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## Atomic Theory of the $\lambda$ Transition in Helium

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It is shown from first principles that, in spite of the large interatomic forces, liquid  $\text{He}^4$  should exhibit a transition analogous to the transition in an ideal Bose-Einstein gas. The exact partition function is written as an integral over trajectories, using the space-time approach to quantum mechanics. It is next argued that the motion of one atom through the others is not opposed by a potential barrier because the others may move out of the way. This just increases the effective inertia of the moving atom. This permits a simpler form to be written for the partition function. A rough analysis of this form shows the existence of a transition, but of the third order. It is possible that a more complete analysis would show that the transition implied by the simplified partition function is actually like the experimental one.

### INTRODUCTION

THE behavior of liquid helium, especially below the  $\lambda$  transition, is very curious.<sup>1</sup> The most successful theoretical interpretations,<sup>2</sup> so far, have been largely phenomenological. In this paper and one or two to follow, the problem will be studied entirely from first principles. We study the quantum-mechanical behavior of strongly interacting atoms of  $\text{He}^4$ . We shall try to show that the main features of these curious phenomena can, in fact, be understood from this point of view. Because of the enormous geometrical complexity involved, we shall not attempt to obtain useful quantitative results. The quantum mechanics will not supplant the phenomenological theories. It turns out to support them.

In this paper we begin the study of the statistical mechanics of the liquid.<sup>3</sup>

London<sup>4</sup> has proposed that the transition between liquid He I and liquid He II is a result of the same process which causes the condensation of an ideal Bose-Einstein gas. This idea could be criticized on the grounds that the strong forces of interaction between the He atoms might make the ideal gas approximation (in which these forces are neglected) even qualitatively

incorrect. We shall argue that London's view is essentially correct. The inclusion of large interatomic forces will not alter the central features of Bose condensation.

The principal point is an argument which shows that in a liquid-like quantum-mechanical system the strong interactions between particles do not prevent these particles from behaving very much as though they move freely among each other.

The exact partition function is first written down as an integral over trajectories, by using the space-time approach to quantum mechanics.<sup>5</sup> The observation that the atoms move very freely among each other is then made. This permits one to write a simpler form [Eq. (7)] for the partition function. This form should be fairly accurate, at least qualitatively. It becomes clear that a transition is to be expected, and that it involves the symmetrical statistics in an essential way.

On the other hand, the geometrical complexity of the problem still prevents us, so far, from giving a very good estimate of the free energy behavior near the transition point and below. A relatively crude approach gives a transition like that of the ideal gas. That is, the specific heat is continuous, contrary to the experimental observation that it appears to be discontinuous. Some of the geometrical problems which might have to be solved to obtain a more satisfactory solution are discussed in an appendix (see also reference 3).

The crude approach should, however, be quite satisfactory a little above the transition point. So there is

<sup>1</sup> W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942).

<sup>2</sup> An excellent summary of the theories of helium II is to be found in R. B. Dingle, *Advances in Phys.* **1**, 112 (1952).

<sup>3</sup> A preliminary report on this work has been published. R. P. Feynman, *Phys. Rev.* **90**, 1116 (1953).

<sup>4</sup> F. London, *Phys. Rev.* **54**, 947 (1938).

<sup>5</sup> R. P. Feynman, *Revs. Modern Phys.* **20**, 367 (1948).

no doubt that at least the existence of the rise of specific heat<sup>1</sup> of He I on cooling toward the  $\lambda$  point can be understood from first principles.

At the opposite extreme of very low temperatures (say below 0.5°K), the situation again can be partially analyzed. This is done in the next paper.<sup>6</sup>

### EXACT EXPRESSION FOR THE PARTITION FUNCTION

To study the thermodynamic properties we must calculate the partition function

$$Q = \sum_i \exp(-\beta E_i), \quad (1)$$

where  $\beta = 1/kT$  and  $E_i$  are the energy levels of the system. In this form the calculation appears hopelessly difficult because the energies  $E_i$  are eigenvalues of such a complex Hamiltonian  $H$ . The expression for  $Q$  is equivalent to the trace of the operator  $\exp(-\beta H)$ . In Eq. (1) the trace is written in a representation in which  $H$  is diagonal. We shall prefer to use the coordinate representation to describe the trace.

To illustrate how this is done, we take the example of a one-dimensional system, of coordinate  $x$  and Hamiltonian  $p^2/2m + V(x) = H$ . The trace of  $\exp(-\beta H)$  is then  $Q = \int dz \langle z | e^{-\beta H} | z \rangle$ . The matrix element  $\langle z | e^{-\beta H} | z \rangle$  is similar in form to the matrix element  $\langle z | \exp(-iH/\hbar) | z \rangle$  which represents the amplitude that the system initially at  $x = z$ , is at time  $t$  also at the point  $x = z$ . This latter is<sup>5</sup> the sum over all paths [signified by  $\int \cdots \mathcal{D}x(t)$ ] which go from  $z$  to  $z$  of  $\exp(iS/\hbar)$ , where  $S$  is the action  $\int_0^t [\frac{1}{2}m\dot{x}^2 - V(x(t))] dt$ . If we replace  $i/\hbar$  by  $\beta$ , we are lead to expect

$$\langle z | e^{-\beta H} | z \rangle = \int_{tr} \exp \left\{ - \int_0^\beta \left[ \frac{m}{2\hbar^2} \left( \frac{dx}{du} \right)^2 + V(x(u)) \right] du \right\} \mathcal{D}x(u), \quad (2)$$

the variable  $u = i/\hbar$  replacing  $t$ , and the various signs adjusted accordingly. The integral  $\int_{tr}$  is to be taken on all trajectories such that  $x(0) = z$  and  $x(\beta) = z$ . It is easily verified that Eq. (2) is exactly correct. The normalization of the path integral is to be such that

$$\int_{tr'} \exp \left[ - \int_0^\beta \frac{m}{2\hbar^2} \left( \frac{dx}{du} \right)^2 du \right] \mathcal{D}x(u) = (m/2\pi\beta\hbar^2)^{1/2} \exp \left[ - \frac{m}{2\beta\hbar^2} (z - z')^2 \right], \quad (3)$$

where the trajectory  $tr'$  runs from  $x(0) = z$  to  $x(\beta) = z'$ . The integral of (2) with respect to  $z$  then gives the partition function.

To apply this to liquid helium two modifications are necessary. First, instead of one variable, we have  $3N$

variables which we take as the  $N$  three-space coordinate vectors  $\mathbf{x}_i$  of each of the  $N$  atoms ( $i = 1$  to  $N$ ). We designate the entire set of coordinates by  $\mathbf{x}^N$  and the integral over them all by  $d^N \mathbf{x}_i = d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N$ . The initial and final values of these we call  $\mathbf{z}_i$ . Secondly, He<sup>4</sup> atoms obey symmetrical statistics. The trace of  $\exp(-\beta H)$  is to be taken only over symmetrical wave functions. This means that if the initial coordinates are  $\mathbf{x}_i(0) = \mathbf{z}_i$ , the final coordinates need not be the same, but may be some permutation of these (signified by  $P\mathbf{z}_i$ ). That is,

$$Q = N!^{-1} \sum_P \int d^N \mathbf{z}_i \int_{trP} \exp \left\{ - \int_0^\beta \left[ \frac{m}{2\hbar^2} \sum_i \left( \frac{d\mathbf{x}_i}{du} \right)^2 + \sum_{ij} V(\mathbf{x}_i - \mathbf{x}_j) \right] du \right\} \mathcal{D}^N \mathbf{x}_i(u), \quad (5)$$

where the integral  $\int_{trP}$  is taken over all trajectories  $\mathbf{x}_i(u)$  of all the particles such that  $\mathbf{x}_i(0) = \mathbf{z}_i$ ,  $\mathbf{x}_i(\beta) = P\mathbf{z}_i$ . That is, the final coordinates  $\mathbf{x}_i(\beta)$  may now be some permutation  $P$  of the initial coordinates  $\mathbf{z}_i$ . The sum is taken over all permutations  $P$  and the integral over all configurations  $\mathbf{z}_i$ .

