

matical "cause" of the transition. As T falls γ rises, until the enormous number of possible orientations of a very long ring more than compensates for the small contribution of each ($\gamma^l \ll 1$, for l large).

There is no doubt of the geometrical fact of large numbers of orientations for long rings, even if these rings may never use the same atom twice (i.e., cannot cross themselves).¹⁶ Therefore there can be no doubt

¹⁶ For example, the number of ways in which a single polygon which does not cross itself can still be oriented in an infinite medium = constant $\times l^3 s^{-3}$, but the value of l is reduced.

that (1-A), and its more complete expression (17), will show a transition from this cause. But the order of the transition need not be the same as that of the approximate evaluations we have made. They neglect the geometrical correlations. For example, if a large chain of K atoms is already formed, are the remaining $N-K$ atoms more (or perhaps less) likely to be contiguous and therefore more easily able to make other chains, than if these $N-K$ atoms were chosen at random from among the N ? Our assumption in deriving (5-A) was that it was equally likely either way.

Atomic Theory of Liquid Helium Near Absolute Zero

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The properties of liquid helium at very low temperatures (below 0.5°K) are discussed from the atomic point of view. It is argued that the lowest states are compressional waves (phonons). Long-range motions which leave density unaltered (stirrings) are impossible for Bose statistics since they simply permute the atoms. Motions on an atomic scale are possible, but require a minimum energy of excitation. Therefore at low temperature the specific heat varies as T^3 and the flow resistance of the fluid is small. The arguments are entirely qualitative—no calculation of the energy of excitation nor of the low-temperature viscosity is given. In an appendix an expression, previously given, for the partition function is modified to include the effects of phonons.

INTRODUCTION

TISZA¹ has suggested the very fruitful concept that He II might be thought of as a mixture of two fluids, "superfluid" and "normal." At zero temperature the helium is pure superfluid. With rising temperature some sort of "excited molecules" form. These constitute the "normal fluid" which behaves very much like a gas. The proportion of normal fluid increases at first slowly, and then rapidly, with temperature until at the transition temperature of 2.19°K (λ point) the liquid, now He I, contains no more superfluid.

Landau² has made even more detailed suggestions. He suggests that there are two kinds of "excited molecules," phonons or quanta of longitudinal compressional waves (sound) and "rotons." The latter are not well understood. It is suggested that they have a minimum energy Δ needed to excite them. For this reason below 0.5°K there are practically only phonons. The rotons can become excited when more energy is available; i.e., at higher temperature. This idea is in agreement with the fact that below 0.5°K the specific heat varies as T^3 in just the manner (and with the correct coefficient) to be expected if only longitudinal sound waves could be excited.

Tisza's view is frankly phenomenological. No serious attempt is made to justify the description from first principles. Landau has made such an attempt by studying the quantum mechanics of a continuous liquid medium. The role of the statistics is not clear in his arguments, however. Furthermore, the magnitudes of energy and inertia that the "rotons" appear to have correspond to a few atoms. A complete understanding of the "roton" state can therefore only be achieved by way of an atomic viewpoint.

A more complete study of liquid helium from first principles might attempt to answer at least three important questions:

(a) Why does the liquid make a transition between two forms, He I and He II?

(b) Why are there no states of very low energy, other than phonons, which can be excited in helium II (i.e., below 0.5°K)?

(c) What is the nature of the excitations which constitute the "normal fluid component" at higher temperatures, say from 1 to 2.2°K?

The first question was answered in a preceding paper.³ We showed that London's suggestion, that it is the analog of the transition in an ideal Bose gas, is correct.

In this note we hope to make a qualitative argument from first principles to answer the second question.

¹ L. Tisza, *Phys. Rev.* **72**, 838 (1947). An excellent summary of the theories of helium II is to be found in R. B. Dingle, *Supplement to Phil. Mag.* **1**, 112 (1952).

² L. Landau, *J. Phys. U.S.S.R.* **5**, 71 (1941).

³ R. P. Feynman, *Phys. Rev.* **91**, 1291 (1953), hereafter called I.

(We have not yet found the answer to the third.*) It is to be understood, therefore, that we are aiming here to explain the properties of the liquid only at extremely low temperatures.

We take, as a model, helium atoms obeying the Schrödinger equation and the symmetrical Einstein-Bose statistics with forces between pairs similar to that worked out by Slater and Kirkwood,⁴ an attraction at large distances and a strong repulsion at small.⁵ (It is sufficient for qualitative purposes, if one wishes, to imagine impenetrable spheres of radius about 2.7Å packed into a space so the mean spacing (cube root of atomic volume) is about 3.6Å.)

At absolute zero the system is in the ground state. Why this is not a solid has been explained by London.⁶ The large zero-point motions of the atoms are capable of "melting" any ordered crystalline arrangement that may be temporarily set up. We begin by describing the wave function for this ground state.

DESCRIPTION OF THE GROUND-STATE WAVE FUNCTION

Wave functions can be described qualitatively in words by giving the amplitude for every configuration of the atoms. The ground state has a positive amplitude for any configuration since the lowest state has no nodes. The amplitude is negligible if any two atoms are so close together that they overlap—that is, that a large negative potential has set in. Thus for any atom surrounded by neighbors, considered for a moment fixed, the amplitude falls to zero when the atom moves over to touch any of the neighbors and is probably bound in such a way that it is maximum when the atom is near the center of its "cage." (This curvature makes a strong kinetic energy tending to blow apart the cage, an energy effect canceled by the long-range attraction of the atoms.) Compressing the atom into a smaller cage requires more kinetic energy, and expansion works against the attractive potential so there is some mean density of equilibrium. Fluctuations away from that mean density are of amplitude distributed in a Gaussian manner. For wavelengths exceeding the atomic spacing they are analogous to zero-point fluctuations of the vacuum electromagnetic field (but are wholly longitudinal, scalar waves, of course).

