

Theory of Quantum Crystals. II. Three-Body Term in the Cluster Expansion*

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In a previous paper, denoted as I, the ground-state properties of crystalline helium were studied by a variational method which used a cluster expansion evaluation of the energy, E_0 . The basic approximation of that work was the truncation of the cluster expansion after the one- and two-particle terms, $E_{01}+E_{02}$. We have tested this approximation by numerical computation of the three-body term, E_{03} , of the expansion. Using the analytic form of the trial wave function given in I, we find, for bcc ^3He , that $E_{03} \approx 10^{-2}E_{02}$ at the minimum in $E_{01}+E_{02}$. Furthermore, when E_{03} is included in the variations, E_{03} remains small and the minimum energy is essentially unchanged, but the values of the wave-function parameters are improved somewhat. These results indicate that the cluster expansion is converging rapidly. The computations are performed as a function of density, and improved results for the ground-state pressure, compressibility, sound velocities, and exchange integral are also presented. Similar calculations at a single density in hcp ^3He and ^4He show that the close packing causes E_{03} to be larger; however, it is still only 1/20 the value of E_{02} , and the truncation of the cluster expansion is probably valid here as well. It is shown that the rate of convergence of the cluster expansion depends on the form of the trial function. A numerical example is given of a form for which the approximation of I breaks down. A critique of the expansion of Brueckner and Froberg is given. On a basis of a numerical test, it is found that they have neglected an important term in truncating their expansion, so that the validity of their variational procedure is uncertain. Some possible improvements in the theory, such as solving a differential equation for the correlation function and including the effects of the phonon spectrum, are discussed. Details of our method of evaluating the three-body terms are given in two Appendices.

I. INTRODUCTION

CRYSTALS of the isotopes of helium and molecular hydrogen, whose zero-point kinetic energies are comparable to their potential energies, may be called "quantum crystals."¹ Because the root-mean-square deviation of an atom from its lattice site in one of these solids is not small compared to the lattice spacing, the classical theory of lattice dynamics cannot be used to treat them.² Further, a very large zero-point motion also implies that correlation effects will be important; hence, a Hartree treatment based on a wave function which is a product of single-particle functions is also a poor approximation.³

The problems of correlations and large zero-point energy were studied in I by means of a variational calculation of the ground-state energy of crystalline helium. The trial wave function used in I is given by

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{i=1}^N \phi(|\mathbf{r}_i - \mathbf{R}_i|) \prod_{j < k} f(r_{jk}). \quad (1.1)$$

In (1.1) we have neglected wave-function symmetry since the exchange energy contribution arising from this property is quite small.^{1,4} The single-particle func-

tion $\phi(|\mathbf{r}_i - \mathbf{R}_i|)$ describes the localization of particle i with coordinate \mathbf{r}_i , about the lattice site at \mathbf{R}_i . The product of the ϕ 's is used, as in a Hartree calculation, to define the crystal structure. Short-range correlation effects are treated by including the product of pair functions, $\prod f(r_{jk})$, where $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$. The ground-state energy E_0 was expressed in I as a cluster expansion

$$E_0 = E_{01} + E_{02} + E_{03} + \dots, \quad (1.2)$$

where E_{0n} gives the contribution to the energy arising *specifically* from the clustering of n particles; that is, the term vanishes if one or more of the n particles is far away from the rest of the particles in the cluster. To give the precise form of the terms of (1.2) we define

$$T(\mathbf{r}_i) \equiv -(\hbar^2/2m)\nabla^2 \ln \phi(|\mathbf{r}_i - \mathbf{R}_i|), \quad (1.3)$$

and an effective potential

$$V(\mathbf{r}) \equiv v(\mathbf{r}) - (\hbar^2/2m)\nabla^2 \ln f(\mathbf{r}), \quad (1.4)$$

where $v(\mathbf{r})$ is the Lennard-Jones potential

$$v(\mathbf{r}) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (1.5)$$

Each of the terms in (1.2) can be split into a part depending on $T(\mathbf{r}_i)$ and a part depending on $V(\mathbf{r})$ [except for E_{01} which depends only on $T(\mathbf{r}_i)$], so that

$$E_0 = E_{01} + (E_{02V} + E_{02T}) + (E_{03V} + E_{03T}) + \dots \quad (1.6)$$

We also define an average of any arbitrary function

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¹ L. H. Nosanow, Phys. Rev. **146**, 120 (1966). We refer to this paper as I.

² F. W. de Wette and B. R. A. Nijboer, Phys. Letters **18**, 19 (1965).

³ L. H. Nosanow and G. L. Shaw, Phys. Rev. **119**, 968 (1962).

⁴ L. H. Nosanow and W. J. Mullin, Phys. Rev. Letters **14**, 133 (1965).

$g(\mathbf{r}_1, \dots, \mathbf{r}_n)$ by

$$\begin{aligned} \langle g(\mathbf{r}_1, \dots, \mathbf{r}_n) \rangle &= \omega^{-n} \int d\mathbf{r}_1 \dots \int d\mathbf{r}_n \left| \phi(|\mathbf{r}_1 - \mathbf{R}_i|) \right|^2 \dots \\ &\quad \left| \phi(|\mathbf{r}_n - \mathbf{R}_n|) \right|^2 g(\mathbf{r}_1, \dots, \mathbf{r}_n), \end{aligned} \quad (1.7)$$

where

$$\omega = \int \left| \phi(|\mathbf{r}_i - \mathbf{R}_i|) \right|^2 d\mathbf{r}_i. \quad (1.8)$$

The leading terms of the expansion are

$$E_{01} = \sum_{i=1}^N \langle T(\mathbf{r}_i) \rangle, \quad (1.9)$$

$$E_{02T} = \sum'_{i,j} \left\{ \frac{\langle T(\mathbf{r}_i) f^2(\mathbf{r}_{ij}) \rangle}{\langle f^2(\mathbf{r}_{ij}) \rangle} - \langle T(\mathbf{r}_i) \rangle \right\}, \quad (1.10)$$

and

$$E_{02V} = \frac{1}{2} \sum'_{i,j} \frac{\langle V(\mathbf{r}_{ij}) f^2(\mathbf{r}_{ij}) \rangle}{\langle f^2(\mathbf{r}_{ij}) \rangle}, \quad (1.11)$$

$$E_{03V} = \frac{1}{2} \sum'_{i,j,k} \left\{ \frac{\langle f^2(\mathbf{r}_{ij}) f^2(\mathbf{r}_{ik}) f^2(\mathbf{r}_{jk}) V(\mathbf{r}_{ij}) \rangle}{\langle f^2(\mathbf{r}_{ij}) f^2(\mathbf{r}_{ik}) f^2(\mathbf{r}_{jk}) \rangle} - \frac{\langle f^2(\mathbf{r}_{ij}) V(\mathbf{r}_{ij}) \rangle}{\langle f^2(\mathbf{r}_{ij}) \rangle} \right\}. \quad (1.12)$$

The form of each of these terms is just what one would expect on physical grounds. This is clearly the case for E_{01} and E_{02V} , since they are, respectively, the single-particle energy and the energy of the interactions of the particles by pairs. Further, the first term of E_{03V} of Eq. (1.12) is the "effective" potential energy of all possible interactions of three particles including terms involving interactions in pairs only. The latter terms have already been accounted for in E_{02V} ; hence the second term subtracts them out of the three-body interaction. A similar interpretation holds for E_{02T} and all other terms of the cluster expansion.

The basic approximation of I was

$$E_0 \cong E_{01} + E_{02V}. \quad (1.13)$$

The purpose of this paper is the investigation of this approximation by the evaluation of the leading correction term as a function of density and as a function of the variational parameters near the minimum of the right side of (1.13).

In I, $E_{01} + E_{02V}$ was varied with respect to the single-particle function ϕ to yield a differential equation for ϕ . It turned out that this solution was always well approximated by a Gaussian so that we may take

$$\phi(\mathbf{r}) = \exp(-A\mathbf{r}^2/2). \quad (1.14)$$

When (1.14) is used

$$T(\mathbf{r}_i) = 3A\hbar^2/4m, \quad (1.15)$$

and all terms of the cluster expansion of the form E_{0nT} , except E_{01} , vanish identically. Since we have already pointed out that the symmetry effects are small, the leading term to be evaluated, to test the validity of the truncation of the cluster expansion, is the term E_{03V} . The use of the Gaussian for ϕ permits E_{02V} to be reduced to a one-dimensional integral and, more importantly, for our present purposes, it allows the rather complicated E_{03V} to be reduced to a numerically tractable form. This reduction is not obvious, however, and is discussed at length in Appendix A.

The analytic form chosen for the correlation function $f(\mathbf{r})$ has been discussed in I; it is

$$f(\mathbf{r}) = \exp\{-K[(\sigma/r)^{12} - (\sigma/r)^6]\}, \quad (1.16)$$

where K is a variational parameter and σ is the "width" of the repulsive core of the Lennard-Jones potential [Eq. (1.5)]. The $f(\mathbf{r})$ of (1.16) is a physically reasonable ansatz since it goes to zero rapidly for $r \rightarrow 0$ and it also has a maximum at $r_{\max} = 2^{1/6}\sigma$ where the Lennard-Jones potential has a minimum. This $f(\mathbf{r})$ is a mathematically convenient form as well; we will show in the next section that it has properties which are necessary if (1.13) is to be a good approximation.

In Sec. II we discuss the validity of the truncation of the cluster expansion and show that the procedure is remarkably good for bcc ^3He and ^4He and is probably also valid for the close-packed forms of ^3He and ^4He . We also discuss at length the conditions which must be imposed on $f(\mathbf{r})$ to justify the neglect of E_{03V} and higher order terms. In Sec. III we show how certain properties of bcc He, such as pressure, compressibility, exchange integral, and sound velocities, are affected by including E_{03V} in the variational computation. A critique of an alternative expansion proposed by Brueckner and Froberg⁵ is given in Sec. IV. In Sec. V we present a summary of our results and a discussion of possible improvements in the theory. The mathematical details of the evaluation of E_{03V} are given in Appendix A, and in Appendix B we discuss the lattice sums involved in that evaluation.

