# Correlation Effects in Quantum Crystals

C. Ebner and C. C. Sung

*Department of Physics, The Ohio State University, Columbus, Ohio* 43210

Correlation effects in the quantum crystals $He^3$ and $He^4$ are studied in detail. The single-particle wave function is obtained in the harmonic effective-field approximation; the parameters of the harmonic-oscillator potential are determined self-consistently from the two-body correlation function and the bare interatomic potential. We determine the two-body correlation function by solving numerically an equation derived by decoupling the three-body correlation function into a product of two-body correlation functions. This equation is similar to one derived on the basis of the $T$-matrix approximation, but yields the correct behavior of the correlation function as the distance between the particles tends to zero. The ground-state energy, pressure, and compressibility are computed over a wide range of molar volume for $He^3$ in the bcc and hcp structures, and for hcp $He^4$. In bcc $He^3$ we employ two different interatomic potentials, the Lennard-Jones 6-12 potential generally used in calculations of this type and also the Yntema-Schneider potential. We find a ground-state energy about $1\frac{1}{2}$ °K too low with the former and about 5 °K too high with the latter, demonstrating that the choice of potential is of considerable importance for detailed comparison of theory and experiment. We also examine the effect of three-body correlations on the equation for the two-body correlation function; the result suggests that the effect is to force the two particles toward one another, which also seems physically reasonable, as the atoms surrounding a particular pair of particles should tend to push them together. We incorporate this effect into the two-particle equation by including a potential linear in the interparticle distance; for a given molar volume, its magnitude is chosen by imposing a constraint on the average interparticle distance. The calculated correlation functions for neighboring particles have peaks at about the corresponding lattice distance, and the numerical results for energy, pressure, and compressibility are in reasonable agreement with experiment. Our approach is compared with other recent theories of quantum crystals.

## I. INTRODUCTION

It was first pointed out by de Wette and Nijboer[1] that when atoms of small mass, such as helium, form crystals, the phonon frequencies cannot be obtained by classical lattice dynamics. The force constant that is calculated from the bare interatomic interaction, usually taken as a Lennard-Jones 6-12 potential or some other acceptable form with a repulsive core and a weak attractive well,[2] is negative and thus gives imaginary frequencies. Similarly, the small atomic mass and the form of the interaction lead to difficulties in the calculation of such quantities as the ground-state energy $E_0$, pressure $P$, and compressibility $K$ of these "quantum crystals" as functions of the molar volume. Numerous theories designed to circumvent these difficulties have been put forward; we mention two rather independent approaches.

The self-consistent phonon formalism was developed by Brenig,[3] Koehler,[4] and Choquard[5] and subsequently applied by Horner[6] and by Koehler, Gillis, and Werthamer.[7] The phonon energy is calculated by assuming sets of force constants which must be determined self-consistently by taking the ensemble average. In principle, there are no externally specified parameters, but in order to determine the force constants from the ensemble average over

the potential, strong short-range correlations have to be introduced in an *ad hoc* manner to remove the singularity in the interaction.

A second approach is based on the single-particle aspect of the system. One starts by describing the crystal as a collection of localized particles with strong short-range correlations. The single-particle wave functions and two-particle correlation functions can be found, for example, from a variational principle involving the ground-state energy $E_0$ which is obtained from a linked-cluster expansion. Nosanow[8] and Hetherington, Mullin, and Nosanow[9] used this approach, giving the single-particle and correlation functions specific forms containing undetermined parameters to be found from the variational principle. A more complicated procedure along the same general lines has been given by Woo and Massey[10]; Guyer[11] and co-workers[12,13] have modified the approach somewhat by assuming at the outset a self-consistent simple harmonic-oscillator potential field at each atomic site in the crystal. The parameters in this potential are determined by minimizing the total energy. Also, Horner[14] and Iwamoto and Namaizawa[15] have developed theories involving the summation of ladder diagrams. Finally we mention similar work by Brueckner and Frohberg.[16]

One weakness of this second approach is that there

is difficulty in the construction of excited states of the crystals,[17] effectively limiting the description to zero temperature.

The numerical results of several of the recent works for the pressure and compressibility as functions of molar volume are in very satisfactory agreement with experiment, and the ground-state energy per particle is generally within several degrees kelvin of the experimentally inferred energy. We should note, however, that these results are achieved using the Lennard-Jones 6-12 potential as the bare interatomic interaction. There are other empirically determined potentials[2] which must be considered acceptable choices also, since there is no one potential which is consistent with all of the measured thermodynamic and transport properties of gaseous and liquid helium. As we discuss below, it turns out that the calculated properties of crystalline He depend rather sensitively on the choice of potential; therefore, we feel that one has to be cautious in interpreting the numerical success of a calculation as a justification of the method or approximations involved.

Because this paper overlaps in some respects with several of the earlier works listed in the second approach above, we wish to point out some of the differences and similarities here. First, we follow Ref. 15 in making a choice of variables such that a two-dimensional equation must be solved for the two-particle correlation function. Also, the self-consistent single-particle effective potential field is determined by expanding the averaged bare interaction as in Ref. 15, rather than by using a variational principle.[11,14]

The equation for the two-particle correlation function is obtained by truncating the hierarchy of equations for $n$-particle correlation functions. Specifically, the three-particle function is written as a product of three two-particle functions. We neglected, in our first attempts at calculation, those purely three-body correlations which still remain in this scheme. The resulting equation for the two-particle function is similar to that obtained in the $T$-matrix approximation,[14] but there is a difference in the behavior of the functions as the interparticle distance goes to zero.

This procedure leads to a calculated ground-state energy $E_0$ which is generally lower than that found by other workers. For example, in the bcc phase of He[3] it is about $4\frac{1}{2}$ °K/particle below the result of Ref. 11 and $1\frac{1}{2}$ °K/particle below the experimentally determined energy. Because the equations obeyed by the two-particle correlation function are quite similar in our work and that in Ref. 11, this difference could well arise from the numerical approximations used in each case to obtain a solution. This point is considered further in Sec. VI.

Our first attempts at quantitative calculation also produced pressures considerably below those found experimentally. We therefore examined our various approximations to see which one might have caused $E_0$ to be insensitive to volume; the most likely source of error seems to be the neglect of three- (and higher) body correlations which would tend to force a given pair of neighboring particles together. It is difficult to evaluate the effect quantitatively, so we have introduced into the two-particle equation a potential-energy term which is proportional to the separation between particles.[18] The magnitude of this potential is determined by requiring that the expectation value of the projection of $\vec{r}_1 - \vec{r}_2$ along the direction of $\vec{R}_i - \vec{R}_j$ be equal to $|\vec{R}_i - \vec{R}_j|$, where $\vec{r}_1$ and $\vec{r}_2$ are the position of particles 1 and 2 and $\vec{R}_i$ and $\vec{R}_j$ are the lattice sites around which the particles are localized. This constraint seems physically reasonable; it is very close to a constraint used by Krumhansl and Wu[19] in a theory of solid hydrogen.

The remainder of this paper is organized as follows. The Green's-function (GF) formalism is in Sec. II; at zero temperature this is unnecessary but makes the approximations more transparent. Section III contains the derivation of the two-particle GF and the decoupling approximation. In Sec. IV the correction designed to approximate the effect of three-body correlations is introduced. Section V is a description of the numerical procedures used to solve the equation, and in Sec. VI we give a discussion of the results and comparison with other theories and with experiment.

## II. GREEN'S-FUNCTION FORMALISM

In a crystalline solid, each particle is associated with a given lattice site and is located in a small volume around that site. Consequently, when the Heisenberg field operators $\Psi^\dagger$ and $\Psi$ are introduced, it is useful to define them such that operators associated with different sites commute with one another[17]; the creation operator is written as $\Psi_i^\dagger(\vec{r}, t)$ and the annihilation operator as $\Psi_i(\vec{r}, t)$, where the subscript $i$ refers to the lattice site located at $\vec{R}_i$. The equal-time commutation relations are

$$\Psi_i(\vec{r}, t)\Psi_j^\dagger(\vec{r}', t) \mp \Psi_j^\dagger(\vec{r}', t)\Psi_i(\vec{r}, t) = \delta_{ij}\delta(\vec{r} - \vec{r}') ,$$

$$\Psi_i(\vec{r}, t)\Psi_j(\vec{r}', t) \mp \Psi_j(\vec{r}', t)\Psi_i(\vec{r}, t) = 0 ,$$

and

$$\Psi_i^\dagger(\vec{r}, t)\Psi_j^\dagger(\vec{r}', t) \mp \Psi_j^\dagger(\vec{r}', t)\Psi_i^\dagger(\vec{r}, t) = 0 ,$$

where the upper (lower) sign is for bosons (fermions). The commutation relations exclude the possibility of exchanging particles on two lattice sites. The exchange probability can be evaluated theoretically and inferred experimentally and is found to be very small,[20] so the neglect of exchange is ac-

ceptable for the calculation of properties not intrinsically dependent on its existence. In what follows, we also make the approximation of neglecting possible double occupancy of a given lattice site.[21]

The Hamiltonian of the system of interacting particles is given in terms of the field operators by[22]

$$H = -(2m)^{-1}\sum_i \int \Psi_i^\dagger(\vec{r}, t)\nabla^2\Psi_i(\vec{r}, t)d^3r + \tfrac{1}{2}\sum_{i,j}\int \Psi_i^\dagger(\vec{r}, t)\Psi_j^\dagger(\vec{r}', t)V(\vec{r} - \vec{r}')\Psi_j(\vec{r}', t)\Psi_i(\vec{r}, t)d^3r\,d^3r' \ , \tag{1}$$

where $V(\vec{r} - \vec{r}')$ is the interatomic interaction which may be taken as the Lennard-Jones 6-12 potential[2] $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, with $\epsilon = 10.2\,^\circ\mathrm{K}$ and $\sigma = 2.556\,\mathrm{\AA}$.

