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The Nature of Higher-Order Phase Transitions with Application to Liquid Helium*

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A general discussion is given of the relation between transitions of various order, especially those which are not concerned with solid lattices. It is shown that third-order transitions bear much the same relation to anomalous first-order transitions as second-order transitions bear to ordinary first-order transitions. The conditions under which higher-order transitions can occur are considered, and it is shown that they may be associated with a dispersed phase. If the transition is second order, the dispersed phase must undergo a transition in itself. The ideas concerning second-order transitions are applied to the λ transition in liquid helium. An argument is given, based on energetic grounds, which indicates that the superfluid in liquid helium is in the form of clusters which are separated in ordinary space as well as in momentum space. If this view is correct, the λ transition corresponds to the appearance of much larger clusters, essentially marking the beginning of long-range orders. It is shown that the Bose-Einstein statistics is quite essential for the formation of the clusters; they cannot appear in He^3, and no λ transition is to be expected in He^3. Finally, a possible explanation is given for Taconis' hypothesis that He^3 is not soluble in the superfluid part of He^4.

1. INTRODUCTION

The λ-point transformation in liquid helium seems to be connected in some way with the Bose-Einstein condensation, as originally suggested by London, and it has been frequently assumed that a qualitative understanding of these phenomena may be obtained if the liquid forces are ignored completely, except insofar as they result in an effective pressure which holds the atoms together in the liquid phase. There are, however, quite definite differences between the behavior of liquid helium and that of the Bose-Einstein gas, which may perhaps best be seen by considering the character of the isotherms. The nature of the isotherms for a Bose-Einstein gas is indicated by Fig. 1. The transition is an anomalous first-order transition, in the nomenclature of Mayer and Streeter,[1] the effective volume of the condensed phase being zero.[2] On the other hand, the transition in liquid helium is second order, and the isotherms are schematically presented in Fig. 2, which takes into account the negative value of the thermal expansion coefficient, $(\partial V/\partial T)_p$, and of the pressure coefficient, $(\partial p/\partial T)_V$, below the λ point. In the latter figure, the effect of the liquid forces is clearly shown. Certainly, considerable modification of the simple Bose-Einstein transformation will be needed before it can be used as a prototype for the transition in liquid helium.

However, since the intermolecular forces depend on the volume, it might be supposed that if the volume is held constant the intermolecular forces would be at least approximately constant, and so perhaps would not contribute to the specific heat at constant volume, C_v. Thus it is suggested that we compare the ideal Bose-Einstein gas with liquid helium at constant volume. This is what is usually done and this procedure has very recently received some theoretical backing, since

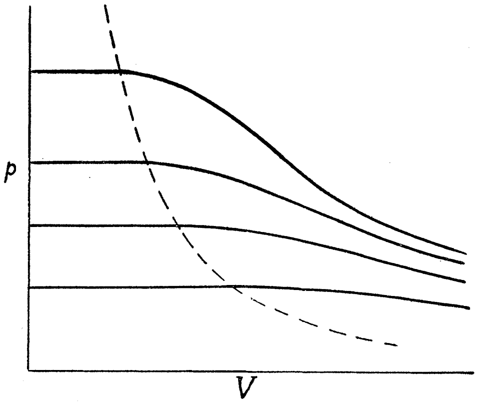

Fig. 1. Isotherms for a Bose-Einstein gas. The broken line is the transition line.

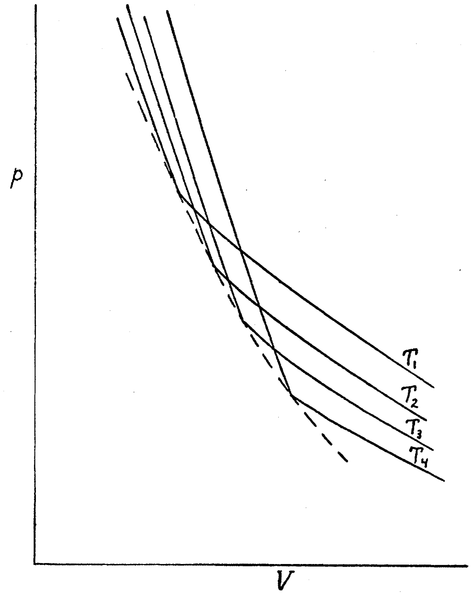

Fig. 2. Isotherms (schematic) for liquid helium. $T_4 > T_3 > T_2 > T_1$. The broken line is the λ line.