II. CONVERGENCE OF THE CLUSTER EXPANSION

A. General Considerations

In this section we test the convergence of the cluster expansion by evaluating the three-body term E_{03V} . In this part of Sec. II we discuss in a general way the factors which affect the size of E_{03V} and higher order terms in the expansion. These factors include the localization of the particles, the short range of the

⁵ K. A. Brueckner and J. Froberg, Progr. Theoret. Phys. (Kyoto), Suppl. (1965). We refer to this paper as BF.

correlation function, the lattice type, and the internal cancellation in the terms. We also present an argument which indicates that the four-or-more-body terms are negligible if the three-body term is small.

A priori, one might reasonably argue that the cluster expansion converges rapidly for a crystal. The most important many-body effect in a crystal, the long-range order, which comes about because each particle is localized about its lattice site by its interactions with its immediate neighbors, is already included in the simple Hartree approximation.³ [Note that one gets to the Hartree theory by taking $f(r)=1$, in which case all terms except E_{01} and E_{02V} vanish; that is, (1.13) becomes exact.] As in I, we say that the Hartree approximation contains an adequate description of the "structural correlations" between particles.

The role of the $f(r)$'s is to provide *short-range* "dynamic" correlations. For example, $f(r)$ prevents two particles from getting too close to one another since it is very small for $r < \sigma$. This greatly lowers the kinetic energy of the system by allowing the single-particle functions to spread out, whereas in the Hartree approximation they were overly localized because they could not overlap. At the position of the potential minimum, $f(r)$ has a maximum and then approaches unity rapidly as r increases.

Because the particles are localized about lattice sites and because the $f(r)$'s are short-range functions, it is improbable that three particles will get close enough together to make the three-body terms important. If we examine the form of E_{03V} in (1.12), we see that for E_{03V} to be large, the product $f^2(r_{ik})f^2(r_{jk})$, on the average, must differ significantly from unity; however, this is not the case since $f(r)$ is near unity at $r \approx R$, the nearest-neighbor distance. Thus a necessary condition on $f(r)$ is that it rapidly approach unity beyond $r = r_{\max}$. In a preliminary account⁶ of this work the correlation function used was

$$f(r) = \exp\{-K[(\sigma/r)^{10} - (\sigma/r)^4]\}.$$

The later version of $f(r)$, given by (1.16) where the second exponent is 6 instead of 4, was introduced^{1,7} to make $f(r)$ approach unity more rapidly as r increases. [The switch of the first exponent from 10 to 12 has no physical significance and was made to place the maximum of $f(r)$ at the position of the potential minimum in a particularly simple way.]

It must be noted that the above argument concerning the small E_{03V} value is probably stronger for a non-close-packed lattice than for a close-packed one for a given correlation function. The body-centered cubic lattice is an open structure in which three particles are unable to approach one another as easily as in a close-packed lattice. This lattice effect, by which one expects E_{03V} to

be larger for an hcp than for a bcc lattice, is shown, in Sec. II B, to occur for solid helium.

Although the condition that $f(r)$ approach unity rapidly is a necessary condition for E_{03V} to be small, it is not a sufficient condition. It turns out that the internal cancellation within E_{03V} due to the contributions of the various kinds of triangles is also crucial. However, this cancellation is not accidental. In Appendix B we indicate that certain kinds of triangles always give negative contributions while others always give positive contributions. Both kinds of triangles are always present in any lattice, so that the cancellation is an important physical feature of the cluster expansion.

In this paper we evaluate only E_{03V} to obtain an indication of the rate of convergence of the cluster expansion, so that even though E_{03V} turns out to be quite small compared to E_{02V} , we have not *proved* that the expansion converges rapidly or even that it converges at all. Indeed it would be useful to have an estimate of E_{04V} . Unfortunately, the computation of E_{04V} is well beyond our present capabilities. However, we can argue that if it is difficult to get three atoms together to make E_{03V} big, it is much more difficult to get four or more together. For the sake of comparison, we give the four-body term

$$E_{04V} = \frac{1}{4} \sum'_{i,j,k,l} \left\{ \left[\frac{\langle V_{ij} f_{ij}^2 f_{ik}^2 f_{il}^2 f_{jk}^2 f_{jl}^2 f_{kl}^2 \rangle}{\langle f_{ij}^2 f_{ik}^2 f_{il}^2 f_{jk}^2 f_{jl}^2 f_{kl}^2 \rangle} - \frac{\langle V_{ij} f_{ij}^2 f_{ik}^2 f_{jk}^2 \rangle}{\langle f_{ij}^2 f_{ik}^2 f_{jk}^2 \rangle} \right] - \left[\frac{\langle V_{ij} f_{ij}^2 f_{ik}^2 f_{jk}^2 \rangle}{\langle f_{ij}^2 f_{ik}^2 f_{jk}^2 \rangle} - \frac{\langle V_{ij} f_{ij}^2 \rangle}{\langle f_{ij}^2 \rangle} \right] \right\}. \quad (2.1)$$

We have written it in this form to demonstrate the kinds of cancellation taking place. There seems no reason why the cancellation between the square brackets, which is the new feature introduced by E_{04V} , should not be as complete as the cancellation within a square bracket which is analogous to that taking place in E_{03V} . Such a result would imply $E_{04V} \ll E_{03V}$. Similar arguments hold for higher order terms in which further cancellations take place.

There is one other indication that these higher order terms are negligible. There have been two Monte Carlo calculations^{8,9} of the energy of close-packed ⁴He. McMillan⁸ uses $f(r_{ij})$ with no single-particle functions; whereas Levesque *et al.*⁹ use a wave function of the general form (1.1) with Gaussian single-particle functions. Although in each case the analytic correlation function used differs from ours and, indeed, is possibly more flexible than ours, the numerical results of these calculations are lower than ours by only about one

⁶ L. H. Nosanow, Phys. Rev. Letters **13**, 270 (1964).

⁷ L. H. Nosanow, in *Proceedings of the Ninth International Conference on Low Temperature Physics* (Plenum Press, Inc., New York, 1965), p. 277.

⁸ W. L. McMillan, Phys. Rev. **138**, A442 (1965).

⁹ D. Levesque, D. Schiff, T. Khiet, and L. Verlet (unpublished report).

TABLE I. Results of a typical calculation on bcc ^3He ($R=3.75 \text{ \AA}$), showing the size of the three-body term E_{03V} in comparison with the one- and two-body terms E_{01} and E_{02V} , and the effect of E_{03V} on the wavefunction in the variational calculation. The energies are in cal/mole and A is in \AA^{-2} .

	At minimum in $E_{01}+E_{02V}$	At minimum in $E_{01}+E_{02V}+E_{03V}$
A	1.30	1.42
$\log_{10}K$	-0.75	-0.76
E_{01}	31.3	34.2
E_{02V}	-21.6	-24.4
E_{03V}	0.1	-0.2
$E_{01}+E_{02V}$	9.7	9.8
$E_{01}+E_{02V}+E_{03V}$	9.8	9.6

calorie per mole. At a nearest-neighbor distance of $R=3.60 \text{ \AA}$ (molar volume = 20 cm^3) we find $E_0=E_{01}+E_{02V}+E_{03V}=-2.6$ cal/mole; whereas they each find $E_0 \cong -4$ cal/mole. We believe this is good evidence that the higher order terms are small and that the truncation of the cluster expansion is valid.

B. Numerical Results

We next present the results of our numerical evaluation of E_{03V} . For bcc ^3He and ^4He we find that E_{03V} is very much smaller than E_{02V} . At the minimum in $E_{01}+E_{02V}$, it varies from a value 100 times smaller at lower densities to 20 times smaller at higher densities; moreover, at the minimum in $E_{01}+E_{02V}+E_{03V}$ it is 100 times smaller than E_{02V} at all densities studied. Including E_{03V} in the variations improves the values of the wave-function parameters, especially at high densities. Calculations on hcp ^3He and ^4He show that E_{03V} is larger than in the bcc calculations; however, it is still about 20 times smaller than E_{02V} . Finally, to illustrate the care one must take in truncating the cluster expansion, we give a numerical example of a parameter variation for which the approximation $E_0 \cong E_{01}+E_{02V}$ is not valid, that is, E_{03V} does not remain small during the variation.

It was indicated in Sec. II A that the bcc lattice should be most favorable for small E_{03V} and this is the case. At low densities, one would expect the cluster expansion to be especially good. Indeed for $R=3.75 \text{ \AA}$ in bcc ^3He , at the values of A and K for which $E_{01}+E_{02V}$ is a minimum, we find $E_{03V}=0.1$ cal/mole. (See the first part of Table I.) This may be compared to the value $E_{02V}=-21.6$ cal/mole (note $E_{01}+E_{02V}=31.3-21.6=9.7$ cal/mole). It is instructive to examine the size of the contribution of some of the triangles to E_{03V} . Table VII in Appendix B lists the important triangles, the number of them occurring in the bcc lattice, and their total contribution to E_{03V} . It was found that the inclusion of the first 12 types of triangles gave sufficient accuracy. (Our accuracy is about 10%.) In Appendix B we give a complete discussion of the triangles needed in the lattice sum. One point is clear from Table VII:

Internal cancellation is an important effect in making E_{03V} small, as we have anticipated above.

The small size of E_{03V} at the position of the minimum in $E_{01}+E_{02V}$ is not the only consideration necessary. We must also require that E_{03V} be slowly varying as a function of the parameters A and K near the position of the minimum in $E_{01}+E_{02V}$. If this is not the case, then it might turn out that the minimum value of $E_{01}+E_{02V}+E_{03V}$ is very different from that of $E_{01}+E_{02V}$ and at very different values of the variational parameters, in which case our approximation procedure would be invalid. When we include E_{03V} in the variational procedure, we find the minimum energy is now 9.6 cal/mole (lower than before by only 0.1 cal/mole) with $E_{03V}=-0.20$ cal/mole. The parameter A at the new minimum is greater by 0.12 \AA^{-2} than its previous value of 1.30 \AA^{-2} , while $\log K$ is less by only 0.01 from the value -0.75 . (See the second part of Table I.)

