[19] Chris Gregory, Phys. Rev. 61, 465 (1942).

[20] Actually, the collisional broadening should be even less important in the 6*s* state since there are fewer atoms with which resonant exchange is possible.

[21] H. Corliss and William R. Bozman, Natl. Bur. Std. (U.S.) Monograph No. 53 (1962).

[22] E. M. Anderson and V. A. Zilitis, Opt. i Spektroskopiya 16, 177 (1964) [translation: Opt. Spectry. (USSR) 16, 99 (1964)].

[23] Wolfgang Zernik, Phys. Rev. 135, A51 (1964); Albert Gold and H. Barry Bebb, Phys. Rev. Letters 14, 60 (1965).

[24] H. A. Kramers, Phil. Mag. 46, 836 (1923); R. W. Ditchburn and U. Öpik, in Atomic and Molecular Processes, edited by D. R. Bates, (Academic Press, Inc., New York, 1962), p. 86.

CALCULATIONS OF SOUND VELOCITIES IN CRYSTALLINE HELIUM AT ZERO TEMPERATURE*

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(Received 16 August 1965)

Solid helium is a crystal which cannot be treated by the traditional theory of lattice dynamics,[1] since its zero-point kinetic energy is approximately equal to its potential energy. In fact, de Wette and Nijboer have recently shown[2] that a calculation of the vibrational frequencies of crystalline helium using the harmonic approximation yields imaginary frequencies for each point of the Brillouin zone. In this Letter, we treat this problem by using the time-dependent Hartree approximation,[3,4] together with the results of variational calculations of the ground-state energy using correlated trial wave functions.[5,6] We report calculations of sound velocities for various densities of crystalline helium at zero temperature, and we estimate the Debye θ as a function of density. Satisfactory agreement with existing experimental information is achieved.

The starting point of our approach is the Hartree approximation, which assumes that the ground-state wave function factors into a product of single-particle functions:

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N)=\prod_{i=1}^{N}\varphi_0(\vec{r}_i-\vec{\tau}_i),$$

where $\vec{\tau}_i$ is the *i*th lattice vector. The main success of this approximation[7] is that it has a solution of crystalline character, i.e., $\varphi_0(\vec{r})$ is localized about $r=0$. However, the Hartree approximation fails to take account of short- and long-range correlations. If the interatomic potential is of short range, then short-range two-body correlations are important in lowering the total energy. In addition, long-range correlations are necessary in order to obtain the correct low-lying spectrum of collective excitations, and thus the correct low-temperature specific heat.

The short-range correlations can be approximately treated within the context of a variational calculation.[5,6] The trial wave function is assumed to be of the form

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N)=\prod_i\varphi_0(\vec{r}_i-\vec{\tau}_i)\prod_{j<k}f(|\vec{r}_j-\vec{r}_k|),\quad(1)$$

where $f(r)=\exp[-Kv(r)]$, and K is a variational parameter. For helium, we take $v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$, with $\epsilon=10.22°\mathrm{K}$ and $\sigma=2.556$ Å. The variational calculation can be carried out by truncating the cluster expansion of the ground-state energy; this method yields an upper bound to the ground-state energy that is accurate to a few percent.[8] It turns out that $\varphi_0(\vec{r})$ calculated in this way is well approximated by a Gaussian, $\varphi_0(\vec{r})\cong(A/\pi)^{3/4}\exp(-Ar^2/2)$, so that the ground-state wave function can be characterized by just two parameters, A and K, which vary with density, mass, and crystal structure. Further, the effect of the correlations can be viewed as replacing the interatomic potential $v(r)$ in the Hartree equation by[9] an effective potential $W(r)$,

$$W(r)=[v(r)+(\hbar^2K/M)\nabla^2v(r)]\exp[-2Kv(r)],\quad(2)$$

where M is the atomic mass. Thus the correlation function not only softens the hard core, but also enhances the attractive part of the well.

The collective modes are a natural consequence of the time-dependent Hartree approximation.[3,4] In this approach, the factorization

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N;t)=\prod_i\varphi(\vec{r}_i-\vec{\tau}_i,t)$$

is assumed for all times in the presence of a weak, space- and time-dependent perturbation. The collective-mode frequencies are the poles of the linear response function. These phonons can be pictured in terms of the individual atoms making transitions to excited states in their own Hartree wells, the phonon being a coherent superposition of these excitations which propagates wavelike through the crystal. No reliance need be placed on the atomic displacements being small.

