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Theory of Exchange in Crystalline ^{3}He†*

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In this work a theory of exchange in crystalline ^{3}He is developed. A spin Hamiltonian is deduced and its matrix elements calculated by cluster-expansion methods. A Heisenberg form of the spin Hamiltonian is found adequate, but with the customary exchange integral replaced by an *exchange operator*, which has matrix elements in phonon space. The diagonal elements of the exchange operator are used to derive an expression for the exchange frequency which depends explicitly on the phonon spectrum of the crystal and on the short-range (hard-core) correlations among particles. Simple arguments are used to show that this expression gives the two outstanding features of exchange in crystalline ^{3}He, viz., that the exchange frequency increases exponentially as the lattice constant increases and that it is antiferromagnetic. The density and the temperature dependence of the exchange frequency are calculated using a phonon spectrum and short-range correlation function obtained in a self-consistent fashion from a variational treatment. Various approximations to the phonon spectrum and the short-range correlation function are used in the calculation of exchange frequency, and the results compared. For example, it is found that the correct form of the short-range correlation function for small interparticle distance and the anisotropy of the pair-distribution function must be considered for good agreement with experimentally deduced results.

I. INTRODUCTION

Because of their small mass and the weakness of their van der Waals interaction, the isotopes of helium have a relatively large zero-point energy. They can be solidified only under pressure even at zero temperature[1] and the rms deviation in the crystalline phase is about 30% of the equilibrium interatomic distance. One effect of these large zero-point oscillations is that there is an unusually large probability for two atoms to exchange lattice sites.[2] This exchange can be detected in ^{3}He since these atoms have a nuclear spin $\frac{1}{2}$.

The exchange interaction energy in crystalline ^{3}He has been measured to be several orders of magnitude greater than the dipole-dipole interaction energy of the nuclear spins.[3–7] This fact makes crystalline ^{3}He unique in nuclear magnetic phenomena. For example, it is expected that the nuclear spins will order at a temperature of about 1 m°K for low densities of the solid. At low temperatures, thermodynamic properties such as specific heat, thermal expansion coefficient, and the melting curve are strongly affected by the ordering of the nuclear spins. Thus for an exchange energy of 1 m°K the thermal expansion coefficient is expected[7] to vanish at $T\sim 0.20°$K and the melting curve is expected[8] to have an inflexion point at about 10.5 m°K. In fact, the slope of the melting curve has been used[7] to measure the exchange energy.

The exchange phenomenon also gives rise to some unusual features in nuclear spin-lattice relaxation[3,4,6] in crystalline ^{3}He, the most notable being the existence of an exchange bath[3,9] in addition to the usual Zeeman and lattice baths. Measurements of spin-lattice relaxation times have also been used to deduce the exchange energy.[3,4,5] The above methods give only the absolute magnitude of the exchange energy. Direct susceptibility measurements can yield both the sign and magnitude of exchange energy. They have been carried out,[5,10,11] but the not with sufficient accuracy to indicate unambiguous deviations from Curie-law behavior.

An adequate theory for the phenomenon of exchange in crystalline ^{3}He can only be built upon an adequate theory of the lattice dynamics of the system. Because of the aforementioned large zero-point energy, it turns out that the traditional theory of lattice dynamics[12] is inapplicable to solid ^{3}He. In the past few years, a theory for such systems has emerged.[13–19] In the present work, we extend this theory to include the effects of the sym-

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metry of the wave function under permutation of particles. Since the effects of exchange are small, the exchange energy being several orders of magnitude lower than the lattice energy, we treat the requirements of antisymmetrization as a small correction. Further, we treat only pair exchanges since we believe, on physical grounds, that these are the most important. The result is that one obtains an effective Hamiltonian H which operates on the unsymmetrized wave functions, i.e., given the usual lattice Hamiltonian H_L,

$$H=H_L+H_S\,, \tag{1.1}$$

where H_S is the Heisenberg Hamiltonian

$$H_S=-\tfrac{1}{2}\sum_{i<j}\mathcal{J}_{ij}\mathbf{I}_i\cdot\mathbf{I}_j\,, \tag{1.2}$$

and $\mathbf{I}_i$ is the spin operator for particle i and $\mathcal{J}_{ij}$ is an operator[20,21] referred to as the *exchange operator* which has matrix elements in phonon space. The introduction of an *exchange operator* is essential, because we are considering the requirements of symmetry on a statistical system with a quasicontinuum of eigenstates. The exchange frequency for the particles at the sites i and j is the statistical average of the matrix elements of the operator $\mathcal{J}_{ij}$.

The plan of the paper is the following: In Sec. II, we give a summary of the existing theory of the lattice dynamics of solid helium. We discuss here the treatment of both the long-range and the short-range correlations in the crystal. In Sec. III, we extend the above theory to include effects of symmetry of the particles and deduce an effective spin Hamiltonian. Further, we calculate the matrix elements of the spin Hamiltonian by cluster-expansion methods that are presented in Appendix A. In Sec. IV, we derive an expression for the exchange frequency using the matrix elements derived in Sec. III. We also qualitatively discuss the physical features of exchange and show that (i) in solid ^{3}He exchange leads to an antiferromagnetic alignment of spins and (ii) the exchange frequency increases as the nearest-neighbor distance in the solid increases. The details of the calculations on which the results of Sec. IV are based are given in Appendix B. In Sec. V, we present results of various calculations of the exchange frequency based on variational calculation of phonon frequency and the short-range correlation functions. We compare them with experimental results and give a physical discussion of the difference between various theoretical results due to the approximations involved. In Appendix C, we discuss various approximations used in this work.

The principal results of this work have been presented briefly earlier.[21]

II. LATTICE DYNAMICS OF QUANTUM CRYSTALS

In this section we summarize the recently developed theory[13–19] of the lattice dynamics of *quantum crystals* (e.g., crystalline helium and hydrogen). There are several special problems in the lattice dynamical theories of such crystals. In the first place, one may not expand the potential in powers of deviations from equilibrium, retain *only* the first few terms, and then obtain phonons through the usual normal mode transformation. Rather, one must obtain the elementary excitations of the system by a partial summation of the *whole* series. Secondly, due to their large excursions, the particles "see" the hard-core of their neighbors and of course avoid it. The dynamics of this "avoidance," or, in other words, the short-range correlations, must be an integral part of the theory.

Here we extend in a straightforward manner one form of the existing zero-temperature theory[17] to finite temperatures which are small compared to the Debye temperature and also point out the deficiencies of the theory and their bearing on the calculations of the exchange energy. In essence, the theory consists of a variational calculation of the free energy using a complete set of trial function states, which are chosen to have the form

$$\psi_{\mathbf{n}}(\mathbf{r})=\varphi_{\mathbf{n}}(\mathbf{r})F_{\mathbf{n}}(\mathbf{r})\,, \tag{2.1}$$

where $\mathbf{r}$ stands for the set of coordinates of all the particles and $\varphi_{\mathbf{n}}(\mathbf{r})$ is the wave function of a harmonic crystal in the state $\mathbf{n}$, $\mathbf{n}$ standing for the set of occupation numbers of all the phonons of wave vector $\mathbf{k}$ and polarization λ. Further, $F_0(\mathbf{r})$ is chosen to be of the form

$$F_0(\mathbf{r})=\prod_{i<j}f(r_{ij})\,, \tag{2.2}$$

with the rest of the $F_{\mathbf{n}}(\mathbf{r})$ being determined, in principle, by an orthogonalization procedure. In this formulation $\varphi_{\mathbf{n}}(\mathbf{r})$ takes into account the long-range correlations and the symmetry of the lattice and $F_{\mathbf{n}}(\mathbf{r})$ takes into account the short-range correlations. The energy of the state $\mathbf{n}$ is assumed to have the harmonic oscillator form

$$E_{\mathbf{n}}=\hbar\sum_{\mathbf{k},\lambda}(n_{k\lambda}+\tfrac{1}{2})\omega_{\mathbf{k}\lambda}\,. \tag{2.3}$$

The frequencies $\omega_{\mathbf{k}\lambda}$, polarization vectors $\epsilon_{\mathbf{k}\lambda\alpha}$, and the function $f(r_{ij})$ are taken to be variational parameters with the restriction that $f(r_{ij})\rightarrow 1$ rapidly when $r_{ij}\gtrsim R$ (R being the nearest-neighbor distance). We are interested in the regime $T\ll\Theta_D$,[22] for which only small $\mathbf{n}$ are occupied, in which case we expect that the short-range correlations may be treated adequately by a cluster expansion since this method works well for $T=0$.[13]

We now calculate the free energy as a function of the variational parameters. In the calculation of the entropy, we neglect the contribution due to the short-

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range correlations (as is justified in Appendix C). The entropy then is simply that for a system of harmonic oscillators, i.e.,

$$S=-k\sum_{\mathbf{k},\lambda}\left[\ln(2\sinh(\tfrac{1}{2}\beta\hbar\omega_{\mathbf{k},\lambda}))\right.$$
$$\left.-(\tfrac{1}{2}\beta\hbar\omega_{\mathbf{k},\lambda})\coth(\tfrac{1}{2}\beta\hbar\omega_{\mathbf{k},\lambda})\right]. \quad (2.4)$$