The one- and two-particle Green's functions are introduced as

$$g_i(1, 1') = -i\langle T(\Psi_i(1)\Psi_i^\dagger(1'))\rangle$$

and

$$G_{ij}(12, 1'2') = (-i)^2\langle T(\Psi_i(1)\Psi_j(2)\Psi_j^\dagger(2')\Psi_i^\dagger(1'))\rangle \ ,$$

where $\langle T(\cdots)\rangle$ denotes the time-ordered ensemble average; the variables $(\vec{r}_1, t_1)$ are abbreviated as (1), etc.[23]

The equation of motion of $g_i(1, 1')$ is

$$\left(\frac{i\partial}{\partial t_1} + \frac{\nabla_1^2}{2m}\right)g_i(1, 1')$$

$$- \sum_j{}'i\int V(1, 2)G_{ij}(12, 1'2^+)\big|_{t_2 = t_1}d^3r_2 = \delta(1 - 1') \ , \tag{2}$$

where the sum over $j$ excludes the term $j = i$. The single-particle self-energy $\Sigma_i$ obeys the equation (where the bar indicates integrated variables)

$$\left(\frac{i\partial}{\partial t_1} + \frac{\nabla_1^2}{2m}\right)g_i(1, 1')$$

$$-\int \Sigma_i(1, \bar{1})g_i(\bar{1}, 1')d\bar{1} = \delta(1 - 1') \tag{3}$$

or

$$\int \Sigma_i(1, \bar{1})g_i(\bar{1}, 1')d\bar{1}$$

$$= i\sum_j{}'\int V(1, 2)G_{ij}(12, 1'2^+)\big|_{t_2 = t_1}d^3r_2 \ . \tag{4}$$

When the interaction $V$ possesses a hard core, the usual approximation is to sum the ladder diagrams, which is equivalent to writing the following equation for $G_{ij}$:

$$G_{ij}(12, 1'2') = g_i(1, 1')g_j(2, 2')$$

$$+ i\int g_i(1, \bar{1})g_j(2, \bar{2})V(\bar{1}, \bar{2})$$

$$\times G_{ij}(\bar{1}\,\bar{2}, 1'2')d\bar{1}d\bar{2} \ . \tag{5}$$

We next introduce the frequency representation of the Green's functions,[24]

$$G_{ij}(12, 1'2')\big|_{t_2 = t_1, t_2' = t_1^+}$$

$$= iT\sum_\nu e^{-i(t_1 - t_1')\omega_\nu}G_{ij}(12, 1'2'; \nu) \ ,$$

where $\omega_\nu = i\pi\nu T + \mu$; $\nu$ is an even (odd) integer for bosons (fermions), while $\mu$ is the chemical potential and $T$ is the temperature. Similar equations hold for $g_i$ and $\Sigma_i$. In the frequency representation, Eq. (5) becomes, for $t_2 = t_1$ and $t_2' = t_1^+$,

$$G_{ij}(12, 1'2'; \nu) = (iT)g_i(1, 1'; \nu)\sum_{\nu'}g_j(2, 2'; \nu') + i\int g_i(1, \bar{1}; \nu)g_j(2, \bar{2}; \nu)V(\bar{1}, \bar{2})G_{ij}(\bar{1}\,\bar{2}, 1'2'; \nu)d^3\bar{r}_1 d^3\bar{r}_2 \ . \tag{6}$$

Similarly, Eq. (4) becomes

$$(\omega_\nu + \nabla_1^2/2m)g_i(1, 1'; \nu)$$

$$-\int \Sigma_i(1, \bar{1}; \nu)g_i(\bar{1}, 1'; \nu)d^3\bar{r}_1 = \delta(r_1 - r_1') \ . \tag{7}$$

Because the particles are localized, $g_i(1, 1')$ is far from being a plane wave in the momentum representation; it is more convenient to solve the equations in coordinate space, although still very difficult. We make the following approximations to simplify the problem:

$$\int \Sigma_i(1, \bar{1}; \nu)g_i(\bar{1}, 1'; \nu)d^3\bar{r}_1 \simeq u_i(1)g_i(1, 1'; \nu) \ , \tag{8}$$

where $u_i$ is approximated as a harmonic-oscillator potential,

$$u_i(1) = u_0 + \alpha^4(\vec{r}_1 - \vec{R}_i)^2/2m \ . \tag{9}$$

From Eqs. (7)–(9), we can solve for $g_i$,

$$g_i(1, 1'; \nu) = \sum_{\mu = 0}[\phi_{i\mu}(1)\phi_{i\mu}(1')/(\omega_\nu - \epsilon_\mu)] \ , \tag{10}$$

where the function $\phi_{i\mu}$ is a (real) solution to the harmonic-oscillator Schrödinger equation in which $u_i(1)$ is the potential; $\epsilon_\mu$ is the corresponding eigenvalue. The ground-state wave function is

$$\phi_{i0}(1) = (\alpha^2/\pi)^{3/4}e^{-\alpha^2(\vec{r}_1 - \vec{R}_i)^2/2} \ , \tag{11}$$

with energy

$$\epsilon_0 = u_0 + 3\alpha^2/2m \ . \tag{12}$$

The one-particle Green's function is completely determined by the constants $u_0$ and $\alpha$ defined in Eqs.

(8) and (9); Eq. (8) amounts to a Hartree approximation for $G_{ij}(12, 1'2; \nu)$ insofar as dependence on $\omega_\nu$ is concerned.

The most general form that $G_{ij}$ can have is

$$G_{ij}(12, 1'2'; \nu) = (-i) \sum_{\rho, \sigma} \phi_{i\rho}(1') \phi_{j\sigma}(2') S_{i\rho, j\sigma}(1, 2; \nu) ,$$

$$(13)$$

where $S_{i\rho, j\sigma}(1, 2; \nu)$ must be proportional to $(\omega_\nu - \epsilon_\rho)^{-1}$ if Eq. (8) is to be satisfied. Difficulties arise from this form because $G_{ij}(12, 1'2; \nu)$ is forced to have the same analytical behavior as $g_i(1, 1'; \nu)$ as a function of $\omega_\nu$; therefore, we may say that $G_{ij}$ describes the motion of particle 1 at site $i$ in the presence of particle 2 at site $j$ without correlations in the motions of the two particles. But we started out at the be-

ginning with the intention of taking the strong short-range interparticle forces into account. This inconsistency has been introduced by neglecting the energy dependence of $\Sigma_i(1, \bar{2}; \nu)$ in Eq. (8). The meaning of Eq. (13) will be clearer below when we give $S$ explicitly.

Equations (4), (8), and (13) can be combined to yield

$$\frac{u_i(1) \phi_{i\mu}(1)}{\omega_\nu - \epsilon_\mu} = \sum_{j, \rho} \int S_{i\mu, j\rho}(1, 2; \nu) \phi_{j\rho}(2) V(1, 2) d^3 r_2 .$$

$$(14)$$

Next, operate on Eq. (6) with $-\omega_\nu - \nabla_1^2/2m - \nabla_2^2/2m + u_i(1) + u_j(2) + V(1, 2)$ and use Eqs. (10) and (13) to find

$$[-\omega_\nu - \nabla_1^2/2m - \nabla_2^2/2m + u_i(1) + u_j(2) + V(1, 2)] S_{i\rho, j\sigma}(1, 2; \nu) - \sum_\mu \left( \int \phi_{i\mu}(1) f(\epsilon_\mu) \phi_{i\mu}(\bar{1}) V(\bar{1}, 2) S_{i\rho, j\sigma}(\bar{1}, 2; \nu) d^3 \bar{r}_1 \right.$$

$$\left. + \int \phi_{j\mu}(2) f(\epsilon_\mu) \phi_{j\mu}(\bar{2}) V(1, \bar{2}) S_{i\rho, j\sigma}(1, \bar{2}; \nu) d^3 \bar{r}_2 \right) = -\frac{\omega_\nu - \epsilon_\rho - \epsilon_\sigma}{\omega_\nu - \epsilon_\rho} \phi_{i\rho}(1) \phi_{j\sigma}(2) f(\epsilon_\sigma) , \quad (15)$$

where we have used

$$T \sum_\nu e^{i\omega_\nu 0^+} (\omega_\nu - \epsilon_\rho)^{-1} = [1 - e^{(\epsilon_\rho - \mu)/T}]^{-1} \equiv f(\epsilon_\rho) .$$