In Eq. (5),  $m$  is the mass of a helium atom, and  $V(\mathbf{R})$  is the mutual potential of a pair of He atoms separated by  $\mathbf{R}$ . The forces between He atoms are, very likely, fairly accurately two-body forces. This potential is given by Slater and Kirkwood.<sup>7</sup> There is a weak attraction of maximum depth (of energy equivalent to  $kT$  at  $T = 7^\circ\text{K}$ ) at radius about 3.0Å. The atomic volume at the transition is (3.6Å)<sup>3</sup>. At 3.6Å,  $V(\mathbf{R})$  is about equivalent to  $kT$  for  $T = 3^\circ\text{K}$ . There is, therefore, a weak attraction at the average atomic distance. There is a violent repulsion if the atoms approach more closely than 2.6Å ( $V = 0$  at 2.6Å).

The expression (5) is an exact<sup>8</sup> quantum-mechanical expression for the partition function (even though no imaginary unit  $i$  appears). We shall use it to develop a qualitative understanding of this function for liquid helium.

The quality  $u$  is of course not the time. However, we shall obtain a vivid representation of (5) by imagining that it is the time. We can say that at one time 0 the coordinates  $\mathbf{x}_i(0)$  of all the atoms form an initial configuration  $\mathbf{z}_i$ , and that as time  $u$  proceeds the particles move about [ $\mathbf{x}_i(u)$ ] in such a manner that at the time  $\beta$  the configuration of atoms appears to be the same (although in fact some of the atoms may have been interchanged). Each mode of motion is weighed by the negative exponential of the time integral of the energy required for the motion, and the sum is taken for all such motions. Finally an average (or rather integral) is taken over all possible initial configurations  $\mathbf{z}_i$ .

We can see immediately that motions which require too large a displacement in the time  $\beta$  have little weight

<sup>7</sup> J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

<sup>8</sup> In so far as the forces can be represented as two-body forces.

<sup>6</sup> R. P. Feynman, Phys. Rev. **91**, 1301 (1953).

because of the high kinetic energy required. Likewise, motions in which the atoms come so close as to appreciably penetrate the radius of their repulsion are of small importance because of the large potential energy which would result. For this reason, also, initial configurations for which the atoms overlap, that is, have centers so close that they would repel, contribute only a small amount. The method of approximation which we shall apply to (5) is to neglect the contributions from motions  $\mathbf{x}_i(u)$  and configurations  $\mathbf{z}_i$  which give small contributions, and to study more carefully only those motions which give the larger contributions to the total in (5). That is, we shall have motions in which the atoms do not move too fast or far in the time  $\beta$  and in which the atoms never overlap.

We emphasize again that these "motions" must not be construed as a real description of what the atoms are doing. It is simply a formal description of the expression for the partition function. An expression "the atom does not move too far in the time  $\beta$ " does not refer to a real motion as  $u$  is not time, but is  $i\dot{u}/\hbar$ . The true behavior of the atoms may have some analogy to the description of the formula (5), but such an analogy need not concern us here. Our reason to continue to call  $u$  and  $\beta$  "time" is to help to make our arguments as vivid as possible so that intuition will be most effective.

#### THE CHARACTER OF THE IMPORTANT TRAJECTORIES

Consider a particular motion in (5) in which some atom  $i$  moves to the site initially occupied by atom  $j$ . Call the displacement  $\mathbf{a} = \mathbf{z}_j - \mathbf{z}_i$ . The atom  $j$  must, of course, move to some other site to leave room for  $i$ . The effect of the motion of  $j$  we will associate with atom  $j$ . We study here the contribution to be expected just from the displacement of the single atom  $i$  by a distance  $\mathbf{a}$ .

Near the transition temperature displacements larger than about  $d$ , the atomic spacing (cube root of atomic volume 3.6A) are not very important [ $\exp(-md^2/2\beta\hbar^2) = 0.3$  at 2.2°K]. Nevertheless we will try to get an idea of the behavior for larger displacements. These will be useful at lower temperatures. Actually our considerations apply to displacements of any size.

Suppose, then, atom  $i$  must make a translation  $\mathbf{a}$  of length  $a$ . We make this, for example, to be nearly along a straight line. Our arguments will apply for any other route.

The central problem is, what is the effect of the potentials of interaction on this translation? As a simple model which retains the essential features imagine the atoms as hard impenetrable spheres. We are, during a time  $\beta$ , to move atom  $i$  from  $\mathbf{z}_i$  to  $\mathbf{z}_j = \mathbf{z}_i + \mathbf{a}$  and at the end to leave all the other atoms in their original positions. The atoms may not overlap at any time.

There may be atoms in the direct line from  $\mathbf{z}_i$  to  $\mathbf{z}_j$ . Nevertheless, a moment's reflection shows that they

will not offer a real potential barrier to the translation of atom  $i$ .

It is evident that it is possible to place atom  $i$  at any position on the route from  $\mathbf{z}_i$  to  $\mathbf{z}_j$ , provided we readjust the positions of the other atoms to make room for it. In the readjusted positions the total potential energy of all the atoms can be made to be very nearly equal to the potential energy of the original configuration. Therefore, atom  $i$  can be moved to any intermediate position without violating any repulsive potential, in fact, without any appreciable modifications of potential energy at all. It is only necessary to move the other atoms around out of the way as atom  $i$  moves along. When  $i$  reaches the final destination  $\mathbf{z}_j$ , the other atoms (except  $j$  of course, as noted above) may all come back to their original positions (or to some permutation thereof<sup>9</sup>).

The readjustment of the other atoms means that their coordinates  $\mathbf{x}_k(u)$  change with time. They contribute just kinetic energy in the exponent in  $Q$ . Beside the kinetic energy  $\frac{1}{2}m(a/\beta)^2$  needed to move atom  $i$  a distance  $a$  in time  $\beta$ , we have also to add the kinetic energy of the readjusting atoms. This we can expect will also vary directly as the square of the velocity of atom  $i$ . The net effect is an energy of the form  $\frac{1}{2}m'(a/\beta)^2$ , where  $m'$  is an effective mass, somewhat larger than the mass of a single atom  $m$ . The difference represents the effective inertia of the atoms which are readjusting.

The time integral of the energy needed for readjustment varies with  $a$  and  $\beta$ , as  $a^2/\beta$ . This is clear for small displacements of  $i$ , for then only a few atoms shift, and they do this with a velocity proportional to that of  $i$ . For large displacements ( $a \gg d$ ) the same form, of course, results. To verify this, imagine that as atom  $i$  moves at velocity  $v (= a/\beta)$  the time it passes near a particular atom is of order  $d/v$ . This atom must adjust through distances of order  $d$  in this time, or move at speed about  $v$ . The time integral of energy needed for this passage is about  $mv^2(d/v) = mdv$ . The number of such atoms which must be jostled to move a total distance  $a$  is of order  $a/d$ . Thus the total time integral of energy of readjustment for all these  $a/d$  atoms varies as  $mdv \cdot a/d = mva = ma^2/\beta$ . It varies with  $a$  and  $\beta$  in the required manner.

The effect of the other atoms is not to offer a potential barrier (time integral varying as  $a\beta$ ) but a kind of kinetic energy barrier (time integral varying as  $a^2/\beta$ ). The effect of the interactions is taken into account by changing the effective mass of a given moving atom.