To calculate the internal energy, the trial density matrix

$$\rho(\mathbf{r},\mathbf{r}')=\sum_{\mathrm{n}} e^{-\beta E_{\mathrm{n}}}\psi_{\mathrm{n}}(\mathbf{r})\psi_{\mathrm{n}}(\mathbf{r}')\bigg/\int d\mathbf{r}\,\psi_{\mathrm{n}}^2(\mathbf{r})$$

is approximated by

$$\rho(\mathbf{r},\mathbf{r}')\simeq\sum_{\mathrm{n}} e^{-\beta E_{\mathrm{n}}}\psi_{\mathrm{n}}(\mathbf{r})\psi_{\mathrm{n}}(\mathbf{r}')\bigg/\sum_{\mathrm{n}} e^{-\beta E_{\mathrm{n}}}\int d\mathbf{r}\,\psi_{\mathrm{n}}^2(\mathbf{r}). \quad (2.5)$$

The validity of this approximation is discussed in Appendix C. If one now uses the partial integration technique derived in Appendix B1(iv) and retains the first two terms of the cluster expansion for short-range correlations, one finds

$$E\simeq\tfrac{1}{4}\hbar\sum_{\mathbf{k},\lambda}\omega_{\mathbf{k}\lambda}\coth(\tfrac{1}{2}\hbar\beta\omega_{\mathbf{k}\lambda})+\sum_{i<j}\left[P(\mathbf{R}_{ij})/Q(\mathbf{R}_{ij})\right], \quad (2.6)$$

where

$$P(\mathbf{R}_{ij})=\langle f^2(r_{ij})\tilde{v}(r_{ij})\rangle,$$
$$Q(\mathbf{R}_{ij})=\langle f^2(r_{ij})\rangle.$$

Here, the brackets indicate a thermal average, $f^2(r_{ij})\tilde{v}(r_{ij})$ is the effective nonsingular potential[13] and

$$\tilde{v}(r_{ij})=v(r_{ij})-(\hbar^2/2m)\nabla^2\ln f(r_{ij}). \quad (2.7)$$

The free energy may now be minimized with respect to $\omega_{\mathbf{k}\lambda}$ and $\epsilon_{\mathbf{k}\lambda\alpha}$. The procedure at finite temperatures is identical to that at $T=0$[17] and yields the self-consistency condition

$$m\omega_{\mathbf{k}\lambda}^2=\sum_{\tau,\alpha\beta}\epsilon_{\mathbf{k}\lambda\alpha}^*\epsilon_{\mathbf{k}\beta\lambda}(1-e^{i\mathbf{k}\cdot\tau})$$
$$\times\left[Q^{-1}(\boldsymbol{\tau})\frac{\partial^2}{\partial\tau_\alpha\partial\tau_\beta}P(\boldsymbol{\tau})\right.$$
$$\left.-Q^{-2}(\boldsymbol{\tau})P(\boldsymbol{\tau})\frac{\partial^2}{\partial\tau_\alpha\partial\tau_\beta}Q(\boldsymbol{\tau})\right], \quad (2.8)$$

where $\boldsymbol{\tau}$ is any lattice vector. A similar procedure has been applied to treat the finite-temperature properties of crystalline neon and argon by Koehler, Gillis, and Werthamer.[22a]

Now we briefly discuss the treatment for the short-range correlations in quantum crystals. The exchange frequency depends strongly on the short-range correlation function. A first-principle solution of the problem has not yet proved possible. The simplest approach[13] to this problem is to assume

$$f(r)=e^{-K\eta(r)}, \quad (2.9)$$

with $\eta(r)=(\sigma/r)^{12}-(\sigma/r)^6$ and use cluster-expansion techniques. This approach gives reasonable values for the energy and good convergence for the cluster expansion.[23] However, for small r, the form (2.9) for $f(r)$ is incorrect; the correct form for a Lenard-Jones potential being

$$f(r)\sim e^{-Cr^{-5}},$$

so that (2.9) gives values for the pair-distribution function which are too small for $r\lesssim\sigma$ and therefore underestimates the exchange frequency.

A better approach to the problem is the determination of $f(r)$ for small r through the derivation of a differential equation for $f(r)$ obtained by varying the energy with respect to $f(r)$. Details of this method will be given in a forthcoming paper by Mullin, Nosanow, and Steinback.[24] This method yields the correct behavior of $f(r)$ for $r\lesssim\sigma$.

III. SPIN HAMILTONIAN FOR CRYSTALLINE ^{3}He

In this section, we discuss the general form of the spin Hamiltonian for crystalline ^{3}He and derive its matrix elements by cluster-expansion methods. In effect, we extend the theory given in Sec. II to include effects of the symmetry requirements on the wave function under permutation of particles. It is important to realize that these symmetry requirements play a part only if there is an overlap of the wave functions of individual particles. Thus, if the effective crystal potential were truly infinite at, say, the surface of the Wigner-Seitz cell around each particle, the question of symmetry under permutations would not arise. Since the potential at the Wigner-Seitz surface is very large even in crystalline helium, the overlap is small and hence the effects of symmetry may be treated as a small perturbation.

It is well known[25] that the effect of the requirement of antisymmetrization of the wave function with respect to permutations of the particles can be expressed in terms of an effective Hamiltonian

$$H=H_L+H_S, \quad (3.1)$$

which operates on the space of unsymmetrized wave functions. Here H_L is the actual Hamiltonian of the system (the lattice Hamiltonian in our case) and H_S, the spin Hamiltonian, takes care of the exchange effects. In what follows, we consider only pair exchanges, since we expect them to be dominant for $T\ll\Theta_D$. This assump-

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tion seems plausible because the exchange frequency is so small and for $T \ll \Theta_D$ the pair distribution vanishes very rapidly as the interparticle distance decreases below $r \cong \sigma$. The latter argument is related to Herring's criterion[25] for the dominance of pair exchanges of electrons in atomic systems. In a crystal, the motion of the particles and therefore the overlap of the wave functions depends upon the state of the whole system $\mathbf{n}$. Therefore the exchange integral for any pair of particles also depends on $\mathbf{n}$. Since the Heisenberg form for H_S follows[25] if we consider only pair exchanges, we may write

$$H_S = -\tfrac{1}{2} \sum_{i<j} \mathcal{J}_{ij} \mathbf{I}_i \cdot \mathbf{I}_j , \tag{3.2}$$

where $\mathbf{I}_i$ is the nuclear spin operator for the ith particle, and $\mathcal{J}_{ij}$ is an operator (referred to as the *exchange operator*[20,21]) which has matrix elements in the phonon space. Thus $\langle \mathbf{n} | \mathcal{J}_{ij} | \mathbf{n} \rangle$ is the exchange integral for the pair (i,j) for the state $\mathbf{n}$. The exchange frequency of the pair (i,j), J_{ij} is the thermal average of such matrix elements and is therefore given by

$$J_{ij} = \mathrm{Tr}(\rho \mathcal{J}_{ij}) , \tag{3.3}$$

where ρ is the phonon density matrix. Thus J_{ij} depends only on the diagonal elements of $\mathcal{J}_{ij}$, whereas the off-diagonal elements of $\mathcal{J}_{ij}$ contribute to spin-lattice relaxation in crystalline ^{3}He. They are important here in contrast to the problem of electron exchange in dielectrics, since the eigenvalues of H_L form a quasi-continuum, whereas in the latter case the eigenvalues are separated by several orders of magnitude greater than the exchange energy.

The Weiss constant in the Curie-Weiss law is proportional to J_{ij}. With the definition of (3.2), a negative value of J_{ij} would give an antiferromagnetic alignment of spins, whereas a positive value would give a ferromagnetic alignment.

The method of obtaining matrix elements of $\mathcal{J}_{ij}$ will now be discussed. The totally antisymmetric wave function

$$\chi_{\mathbf{n}} = \mathcal{A}(\psi_{\mathbf{n}} \xi) \tag{3.4}$$

is considered, where $\mathcal{A}$ is the antisymmetrization operator, and ξ is the product of the spin functions of all the particles. In Appendix A, the matrix elements $E_{\mathbf{mn}} \equiv \langle \chi_{\mathbf{m}} | H_0 | \chi_{\mathbf{n}} \rangle$ are calculated by a cluster-expansion scheme which can be used to treat off-diagonal as well as diagonal elements of the Hamiltonian. The cluster expansion is performed only with respect to the short-range correlations and the antisymmetrization, but not with respect to the phonons. Retaining only the one- and two-body terms of the cluster expansion, one obtains

$$E_{\mathbf{mn}} = \sum_i (E_i)_{\mathbf{mn}} + \sum_{i<j} \left[(E_{ij}{}^{\pm})_{\mathbf{mn}} - (E_i)_{\mathbf{mn}} - (E_j)_{\mathbf{mn}} \right] , \tag{3.5}$$

where

$$(E_i)_{\mathbf{mn}} \equiv (\varphi_{\mathbf{m}}, H_i \varphi_{\mathbf{n}}) , \tag{3.6}$$

$$(E_{ij}{}^{\pm})_{\mathbf{mn}} \equiv (N_{ij}{}^{\pm})_{\mathbf{mn}} / (D_{ij}{}^{\pm})_{\mathbf{mm}}{}^{1/2} (D_{ij}{}^{\pm})_{\mathbf{nn}}{}^{1/2} , \tag{3.7}$$

where the plus sign is associated with the singlet spin state of the pair (i,j), the minus sign with the triplet state, and

$$(N_{ij}{}^{\pm})_{\mathbf{mn}} \equiv [\varphi_{\mathbf{m}} f_{ij}, H_{ij} f_{ij} (1 \pm P_{ij}) \varphi_{\mathbf{n}}] , \tag{3.8}$$

$$(D_{ij}{}^{\pm})_{\mathbf{mn}} \equiv [\varphi_{\mathbf{m}}, f_{ij}{}^2 (1 \pm P_{ij}) \varphi_{\mathbf{n}}] , \tag{3.9}$$

and H_i and H_{ij} are, respectively, the one- and two-particle Hamiltonians and P_{ij} is the permutation operator for the pair (i,j). Since the exchange integral for the pair (i,j) is defined as twice the difference between the singlet and triplet states, it is natural to write

$$(\mathcal{J}_{ij})_{\mathbf{mn}} \equiv 4[(E_{ij}{}^{+})_{\mathbf{mn}} - (E_{ij}{}^{-})_{\mathbf{mn}}] . \tag{3.10}$$