At high densities one expects the cluster expansion to be poorer than at low densities; and in a certain sense this is the case. The results for $R=3.45 \text{ \AA}$ are given in Table II. The minimum in $E_{01}+E_{02V}$ is 18.6 cal/mole with $A=1.73 \text{ \AA}^{-2}$, $\log K=-0.79$. There, $E_{03V}=1.3$ cal/mole which, indeed, is much larger than for $R=3.75 \text{ \AA}$. However, if E_{03V} is included in the variational procedure, the best parameters are changed to $A=2.08$ and $\log K=-0.83$ for which $E_{03V}=+0.20$. The minimum energy is changed from 18.6 cal/mole to 19.3 cal/mole. From the point of view of the variational parameters the cluster expansion is not quite as good at high densities, that is, E_{03V} has more of an effect on the position of the minimum. But given an accurate wave function, the small size of E_{03V} indicates that the cluster expansion convergence is about the same at all densities. The inclusion of E_{03V} in the calculations has changed the energy by only a small amount (at most by 0.7 cal/mole). E_{03V} is smaller, by two orders of magnitude, than E_{02V} which is about -25 cal/mole for all densities. In Fig. 1 we plot the minimum value of $E_{01}+E_{02V}$ and that of $E_{01}+E_{02V}+E_{03V}$ as a function of the molar volume. We also plot the values of the variational parameters for the two minimizations in Fig. 2.

We have computed the ground-state energy for bcc ^4He at only one density since it exists over a small

TABLE II. Results similar to those of Table I for bcc ^3He at a higher density ($R=3.45 \text{ \AA}$). At higher densities E_{03V} has a larger effect on the wave function.

	At minimum in $E_{01}+E_{02V}$	At minimum in $E_{01}+E_{02V}+E_{03V}$
A	1.73	2.08
$\log_{10}K$	-0.79	-0.83
E_{01}	41.5	48.8
E_{02V}	-22.9	-29.7
E_{03V}	1.3	0.2
$E_{01}+E_{02V}$	18.6	19.1
$E_{01}+E_{02V}+E_{03V}$	19.9	19.3

TABLE III. Results similar to those of Tables I and II for hcp ^3He ($R=3.75 \text{ \AA}$, upper table) and ^4He ($R=3.60 \text{ \AA}$, lower table).

	At minimum in $E_{01}+E_{02V}$	At minimum in $E_{01}+E_{02V}+E_{03V}$
A (\AA^{-2})	1.53	1.65
$\log_{10}K$	-0.79	-0.78
E_{01}	36.7	39.6
E_{02V}	-24.4	-27.3
E_{03V}	-1.2	-1.4
$E_{01}+E_{02V}$	12.3	12.3
$E_{01}+E_{02V}+E_{03V}$	11.1	10.9
A (\AA^{-2})	2.00	2.10
$\log_{10}K$	-0.74	-0.74
E_{01}	34.8	36.5
E_{02V}	-35.8	-37.4
E_{03V}	-1.5	-1.7
$E_{01}+E_{02V}$	-1.0	-0.9
$E_{01}+E_{02V}+E_{03V}$	-2.5	-2.6

region of temperature and pressure. At a molar volume of 21.01 cm^3 , the minimum values are $E_{01}+E_{02V} = -2.4 \text{ cal/mole}$ and $E_{01}+E_{02V}+E_{03V} = -2.8 \text{ cal/mole}$.

The computation of E_{03V} for the hcp lattice consumes far more computer time than for the bcc lattice since there are many more triangles in this lattice. (See the listing in Table VIII in Appendix B.) One useful simplification that can be made is to replace the hcp by an fcc lattice, which has far fewer significant triangles in its lattice sum. This is a reasonable approximation because the three-body energies of the two lattices are almost identical in static lattice calculations,¹⁰ and values of E_{02V} for the two structures are very nearly equal in our own calculations. We have checked this approximation in one case and have found that, for $R=3.60 \text{ \AA}$ in ^4He , the fcc $E_{03V} = -1.8 \text{ cal/mole}$ while the hcp $E_{03V} = -1.7 \text{ cal/mole}$. The difference is negligible for our purposes.

For hcp helium (either isotope) use of the same trial correlation function (1.16) gives an E_{03V} which is about 10 times larger than in bcc helium. The reason for this seems to be the lattice effect mentioned above. Table III illustrates hcp calculations for typical sets of

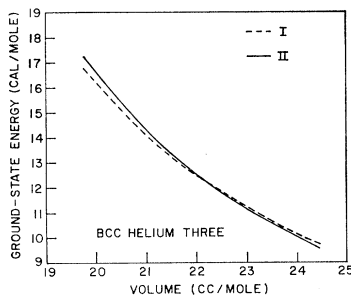


FIG. 1. Energy (in cal/mole) versus molar volume. Curve I, from Ref. 1 is based on minimizing $E_{01}+E_{02V}$; curve II is the calculation of this paper based on minimizing $E_{01}+E_{02V}+E_{03V}$.

¹⁰ See, for example, B. M. Axilrod, J. Chem. Phys. **19**, 724 (1951) or L. Jansen and R. T. McGinnies, Phys. Rev. **104**, 961 (1956).

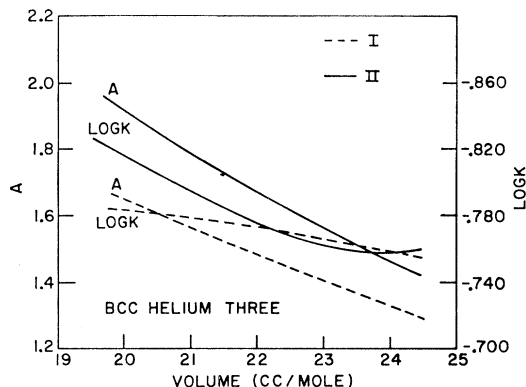


FIG. 2. Variational parameters A (in \AA^{-2}) and $\log_{10}K$ versus molar volume. Curve I, from Ref. 1, gives the parameters that minimize $E_{01}+E_{02V}$; curve II gives those that minimize $E_{01}+E_{02V}+E_{03V}$. Larger A means greater localization of the particles about their lattice sites.

parameters. (Compare with Table I.) Note in Table III that although E_{03V} is larger than the bcc case, it is still about 20 times smaller than E_{02V} . The energy values change only slightly in going from the minimum in $E_{01}+E_{02V}$ to the minimum in $E_{01}+E_{02V}+E_{03V}$. The wave function changes no more than in the bcc ^3He case. It is interesting that the primary effect of the three-body term on the wave function in these and in our bcc calculations is an increase in the localization of a particle; the parameter A is always increased. (See Tables I-III or, Fig. 2.) This is not surprising since the presence of surrounding third particles, with their repulsive cores, further limits the motion of the first particle while it is interacting with the second.

We have not performed calculations of E_{03V} as a function of density for the hexagonal phase of either helium isotope, but only at a single density for each.

We have stressed above that it is necessary to limit the variations in $f(r)$ to those for which E_{03V} is small so that the cluster expansion truncation after E_{02V} is meaningful. We can demonstrate a variation which violates that rule. If we replace σ in the $f(r)$ of Eq. (1.16) by a variational parameter η , then

$$f(r) = \exp\{-K[(\eta/r)^{12} - (\eta/r)^6]\}. \quad (2.2)$$

For each value of η used, we find the A and K for which

TABLE IV. Results of the variation of the correlation function parameter η to illustrate how the approximation $E_0 = E_{01}+E_{02V}$ can break down if E_{03V} becomes large. The quantity $E_{01}+E_{02V}$ has no minimum as a function of η , but $E_{01}+E_{02V}+E_{03V}$ behaves reasonably. The units of η , A , and the energies are \AA , \AA^{-2} , and cal/mole, respectively. The values of A and K are those which minimize $E_{01}+E_{02V}$ for the η given.

η	2.50	2.556	2.60	2.65
A	1.55	1.44	1.37	1.22
$\log_{10}K$	-0.66	-0.77	-0.84	-0.90
$E_{01}+E_{02V}$	12.7	11.7	11.1	10.3
E_{03V}	-0.5	0.3	0.9	2.3
$E_{01}+E_{02V}+E_{03V}$	12.2	12.0	12.0	12.6

$E_{01}+E_{02V}$ is a minimum. The value of E_{03V} is then computed. Table IV shows the results. As η increases, $E_{01}+E_{02V}$ decreases in the range shown; indeed, there is no real minimum at all in this quantity as a function of η . As η increases, the best value of A becomes so small that the calculation is clearly meaningless. It is only the inclusion of E_{03V} in the variation that makes good sense out of the calculation; E_{03V} increases until a minimum appears in $E_{01}+E_{02V}+E_{03V}$ as a function of η . This injunction against arbitrary variations in $f(r)$ was pointed out in I and has also been stressed by Brueckner and Froberg.⁵ However, despite statements to the contrary in BF, this restriction does not rule out the validity of truncating the cluster expansion after E_{02V} when the analytic form of $f(r)$ is limited to one for which E_{03V} is always small, as for example, the $f(r)$ of (2.2) with $\eta \leq \sigma$. It is true, of course, that including E_{03V} as a correction (when $\eta = \sigma$) does improve the calculation, especially in reference to the wave function. If a differential equation is derived for $f(r)$, as has been done by Brueckner and Froberg⁵ and by us,¹¹ then this amounts to an arbitrary variation so that E_{03V} must be included in the calculations.

We should point out that we have not studied the effect of varying η in the calculations for the hcp lattice. The fact that E_{03V} is 10 times larger there than in the bcc case may be due to a poorer choice of η , i.e., $\eta = \sigma$. Indeed, we expect E_{03V} to increase from its negative value, pass through zero, and then become positive as η increases. (See Table IV.) It may be that the minimum in $E_{01}+E_{02V}+E_{03V}$, as a function of η , will occur when E_{03V} is nearer zero than it is presently. This possibility will be studied in future work.

III. FURTHER RESULTS FOR bcc He

Since the inclusion of the three-body term in the variational calculation has improved the wave function

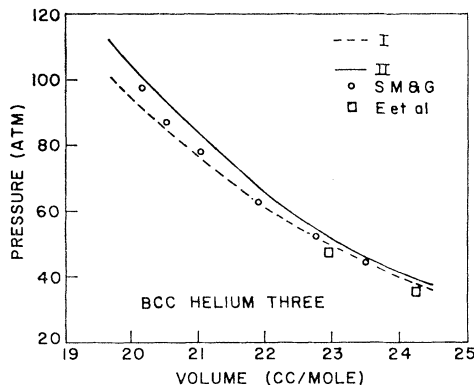


FIG. 3. Pressure P versus molar volume, Curve I, is from Ref. 1; curve II, from this work. The data are those of Sydorik, Mills, and Grilly (Ref. 12) and of Edwards, Baum, Brewer, Daunt, and McWilliams (Ref. 13).