To get some idea of the order of  $m'$ , we recall that the effective mass of a sphere moving through an ideal fluid of the same density is classically  $(\frac{3}{2})m$ , the extra  $\frac{1}{2}$  being the energy of motion of the fluid making way for the sphere. The effect of the attractive forces may in-

<sup>9</sup> The effect of a moving atom in permuting other atoms might have to be considered in more detail if we were to apply these ideas to the case of Fermi-Dirac statistics. It may mean that the  $m'$  (discussed further on) is somewhat larger in that case.

crease this somewhat. We may expect  $m'$  not to be very much greater than  $m$ —perhaps not more than 2 or 3  $m$ .

The effect of the relatively weak attractive potentials may be to alter the motions a bit, in that adjacent atoms tend to stick together a little. Thus the atom  $i$  may have a tendency to drag some atoms with it from time to time, possibly increasing  $m'$  a little more. On the other hand, in He the zero-point energy<sup>10</sup> is high enough to shake these others loose readily. If the potential were much stronger the group attraction might become accumulative, raising  $m'$  very much. It is possible that this would result in solidification.

For short displacements  $a$  of order  $d$ , proportionately less adjustment need be made, so that it is likely that  $m'$  may be somewhat less. For high velocities, it may represent less energy to violate the real potential restrictions a little. Thus the readjustments need not be complete, so that  $m'$  again may decrease a little with velocity  $a/\beta$ , approaching  $m$  as  $a/\beta \rightarrow \infty$ .

As this is meant to be a first approach to the problem, we shall not attempt to calculate the  $m'$ : The geometrical complexity is very great. Further, we shall neglect the variation of  $m'$  with  $a$  and velocity. It is to be expected that this neglect may not alter our conclusions qualitatively. It is always possible, later, to include such finer details. Nor shall we discuss the variation (expected rise) of  $m'$  with increasing density of the fluid.

For every trajectory the atom acts like a free particle of effective mass  $m'$ . Hence we may take the integral over all paths  $\mathbf{x}_i$  for atom  $i$  to go a distance  $a$  to be proportional to

$$(m'/2\pi\beta\hbar^2)^{3/2} \exp(-m'a^2/2\beta\hbar^2). \quad (6)$$

The normalization factor has been written as  $(m'/2\pi\beta\hbar^2)^{3/2}$  for convenience. That it varies as  $\beta^{-3/2}$  may be shown by dimensional analysis [compare Eq. (3)]. Actually a change in this factor will just change the partition function by a factor. It will be easiest to discuss the normalization of the entire partition function.

Therefore, we can approximate  $Q$  by

$$Q = \frac{K_\beta}{N!} \left( \frac{m'}{2\pi\beta\hbar^2} \right)^{3N/2} \int \sum_P \exp \left[ -\frac{m'}{2\beta\hbar^2} \sum_i (\mathbf{z}_i - P\mathbf{z}_i)^2 \right] \times \rho(\mathbf{z}_1, \mathbf{z}_2, \dots, \mathbf{z}_N) d^N \mathbf{z}_i. \quad (7)$$

The factor  $K_\beta$  we shall estimate later. The function  $\rho(\mathbf{z}_1, \dots, \mathbf{z}_N) = \rho(\mathbf{z}^N)$  represents a density associated with each configuration. It is discussed in the next

<sup>10</sup> The zero-point energy referred to appears in the integral for  $Q$  in the following guise. Suppose we restrict the motion of a certain atom  $k$  so that, for example, it tries to move along close to  $i$  to take advantage of some extra attractive potential between  $k$  and  $i$ . Then the trajectories of  $k$  are restricted, and we lose a great deal in the integral over possible paths of  $k$  because we are not adding contributions from very many paths. We lose "volume in path-space." This will suffice to offset the attraction if, in the conventional language, the zero-point motion is sufficiently large.

section. This expression (7) for  $Q$  may be rewritten, using Fourier transforms as

$$Q = \int F(\mathbf{k}^N) \exp[-(\beta\hbar^2/2m') \sum_i \mathbf{k}_i^2] d^N \mathbf{k}_i (2\pi)^{-3N}, \quad (7a)$$

where

$$F(\mathbf{k}^N) = K_\beta (N!)^{-1} \int \sum_P \exp[i \sum_i \mathbf{k}_i \cdot (\mathbf{z}_i - P\mathbf{z}_i)] \times \rho(\mathbf{z}^N) d^N \mathbf{z}_i.$$

This form is especially useful near absolute zero, but we will not need it in this paper.

It should be emphasized that the argument which leads to the free particle approximation for the motion of an atom is of greater generality. The argument results simply from a consideration of the limitations to the true trajectories which result from the interatomic potentials. They therefore apply as well to the non-diagonal element of  $\exp(-\beta H)$ , as to the diagonal element which appears in  $Q$ . Likewise, they are applicable to the true quantum-mechanical kernel, which is the nondiagonal element of  $\exp(-itH/\hbar)$ . The imaginary weights in this case also restrict the atoms not to overlap at low energy, etc.

This principle may have uses in other branches of physics, for example, in nuclear physics. Here there is the puzzling fact that single nucleons often act like independent particles in spite of strong interactions. The arguments we have made for helium may apply to this case also.<sup>9</sup>

#### THE CONFIGURATIONS OF IMPORTANCE

Not all configurations  $\mathbf{z}_N$  are to be weighed equally. If  $\mathbf{z}_i$  and  $\mathbf{z}_j$  are closer than the distance at which strong repulsion sets in (2.6A) the configuration should be given very little weight [i.e.,  $\rho$  in (7) is nearly zero if atoms overlap]. We shall discuss this effect first for the case of low temperature ( $\beta$  large).

Suppose initially in (5) two atoms overlap, say by a distance  $x$ , and suppose that this results in an extremely high (relative to  $1/\beta$ ) potential  $V$ . If they move a distance  $x$  further apart, suppose  $V$  goes to 0, and take  $V$  independent of  $x$  for simplicity. During the interval  $u=0$  to  $\beta$ , if the atoms remain overlapped for a time  $\tau$ , the contribution is the negative exponential of  $V\tau$ . This contribution is extremely small unless  $\tau$  is very short (if  $V\beta \gg 1$  then  $\tau \ll \beta$ ). The most important trajectories are then those that release  $V$  as quickly as possible. This can only be done by a high kinetic energy  $m'x^2/2\tau^2$ . Thus the integral of energy has the value  $m'x^2/2\tau\hbar^2 + V\tau$ , which is least if  $\tau = (m'x^2/2V\hbar^2)^{1/2}$ , in which case it has the value  $(2m'V)^{1/2}x/\hbar$ . The contribution varies as  $\exp[-(2m'V)^{1/2}x/\hbar]$ . This is just the quantum-mechanical penetration factor. In  $\rho$  it appears twice, for again we must get into the overlapped condition at the end of the interval  $\beta$ . This argument fails if  $\beta$  does not exceed

2τ. In that case a larger penetration results. It is due, of course, to the high kinetic energy that such a small β implies. For the large repulsions V at low temperatures involved here this penetration is very small.

In addition, ρ would not be quite uniform even if there is no overlap of the atoms, and even if they are considered as impenetrable spheres. In fact, ρ would be larger if atoms are well spaced than if they are nearly adjacent (for large β). If two atoms are adjacent initially, the available paths are limited to those which move them apart—for they must not come to overlap. This decreases the effective volume of path space for a short time. Actually this effect is offset partly by the actual attractive potential which results upon the closer approach of the two atoms. Thus ρ represents the effects of short-time adjustments (times ≪ β) while the longer-time effects<sup>11</sup> are contained in the exponential factor in (7) [that is, expression (12) below]. For large β, low T, ρ can be taken as nearly temperature independent, and the main temperature dependence comes from the other factor (12). This ρ as β → 0 is the density corresponding to the ground-state wave function. For approximate purposes we can take it to be simply the density function ρ for a classical gas of impenetrable atoms of diameter b. That is, ρ = 0 if any two z<sub>i</sub>'s are closer to each other than b, and is 1 otherwise. This neglects the variations with distance due to the quantum-mechanical effect discussed above of restricted path-space volume, and due to the attractive part of the potential.