This expression involves $P_{ij} \varphi_{\mathbf{n}}$ in an essential way. Because $\varphi_{\mathbf{n}}$ involves the normal modes which depend on coordinates of all the particles, $P_{ij} \varphi_{\mathbf{n}}$ may be looked upon as a phonon wave function in which the forces between the pair (i,j) and all the neighboring particles are altered. This alteration decreases as one moves away from the pair (i,j). Further, the exchange operator when written in coordinate space, i.e., $\langle \mathbf{r} | \mathcal{J}_{ij} | \mathbf{r}' \rangle$ is nondiagonal and cannot be approximated by any form depending only on the coordinates of (i,j). This fact has an important bearing on the spin-lattice relaxation in solid ^{3}He.

IV. DERIVATION OF EXCHANGE FREQUENCY

In this section, we derive an expression for the exchange frequency using the matrix elements of $\mathcal{J}_{ij}$ given in Sec. III. The exchange frequency J_{ij} is given by (3.3). Using (3.7) and (3.10), we have

$$J_{ij} = 4 \sum_{\mathbf{n}} \rho_{\mathbf{n}} \left[\frac{(N_{ij}{}^{+})_{\mathbf{nn}}}{(D_{ij}{}^{+})_{\mathbf{nn}}} - \frac{(N_{ij}{}^{-})_{\mathbf{nn}}}{(D_{ij}{}^{-})_{\mathbf{nn}}} \right] , \tag{4.1}$$

which, using the low-temperature approximation discussed in Appendix C, may be written

$$J_{ij} \simeq 4[\langle N_{ij}{}^{+} \rangle / \langle D_{ij}{}^{+} \rangle - \langle N_{ij}{}^{-} \rangle / \langle D_{ij}{}^{-} \rangle] . \tag{4.2}$$

Using Eqs. (4.8) and (4.9) for $\langle D_{ij}{}^{\pm} \rangle$ and $\langle N_{ij}{}^{\pm} \rangle$ and the expressions derived in Appendix B for $\langle H_{ij} \rangle$ and $\langle P_{ij} H_{ij} \rangle$, after some cancellation we obtain

$$J_{ij} \simeq 4 \{ f_{ij}{}^2 \}^{-1} [\{ f_{ij}{}^2 \tilde{v}_{ij} \}_x + (\hbar^2/2m) \times \{ f_{ij}{}^2 \}_x (\mathrm{Tr}\mathbf{F}_{ij} - \mathrm{Tr}\mathbf{G}_{ij} - 2\mathbf{R}_{ij} \cdot \mathbf{F}_{ij} \cdot \mathbf{R}_{ij})] , \tag{4.3}$$

where for any arbitrary function $g(r_{ij})$

$$\{ g_{ij} \} = \pi^{-3/2} | \mathbf{F}_{ij} |^{1/2} \int d\mathbf{r}_{ij} \, g(\mathbf{r}_{ij}) \times \exp[-(\mathbf{r}_{ij} - \mathbf{R}_{ij}) \cdot \mathbf{F}_{ij} \cdot (\mathbf{r}_{ij} - \mathbf{R}_{ij})] \tag{4.4}$$

and

$$\{g_{ij}\}_x \equiv \pi^{-3/2} |\mathbf{F}_{ij}|^{1/2} \exp(-\mathbf{R}_{ij}\cdot\mathbf{F}_{ij}\cdot\mathbf{R}_{ij}) \times \int d\mathbf{r}_{ij}\, g(\mathbf{r}_{ij}) \exp(-\mathbf{r}_{ij}\cdot\mathbf{G}_{ij}\cdot\mathbf{r}_{ij}) . \quad (4.5)$$

Further, $\mathbf{F}_{ij}$ and $\mathbf{G}_{ij}$ are 3×3 matrices with elements given by

$$(\mathbf{F}_{ij}^{-1})_{\alpha\beta} = (2\hbar/mN) \sum_{\mathbf{k}\lambda} \epsilon_{\mathbf{k}\lambda\alpha}\epsilon_{\mathbf{k}\beta\lambda}(1-\cos\mathbf{k}\cdot\mathbf{R}_{ij}) \times \omega_{\mathbf{k}\lambda}^{-1} \coth(\tfrac{1}{2}\beta\hbar\omega_{\mathbf{k}\lambda}) , \quad (4.6)$$

$$(\mathbf{G}_{ij})_{\alpha\beta} = (m/2\hbar N) \sum_{\mathbf{k}\lambda} \epsilon_{\mathbf{k}\lambda\alpha}\epsilon_{\mathbf{k}\beta\lambda}(1-\cos\mathbf{k}\cdot\mathbf{R}_{ij}) \times \omega_{\mathbf{k}\lambda} \coth(\tfrac{1}{2}\beta\hbar\omega_{\mathbf{k}\lambda}) , \quad (4.7)$$

where we have assumed a Bravais lattice. In the derivation of (4.3), the term $\{P_{ij}f_{ij}^2\}/\{f_{ij}^2\}$ has been neglected because it is small for $T \ll \Theta_D$.

Equation (4.3) for J_{ij} includes the symmetry of the lattice through the matrices $\mathbf{F}_{ij}$ and $\mathbf{G}_{ij}$ and includes the short-range correlations through the function $f(r)$. If we consider the limit $T=0$ and use the Einstein approximation for the phonon spectrum, we have $\mathbf{F}_{ij} = (\frac{1}{2}A)\mathbf{I} = \mathbf{G}_{ij}$, where $\mathbf{I}$ is the identity matrix; in this case (4.3) reduces to the expression derived by Nosanow and Mullin.[26]

V. PHYSICAL PICTURE OF EXCHANGE

Before we present the results of our numerical calculations of J_{ij}, we wish to recapitulate the basic ideas of the preceding analysis and extract the qualitative physical results through simple physical arguments.[27] The basic approach is to focus attention on two particles i and j and consider their motion in the field of the rest of the particles. The exchange frequency is proportional to the energy difference between the singlet and triplet states which is calculated by cluster-expansion methods.

At $T=0$, the exchange frequency is $\langle 0|\mathcal{J}_{ij}|0\rangle$, and by (3.10) [neglecting terms $(1-\langle f_{ij}^2\rangle)^2$ and S_{ij}^2 as small compared to unity]

$$\tfrac{1}{8}J_{ij} \simeq [P_{ij}(\varphi_0 f_{ij}), H_{ij}(f_{ij}\varphi_0)] - S_{ij}[\varphi_0 f_{ij}, H_{ij}(\varphi_0 f_{ij})] , \quad (5.1)$$

where

$$S_{ij} = [P_{ij}(\varphi_0 f_{ij}), \varphi_0 f_{ij}] .$$

It must now be noted that $f_{ij}\varphi_0$ is not an eigenfunction of H_{ij}; if it were, J_{ij} would be zero by (5.1). Since both terms of (5.1) involve $f_{ij}\varphi_0$ and $P_{ij}(f_{ij}\varphi_0)$, we may write

$$J_{ij} \sim S_{ij} , \quad (5.2)$$

on intuitive grounds. For simplicity, we may now use the Einstein approximation to evaluate (5.2), so that for nearest neighbors

$$J \sim \left(\frac{2A^3}{\pi}\right)^{1/2} e^{-AR^2/2} \int_0^\infty dr\, r^2 f^2(r) e^{-Ar^2/2} . \quad (5.3)$$

From (5.3) we deduce that $|J|$ increases in an exponential way as R increases. Since A decreases as R increases such that AR^2 is approximately constant, the decrease in A gives more weight to the region in the integral in (5.3) in which $f^2(r)$ is larger. Further, in this region $f^2(r)$ is well represented by exp(function of r), so that the increase in J is exponential. In physical terms (5.3) implies that the increase in J is due to the fact that, for larger R, there is more "room" for particles to get around one another.