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* Work supported by the U. S. Office of Naval Research.

[1] J. E. Mayer and S. F. Streeter, J. Chem. Phys. 7, 1019 (1939).

[2] B. Kahn and G. E. Uhlenbeck, Physica 5, 399 (1938).

work of Feynman[3] has indicated that a λ transition should occur even though there are strong interatomic forces. Feynman's general argument is that the motion of the atoms is not sufficiently altered by the interatomic forces but that the general character of the transition remains unaltered. He effectively assumes that the attractive forces do not have any specific effect, only the general effect of holding the atoms together. Within the liquid, the atoms would act much like hard spheres. Feynman then finds that the λ transition should be like the transition in the Bose-Einstein gas, in that there should be no break in C_v, but only a change in slope. Actually, of course, C_v shows a break rather than a mere change in slope, and it is quite possible that this arises from the attractive forces. It was shown by Bijl, de Boer, and Michels[4] that such a break in C_v would appear if the lowest energy level into which the molecules "condense" were lower compared with the higher energy levels than would be the case with the ideal gas, this lowering of the lowest energy being produced by the liquid forces.

Under the circumstances it may be profitable to consider the difference between the λ phenomenon in helium and the transition in an ideal Bose-Einstein gas in the light of the available experimental data, still bearing in mind, however, the great probability that the phenomena are related. The first step will be to consider the general characteristics of second-order transitions, especially those which are not concerned with solid lattices, and in particular to note some of the relationships between transitions of various types.

Before turning to this development, however, we wish to set down the Keesom-Ehrenfest equation, for future reference, in the following form:

$$\Delta C_p = (dp/dT)T\Delta(\partial V/\partial T)_p. \qquad (1)$$

Here C_p is the molal heat capacity at constant pressure, the total derivative dp/dT refers to the change of pressure with temperature along the second-order transition line, V is the molal volume and Δ indicates that the value of quantity on the low-temperature side of the transition is to be subtracted from the value just across the transition line on the high-temperature side.

We can also write

$$\Delta C_v = -(dV/dT)T\Delta(\partial p/\partial T)_V. \qquad (2)$$

This equation is implied but not actually written down by Semenchenko,[5] and can be derived by considering the entropy S as a function of V and T, writing

$$\begin{aligned} dS &= (\partial S/\partial T)_V dT + (\partial S/\partial V)_T dV \\ &= (C_v/T)dT + (\partial p/\partial T)_V dV. \end{aligned}$$

Now noting that S does not change at a second-order transition, so that along the transition line,

$$d\Delta S = (\Delta C_v/T)dT + \Delta(\partial p/\partial T)_V dV = 0,$$

we see that Eq. (2) follows immediately.

For helium, we may note that application of Eqs. (1) and (2) makes it highly probable that C_p and C_v actually have definite breaks rather than merely sharp maxima at the λ point. For both $(\partial V/\partial T)_p$ and $(\partial p/\partial T)_V$ actually change sign at the λ-point, and there is no evidence to indicate that they do not change suddenly. In fact, they appear to increase in magnitude as the λ point is approached from below, and not to change rapidly as it is approached from above.[6] Though it is impossible to prove a point of this sort absolutely, the evidence is thus exceedingly good that we are dealing with a true second-order transition.

2. GENERAL DISCUSSION OF PHASE TRANSITIONS OF VARIOUS ORDERS

Gorter[7] has pointed out that if we cooled a vapor in a closed, opaque container of constant volume, we would find a discontinuity in the slope, $(\partial p/\partial T)_V$, of the pressure-temperature curve when we reached the point of condensation. If we were unaware of the separation of phases, we might infer that a second-order transition had occurred. If we tried the experiment with systems of different density we could find dp/dT and dV/dT for the transition, and it would, in fact, be entirely proper to apply Eqs. (1) and (2). However, we would also find, that, in what we know to be the two-phase region, $(\partial p/\partial V)_T=0$. Since $(\partial p/\partial T)_V$ does not vanish, this means that $(\partial T/\partial V)_p=0$ or $(\partial V/\partial T)_p$ is infinite. C_p, which, in the transition region, includes the heat effects arising from evaporation or condensation, also becomes infinite, so that dp/dT cannot be determined from Eq. (1). However, we can consider this to be a limiting case in the application of Eq. (1). If $(\partial p/\partial V)_T$ in the two-phase region were very small but not zero, $(\partial V/\partial T)_p$ would be very large but not infinite, as would C_p. We could then, in comparison, neglect $(\partial V/\partial T)_p$ and C_p for the one-phase region, and write Eq. (1) as