For purposes of computing the phonon spectrum of crystalline helium, it is necessary to take account of both short- and long-range correlations. We use the time-dependent Hartree approximation, together with the replacement of $v(r)$ by $W(r)$. We thus assume that the short-range correlations are not significantly influenced by the weak, time-dependent disturbance.

The calculation of the phonon spectrum, in principle, requires[4] all of the eigenvalues and eigenfunctions of the Hartree potential obtained with $W(r)$. Unfortunately, computation of the excited states has not yet been carried out. Such eigenstates would have to be regarded as less reliable than the ground state, since they are progressively more sensitive to $f(r)$. Furthermore, the energy of the first excited state for helium can be estimated to lie very near to the top of the Hartree well, so that the state might actually be a virtual, resonant scattering level rather than a true bound state. In order to circumvent these gaps in our knowledge, we have resorted to the simplifying assumption that only the first excited state is significant for determining the phonon frequencies. In addition, since φ_0 is so nearly Gaussian, we also assume that the (triply degenerate) first excited states are given by

$$\varphi_\xi(\vec{r}) = \langle \vec{r} \,|\, \xi \rangle \cong (2/A)^{1/2} \partial \varphi_0(\vec{r})/\partial \xi, \tag{3}$$

where $\xi = x, y, z$, and the excitation energy is $\Omega_{10} \cong \hbar^2 A/M$. We have tested the validity of these approximations by using the rigorous sum rule[10]

$$\langle 0 \,|\, \vec{r} \,|\, \xi \rangle \Omega_{10}{}^2$$

$$= -2 \sum\nolimits_\gamma \langle 00 \,|\, \sum\nolimits_{\vec{\tau}}{}' W(\vec{r} - \vec{r}\,' + \vec{\tau}) \,|\, \xi\gamma \rangle \Omega_{\gamma 0} \langle 0 \,|\, \vec{r} \,|\, \gamma \rangle, \tag{4}$$

where γ runs over all excited states. Assuming that only the first excited state contributes to the sum in (4), we obtain

$$\Omega_{10} \cong -2 \langle 00 \,|\, \sum\nolimits_\tau{}' W(\vec{r} - \vec{r}\,' + \vec{\tau}) \,|\, \xi\xi \rangle. \tag{5}$$

We find that with approximation (3), Relation (5) is satisfied numerically to within 3%, thus confirming that the single excited state (3) nearly saturates the sum rule.

With all of these approximations, the formulas of FW simplify substantially. The phonon frequencies $\omega_{\vec{k}\lambda}$ are the roots of[11]

$$\det \left| M \omega_{\vec{k}\lambda}{}^2 \delta_{\xi,\xi'} - \sum_{\vec{\tau}} (1 - e^{-i\vec{k}\cdot\vec{\tau}}) \frac{\partial^2}{\partial \tau_\xi \partial \tau_{\xi'}} \times \langle 00 \,|\, W(\vec{r} - \vec{r}\,' + \vec{\tau}) \,|\, 00 \rangle \right| = 0. \tag{6}$$

This equation for the frequencies is very similar to that of the traditional harmonic approximation, but with two important changes in the dynamical matrix: the replacement of $v(r)$ by $W(r)$, and the averaging of $W(r)$ over the mean positional probability of the two interacting atoms. It is these differences which convert the dynamical matrix from negative to positive definite. It should be pointed out that the use of the Hartree approximation im-

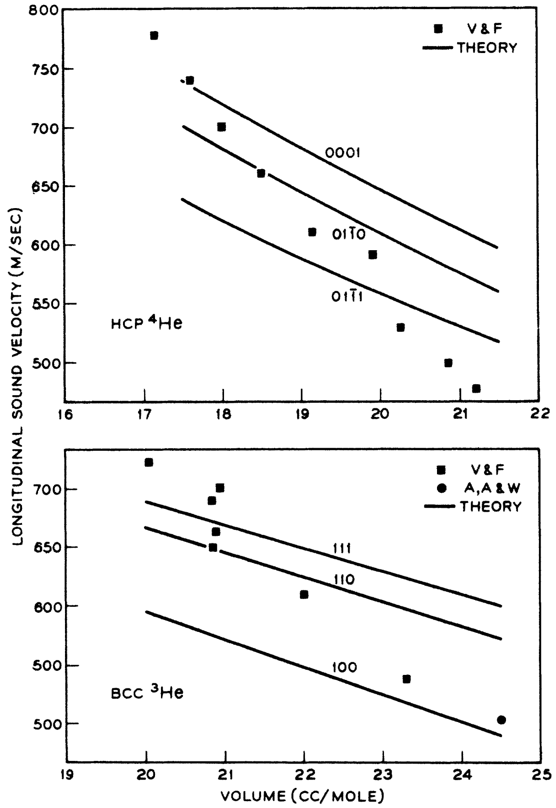

FIG. 1. Longitudinal sound velocities, in meters per second, versus molar volume, for hcp ^{4}He and bcc ^{3}He, in several symmetry directions. Measurements taken from references 12 and 13.