¹¹ W. J. Mullin and L. H. Nosanow, *Bull. Am. Phys. Soc.* **11**, 126 (1966).

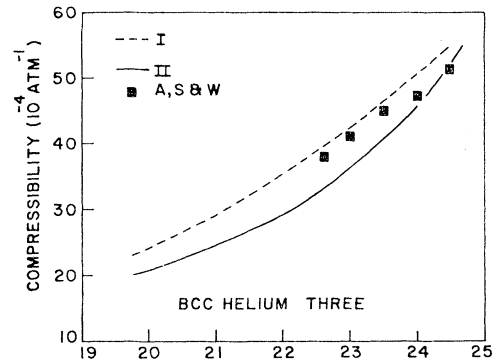


FIG. 4. Compressibility κ versus molar volume. Curve I, is from Ref. 1; curve II, from this work. The data are those of Adams, Straty, and Wall (Ref. 14).

for bcc ^3He , it is worth while computing the other zero-temperature properties of bcc ^3He . We use the new values of A and K to compute the pressure, compressibility, sound velocities, Debye temperature, and exchange integral, as a function of density. We also compute the sound velocities for bcc ^4He .

We can obtain the pressure and compressibility by use of the formulas $P = -dE_0/dV$ and $\kappa = -(dV/dP)/V$. We numerically differentiate $E_{01}+E_{02V}+E_{03V}$ and compare the results with those obtained in I where $E_{01}+E_{02V}$ was analyzed. Figures 3 and 4 show our results. The dashed curves are the results of I for a Gaussian ϕ . The agreement with experiment¹²⁻¹⁴ is not changed much; the pressure is perhaps a bit too high now and the compressibility a bit too low.

The pressure and compressibility results presented here are in much better agreement with experiment than are the ground-state energy calculations. We repeat an argument given in I to explain this effect. Our values for E_0 for bcc ^3He are about 10 cal/mole too high. A typical value of E_0 is 10 cal/mole which is composed of $E_{01} = 34$ cal/mole and $E_{02V}+E_{03V} = -24$ cal/mole. Improvements in the theory will probably lower both E_{01} and $E_{02V}+E_{03V}$; a 10% to 15% lowering in each would bring about agreement with the correct energy. Hence, each of the quantities is probably accurate to $\sim 15\%$. Since it turns out that $E_{02V}+E_{03V}$ is nearly constant over the whole density range with E_{01} containing almost all of the density dependence, it is reasonable that we can obtain the pressure and compressibility to about 15%.

It is useful to try to understand why including E_{03V} in the variational procedure has had the effects illustrated in Figs. 3 and 4, and perhaps to try to explain some of the discrepancies found. In I, the fact that the calculated pressures were somewhat too low and the

¹² S. G. Sydorik, R. L. Mills, and E. R. Grilly, *Phys. Rev. Letters* **4**, 495 (1960).

¹³ D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, *Helium Three* (Ohio State University Press, Columbus, Ohio, 1960).

¹⁴ E. D. Adams, G. C. Straty, and E. L. Wall, *Phys. Rev. Letters* **15**, 549 (1965).

compressibilities too high (when the numerical ϕ was used) was blamed on deficiencies in $f(r)$. (See Sec. VII of I.) It was claimed that $f(r)$ "softened" the hard core of the effective potential too much by vanishing too rapidly for small r . [That is, the small r form of $f(r)$ should be $\exp(-\text{constant}/r^5)$ rather than our $\exp(-\text{constant}/r^{12})$ as discussed after Eq. (2.8) of I.] While this deficiency is really present in $f(r)$, it is of importance only for $r \ll \sigma$; the pressure and compressibility depend on $f(r)$ more strongly in the region $r \cong \sigma$. Thus, we now feel that explanation is insufficient and that an important cause of the low pressures and high compressibilities of I is the neglect of E_{03V} in that paper. The effect that a third particle has on a pair of interacting particles, especially at high densities, is to restrict the motion of the particles. From a single-particle point of view, one would expect that a particle would now see an effective potential well which has a higher barrier. For Gaussian single-particle functions this means the parameter A will be increased, and by a greater amount at larger densities. This effect is shown in Fig. 2 where the old and new A values are plotted. Since the slope of the new A vs molar volume curve is more negative than that of I, the pressures computed are somewhat larger and the compressibility lower. If now one were able to make use of the more accurate numerical ϕ , rather than the Gaussian, we know from I that the pressures would be slightly lowered and the compressibility slightly raised, bringing them into even better

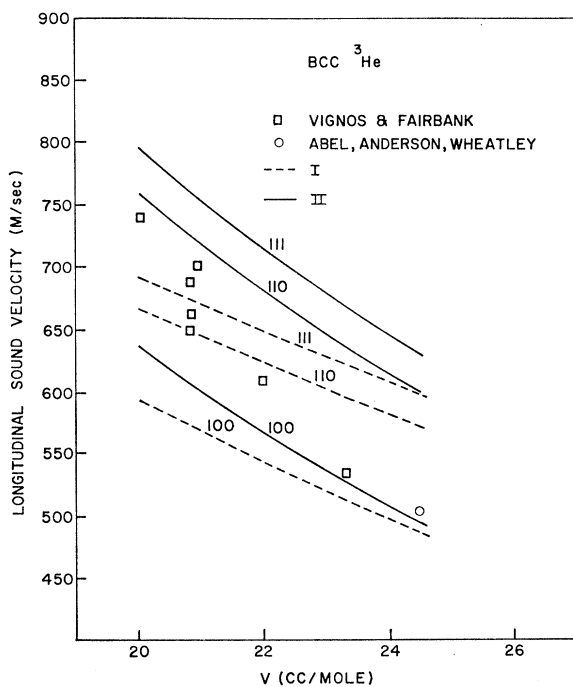


FIG. 5. Longitudinal sound velocities versus molar volume, in several symmetry directions. Curves I, from Ref. 15, are based on the parameters which minimize $E_{01} + E_{02V}$; curves II are based on the parameters calculated in this work. Data are from Ref. 17.

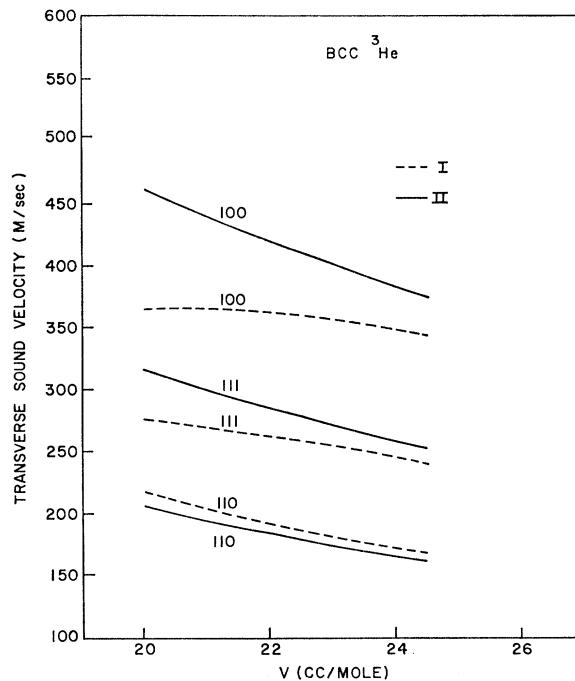


FIG. 6. Transverse sound velocities versus molar volume in several symmetry directions. Curve I is from Ref. 15; curve II from this work.

agreement with experiment. However, as stated above, our inaccuracy in pressure and compressibility due to the uncertainty in E_{01} is about 15%, and the discrepancies we are considering are not very much larger than that. Hence a discussion of discrepancies in those two quantities will be more meaningful when the ground-state energy, and E_{01} , have been more accurately computed.

We have also recomputed the sound velocities¹⁵ in bcc ^3He and ^4He . The results are shown in Figs. 5 and 6 and in Table V. The experimental results¹⁶ are also shown. The density dependence of the calculated longitudinal sound velocities is improved over those

TABLE V. The results of our calculation of the sound velocities (in m/sec) for bcc ^4He at a molar volume of 21.01 cm³.

Symmetry direction	Longitudinal	Transverse
100	449	360(2)
110	555	152
111	586	360
expt	540-555 ^a	337-351 ^b

^a See Ref. 16.

^b F. P. Lipschultz and D. M. Lee, Phys. Rev. Letters 14, 1017 (1965).

¹⁵ L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters 15, 618 (1965).

¹⁶ J. H. Vignos and H. A. Fairbank, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (Butterworth Scientific Publications, Ltd., London, 1962); W. R. Abel, A. C. Anderson, and J. C. Wheatley, Phys. Rev. Letters 7, 299 (1961).