Next, $S_{i\rho, j\sigma}$ is expanded in terms of functions $\theta_{ij\alpha}(1, 2)$ which are defined as the solutions to the equation

$$\{-\lambda_\alpha - \nabla_1^2/2m - \nabla_2^2/2m + u_i(1) + u_j(2) + V(1, 2)\} \theta_{ij\alpha}(1, 2) - [\sum_\mu \int \phi_{i\mu}(1) f(\epsilon_\mu) \phi_{i\mu}(\bar{1}) V(\bar{1}, 2) \theta_{ij\alpha}(\bar{1}, 2) d^3 \bar{r}_1$$

$$+ \sum_\mu \int \phi_{j\mu}(2) f(\epsilon_\mu) \phi_{j\mu}(\bar{2}) V(1, \bar{2}) \theta_{ij\alpha}(1, \bar{2}) d^3 \bar{r}_2] = 0 . \quad (16)$$

Equation (16) determines $\theta_{ij\alpha}$ up to a normalization constant. We expand $S$ as a linear combination of $\theta$'s,

$$S_{i\rho, j\sigma}(1, 2; \nu) = \sum_\alpha C_{i\rho, j\sigma}(\alpha, \nu) \theta_{ij\alpha}(1, 2) , \quad (17)$$

where

$$C_{i\rho, j\sigma}(\alpha, \nu) = \frac{\omega_\nu - \epsilon_\rho - \epsilon_\sigma}{(\omega_\nu - \lambda_\alpha)(\omega_\nu - \epsilon_\rho)}$$

$$\times \int \theta_{ij\alpha}(1, 2) \phi_{i\rho}(1) \phi_{j\sigma}(2) f(\epsilon_\sigma) d^3 r_1 d^3 r_2 . \quad (18)$$

Because $S_{i\rho, j\sigma}(1, 2; \nu)$ must be proportional to $(\omega_\nu - \epsilon_\rho)^{-1}$, and $f(\epsilon_\rho) = 1$ for $\rho = 0$ while $f(\epsilon_\rho) = 0$ for $\rho \neq 0$ at $T = 0$, we may approximate Eq. (18) in this limit as

$$S_{i\rho, j\sigma}(1, 2; \nu) = (\omega_\nu - \epsilon_\rho)^{-1} \theta_{ij0}(1, 2) \delta_{\rho 0} \delta_{\sigma 0} . \quad (19)$$

Here $\theta_{ij0}$ is that function $\theta_{ij\alpha}$ having the lowest eigenvalue $\lambda_\alpha$.

The normalization of $\theta_{ij0}$ is determined from[25]

$$1 = \int G_{ij}(12, 12^+)|_{t_2 = t_1} d^3 r_1 d^3 r_2$$

$$= T \sum_\nu \int S_{ij}(1, 2; \nu) \phi_i(1) \phi_j(2) d^3 r_1 d^3 r_2$$

$$= \int \theta_{ij}(1, 2) \phi_i(1) \phi_j(2) d^3 r_1 d^3 r_2$$

$$\equiv \int \chi_{ij}(1, 2) \phi_i^2(1) \phi_j^2(2) d^3 r_1 d^3 r_2 , \quad (20)$$

where we have factored $\theta_{ij}$ into $\chi_{ij}$ times $\phi_i \phi_j$; $\chi_{ij}$ is the pure correlated part of $\theta_{ij}$.

Notice that $S_{ij}(1, 2; \nu)$ in Eq. (19) has only a single pole, located at $\epsilon_0$, while the exact $S_{i\rho, j\sigma}$ from Eqs. (17) and (18) has additional poles at $\omega_\nu = \lambda_\alpha$. The approximation of taking the pole at $\epsilon_0$ alone is implied by writing Eq. (8) for the self-energy.

Note also that the claim $f(\epsilon_\rho) = 0$ for $\rho \neq 0$ cannot really be justified except in terms of the $T = 0$ result for $\mu$, which is to say, in terms of the ground-state energy per particle $E_0$, since $\mu \equiv E_0$ in this limit.

Equations (16) and (20) are the basis of the $T$-matrix program of calculation. Before proceeding to Sec. III, let us summarize the approximations to this point.

(a) No double occupancy or exchange is allowed.

(b) The self-energy is approximated according to Eq. (8); in particular, its energy dependence is ignored.

(c) The effective field $u_i$ is treated within the harmonic approximation.

(d) The $T$-matrix approximation is used for $\theta_{ij\alpha}$

in Eq. (16).

The first assumption should be quite valid, but the second and third depend on how well particles are localized around their lattice positions. However, it is possible to compute the corrections to these simple approximations if assumption (d) can be accepted. The validity of the latter can only be judged from the final results. It contains one undesirable feature; namely, at small interparticle distances $r_{12} \equiv |\vec{r}_1 - \vec{r}_2| \approx 0$, Eq. (16) should describe two particles interacting with a hard core. The Lennard-Jones 6-12 potential gives $\ln\chi(r_{12}) \sim - r_{12}^{-5}$ in the limit of small $r_{12}$,[15] but this is not true in Eq. (16). Whether or not this feature affects the numerical results is hard to assess. The trouble originates from the fact that Eq. (16) is not the $T$-matrix approximation describing two "free" particles, but describes instead two particles under the influence of all other surrounding particles. The square-bracketed terms in Eq. (16) are supposed to cancel the contribution of particle 2 at site $j$ to $u_i(1)$ and also that of particle 1 at site $i$ to $u_j(2)$, but they do not seem to actually do so.

In addition, the $T$-matrix approximation contains two-body correlations only, and there is no way that one may estimate many-body correlation effects in this approximation.

## III. CORRELATION FUNCTION

In this section we derive an equation for $\theta_{ij\alpha}(1, 2)$ by decoupling the three-particle Green's function. The starting point is the equation of motion for $G_{ij}$,

$$\left(-i\frac{\partial}{\partial t_1} - i\frac{\partial}{\partial t_2} - \frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} + V(1, 2)\right)G_{ij}(12, 1'2')$$

$$+i{\sum_k}' \int [V(1, 3) \mathcal{G}_{ijk}(123, 1'2'3^+)|_{t_3=t_1} + V(2, 3)\mathcal{G}_{ijk}(123, 1'2'3^+)|_{t_3=t_2}]d^3r_3 = -\delta(1 - 1')g_j(2, 2') - \delta(2 - 2')g_i(1, 1') ,$$

$$(21)$$

where the sum over $k$ excludes the terms $k = i$, $j$; $\mathcal{G}_{ijk}$ is the three-particle Green's function defined as

$$\mathcal{G}_{ijk}(123, 1'2'3')$$

$$= (-i)^3 \langle T(\Psi_i(1)\Psi_j(2)\Psi_k(3)\Psi_k^\dagger(3')\Psi_j^\dagger(2')\Psi_i^\dagger(1'))\rangle .$$

Equation (21) is derived assuming no double occupancy of lattice sites. Now let $t_2' \rightarrow t_2^+$ and $t_2 \rightarrow t_1$. Then the equation of motion is, in the spectral representation,

$$[-2\omega_\nu - \nabla_1^2/2m - \nabla_2^2/2m + V(1, 2)]G_{ij}(12, 1'2'; \nu)$$

$$+i{\sum_k}' \int \mathcal{G}_{ijk}(123, 1'2'3; \nu)[V(1, 3) + V(2, 3)]d^3r_3$$

$$= \delta(\vec{r}_1 - \vec{r}_1')g_j(2, 2')|_{t_2 = t_2^+} ; \quad (22)$$

$\mathcal{G}_{ijk}$ is given in terms of its frequency components by

$$\mathcal{G}_{ijk}(123, 1'2'3^+)|_{t_3=t_1, t_2'=t_2^+, t_2=t_1}$$

$$= iT{\sum_\nu} e^{-i(t_1 - t_1')\omega_\nu} \mathcal{G}_{ijk}(123, 1'2'3; \nu) .$$

For simplicity of notation, we will work in the zero-temperature limit where summation over excited states is unnecessary. Then we may drop subscripts which refer to the state, as in Sec. II.[25] In this limit,

$$G_{ij}(12, 1'2'; \nu) = \phi_i(1')\phi_j(2')\theta_{ij}(1, 2)/(\omega_\nu - \epsilon_0) ,$$

where $\theta_{ij}$ satisfies the equation

$$[-\lambda_0 - \nabla_1^2/2m - \nabla_2^2/2m + V(1, 2)]\theta_{ij}(1, 2)$$

$$+{\sum_k}' \int \theta_{ijk}(1, 2, 3)\phi_k(3)[V(1, 3) + V(2, 3)]d^3r_3 = 0 ,$$

$$(23)$$

and $\theta_{ijk}$ is related to $\mathcal{G}_{ijk}$ by

$$\mathcal{G}_{ijk}(123, 1'2'3; \nu)$$

$$= -i\phi_i(1')\phi_j(2')\phi_k(3)\theta_{ijk}(1, 2, 3)/(\omega_\nu - \epsilon_0) . \quad (24)$$

This is the most general form that $\theta_{ijk}$ can have consistent with the effective-field approximation equation (8).

We now approximate $\theta_{ijk}$ by products of two-particle functions, thereby truncating the hierarchy of equations for $n$-particle functions. First, we introduce $\chi_{ijk}$ in analogy with $\chi_{ij}$,

$$\theta_{ijk}(1, 2, 3) = \phi_i(1)\phi_j(2)\phi_k(3)\chi_{ijk}(1, 2, 3) .$$

The most obvious choice of $\chi_{ijk}$ is

$$\chi_{ijk}(1, 2, 3) = \chi_{ij}(1, 2)\chi_{jk}(2, 3)\chi_{ik}(1, 3) . \quad (25)$$

A simpler choice which should preserve those important features of $\chi_{ijk}$ in the present problem is to use

$$V(1, 3)\chi_{ijk}(1, 2, 3) = V(1, 3)\chi_{ij}(1, 2)\chi_{ik}(1, 3)$$

and

$$V(2, 3)\chi_{ijk}(1, 2, 3) = V(2, 3)\chi_{ij}(1, 2)\chi_{jk}(2, 3) \quad (26)$$

in the integrand of Eq. (23). This amounts to keeping short-range correlation where necessary to screen out the short-range repulsive interaction.

