculation of exchange interaction J, as a function of molar volume and crystal structure.

Figure 4 shows that not only the Gaussian approximation is very poor far from the origin but that the single-particle density is not isotropic and is not even a monotonic function.

We then computed the cohesive energy by means of equation (12). To do this we used an IBM 7094 computer to find the second derivatives, thus the G matrix for the single-particle density

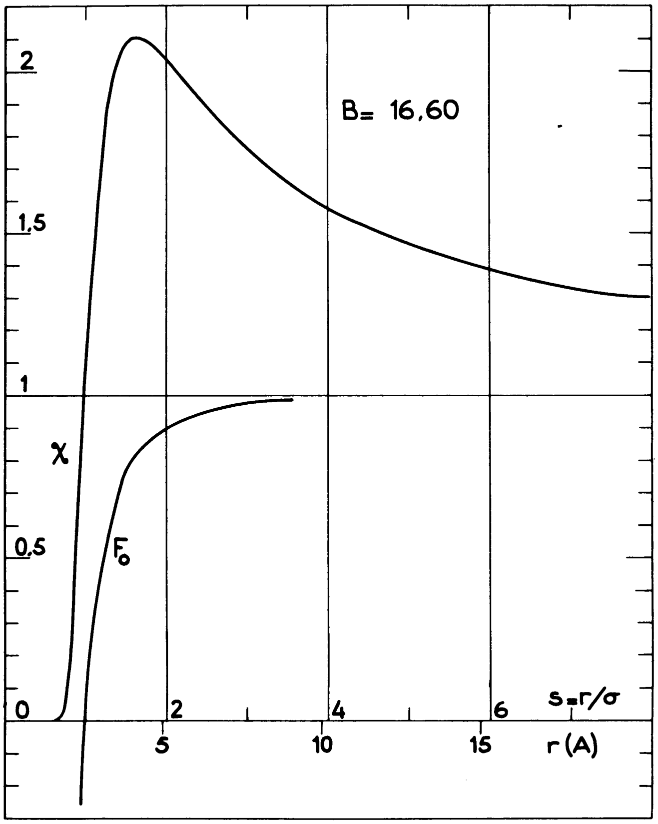

FIGURE 3

The correlation function χ is plotted against interatomic separation r. χ goes to zero for zero interatomic separation. F_0 is one special solution for equation (23), used as a correlation function by Saunders and referred to as χ in Figure 1 of reference 1.

γ given by equation (10) and shown on Fig. 4. The results of these calculations are exhibited in Table 2, for both bcc and hcp lattices.

We then tried a mean-square fitting of these results to the following analytical expression:

$$<E> = (\hbar^2/24m\sigma^2)\ \{T - (V/V_0) + (1/\mu)(V_1/V)^{\mu}\} \tag{25}$$

which was possible with a root-mean-square deviation of the order of 10^{-4} $<E>$. Equation (25) was chosen because it makes it very easy to calculate the compressibility K:

$$1/K = A\,V\frac{\partial^2}{\partial V^2} <E> = A(\hbar^2/24m\sigma^2)(1 + \mu)\ (1/V_1)(V_1/V)^{\mu+1} \tag{26}$$

and thus to predict the variation of the Debye temperature θ with molar volume, i.e. the Gruneisen coefficient:

$$\Gamma = -d \ln \theta/d \ln V = 1/3 + \mu/2 \tag{27}$$

In the case of the bcc lattice, assumed elastically isotropic and assumed to obey the Cauchy

TABLE 2

For bcc and hcp lattice structures, the molar cohesive energy $A\langle E\rangle$ is given for various molar volumes; it has been calculated using the pair wave function χ shown by Fig. 3. A is the Avogadro number. These results for cohesive energy have been fitted to an analytical form:

$$\langle E\rangle = (\hbar^2/24\, m\sigma^2)\ [T - (V/V_0) + (1/\mu)(V_1/V)^{\mu}]$$

where μ is related to the Gruneisen coefficient:

$$\Gamma = (1/2)\mu + 1/3 \quad .$$

The coefficients Γ, T, V_0, V_1 are given for both lattice structures.