We may consider (5.1) again to place the above argument on a somewhat firmer footing and also deduce the sign of J_{ij} by taking into account the properties of the short-range correlation function, which is determined by the interatomic potential. It is already obvious from (5.3) that the important region of $f(r)$ for exchange is $r \lesssim \sigma$. In this region $f(r)$ is essentially the wave function of two helium atoms in vacuum so that we have

$$H_{ij} f(r) \simeq \epsilon f(r) . \quad (5.4)$$

To use this result, we write (5.1) as

$$\begin{aligned}\tfrac{1}{8}J_{ij} \simeq{}& [P_{ij}(\varphi_0 f_{ij}), \varphi_0 H_{ij} f_{ij}] \\ &+ (\hbar^2/2m)\{[f_{ij}\nabla_i(P_{ij}\varphi_0), f_{ij}\nabla_i\varphi_0] \\ &+ [f_{ij}\nabla_j(P_{ij}\varphi_0), f_{ij}\nabla_j\varphi_0]\} \\ &- S_{ij}(\varphi_0 f_{ij}, \varphi_0 H_{ij} f_{ij}) \\ &- S_{ij}(\hbar^2/2m)[(f_{ij}\nabla_i\varphi_0, f_{ij}\nabla_i\varphi_0) \\ &+ (f_{ij}\nabla_j\varphi_0, f_{ij}\nabla_j\varphi_0)] . \quad (5.5)\end{aligned}$$

Now, by (5.4) the first and third terms of (5.5) approximately cancel.[22] Further, after some manipulation and use of the Einstein approximation, we find

$$\tfrac{1}{8}J \simeq -(\hbar^2 A/4m)(A/2\pi)^{3/2} e^{-AR^2/2} \times \int d\mathbf{r}\, f^2(r) e^{-Ar^2/2} [\tfrac{9}{2} + A(R^2 - r^2)] . \quad (5.6)$$

The argument regarding the density dependence of J is the same as that given for (5.3). In addition, (5.6) shows that $J<0$ because the integrand is appreciable only for $r \lesssim \sigma < R$.

In summary then, it follows from simple physical arguments that (1) $J<0$ (i.e., antiferromagnetic); (2) $|J|$ *increases* as R *increases* (i.e., as the density decreases).

VI. RESULTS

In this section we present the results of our numerical calculations of the nearest-neighbor exchange fre-

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[26] L. H. Nosanow and W. J. Mullin, Phys. Rev. Letters **14**, 133 (1965).

[27] In this discussion, an error made in Ref. (21), viz., the omission of the second term of (5.1), has been rectified. This accounts for the difference in Eq. (5.5) and Eq. (17) of Ref. (21) and allows the substitution of the better approximation (5.4) for the approximation $Hf \approx 0$ used therein. Further, Eqs. (17) and (18) of Ref. (21) are too small by a factor of 2.

quency. We do this by evaluating (4.3) under the approximations discussed in Appendix C.

The results of various calculations and the experimental results are shown in Figs. 1 and 2. The result[26] labeled MN was obtained with an Einstein spectrum for the phonons together with a short-range correlation of the form (2.9). For NVI and NVII the same form of the short-range correlation function is used but the one- and two-branch approximations (see Appendix C) are used for the phonon spectrum. The two-branch approximation takes into account, in an approximate fashion, the anisotropy of the wave function. The results show that the inclusion of a phonon spectrum is important both for the magnitude and the density dependence of the exchange frequency. Further, the proper treatment of the anisotropy of the wave function increases the magnitude of the exchange frequency, although the density dependence remains essentially unchanged.

We ascribe the disagreement of the magnitude and the detailed density dependence of NVII to the inadequacy of a short-range correlation function of the form (2.9). As discussed earlier, (2.9) is too small for $r \lesssim \sigma$ and overemphasizes the hard core, thus reducing exchange.

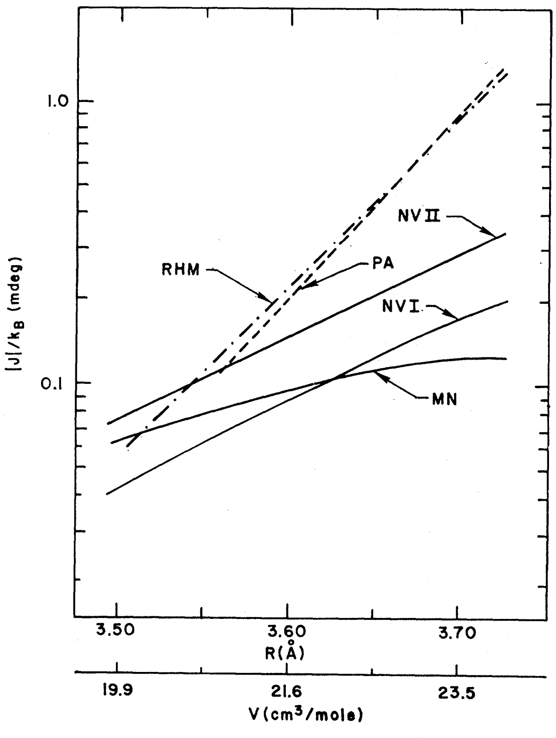

FIG. 1. Nearest-neighbor exchange frequency $|J|$ in bcc ³He as a function of the nearest-neighbor distance R or the molar volume V. The dashed curves are the results deduced from experiment and the solid curves are results of theoretical calculations at $T=0$. RHM (Ref. 6) deduced $|J|$ from NMR measurements, while PA [M. F. Panczyk and E. D. Adams (private communication)] deduced it from $(dP/dT)_V$ measurements. The theoretical curves are described in the text in Sec. VI.

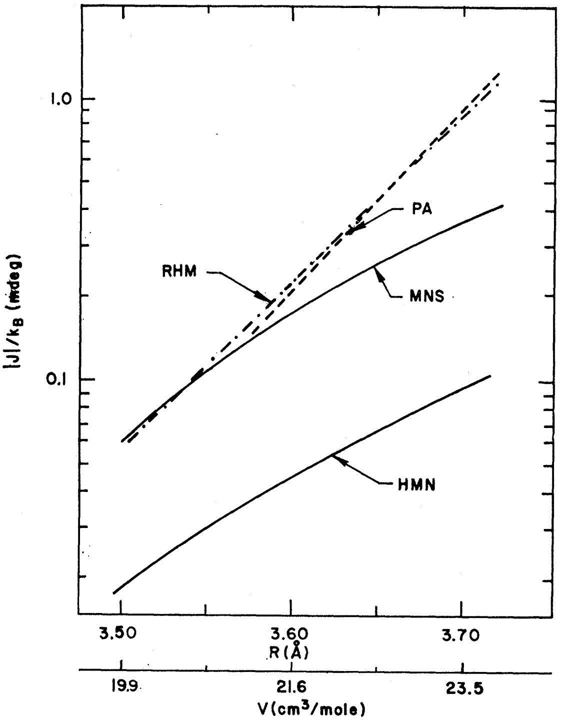

FIG. 2. Nearest-neighbor exchange frequency $|J|$ in bcc ³He as a function of the nearest-neighbor distance R or the molar volume V. The experimental curves (dashed lines) are the same as in Fig. 1 and the theoretical curves (solid lines) are described in the text in Sec. VI.

In Fig. 2, HMN labels the results of an earlier calculation[23] using an Einstein spectrum for the phonons and with a short-range correlation of the form (2.9) calculated, however, with the inclusion of three-body clusters in the evaluation of the variational parameter. A comparison with MN of Fig. 1 shows that the density dependence is improved considerably by a better short-range correlation function. The curve MNS reproduces results[24] of a calculation with an Einstein spectrum and with the small r region of the short-range correlation function evaluated through a differential equation, as discussed in Sec. II. It is clear that the "softer" short-range correlation is important in understanding the magnitude of the exchange frequency.

From the results given in Figs. 1 and 2, it is evident that a calculation of the exchange frequency depends in an important way on the treatment of the short-range correlations and the phonon excitations of the crystal. We have also calculated the temperature dependence of J_{ij} in the one branch approximation. In this approximation, we find that $|J_{ij}|$ increases at each density and at low temperatures has the form

$$J_{ij}(T)=J_{ij}(0)[1+\delta(T/\Theta_D)^4].$$

The results for δ are shown in Table I. These results may be compared with those of Thouless, who obtained $\delta \simeq 4000$ at $R=3.75$ Å from phenomenological considera-

TABLE I. Results for δ.

R(Å)	Θ_D(°K)	δ
3.55	32.6	302
3.65	28.8	179
3.75	25.6	81

tions. We might look upon the increase of $|J_{ij}|$ with temperature as due to the broadening of the pair distribution function.

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APPENDIX A: CLUSTER EXPANSION OF OFF-DIAGONAL ELEMENTS

In the theory of crystalline helium, the cluster expansion has been used extensively.[13] The usual method cannot be used, however, to cluster-expand the off-diagonal elements of the Hamiltonian. Here, a method of cluster expanding with respect to short-range correlations and the antisymmetrization of the wave function is devised, which can be used for any matrix element and which for diagonal elements reduces to the standard result.