There are a large number of configurations with densities near the most likely density, in all of which the atoms tend to keep separate from one another. They differ from one another mainly in the location of the atoms. The various configurations differ only in that one may be "stirred" into another with a little reshuffling or stirring of the atoms. We may take it

that all configurations which have nearly the same type of density fluctuations and which can be essentially just stirred from one to another have the same amplitude in the ground state.

THE CHARACTER OF LOW-ENERGY STATES

We must next determine the character of the low-energy states near the ground state. We aim to show that the only states which differ from the ground state by an infinitesimal energy are the phonons.

First we can take it that the lowest states are those involving large numbers of atoms or large distances. Consider, for example, a tiny region of the liquid, say a cube 3 or 4 atomic spacings on a side. If the atoms in this region are confined in this region (so we have a submicroscopic sample of liquid He) the excitations above the ground state will all involve one node somewhere among the configurations and hence a wavelength of order of a . This must mean an excess kinetic energy of the order \hbar^2/a^2m , or at least of order \hbar^2/Na^2m , where N is the number of atoms and m is the mass of each—leaving an appreciable gap from the ground state.

This argument fails if in the ground state there are two (or more) regions of configuration space in both of which the amplitude is large and which are completely separated by a region of very small amplitude. (Analogous to a particle in a potential with two wells separated by a barrier.) If the nodal surface is passed through the region of small amplitude (the barrier) very little change in energy results. But we have seen that the states of large amplitude are just all those in which the atoms are reasonably well separated. We can assume that we can get from one to any other without crossing any high potential barrier. We suppose all possible rearrangements may be achieved without the atoms coming too close together at any time. That this is reasonable can be seen by comparing the size of the atoms to their spacing. For example, if at some point they are locally roughly on a cubic close-packed lattice, the nearest neighbors are 4.0Å apart (corresponding to the observed atomic volume⁵ of 45Å³). The diameter of the atoms is 2.7Å, the radius at which Slater and Kirkwood's potential passes from minus to plus. The cube edge of the lattice is 5.6Å, so a face-centered atom could even pass between those at the corners of the cube! Clearly, if they are allowed to vary their mutual distances a little, all kinds of rearrangements can be made. It is likely that the condition that there be no effective barrier between configurations is equivalent to the condition that the He II is liquid in the lowest state. We assume it valid for He II.

If we are to find extremely low-energy states we must therefore look to excitations involving large groups of atoms or long wavelengths. One possibility is in the compression waves. Suppose the atoms are compressed to a small excess density over a large volume and a rarefaction left adjacently. The only way this fluctuation could even out is for a considerable number of atoms to move, each a little bit. This involves, effectively, the motion of a large mass and can have low kinetic energy. There is, therefore, little doubt that such compressional waves represent a true mode of excitation in the helium, and a mode of very low energy. If the speed of sound is called c and the wave number of the waves K , the frequency $\omega = cK$ and quantum

* Note added in proof:—This problem has now been solved. Its solution will appear in a forthcoming publication.

⁴ J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

⁵ For a detailed account of the properties of helium see W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942).

⁶ F. London, *Nature* **141**, 643 (1938).

energy $\hbar cK$ can be as small as desired. Thus there is no reason why we should not expect the specific heat, varying as T^3 , from these modes.⁷

We have assumed that the way to release a density fluctuation in a given time which requires the least kinetic energy is to move many atoms a short distance. If only a fraction f of the atoms move, the velocity required is $1/f$ times higher. This means a higher kinetic energy if the kinetic energy varies as the velocity squared.

There are cases, however, in which the kinetic energy does not vary in this way. In a degenerate Fermi gas a single atom excited by a small excess momentum p above the Fermi surface of momentum p_0 has an energy $((p_0+p)^2 - p_0^2)/2m$ or $(p_0/m)p$. This linear dependence of energy on momentum means that the group velocity of such waves is energy independent. It is p_0/m . The speed of sound calculated from the compressibility and density of the ideal gas is $3^{-1/2}p_0/m$. The single atoms will run ahead of the sound. Fluctuations are reduced by a process more like diffusion than sound. The specific heat near $T=0$ varies as T instead of T^3 because the density of states for exciting single atoms exceeds that for sound. As we shall see, for Bose helium there are no states, except phonons, whose energy approaches zero as their momentum approaches zero. The sound has no competitor capable of discharging pressure.⁸

LOW-ENERGY STATES DISREGARDING STATISTICS

The Bose statistics play an essential part in the discussion of other possible states of very low-excitation energy. To make this role clear by contrast, we shall first analyze the situation, disregarding the statistics. More precisely we consider in this section an imaginary quantum liquid made of atoms which are, in principle, distinguishable ("Boltzman" statistics). The ground state for Boltzman statistics is the same as for Bose statistics, since the lowest state is, in either case, symmetrical.

We must try to find modes of excitation involving long wavelengths which do not involve changes in mean density. The density fluctuation modes have already been considered. To simplify the argument consider first the following crude model. We consider a set of cells, each of which contains one atom. Each atom is free to wander in its cell and may occupy therefore some ground-state wave function, say constant amplitude in the cell. We are to consider states which can be made solely by rearranging the atoms among the cells. No two atoms may go into the same cell, for that corresponds to a density fluctuation, and we do not wish to consider those.