For high temperatures, the exponential terms in (7), representing diffusion, are unimportant, and ρ should approach the classical distribution function. Now the attractive forces are weak and unimportant so again can be roughly represented by an impenetrable sphere model. The radius b should be somewhat smaller. We shall neglect this variation of b with temperature.

To summarize, ρ is qualitatively similar to the density distribution of a classical gas. It changes somewhat with temperature.

PROPERTIES OF THE PARTITION FUNCTION

A partition function has several formal properties, and we may test our approximate expression (7) to see how well it satisfies these conditions. Another important function is the nondiagonal element of

<sup>11</sup> There is a kind of distortion that takes a long time τ to release, namely, a general increase in density over a large area. This restricts the path-space volume for each atom in the area and results in a factor e<sup>-βE</sup> for each particle, where E is the excess energy per particle induced by compression. The energy E can only be released by moving many particles, distributed over the area. These density fluctuations are sound waves. If the wavelength of the fluctuation is λ = 2π/c, the time needed to release it is τ = 1/ħω = 1/ħcK, where c is the speed of sound. This exceeds β if λ > 2πħT/ħc or λ > 2π · 8Å for 2.2°K. (This exceeds the diffusion distance d ≈ 3.6Å even at 2.2°K, so will not be of concern to us near the transition.) Thus (7) is incomplete in that it does not correctly describe long wave-sound fluctuations. This matter is discussed in a subsequent paper.

exp(-βH). That is, G<sub>β</sub>(z', z) = (z' | exp(-βH) | z), or

$$G_{\beta}(\mathbf{z}'^N, \mathbf{z}^N) = (N!)^{-1} \sum_P \int_{trP'} \exp \left[ - \int_0^{\beta} \left( \frac{m}{2\hbar^2} \sum_i \left( \frac{d\mathbf{x}_i}{du} \right)^2 + \sum_{ij} V(\mathbf{x}_i - \mathbf{x}_j) \right) du \right] \mathfrak{D}^N \mathbf{x}_i(u), \quad (8)$$

the integral being taken over all trajectories trP' such that x<sub>i</sub>(0) = z<sub>i</sub>, x<sub>i</sub>(β) = Pz<sub>i</sub>'. The final configuration z<sub>i</sub>' may differ from the initial configuration. Of course, Q = ∫ G<sub>β</sub>(z<sup>N</sup>, z<sup>N</sup>) d<sup>N</sup>z<sub>i</sub>.

For large β we have given an argument for behavior of the function ρ(z<sup>N</sup>), which represented it as the square of a function, say φ(z<sup>N</sup>). One factor was for leaving an unfavorable (say overlapping) configuration. The second was for entering it again. At low temperature φ(z<sup>N</sup>) is the ground-state wave function. The same arguments give for G<sub>β</sub>(z<sup>N</sup>, z<sup>N</sup>) the approximate expression,

$$G_{\beta}(\mathbf{z}'^N, \mathbf{z}^N) = K_{\beta} (N!)^{-1} \sum_P \phi(\mathbf{z}'^N) \phi(\mathbf{z}^N) \times \exp \left[ - \frac{m'}{2\beta\hbar^2} \sum_i (\mathbf{z}_i - P\mathbf{z}_i')^2 \right] \left( \frac{m'}{2\pi\beta\hbar^2} \right)^{3N/2}. \quad (9)$$

Since exp(-β<sub>1</sub>H) exp(-β<sub>2</sub>H) = exp[-(β<sub>1</sub>+β<sub>2</sub>)H], we have the condition of matrix multiplication, namely, that

$$G_{\beta_1+\beta_2}(\mathbf{z}'^N, \mathbf{z}^N) = \int G_{\beta_1}(\mathbf{z}'^N, \mathbf{z}''^N) G_{\beta_2}(\mathbf{z}''^N, \mathbf{z}^N) d^N \mathbf{z}_i''.$$

This requires that (β = β<sub>1</sub>+β<sub>2</sub>)

$$K_{\beta} \left( \frac{m'}{2\pi\beta\hbar^2} \right)^{3N/2} \sum_P \exp \left[ - \frac{m'}{2\beta\hbar^2} \sum_i (\mathbf{z}_i - P\mathbf{z}_i')^2 \right] = K_{\beta_1} K_{\beta_2} \left( \frac{m'}{2\pi\beta_1\hbar^2} \right)^{3N/2} \left( \frac{m'}{2\pi\beta_2\hbar^2} \right)^{3N/2} \int N!^{-1} \sum_P \sum_{P'} \times \exp \left[ - \frac{m'}{2\beta_1\hbar^2} \sum_i (P\mathbf{z}_i' - \mathbf{z}_i'')^2 - \frac{m'}{2\beta_2\hbar^2} \sum_i (P'\mathbf{z}_i'' - \mathbf{z}_i)^2 \right] \times [\phi(\mathbf{z}''^N)]^2 d^N \mathbf{z}_i''.$$

Now, in the exponent we can relabel i (by permuting the names) as P'i, since the sum in on all i. That is, ∑<sub>i</sub> (Pz<sub>i</sub>' - z<sub>i</sub>'')<sup>2</sup> = ∑<sub>i</sub> (PP'z<sub>i</sub> - P'z<sub>i</sub>'')<sup>2</sup>. Now call PP' = P'', and the sum on all P is equivalent to a sum on all P''. Finally, since z<sub>i</sub>'' are variables of integration in a symmetrical factor [(φ(z''<sup>N</sup>)]<sup>2</sup> = ρ(z''<sup>N</sup>) = ρ(P'z''<sup>N</sup>) for any P', the z''<sup>N</sup> integral does not depend on P', and ∑<sub>P'</sub> just gives a factor N!

Now the weight function ρ(z''<sup>N</sup>) prevents various z<sub>i</sub>'' from being too close together. If, however, β<sub>1</sub> and β<sub>2</sub> are so low that exp(-m'd<sup>2</sup>/2β<sub>1</sub>ħ<sup>2</sup>) is fairly close to 1, the variations in the exponents due to this restriction

is very small. [That is, in the integrand,  $\rho(\mathbf{z}'^N)$  varies rapidly while the other factor is smooth.] Therefore, we replace  $\rho(\mathbf{z}'^N)$  by an average value and integrate over all  $\mathbf{z}'^N$ . The effect of  $\rho(\mathbf{z}'^N)$  just restricts the volume available to the configuration variables. Let us call

$$V_N = \int \rho(\mathbf{z}^N) d^N \mathbf{z}_i, \quad (10)$$

so that the average value of  $\rho$  is  $V_N/V^N$ . The integral on  $\mathbf{z}_i''$  is now easy, and we find

$$K_{\beta_1+\beta_2} = K_{\beta_1} K_{\beta_2} V_N/V^N.$$

[This verifies our choice of the  $\beta^{-3}$  dependence in (6).] This means that  $K_\beta$  must have the form

$$K_\beta = V^N V_N^{-1} e^{-\beta E_0}, \quad (11)$$

where  $E_0$  is a constant. Such a constant means, in  $Q$ , a constant energy (the energy at absolute zero). We will not try to determine this energy. Let us measure energies above this as a zero level. Then it can be ignored. Our final partition function is then (17) with  $K_\beta = V^N/V_N$ .