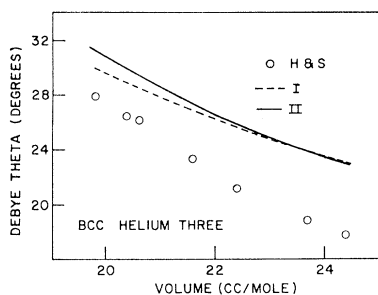


FIG. 7. Debye θ versus molar volume. Curve I is from Ref. 15; curve II is from this work. Measurements are from Ref. 17.

calculated in Ref. 15 because of the better A values used; however, the sum rule [Eq. (5) of Ref. 15] which was used as a test of the approximations of Ref. 15 is now satisfied to within 10% (instead of the 3% found with the previous wave function). The zero-temperature limit of the Debye Θ is again computed by the method of Ref. 15, and the curves are shown in Fig. 7. The experimental points are those of Heltemes and Swenson.¹⁷

We use the new values of the wave-function parameters, A and K , gotten by minimizing $E_{01} + E_{02V} + E_{03V}$, and the cluster expansion methods described in a previous paper⁴ to calculate improved values of the exchange integral J as a function of density for bcc ^3He . Figure 8 is a plot of the spin alignment temperature, given by

$$T_c = \frac{1}{4} z |J|, \quad (3.1)$$

where z is the number of nearest neighbors. The previous calculation, with results denoted by I in the figure, gave T_c values of nearly the right magnitude but they have the wrong density dependence when compared with the experimental results.¹⁸ Use of the new parameters leads to results, indicated by II, which still have the correct order of magnitude and now have an improved density dependence. In Ref. 4, we correctly attributed the mistaken density dependence of our T_c to errors in $\phi(r)$, although for the wrong reasons. At that time we did not realize the large effect that E_{03V} would have on the single-particle function. Since the exchange integral depends sensitively on the overlap of neighboring single-particle functions, the increase in A values, from the inclusion of E_{03V} in the variations, makes the computed $|J|$ values smaller than those of Ref. 4 at high densities. The change in K (Fig. 2) at high densities has negligible effect on J . Apparently the decrease of the exchange integral with increasing density occurs because the exchange of two particles is impeded by the

¹⁷ E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

¹⁸ R. L. Garwin and A. Landesman, Phys. Rev. **133**, A1503 (1964); M. G. Richards, J. Hatton, and R. P. Giffard, in *Proceedings of the Ninth International Conference on Low Temperature Physics* (Plenum Press, Inc., New York, 1965), p. 219; R. C. Richardson, E. Hunt, and H. Meyer, Phys. Rev. **138**, A1326 (1965); and R. C. Richardson, A. Landesman, E. Hunt, and H. Meyer, *ibid.* **146**, 244 (1966).

presence of the hard cores of the surrounding particles, and, of course, this effect is greater at larger densities.

Our new T_c values are uniformly lower than experiment because of the remaining inaccuracies of our analytic wave function. The tail of the Gaussian single-particle function ϕ cuts off somewhat faster than that of the numerical ϕ . (This is shown, for example, in Figs. 1 and 2 of I.) The more accurate tail of the numerical ϕ will increase the overlap and hence $|J|$ as well. Certainly the replacement of our analytic $f(r)$ by one which is more accurate at small r values will also have an effect on the value of $|J|$, but at this time it is not clear to us just what this effect will be.

IV. THE BRUECKNER-FROHBERG EXPANSION

In a recent paper,⁵ Brueckner and Frohberg have outlined a variational calculation in which the energy upper-bound is evaluated by an expansion which appears to be similar to ours. Here we wish to point out the fundamental differences between their expansion and ours. Further, we report a few calculations of the leading correction term of their expansion. On a basis of these results, it seems likely that their expansion converges too slowly to be useful in calculating the

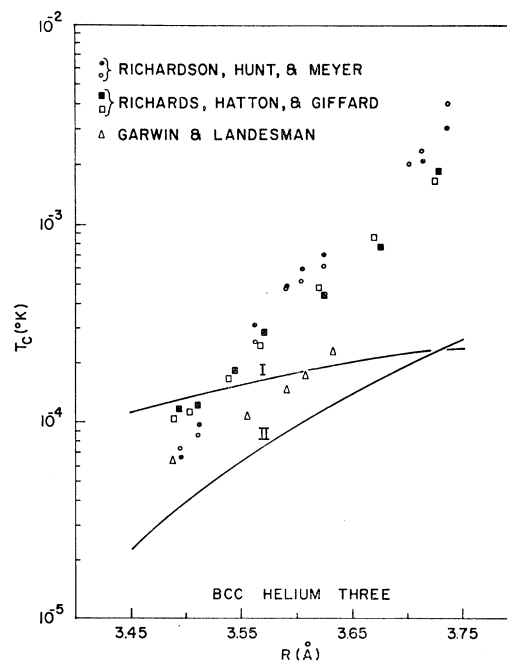


FIG. 8. Spin-alignment temperature T_c versus nearest-neighbor distance R . Curve I is from Ref. 4; curve II is gotten using the variational parameters computed in this paper by including E_{03V} in the energy minimization. The density dependence of curve II is now in improved agreement with the experiments of Ref. 18. Curve II is too low for reasons discussed in the text. The experimental curve of Garwin and Landesman (Ref. 18) should be in close agreement with the other data, but they failed to take the "10/3 effect" into account. [See the paper of Richardson, Landesman, Hunt, and Meyer (Ref. 18) for a discussion of this.]

properties of crystalline helium by the method they propose.

The BF expansion requires the wave function to be factorable into a product of single-particle and pair functions. Hence, it is not as general as the cluster expansion used in I, which is valid for an *arbitrary* wave function. The BF expansion is written in terms of pair indices, α, β , etc., which represent, for example, ij, ik , etc. The energy is

$$E_0 = \mathcal{E}_0 + \sum_{\alpha} \mathcal{E}_1(\alpha) + \sum_{\alpha, \beta} \mathcal{E}_2(\alpha\beta) + \sum_{\alpha, \beta, \gamma} \mathcal{E}_3(\alpha\beta\gamma) + \dots, \quad (4.1)$$

where the sums are restricted so that each pair is counted only once. Here $\mathcal{E}_n(\alpha\beta\cdots)$ is *not* an n -particle term, but contains, as its leading elements, all possible configurations which have n factors of f^2 regardless of how many single-particle coordinates appear in each of these elements. Thus, \mathcal{E}_1 is strictly a two-particle term; but the \mathcal{E}_2 terms describe only part of the three-particle interaction, and the \mathcal{E}_3 terms describe the rest of the three-particle interaction as well as part of the four-particle interaction. These terms, which we also convert to single-particle notation, are $\mathcal{E}_0 = 3AN\hbar^2/4m$,

$$\begin{aligned} \sum_{\alpha} \mathcal{E}_1(\alpha) &= \sum_{\alpha} \frac{\langle V_{\alpha} f_{\alpha}^2 \rangle}{\langle f_{\alpha}^2 \rangle} = \frac{1}{2} \sum'_{i,j} \frac{\langle V_{ij} f_{ij}^2 \rangle}{\langle f_{ij}^2 \rangle}, \\ \sum_{\alpha\beta} \mathcal{E}_2(\alpha\beta) &= \sum_{\alpha\beta} \left\{ \frac{\langle (V_{\alpha} + V_{\beta}) f_{\alpha}^2 f_{\beta}^2 \rangle}{\langle f_{\alpha}^2 f_{\beta}^2 \rangle} - \mathcal{E}_1(\alpha) - \mathcal{E}_1(\beta) \right\} \\ &= \sum'_{i,j,k} \left\{ \frac{\langle V_{ij} f_{ij}^2 f_{ik}^2 \rangle}{\langle f_{ij}^2 f_{ik}^2 \rangle} - \frac{\langle V_{ij} f_{ij}^2 \rangle}{\langle f_{ij}^2 \rangle} \right\}, \quad (4.2) \\ \sum_{\alpha\beta\gamma} \mathcal{E}_3(\alpha\beta\gamma) &= \sum_{\alpha\beta\gamma} \left\{ \frac{\langle (V_{\alpha} + V_{\beta} + V_{\gamma}) f_{\alpha}^2 f_{\beta}^2 f_{\gamma}^2 \rangle}{\langle f_{\alpha}^2 f_{\beta}^2 f_{\gamma}^2 \rangle} \right. \\ &\quad \left. - \mathcal{E}_2(\alpha\beta) - \mathcal{E}_2(\alpha\gamma) - \mathcal{E}_2(\beta\gamma) \right. \\ &\quad \left. + \mathcal{E}_1(\alpha) + \mathcal{E}_1(\beta) + \mathcal{E}_1(\gamma) \right\}. \end{aligned}$$

Note that the first two BF terms are the same as ours. The three-body part of $\sum \mathcal{E}_3$ is

$$\begin{aligned} \left(\sum_{\alpha\beta\gamma} \mathcal{E}_3 \right)_{3\text{-body}} &= \frac{1}{2} \sum'_{i,j,k} \left\{ \frac{\langle V_{ij} f_{ij}^2 f_{jk}^2 f_{ik}^2 \rangle}{\langle f_{ij}^2 f_{jk}^2 f_{ik}^2 \rangle} \right. \\ &\quad \left. - 2 \frac{\langle V_{ij} f_{ij}^2 f_{ik}^2 \rangle}{\langle f_{ij}^2 f_{ik}^2 \rangle} + \frac{\langle V_{ij} f_{ij}^2 \rangle}{\langle f_{ij}^2 \rangle} \right\}. \quad (4.3) \end{aligned}$$

Two kinds of four-body terms containing factors like $\langle V_{ij} f_{ij}^2 f_{jk}^2 f_{kl}^2 \rangle$ and $\langle V_{ij} f_{ij}^2 f_{ik}^2 f_{il}^2 \rangle$, respectively, also appear in $\sum \mathcal{E}_3$, since they each have three f_{α}^2 's. The total three-body term (no other sums over just three

TABLE VI. Test of the Brueckner-Frohberg expansion. The higher order term $\sum \mathcal{E}_2$ is retained in BF (Ref. 5) while another three-body term ($\sum \mathcal{E}_3$)_{3 body} is neglected; the sum of these two is our three-body term E_{03V} . The neglect of ($\sum \mathcal{E}_3$)_{3 body}, which is larger than $\sum \mathcal{E}_2$ during the variation of the parameter η , has a substantial effect on the energy and wave function results since the BF energy estimate, $\mathcal{E}_0 + \sum \mathcal{E}_1 + \sum \mathcal{E}_2$, has no minimum for $\eta < 2.65 \text{ \AA}$, while our estimate, $E_{01} + E_{02V} + E_{03V}$, has a minimum near $\eta = 2.556 \text{ \AA}$. Note $\mathcal{E}_0 + \sum \mathcal{E}_1 \equiv E_{01} + E_{02V}$. Energies are in cal/mole. The values of A, K , and $E_{01} + E_{02V} + E_{03V}$ are from Table IV.