Using the second decoupling scheme in Eq. (23), we find after some algebra that

$$\{- \lambda_0 - \nabla_1^2 / 2m - \nabla_2^2 / 2m + u_i(1) + u_j(2) + V(1, 2)$$

$$- [ \int \phi_j^2(\bar{2}) V(1, \bar{2}) \chi_{ij}(1, \bar{2}) \, d^3 \bar{r}_2$$

$$+ \int \phi_i^2(\bar{1}) V(\bar{1}, 2) \chi_{ij}(\bar{1}, 2) \, d^3 \bar{r}_1 ] \}$$

$$\times \phi_i(1) \phi_j(2) \chi_{ij}(1, 2) = 0 \ . \quad (27)$$

In order to obtain this equation, it is necessary to employ the definition of the effective field $u_i$.

Note that the $T$-matrix approximation equation (16) corresponds to replacing $V(1, 3) \chi_{ijk}(1, 2, 3)$ by $V(1, 3) \chi_{ik}(1, 3)$ in Eq. (23). It is interesting that the equation used in Ref. 14 to determine the correlation function is similar to Eq. (16).

The difference between choices (25) and (26) for the three-particle function $\theta_{ijk}$ can be examined by treating this difference as a perturbation in Eq. (27).

The equation of motion which results when Eq. (26) is used may be written as

$$\{- \lambda_0 - \nabla_1^2 / 2m - \nabla_2^2 / 2m + u_i(1) + u_j(2) + V(1, 2)$$

$$- [ \int \phi_j^2(\bar{2}) V(1, \bar{2}) \chi_{ij}(1, \bar{2}) \, d^3 \bar{r}_2$$

$$+ \int \phi_i^2(\bar{1}) V(\bar{1}, 2) \chi_{ij}(\bar{1}, 2) \, d^3 \bar{r}_1 ]$$

$$+ \Delta_{ij}(1, 2) \} \phi_i(1) \, \phi_j(2) \chi_{ij}(1, 2) = 0 \ , \quad (28)$$

where

$$\Delta_{ij}(1, 2) = \sum_k{}' \int \phi_k^2(3) \{ \ V(1, 3) [\chi_{jk}(2, 3) - 1] \chi_{ik}(1, 3)$$

$$+ V(2, 3) [\chi_{ik}(1, 3) - 1] \chi_{jk}(2, 3) \} d^3 r_3 \quad (29)$$

represents the difference between using Eq. (26) to decouple $\chi_{ijk}$ and using Eq. (25). This term can be considered as a perturbation and its effect analyzed qualitatively as follows. First $\chi_{jk}(2, 3)$ is close to unity except when $r_{23} \equiv |\vec{r}_2 - \vec{r}_3|$ is smaller than the radius of the hard core in the interaction, in which case it is essentially zero. Now consider the first term in curly brackets in Eq. (29). There we see that the difference between using Eq. (25) and using Eq. (26) is that the former effectively excludes integration of $\vec{r}_3$ over a "hard-core volume" around $\vec{r}_2$, the position of particle 2, whereas the latter allows integration over this region. The region moves with particle 2, so that it is close to or far from particle 1 according to the position of particle 2. Because $V(1, 3)$ is large and positive for $\vec{r}_3$ near $\vec{r}_1$ and negative or zero for $\vec{r}_3$ far from $\vec{r}_1$, we may conclude that $\Delta_{ij}(1, 2)$ should increase with $r_{12}$. Qualitatively, then, $\Delta_{ij}(1, 2)$ acts as an attractive potential. It is a complicated function of $\vec{r}_1$ and $\vec{r}_2$ but for small deviations of $r_{12}$ from $R_{ij} = |\vec{R}_i - \vec{R}_j|$ it will be essentially of the form $a_0 + p(r_{12} - R_{ij}) + \cdots$, where $a_0$ is a constant and may be ignored and $p > 0$. We have evaluated $\Delta_{ij}$ numerically for several configurations of particles 1 and 2 using our solutions $\chi_{ij}$ from Eq. (27) and find that this is indeed the

case. In actual calculations we do not treat $\Delta_{ij}$ as in Eq. (29) because of the length of the computations that would be necessary; instead, a simple potential of the form $p(r_{12} - R_{ij})$ is used; this point is discussed in Sec. IV.

Finally, we should remark that the three-particle correlation effect is important only when particles 1 and 2 are nearest neighbors while particle 3 is no further away than a nearest neighbor of one and a next nearest neighbor of the other.

## IV. CONSTRAINT

In Sec. III we argued that the principal effect of three-body correlations is to force nearest-neighbor particles closer together. This is accomplished through the term $\Delta_{ij}(1, 2)$ in Eq. (28); rather than use the complicated form (29) for $\Delta_{ij}$, which would require extensive numerical computation, we have chosen to approximate it as

$$\Delta_{ij}(1, 2) \to p(r_{12} - R_{ij}) \ ; \quad (30)$$

$p$ is a positive constant. This expression may be regarded as the first term in an expansion of $\Delta_{ij}$ in the displacements of particles 1 and 2 from $\vec{R}_i$ and $\vec{R}_j$, although the actual expression will be considerably more complicated in appearance. It is possible to estimate $p$ from

$$p = \left( \frac{\partial \Delta_{ij}(1, 2)}{\partial r_{12}} \right) \Big|_{r_{12} = R_{ij}}$$

but this in turn cannot be evaluated except as some sort of average over the positions of particles 1 and 2 subject to the condition $r_{12} = R_{ij}$. Thus the determination of $\Delta_{ij}$ from Eq. (30) rather than Eq. (29) creates a problem in that we need a method of choosing the constant $p$. It can be estimated from Eq. (29) or determined from some criterion placed on the correlation function. Needless to say, the latter method is reasonable only if it leads to a $p$ which is comparable with that inferred from the former method.

Because the size of $p(r_{12} - R_{ij})$ depends directly on $r_{12}$, the criterion may be conveniently related to the average interparticle distance. One possible choice is

$$\langle \vec{r}_{12} \cdot \vec{R}_{ij} \rangle = R_{ij}^2 \ , \quad (31)$$

where $\langle f \rangle$ denotes the expectation value of $f$. In the present formalism, we shall take for this expectation value the integral of $f$ over the two-particle Green's function,[25]

$$\langle f \rangle_{ij} = \int f(1, 2) G_{ij}(12, 12) \big|_{t_2 = t_1} d^3 r_1 d^3 r_2 \ . \quad (32)$$

It is probably more nearly correct to define the average as an integral over the three-particle Green's function,

$$\langle f \rangle_{ij}$$

$$= \sum_k{}' \int f(1,2) \, g_{ijk}(123,123) \big|_{t_1 = t_2 = t_3} d^3 r_1 \, d^3 r_2 \, d^3 r_3 \,, \tag{33}$$

where the sum on $k$ excludes $k = i$, $j$ and $g_{ijk}$ is given according to our decoupling scheme. The difference between these averages hardly affects our results, so we have used Eq. (32) because it is numerically much simpler.

The criterion (31) is certainly not unique; a different condition has been used by Krumhansl and Wu,[19] namely,

$$d\chi_{ij}(r_{12})/dr_{12} \big|_{r_{12} = R_{ij}} = 0 \,, \tag{34}$$

where the correlation function is approximated as depending on the interparticle distance $r_{12}$ alone. This means that the correlation function has a maximum at the lattice distance which seems very reasonable from a physical point of view. It turns out that Eq. (31) is a very similar condition; it results in a correlation function having a peak at a slightly smaller distance, but the peak is broad enough that $\chi_{ij}(R_{ij})$ is almost equal to the maximum value of $\chi_{ij}$. In other words, Eqs. (31) and (34) have essentially the same effect on $\chi_{ij}$.

We have generally used condition (31) to calculate the results which are presented in Sec. VI. We have also investigated the choice of $p = 0$, or no three-body correlations at all. This calculation was done only on bcc He$^3$ and is included mainly for comparison.