For extremely large  $\beta$ ,  $Q$  should approach 1 from its original definition as  $\sum_i e^{-\beta E_i}$  and the choice  $E_0=0$ . For such large  $\beta$ , the sum on permutations  $P$  means that  $P\mathbf{z}_i$  goes successively over every site, while the exponential  $\exp[-(m'/2\beta\hbar^2)(\mathbf{z}_i - P\mathbf{z}_i)^2]$  varies smoothly. It is approximated by writing it as  $\exp[-(m'/2\beta\hbar^2) \times (\mathbf{z}_i - \mathbf{z}_i')^2]$  and integrating over all  $\mathbf{z}_i'$  but dividing by the atomic volume  $V_A = V/N$  for each  $\mathbf{z}_i'$ . However, this does not take into account the restriction that all the  $\mathbf{z}_i'$  are on different sites. So an additional  $N!/N^N$  is needed. Thus the total factor is  $N!/(NV_A)^N$  or  $N!/V^N$ . The integrals give  $(2\pi\beta\hbar^2/m')^{3/2}$  per degree of freedom, so we see that  $Q$  approaches

$$Q \sim (K_\beta/V^N) \int \rho(\mathbf{z}^N) d^N \mathbf{z}_i = 1$$

as  $\beta \rightarrow \infty$ , as required.

This value of  $K_\beta$  was obtained by an argument involving large  $\beta$ . Let us study its behavior for small values of  $\beta$ . For small  $\beta$  (high  $T$ ) no permutation is important in (17) except the identity. For no atoms are closer than  $b=2.6\text{\AA}$ , and  $(m'/2\beta\hbar^2)(\mathbf{z}_i - P\mathbf{z}_i)^2$  would be at least  $b^2 m'/2\beta\hbar^2$ , if  $P\mathbf{z}_i \neq \mathbf{z}_i$ . For small  $\beta$  this results in a large negative exponent. Thus  $Q$  approaches the value

$$Q = K_\beta (N!)^{-1} (m'/2\pi\beta\hbar^2)^{3N/2} \int \rho(\mathbf{z}^N) d^N \mathbf{z}_i.$$

The correct limit, according to the classical theory, should be

$$Q = N!^{-1} (m'/2\pi\beta\hbar^2)^{3N/2} \int \rho(\mathbf{z}^N) d^N \mathbf{z}_i.$$

Since  $m'$  approaches  $m$ ,  $K_\beta$  must approach 1 as  $\beta \rightarrow 0$ .

This means that  $K_\beta$  must be a function of  $\beta$  which varies from  $V^N/V_N$  to 1 as  $\beta$  varies from large to small values.

An accurate quantitative analysis of this problem would require close attention to the variation with temperature and density of  $m'$ , of  $K$  and of  $b$  (or, more completely, of  $\rho$ ).

#### EXISTENCE OF THE TRANSITION

We can use this partition function (7) and the ideas associated with it to understand many of the properties of liquid helium. The behavior of the liquid at very low temperature (below  $0.5^\circ\text{K}$ ) will concern us in the following paper.<sup>6</sup> Here we will study the behavior in the region of a few degrees and shall show that a transition should occur.

In the qualitative study of such a transition we need not concern ourselves with the continuous variations in the effective constants  $m'$ ,  $K_\beta$ ,  $b$ . It might be well to remark, however, that  $2.2^\circ\text{K}$  the expression  $mx^2/2\beta\hbar^2$  is unity for  $x=3.4\text{\AA}$ . This is just the order of the average spacing of the atoms. Therefore, we are not going to be involved in very long displacements, and it may be that  $m'$  does not differ too much from  $m$ .

It is not hard to understand that (17) gives a transition. If  $\rho$  were a constant it would be the same as the partition function for an ideal gas. The fact that  $\rho$  is not perfectly uniform cannot change this much.

To see in more detail how this transition arises, consider the factor

$$\sum_P \exp[-(m'/2\beta\hbar^2) \sum_i (\mathbf{z}_i - P\mathbf{z}_i)^2] \quad (12)$$

in the partition function (7).

Each permutation may be divided into cycles. A cycle of length  $s$  is a chain of permutations, such as 1 goes to 2, 2 goes to 3, 3 goes to 4, etc. until  $s-1$  goes to  $s$  and finally  $s$  goes to 1. Such a cycle contributes to a term in (12) the factor

$$\exp[-(m'/2\beta\hbar^2)(\mathbf{z}_{12}^2 + \mathbf{z}_{23}^2 + \cdots + \mathbf{z}_{s1}^2)], \quad (13)$$

where  $\mathbf{z}_{ij} = \mathbf{z}_i - \mathbf{z}_j$  and  $\mathbf{z}_1, \mathbf{z}_2$ , etc., are the positions of the particular atoms in the cycle. The total contribution from a given permutation is the product of all these factors, one from each of its cycles. For a given configuration we are to sum such a product over all permutations, that is, over all possible ways of laying out cycles on the configuration.

Consider a permutation of a certain "type," that is, having a certain number of each kind of cycle. That is,  $P$  has  $n_1$  cycles of length 1 (i.e.,  $n_1$  atoms are not permuted),  $n_2$  cycles of length 2,  $\cdots n_s$  of length  $s$ , etc. The total number of atoms is  $N$ , so that

$$N = \sum_s s n_s. \quad (14)$$

To these cycles there correspond  $n_1$  atoms,  $n_2$  polygons of 2 sides,  $n_3$  triangles,  $\cdots$ , etc. drawn on the configuration, and each contributes its factor (13).

Next we may sum over all permutations of the same type. This means that each polygon will change its shape and location (but not its number of sides) as we go from one permutation to another in the sum. Eventually a given polygon can be considered as taking up all possible forms—that is, a polygon of  $s$  sides will have had every possible set of  $s$  atom sites for its vertices.<sup>12</sup> As a given polygon changes, of course, the others must change too, for no atom may be a member of more than one polygon in any given permutation  $P$ . This presents an enormously complicated mathematical problem.

We shall try to simplify it by an assumption that the various geometrical forms that a given polygon can take are roughly independent of the shapes of the other polygons. That is, we shall assume that the contribution of a polygon of a given size is the average for such a polygon over all possible forms the polygons can take without restriction. That is, *we assume the average factor contributed by a given polygon does not depend on what type the other polygons are.* This assumption is probably not sufficiently accurate to give an exact description of the order of the transition.

We shall actually use, for the contribution of a polygon, the total effect it would have if it were alone. In the various integrations over many polygons, the fact that no atom may be used twice actually restricts the volume of configuration space. It is  $V_N$  [Eq. (10)]. To include this effect we will have an additional factor  $V_N/V^N$ .

Making these assumptions the total contribution to (12) of all permutations of a given type is

$$V_N V^{-N} C(n_1, n_2, \dots) f_1^{n_1} f_2^{n_2} \dots f_s^{n_s} \dots, \quad (15)$$

where  $C(n_1, n_2, \dots) = N! / \prod_s n_s! s^{n_s}$  is the total number of permutations of a given type, and  $f_s$  is the contribution of a polygon of type  $s$ , for a given configuration calculated as though it were alone. We may average this over the possible configurations also. That is,

$$f_s = V \int \exp \left[ -\frac{m'}{2\beta\hbar^2} (\mathbf{z}_1^2 + \mathbf{z}_2^2 + \dots + \mathbf{z}_s^2) \right] \times \rho^{(s)}(\mathbf{z}_1, \mathbf{z}_2, \dots, \mathbf{z}_s) d\mathbf{z}_1 \dots d\mathbf{z}_s, \quad (16)$$

where  $\rho^{(s)}(\mathbf{z}_1, \dots, \mathbf{z}_s)$  is the chance of finding  $s$  atoms with their centers at  $\mathbf{z}_1, \mathbf{z}_2, \dots, \mathbf{z}_s$ . That is,

$$\rho^{(s)}(\mathbf{z}_1, \dots, \mathbf{z}_s) = \int \rho(\mathbf{z}_1, \mathbf{z}_2, \dots, \mathbf{z}_s, \mathbf{z}_{s+1}, \dots, \mathbf{z}_N) d\mathbf{z}_{s+1} \dots d\mathbf{z}_N,$$

where  $\rho(\mathbf{z}^N)$  is the configuration density of (7). The factor  $V$  comes in (16) from the fact that  $\mathbf{z}_1$  can be anywhere and has been integrated out.