	$\eta = 2.556 \text{ \AA}$ $A = 1.44 \text{ \AA}^{-2}$ $\log_{10} K = -0.77$	$\eta = 2.65 \text{ \AA}$ $A = 1.22 \text{ \AA}^{-2}$ $\log_{10} K = -0.90$
$\sum \mathcal{E}_2$	-0.1	1.0
$(\sum \mathcal{E}_3)_{3 \text{ body}}$	0.4	1.3
E_{03V}	0.3	2.3
$\mathcal{E}_0 + \sum \mathcal{E}_1 + \sum \mathcal{E}_2$	11.6	11.3
$E_{01} + E_{02V} + E_{03V}$	12.0	12.6

indices appear anywhere else in the expansion) is

$$\begin{aligned} \sum_{\alpha\beta} \mathcal{E}_2 + \left(\sum_{\alpha\beta} \mathcal{E}_3 \right)_{3 \text{ body}} &= \frac{1}{2} \sum'_{i,j,k} \left\{ \frac{\langle V_{ij} f_{ij}^2 f_{jk}^2 f_{ik}^2 \rangle}{\langle f_{ij}^2 f_{jk}^2 f_{ik}^2 \rangle} - \frac{\langle V_{ij} f_{ij}^2 \rangle}{\langle f_{ij}^2 \rangle} \right\}. \quad (4.4) \end{aligned}$$

The term $\langle V_{ij} f_{ij}^2 f_{jk}^2 f_{ik}^2 \rangle / \langle f_{ij}^2 f_{jk}^2 f_{ik}^2 \rangle$, which does not appear at all in the usual cluster expansion for a liquid or a gas, has *cancelled out* leaving just the complete three-body term, E_{03V} , which we have treated in this paper. Thus it may be that the cluster expansion used in I is a partial summation of the BF expansion.

The analysis described in BF involves truncating the expansion after the $\sum \mathcal{E}_2$ term. The terms retained are varied to yield a differential equation for f_{ij} , and it is the contention of the authors that the inclusion of the $\sum \mathcal{E}_2$ term will allow such a variation to be made. We have tested this truncation procedure by numerical evaluation of $\sum \mathcal{E}_2$ and $(\sum \mathcal{E}_3)_{3 \text{ body}}$ using (2.2). As a typical example, we take $R = 3.65 \text{ \AA}$ in bcc ^3He with $\eta = 2.556 \text{ \AA}$ and 2.65 \AA ; the appropriate values of A and $\log_{10} K$ are taken from Table IV. For $\eta = 2.556 \text{ \AA}$ we see, in Table VI, that the higher order term $(\sum \mathcal{E}_3)_{3 \text{ body}}$, which is dropped, is actually larger in magnitude than the higher order term $\sum \mathcal{E}_2$, which is kept. However, both terms are quite small compared to $\sum \mathcal{E}_1 (\equiv E_{02V}) \cong -25$ cal/mole. The calculation for $\eta = 2.65 \text{ \AA}$ demonstrates how the neglect of part of the total three-body term has a serious effect on the wave function. Table VI shows that the neglected term, $(\sum \mathcal{E}_3)_{3 \text{ body}}$, is sufficiently large that the quantity $\mathcal{E}_0 + \sum \mathcal{E}_1 + \sum \mathcal{E}_2$ has not yet reached a minimum at $\eta = 2.65 \text{ \AA}$ and that it can only reach a minimum when $\sum \mathcal{E}_2$ is so large that the convergence of the expansion is doubtful. On the other hand, in our η variation (Table IV and the last line of Table V) we found that including the total three-body term E_{03V} pushed the minimum back to $\eta \approx 2.56 \text{ \AA}$, where E_{03V} is very small.

Thus, not only are the wave functions given by the two methods very different, but also the rate of convergence of our expansion in the neighborhood of the minimum seems to be faster than for the BF expansion.

It might be argued that our regrouping of the BF terms, that is, the splitting of \mathcal{E}_3 into $(\sum \mathcal{E}_3)_{3 \text{ body}} + (\sum \mathcal{E}_3)_{4 \text{ body}}$, is not a valid way of analyzing their method, so that, although $(\sum \mathcal{E}_3)_{3 \text{ body}}$ is not small compared to $\sum \mathcal{E}_2$, the complete $\sum \mathcal{E}_3$ is small because of cancellation. Although we cannot prove that this cancellation does not occur, we see no physical reason why it should.

We must note that we have used *our* correlation function in this analysis, although the BF function should be quite different. In principle, the BF method gives a separate correlation function for each pair of particles and coupled differential equations are solved for each function; also, the boundary condition to be imposed on each function at large distances may differ from ours. However, since the method involves *arbitrary* variations with respect to each correlation function, it seems quite possible that a situation analogous to the one we have described will arise, that is, one for which the minimum in the retained terms of the expansion occurs when the neglected three-body terms are important, so that the calculated wave function is not a good approximation to the actual one. In order to avoid this undesirable situation we feel that further constraints must be placed on the solutions of their differential equations. Perhaps including all of E_{03V} is sufficient to keep all higher order terms small; however, some recent work by us¹¹ indicates that even further constraints will be necessary to remove long-range correlation effects which cannot be treated by cluster expansion techniques. We will discuss the significance of such long-range effects further in the next section.

V. SUMMARY AND DISCUSSION

The calculations reported in this paper indicate that the physical properties of the state given by our trial wave function are adequately described within the approximation of I, in which the cluster expansion was truncated at $E_0 \cong E_{01} + E_{02V}$. This fact was demonstrated by showing that the inclusion of E_{03V} causes only small changes in the energy. Furthermore, the reasonable agreement of the calculated quantities with the experimental properties of solid helium indicates that our trial wave function is a fair approximation to the true ground state. Of course, the approximation of I limits the types of trial correlation functions that we can use. The variation of η in Sec. II showed that, if we do not keep $f(r)$ short-ranged, the higher order terms in the cluster expansion can become large.

Although the three-body term is small and $E_{01} + E_{02V}$ is a good approximation to the upper bound on the ground-state energy E_0 , the inclusion of E_{03V} in the calculation does give a noticeable improvement in the

accuracy of the wave function. The values of the wave-function parameters A and K are changed, especially at high densities. When other ground-state properties of bcc ^3He are computed as a function of density using the improved wave function, it is found that agreement with experiment is either essentially unchanged or improved.

Since the calculated energies are still about 10 cal/mole higher than the experimental ones, it is clear that the trial wave function needs to be improved. We have already shown in I that using a numerical single-particle function will only lower the energy by about one cal/mole, hence, this is not the answer. We have made some efforts¹¹ to derive and solve a differential equation for an $f(r)$ which is constrained to be short-ranged so that the cluster expansion will converge. Although this work is not yet complete, it is likely that the energy will be lowered by only a few cal/mole. Since the remaining discrepancy is about 5 cal/mole, we feel that it is probably a basic physical effect and will not be remedied without a fundamental change in the trial wave function. One major possibility is that this energy might come from including a more realistic phonon spectrum in the problem.^{15,19,20} In effect, this means including long-range correlations, which cannot be treated by cluster expansion methods. In his calculations on neon, Koehler²⁰ has found that this effect lowers the energy by 12% of the kinetic energy; if the same lowering were to obtain in solid helium, it would amount to approximately 4 cal/mole.

ACKNOWLEDGMENT

We wish to thank Paul Steinback for his help in the numerical work.

APPENDIX A: REDUCTION OF THE THREE-BODY INTEGRAL

Here we show how to reduce the integral $\langle V_{ij} f_{ij}^2 f_{jk}^2 f_{kr}^2 \rangle$ to a form suitable for numerical evaluation so that the three-body term E_{03V} given by Eq. (1.12) may be studied. Using normalized Gaussian single-particle functions, we have

$$\begin{aligned} I &\equiv \langle V_{12} f_{12}^2 f_{23}^2 f_{31}^2 \rangle \\ &= (A/\pi)^{9/2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 V(u) f^2(u) f^2(v) f^2(w) \\ &\quad \times \exp\{-A[(\mathbf{r}_1 - \mathbf{R}_1)^2 + (\mathbf{r}_2 - \mathbf{R}_2)^2 + (\mathbf{r}_3 - \mathbf{R}_3)^2]\}, \quad (\text{A1}) \end{aligned}$$

where u , v , and w are the magnitudes of the vectors

$$\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2, \quad \mathbf{v} = \mathbf{r}_2 - \mathbf{r}_3, \quad \mathbf{w} = \mathbf{r}_3 - \mathbf{r}_1, \quad (\text{A2})$$

and $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$ are the positions of the three lattice

¹⁹ D. R. Fredkin and N. R. Werthamer, Phys. Rev. 138, A1527 (1965).

²⁰ T. R. Koehler, Phys. Rev. 144, 789 (1966).

sites. We want to reduce the ninefold integral of (A1) to a three-dimensional integration over the variables u , v , and w .

For convenience let

$$\mathbf{a} = \mathbf{R}_1 - \mathbf{R}_2, \quad \mathbf{b} = \mathbf{R}_2 - \mathbf{R}_3, \quad \mathbf{c} = \mathbf{R}_3 - \mathbf{R}_1 \quad (\text{A3})$$

and then take the origin of coordinates at \mathbf{R}_1 . The exponential factor in (A1) becomes

$$\exp\{-A[(\mathbf{r}_1)^2 + (\mathbf{r}_2 + \mathbf{a})^2 + (\mathbf{r}_3 - \mathbf{c})^2]\}.$$

The three integrations over the center-of-mass coordinates may be carried out immediately. After substituting \mathbf{u} and \mathbf{w} for \mathbf{r}_2 and \mathbf{r}_3 and then integrating over \mathbf{r}_1 , we find

$$\begin{aligned} I = & 3^{-3/2}(A/\pi)^3 \int_0^\infty du u^2 V(u) f^2(u) \int_0^\infty dw \\ & \times w^2 f^2(w) \int d\Omega_u \int d\Omega_w f^2(v) \\ & \times \exp\{- (A/3)[u^2 + v^2 + w^2 + a^2 + b^2 + c^2 \\ & - 2\mathbf{u} \cdot (\mathbf{b} - \mathbf{a}) - 2\mathbf{w} \cdot (\mathbf{b} - \mathbf{c})]\}, \quad (\text{A4}) \end{aligned}$$

where $d\Omega_u$ and $d\Omega_w$ are the elements of solid angle of vectors \mathbf{u} and \mathbf{w} , respectively, and where we have used the equality $\mathbf{v} = -(\mathbf{u} + \mathbf{w})$.