## V. NUMERICAL PROCEDURE

We first reduce Eq. (28) to a simpler approximate equation which is tractable for numerical calculation; our notation and procedure parallel those used by Iwamoto and Namizawa.[15] With $\Delta_{ij}(1,2)$ replaced by $p(r_{12} - R_{ij})$, Eq. (28) is

$$[-\lambda_0 - \nabla_1^2/2m - \nabla_2^2/2m$$

$$+ u_i(1) + u_j(2) + V(1,2) - W_{ij}(1,2)$$

$$+ p(r_{12} - R_{ij})] \, \phi_i(1) \, \phi_j(2) \, \chi_{ij}(1,2) = 0 \,, \tag{35}$$

where

$$W_{ij}(1,2) = \int \phi_j^2(\bar{2}) \, V(1,\bar{2}) \chi_{ij}(1,\bar{2}) \, d^3\bar{r}_2$$

$$+ \int \phi_i^2(\bar{1}) V(\bar{1},2) \chi_{ij}(\bar{1},2) \, d^3\bar{r}_1 \,. \tag{36}$$

It is convenient to work with variables $\vec{\eta}$ and $\vec{X}$, defined as $\vec{\eta} = (\vec{r}_1 - \vec{R}_i) - (\vec{r}_2 - \vec{R}_j)$ and $\vec{X} = \frac{1}{2}[(\vec{r}_1 - \vec{R}_i) + (\vec{r}_2 - \vec{R}_j)]$; the dependence of $\chi_{ij}$ on $\vec{X}$, the center-of-mass variable, is very weak; in the absence of the "effective potential" $W_{ij}$, which is a weak perturbation compared to the other potentials in Eq. (35), $\chi_{ij}$ is independent of $\vec{X}$ in the state corresponding to the smallest $\lambda_0$. We shall approximate $\chi_{ij}$ as a function of $\vec{\eta}$ alone. Then the equation becomes

$$\left( -\lambda_0 + \frac{3}{2}\frac{\alpha^2}{m} - \frac{1}{m} \nabla_\eta^2 + \frac{\alpha^4}{4m}\eta^2 + V(|\vec{\eta} + \vec{R}_{ij}|) - W_{ij}(\vec{\eta}, \vec{X}) \right.$$

$$\left. + p(|\vec{\eta} + \vec{R}_{ij}| - R_{ij}) \right) e^{-\alpha^2 X^2} e^{-\alpha^2 \eta^2/4} \chi_{ij}(\vec{\eta}) = 0 \,. \tag{37}$$

Because $\chi_{ij}$ has been taken independent of $\vec{X}$, the dependence of $W_{ij}$ on $\vec{X}$ must also be removed. We have accomplished this by integrating Eq. (37) over $\vec{X}$, which in effect averages $W_{ij}$ in some way. This is only one of several reasonable procedures; alternatively, we might evaluate $W_{ij}$ at the most probable value of $\vec{X}$. Insofar as the eventual numerical results are concerned, the difference between these choices is quite negligible, which supports the assumption that the dependence of $\chi_{ij}$ on $\vec{X}$ is unimportant. After the averaging is performed, Eq. (37) becomes

$$\left( -\lambda_0 + \frac{3}{2}\frac{\alpha^2}{m} - \frac{1}{m}\nabla_\eta^2 + \frac{\alpha^4}{m}\eta^2 + V(|\vec{\eta} + \vec{R}_{ij}|) - W_{ij}(\vec{\eta}) \right.$$

$$\left. + p(|\vec{\eta} + \vec{R}_{ij}| - R_{ij}) \right) e^{-\alpha^2 \eta^2/4} \chi_{ij}(\vec{\eta}) = 0 \,, \tag{38}$$

where

$$W_{ij}(\vec{\eta}) = (\alpha^2/\pi)^{3/2} \int W_{ij}(\vec{\eta}, \vec{X}) \, e^{-\alpha^2 X^2} d^3 X \,. \tag{39}$$

The solution of Eq. (38) which corresponds to the smallest eigenvalue $\lambda_0$ is invariant under rotation around the direction of $\vec{R}_{ij}$ and may be written as a function of the variables $\eta \equiv |\vec{\eta}|$ and $\xi = |\vec{\eta} + \vec{R}_{ij}|$; $\xi$ is the interparticle distance, and $\chi_{ij}$ will depend much more strongly on this variable than on $\eta$. Our first simplification is to ignore the dependence of the correlation function on $\eta$; this is less easy to justify than ignoring its dependence on $\vec{X}$, and it turns out that the manner in which one subsequently averages $\vec{\eta}$ in Eq. (38) does make a difference in the numerical results. Given this approximation, Eq. (38) is

$$\left( -\lambda_0 + 3\frac{\alpha^2}{m} - \frac{1}{m}\frac{1}{\xi}\frac{\partial^2}{\partial \xi^2}\xi + V(\xi) + \frac{\alpha^2}{2m}\frac{\eta^2 + \xi^2 - R_{ij}^2}{\xi}\frac{\partial}{\partial \xi} \right.$$

$$\left. - W_{ij}(\xi, \eta) + p(\xi - R_{ij}) \right) e^{-\alpha^2 \eta^2/4} \chi_{ij}(\xi) = 0 \,, \tag{40}$$

where $W_{ij}(\xi, \eta) \equiv W_{ij}(\vec{\eta})$. The averaging procedure we employ is to integrate Eq. (40) over allowed values of $\eta$, $|R_{ij} - \xi| < \eta < |R_{ij} + \xi|$, using the appropriate volume element. The result is

$$\left( -\lambda_0 + \frac{3\alpha^2}{m} - \frac{1}{m}\frac{d^2}{d\xi^2} + V(\xi) + \frac{\alpha^2}{m}(\xi - R_{ij})\frac{d}{d\xi} \right.$$

$$\left. - W_{ij}(\xi) + p(\xi - R_{ij}) \right) \chi_{ij}(\xi) = 0 \,, \tag{41}$$

where

$$W_{ij}(\xi) = \frac{1}{2}\alpha^2 e^{-\alpha^2(\xi - R_{ij})^2/4}$$

$$\times \int_{|\xi - R_{ij}|}^{|\xi + R_{ij}|} \eta \, d\eta \, W_{ij}(\xi, \eta) \, e^{-\alpha^2 \eta^2/4} \,. \tag{42}$$

In obtaining Eq. (41), terms of relative order $e^{-\alpha^2 R_{ij}^2}$ have been dropped.

Various alternatives to this method are probably equally acceptable. One that has been used by

Horner[14] and by Guyer[11] is to set $\eta$ equal to the smallest possible value, which is also the most probable value, $\eta = |\xi - R_{ij}|$. This corresponds to constraining $\vec{\eta}$ to be parallel to $\vec{R}_{ij}$, which effectively reduces the motion of the particles to one dimension. For purposes of comparison, we have used both this reduction scheme and the average described above in the particular case of bcc He[3]. The results are discussed in Sec. VI.

It is easier to solve Eq. (41) numerically if an integrating factor is introduced to remove the first derivative; also, this makes the choice of boundary condition for $\xi \to \infty$ more obvious. We define the function $y_{ij}(\xi) = e^{-\alpha^2(\xi - R_{ij})^2/4} \chi_{ij}(\xi)$ and substitute into the differential equation for $\chi_{ij}(\xi)$, finding

$$\frac{d^2 y_{ij}}{d\xi^2} = [-m\lambda_0 + 2\alpha^2 + mV(\xi) + \tfrac{1}{4}\alpha^4(\xi - R_{ij})^2$$
$$- mW_{ij}(\xi) + mp(\xi - R_{ij})] y_{ij} ; \quad (43)$$

the boundary condition at $\xi \to 0$ is $y_{ij} = 0$, while for $\xi \to \infty$ the only choice which keeps $y_{ij}$ from diverging is $y_{ij}(\xi) \to 0$ as $\xi \to \infty$.

This equation has been solved using a Fox-Goodwin[26] numerical integration procedure. The effective potential $W_{ij}(\xi)$ depends on the solution itself; consequently the equation must be solved repeatedly until self-consistency of $W_{ij}$ and $y_{ij}$ is achieved. The form of $W_{ij}$ is described in the Appendix.

When $\vec{R}_i$ and $\vec{R}_j$ are not nearest-neighbor lattice positions, the parameter $p$ is taken equal to zero, since Eq. (31) is always satisfied to considerably better than 1% and generally to better than 0.1%. When nearest neighbors are treated, $p$ is chosen such that Eq. (31) is satisfied. Calculations with $p = 0$ for nearest neighbors have been done in bcc He[3] for purposes of comparison.

And, finally, $\alpha$ must be such that Eqs. (4), (8), and (9) are satisfied when the right-hand side of Eq. (4) is expanded to second order in the displacement of particle 1 from its equilibrium position. Equation (4) includes a summation over all positions $j$ around position $i$; we sum over as many shells of neighbors as necessary to obtain convergence of the ground-state energy to within 0.1 °K/particle. This energy is given in terms of $u_0$ and $\alpha$ by $E_0 = \tfrac{1}{2} u_0 + 9\alpha^2/8m$. The number of shells depends on the crystal structure but is always more than ten.

In order to satisfy simultaneously all of the conditions listed above, a fairly extensive amount of computing is necessary. With a little experience in choosing starting values of the various parameters, we were able to determine the solution at a given molar volume in about 10 sec of computing time on an IBM 360/75.

Numerical calculations have been done for crystalline He[3] and He[4] at $T = 0$; He[4] occurs in the hcp structure and He[3], in the bcc or hcp structure depending on molar volume (or pressure). The bcc

phase of He[3] is used for comparing the constraints described in Sec. IV and also for comparing the one-dimensional approximation $\eta = |R_{ij} - \xi|$ with the averaging procedure given in Eq. (42). Also, the effect of using an interaction different from the Lennard-Jones 6-12 potential is examined in the bcc phase of He[3]. In the hcp phase of He[3] and in He[4], the constraint $\langle \vec{R}_{ij} \cdot \vec{r}_{12} \rangle = R_{ij}^2$, the average equation (42), and the Lennard-Jones potential are used exclusively. We turn now to the presentation and discussion of the results.