⁷ The partition function discussed previously (reference 3) is extended to include a description of the phonons in the Appendix to this paper.

⁸ For an ideal Bose gas, as $T \rightarrow 0$, the sound velocity approaches zero, so that the expected T^3 specific heat does not appear. It is replaced by T^1 . Density fluctuations are much more restricted in liquid helium than they are in the ideal gas. This is the origin of many differences in behavior for the two cases.

In the ground state, the amplitude is the same for any rearrangement of the atoms among the cells. The lowest states can now be analyzed as follows. We neglect the statistics, that is, we assume Boltzmann statistics to apply. We can describe a wave function which corresponds to a very low excitation as follows: Pick out a certain atom, A , say. Put it in a given cell. Then all rearrangements of the other atoms among the other cells can be taken to have the same amplitude. If atom A is in a different cell, the amplitude may be different, but again independent of the arrangement of the other atoms. We thus can specify this wave function by giving just the amplitude for various positions of atom A . The function is independent of the position of the others. We may take this as $\exp(iK \cdot R_A)$, where R_A is the position of the center of the cell in which atom A is. We may, with enough accuracy, let R_A be just the position of atom A . The K can be a long wave fitting into the volume V in which the helium is contained. The energy of this state is $\hbar^2 K^2/2m'$ where m' is the effective mass needed to move atom A . This energy can be very small, for K can be small.

This effective mass is not far from the mass of one helium atom. It is discussed in a previous paper.³ We summarize the argument here. To push a single atom along, we need not go over any potential barriers. The other atoms may move out of the way. No matter where atom A is located the other atoms can arrange themselves into a state of minimum energy and this minimum energy is independent of the location of atom A . However, as A moves, the others must readjust themselves into the state of minimum energy for the new position of A . That is, in addition to the kinetic energy of A there is a kinetic energy of the other atoms which must move away to make room for A .

Thus there would be low-lying states, of energy $\hbar^2 K^2/2m'$. The number of such states would be very large, for the wave function could depend in similar ways on the coordinates of other atoms also. [For example, we could choose two atoms A, B and have the wave function vary with their location as $\exp(iK_1 \cdot R_A) \exp(iK_2 \cdot R_B)$ and be otherwise independent of the distribution of the others in the cells, etc.] The large density of low-lying states would result in a large specific heat near absolute zero.

LOW STATES WITH SYMMETRICAL STATISTICS

However, if the atoms obey Bose statistics none of these states can exist. For in our model, whether atom A is at one location or another is merely an interchange of which atom is which. This cannot change the wave function. In fact, for the model of one atom in a cell no excited state at all can exist for Bose particles without excitation of the atom within the cell.

For the real liquid a similar situation holds—aside from the phonons, there can be no low-lying state. The wave function must have the property that any change, that just means an interchange among the atoms, must not alter the wave function. The excited state must be orthogonal to the ground state, of course. Starting at any configuration and supposing the amplitude is

the same as for the ground state, we must find a new configuration that represents a kind of stirring of the old configuration (to omit phonon states) such that the amplitude is now reversed in sign. It is clear that *every* configuration is close to the original one, albeit with some atoms interchanged. So it is hard to find a configuration to give the minus amplitude which is sufficiently far (in configuration space) from the original positive amplitude configuration to have a slow rate of decay and thus a low energy.

There are some possibilities of this kind which might at first sight seem allowable. Consider among the atoms a set of adjacent ones forming a large ring. Suppose l atoms are in the ring and let us imagine the wave function is such that, if all move together half an atomic spacing a , the phase changes by π , so when they turn about another $a/2$ the phase changes by 2π , as required by the Bose statistics. (For a shift of a just changes each atom for the one behind.) The mass moving is $m'l$, and the momentum is \hbar/a (for the wavelength is a) so that the energy is $\frac{1}{2}(m'l)^{-1}(\hbar/a)^2$. This may be made low by choosing l very large. (If it were not for the Bose statistics we could have taken the wavelength to be la and the energy would be even lower, varying as $1/l^3$.)

The argument for calculating this energy is incorrect, however. By assuming that all the atoms must move together, degrees of freedom (in which parts of the ring turn by themselves) have been restricted. This tacitly adds a considerable energy by the uncertainty principle.

To understand better the failure of the argument, consider by the same reasoning the case that one had two equal rings parallel to each other. We may argue as before that now the entire mass $2m'l$ moves together with momentum \hbar/a and thus expect an energy $\frac{1}{2}(2m'l)^{-1}(\hbar/a)^2$ for the energy of the lowest state. But this is certainly wrong, for if we consider the rings as independent, the lowest state but one is surely that one for which one of the rings is excited and the other not (momentum 0), an energy $\frac{1}{2}(m'l)^{-1}(\hbar/a)^2$, larger than our previous lowest estimate! The error for the first figure of $\frac{1}{2}(2m'l)^{-1}(\hbar/a)^2$ consisted in this. In describing the wave function, the possibility that the two rings could turn independently was omitted. To force the rings to move together would be to force the difference between their displacements to be fixed at zero. Thus the momentum conjugate to this difference coordinate would be very high, and the energy associated with this coordinate very large. Thus the system does not have just the energy estimated but, in fact, a very much higher one. We have not completely specified the wave function. We have not said what the amplitude is to be for configurations in which only one of the rings moves.