$$C_p = (dp/dT)T(\partial V/\partial T)_p,$$

where C_p and $(\partial V/\partial T)_p$ are for the two-phase region. Since $C_p = T(\partial S/\partial T)_p$ we see that this yields

$$dp/dT = (\partial S/\partial V)_p.$$

In the limit, where $(\partial p/\partial V)_T=0$, this is

$$dp/dT = (\partial S/\partial V)_T.$$

Interpreting the right-hand side of this equation in terms of the behavior of the two coexisting phases, we see that $(\partial S/\partial V)_T = \Delta S/\Delta V$, and we recover the Clapeyron equation.

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[3] R. P. Feynman, Phys. Rev. **91**, 1291 (1953).

[4] Bijl, de Boer, and Michels, Physica 8, 655 (1941).

[5] V. K. Semenchenko, Zhur. Fiz. Khim. **21**, 1461 (1947).

[6] W. H. Keesom, *Helium* (Elsevier Publishing Company, New York, 1942), Sec. 4.7.

[7] See reference 6, p. 259.

In the case of Eq. (2) there is no difficulty in applying the equation when $(\partial p/\partial V)_T=0$, for, as we have noted $(\partial p/\partial T)_V$ remains finite, and so, unless dV/dT is infinite, C_v will remain finite also.

This discussion will indicate the desirability of considering a little more closely the relation between first- and second-order transitions. Let us suppose that we have a transition which resembles a first-order transition, except that the slope of an isotherm in the transition region is not quite zero. Then the isotherms will appear as shown in Fig. 3. This represents a set of ordinary second-order transitions, or rather two sets of such transitions, one set on the left-hand branch of the transition curve and the other on the right-hand branch. Is there any way that we can still interpret the transition at the right-hand branch (vapor) as the formation of some of the left-hand phase (liquid)? Suppose that the Gibbs free energy of the vapor at some given temperature is G_g and that it is at a pressure p_g. The free energy of liquid at pressure p_l is

$$G_g+\int_{p_g}^{p_l} Vdp.$$

The free energy of liquid at p_g is

$$G_l(p_g)=G_g+\int_{p_g}^{p_l} Vdp-\int_{p_g}^{p_l} V_l dp. \tag{3}$$

Since the average value of V involved in the first integral is greater than the average value of V_l in the second, we see that

$$G_l(p_g)>G_g. \tag{4}$$

Of course this is why an ordinary liquid phase does not appear at the transition line. Unless some device can be found to lower the free energy of the liquid, the interpretation we have proposed cannot stand. However we know that if the liquid is dispersed in the gas its entropy will be increased and its enthalpy *may* be lowered. Both effects can contribute to the lowering of the chemical potential of the liquid so as to bring it down to the chemical potential of the gas.[8]

If we approach the left-hand transition curve from the liquid side we find, in an entirely similar manner,

$$G_g(p_l)=G_l+\int_{p_l}^{p_g} Vdp-\int_{p_l}^{p_g} V_g dp. \tag{5}$$

In this case the integrals are negative since $p_g<p_l$ and the average value of V_g will be expected to be greater than the average value of V, since the compressibility of the gas is less than that of the mixture of gas and liquid. Therefore, in this case,

$$G_g(p_l)>G_l. \tag{6}$$

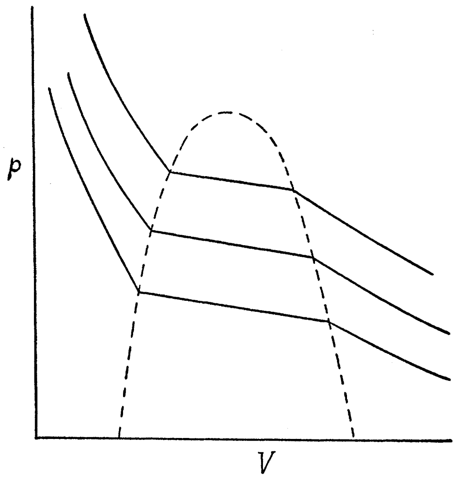

FIG. 3. Isotherms, illustrating a possible type of second-order transition. The broken line is the transition line.