## VI. DISCUSSION

Before discussing our results and comparing them with other theories and experiments, we wish to emphasize the importance of the bare potential used in the calculation. In addition to the Lennard-Jones (LJ) 6-12 potential, there are several other empirically determined interactions that must be considered equally acceptable.[2] In the present problem, where there is a delicate balance of kinetic and potential energies, a small change in the potential can produce a large change in the calculated ground-state energy and related quantities. To investigate the size of this effect, we have calculated $E_0$ in bcc He[3] using both the LJ potential and the Buckingham potential which Yntema and Schneider fitted to their high-temperature second-virial-coefficient measurements.[27] The latter potential (YS) is $V(r) = [1200 e^{-4.72r} - 1.24/r^6 - 1.89/r^8] \times 10^{-12}$ erg, where $r$ is in angstroms. The two potentials are shown in Fig. 1; the calculated $E_0$ for bcc He[3] is plotted as a function of molar volume. As can be seen, the YS potential is several degrees less attractive than the LJ potential and also has a hard core of larger radius. The effect on $E_0$ is quite sizable, all the more so when one realizes that a small change in $E_0$ at one end of the curve can change the calculated pressure and compressibility from good agreement to poor agreement (or vice versa) with experimental results. The size of the hard core is very important in this respect and this part of each potential is entirely empirically determined.

In view of the uncertainty in the potential and the approximations made, it should be clear that the merits of a calculation cannot be judged entirely on the basis of agreement or disagreement with experiment. To facilitate the comparison of our work with the work of others, we have used the LJ potential exclusively to calculate the results described below.

The most important calculated quantities are $\alpha^2$ and $u_0$, which we obtain according to Eqs. (4), (8), and (9); specifically, the right-hand side of Eq. (4) is expanded to second order in powers[28] of $(\vec{r}_1 - \vec{R}_i)^2$ and a consistent choice of $\alpha$ is found. There is no arbitrariness in this choice; $\alpha$ and $u_0$ are uniquely

determined. In Ref. 14, on the other hand, $\alpha^2/2m$
is determined by minimizing $\epsilon_0$, and, in Ref. 11,
by minimizing $E_0$. It is clear theoretically why one
should treat $\alpha^2/2m$ as a variational parameter.
We believe that the self-consistent method of
Iwamoto and Namaizawa[15] is the most straightfor-
ward and least ambiguous. At the same time, it
is not completely satisfactory because the expansion
of the right-hand side of Eq. (4) may not converge
sufficiently rapidly for the self-consistent field
$u_i(1)$ to be accurately determined in the harmonic
approximation. We have checked this point by com-
paring the averages

$$I_1 = \int \phi_i^2(1) u_i(1) \, d^3r_1$$
and
$$I_2 = \sum_j{}' \int V(1,2) \chi_{ij}(1,2) \phi_i^2(1) \phi_j^2(2) \, d^3r_1 d^3r_2$$

using the functions $\phi_i$ and $\chi_{ij}$ calculated as de-
scribed above. If the expansion of Eq. (4) is good,
these integrals should be equal. The case for which
it is least likely to be good is bcc He$^3$, where the
atoms have the largest zero-point motion. For this
case, we find that $I_1$ and $I_2$ differ by about 4%, which,
if the difference is ascribed totally to an inaccuracy
in $\alpha$, suggests an error of about $1\,^\circ$K/particle in the
ground-state energy.

To investigate this point further, we also calcu-
lated $\alpha$ self-consistently by demanding that the
averages $I_1$ and $I_2$ be equal instead of by using the
expansion procedure; in this calculation, $u_0$ was
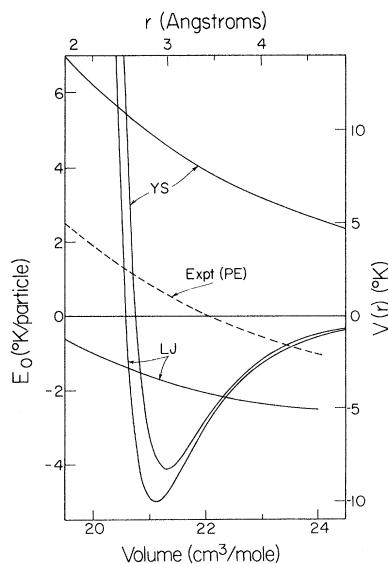taken to be $u_i(\vec{r}_1 = \vec{R}_i)$ as before. The result is a



FIG. 2. Ground-state energy per particle of He$^3$ and
He$^4$ as a function of molar volume. The dashed lines are
experimentally obtained; DF is from Ref. 29, EP from
Ref. 30, and PE from Ref. 31. The present theory is
PT. The theoretical results of Refs. 14 (H), 11 (G), and
9 (HMN) are also given for bcc He$^3$.

curve for $E_0$ for bcc He$^3$ which is almost exactly
$1\,^\circ$K above the theoretical curve in Fig. 2, the
latter being the same as curve B in Fig. 3. Curve
B is the one with which the present calculation
should be compared because, aside from the method
for choosing $\alpha$, it was determined under the same
conditions (see below).

As can be seen, rather better agreement with
experiment is obtained using the average, but this
may well be coincidental. What this check does
show, we feel, is that the method by which $\alpha$ and $u_0$
are chosen is of some importance, although the
change from average to expansion does not have a
remarkable effect.

In principle, we should incorporate terms of the
form $(r_1 - R_i)^4$ in the expansion of $u_i(1)$. The re-
sult of this correction in addition to the effects of
other approximations mentioned in this paper will
be studied in the future.

In Fig. 2, we plot the ground-state energy $E_0$ as
a function of molar volume in hcp He$^4$ and in hcp
and bcc He$^3$. The results of several other theories
are shown for bcc He$^3$; the prominent difference
between our results and those of the other workers
is that our energy is consistently lower by several
degrees. This is also true in He$^4$ and hcp He$^3$.
It is difficult to pinpoint the origin of this feature
because there are many differences between the
procedures, the effect of which is not always obvi-
ous; however, we think that one important factor is
the method of handling the second variable, $\eta$, in
Eq. (40). We also tried using $\eta = |\xi - R_{ij}|$, as in



FIG. 1. Lennard-Jones (LJ) and Yntema-Schneider
(YS) potentials $V(r)$ are plotted as functions of $r$; the bcc
He$^3$ ground-state energy per particle calculated from
each potential is plotted as a function of molar volume.
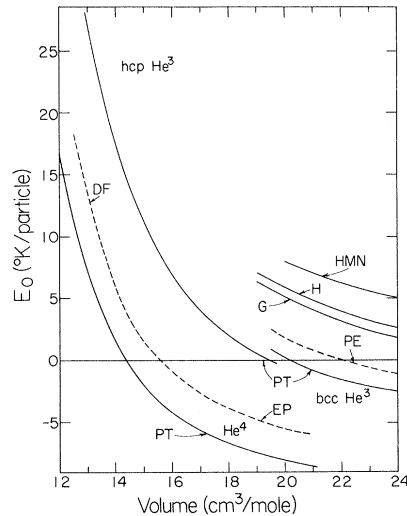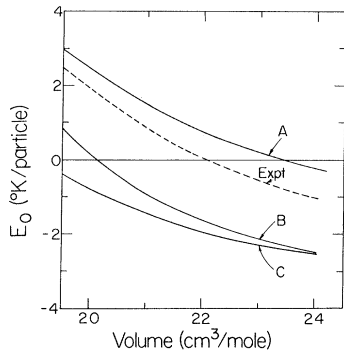The dashed line is the experimental ground-state energy
from Ref. 31.

FIG. 3.  Ground-state energy per particle in bcc He³
as a function of molar volume.  The theoretical curves
A–C were obtained using different constraints on $\langle r_{12} \rangle$
and/or different treatments of the variable $\eta$ as explained
in the text.  The experimental curve is from Ref. 31.

Refs. 11 and 14, in the bcc He³ calculation.  The
result is the curve labeled A in Fig. 3; it should
be compared with curve B, which was obtained by
treating $\eta$ according to Eq. (42).  This illustrates
the point that in one dimension the repulsive core
occupies relatively more space than in three di-
mensions.

Curves A and B in Fig. 3 were calculated using
the constraint equation (31); curve C, on the other
hand, was obtained by setting $p = 0$, or by ignoring
three-body correlations altogether.  The variable
$\eta$ was treated according to Eq. (42), so this curve
should be compared with curve B.  The pressure
obtained from curve C is very low because this cal-
culation gives an $E_0$ which is too insensitive to
changes in the molar volume.

The question arises as to why it is necessary to
introduce the constraint at all, since it is not used
in any previous theories of solid helium although
these theories often given good $P$-$V$ curves.  Also,
it is generally claimed in the literature that the ef-
fect of three-body correlations, which we use to in-
troduce the constraint, is small; yet it plays an
important role in our work.  We believe that the
reason for the discrepancy is as follows.

The three-particle correlations have the same
effect in Eq. (28) as $W_{ij}$, the term in square brack-
ets, has; this is to force particles 1 and 2 into the
proper positions in the lattice.  The magnitude and
functional form of $W_{ij}$ are, of course, all-important
in determining how effectively this "potential" draws
the particles together.  However, in order to be con-
sistent with our harmonic approximation to the self-
energy, we have to treat $W_{ij}$ approximately by ex-
panding it to second order also, as described in the
Appendix.  After expansion, we find that the strength
of $W_{ij}$ is somewhat too weak to produce a $\chi_{ij}$ which
satisfies Eq. (31).  On the other hand, the value of
$p$ estimated from Eqs. (29) and (30) is such that

when the term $p(\xi - R_{ij})$ is added to $W_{ij}$, the com-
bined effect is of very nearly the size necessary to
satisfy Eq. (31).  The relative importance of the
two terms in achieving this effect is about unity.