It is possible to simplify considerably the dot products in (A4) before doing the angular integrations. We choose the z axis for \mathbf{u} along $\mathbf{b} - \mathbf{c}$ and the x axis in the plane of the triangle of lattice vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} . We may then write $\mathbf{b} - \mathbf{c}$ and $\mathbf{b} - \mathbf{a}$ in component form

$$\mathbf{b} - \mathbf{c} = \alpha \mathbf{i}_z, \quad (\text{A5})$$

$$\mathbf{b} - \mathbf{a} = \beta \mathbf{i}_x + \gamma \mathbf{i}_z, \quad (\text{A6})$$

where \mathbf{i}_x and \mathbf{i}_z are unit vectors and

$$\begin{aligned} \alpha &= (2b^2 + 2c^2 - a^2)^{1/2}, \\ \beta &= 6\Delta_{abc}/\alpha, \\ \gamma &= (5b^2 - a^2 - c^2)/2\alpha, \end{aligned} \quad (\text{A7})$$

with the area of the triangle with sides a , b , and c given by

$$\Delta_{abc} = \frac{1}{4}[2(a^2b^2 + b^2c^2 + c^2a^2) - (a^4 + b^4 + c^4)]^{1/2}. \quad (\text{A8})$$

The next step is to express \mathbf{w} in a coordinate system whose z axis is aligned along \mathbf{u} . Then the simplest way to compute the dot product $\mathbf{w} \cdot (\mathbf{b} - \mathbf{c})$ is to construct a rotation matrix²¹ to express \mathbf{w} in this new coordinate system. One finds

$$\mathbf{w} \cdot (\mathbf{b} - \mathbf{c}) = w\alpha(\cos\theta_u \cos\theta_w - \sin\theta_w \cos\phi_w \sin\theta_u), \quad (\text{A9})$$

$$\mathbf{u} \cdot (\mathbf{b} - \mathbf{a}) = u(\beta \cos\phi_u \sin\theta_u + \gamma \cos\theta_u), \quad (\text{A10})$$

where θ_u and ϕ_u are the angular coordinates of \mathbf{u} in the fixed coordinate system and θ_w and ϕ_w are the angular

coordinates of \mathbf{w} in the coordinate system whose z axis lies along \mathbf{u} . Note that (A9) is independent of ϕ_u because the fixed z axis has been chosen along $\mathbf{b} - \mathbf{c}$, and that v is independent of ϕ_w because of our choice of coordinate system for \mathbf{w} .

Our integral (A4) now becomes

$$\begin{aligned} I = & 3^{-3/2}(A/\pi)^3 \int_0^\infty du u^2 V(u) f^2(u) \int_0^\infty dw \\ & \times w^2 f^2(w) \int_0^\pi d\theta_w (\sin\theta_w) f^2(v) \\ & \times \exp[-(A/3)(u^2 + v^2 + w^2 + a^2 + b^2 + c^2)] \\ & \times \int_0^\pi d\theta_u (\sin\theta_u) \int_0^{2\pi} d\phi_u \int_0^{2\pi} d\phi_w \\ & \times \exp[(2A/3)(u\beta \cos\phi_u \sin\theta_u + u\gamma \cos\theta_u \\ & + w\alpha \cos\theta_u \cos\theta_w - w\alpha \sin\theta_w \cos\phi_w \sin\theta_u)]. \quad (\text{A11}) \end{aligned}$$

If we let

$$\begin{aligned} \lambda &= \cos\theta_w, \\ D &= (2A/3)(u\gamma + w\alpha\lambda), \\ E &= (2A/3)(u\beta), \\ F &= (2A/3)w\alpha(1 - \lambda^2)^{1/2}, \end{aligned} \quad (\text{A12})$$

then the last three angular integrations of (A11) may be written

$$\begin{aligned} I_1 = & \int_0^{2\pi} d\phi_w \int_0^{2\pi} d\phi_u \int_0^{2\pi} d\theta_u \sin\theta_u \\ & \times \exp\{D \cos\theta_u + (E \cos\phi_u + F \cos\phi_w) \sin\theta_u\}. \quad (\text{A13}) \end{aligned}$$

The ϕ_u and ϕ_w integrations now could be performed immediately but that is not the best way to proceed. Instead note that

$$\begin{aligned} & E \cos\phi_u + F \cos\phi_w \\ & = (E + F) \cos\left(\frac{\phi_u + \phi_w}{2}\right) \cos\left(\frac{\phi_u - \phi_w}{2}\right) \\ & \quad - (E - F) \sin\left(\frac{\phi_u + \phi_w}{2}\right) \sin\left(\frac{\phi_u - \phi_w}{2}\right), \quad (\text{A14}) \end{aligned}$$

so that the substitutions

$$\Phi = \frac{1}{2}(\phi_u + \phi_w), \quad \Psi = \frac{1}{2}(\phi_u - \phi_w) \quad (\text{A15})$$

lead to

$$\begin{aligned} I_1 = & \int_0^{2\pi} d\Psi \int_0^{2\pi} d\Phi \int_0^{2\pi} d\theta \sin\theta \\ & \times \exp[(E - F) \cos\Psi \cos\Phi \sin\theta \\ & + (E + F) \sin\Psi \sin\Phi \sin\theta + D \cos\theta], \quad (\text{A16}) \end{aligned}$$

²¹ See, for example, H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Cambridge, Massachusetts, 1953), p. 107.

where we have made use of the symmetries of the integrand to fix the Ψ and Φ limits of integration at the values shown. Equation (A16) has the form

$$I_1 = \int_0^{2\pi} d\Psi \int d\Omega_s \exp\{\mathbf{p} \cdot \mathbf{s} / |\mathbf{s}|\} \\ = 4\pi \int_0^{2\pi} d\Psi \sinh|\mathbf{p}| / |\mathbf{p}|, \quad (\text{A17})$$

where the vector \mathbf{p} has components

$$\mathbf{p} = ((E-F) \cos\Psi, (E+F) \sin\Psi, D), \quad (\text{A18})$$

so that

$$|\mathbf{p}| = (D^2 + (E+F)^2 - 4EF \cos^2\Psi)^{1/2}. \quad (\text{A19})$$

If we define

$$P^2 = D^2 + (E+F)^2, \quad (\text{A20}) \\ Q = 4EF/P^2,$$

then

$$I_1 = 4\pi \int_0^{2\pi} d\Psi \frac{\sinh(P(1-Q \cos^2\Psi)^{1/2})}{P(1-Q \cos^2\Psi)^{1/2}}. \quad (\text{A21})$$

Our integral (A11) has now been reduced to a four-dimensional form with a rather simple integrand. It is possible to evaluate it numerically in its present form; however, we find that expressing I_1 in a power series is more convenient. If we let

$$t = -PQ \sin^2\Psi/2 \quad (\text{A22})$$

and if

$$i_n = (\pi/2P)^{1/2} I_{n+1/2}(P)$$

is the modified spherical Bessel function, then a series for the integrand of (A21) may be derived by differentiating the identity²²

$$\cosh((P^2+2Pt)^{1/2})/P = \sum_{n=0}^{\infty} t^n i_{n-1}(P)/n! \quad (\text{A23})$$

with respect to t . We integrate the resulting series term by term to give finally

$$I_1(P, Q) = 8\pi^{3/2} \sum_{n=0}^{\infty} \Gamma(n + \frac{1}{2}) \\ \times (-PQ/2)^n i_n(P) / (\Gamma(n+1))^2. \quad (\text{A24})$$

This expression is useful for small PQ . For larger PQ , say $PQ > 15$, we have found a suitable asymptotic series given by

$$I_1(P, Q) = \frac{8\pi}{(P^2Q)^{1/2}} \sum_{n=0}^{\infty} (\Gamma(n + \frac{1}{2}))^2 \\ \times I_n(P) \left(\frac{2}{PQ}\right)^n / \Gamma(n+1). \quad (\text{A25})$$

²² H. A. Antosiewicz, in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964), Appl. Math. Ser. 55, p. 445.

This series may be derived by expressing the series (A24) as a Barnes's contour integral²³ and then deforming the infinite semicircle of the contour from the right half-plane to the left half-plane.

We may now write down the final form for the integral I. We replace the θ_w integration of (A11) with an integration over v by using

$$v^2 = u^2 + w^2 + 2uw \cos\theta_w, \quad (\text{A26})$$

which finally leads us to

$$I = (A/\pi\sqrt{3})^3 \int_0^{\infty} du \int_0^{\infty} dw \int_{|u-w|}^{u+w} dv \\ \times V(u) f^2(u) f^2(v) f^2(w) uvw \\ \times \{\exp[-(A/3)(u^2+v^2+w^2+a^2+b^2+c^2)]\} I_1(P, Q), \quad (\text{A27})$$

where the combination of (A7), (A12), (A20), and (A26) yields

$$P = (2A/3)[3(u^2a^2+v^2b^2+w^2c^2) \\ - \frac{1}{2}(u^2+v^2+w^2)(a^2+b^2+c^2) + 24\Delta_{uvw}\Delta_{abc}]^{1/2}, \quad (\text{A28})$$

and

$$Q = (2A/3)^2 48\Delta_{uvw}\Delta_{abc}/P^2,$$

with Δ_{uvw} and Δ_{abc} given by (A8).

The study of E_{03V} is based on the numerical evaluation of the power series for $I_1(P, Q)$ and then of the triple integral indicated in (A27). Since internal cancellation always causes the loss of at least one significant digit, we always computed integrals like I to four figures to insure two digits in E_{03V} .

APPENDIX B: TRIANGLES IN THE LATTICE SUM

In this Appendix we list the important triangles of the lattice sum of the calculation of E_{03V} ; we give typical values for the contributions of these; and we discuss some physical reasons why certain important triangles should make the contributions indicated. We will not go into the details of the triangle counting method; such methods are not difficult to devise.

In the bcc lattice, it was found that including 12 types of triangles gave E_{03V} with an accuracy of better than 10%. In Table VII we list these important triangles, the number of each occurring in the bcc lattice, and the total contribution of each type to E_{03V} . The most important triangles in the lattice sum are given in the upper half of Table VII. The lower half shows the contributions of the most important of the triangles which were dropped from the lattice sum in all calculations of E_{03V} except for a few test cases. It turns out that a triangle's contribution is small if the side

²³ E. T. Whittaker and G. N. Watson, *A Course in Modern Analysis* (Cambridge University Press, Cambridge, England, 1952), 4th ed., p. 86.