	bcc Lattice		hcp Lattice	
	Molar volume V(cm^3/mole)	Cohesive energy $A\langle E\rangle$ (cal/mole)	Molar volume V(cm^3/mole)	Cohesive energy $A\langle E\rangle$ (cal/mole)
	20.12	14.37	17.80	17.99
	21.10	13.19	18.55	16.52
	21.70	12.55	19.30	15.29
	22.05	12.20	20.70	13.47
	22.48	11.79		
Grüneisen coefficient Γ	2.265		2.518	
T	100.7		76.39	
V_0(cm^3)	0.4036		0.6985	
V_1(cm^3)	61.60		57.11	

relations, it is even possible to calculate the Debye temperature itself:

$$\theta = \theta_0(V/V_1)^{-\Gamma} = 26.0\ (V/20.0\ \mathrm{cm}^3)^{-2.265} \qquad (28)$$

where

$$\theta_0 = (2/B)(\varepsilon/k)(6\pi^2 A\sigma^3/V_1)^{1/3} \left(\frac{3}{1+\sigma\sqrt{3}}\right)^{1/3} \sqrt{\frac{3(1+\mu)}{10}} \qquad (28')$$

The result of equation (28) is to be compared with the experimental results [13] which can be written as:

$$\theta = 28.5 \qquad (V/20.0\ \mathrm{cm}^3)^{-2.50}$$

The good agreement of the Debye temperature given by equation (28) must be considered as somewhat fortuitous, considering the implausibility of the Debye theory of thermal vibrations in solid He^3.

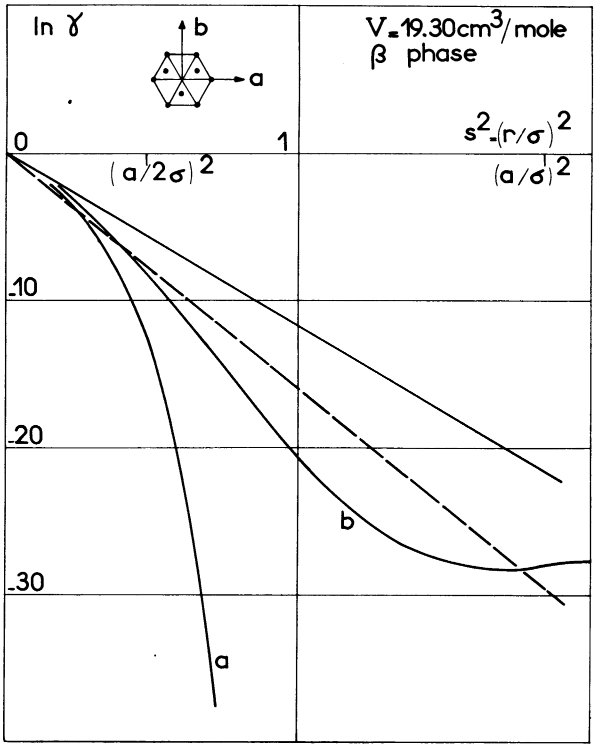

FIGURE 4

The logarithm of the single-particle probability density of solid He^3 in β phase (V = 19.30 cm^3/mole) versus the reduced square distance from the origin lattice site $s^2 = (r/\sigma)^2$. The single-particle density is normalized so that $\gamma(0) = 1$. The curve a is along a line a joining nearest neighbors in the basal plane. The curve b is along a line b perpendicular to a and in the direction shown in the upper left of the figure. The solid straight line is a Gaussian $\ln\gamma \doteq -\delta^2 r^2$, where the parameter δ^2 has been calculated using equation (16) and Table 2: $\delta^2 = (4m\,\langle E\rangle/\hbar^2) = 1.91\ A^{-2}$. The dashed straight line is a Gaussian with δ^2 taken from Saunders' theory (Fig. 2): $\delta^2 = 2.448\ A^{-2}$.

As for the hcp lattice, the only possible comparison still to be made is that of the experimental [13] Gruneisen coefficient equal to 2.50 with that given by Table 2, since the Cauchy relations do not hold when the lattice sites are not centers of symmetry for the crystal.