Again we are led to the idea of a dispersed phase, this time gas in liquid. Of course a dispersion of gas in liquid could merge gradually, as the proportion of gas increased, into a dispersion of liquid in gas.

If there were no discontinuity in the slope $(\partial p/\partial V)_T$ of the isotherms at the transition line of Fig. 3, but only a discontinuity in $(\partial^2 p/\partial V^2)_T$, then the transition would be third order instead of second order. It is seen that when $(\partial p/\partial V)_T$ in the transition region within the transition line approaches zero the third-order transformation approaches an anomalous first-order transition. In this case $(\partial V/\partial T)_p$ and C_p increase without limit and become infinite at the transition line, but $(\partial p/\partial T)_V$ and C_v [by Eq. (2)] remain continuous and finite. However, since $(\partial p/\partial T)_V$ is constant in the transition region in the anomalous first-order transition, the rates of change of $(\partial p/\partial T)_V$ and, hence, of C_v, change abruptly. This is just the situation in the Einstein-Bose transition. The Clapeyron equation in its usual form will hold for the anomalous first-order transition, as for the ordinary first-order transition.

The relation between the third-order transition and the anomalous first order is exactly similar to the relation between the second-order transition and the ordinary first order, and if the third-order transition is to be described in terms of two phases, as we described the second-order one, we must again think of one phase dispersed in the other.

When a first-order transition takes place certain pretransition phenomena will in general occur. Thus, when a vapor is compressed isothermally clusters of molecules will appear.[9] The larger clusters will resemble the liquid but will have surface free energy. The surface free energy will tend to favor coalescence of clusters, but the entropy effect will tend to favor separation into

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[8] Compare V. K. Semenchenko, Zhur. Fiz. Khim. 21, 1461 (1947).

[9] J. Frenkel, J. Chem. Phys. 7, 200, 538 (1939); W. Band, J. Chem. Phys. 7, 324, 927 (1939).

smaller clusters.[10] At high dilution the entropy effect will be more important, and there will be but few clusters formed. At a certain stage in the compression these two effects will balance each other for large clusters, and further compression will result in the sudden onset of condensation.

If the surface tension is zero or negative this sudden condensation will not occur. It might off-hand be expected that in this case there would no longer be any tendency to form clusters. However, it seems probable that, at least in the case of compression just above the critical point, there is cluster formation; although the surface free energy is negative and the surface tends to increase, so that a cluster becomes porous and open, there is a limit to this process because of dependence of the surface free energy on the curvature of the surface. Coalescence of the clusters, however, is never favored, and will not occur until the free volume of large clusters is reduced to zero. The size of the clusters simply increases gradually up to this point, and then there is just one big, but spongy cluster. This can be further compressed, but with a somewhat different law of compression. However, it appears from a discussion of this case,[11] and especially because the individual clusters are already subject to compression even before coalescence so that the whole process takes place gradually, that $(\partial p/\partial V)_T$ will probably be continuous, though $(\partial^2 p/\partial V^2)_T$ may very well not be. Except in the special case when the surface tension is zero $(\partial p/\partial V)_T$ should not become zero, so this situation corresponds to the third-order transition. It will be seen that the spongy coalesced cluster is really a dispersion, but depends for stabilization on its negative surface tension, as well as upon its configurational entropy, which arises because it does not have a fixed shape. Indeed, the two factors are closely interrelated, and one can say that the fact that the convoluted surfaces of the dispersed phase are mobile adds to the surface entropy.

To have a second-order transition an intermediate situation must exist.[12] The tendency for dispersal must exist, as though the system had a negative or at least near-zero surface tension. On the other hand, there must also be some special stability of a condensed phase, which is in this case an extended dispersed phase with configuration entropy. Thus clusters would be formed on compression, but they would not be compact, but rather disperse clusters. But on further compression, as their entropy of translation as a whole decreased so that the entropy of coagulation would not be so great, there would begin to appear a very large cluster, a condensed but still dispersed phase, as though for this process of coalescence the surface tension were positive. This large cluster is the "condensed phase." The question which now arises is why this condensed phase does not continue to form on compression without change of free energy, until it fills the volume and encompasses all the dispersed clusters. If this happened the transition would have a, perhaps small but nonetheless real, first-order region with a finite latent heat. The answer is that the large cluster described still has an entropy of mixing, for it is not confined to any one part of the system, in essential contrast to the condensed phase in an ordinary condensation. Thus the coalescence of the clusters really occurs simply when the point arises at which much larger, but not "infinite" or macroscopic clusters reach as low a free energy as the already large, but not *that* large (intermediate sized) clusters which were previously present. The sudden appearance of clusters of a much larger size signals the second-order transition, after which further compression results in the further building up of the much larger clusters, both by having them grow at the expense of the intermediate clusters, and ultimately (and to some extent simultaneously) at the expense of the vapor molecules, i.e., molecules which are not combined into clusters, or which are present in very small clusters. Since the intrinsic free energy involved in going from intermediate clusters to very large clusters is certain to be very small, it is not to be expected that such a transition would occur until the concentration of the intermediate clusters was sufficiently large so that their free volume would be greatly restricted.