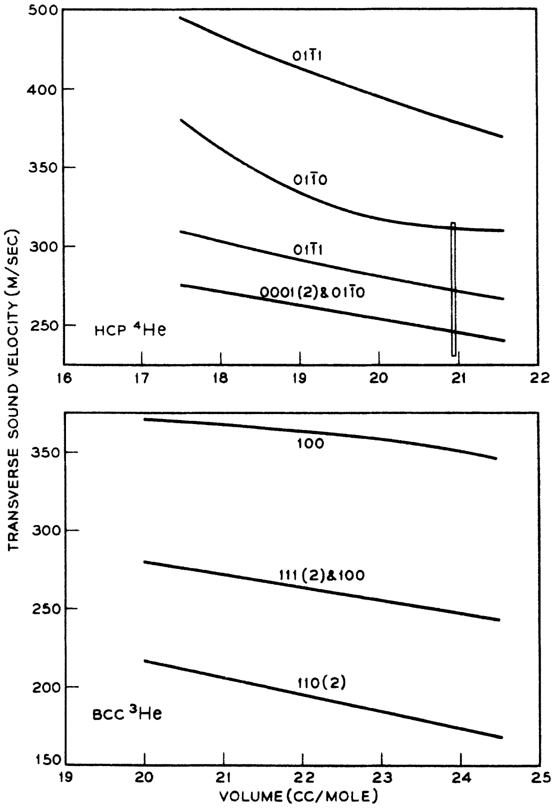

FIG. 2. Transverse sound velocities, in meters per second, versus molar volume, for hcp ^{4}He and bcc ^{3}He, in several symmetry directions. Measurements taken from reference 14.

plies that the phonons are undamped.

We have used (6) to compute the long-wavelength sound velocities $s_\lambda(\hat{k})$ along several symmetry directions for both ^{3}He and ^{4}He, in both the bcc and hcp phases. The results for bcc ^{3}He and hcp ^{4}He are given in Figs. 1 and 2, along with experimental results of Vignos and Fairbank,[12] Abel, Anderson, and Wheatley,[13] and Lipschultz and Lee.[14] The results for bcc ^{4}He are given in Table I. We have not presented the results for hcp ^{3}He, as this phase occurs only at high densities where our approximations break down,[15] due to the inadequacy of the choice of $f(r)$.

In addition, we have used the calculated sound velocities to estimate the zero-temperature limit of the Debye Θ. We have adopted the elementary expression[16]

$$k_B\Theta = \hbar[18\rho\pi^2/\textstyle\sum_\lambda \int d\hat{k}\, s_\lambda^{-3}(\hat{k})]^{1/3}, \tag{7}$$

where ρ is the number density, and have applied

Table I. The results of the calculations of sound velocities, in meters per second, in bcc ^{4}He.

molar volume	longitudinal 111	110	100	transverse 111	110	100
19.88 cc	582	556	471	244(2)	174(2)	343 244
21.63 cc	547	520	425	230(2)	152(2)	335 230
expt.	540-555[a]			337-351[b]		

[a] See reference 12.

[b] See reference 14.

Houston's method[16] to approximate the angular average. The results for bcc ^{3}He and hcp ^{4}He are given in Fig. 3, along with the experimental results of Heltemes and Swenson[17] and Edwards and Pandorf.[18]

In view of the many approximations we have made, the agreement between our calculations and experiment is quite good. The fact that the agreement is better for bcc ^{3}He than for hcp ^{4}He may be due to our use of a spherically symmetric $\varphi_0(r)$, an approximation more appropriate for a cubic than for a hexagonal lattice. In all cases, the calculated quantities