In an analogous way, the estimate of energy for the single ring, $\frac{1}{2}(m'l)^{-1}(\hbar/a)^2$, is incorrect. We have specified the amplitude for the case that *all* of the atoms are simultaneously in the mid positions. What is to be the amplitude if only a few move to mid positions? (This may be accomplished without doing violence to the potentials by using the atoms adjacent to the ring and by turning on smaller rings of 4 or 5 atoms.) If the motion (all to $\frac{1}{2}$ position) can be made up of smaller parts moving in concert, and if these smaller parts could also have moved independently, the energy cannot be lower than that corresponding to just one of independent parts being excited.

Since we may well imagine that any motion of the atoms could be made up of combinations of motions of small groups (say 3 or 4 revolving about each other) the lowest energy is the excitation of one of these small groups. These we can identify with Tisza's excited molecules or Landau's rotons (but see next paragraph). Any such small ring of r atoms must, of course, have

its first state of excitation of angular momentum $r\hbar$ (or $p=\hbar/a$) because of the statistics. Landau's arguments² that such angular momentum must have an excitation energy was made in a way that does not involve the statistics of the atoms. It is possibly equivalent to our argument that large rings need not be considered if their motion is analyzable in smaller parts. The central importance of the statistics would not seem to be here, but rather in the previous argument which shows that no states corresponding to the slow linear motion of a single atom are permitted.

It is not obvious whether the lowest excited state, excluding the phonons, is actually a small ring of atoms turning. The arguments do not exclude the possibility that these are all higher than another type of mode; namely, the rapid motion of a single atom. In our cell model a state which depends on atom A as $\exp iK \cdot R_A$ with $Ka=2\pi$ is, of course, possible. Another possibility is the analog of the excitation of a single atom in a cell. (This may be the same as the single atom motion.) All of these states differ from the ground state by a finite energy. But which is lowest is hard to determine.

Any such excitation can, of course, move through the fluid. (In fact, the lowest state is that in which it has equal amplitude of being anywhere in the fluid.) That is, the wave function could vary as $\exp(iK \cdot R)$, where R is the location of the center of excitation. Then the energy of these excitations might have the form, suggested by Landau,² $\Delta + K^2/2\mu$, where Δ is the energy needed to excite the ring or other excitation, and μ is a sort of effective mass.

Our primary purpose was to show that no states close to the ground state exist, exclusive of the phonons. We are not yet able to calculate the energy, nor to give a clear picture of the other modes of excitation.

DESCRIPTION OF SOME PROPERTIES OF THE LIQUID

In concluding that only phonons exist at low temperature, we concur with the opinion of the phenomenological theories. Therefore, a description of how some of the properties of helium arise, according to this model, will repeat much that has already been pointed out by others.^{1,2} We limit ourselves, therefore, to a very brief summary from a kinetic theory point of view.

First, consider the motion of an object, such as a small sphere through the liquid. If the object is stationary at a fixed position R , the liquid may get into a certain state which, omitting phonons for a moment, is like the ground state (except that now part of the space occupied by the object is not available to the helium). Let the wave function of the helium be ψ_R . It is a function of all the helium atoms and depends, say parametrically, on R . If R is changed, ψ is also, but the energy of the fluid is not changed. For, rearranging the fluid to a new shape at the same density does not alter the energy. Now if we alter the R from R_1 to R_2 nearby, we will only need to add a little kinetic energy to push the helium atoms out of the

way. The overlap of ψ_{R_1} and ψ_{R_2} will be nearly perfect (except near the surface of the object which is a different volume of space in the two cases, $R=R_1$ and $R=R_2$). The object can move therefore with an energy equal to just the kinetic energy of itself and the liquid which flows around it. The fluid will move so that the curl of the velocity is zero, because circulation corresponds to permutation of atoms, and the Bose statistics will not permit such motions, as we have seen.⁹

What will be the losses of energy suffered by such an object? If it loses energy it can do so only by exciting the helium. First, can it excite the molecular excitations? These take a certain energy Δ to excite, but a massive object even moving very slowly may have sufficient energy. On the other hand, for such an object to change energy by Δ its momentum must change by an enormous amount. To create an excitation of very high momentum may take much more energy than Δ . As Landau has shown,² if the energy to excite a roton of momentum p is taken to be of the form $\Delta + p^2/2\mu$, the laws of conservation of energy and momentum show that slowly moving objects [velocity less than $(2\mu\Delta)^{1/2}$] can produce no excitations. Likewise, objects moving at velocities below that of sound cannot lose energy by creating phonons. Therefore, at absolute zero and for not too high velocity, a moving object will suffer no viscous drag.

At low temperatures, there are, however, some phonons already existing in the liquid. They can scatter off of the object (changing their energy by the Doppler effect) and in this way the object can lose a little energy. A phonon of energy $\hbar\omega$ carries momentum $\hbar\omega/c$ and behaves very much like a particle of mass $\hbar\omega/c^2$ moving at velocity c . The phonons act in most respects like a gas of such particles, and the resistance suffered by our object is just like the viscosity that would be suffered by an object moving through such a gas.

The actual calculation of this energy loss means a calculation of the viscous drag of such a gas. This requires a knowledge of the mean free path for collision among the phonons. The phonons scatter from one another because the medium is not linear. The speed of sound depends a little on the density. Therefore speaking classically, if a wave is present, another wave impinging finds the index of refraction varying sinus-

oidally and is thereby scattered. The same thing happens in the quantum mechanical system.

The mean free path should rise rapidly as the temperature falls, because the density of phonons decreases (the scattering cross section also decreases). Interesting phenomena should result when this free path becomes comparable to the dimensions of the apparatus.