3. *Calculation of the exchange interaction*

As usual we shall only consider the exchange interaction between nearest neighbors. In β phase, if the wave functions of the atoms in the crystal are not spherically symmetric, there are two different values for that interaction according to whether the two nearest neighbor atoms are in the same basal plane or not. In the first case the vector joining them is a translation vector for the hcp lattice, while in the second case it is not; all nearest neighbors of a given atom are then not equivalent. Although one really measures some kind of average exchange, from the theoretical point of view this is indeed a complication which does not arise in the case of a bcc lattice (α phase).

Let us assume two atoms numbered i and j, the probability densities of which are centered around two nearest neighbor lattice sites A and B. What we need is to compute the two quantities E and Δ which enter equation (20) giving the exchange interaction. For both quantities we propose to use the following method (method of "steepest descents"), very similar to the one EMS used, except for the fact that he only applied it to the total energy $\langle E \rangle$ of the system and not for Δ or E. These quantities are given by the integration over the whole space of some integrand which presents a small number of very sharp maxima (equivalent under the lattice symmetry). We shall assume that the main contribution to such an integration comes from the neighborhood of these maxima and we shall fit the integrand to a Gaussian which has the same curvature at the maximum.

Suppose we want to calculate:

$$K = \int I(\mathbf{r})\ d^3\mathbf{r} \tag{29}$$

and we know $I(\mathbf{r})$ has one maximum at $\mathbf{r} = \mathbf{r}_0$ around which it can be expanded as:

$$I(\mathbf{r}) = I_{\max} \{1 - 1/2\sigma^2(\mathbf{r} - \mathbf{r}_0)\ G\ (\mathbf{r} - \mathbf{r}_0) + \dots \} \tag{30}$$

We replace in equation (29) the integrand by:

$$I(\mathbf{r}) = I_{\max} \exp \{ - 1/2\sigma^2(\mathbf{r} - \mathbf{r}_0)\ G\ (\mathbf{r} - \mathbf{r}_0)\} \tag{31}$$

which yields:

$$K = \sigma^3\ I_{\max}\ \sqrt{8\pi^3 / \|G\|} \tag{32}$$

The first quantity to calculate by this procedure is really the constant on the right-hand side of equation (18) in order to satisfy the normalization condition of equation (19), which constant we shall write as $(K_3)^{-1/2}$ · K_3 is defined as:

$$K_3 = \int \pi_{k \neq i}\ \chi^2(u_{ik}) d^3\mathbf{r} \tag{33}$$

and calculated by the standard method just explained. It is shown in Appendix C how we computed numerically the maximum of the integrand on the right-hand side of equation (33). As for its G matrix, it is really a constant and was already computed for the calculation of the cohesive energy described in the second part of this Section.

The quantity E, given by equation (21), can easily be seen to be the major contribution to J; we can separate the integrations on the variables of the two atoms and write:

$$E = -(\hbar^2/3m)(K_1K_2/K_3) \tag{34}$$

K_1 and K_2 being defined as follows:

$$K_1 = \int \pi_{k\neq i}\ \chi(u_{ik})\ \pi_{k\neq j}\ \chi(u_{ik})d^3\mathbf{r} \tag{35}$$

$$K_2 = \int \pi_{k\neq i}\ \chi(u_{ik})\ \nabla^2\pi_{k\neq j}\ \chi(u_{ik})d^3\mathbf{r} \tag{36}$$

In order to calculate these integrals by "steepest descents" the maxima of the integrands are calculated by an automatic maximization routine on the IBM 7094, the "Variable-Metric Method" [14]. To find the maximum of some integran $I(\mathbf{r})$ (like those of equations (35) and (36)), using the procedure of Appendix C to calculate the single-particle density $\gamma(\mathbf{r}_1)$ at an arbitrary point of a crystal of given molar volume, the program calculates the value ln $I(\mathbf{r})$ for a given $\mathbf{r}$, computes also the gradient of ln $I(\mathbf{r})$ and then extrapolates in a sophisticated manner to locate the maximum I_{max}. A byproduct of the procedure is the G matrix (Hessian matrix). Indeed, that maximum is not unique, either for the integrand of K_1 or for that of K_2. The number of the maxima, which are found equivalent, can be accounted for by considerations of symmetry and