<sup>12</sup> Actually the only contributions (near 2°K) come from polygons formed from nearly adjacent atoms. The factor (13) is very small if any of the sides are very long. The polygons of importance may be of any total perimeter (for large  $s$ ), of course. It is only their individual sides which are limited.

Next we must sum over all permutation types. That is, over all values of  $n_1, n_2, \dots$  subject to (14). Signifying this by  $\sum'$  and substituting into (7) we find

$$Q = (K_\beta V_N / V^N) (m' / 2\pi\beta\hbar^2)^{3N/2} \sum' \prod_s (f_s^{n_s} / n_s! s^{n_s}).$$

The factor  $K_\beta V_N / V^N$  presumably varies exponentially with  $N$ . We could write it as  $\exp(N\alpha)$  where  $\alpha$  is independent of  $N$  and varies slowly with temperature, vanishing as  $T \rightarrow 0$ . It will make no essential difference in our study of the transition (it just adds  $NkT\alpha$  to the free energy  $A$ ) so we will not bother to carry it along.

The sum is very difficult because of the restriction (14). However, we may use the usual methods of steepest descents. We multiply  $Q$  by a factor of the form  $\exp(\mu N / kT)$  ( $\mu$  is the chemical potential) and sum over  $N$ . If we then put  $N = \sum_s n_s$ , we can sum on all  $n_s$  without restriction. Further, if the free energy  $A$  is

$$A = -kT \ln Q$$

and the sum is written  $\exp(-B/kT)$ , we can determine  $A$  from

$$A = B + \mu N \quad (18)$$

and

$$\bar{N} = -\partial B / \partial \mu \quad (19)$$

in the usual way. ( $\bar{N}$  is the mean number of atoms.) Hence, putting

$$x = (m' / 2\pi\beta\hbar^2)^{\frac{3}{2}} \exp(\mu / kT), \quad (20)$$

we can write

$$\begin{aligned} \exp(-B/kT) &= \sum_{\text{all } n_s} x^N \prod_s (f_s^{n_s} / n_s! s^{n_s}) \\ &= \prod_s \sum_{n_s} (f_s^{n_s} x^{n_s} / n_s! s^{n_s}) \\ &= \prod_s \exp(f_s x^s / s), \end{aligned}$$

or

$$-B = kT \sum_s f_s x^s / s; \quad (21)$$

and (19) gives

$$N = \sum_s f_s x^s. \quad (22)$$

This pair of equations together with (20), (18) determines  $A$  and thereby all the thermodynamic functions. The  $x$  is determined from the second Eq. (22), by the condition that  $\bar{N}$  equal  $N$ , the actual number of atoms.

To proceed further we shall have to evaluate  $f_s$ . This we do approximately; for the calculation  $f_s$  from (16) is difficult. The distribution  $\rho^{(s)}$  does not permit atoms to be too close together. This is important for atoms adjacent in the polygon, such as 1 and 2. On the other hand, it is not of great geometrical importance for links much further apart (like 1 and 5). The important polygons correspond to random walks of  $s$  steps from each atom to a neighbor, finally returning to the origin. In three dimensions the chance, after a few steps, of coming back to the origin before the final step is not large. In averaging (16) over the polygons, if we include self-crossing polygons in the average we may not be

far off. There are not many of them so they probably do not alter the average very much. This is a second assumption. It is similar to the first. To be more explicit we shall approximate  $\rho^{(s)}$  in (16) by

$$\rho^{(s)}(\mathbf{z}_1, \mathbf{z}_2, \dots, \mathbf{z}_s) = p(\mathbf{z}_{12})p(\mathbf{z}_{23}) \cdots p(\mathbf{z}_{s1}), \quad (23)$$

where  $p(\mathbf{z}_{12})$  is the probability per unit atomic volume, of finding an atom located at  $\mathbf{z}_2$  if one is known to be at  $\mathbf{z}_1$  (and  $\mathbf{z}_{12} = \mathbf{z}_1 - \mathbf{z}_2$ ). It is a function only of the radial distance  $p(r)$ ,  $r^2 = \mathbf{z}_{12}^2$ , which approaches unity as  $r$  gets beyond a few times the atomic spacing  $d$  [ $p(\mathbf{z}_{12})$  is proportional to  $\rho^{(2)}(\mathbf{z}_1, \mathbf{z}_2)$ .]

Thus, approximately,

$$f_s = V \int \exp[-(m'/2\beta\hbar^2)(\mathbf{z}_{12}^2 + \mathbf{z}_{23}^2 + \cdots + \mathbf{z}_{s1}^2)] \times p(\mathbf{z}_{12})p(\mathbf{z}_{23}) \cdots p(\mathbf{z}_{s1}) d\mathbf{z}_2 \cdots d\mathbf{z}_s. \quad (24)$$

This formula is wrong for  $s=1$ , for, of course,  $f_1 = V$ . For  $s=2$ , (24) is not very good, for (24) averages with weight  $p(\mathbf{z}_{12})^2$  while the correct weight in (16) should be  $p(\mathbf{z}_{12})$ . Short rings are not important in determining the existence nor order of the transition, however.

The expression (24) is nearly in the form of a convolution and can therefore easily be simplified. If the last point of the polygon were not 1 but some other location, say  $\mathbf{z}_0$  [i.e., replace  $\mathbf{z}_{s1}$  by  $\mathbf{z}_{s0}$  in (24)], the expression ( $\div V$ ) would depend on  $\mathbf{z}_1 - \mathbf{z}_0$  or  $\mathbf{z}_{10}$ . Call it  $g_s(\mathbf{z}_{10})$ . Its Fourier transform,  $\int g_s(\mathbf{z}_{10}) \exp(i\mathbf{K} \cdot \mathbf{z}_{10}) \times d\mathbf{z}_{10}$ , is the  $s$  power of the Fourier transform,

$$\Gamma(\mathbf{K}) = \int \exp(-m'\mathbf{z}^2/2\beta\hbar^2) p(\mathbf{z}) \exp(i\mathbf{K} \cdot \mathbf{z}) d\mathbf{z}. \quad (25)$$

Therefore  $g_s(\mathbf{z}) = \int \exp(-i\mathbf{K} \cdot \mathbf{z}) (\Gamma(\mathbf{K}))^s d\mathbf{K} (2\pi)^{-3}$ , and since  $f_s = g_s(0)$ , we find

$$f_s = V \int \Gamma(\mathbf{K})^s d\mathbf{K} (2\pi)^{-3}. \quad (26)$$

This is not true for  $s=1$ . For  $s=1$  the true  $f_1$  is  $V$ , while this gives  $f_1 = V \int \Gamma(\mathbf{K}) d\mathbf{K} (2\pi)^{-3} = V p(0)$  from (25). This  $p(0)$  should be practically 0, but for generality we retain it. Substitution of this into (21) we get ( $f_1 = V$ )

$$-B = kTV \sum_{s=2} \int (x^s \Gamma(\mathbf{K})^s / s) d\mathbf{K} (2\pi)^{-3} + kTVx,$$

or

$$-B = kTV \int \ln(1 - x\Gamma(\mathbf{K})) d\mathbf{K} (2\pi)^{-3} + kTV[1 - p(0)]x; \quad (27)$$

and, similarly,

$$\bar{N}/V = \int [1 - x\Gamma(\mathbf{K})]^{-1} d\mathbf{K} (2\pi)^{-3} + [1 - p(0)]x. \quad (28)$$

To study the transition more closely, we study the effects of the longer cycles. We need  $f_s$  for very large  $s$ .