If the viscosity is measured by connecting two vessels with a capillary, a different situation arises. The phonons cannot readily work their way through the long capillary, but the bulk liquid can move through it. There is work done on the phonons as the piston moves down in one of the vessels, again by the Doppler effect on the phonons bouncing off of the moving piston. But this work just goes into increasing the phonon energy—that is, the liquid in one vessel is heated, in the other cooled. If isothermal conditions are maintained it goes as heat to the walls of the first container and from the walls of the second. No net work is done in this case and the viscosity appears to vanish. There is essentially no energy loss because there is no real viscous flow of our phonon “gas” through the capillary. The reason that, experimentally, resistance appears⁵ if the flow velocity exceeds a certain critical velocity is not clear. Perhaps in passing sharp protuberances in the capillary wall the velocity locally exceeds that needed to create excitations or new phonons. It cannot very well be a kind of turbulence because presumably the velocity field should be always free of circulation.

In two volumes of liquid helium connected by a capillary, the hotter one will exert the higher pressure (fountain effect). The larger number and higher average momentum of phonons in the hotter region results, from wall bombardment, in a higher pressure there. The pressure can only be released slowly by phonons passing through the long capillary. This would be the mechanism of heat conductivity through capillaries. The rate of such conduction would depend on the relative size of the capillaries and the phonon mean free path.

If temperature varies from one point to another in the bulk liquid, then the phonon density varies. What happens depends on the mean free path. If it is long compared to the distances over which the variations occur, the variations are almost immediately evened out by the diffusion of phonons rushing from one place to another (at the speed c). If the mean free path is shorter than the distances involved in the variation, no single phonon can go directly from a high- to low-density region. Instead, a cooperative movement sets in. If we consider the analogy to a gas of phonon “particles,” a pressure variation is released by body motion—that is, by sound waves. The speed of this sound is $3^{-1/2}$ times the individual particle velocities. In our case, this “second sound” representing waves of phonon density (i.e., temperature) should travel at a velocity $3^{-1/2}c$. At low temperatures it will be experimentally hard to keep the mean free path very small compared to the wave-

⁹ For a liquid contained in a simply connected region, the circulation vanishes everywhere if it vanishes locally. But in a region of connectivity like the inside of a torus, although the curl is everywhere zero, the circulation around the ring may not be zero. Such a circulation cannot be compounded of smaller independent units. Therefore, it should be possible to demonstrate circulatory motions in such a vessel which will maintain themselves for a long time. Circulation may be created by rotating the vessel containing He I and cooling to the temperature desired below the λ point. Stopping the rotating vessel should leave the interior liquid with a nearly permanent angular momentum, which could be demonstrated, for example, by its gyroscopic effects. The liquid must be completely confined with no free surface because the exchange of atoms between the rotating liquid and the stationary gas above it might cause a rapid damping of the angular momentum.

length, so that second sound would show appreciable damping and dispersion. At extremely low temperatures the free path may be larger than the apparatus. Then, if a pulse of heat at one point creates extra phonons, these will rush away at speed c so that temperature rise will begin at a distant point delayed only by the time required for *first* sound to traverse the apparatus.¹⁰

EFFECTS OF He³ ATOMS AT LOW CONCENTRATIONS

If a foreign atom, say an atom of He³, is in the liquid, our arguments indicate that it will move about essentially as a free particle, albeit with an effective mass m'' larger than its true mass. (This m'' should be about one atomic mass unit less than the effective mass m' of a He⁴ atom.) Such He³ atoms put into He⁴ at low concentration should behave as a perfect gas. Consider, as an example, a concentration of 0.1 percent. The mean spacing of the atoms is so large that the gas is not degenerate, except at a few hundredths of a degree. (The statistics can only be of importance if the atoms can permute. This occurs only if $\exp(-m''D^2kT/2\hbar^2)$ is not too small. Here, D is the mean spacing of the atoms, which is 36Å in our example.) The specific heat contributed by the He³ is then k per atom. This can exceed the specific heat of the phonons (below 0.4° in our example). A temperature pulse would then go mainly into increasing the energy of the He³ gas. The speed of sound in this gas is of the order of the He³ atom velocity, and therefore the observed second sound velocity should vary as $(kT/m'')^{1/2}$ in this region.¹⁰ A more detailed analysis of the intermediate region in which both He³ and phonons contribute requires a study of the collision cross sections for phonon-phonon, phonon-He³, and He³-He³ collisions. Higher concentrations of He³ require a study of the degenerate Fermi gas. The entire analysis of this paper fails to apply to pure He³, because the ground state from which we begin is different.

An atom of He³ should show an appreciably higher free energy when dissolved in He⁴, than if that atom is replaced by He⁴. This is because, as discussed in a previous paper,³ for pure He⁴ the partition function is the sum on all trajectories which start at some configuration of the atoms \mathbf{z}_i and return to *any* permutation of the original configuration $P\mathbf{z}_i$. With a He³ atom at \mathbf{z}_1 say (and no others nearby), the final configuration is limited to only those permutations for which this atom returns to \mathbf{z}_1 . We can estimate the effect as follows: Neglect the mass difference of He³ and He⁴. Consider the nondiagonal matrix element $\langle \mathbf{z}' | e^{-\beta H} | \mathbf{z} \rangle$ in which the final state differs from the initial state only in that the atom \mathbf{z}_1 is moved to another site \mathbf{z}'_1 . All the other atoms may go to some permutation of the original positions. From what we have said in I, this should depend upon \mathbf{z}_1 and \mathbf{z}'_1 approximately