The matrix element

$$E_{\mathrm{mn}}^{(N)}(1,\cdots,N)\equiv\frac{(\chi_{\mathrm{m}},H\chi_{\mathrm{n}})}{(\chi_{\mathrm{m}},\chi_{\mathrm{m}})^{1/2}(\chi_{\mathrm{n}},\chi_{\mathrm{n}})^{1/2}}=\frac{(\psi_{\mathrm{m}}\xi,H\chi_{\mathrm{n}})}{(\psi_{\mathrm{m}}\xi,\chi_{\mathrm{m}})^{1/2}(\psi_{\mathrm{n}}\xi,\chi_{\mathrm{n}})^{1/2}} \tag{A1}$$

is considered, where H, χ_{m}, ψ_{m}, and ξ are defined in Sec. III. The one-particle cluster term $(E_i)_{m,n}$ is defined by

$$E_{\mathrm{m,n}}^{(1)}(i)=\frac{(\varphi_{\mathrm{m}},H_i\varphi_{\mathrm{n}})}{(\varphi_{\mathrm{m}},\varphi_{\mathrm{m}})^{1/2}(\varphi_{\mathrm{n}},\varphi_{\mathrm{n}})^{1/2}}=(E_i)_{\mathrm{m,n}}, \tag{A2}$$

and the two-particle cluster term $(E_{ij}{}^{\pm})_{\mathrm{mn}}$ by

$$\begin{aligned}E_{\mathrm{m,n}}^{(2)}(i,j)&=\frac{[\varphi_{\mathrm{m}}\xi_{ij},f_{ij}H_{ij}f_{ij}\mathcal{A}_{ij}(\varphi_{\mathrm{n}}\xi_{ij})]}{\{[\varphi_{\mathrm{m}}\xi_{ij},f_{ij}{}^2\mathcal{A}_{ij}(\varphi_{\mathrm{m}}\xi_{ij})][\varphi_{\mathrm{n}}\xi_{ij},f_{ij}{}^2\mathcal{A}_{ij}(\varphi_{\mathrm{n}}\xi_{ij})]\}^{1/2}}\\&=\frac{[\varphi_{\mathrm{m}},f_{ij}H_{ij}f_{ij}(1\pm P_{ij})\varphi_n]}{\{[\varphi_{\mathrm{m}},f_{ij}{}^2(1\pm P_{ij})\varphi_{\mathrm{m}}][\varphi_{\mathrm{n}},f_{ij}{}^2(1\pm P_{ij})\varphi_{\mathrm{n}}]\}^{1/2}}\\&\equiv(E_i)_{\mathrm{m,n}}+(E_j)_{\mathrm{m,n}}+(E_{ij}{}^{\pm})_{\mathrm{m,n}},\end{aligned} \tag{A3}$$

where the plus sign is associated with the singlet state of the pair (i,j) and the minus with the triplet state, and where $\varphi_{\mathrm{m}}, f_{ij}{}^2$, P_{ij}, H_i, and H_{ij} are defined in Secs. II and III. Continuing in a similar fashion, one can define the general cluster term. Using (A3), the first two terms in the cluster expansion for $E_{\mathrm{m,n}}^{(N)}(1,\cdots,N)$ are

$$E_{\mathrm{m,n}}^{(N)}(1,\cdots,N)=\sum_i(E_i)_{\mathrm{m,n}}+\sum_{i<j}[E_{\mathrm{m,n}}^{(2)}(i,j)-(E_i)_{\mathrm{m,n}}-(E_j)_{\mathrm{m,n}}]+\cdots, \tag{A4}$$

where

$$(E_i)_{\mathrm{m,n}}\equiv\frac{(\varphi_{\mathrm{m}},H_i\varphi_{\mathrm{n}})}{[(\varphi_{\mathrm{m}},\varphi_{\mathrm{m}})(\varphi_{\mathrm{n}},\varphi_{\mathrm{n}})]^{1/2}}, \tag{A5}$$

$$E_{\mathrm{mn}}^{(2)}(i,j)\equiv\frac{(N_{ij}{}^{\pm})_{\mathrm{m,n}}}{[(D_{ij}{}^{\pm})_{\mathrm{mm}}(D_{ij}{}^{\pm})_{\mathrm{nn}}]^{1/2}}, \tag{A6}$$

and

$$(N_{ij}{}^{\pm})_{\mathrm{mn}}\equiv[\varphi_{\mathrm{m}}f_{ij},H_{ij}f_{ij}(1\pm P_{ij})\varphi_{\mathrm{n}}], \tag{A7}$$

$$(D_{ij}{}^{\pm})_{\mathrm{mm}}\equiv[\varphi_{\mathrm{m}},f_{ij}{}^2(1\pm P_{ij})\varphi_{\mathrm{m}}]. \tag{A8}$$

Equation (A4) is used in Sec. III to derive matrix elements of the exchange operator.

APPENDIX B: CALCULATION OF EXCHANGE FREQUENCY

The quantities needed for the evaluation of the exchange frequency J_{ij} will be calculated here. Since they involve a rather long calculation, it is performed in steps. In Sec. B1 some useful results are derived or mentioned. In B2, J_{ij} is derived from cluster expansion methods using certain averages calculated in B3.

1. Some Useful Results

i. Normal Coordinate Transformation

The variables in the particle coordinate space are taken to be $u_{i\alpha}\equiv(r_{i\alpha}-R_{i\alpha})$, where α denotes Cartesian direction and $\mathbf{r}_i$ is the instantaneous position of particle i, whose equilibrium position is $\mathbf{R}_i$. In normal coordinate space the variables taken to be real are $q_{\mathbf{k}\lambda}$, where $\mathbf{k}$ is the quasicontinuum of wave vectors, and λ denotes polarization. The transformation between $u_{i\alpha}$ and $q_{\mathbf{k}\lambda}$

can be written in the form[12] (in this section $\hbar=1$)

$$u_{i\alpha}=\left(\frac{2}{mN}\right)^{1/2}\overline{\sum_{\mathbf{k},\lambda,\sigma=1,2}}\epsilon_{\mathbf{k},\lambda\alpha}\Omega_\sigma(\mathbf{k}\cdot\mathbf{R}_i)q_{\sigma\mathbf{k}\lambda}, \tag{B1}$$

where $\epsilon_{\mathbf{k}\lambda\alpha}$ is a polarization vector and the Brillouin zone has been split into two equal parts by introducing σ; the bar over the summation indicates that only half the Brillouin zone must be summed over, and

$$\begin{aligned}\Omega_\sigma(x)&=\cos x, &&\text{for}\quad \sigma=1\\ &=-\sin x, &&\text{for}\quad \sigma=2.\end{aligned}$$

The polarization vectors of a Bravais lattice may be chosen to be real and have the property that $\epsilon_{\mathbf{k}\lambda\alpha}=\epsilon_{\mathbf{k}\alpha\lambda}=\epsilon_{\mathbf{k}\lambda\alpha}{}^{-1}$. Using this property, one may write the inverse transformation of (C1):

$$q_{\mathbf{k}\lambda\sigma}=\left(\frac{2m}{N}\right)^{1/2}\sum_{i,\alpha}\epsilon_{\mathbf{k}\lambda\alpha}\Omega_\sigma(\mathbf{k}\cdot\mathbf{R}_i)u_{i\alpha}. \tag{B2}$$

ii. Phonon Density Matrix

The phonon density matrix in normal coordinate space,

$$\rho(\mathbf{q},\mathbf{q}')=\frac{1}{Z}\sum_{\mathbf{n}}e^{-\beta E_{\mathbf{n}}}\varphi_{\mathbf{n}}(\mathbf{q})\varphi_{\mathbf{n}}(\mathbf{q}'), \tag{B3}$$

is considered, where $\mathbf{n}$ stands for the set of all phonon occupation numbers and $\mathbf{q}$ for the set of all normal coordinates; $\varphi_{\mathbf{n}}$ is the wave function of harmonic oscillators in the $\mathbf{n}$th state and

$$Z=\sum_{\mathbf{n}}e^{-\beta E_{\mathbf{n}}}. \tag{B4}$$

It is well known that $\rho(\mathbf{q},\mathbf{q}')$ is a product of Gaussians:

$$\rho(\mathbf{q},\mathbf{q}')=\prod_{\mathbf{k},\lambda,\sigma}\rho_{\mathbf{k},\lambda}(q_{\mathbf{k}\lambda\sigma},q_{\mathbf{k}\lambda\sigma}'), \tag{B5}$$

with

$$\begin{aligned}\rho_{\mathbf{k},\lambda}(q_{\mathbf{k}\lambda\sigma},q_{\mathbf{k}\lambda\sigma}')&=(\xi_{\mathbf{k}\lambda}/\pi)^{1/2}\\ &\times\exp[-\xi_{\mathbf{k}\lambda}(q_{\mathbf{k}\lambda}{}^2+q_{\mathbf{k}\lambda}'^2)-\tfrac{1}{2}\eta_{\mathbf{k}\lambda}(q_{\mathbf{k}\lambda}-q_{\mathbf{k}\lambda}')^2],\end{aligned} \tag{B6}$$

where

$$\xi_{\mathbf{k}\lambda}=\omega_{\mathbf{k}\lambda}\tanh(\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}) \tag{B7}$$

and

$$\eta_{\mathbf{k}\lambda}=\omega_{\mathbf{k}\lambda}\,\mathrm{csch}(\beta\omega_{\mathbf{k}\lambda}). \tag{B8}$$