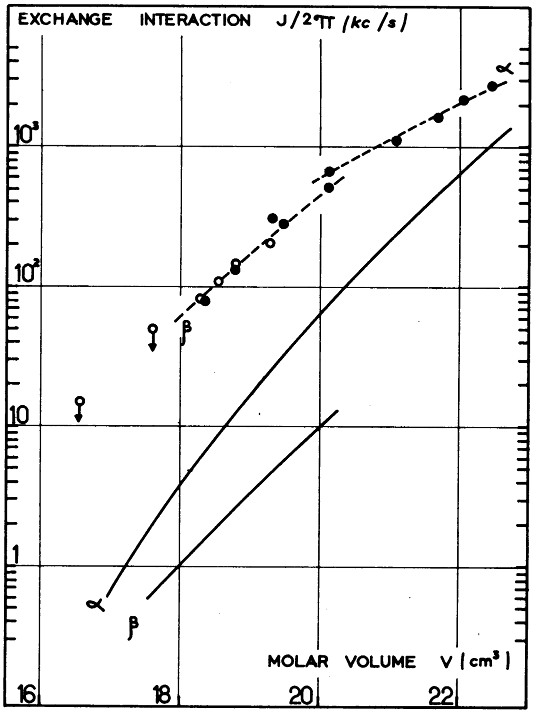

FIGURE 5

The exchange interaction $J/2\pi$, in kilocycles per second, versus the molar volume V in solid He^3, in α and β phases. The solid lines are the results of the calculations presented in this paper. The circles are experimental points for the exchange interaction, the same ones as on Fig. 1.

happens to be 6 for bcc lattice and 2 for hcp lattice, for K_1 or K_2. We then multiply the contribution to the integral from one maximum by this multiplicity factor.

These calculations were made for both hcp and bcc lattice structures and various molar volumes. They are summarized by the solid curves of Fig. 5 which give the resulting exchange interaction $J/2\pi$ between nearest neighbors, versus molar volume for both lattice structures. For the hcp phase, the calculation was made for both kinds of nearest neighbor of a given atom. It was found that the exchange interaction with the second kind of neighbor (out of the basal plane) is 5 to 9% larger than the interaction with the first kind of neighbor (in the basal plane). This difference being rather small, the average of the two exchange interactions was plotted for hcp phase on Fig. 5.

Comparison of our results with those of EMS, given by Fig. 1, shows that ours are not closer to the experimental results than his, although ours seem to be systematically smaller and his systematically larger. Still we must point out that we tried to use our correlation function χ (Fig. 3) with EMS procedure of using the Gaussian probability density (11) in the whole space and found exchange interactions larger than those we found and showed on Fig. 5 by 2, 3, or 4 orders of magnitude.

4. Conclusion

The Pluvinage method extensively used in this paper, just as in reference 1, should be completed by an estimation of the mean value of the "perturbation term", i.e. of the part $\mathscr{H}'$ of the total Hamiltonian (see equation (5)). EMS, using the function F_0 (Fig. 3) as a correlation function, found the mean value $<\mathscr{H}'>$ to be of the same order as the cohesive energy $<E>$. Using our correlation function χ, we too found $<\mathscr{H}'>$ to be comparable with $<E>$, and possibly somewhat larger. This is obviously an indication of a major weakness of our calculations, which, however, do present two advantages.

First, we concentrate on calculating the exchange interactions and for that purpose we studied the wings of the wave functions, the only regions which contribute significantly to the exchange interaction. Our procedure may be valuable even when abandoning the Pluvinage and Saunders method.

Then we must point out that the theoretical problems generally concerning the mixtures of little He^3 and He^4 have still received no attention [33]: phase separation [12], anomalour exchange heat capacity [7,8,15,16], diffusion of an atom of one isotope through a crystal either of the same one or of the other one. We feel that EMS's method, as we have modified it, which involves comparatively simple calculations, could perhaps be extended to treat these problems more easily than other theories of solid helium.

A recent theory of L.H. Nosanow [17,18] attempts to find a many-body wave function analogous to that of equation (4), except for the fact that the one-particle wave functions $\Phi(\mathbf{r}_i)$ are localized functions rather than standing waves. His correlation function presents a maximum and has the qualitative behavior of ours, though with a shorter range. To progress in his variational calculation with the many-body function as a trial function, Nosanow assumes one is allowed to make a cluster expansion. A quantitative estimation [19] of the error made in such an expansion appears to be very delicate.