through a factor $(\beta=1/kT)$,

$$(m'/2\pi\beta\hbar^2)^{3/2} \exp[-m'(\mathbf{z}_1-\mathbf{z}'_1)^2/2\beta\hbar^2], \quad (1)$$

since the atom acts essentially as a free particle of mass m' . To get the partition function if the atom 1 is He⁴, we must sum this over all possible sites \mathbf{z}'_1 . At low temperatures, where the diffusion distance $(2\beta\hbar^2/m')^{1/2}$ exceeds the atomic spacing $d=(V_A)^{1/3}$, this is approximately the integral of (1) over all \mathbf{z}'_1 divided by V_A , the atomic volume. This gives V_A^{-1} for He⁴. For He³, \mathbf{z}'_1 must coincide with \mathbf{z}_1 so (1) gives $(m'/2\pi\beta\hbar^2)^{3/2}$. The ratio of the partition function for He⁴ to that in which a He⁴ atom is replaced by He³ is therefore $(m'kT/2\pi\hbar^2)^{-3/2}V_A^{-1}$ (at low concentration). The extra free energy per atom of He³ is therefore $(3/2)kT \ln(2\pi\hbar^2/m'kTV_A^{3/2})$ at low temperatures. (Since He³ is lighter than He⁴, m' is replaced by m'' .)¹¹

DISCUSSION

A number of problems are suggested by this work.

First, a detailed quantitative analysis of all of the properties of liquid He⁴ below 0.5°K should be undertaken with the confidence that the problem is relatively simple. Only the phonons should be involved. Their wavelengths are long compared to atomic dimensions, and we have to do essentially with a continuous medium. The statistical mechanical aspects are considered in the appendix. The mean free path for phonon collisions could be computed if the nonlinearity of the medium is included. Work in this direction has been done by Landau and Khalatnikov.¹² An extension could be made to include the effects of small concentrations of He³.

A more difficult class of problem, and one which we have left completely untouched, is the answer to question (c) of the introduction. Namely, what is the detailed nature of the excitations involved at the higher temperatures of 1 to 2.2°K? Most of the experimental work has been done in this region. The atomic viewpoint cannot claim a real understanding of the situation in liquid He II until this problem is solved. (See note added in proof.)*

There is a third group of problems which has not been touched upon. They involve the question,

(d) What is the mechanism of the Rollin film?⁵

This seems to be a problem of the very low-temperature behavior and should properly have been discussed in this paper. A suggestion of Bijl, de Boer, and Michels¹³ involves the idea that the energy of a layer of the

¹¹ To the effect considered in the text, there must be added the large free-energy difference at absolute zero, which arises from the difference in zero-point energy occasioned by the difference in atomic mass. In first approximation, the wave function is unaltered but the kinetic energy, $-(\hbar^2/2m)\nabla^2$, is higher, for m is 3 instead of 4. This difference is, therefore, close to $\frac{1}{4}$ of the mean kinetic energy, per He⁴ atom, in the ground state.

¹² L. D. Landau and I. M. Khalatnikov, J. Exptl. Theoret. Physik (U.S.S.R.) **19**, 637, 709 (1949).

¹³ Bijl, de Boer, and Michels, Physica **8**, 655 (1941).

¹⁰ I am indebted to F. G. Brickwedde for calling my attention to this phenomenon.

liquid depends strongly on the thickness of the layer, decreasing for thicker layers, even up to 100 atoms thick. If this view is correct, we should look for the answer by studying the energy of the ground state, to see if it is dependent on the shape of the container. It is possible that such a dependence exists, even for thick layers, because of the very long permutation rings involved at low temperatures in the condensed phase. These rings are long enough to wander over the entire volume of the liquid, so that the energy may be sensitive to the shape. We have not yet been able to verify quantitatively the correctness of this idea.

Finally, the problem of critical flow velocities, and the resistance to high-speed motions, remains unsolved.

The analysis of pure liquid He³ requires a new start because our physical arguments so far have depended so strongly on the Bose statistics.

The author has profited from conversations with E. Wigner, H. A. Bethe, and R. F. Christy.

APPENDIX

In a previous paper,³ I, an approximate partition function was proposed for liquid helium. Without modification it will not describe the phonon states correctly. The necessary modifications are discussed here.

In I, it was noted that the partition function of helium is the integral over all configurations \mathbf{z}_i of the quantity

$$W(\mathbf{z}^N) = N!^{-1} \sum_P \int_{\text{tr}_P} \exp \left\{ - \int_0^\beta \left[\frac{m}{2\hbar^2} \sum_i \left(\frac{d\mathbf{x}_i}{du} \right)^2 + \sum_{ij} V(\mathbf{x}_i - \mathbf{x}_j) \right] du \right\} \mathcal{D}^N \mathbf{x}_i(u), \quad (2)$$

using the notation of that paper [I, Eq. (5)]. The integral \int_{tr_P} is taken over all trajectories $\mathbf{x}_i(u)$ of the atoms which start from the positions $\mathbf{x}_i(0) = \mathbf{z}_i$ and end up at some permutation $\mathbf{x}_i(\beta) = P\mathbf{z}_i$ of \mathbf{z}_i . The sum is taken on all permutations P . It was pointed out that if a configuration \mathbf{z}_i contained atoms nearly overlapping, or in some other unfavorable arrangement, the important trajectories $\mathbf{x}_i(u)$ would almost immediately move to release the energy of the unfavorable arrangement (for example, overlapping atoms would spring apart). The time for this was generally much less than β . Thus the various configurations could be given a weight $\rho(\mathbf{z}_1, \mathbf{z}_2 \cdots \mathbf{z}_N) = \rho(\mathbf{z}^N)$. The slower motions of atomic diffusion contributed an additional exponential factor, so an approximate expression [I Eq. (7)],