At the same time, we must point out that the
addition of the three-body correlation effect alters
$E_0$ by only a small amount; nevertheless, its exis-
tence cannot be denied and its importance should,
we feel, be checked in any calculation.  A small
change of $E_0$ over part of the $E_0$-vs-$V$ curve can
have a sizable effect on the calculated pressure.

The term $W_{ij}$ also appears in Refs. 11 and 14 and
is handled by a different numerical procedure in
each case.  A direct comparison of the treatments
does not seem to be possible.

Finally, let us repeat that numerical results are
dominated by $\alpha^2$ and $u_0$, which are probably more
affected by the scheme according to which they are
chosen than anything else.

The results for the ground-state energy are
plotted in Fig. 2, while the pressure and compres-
sibility are given in Figs. 4 and 5.  The dashed
curves are the experimental results of Dugdale
and Franck[29] (DF) and of Edwards and Pandorf[30]
(EP) and Pandorf and Edwards[31] (PE).  As we noted
above, our $E_0$-vs-$V$ curves lie several degrees be-
low those of other workers and are also below the
experimental curves.  We have not plotted other
theoretical results for the pressure and compres-
sibility but should remark that some of these, e.g.,
Refs. 8, 11, and 14, are in very good agreement
with experiment.

In Fig. 6, we plot the correlation functions $\chi_{ij}(r)$
for the first two shells in bcc He³ at a volume of
21.4 cm³.  Along the abscissa, the variable is $r/R_{ij}$,
where $R_{ij} = a$ for the first shell and $a\, 2/\sqrt{3}$ for the
second.  The correlation functions for large shells
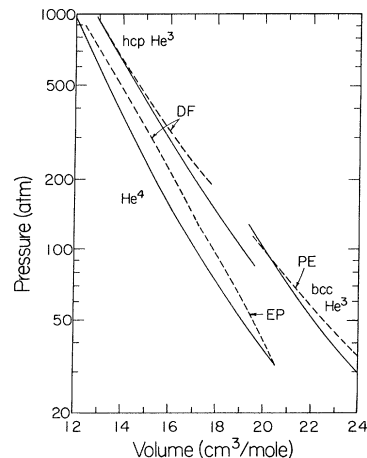become progressively flatter away from the hard-



FIG. 4.  Pressure as a function of molar volume in
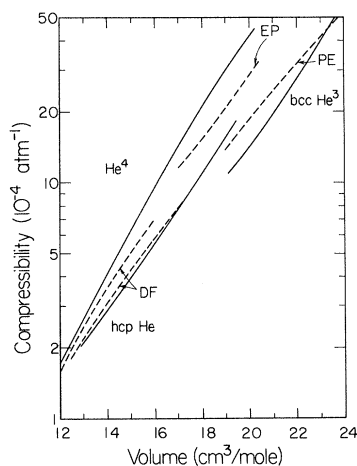He³ and He⁴; the labels are as in Fig. 2.

FIG. 5. Compressibility as a function of molar volume in $He^3$ and $He^4$; the labels are as in Fig. 2.

core region. The distance at which $\chi_{ij}(r)$ rises from zero is determined mainly by the hard-core radius and so is relatively insensitive to the molar volume. On the other hand, for nearest neighbors the position of the peak tends to vary as the lattice distance or $V^{1/3}$, so that the shape of the correlation function changes with molar volume.

A comparison of our correlation function for nearest neighbors with those of Hetherington, Mullin, and Nosanow[9] and of Horner[14] is made in Fig. 7 for bcc $He^3$ at a molar volume of 24 cm³. Because of the different method Guyer[11,12] has used to separate the single-particle and correlation functions, we cannot make a meaningful comparison with his correlation function.
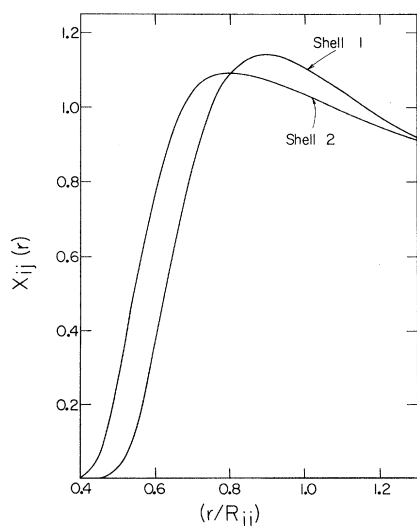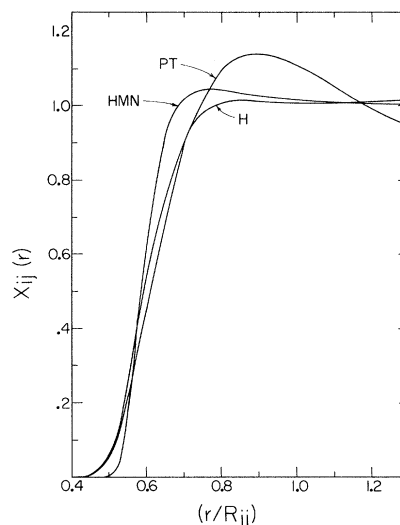


FIG. 7. Correlation function $\chi_{ij}(r)$ vs $r/R_{ij}$ for nearest neighbors at a molar volume of 24 cm³. That of the present theory is labeled PT; those of Refs. 9 and 14 are labeled HMN and H, respectively.

In Fig. 8, $\alpha^2 a^2$ is shown as a function of molar volume, where $a$ is the nearest-neighbor lattice distance. This quantity depends quite strongly on volume, increasing as $V$ decreases, corresponding to increasing localization of the particles. This will lead to a strong dependence on volume of such quantities as the exchange constant and phonon dispersion relation, as discussed by Guyer.[11] We will present calculations of these quantities based on the present results in a forthcoming paper.

On the basis of our calculations, we draw the following conclusions:

(i) The potential used in the calculation is extremely important insofar as the numerical results are
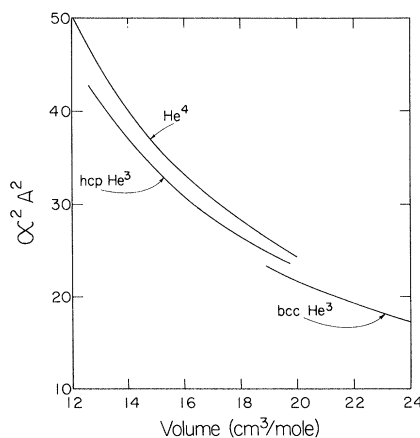


FIG. 6. Correlation function $\chi_{ij}(r)$ for nearest and for next nearest neighbors as functions of $r/R_{ij}$ for bcc $He^3$ at a molar volume of 21.4 cm³.



FIG. 8. Quantity $\alpha^2 a^2$ plotted as a function of molar volume in $He^3$ and $He^4$; $a$ is the nearest-neighbor lattice separation.

concerned. Small changes in the depth of the attractive well or the hard-core radius can significantly alter these results; in the absence of a "best" potential, comparison with experiment cannot in itself be a satisfactory test of a theory.

(ii) A self-consistent calculation defined in our program and which ignores three-body correlations will produce $E_0$ too low at small molar volume and an average interparticle distance which is too large. We believe that this feature is caused by taking exclusively the two-particle hard-core effects without considering the fact that the particles are also surrounded by other particles which constrain them to be a certain distance apart on the average.

(iii) We find that the three-body correlations have the effect of producing a two-particle function $\theta_{ij}$ which describes two particles localized at $\vec{R}_i$ and $\vec{R}_j$ and in close agreement with either of Eqs. (31) and (34). In actual calculations this effect is approximated by a simple potential whose magnitude is such that Eq. (31) is satisfied. It is important to have some such well-defined theoretical criterion because, by choosing the magnitude $p$ of this potential more arbitrarily, the volume dependence of $E_0$ could be significantly altered. In particular, it would not be necessary to change $p$ by as much as a factor of 2 to obtain perfect agreement of the calculated pressure with experiment. This point also illustrates the importance of achieving self-consistency in treating $W_{ij}$ in Eq. (35).