As for solid He^4, Saunders' theory is completely inadequate, because of the enormous amplitude of the correlation function of Fig. 6, due to the vicinity of a bound state for a He^4-He^4

pair. An attempt to use it yields a cohesive energy of several thousand calories per mole (and positive, of course), a ridiculous figure.

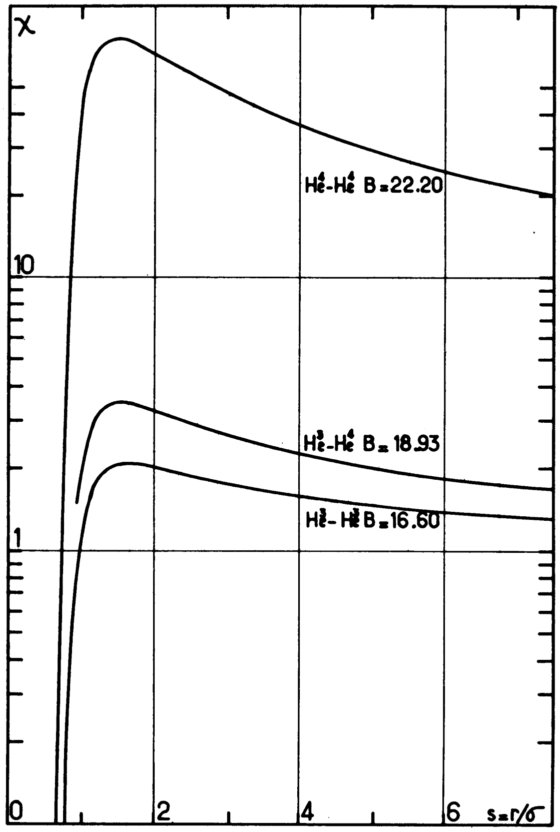

FIGURE 6

The correlation function χ, solution for equation (23), for different values of the parameter $B = 4\, m\sigma^2\varepsilon/\hbar^2$: $B = 16.60$ (He^3-He^3 pair); $B = 18.93$ (He^3-He^4 pair); $B = 22.20$ (He^4-He^4 pair).

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APPENDIX A

The Experimental Value for the Cohesive Energy of Helium

The cohesive energy is the energy to be supplied to atoms at infinite mutual distance (i.e. at zero pressure) in order to have solid at 0°K of given density. Let us call E_0 the cohesive energy of solid helium of minimum density at 0°K, i.e. of the solid in presence of liquid.

$$E_0 = -\Delta H_v(0) + W_c(0) + W_m(0) \qquad \text{(A1)}$$

The positive quantity $\Delta H_v(T)$ is the heat of vaporization of the liquid at temperature T. $W_c(T)$ is the work to be supplied to liquid taken at vaporization pressure $P_v(T)$ to compress it isothermally to melting pressure $P_m(T)$: The melting work $W_m(T)$ is given by:

$$W_m(T) = P_m(T) \times \Delta V_m(T) \qquad (A2)$$

$\Delta V_m(T)$ being the volume change on melting at constant temperature T. Extrapolating to 0°K the quantities $\Delta H_v(T)$, $W_c(T)$, and $W_m(T)$ one gets the quantities entering equation (A1).

(a) Cohesive energy of He^3. The heat of vaporization extrapolated to 0°K is [20]:

$$\Delta H_v(0) = 5.05 \text{ cal/mole} = 2.54°\text{K/atom}$$

The density of liquid He^3 has been measured as a function of pressure and temperature down to 0.1°K [21,22]. Data of references 21, 23, and 24 enable us to calculate:

$$W_c(0.1°\text{K}) = 1.424°\text{K/atom}$$

which we assume to be little different from $W_c(0)$. The melting pressure and the volume change on melting have been measured down to 0.03°K [11]; these measurements enable us to calculate $W_m(T)$ which is a monotonic function increasing when T decreases down to 0.03°K and exptrapolating to $W_m(0) = 0.521$°K/atom. For solid He^3 at minimum density at 0°K ($V \sim 24.8$ cm^3/mole [11], the nearest neighbor distance being a $\sim$ 3.77 A if the structure is still body-centered cubic), the cohesive energy is then:

$$E_0 = -0.6°\text{K/atom} = -1.2 \text{ cal/mole}$$

(b) Cohesive energy of He^4. The heat of vaporization extrapolated to 0°K is found in reference 25:

$$\Delta H_v(0) = 59.50 \text{ J/mole} = 7.313°\text{K/atom}$$

The density of liquid He^4 has been measured down to 1.5°K [26] below which temperature it does not seem to vary further with temperature. The compression work then extrapolates to to 1.28°K and extrapolates to $W_m(0) = 0.62$°K. For solid He^4 at minimum density at 0°K ($V \sim$ 21 cm^3/mole [28], the nearest-neighbor distance in that hexagonal-close packed crystal being a $\sim$ 3.67 A), the cohesive energy is then:

$$E_0 = -6.1°\text{K/atom} = -12.2 \text{ cal/mole}$$

very close to the experimental value quoted in reference 29.

It is hard to make an estimate of the error in this procedure. In the case of He^3, E_0 appears as the difference between quantities considerably larger than E_0, which weakens the result, the more so since the melting curve of He^3 is still expected to have a maximum [30] below 0.03°K.

APPENDIX B

Numerical Calculation of the Correlation Function

Writing $\chi(r) \equiv [\Psi(r)/r]$, equation (23′) becomes:

$$\frac{d^2\Psi}{ds^2} - B\Psi(s^{-12} - s^{-6}) = 0 \tag{B1}$$

For $s \ll 1$, $\Psi(s) \to 0$. The solution to equation (B1) is thus indistinguishable except by a constant factor from that for

$$\Psi''(s) - Bw(s)\ \Psi(s) = 0 \tag{B2}$$

with $w(s) = s^{-12} - s^{-6} \qquad s \geqslant s_0$

$w(s) = \infty \qquad s < s_0$

and with $\Psi(s_0) = 0$ and $\Psi'(s_0) = 1$ for some particular $s_0 \ll 1$, i.e. the same problem with the Lennard-Jones potential supplemented by a (non-physical) hard core, within some distance $s_0\sigma$. We have taken $s_0 = 0.500$, ($V(0.5\ \sigma) = 16128\ \varepsilon$), and calculated by a Runge-Kutta integration, obtaining and storing on punched cards for several values of B: s, χ, $\ln \chi$ and the dimensionless quantity $\sigma^2 g(r)$, where $g(r)$ is given by equation (14′) and is utilized in equations (14) and (15). This was done for several values of B as is shown by Fig. 6 giving versus s the correlation function χ for $B = 16.60$ (He^3-He^3 pair), $B = 18.93$ (He^3-He^4 pair) and $B = 22.20$ (He^4-He^4 pair). For large s it is evident from equation (B1) that $\Psi = k(s + C_1)$, where $+ C_1$ is the "zero-energy scattering length". A bound state at zero energy occurs [31] for $C_1 \to \infty$, which arises for $B = 22.3$. This value for B means that a pair of helium atoms of mass exceeding 4.049 a.m.u. will be bound in a molecule. Thus the Lennard-Jones potential (equation (2)) implies a very large resonant scattering cross-section for He^4-He^4 collisions at low energy.

For rare gases heavier than helium, the parameter B is much larger and one might look for evidence of diatomic molecules of these gases. The binding energy of such molecule would be at most of the order of ε, thus weaker by many orders of magnitude than the usual binding energies of covalent molecules. Nuclear-magnetic-resonance studies of Xe^{129} in xenon gas [32] have indeed shown that the observed values of spin-lattice relaxation times are well accounted for, for various densities, by the assumption that during collisions two atoms get sufficiently close to interact and form a diatomic xenon system in which the chemical shift of Xe^{129} is different from what it is in an isolated atom. For xenon, the depth of the Lennard-Jones well is $\varepsilon/k = 226°K$; it is then not surprising that the diatomic system is highly labile and transient in the above-mentioned experiments, made between 201°K and 273°K.