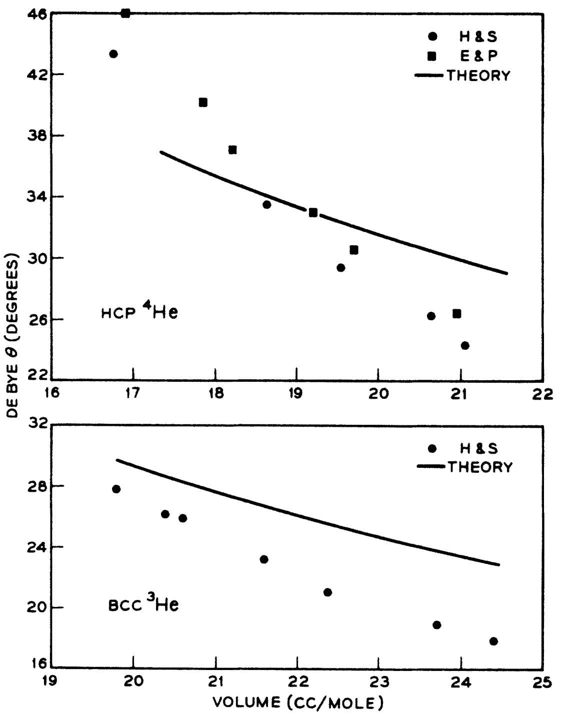

FIG. 3. Debye Θ, in °K, versus molar volume, for hcp ^{4}He and bcc ^{3}He. Measurements taken from references 17 and 18.

do not increase sufficiently rapidly with density; again, the choice of analytic form for $f(r)$ is probably responsible.[15] One other discrepancy between theory and experiment is quite puzzling. We find anisotropies of the order of 100 m/sec for the longitudinal modes and 150 m/sec for the transverse modes, whereas anisotropies of this size have been observed[14] only in the transverse velocity of hcp ^{4}He. Since crystalline helium is thought[19] to solidify into one or several large crystallites, it is not clear why these anisotropies have not been observed, although we note that no measurements have yet been made on an oriented sample.

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*Work supported in part by the Air Force Office of Scientific Research.

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[1] See, e.g., M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Clarendon Press, Oxford, England, 1954).

[2] F. W. de Wette and B. R. A. Nijboer, to be published.

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

[4] D. R. Fredkin and N. R. Werthamer, Phys. Rev. 138, A1527 (1965); we refer to this paper as FW.

[5] L. H. Nosanow, Phys. Rev. Letters 13, 270 (1964).

[6] L. H. Nosanow, Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964 (to be published).

[7] L. H. Nosanow and G. L. Shaw, Phys. Rev. 119, 968 (1962).

[8] The three-body terms in the cluster expansion have recently been calculated by J. H. Hetherington, W. J. Mullin, and L. H. Nosanow. For bcc ^{3}He with a nearest-neighbor distance of 3.65 Å, the first two terms give 10.6 cal, whereas the three-body term gives −0.3 cal.

[9] We neglect a 1% correction to $W(r)$ involving averages of f^2 in the denominator.

[10] See Eqs. (38) and (39) of FW.

[11] In the notation of FW reference 5, Eq. (6) follows directly from the single approximation $\mathrm{Tr}\{AM^{-1}A\} \simeq \mathrm{Tr}\{(AMA)^{-1}\}$.

[12] J. H. Vignos and H. A. Fairbank, Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962, edited by R. O. Davies (Butterworths Scientific Publications, Ltd., London, 1962).

[13] W. R. Abel, A. C. Anderson, and J. C. Wheatley, Phys. Rev. Letters 7, 299 (1961).

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

[15] See the discussion of this point in L. H. Nosanow and W. J. Mullin, Phys. Rev. Letters 14, 133 (1965).

[16] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation (Academic Press, Inc., New York, 1963).

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

[18] D. O. Edwards and R. C. Pandorf, to be published.

[19] W. H. Keeson and K. W. Taconis, Physica 5, 161 (1958); A. F. Schuch, Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 30 August 1957, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958); D. G. Henshaw, Phys. Rev. 109, 328 (1958).

INTERFACIAL DENSITY PROFILE FOR FLUIDS IN THE CRITICAL REGION

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(Received 16 September 1965)

Webb and collaborators[1] recently measured the reflectivity of the interface in a cyclohexane-methanol mixture just below the consolute temperature T_c, with a view toward establishing the temperature dependence of interfacial width. The data were analyzed in terms of a concentration profile of the form imposed by the Maxwell–van der Waals theory,[2]

$$\rho(z) = \tfrac{1}{2}[\rho_1 + \rho_2 - (\rho_1 - \rho_2)\tanh(2z/L)], \tag{1}$$

where z is vertical height, and $\rho(z)$ is the concentration of that species whose lower and upper bulk phase values are ρ_1 and ρ_2, respectively. On this basis the experiments indicated that the characteristic interfacial width parameter L varied as $(T_c - T)^{-\mu}$, with $\mu = 0.76 \pm 0.1$. It is our purpose in this note to sketch results of a general theory of interfacial structure, based in part upon use of capillary waves as