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### APPENDIX: EFFECTIVE POTENTIAL

In Sec. III, we derive an "effective potential" given by

$$W_{ij}(1, 2) = \int \phi_j^2(\bar{2}) V(1, \bar{2}) \chi_{ij}(1, \bar{2}) d^3\vec{r}_2$$
$$+ \int \phi_i^2(\bar{1}) V(\bar{1}, 2) \chi_{ij}(\bar{1}, 2) , \quad (A1)$$

which we wish to reduce to a form consistent with the harmonic approximation used for the single-particle self-energy. In the first integral, define $\bar{q} = |\vec{r}_2 - \vec{R}_j|$ and $\bar{\xi} = |\vec{r}_1 - \vec{r}_2|$ and make a similar transformation of variables in the second integral. Also, assume $\chi_{ij}(1, \bar{2})$ depends only on $\bar{\xi}$, as in Sec. V; then

$$W_{ij}(1, 2) = 2\pi \left(\frac{\alpha^2}{\pi}\right)^{3/2} \int_0^\infty \bar{\xi} d\bar{\xi} \, V(\bar{\xi}) \chi_{ij}(\bar{\xi})$$
$$\times \left( \int_{|\bar{\xi} - A_{1j}|}^{\bar{\xi} + A_{1j}} \bar{q} d\bar{q} \frac{e^{-\alpha^2\bar{q}^2}}{A_{1j}} + \int_{|\bar{\xi} - A_{2i}|}^{\bar{\xi} + A_{2i}} \bar{q} d\bar{q} \frac{e^{-\alpha^2\bar{q}^2}}{A_{2i}} \right), \quad (A2)$$

where $A_{1j} = |\vec{r}_1 - \vec{R}_j|$ and $A_{2i} = |\vec{r}_2 - \vec{R}_i|$. The integration over $\bar{q}$ can be done, and the result expanded in powers of the center-of-mass and relative variables $\vec{X}$ and $\vec{\eta}$, as far as second order, which is consistent with Eq. (9). Also, it is convenient to drop the subscripts $i$, $j$ and to define the averages

$$V_n = (\alpha R/\sqrt{\pi}) \int_0^\infty x dx \, e^{-\alpha^2 R^2 (x-1)^2} V(Rx) \chi(Rx)(x - 1)^n . \quad (A3)$$

The resulting expression for $W$ is

$$W(\vec{\eta}, \vec{X}) = 2V_0 - \eta \cos\theta_\eta (V_0 - 2\alpha^2 R^2 V_1)/R + [2X^2 P_2(\cos\theta_X)/R^2 + \eta^2 P_2(\cos\theta_\eta)/2R^2](V_0 - 2\alpha^2 R^2 V_1)$$

$$+ [2X^2(\cos^2\theta_X)/R^2 + \eta^2(\cos^2\theta_\eta)/2R^2](- 4\alpha^2 R^2 V_0 + 8\alpha^4 R^4 V_2) , \quad (A4)$$

where $\cos\theta_\eta = (\vec{\eta} \cdot \vec{R}_{ij})/R^2$, $\cos\theta_X = (\vec{X} \cdot \vec{R}_{ij})/R^2$, and $P_2$ is the second Legendre polynomial.

Next, the average over $\vec{X}$ defined in Eq. (38) is performed:

$$W(\vec{\eta}) = V_0 - \alpha^2 R^2 V_2 - \eta \cos\theta_\eta(V_0 - 2\alpha^2 R^2 V_1)/R$$
$$+ \eta^2 P_2(\cos\theta_\eta)(V_0 - 2\alpha^2 R^2 V_2)/R^2$$
$$+ \eta^2 \cos^2\theta_\eta(- 4\alpha^2 R^2 V_0 + 8\alpha^4 R^4 V_2)/R^2 , \quad (A5)$$

and, finally, the average over $\eta$ given by Eq. (41) is done. In this context, it is useful to note that $\xi = |\vec{R} + \vec{\eta}|$ or $\cos\theta_\eta = (\xi^2 - \eta^2 - R^2)/2\eta R$. We find for the average

$$W(\xi) = 2[B_0 + B_1(\xi - R)/R + B_2(\xi - R)^2/R^2] , \quad (A6)$$
where

$$B_0 = (\tfrac{1}{2} + 3/\alpha^4 R^4)V_0 - (1 + 6/\alpha^2 R^2)V_1 + (\alpha^2 R^2 + 4)V_2 ,$$

$$B_1 = (\tfrac{1}{2} - 3/2\alpha^2 R^2)V_0 + (\alpha^2 R^2 + 3)V_1 - 2\alpha^2 R^2 V_2 , \quad (A7)$$

$$B_2 = (- \tfrac{1}{4}\alpha^2 R^2 + \tfrac{1}{4})V_0 - (\tfrac{1}{2}\alpha^2 R^2)V_1 + (\tfrac{1}{2}\alpha^4 R^4)V_2 .$$

Equation (A6) gives the function $W_{ij}(\xi)$ which appears in Eq. (42), provided, of course, $\eta$ is averaged as in Eq. (41). If some other scheme is used to remove $\eta$ from the equation for $\chi_{ij}$, then Eqs. (A7) are modified somewhat but remain linear combinations of $V_0$, $V_1$, and $V_2$.

[1] F. W. de Wette and B. R. A. Nijboer, Phys. Letters 18, 19 (1965).

[2] See, e.g., J. O. Hirschfelder, C. F. Curtis, and

R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954), p. 197.

[3] W. Brenig, Z. Physik 171, 60 (1963).

[4]T. R. Koehler, Phys. Rev. Letters 17, 89 (1966).

[5]P. Choquard, *The Anharmonic Crystal* (Benjamin, New York, 1967).

[6]H. Horner, Z. Physik 205, 72 (1967).

[7]T. R. Koehler, N. S. Gillis, and N. R. Werthamer, Phys. Rev. 165, 951 (1968).

[8]L. H. Nosanow, Phys. Rev. 146, 20 (1966).

[9]J. H. Hetherington, W. J. Mullin, and L. H. Nosanow, Phys. Rev. 154, 175 (1967).

[10]C. W. Woo and W. E. Massey, Phys. Rev. 169, 241 (1968).

[11]R. A. Guyer, Solid State Commun. 7, 315 (1969); in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 413; R. A. Guyer and L. I. Zane, Phys. Rev. 188, 445 (1969).

[12]B. Sarkissian, Ph. D. thesis (Duke University, 1969) (unpublished).

[13]When discussing the work of Guyer and Sarkissian, we will generally use the single reference 11. It should be pointed out, however, that many of the numerical results described in these articles were first calculated by Sarkissian in Ref. 12, which is less readily available.

[14]H. Horner, Phys. Rev. A 1, 1722 (1970).

[15]F. Iwamoto and H. Namaizawa, Progr. Theoret. Phys. (Kyoto) Suppl. 37/38, 234 (1966); and unpublished.

[16]K. A. Brueckner and J. Frohberg, Progr. Theoret. Phys. (Kyoto) Suppl. Ext. 383 (1965).

[17]N. S. Gillis and N. R. Werthamer, Phys. Rev. 167, 607 (1968).

[18]Such a potential has the effect of drawing the particles together; if one expands the contribution of three-particle correlations to the two-particle equation, the leading term in the expansion will have approximately the same form.

[19]J. A. Krumhansl and S. Y. Wu, Phys. Letters 28A, 263 (1968).

[20]H. Meyer, J. Appl. Phys. 39, 390 (1968).

[21]Because exchange is not included and particles are treated as distinguishable, the statistics of the particles will not actually play any role. We will write equations appropriate for Bose statistics only to simplify the notation.

[22]We use units such that Planck's constant divided by $2\pi$ and Boltzmann's constant are equal to unity.

[23]The notation is generally the same as in L. P. Kadanoff and G. A. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1962).

[24]Note that in the frequency component of $G$, $G_{ij}(12, 1'2; \nu)$, the symbols 1, 2, and 1' represent only the space variables $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_1'$.

[25]Because the subscripts $\rho$, $\sigma$, and $\alpha$ are all zero starting from this point, we drop them altogether. Also appropriate time ordering is taken here.

[26]L. Fox and E. T. Goodwin, Proc. Cambridge Phil. Soc. 45, 372 (1949).

[27]J. L. Yntema and W. G. Schneider, J. Chem. Phys. 18, 646 (1950).

[28]In the hcp structure, the harmonic expansion is not spherically symmetric beyond the second shell; for more distant shells we use an isotropic approximation as in Ref. 15.

[29]J. S. Dugdale and J. P. Franck, Phil. Trans. Roy. Soc. London A257, 1 (1964).

[30]D. O. Edwards and R. C. Pandorf, Phys. Rev. 140, A816 (1965).

[31]R. C. Pandorf and D. O. Edwards, Phys. Rev. 169, 222 (1968).

# High-Energy Neutron Scattering from Liquid Helium in the Impulse Approximation*

H. A. Gersch and Phil N. Smith
*School of Physics, Georgia Institute of Technology, Atlanta, Georgia* 30332
(Received 19 November 1970)

The impulse approximation is used to describe the inelastic cross section for high-energy neutron scattering from superfluid helium in terms of a ground-state momentum distribution of the helium atoms as given by existing variational calculations. The predicted shape of the cross section is compared with recent experimental data and with a previous theory which approximated the noncondensate contribution to the dynamic structure factor by a single-Gaussian function. In contrast to conclusions obtained using the single-Gaussian approximation, our predicted inelastic cross section omitting a condensate contribution provides an acceptable fit to the experimental data. This fit is worsened by introducing a contribution from a condensate fraction in the amount consistent with the variational calculations, namely 11%. If the condensate fraction is arbitrarily reduced from this value, it is found that a much smaller value, with an upper limit of about 3%, is consistent with the available experimental data. It appears that unique assignments of condensate-fraction contributions to inelastic neutron scattering, for the range of neutron energies presently available, will require an improved theory of final-state effects on the shape of the condensate contribution.

## I. INTRODUCTION

Central to microscopic superfluid theory is the concept of the existence of a condensate fraction of helium particles having zero momentum.[1,2] Recently, experiments in high-energy scattering of neutrons from superfluid helium have been carried out,[3,4] the aim being to measure the momentum distribution of the individual He[4] atoms and thus the strength of occupation of the zero-momentum level.[5]