The diagonal element $\rho(\mathbf{q},\mathbf{q})$ can be written as

$$\rho(\mathbf{q},\mathbf{q})=\Big[\prod_{k,\lambda,\sigma}(\xi_{\mathbf{k}\lambda}/\pi)^{1/2}\Big]e^{-Q}, \tag{B9}$$

where

$$Q=\sum_{\mathbf{k},\lambda,\sigma}\xi_{\mathbf{k}\lambda}q_{\mathbf{k}\lambda\sigma}{}^2. \tag{B10}$$

iii. "Exchanged" Phonon Density Matrix

The expression (3.5) for J_{ij} involves the lattice average $\sum_{\mathbf{n}}\exp(-\beta E_{\mathbf{n}})(\varphi_{\mathbf{n}},H_{ij}P_{ij}\varphi_{\mathbf{n}})$. It is essential for the evaluation of such an average that the exchanged phonon density matrix

$$\rho_x(\mathbf{q},\mathbf{q}')=(1/Z)\sum_{\mathbf{n}}e^{-\beta E_{\mathbf{n}}}[P_{ij}\varphi_{\mathbf{n}}(\mathbf{q})]\varphi_{\mathbf{n}}(\mathbf{q}') \tag{B11}$$

be evaluated. The result for $\rho_x(\mathbf{q},\mathbf{q}')$ can be obtained by noting that $P_{ij}\varphi_{\mathbf{n}}(\mathbf{q})$ is the same function of the set $\hat{\mathbf{q}}$ that $\varphi_{\mathbf{n}}(\mathbf{q})$ is of the set $\mathbf{q}$, where the set $\hat{\mathbf{q}}$ is obtained by the transformation

$$\begin{aligned}\hat{q}_{\mathbf{k}\lambda\sigma}&=P_{ij}q_{\mathbf{k}\lambda\sigma}\\ &=(2m/N)^{1/2}\sum_{\alpha}[\Omega_\sigma(\mathbf{k}\cdot\mathbf{R}_i)(\mathbf{r}_j-\mathbf{R}_i)_\alpha\\ &\qquad+\Omega_\sigma(\mathbf{k}\cdot\mathbf{R}_j)(\mathbf{r}_i-\mathbf{R}_j)_\alpha+\sum_{l\neq i,j}\Omega_\sigma(\mathbf{k}\cdot\mathbf{R}_l)]\mathbf{u}_{l\alpha}\\ &=q_{\mathbf{k}\lambda\sigma}+(2m/N)^{1/2}\sum_{\alpha}\epsilon_{\mathbf{k}\lambda\alpha}[\Omega_\sigma(\mathbf{k}\cdot\mathbf{R}_i)\\ &\qquad\qquad-\Omega_\sigma(\mathbf{k}\cdot\mathbf{R}_j)](\mathbf{r}_j-\mathbf{r}_i)_\alpha.\end{aligned} \tag{B12}$$

Thus, on substituting $\hat{\mathbf{q}}$ for $\mathbf{q}$ in (B6), one obtains for $\rho_x(\mathbf{q},\mathbf{q}')$,

$$\rho_x(\mathbf{q},\mathbf{q}')=\overline{\prod_{\mathbf{k},\lambda,\sigma}}\rho_{\mathbf{k}\lambda}(\hat{q}_{\mathbf{k}\lambda\sigma},q_{\mathbf{k}\lambda\sigma}'), \tag{B13}$$

where

$$\begin{aligned}\rho_{\mathbf{k},\lambda}(\hat{q}_{\mathbf{k}\lambda\sigma}q_{\mathbf{k}\lambda\sigma}')&=(\xi_{\mathbf{k}\lambda}/\pi)^{1/2}\exp[-\tfrac{1}{2}\xi_{\mathbf{k}\lambda}(\hat{q}_{\mathbf{k}\lambda\sigma}{}^2+q_{\mathbf{k}\lambda\sigma}'^2)\\ &\qquad-\tfrac{1}{2}\eta_{\mathbf{k}\lambda}(\hat{q}_{\mathbf{k}\lambda\sigma}-q_{\mathbf{k}\lambda\sigma}')^2].\end{aligned} \tag{B14}$$

The diagonal element in (B14) can be written

$$\rho_x(\mathbf{q},\mathbf{q})=\Big[\prod_{\mathbf{k},\lambda}(\xi_{\mathbf{k}\lambda}/\pi)^{1/2}\Big]\exp[-\tfrac{1}{2}(Q+Q_Z+Q_3)] \tag{B15}$$

where

$$Q=\overline{\sum_{\mathbf{k},\lambda,\sigma}}\xi_{\mathbf{k}\lambda}q_{\mathbf{k}\lambda\sigma}{}^2, \tag{B16}$$

$$Q_z=\overline{\sum_{\mathbf{k},\lambda,\sigma}}\xi_{\mathbf{k}\lambda}\hat{q}_{\mathbf{k}\lambda\sigma}{}^2, \tag{B17}$$

and

$$\begin{aligned}Q_3&=\overline{\sum_{\mathbf{k},\lambda,\sigma}}\eta_{\mathbf{k}\lambda}(q_{\mathbf{k}\lambda\sigma}-\hat{q}_{\mathbf{k}\lambda\sigma})^2\\ &=(4m/N)\sum_{\alpha,\beta}\sum_{\mathbf{k},\lambda}(1-\cos\mathbf{k}\cdot\mathbf{R})\epsilon_{\mathbf{k}\lambda\alpha}\epsilon_{\mathbf{k}\beta\lambda}\eta_{\mathbf{k}\lambda}r_\alpha r_\beta,\end{aligned} \tag{B18}$$

where

$$\mathbf{R}=\mathbf{R}_i-\mathbf{R}_j$$

and

$$\mathbf{r}=\mathbf{r}_i-\mathbf{r}_j.$$

Thus Q_3 depends only on the coordinates of particles i and j.

iv. Generalization of the Jackson-Feenberg Method

Here a transformation originally derived by Jackson and Feenberg[28] will be generalized. It has been used

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[28] H. W. Jackson and E. Feenberg, Ann. Phys. (N. Y.) **15**, 266 (1961).

several times in the present work. The integral

$$I=\int d\mathbf{r}\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r}')\nabla_r^2[f(\mathbf{r})\rho(\mathbf{r},\mathbf{r}')] \quad \text{(B19)}$$

is considered where ∇_r^2 is the Laplacian acting on $\mathbf{r}$. Integrating (B19) by parts with respect to $\mathbf{r}$, one finds

$$I=\int d\mathbf{r}\int d\mathbf{r}'\nabla_r[\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r}')]\cdot\nabla_r[f(\mathbf{r})\rho(\mathbf{r},\mathbf{r}')]. \quad \text{(B20)}$$

Using $\nabla_r\delta(\mathbf{r}-\mathbf{r}')=-\nabla_{r'}\delta(\mathbf{r}-\mathbf{r}')$ in (B20) and integrating by parts with respect to r', one has

$$I=-\int d\mathbf{r}\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')\nabla_{r'}\times\{f(\mathbf{r}')\nabla_r[f(\mathbf{r})\rho(\mathbf{r},\mathbf{r}')]\}. \quad \text{(B21)}$$

Alternatively, integrating (B20) by parts with respect to $\mathbf{r}$, one finds

$$I=\int d\mathbf{r}\int d\mathbf{r}'\nabla_r^2[\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r})f(\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')] \quad \text{(B22)}$$

$$=\int d\mathbf{r}\int d\mathbf{r}'\nabla_{r'}^2[\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r})f(\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')]. \quad \text{(B23)}$$

Integrating (B22) by parts twice with respect to $\mathbf{r}$ and (B23) with respect to $\mathbf{r}'$, one gets successively

$$I=\int d\mathbf{r}\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r})\nabla_{r'}^2[f(\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')] \quad \text{(B24)}$$

$$=-\int d\mathbf{r}\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')\nabla_r\{f(\mathbf{r})\nabla_{r'}[f(\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')]\}. \quad \text{(B25)}$$

Adding (B19), (B21), (B24), and (B25) and dividing by 4, one finds

$$I=\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')(f(\mathbf{r}')\nabla_r^2[f(\mathbf{r})\rho(\mathbf{r},\mathbf{r}')] + f(\mathbf{r})\nabla_{r'}^2[f(\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')]-\nabla_{r'}\{f(\mathbf{r}')\nabla_r[f(\mathbf{r})\rho(\mathbf{r},\mathbf{r}')]\} -\nabla_r\{f(\mathbf{r})\nabla_{r'}[f(\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')]\}). \quad \text{(B26)}$$

Expanding each term in (B26) and then regrouping terms, one has on integration where possible by using the δ function and regrouping terms:

$$I=\frac{1}{2}\int d\mathbf{r}f^2(\mathbf{r})\rho(\mathbf{r},\mathbf{r})\nabla^2\ln f(\mathbf{r}) +\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r}')f(\mathbf{r})(\nabla_r-\nabla_{r'})^2\rho(\mathbf{r},\mathbf{r}'). \quad \text{(B27)}$$

v. Integration Formula

Consider the integral

$$I=\int d\mathbf{q}\exp(-\mathbf{q}\cdot\mathsf{M}\cdot\mathbf{q}), \quad \text{(B28)}$$

where $\mathbf{q}$ is a column vector with n elements, which is further written as $\mathbf{q}=(\mathbf{q}_x\ \mathbf{q}_y)$, where $\mathbf{q}_x$ and $\mathbf{q}_y$ are column vectors with n_x and n_y elements, respectively. Further, M is an $n\times n$ matrix

$$\mathsf{M}=\begin{bmatrix}\mathsf{M}_{xx} & \mathsf{M}_{yy}\\ \mathsf{M}_{yx} & \mathsf{M}_{yy}\end{bmatrix}, \quad \text{(B29)}$$

where M_{xx} and M_{yy} are $n_x\times n_x$ and $n_y\times n_y$ matrices, respectively. Then it is known that[17]

$$I=\pi^{n_y/2}|\mathsf{M}|^{-\frac{1}{2}}|\mathsf{M}^{-1}{}_{xx}|^{-\frac{1}{2}}\int d\mathbf{q}_x \times\exp[-\mathbf{q}_x\cdot(\mathsf{M}^{-1}{}_{xx})^{-1}\cdot\mathbf{q}_x], \quad \text{(B30)}$$

where $\mathsf{M}^{-1}{}_{xx}$ is defined by

$$\begin{bmatrix}\mathsf{M}_{xx} & \mathsf{M}_{xy}\\ \mathsf{M}_{yx} & \mathsf{M}_{yy}\end{bmatrix}\begin{bmatrix}\mathsf{M}^{-1}{}_{xx} & \mathsf{M}^{-1}{}_{xy}\\ \mathsf{M}^{-1}{}_{yx} & \mathsf{M}^{-1}{}_{yy}\end{bmatrix}=\begin{bmatrix}\mathsf{I} & 0\\ 0 & \mathsf{I}\end{bmatrix}. \quad \text{(B31)}$$