Since  $\Gamma(\mathbf{K})$  in (25) falls as  $\mathbf{K}$  rises and is maximum for  $\mathbf{K}=0$ , we expand  $\ln\Gamma(\mathbf{K})$  in powers of  $\mathbf{K}^2$  and carry only the first two terms in the form

$$\ln\Gamma(\mathbf{K}) \sim \ln\delta - \frac{1}{2}w^2\mathbf{K}^2. \quad (29)$$

Here

$$\delta = \int \exp(-m'r^2/2\beta\hbar^2) p(r) 4\pi r^2 dr, \quad (30)$$

and

$$w^2\delta = \frac{1}{3} \int r^2 \exp(-m'r^2/2\beta\hbar^2) p(r) 4\pi r^2 dr. \quad (31)$$

Then for large  $s$ , asymptotically,

$$f_s \sim V\delta^s \int \exp(-\frac{1}{2}sw^2\mathbf{K}^2) d\mathbf{K} (2\pi)^{-3} = V\Delta\delta^s/s^{\frac{3}{2}}, \quad (32)$$

with  $\Delta = (2\pi w^2)^{-\frac{3}{2}}$ . If we use this asymptotic form for all  $s > 1$ , we make errors for the first few terms. But the transition occurs because of the character of the convergence of the series for large  $s$ . Therefore the predicted character of the transition may be found by studying the sums (21), (22) with the asymptotic form (32) for  $f_s$ . For example, the  $\bar{N}/V$  sum is [putting  $p(0)=0$ ]

$$\bar{N}/V = \Delta \sum_{s=1} (\delta x)^s / s^{\frac{3}{2}} + (1 - \Delta\delta)x, \quad (33)$$

and the expression for  $B$  is

$$-B = kTV[\Delta \sum_{s=1} (\delta x)^s / s^{5/2} + (1 - \Delta\delta)x]. \quad (34)$$

The same situation exists here as for the ideal gas case. The sum in (33) cannot exceed 2.612 (for  $x=1/\delta$ ) and  $2.612\Delta + (1 - \Delta\delta)/\delta$  may be less than the actual  $\bar{N}/V$  desired. This will not occur for high temperature ( $\delta$  small), but on lowering  $T$  the difficulty suddenly sets in.

What one must do, as is well known,<sup>4</sup> is to note that the  $d\mathbf{K}$  integral in (32) is really a sum over the values of  $\mathbf{K}$  which fit in the box of volume  $V$ . The lowest state ( $\mathbf{K}=0$ , using running waves) is distant  $d\mathbf{K} = (2\pi)^3/V$  from the next. It suffices to sum on this one and integrate the others. Thus we should add a factor  $1 + (2\pi)^3 V^{-1} \delta(\mathbf{K})$  to the integrand of (32),<sup>13</sup> so that the sum is more closely

$$f_s = V\Delta\delta^s s^{-\frac{3}{2}} + \delta^s, \quad (32a)$$

and (33) becomes

$$\bar{N}/V = \Delta \sum_{s=1} (\delta x)^s s^{-\frac{3}{2}} + (1 - \Delta\delta)x + V^{-1}(1 - \delta x)^{-1}. \quad (33a)$$

Now  $\delta x$  can become very nearly 1, to order  $1/V$  (e.g., put  $\delta x = 1 - 1/gV$ ) and the sum in this region is  $\bar{N}/V = 2.612\Delta + (1 - \Delta\delta)\delta^{-1} + g$  which can be satisfied for proper choice of  $g$ . For higher temperatures (smaller  $\delta$ ) we can use the original expansion (33). This change in

<sup>13</sup> The validity of this procedure has sometimes been questioned. A method of arriving at the result (32') which avoids the use of this procedure is given in the Appendix.



behavior for the two regions of  $T$  reflects in  $B$  (34) as a phase transition. This shows the existence of the transition. As temperature falls  $\delta$  in (30) rises without limit. Since  $\rho(r) \sim 1$  for large  $r$ , as  $\beta$  rises  $\delta$  eventually behaves as  $(2\pi\beta\hbar^2/m')^3$ . Likewise, eventually  $w^2$  becomes  $\beta\hbar^2/m'$ , so that  $\Delta = (2\pi w^2)^{-3}$  approaches  $\delta^{-1}$ . Therefore  $2.612\Delta + (1 - \Delta\delta)\delta^{-1}$  tends toward zero (as  $T^3$ ) and must eventually fall below  $N/V$ . Actually by putting in very reasonable values for the parameters, it is easy to obtain a transition at about the right place.

If we do not use the asymptotic form (29) for  $\Gamma$ , nothing is fundamentally changed. In (28) the integral on  $\mathbf{K}$  should have its factor  $1 + (2\pi)^3 V^{-1} \delta(\mathbf{K})$  as explained, and the equation to determine  $x$  becomes (calling  $\Gamma(0) = \delta$ )

$$\bar{N}/V = \int [1 - x\Gamma(\mathbf{K})]^{-1} d\mathbf{K} (2\pi)^{-3} + [1 - \rho(0)]x + V^{-1}(1 - \delta x)^{-1}. \quad (36)$$

Above the transition the last term is not required. Below,  $\delta x = 1 - 1/gV$  and  $\bar{N}/V = \int [1 - \delta^{-1}\Gamma(\mathbf{K})]^{-1} d\mathbf{K} \times (2\pi)^{-3} + [1 - \rho(0)]\delta^{-1} + g$ , with analogous expressions for  $B$ .

#### RELATION TO EXPERIMENT

It would not be worth while to substitute numbers in these expressions as too many small approximations have been made. In addition, it is difficult to estimate  $m'$ . The function  $\rho(r)$  might be calculated roughly for the smaller  $r$  by using the corresponding function required for the quantum-mechanical second virial coefficient. This assumed that any two colliding atoms are independent of the others. Alternatively,  $\rho(r)$  could be taken experimentally from x-ray or neutron scattering data.

On the other hand, the formulas (27), (28) have even qualitative faults when compared to experiment. They predict that helium, like the ideal Bose gas, would show a third-order transition (specific heat continuous but discontinuous slope). The experimental data<sup>1</sup> do not agree (apparently the specific heat is discontinuous). This disagreement probably stems from the neglected geometrical correlations among the rings.<sup>14</sup>

In order to study this in greater detail, it was thought that a careful study of the situation at extremely low temperature would be of value. The character of the transition must depend on an accurate description of the phase into which the liquid changes as it cools past the  $\lambda$  point. This phase is represented in an extreme form near absolute zero. In this region Eqs. (27), (28) fail very badly. They predict a specific heat varying as  $T^3$  while experimentally it varies as  $T^2$ . In the following paper<sup>6</sup> we shall see that this discrepancy is a result

<sup>14</sup> Assumptions about the temperature variation of the parameters  $m$ ,  $\rho(r)$ ,  $K_\beta$  cannot alter the order of the predicted transition. The effect of modifying (7) in the manner indicated in footnote 11 is discussed in the paper to follow. The change, if anything, is in the wrong direction.

of the error produced by the geometrical approximations made in passing from (7) to (27), (28). The approximations here permit much larger fluctuations in density than is available to the true liquid, and this qualitatively alters the behavior of the specific heat at low temperature.

The experimental specific heat curve shows<sup>1</sup> a slight rise in the He I region as the  $\lambda$  point is approached from above. This is also a property of our expression (34). In this region only a few chains are starting to form. The restriction that no atom may be in more than one chain is not yet of importance. Therefore, in this region our geometrical approximations should be valid. The very least we can say, then, is that the rapid rise in specific heat of He I with falling temperature is completely explained.

#### SUMMARY

Starting with an exact quantum-mechanical partition function, we have derived an approximate expression [Eq. (7)] which should be qualitatively accurate. It has been shown to be in agreement with experiment in predicting a transition which depends in an essential manner on the statistics.

Further mathematical approximations have not been accurate enough to show whether (7) will correctly predict the order of the transition and the temperature dependence of the specific heat near absolute zero. They do suffice at high temperatures to show the rise in specific heat of He I as the transition is approached.

It is proposed that a more careful analysis of (7) would show more complete agreement with the experimental facts.<sup>1</sup> In the next paper<sup>6</sup> the situation near absolute zero is studied in detail, and it is found that (7) (corrected for the effect mentioned in footnote 11) very likely does predict the correct behavior in this region.