$a(=|\mathbf{R}_i-\mathbf{R}_j|/R)$ is large [because the potential $V(r_{ij})$ becomes small] or if either b or $c(=|\mathbf{R}_j-\mathbf{R}_k|/R$ and $|\mathbf{R}_k-\mathbf{R}_i|/R)$ is large (because correlation effects are important at short range only). Note, however, that it is again internal cancellation which makes the total contribution of these "higher order" triangles small. In Table VIII we give a simultaneous listing of the primary triangles for the fcc and hcp lattices. In the one case tested, we found that the truncation of the lattice sum at the 16 fcc triangles and 25 hcp triangles listed in the table caused only a 2% error. We should note that a crude estimate of the values of the parameters, A and K , that minimize $E_{01}+E_{02V}+E_{03V}$ may be obtained by approximating E_{03V} with the contributions from only the first four types of triangles in the bcc lattice or the first six in the fcc. This means that the contributions from the remaining triangles in the lattice sum are less sensitive to changes in A or K .

A quick examination of the individual triangle contributions in the tables shows that internal cancellation is an important factor in making E_{03V} small. For example, we have always found that triangle No. 1 yields a negative contribution and No. 2 a positive one for all lattice types. It is useful to understand why some

TABLE VII. Listing of triangles in the bcc lattice and their contribution to E_{03V} [Eq. (1.12)] in cal/mole for a set of typical parameters. The triangle sides a , b , and c are given in units of the nearest-neighbor distance. Note that a is the side connecting particles interacting through the Lennard-Jones potential in E_{03V} . The upper half of the table lists the triangles which were included in every E_{03V} calculation and the sum of their contributions. The lower half lists the most important of the triangles which were neglected in the E_{03V} lattice sum to show the approximate error in that sum. Results are for bcc ^3He with $R=3.65 \text{ \AA}$ ($A=1.44 \text{ \AA}^{-2}$ and $\log_{10}K=-0.75$).

a^2	b^2	c^2	Number of triangles	Contribution to E_{03V}
1	1	4/3	48	-0.60
1	1	8/3	48	1.69
1	1	4	16	-0.03
1	4/3	11/3	48	-0.49
4/3	1	1	24	-0.27
4/3	1	11/3	48	-0.62
4/3	4/3	8/3	48	-0.004
4/3	4/3	16/3	12	-0.03
8/3	1	1	24	0.46
8/3	1	11/3	96	-0.10
11/3	1	4/3	48	0.16
11/3	1	8/3	96	0.11
total				0.28
1	8/3	11/3	96	0.04
4/3	8/3	4	48	-0.005
8/3	4/3	4/3	24	0.02
8/3	4/3	4	48	-0.06
8/3	8/3	8/3	48	-0.03
8/3	8/3	16/3	48	-0.01
11/3	1	4	48	0.002
11/3	1	16/3	48	-0.03
11/3	4/3	11/3	96	-0.01
11/3	8/3	11/3	144	-0.01
4	1	1	8	0.05
4	1	11/3	48	0.02
4	4/3	8/3	48	-0.01
total				-0.04

TABLE VIII. Listing similar to Table VI of important triangles in the fcc and hcp lattice sums of E_{03V} . We have used the fcc lattice sum, which has many fewer triangles, in place of the hcp sum, in the calculation of Sec. II, because of the approximate equality of the two sums. Results are for close-packed ^4He , $R=3.50 \text{ \AA}$ ($A=2.15 \text{ \AA}^{-2}$ and $\log_{10}K=-0.75$).

a^2	b^2	c^2	(fcc lattice)		(hcp lattice)	
			Number of triangles	Contribution to E_{03V}	Number of triangles	Contribution to E_{03V}
1	1	1	48	-1.68	48	-1.68
1	1	2	48	-0.70	48	0.70
1	1	8/3	0	0	12	0.05
1	1	3	96	-0.30	72	-0.22
1	1	11/3	0	0	24	-0.44
1	1	4	24	-0.60	12	-0.30
1	2	3	48	0.003	36	0.002
1	2	11/3	0	0	24	-0.04
1	2	5	48	-0.14	24	-0.07
1	2	17/3	0	0	12	-0.04
2	1	1	24	0.39	24	0.39
2	1	3	48	-0.08	36	0.01
2	1	11/3	0	0	24	-0.06
2	1	5	48	-0.15	24	-0.08
2	1	17/3	0	0	12	-0.04
3	1	1	48	0.28	36	0.21
3	1	2	48	0.04	36	0.03
3	1	3	96	0.02	72	0.02
3	1	4	0	0	24	-0.004
3	1	4	96	-0.03	48	-0.01
3	1	5	96	-0.06	48	-0.03
3	1	17/3	0	0	24	-0.02
3	1	6	48	-0.04	36	-0.03
3	1	20/3	0	0	24	-0.02
3	1	7	96	-0.07	48	-0.04
Total				-1.71		-1.72

triangles give a positive or negative contribution so that cancellation may take place. In the bcc lattice, triangle No. 1 is almost equilateral with sides in the ratio 1:1:1.15 (it is equilateral in the close-packed case). Because the hard core of the third particle can come in between them, this means that two interacting nearest neighbors are held farther apart on the average than if the third particle were not present. [See Fig. 9(a).] Because the two particles are held farther apart, they see less of each other's repulsive potential and more of the attractive part. Hence the first term of E_{03V} , Eq. (1.12), is more negative than the second and their

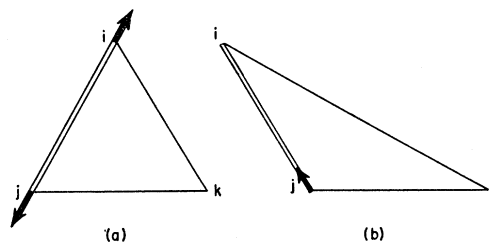


FIG. 9. Two types of triangles in the lattice sum. (a) Particles i and j interact via the Lennard-Jones potential (double line); particle k can interpose its hard core in between i and j in an equilateral triangle and force them farther apart on the average than if k were absent. This makes triangle (a)'s contribution to E_{03V} negative if i and j are nearest neighbors. (b) In an obtuse triangle, particle k tends to push j toward i which makes (b)'s contribution to E_{03V} positive if i and j are nearest neighbors.

difference is negative. Triangle No. 2, on the other hand, is obtuse, with the two particles, i and j , which interact via the Lennard-Jones potential on one leg of the obtuse angle. Thus the hard core of the third particle, k , tends to push j toward i [Fig. 9(b)], so that if i and

j are nearest neighbors, they see more of each other's repulsive potential. The first term of E_{03V} is larger than the second, so the difference is positive. Since obtuse and acute triangles occur in every lattice, there will always be cancellation in the sum.

Power Series of Kinetic Theory. I. Perturbation Expansion*

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In recent years intensive efforts have been made to develop, from first principles, systematic corrections to the established kinetic equations, and thereby obtain an understanding of the approach to thermal equilibrium for arbitrary macroscopic systems. These efforts, dominated by Bogoliubov's synchronization technique and "functional assumption," have met with only partial success. In fact, the method of synchronization has been shown to lead to serious difficulties when carried beyond the lowest order results, so that an H theorem is lacking for the higher order terms. To discuss the problem in full generality, we construct in this paper the direct perturbation series (and in the follow paper, Bogoliubov's synchronized series) to *all* orders in a parameter ϵ that can be identified with the potential strength. An explicit expression is obtained for the ν th-order term of the s -body distribution function and a simple, systematic graphical representation of all the terms is derived. The result is obtained by the use of a matrix formalism that allows an effective decoupling of the Bogoliubov-Born-Green-Kirkwood-Yvon equations, and thereby, for a detailed analysis of the perturbation series. Bogoliubov's basic result concerning the secular behavior of perturbation theory ($F^{(s)} \sim t$) is deduced here as a special case of a general theorem: The ν th-order term for the s -body distribution grows for large times as a polynomial in time whose leading power is $[\nu/2]$ independent of s .

I. INTRODUCTION

THE aim of nonequilibrium statistical mechanics is to determine the evolution in time of systems containing a large number of interacting particles, and thereby describe the irreversible approach to thermal equilibrium. From the basic dynamical equations one seeks an equation of the form

$$\partial f / \partial t = A[f], \quad (1.1)$$

called the kinetic equation, where A is a functional of the one particle distribution function $f(\mathbf{x}, \mathbf{p}, t)$, and has no explicit time dependence. Outstanding examples of such Markovian¹ equations which correspond to different gaseous regimes, are the Boltzmann equation for neutral, dilute gases, the Landau² equation for weakly interacting, high-temperature systems, and the kinetic equation with Debye shielding originally discovered by Bogoliubov,³ and referred to as the Balescu-

Guernsey-Lenard equation. These equations constitute the lowest order term in expansions of Liouville's equation appropriate for the regime considered.⁴ In this work we will be concerned with an expansion of the Liouville equation which we shall analyze to all orders.⁵

(i) The outstanding *open problem* in nonequilibrium theory is that of determining systematically the higher order corrections to these kinetic equations, if they exist. For example, the Boltzmann equation is a valid description of dilute, short-range gases, so that only binary collisions are taken into account. This restriction has the consequence that the transport coefficients are independent of the density. Furthermore, the bulk viscosity coefficient is not given by the Boltzmann equation (it vanishes identically). However, for dense gases, ($p \geq 5$ atm, $T \sim 300^\circ\text{K}$), the transport coefficients of monatomic gases are known to be density-dependent and the bulk viscosity is nonzero. Therefore, a more general theory is required which should yield the well-established kinetic equations in lowest approximation. If such general kinetic equations could be derived from

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¹ I. Oppenheim and K. Shuler, *Phys. Rev.* **138**, B1007 (1965).

² L. Landau, *J. Phys. (USSR)* **10**, 25 (1946). See also J. Enoch, *Phys. Fluids* **3**, 353 (1960).

³ N. Bogoliubov, *Problems of a Dynamical Theory in Statistical*

Physics (Moscow, 1946) [English transl.: E. Gora, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962), Vol. I.]

⁴ G. Sandri, *Ann. Phys. (N. Y.)* **24**, 332 (1963); **24**, 380 (1963).

⁵ P. Goldberg and G. Sandri, *Bull. Am. Phys. Soc.* **11**, 555 (1966).