Further, it can be shown that

$$\mathsf{M}^{-1}{}_{xx}=\mathsf{M}_{xx}-\mathsf{M}_{xy}\mathsf{M}^{-1}{}_{yy}\mathsf{M}_{yx}. \quad \text{(B32)}$$

If $(\mathbf{x})=(\mathbf{u}_i\ \mathbf{u}_j)$, where $\mathbf{u}_i$ is the deviation of the ith particle from equilibrium, it is possible to write

$$\mathsf{M}^{-1}{}_{xx}=\begin{bmatrix}\mathsf{P}_{ij} & -\mathsf{P}_{ij}\\ -\mathsf{P}_{ij} & \mathsf{P}_{ij}\end{bmatrix}, \quad \text{(B33)}$$

where P_{ij} is a 3×3 matrix with elements given by[17]

$$(\mathsf{P}_{ij}{}^{-1})_{\alpha\beta}=(2\hbar/mN)\sum_{\mathbf{k},\lambda}\epsilon_{\mathbf{k}\lambda\alpha}{}^*\epsilon_{\mathbf{k}\beta\lambda} \times(1-\cos\mathbf{k}\cdot\mathbf{R}_{ij})\omega_{k\lambda}{}^{-1}, \quad \text{(B34)}$$

where $\omega_{\mathbf{k},\lambda}$ are the phonon frequencies obtained from the matrix M by well-known transformations.[12]

2. Calculation of $\langle H_{ij}\rangle$ and $\langle P_{ij}H_{ij}\rangle$

The quantities

$$\langle H_{ij}\rangle=\langle f_{ij}{}^2\rangle^{-1}\int d\mathbf{r}\int d\mathbf{r}'f(r'_{ij})f(r_{ij})\prod_k\delta(\mathbf{r}_k-\mathbf{r}_k{}') \times[-(\hbar^2/2m)(\nabla_i{}^2+\nabla_j{}^2)+v_{ij}]\rho(\mathbf{r},\mathbf{r}') \quad \text{(B35)}$$

and

$$\langle P_{ij}H_{ij}\rangle=\langle f_{ij}{}^2\rangle^{-1}\int d\mathbf{r}\int d\mathbf{r}'f(r'_{ij})f(r_{ij})\prod_k\delta(\mathbf{r}_k-\mathbf{r}_k{}') \times[-(\hbar^2/2m)(\nabla_i{}^2+\nabla_j{}^2)+v_{ij}]\rho_x(\mathbf{r},\mathbf{r}') \quad \text{(B36)}$$

are considered, where **r** stands for the set of coordinates of all the particles.

One may employ integration formula (B30) to get

$$\langle P_{ij}H_{ij}\rangle=\langle f_{ij}^2\rangle^{-1}\int d\mathbf{r}\, f_{ij}^2\tilde{v}_{ij}\rho_x(\mathbf{r},\mathbf{r}')$$

$$-\frac{\hbar^2}{8m}\langle f_{ij}^2\rangle^{-1}\int d\mathbf{r}\int d\mathbf{r}'\prod_k \delta(\mathbf{r}_k-\mathbf{r}_k')f(r_{ij}')f(r_{ij})$$

$$\times[(\nabla_i-\nabla_i')^2+(\nabla_j-\nabla_j')^2]\rho_x(\mathbf{r},\mathbf{r}'). \quad \text{(B37)}$$

The first integral is straightforward; it is denoted by $\langle P_{ij}\tilde{v}_{ij}\rangle$ and is given by Eq. (4.5). The second integral may be written $(-\hbar^2/8m)(M_i+M_j)$, where M_i denotes the integral which has $(\nabla_i-\nabla_i')^2$ in the integrand. It is clear that $M_i=M_j$. One may integrate in M_i with respect to all primed coordinates but $\mathbf{r}_i'$ to get

$$M_i=\langle f_{ij}^2\rangle^{-1}\int d\mathbf{r}_i\int d\mathbf{r}_j'\int dr_i'$$

$$\times\delta(\mathbf{r}_i-\mathbf{r}_i')f^2(r_{ij})[\nabla_i-\nabla_i']^2\rho_x(\mathbf{r},\mathbf{r}'). \quad \text{(B38)}$$

In Eq. (B13) for $\rho_x(\mathbf{r},\mathbf{r}')$, the exponent is $\frac{1}{2}(Q+Q_z'+Q_3)$. Transforming to coordinate space by (B2) and with some manipulation, one has

$$\tfrac{1}{2}(Q+Q_z')=\tfrac{1}{4}(\mathbf{x}-\mathbf{z}')\cdot\mathbf{C}_{xx}\cdot(\mathbf{x}-\mathbf{z}')+\boldsymbol{\eta}\cdot\mathbf{C}\cdot\boldsymbol{\eta}, \quad \text{(B39)}$$

where $\mathbf{C}$ is the $3N\times3N$ matrix of force constants and C_{xx} is the 6×6 matrix:

$$\mathbf{C}_{xx}=\begin{pmatrix}\mathbf{C}_{ii} & \mathbf{C}_{ij}\\ \mathbf{C}_{ji} & \mathbf{C}_{jj}\end{pmatrix},$$

where $\mathbf{C}_{ii}=\mathbf{C}_{jj}$, $\mathbf{C}_{ij}=\mathbf{C}_{ji}$ are 3×3 matrices. Further,

$$\mathbf{x}=\begin{pmatrix}\mathbf{r}_i-\mathbf{R}_i\\ \mathbf{r}_j-\mathbf{R}_j\end{pmatrix}, \quad \mathbf{z}=\begin{pmatrix}\mathbf{r}_j-\mathbf{R}_i\\ \mathbf{r}_i-\mathbf{R}_j\end{pmatrix},$$

$$\boldsymbol{\eta}=\begin{pmatrix}\boldsymbol{\xi}'\\ \mathbf{y}\end{pmatrix}, \qquad \boldsymbol{\xi}'=\tfrac{1}{2}(\mathbf{x}+\mathbf{z}'),$$

and **y** is the column vector containing all $(\mathbf{r}_k-\mathbf{R}_k)$, $k\neq i,j$; as elements. With Eq. (B18) for Q_3, it is possible to write

$$\tfrac{1}{4}(\mathbf{x}-\mathbf{z}')\cdot\mathbf{C}_{xx}\cdot(\mathbf{x}-\mathbf{z}')+\tfrac{1}{2}Q_3=\tfrac{1}{4}(\mathbf{r}_{ij}'-\mathbf{s}_{ij}')$$

$$\times\begin{bmatrix}\mathbf{C}_{ii}+4\mathbf{P}_{ii} & \mathbf{C}_{ij}+4\mathbf{P}_{ij}\\ \mathbf{C}_{ij}+4\mathbf{P}_{ij} & \mathbf{C}_{ii}+4\mathbf{P}_{ii}\end{bmatrix}\cdot\begin{bmatrix}\mathbf{r}_{ij}'\\ -\mathbf{s}_{ij}'\end{bmatrix}, \quad \text{(B40)}$$

where $\mathbf{r}_{ij}'=\mathbf{r}_i-\mathbf{r}_j'$; $\mathbf{s}_{ij}'=\mathbf{r}_i+\mathbf{r}_j'$, and

$$(P_{ii})_{\alpha\beta}=(2m/N)\sum_{\mathbf{k},\lambda}\eta_{\mathbf{k}\lambda}\epsilon_{\mathbf{k}\lambda\alpha}^*\epsilon_{\mathbf{k}\beta\lambda}, \quad \text{(B41)}$$

$$(P_{ij})_{\alpha\beta}=(2m/N)\sum_{\mathbf{k},\lambda}\cos(\mathbf{k}\cdot\mathbf{R}_{ij})\eta_{\mathbf{k}\lambda}\epsilon_{\mathbf{k}\lambda\alpha}^*\epsilon_{\mathbf{k}\beta\lambda}. \quad \text{(B42)}$$