APPENDIX C

Calculation of the Single-Particle Density

We want to compute

$$\gamma(\mathbf{r}_1) = \prod_{k=2}^{k=\infty} \chi^2(r_{1k}) \tag{C1}$$

as an approximation to the single-particle density of atom (1) near the origin. $\chi^2(r_{1k})$ is the square of the (spherical) pair function computed as outlined in Section 2 and shown in Fig. 3. The independent variable r_{1k} is the distance from atom 1 to the lattice site k (i.e. $r_{1k} = \mathbf{R}_k - \mathbf{r}_1$). The product $\prod_{k=2}^{\infty}$ runs, in principle, over all other lattice sites of the crystal.

The numerical calculations were performed on an IBM 7094. Our method of numerical calculation is to write

$$\ln \gamma(\mathbf{r}_1) = 2\sum_{k=2}^{\infty} \ln \chi(r_{1k}) = 2\sum_{k=2}^{N} \ln \chi(r_{1k}) + \frac{2A}{V}\int_{R_0}^{\infty} \ln \chi(r_{1k}) d^3\mathbf{R}_k \tag{C2}$$

thus replacing the detailed consideration of atoms beyond a large sphere R_0 (centered on the lattice site R_1) by an integral over the (grossly) spatially uniform density. In a preliminary calculation, the crystal lattices of the bcc and hcp phases are generated and stored on punched cards as normalized vectors ρ_k for nearest-neighbor distance unity. Since one quite often wishes to perform the type of separation indicated in equation (C2), i.e., a detailed sum over the nearest N atoms and a correction integral to infinity, the positions were computed for N atoms with $\rho_k^2 \leqslant R_0^2$. Using then the values of ln $\chi(s)$ obtained and stored as indicated in Appendix B for B = 16.60 for equal intervals of s ($0.5 \leqslant s \leqslant 10$), the 7094 calculated (for a given phase and a specified molar volume V) first the nearest-neighbor distance a_0, then the actual atomic positions $\mathbf{R}_k = a_0\rho_k$, the inner cutoff for the integral $R_0 = \sigma S_0$ from the relation

$$\frac{4\pi}{3} R_0^{\,3} = \frac{NV}{A} \tag{C3}$$

and, finally, for each required position r_1 (in units of σ; sometimes in a mesh, sometimes as part of the maximization program) the sum $\sum_{k=2}^{N} \ln \chi(S_k)$ with $S_k^2 = (\mathbf{R}_k - \mathbf{r}_1)^2/\sigma^2$. Then ln (S_k) is obtained from the neighboring tabulated values of ln $\chi(s)$ by fourth-order interpolation.

Having run through the $(N - 1)$ contributions to $\sum_{k=2}^{N}$, the program calculates the correction integral:

$$I \equiv \int_{|R_k| = R_0}^{\infty} \ln \chi(r_{1k}) d^3\mathbf{R}_k \tag{C4}$$

Since $\chi(r)$ is given for $r \gg \sigma$ by equations (23a), (23b), and (24), I diverges. In actuality, γ as defined in equation (C1) is not yet normalized, and we may provisionally calculate

$$\frac{\gamma(r_1)}{\gamma(r_1 = 0)} \equiv \gamma'(r_1).$$

$$\ln \gamma'(r_1) = \ln \gamma(r_1) - \ln \gamma(r_1 = 0) =$$

$$2\left[\sum_{k=2}^{N} \ln \chi(r_{1k}) - \sum_{k=2}^{N} \ln \chi(R_k)\right] + \frac{2A}{V} I'$$

with

$$I' \equiv \int_{|R_k|=R_0}^{\infty} \left[\ln \chi(r_{1k}) - \ln \chi(R_k)\right] d^3\mathbf{R}_k \tag{C5}$$

For $R_0 >> a_0$, the density of atoms is almost uniform, and $I'(r_1)$ may be expanded as a Taylor series in $\mathbf{r}_1$. I' is isotropic, and we keep only the first term in the expansion - than in $|\mathbf{r}_1|^2$. Thus we want

$$I' = \int_{R_0}^{\infty} \Delta F(r_{1k}) d^3\mathbf{R}_k \tag{C6}$$

with

$$F(r) = \ln \left(1 - \frac{B}{12r^4} + \frac{C_1}{r} - \frac{BC_1}{20r^5} + \ldots\right) \tag{C7}$$

from equation (23a) and equation (23b).