$$W(\mathbf{z}^N) = N!^{-1} K_\beta \left(\frac{m'}{2\pi\beta\hbar^2} \right)^{3N/2} \times \sum_P \exp \left[- \frac{m'}{2\beta\hbar^2} \sum_i (\mathbf{z}_i - P\mathbf{z}_i)^2 \right] \rho(\mathbf{z}^N), \quad (3)$$

was proposed. The factor ρ was to be (for low temperatures, large β) nearly independent of β , as it represents the effect of rapid local motions. It is $\phi(\mathbf{z}^N)^2$, where ϕ is the ground-state wave function.

On the other hand, it was remarked (footnote 11 of I) that general variations in density over large distances would not be so rapidly released. We now consider in detail the effect of these compressional waves.

To a sound wave of wave number K , and frequency $\omega = cK$, where c is the speed of sound, correspond phonons of energy $\hbar\omega$. A density fluctuation of this wavelength $\lambda = 2\pi K^{-1}$ would take a time τ of order $1/\hbar\omega$ to decay (calling u "time" as in I). This time will exceed β , for wavelengths $\lambda > 2\pi\hbar c/kT = 2\pi \cdot 17\text{\AA}/T^\circ K$. Since this distance exceeds the atomic spacing 3.6\AA and the diffusion distance $(2\beta\hbar^2/m)^{1/2} = 4.8\text{\AA}/(T^\circ K)^{1/2}$, there is clear separation of these waves from local atomic motions. Therefore, an expression like (3) is correct locally, for a density fluctuation over a small region is rapidly released so that its effect can be contained in ρ (by having ρ smaller for such fluctuations). But a fluctuation over long distances will not even out in a time β and is not correctly described in (3).

Choose a length $1/K_0$ exceeding the atomic spacing, but below the wavelength of sound excited at the given temperature ($\hbar c K_0 \beta \gg 1$). For distances inside $1/K_0$ no new considerations are necessary, and (3) is locally correct. For long distances it must be altered. Let $n(\mathbf{R})$ be the average number density at \mathbf{R} in the configuration \mathbf{z}_i —the average being taken over a region of volume $1/K_0^3$. We shall determine how the probability of this configuration depends on $n(\mathbf{R})$ [the result is (9) below].

We may describe the motions $\mathbf{x}_i(u)$ as local atomic movements (within distances K_0^{-1}) and general drift motions of the center of gravity of the atoms in a volume K_0^{-3} . It is convenient to describe the initial density distribution by imagining that it arose from an initially uniform distribution of density n_0 by a displacement. If the atoms originally at \mathbf{R} were displaced by $\mathbf{D}_0(\mathbf{R})$, the density is $n(\mathbf{R}) = n_0(1 + \nabla \cdot \mathbf{D}_0)$, where $n_0 = V_A^{-1}$ is the density averaged over the entire fluid. As the trajectories in (2) move, there is a general drift which we will describe by giving the displacement $\mathbf{D}(\mathbf{R}, u)$ as a function of u . What is the energy associated with this drift? First, to the kinetic energy of the atoms due to local motion there is an extra contribution from the general drift $(m/2V_A)(\partial\mathbf{D}/\partial u)^2$ per unit volume. Further, suppose a region temporarily has an extra high local density. This will limit the path-space volume available (and also change the average mutual potential energies). Therefore there will be an extra factor accumulated in each little interval of time. This we can write as a factor $e^{-E\,dudV}$ for the volume dV in time du . This E (the energy resulting from the compression) depends just on the density, hence on $\nabla \cdot \mathbf{D}$. We expand it in powers of $\nabla \cdot \mathbf{D}$. The constant term may be omitted by changing the zero from which we

measure energy. The linear term gives nothing for its integral over all the liquid vanishes $\int \nabla \cdot \mathbf{D} dV = 0$ from the conservation of mass. The quadratic term is written conveniently as $(1/2)mc^2V_A^{-1}(\nabla \cdot \mathbf{D})^2$, for c defined this way becomes the speed of sound. Higher-order terms produce phonon-phonon scattering, but we neglect them here. Thus, in addition to the features which go to make up (3) locally, there is a factor controlling the large scale motions,

$$\exp \left[-\frac{m}{2V_A \hbar^2} \int_0^\beta \int \left(\left(\frac{\partial \mathbf{D}}{\partial u} \right)^2 + \hbar^2 c^2 (\nabla \cdot \mathbf{D})^2 \right) dV du \right] \mathfrak{D} \mathbf{D}(\mathbf{R}, u), \quad (4)$$

where the \mathbf{D} are to be summed over all displacement fields such that¹⁴ $\mathbf{D}(\mathbf{R}, 0) = \mathbf{D}_0 = \mathbf{D}(\mathbf{R}, \beta)$, with

$$\nabla \cdot \mathbf{D}_0 = V \Delta n(\mathbf{R}) - 1.$$

This is best analyzed in momentum space. We put

$$\mathbf{D}(\mathbf{R}, u) = \int \mathbf{A}(\mathbf{K}, u) \exp(i\mathbf{K} \cdot \mathbf{R}) d^3 \mathbf{K} (2\pi)^{-3}.$$