With the exponent in $\rho_x(\mathbf{r},\mathbf{r}')$ in this form, it is easy to see that the integration over $\mathbf{r}_k$ $(k\neq i,j)$ in M_i can be carried out by the Kohler formula to get

$$M_i=\pi^{-3}\langle f_{ij}^2\rangle^{-1}|\boldsymbol{\Gamma}_{xx}^{-1}|^{1/2}\int d\mathbf{r}_i\int d\mathbf{r}_j\int d\mathbf{r}_i'\int d\mathbf{r}_j'$$

$$\times\delta(\mathbf{r}_i-\mathbf{r}_i')\delta(\mathbf{r}_j-\mathbf{r}_j')f(\mathbf{r}_{ij})f(\mathbf{r}_{ij}')(\nabla_i-\nabla_i')^2$$

$$\times\exp[-\tfrac{1}{4}(\mathbf{x}-\mathbf{z}')\cdot\mathbf{C}_{xx}\cdot(\mathbf{x}-z')$$

$$-\tilde{\xi}'\boldsymbol{\Gamma}_{xx}^{-1}\xi-\tfrac{1}{2}Q_3'], \quad \text{(B43)}$$

where

$$\boldsymbol{\Gamma}_{xx}^{-1}=\begin{bmatrix}\mathbf{F}_{ij} & -\mathbf{F}_{ij}\\ -\mathbf{F}_{ij} & \mathbf{F}_{ij}\end{bmatrix},$$

and where $\mathbf{F}_{ij}$ is a 3×3 matrix with elements given by (4.6). Next, the partial differentiation in (B38) is performed and the δ function used to integrate over the primed variables; the center-of-mass integration of coordinates i and j is then performed to get

$$M_i=\pi^{-3/2}\langle f_{ij}^2\rangle^{-1}|\mathbf{F}_{ij}|^{1/2}D[\exp(-\mathbf{R}_{ij}\cdot\mathbf{F}_{ij}\cdot\mathbf{R}_{ij})]$$

$$\times\int d\mathbf{r}_{ij}f^2(\mathbf{r}_{ij})\exp(-\mathbf{r}_{ij}\cdot\mathbf{G}_{ij}\cdot\mathbf{r}_{ij}), \quad \text{(B44)}$$

where

$$D=-2\,\mathrm{Tr}F-\mathrm{Tr}(\mathbf{C}_{ii}+\mathbf{C}_{ij}+4\mathbf{P}_{ii}+4\mathbf{P}_{ij})$$

$$+4\mathbf{R}\cdot\mathbf{F}^2\cdot\mathbf{R}, \quad \text{(B45)}$$

and $\mathbf{G}_{ij}$ is a 3×3 matrix with elements

$$(\mathbf{G}_{ij})_{\alpha\beta}=\tfrac{1}{2}(\mathbf{C}_{ii}+4\mathbf{P}_{ii}-\mathbf{C}_{ij}-4\mathbf{P}_{ij})_{\alpha\beta},$$

which may be expressed as in (4.7). Finally,

$$\langle P_{ij}H_{ij}\rangle=\langle P_{ij}\tilde{v}_{ij}\rangle-(\hbar^2/4m)M_i. \quad \text{(B46)}$$

The quantity $\langle H_{ij}\rangle$ is much easier to evaluate; the result is merely quoted:

$$\langle H_{ij}\rangle=\langle\tilde{v}_{ij}\rangle+(\hbar^2/2m)\,\mathrm{Tr}\mathbf{C}_{ii}. \quad \text{(B47)}$$

Since $\mathrm{Tr}\mathbf{C}_{ii}$ is the sum of the phonon frequencies, the second term in (B47) is the kinetic energy contribution to $\langle H_{ij}\rangle$.

APPENDIX C: APPROXIMATIONS USED IN THE SELF-CONSISTENT PHONON CALCULATION

Since the exchange integral is sensitive only to averages over the phonon spectrum, it is not necessary to do the calculation of the phonon spectrum exactly. We have used the following two approximations for the self-consistent phonon trial wave function.

(1) The "one-branch" approximation (OBA):

$$\omega_{\mathbf{k}\lambda}\simeq\omega_k; \quad \text{(C1)}$$

(2) The "two-branch" approximation (TBA):

$$\begin{aligned}\omega_{\mathbf{k}\lambda}&\simeq\omega_{kl}, && \text{longitudinal mode}\\ &\simeq\omega_{kt}, && \text{each transverse mode}\\ \epsilon_{\mathbf{k}\lambda\alpha}&\simeq k_\alpha/k, && \text{longitudinal mode.}\end{aligned} \quad \text{(C2)}$$

TABLE II. Calculations of the ground-state energy E_0 for a nearest-neighbor distance $R=3.65$ Å. Here EA and SCPA refer to calculations using the Einstein approximation (Ref. 13) and the self-consistent-phonon approximation (Ref. 17), respectively.

Approx	EA	OBA	TBA	SCPA
E_0 (cal/mole)	11.7	10.1	7.7	7.3

These equations together with the orthonormality relation for a Bravais lattice,

$$\sum_{\lambda} \epsilon_{\mathbf{k}\lambda\alpha}\epsilon_{\mathbf{k}\lambda\beta}=\delta_{\alpha\beta}\,, \tag{C3}$$

define the approximations.

In both of these approximations, the matrix $(\mathbf{F}_{ij})_{\alpha\beta}$ of (4.6) is diagonal. In the OBA the results are

$$(\mathbf{F}_{ij}^{-1})_{\alpha\beta}=\delta_{\alpha\beta}\frac{\hbar}{m\rho\pi^2}\int_0^{k_m} dk\frac{k^2}{\omega_k} \times[1-\sin(kR_{ij})/kR_{ij}]\coth(\tfrac{1}{2}\beta\hbar\omega_k)\,; \tag{C4}$$

in the TBA they are

$$(\mathbf{F}_{ij}^{-1})_{\alpha\beta}=\delta_{\alpha\beta}\frac{\hbar}{4m\rho\pi^3}\int_{0\leq k\leq k_m} d\mathbf{k}(1-\cos\mathbf{k}\cdot\mathbf{R}_{ij}) \times[\omega_{kl}^{-1}\epsilon_{\mathbf{k}l\alpha}^2\coth(\tfrac{1}{2}\beta\hbar\omega_{kl}) +\omega_{kt}^{-1}(1-\epsilon_{\mathbf{k}l\alpha}^2)\coth(\tfrac{1}{2}\beta\hbar\omega_{kt})]\,. \tag{C5}$$

The virtue of the "two-branch" approximation is that $(\mathbf{F}_{ij}^{-1})_{\alpha\beta}$ has the correct form for nearest and next-nearest neighbors. If the z axis is taken along $\mathbf{R}_{ij}$, the matrix is diagonal with the x and y components equal. In both approximations the analog of (2.8) can be obtained straightforwardly by operating on (2.8) with $(4\pi)^{-1}\int d\Omega_{\mathbf{k}}$ and using (C1)–(C3). To apply these results to calculations of exchange we need the matrix $(\mathbf{G}_{ij})_{\alpha\beta}$ defined by (4.7). The results are straightforward to obtain and quite analogous to (C3) and (C4).

Typical numerical results obtained using these approximations are given in Tables II and III along with various comparisons to other calculations. In all cases, the short-range correlations were treated using the analytic form of Ref. 13. From Table II we see that the TBA is almost as good as the SCPA in calculating E_0, a quantity which also depends on an average over the phonon spectrum. In Table III, we see how the "width" parameters change as better approximations are adopted (note that $F_{\parallel}=\frac{1}{2}A$ in the EA, to make a comparison with earlier work). It is the difference between $F_{\parallel}(G_{\parallel})$ and $F_{\perp}(G_{\perp})$ which leads to all improvements obtained from self-consistent calculations.

TABLE III. Calculations of the width parameters important to the exchange integral calculation for the various approximations. Here R is the nearest-neighbor distance in angstroms and V is the volume in cm³/mole. The quantities $F_{\parallel}(G_{\parallel})$ and $F_{\perp}(G_{\perp})$ are the components parallel and perpendicular to $\mathbf{R}$, respectively. In the EA, there is no distinction between F and G; in the OBA there is no distinction between parallel and perpendicular components.

			$F_{\parallel}$		$F_{\perp}$	$G_{\parallel}$		$G_{\perp}$
R	V	EA	OBA	TBA	TBA	OBA	TBA	TBA
3.45	19.0	0.864	0.993	0.973	0.847	0.935	1.000	0.867
3.55	20.7	0.794	0.895	0.878	0.767	0.843	0.884	0.768
3.65	22.5	0.719	0.801	0.787	0.669	0.755	0.786	0.685
3.75	24.5	0.649	0.718	0.705	0.618	0.676	0.703	0.613

APPENDIX D: LOW-TEMPERATURE APPROXIMATIONS

We shall now discuss the approximation leading to (2.5), which is necessary because of the nonorthogonality of the set (2.1). Equation (2.5) is exact for $T=0$, and it is a good approximation as long as $\langle 0|f_{ij}^2|0\rangle\simeq\langle\mathbf{n}|f_{ij}^2|\mathbf{n}\rangle$ for those excited states of importance. For $T\ll\Theta_D$ only low-lying excited states are important and the choice of an $f(r_{ij})$, which is nearly unity for $r_{ij}\gtrsim\sigma$, makes it likely that the above condition is satisfied. In fact, our calculations have shown that $\langle f^2\rangle\simeq\langle 0|f^2|0\rangle$ for $T\ll\Theta_D$, a result which further supports the use of this approximation. The above argument also supports the derivation of (4.2) from (4.1), so long as overlap integrals between important excited states are not large.

In Sec. II, we have taken the density matrix ρ for the system to be that of a set of harmonic oscillators. Thus we have neglected the contribution of the short-range correlations to the entropy. The correct expression for ρ is

$$\rho(\mathbf{r},\mathbf{r}')=\sum_{\mathrm{n}} e^{-\beta E_{\mathrm{n}}}\left[\psi_n(\mathbf{r})\psi_{\mathrm{n}}(r')\Big/\int d\mathbf{r}\,\psi_{\mathrm{n}}^2(\mathbf{r})\right].$$

Now

$$S=-k\rho\ln\rho\,;$$

and if we write $f_{ij}\approx 1+x$, then, on expanding the logarithm, the contribution of the short-range correlations to the entropy is $O(\langle x^2\rangle)\ll 1$ for the $f(r_{ij})$ used in this work.