$$\Delta F(r_{1k}) = \left\{\frac{dF}{dr_{1k}}\right\}_{R_k} \times |\Delta r_{1k}| + \left\{\frac{d^2F}{dr^2_{1k}}\right\}_{R_k} \times$$

$$\Delta r_{1k}|^2 + \frac{1}{6} \left\{\frac{d^3F}{dr^3_{1k}}\right\}_{R_k} \times |\Delta r_{1k}|^3 + \ldots \tag{C8}$$

$$\frac{dF}{dr_{1k}} = \frac{1}{\chi} \frac{d\chi}{dr_{1k}},$$

$$\frac{d^2F}{dr^2_{1k}} = \left[\frac{-1}{\chi^2} \left(\frac{d\chi}{dr_{1k}}\right)^2 + \frac{1}{\chi} \frac{d^2\chi}{dr^2_{1k}}\right] \tag{C9}$$

$$\Delta r_{1k}| = R_k \left\{\left[1 + \frac{r^2{}_1}{R^2{}_k} - \frac{2(\mathbf{r}_1 \cdot \mathbf{R}_k)}{R^2{}_k}\right]^{1/2} - 1\right\}$$

$$= R_k \left\{\frac{1}{2} \frac{r^2{}_1}{R^2{}_k} - \frac{(\mathbf{r}_1 \cdot \mathbf{R}_k)}{R^2{}_k} - \frac{1}{2} \frac{(\mathbf{r}_1 \cdot \mathbf{R}_k)^2}{R^4{}_k} + \ldots\right\} \tag{C10}$$

to terms in $r^2{}_1$.

$$|\Delta r_{1k}|^2 = R^2{}_k \left\{\frac{(\mathbf{r}_1 \cdot \mathbf{R}_k)^2}{R^4{}_k}\right\}, \quad \text{and} \quad |\Delta r_{1k}|^3 = 0, \quad \text{both to terms in } r^2{}_1.$$

The angular integral over $(\mathbf{r}_1 \cdot \mathbf{R}_k)$ gives zero, and that over $(\mathbf{r}_1 \cdot \mathbf{R}_k)^2$ gives $r^2{}_1 R^2{}_k/3$.

Thus equation (C6) becomes

$$I' = \int_{R_0}^{\infty} \left\{ \left(\frac{1}{\chi}\frac{d\chi}{dr}\right)_{r=R} \left[\frac{1}{2}\frac{r_1^2}{R} - \frac{1}{6}\frac{r_1^2}{R}\right] + \left[\frac{1}{\chi}\frac{d^2\chi}{dr^2} - \frac{1}{\chi^2}\left(\frac{d\chi}{dr}\right)^2\right]_{r=R} \times \left(\frac{1}{6} r^2\right) 4\pi R^2 dR \right\} \tag{C11}$$

$$= \frac{2\pi}{3} r_1^2 \int_{R_0}^{\infty} \left\{ \frac{2R}{\chi}\frac{d\chi}{dR} + \frac{R^2}{\chi}\frac{d^2\chi}{dR^2} - \frac{R^2}{\chi^2}\left(\frac{d\chi}{dR}\right)^2 \right\} dR$$

Substituting equation (23a) and equation (23b) and keeping terms through R^{-5} in the integrand, we find

$$I' = -\frac{2\pi r_1^2}{3} \left\{ \frac{C_1^2}{S_0} - \frac{C_1^3}{S_0^2} + \frac{(B/3 + C^4)}{S_0^3} - \frac{C^5 + \frac{BC}{6}}{S_0^4} \right\} \tag{C12}$$

Thus

$$I' = -\frac{2\pi r_1^2 C_1^2}{3S_0} \left\{ \frac{S_0}{S_0 + C_1} + \frac{B}{3C_1^2 S_0^2} - \frac{B}{6C_1 S_0^3} \right\} \tag{C13}$$

This approximation is sufficiently accurate that the results of calculations of $\gamma(r_i)$ with $N = 51$ or $N = 991$ atoms explicitly considered in equation (C2) differed fractionally by only 10^{-4} to 0^{-3}; we thus made all "production calculations" with $N = 51$ atoms (hcp phase or bcc phase).

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