The \mathbf{A} field can be separated into transverse components \mathbf{A}_1 and \mathbf{A}_2 and a longitudinal component $B = \mathbf{A} \cdot \mathbf{K} / K$. Thus

$$\nabla \cdot \mathbf{D} = \int KB(\mathbf{K}, u) e^{i\mathbf{K} \cdot \mathbf{R}} d^3 \mathbf{K} (2\pi)^{-3}, \quad (5)$$

and (4) becomes

$$\exp \left[-\frac{m}{2V_A \hbar^2} \int_0^\beta \int \left[\left(\frac{\partial B}{\partial u} \right)^2 + \hbar^2 c^2 \mathbf{K}^2 B^2 + \left(\frac{\partial \mathbf{A}_1}{\partial u} \right)^2 + \left(\frac{\partial \mathbf{A}_2}{\partial u} \right)^2 \right] d^3 \mathbf{K} (2\pi)^{-3} du \right] \mathfrak{D} \mathbf{A}_1(\mathbf{K}, u) \mathfrak{D} \mathbf{A}_2 \mathfrak{D} B. \quad (6)$$

The transverse displacements act as free particle motions, for there is no restoring force. They contribute a factor $(m/2\pi\beta\hbar)^3$ per mode. This is already contained in (3) (but with m' for m , which makes little difference for the small fraction $V_A K_0^3$ of modes involved). We need not count them again in (6).

For each longitudinal mode, we must integrate an expression of the form

$$\exp \left\{ -\frac{m\delta}{2V_A \hbar^2} \int_0^\beta \left[\left(\frac{dB}{du} \right)^2 + \hbar^2 c^2 K^2 B^2 \right] du \right\} \mathfrak{D} B(u),$$

where δ is the K -space volume per mode for all $B(u)$ which begin and end at B_0 . This may be easily done by a method explained in another connection by the

¹⁴ In principle the final displacements could differ from the initial by an atomic spacing d (because atoms may be permuted). But the actual displacements permitted by (4) are very much smaller than d , so that the only important term from (4) is that for which the configuration is restored atom by atom.

author.¹⁵ There results ($\omega = cK$),

$$\left(\frac{m\delta\omega}{2\pi V_A \hbar \sinh(\omega\beta\hbar)} \right)^{\frac{1}{2}} \exp \left[-\frac{m\delta\omega}{V_A \hbar} B_0^2 \tanh \left(\frac{\omega\beta\hbar}{2} \right) \right]. \quad (7)$$

The complete partition function is the integral (2) over all initial configurations. We therefore integrate (7) over B_0 to get the contribution from this mode. The integral yields

$$\begin{aligned} [2 \sinh(\omega\beta\hbar) \tanh(\frac{1}{2}\omega\beta\hbar)]^{-\frac{1}{2}} &= [2 \sinh(\frac{1}{2}\omega\beta\hbar)]^{-1} \\ &= \exp(-\frac{1}{2}\omega\beta\hbar) [1 - \exp(-\omega\beta\hbar)]^{-1}, \end{aligned}$$

the usual partition function from such a mode. All the modes together contribute

$$\exp \left\{ - \int \ln [2 \sinh(\frac{1}{2}\omega\beta\hbar)] d^3 \mathbf{K} (2\pi)^{-3} V \right\}, \quad (8)$$

the integral extending over all modes of wave number less than K_0 . This factor in the partition function gives the usual Debye specific heat, varying as T^3 as long as our temperatures are, as we have assumed, small enough that $K_0 c \hbar \beta \gg 1$.

Multiplication of the factors (7) for all modes tells us that density fluctuations have a probability proportional to

$$\exp \left\{ -\frac{mc^2}{V_A \hbar} \int [KB_0(\mathbf{K})]^2 \tanh \left(\frac{\omega\beta\hbar}{2} \right) \frac{d^3 \mathbf{K}}{(2\pi)^3 \omega} \right\}, \quad (9)$$

where KB_0 is the Fourier transform of the density fluctuation [from (5)],

$$KB_0(\mathbf{K}) = V_A \int (n(\mathbf{R}) - n_0) e^{i\mathbf{K} \cdot \mathbf{R}} d^3 \mathbf{R}. \quad (10)$$

Since, for large $\omega\beta\hbar$, $\tanh(\frac{1}{2}\omega\beta\hbar)$ is nearly 1, the density fluctuations of short wavelength are independent of the temperature. For these the factor (9) could just as well be combined with the temperature independent factor ρ to make a new effective ρ . This shows that the results do not depend on the exact choice of K_0 . For long waves $\tanh(\frac{1}{2}\omega\beta\hbar)$ falls below 1 and wider fluctuations are permitted than would be expected from (3). A more accurate representation of (2) is then (3) with ρ containing general variations in density, these variations being weighed by multiplying by the factor (9), normalized. A factor $(m'/2\pi\beta\hbar^2)^{N/2} \omega$ should be replaced by (8).

The purpose of this appendix is just to note that (3) does not automatically contain the phonon effects, but must be modified to include them. The study of such questions as the nature of higher-energy excitations and the character of the transition can presumably be made using (3) without modification. It is convenient that the sound wavelengths are so long that a nearly complete separation can be made of the local behavior and the behavior of the overlying compressional waves.

¹⁵ R. P. Feynman, Phys. Rev. **84**, 108 (1951) Appendix C. The explicit answer is given in R. P. Feynman, Revs. Modern Phys. **20**, 367 (1948) on page 386, by substituting $\gamma=0$, $q_i=q_0 = B_0$, $\hbar = -iV_A \hbar^2 / m\delta$, $\omega = i\omega\hbar$, $T = \beta$.