The physical idea which plays a central role is that in a quantum-mechanical Bose liquid the atoms behave in some respects like free particles.

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#### APPENDIX

We give here another derivation of the approximate partition function (33a), (34). It has the advantage of showing more clearly the origin of the transition. We will treat it in a very approximate manner as we have already given more complete formulas. (It is the first derivation that the author made.)

Near the transition only permutations involving shifts of each atom to the position of its neighbor, at some mean distance  $d$ , are important. The exponential factor from such a shift is  $\gamma = \exp(-m'd^2/2\beta\hbar^2)$ .

Each permutation can be broken into cycles. We now only count those cycles for which all atoms are adjacent,

forming a closed chain or ring. If a ring contains  $s$  atoms, its contribution is  $y^s$ . If we have  $n_2$  rings of 2 atoms,  $n_3$  of 3 atoms, etc., the contribution is  $y^{2n_2+3n_3+\dots}$ . The part of the partition function which determines the transition is then

$$q = \sum G(n_2, n_3, \dots) y^{2n_2+3n_3+\dots} \tag{1-A}$$

where  $G(n_2, n_3, \dots)$  is the number of ways we can lay out polygons,  $n_2$  of 2 sides,  $n_3$  triangles, etc., on the configuration—the sides of the polygons consisting of lines joining nearest neighbors (length  $d$ ). The sum is restricted for the number of single atoms  $n_1 = N - \sum_{s=2} n_s$  must not be negative.

Here again we shall make the error of neglecting the geometrical interference of polygons due to the restriction that each atom be a vertex of only one polygon. We shall include the competition among the polygons for the total number of available atoms by saying that there is an average probability  $t$  that any site is unoccupied. This  $t$  will later be determined so that the average number of atoms occupied is  $\bar{N} = N$ . (This can be done in detail by steepest descents, but it amounts to the same thing.) Therefore, instead of  $q$  we calculate  $t^N q$  and call it  $\exp(-B/kT)$ .

The polygons can now be considered as independent. If  $R_s$  is the total number of  $s$  gons that can be drawn on the configuration, each  $s$  gon can be chosen in  $R_s$  ways, and all  $n_s$  of them in  $R_s^{n_s}/n_s!$  ways. The  $n_1$  single atoms can be chosen in  $N^{n_1}/n_1!$  ways. Thus

$$\begin{aligned} \exp(-B/kT) &= \sum_{n_1} \prod_{s=2} R_s^{n_s} (n_s!)^{-1} y^{s n_s} t^{s n_s} N^{n_1} (n_1!)^{-1} \\ &= \exp[Nt + \sum_{s=2} R_s (ty)^s], \end{aligned}$$

or

$$-B = kT [Nt + \sum_{s=2} R_s (ty)^s]. \tag{2-A}$$

The average number of atoms  $\bar{N}$  used in sites is  $t(\partial q/\partial t)q^{-1}$ , so we have

$$\bar{N} = Nt + \sum_{s=2} s R_s (ty)^s. \tag{3-A}$$

Now we calculate  $R_s$ . We call  $h_s$  the total number of ways that we can, starting at an atom and making successive steps to adjacent atoms, return after exactly  $s$  steps. This forms a closed  $s$  gon. We may start at any of the  $N$  atoms. The total  $Nh_s$  measure the total number of  $s$  gons, but counts each  $s$  times (for you could start at any of the  $s$  atoms as the "first"). Hence we have,  $R_s = Nh_s/s$ , and

$$-B = kTN [t + \sum_{s=2} h_s (ty)^s / s], \tag{4-A}$$

where  $t$  is a parameter determined from  $\bar{N} = N$ , in (3-A), or

$$1 = t + \sum_{s=2} h_s (ty)^s. \tag{5-A}$$

We shall bother to determine the form of  $h_s$  for large  $s$  only. In the random walk, each step is length  $d$ , and may be made to any of the adjacent atoms, which we shall say are  $l$  in number, on the average. Each step can be made in  $l$  ways, the entire  $s$  steps in  $l^s$  ways. There are  $l^s$  walks in total but only a certain number return to the origin. As is well known, the probability of being at a given point, per unit volume, radius  $r$  from the starting point is

$$(2\pi d^2 s/3)^{-\frac{3}{2}} \exp(-3r^2/2sd^2) = \Delta s^{-\frac{3}{2}} \exp(-r^2/2sw^2),$$

putting  $w^2 = d^2/3$  and  $\Delta = (2\pi w^2)^{-\frac{3}{2}}$ . The chance we are back at the original atom (that is, within a space of one atomic volume  $V_A = V/N$  near the origin) is  $V_A \Delta s^{-\frac{3}{2}}$ , so that

$$h_s = V_A \Delta s^{-\frac{3}{2}} l^s.$$

The reason for the dependence on the  $s^{-\frac{3}{2}}$  is easy to see. After  $s$  steps we have wandered out to a mean radius of order  $s^{\frac{1}{2}}$ , or over a volume  $s^{\frac{3}{2}}$ . Hence, the chance that in this volume we are back at the original atom varies as  $s^{-\frac{3}{2}}$ . This is correct except for enormous chains  $s \gtrsim N^{\frac{2}{3}}$ , which are long enough to wander all over the liquid. Then the available volume no longer increases. The chance that one is back at the original atom instead of one of the other roughly equally likely atoms is  $1/N$ . For such large  $s$ , then,  $h_s = l^s/N$ . The formula,

$$h_s = (V_A \Delta s^{-\frac{3}{2}} + 1/N) l^s, \tag{6-A}$$

takes care of both cases, because for small  $s$  the first term dominates, and for large  $s$  the second takes over, as it should.<sup>15</sup> Substitution into (3-A) gives

$$1 = t + V_A \Delta \sum_{s=2} (lyt)^s s^{-\frac{3}{2}} + N^{-1} (1 - lyt)^{-1}. \tag{7-A}$$

This may be compared to (33a). To do so, note that our interpretation of  $3w^2$  as the mean square length of a step agrees with (31). Further  $ly$  is the number of atoms available per step,  $l$ , multiplied by the weight  $y = \exp(-m'd^2/2\beta\hbar^2)$ . In the more general case it becomes  $\delta/V_A$  as an inspection of (30), the expression for  $\delta$ , shows. Finally, the parameter  $t$  can as well be called  $V_A x$ , and Eq. (7-A) is seen to be identical to (33a) (times  $V_A$ ). Likewise, substitution of (6-A) into (4-A) gives the corresponding equation (34) for  $B$ .

This derivation throws some light on the mathe-

<sup>15</sup> According to (6-A) the chance to return is higher than for an infinite medium. It might be objected that there should be fewer paths available when there are a finite number of atoms in an enclosed space. What we have done corresponds to working with a periodic boundary condition, and the excess arises from the chance to return to one of the images of the origin, instead of to the origin itself. With the more physical boundary condition—that paths cannot cross the liquid surface—the total number of paths for high  $s$  is not  $l^s$ , but is reduced. It becomes eventually proportional to  $e^{-\epsilon l^s}$ , where  $\epsilon$  is a very small number of order  $N^{-\frac{1}{3}}$ . It makes no essential difference in the result. In the momentum representation of the text it corresponds to taking the lowest state to have a wavelength controlled by the size of the box. I am indebted to Herman Kahn for pointing out this possible objection to (6-A).

matical "cause" of the transition. As  $T$  falls  $\gamma$  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).<sup>16</sup> Therefore there can be no doubt

<sup>16</sup> 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

TISZA<sup>1</sup> 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 ( $\lambda$  point) the liquid, now He I, contains no more superfluid.

Landau<sup>2</sup> 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  $\Delta$  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.<sup>3</sup> 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.

<sup>1</sup> 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).

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

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