3. THE λ TRANSITION IN LIQUID HELIUM

We shall base our discussion of liquid helium upon the fundamental assumption that the λ phenomenon depends upon some of the atoms going into a low-energy state, and that the superfluid properties result from these atoms. These atoms, then, essentially form the superfluid, and in using the language of the two-fluid hypothesis of Tisza we shall assume that it has some actual physical significance. With this fairly definite picture in mind we desire to inquire how it can be fitted into the general picture of a second-order transition, as presented in the preceding section.

If, below the normal λ temperature, we start with helium I at a high pressure which is gradually lowered, we will eventually reach the transition curve where the change to helium II occurs. The situation is not very different from that which we find at the left-hand side of Fig. 3. The transition is, as we have seen, presumably a second-order one; therefore the pressure will continue to decrease after it occurs. In terms of the two-fluid theory we will say that superfluid appears at the transition, or at least that it there first takes a form in which the superfluid properties become evident, and the amount of superfluid continues to increase as the pressure is lowered, until at some pressure (which may be negative but practically is around zero pressure

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[10] See O. K. Rice, J. Phys. and Colloid. Chem. **54**, 1293 (1950).

[11] O. K. Rice, J. Chem. Phys. **15**, 314 (1947); *Thermodynamics and Physics of Matter* (Vol. I of *High Speed Aeronautics and Jet Propulsion*) (Princeton University Press, Princeton, to be published), Sec. 7, Art. 6.

[12] There are of course other ways that second-order transitions can occur, especially in solid lattice.

below 1°K) the system consists almost entirely of superfluid.

Though the isobars given by Keesom[6] indicate $-(\partial p/\partial V)_T$ decreases discontinuously at the transition line, the situation at the other end of the transition (i.e., corresponding to the right-hand branch of Fig. 3) is not so clear since there is no definite sign of another transition. However, the slope of the isobars $(\partial \rho/\partial T)_p$ (where ρ is the density) becomes practically zero around 1°K where presumably the liquid has become pure superfluid. We therefore conclude that the properties of the superfluid do not depend appreciably on the temperature, but only upon the pressure or density. Furthermore, we find that at any pressure $(\partial p/\partial V)_T$ is greater for superfluid (i.e., near 0°K) than it is where there is a mixture of superfluid and normal fluid near the λ-transition pressure. Also V is larger for superfluid than for normal fluid. Thus the conditions by which the inequality (6) is derived from Eq. (5) (with the superfluid taking the place of the gas and the normal fluid taking the place of the liquid) are fulfilled. Thus, where the transition occurs, the superfluid must have a lower chemical potential than pure superfluid would have. In other words, in terms of partial molal quantities (with subscript s referring to superfluid and subscript λ referring to the condition at the transition line) we must have either

$$\bar{S}_{s,\lambda}>S_s, \tag{7}$$

or

$$\bar{H}_{s,\lambda}<H_s, \tag{8}$$

or both, where the quantities on the right-hand side refer to the pure superfluid. From consideration of the conditions of equilibrium in the two-fluid theory, I have already come to these conclusions, and I have developed the thermodynamics of liquid helium[13] on the basis of the assumption $\bar{S}_{s,\lambda}>S_s$ and $\bar{H}_{s,\lambda}=H_s$, which implies an entropy of mixing, while Gorter[14] has developed the thermodynamics on assumptions which are equivalent to taking $\bar{S}_{s,\lambda}=S_s$ and $\bar{H}_{s,\lambda}<H_s$, implying an enthalpy of mixing.

This is a difference between the transition in liquid helium and the transition in the Bose-Einstein gas which is of some importance, and should be taken into account in any theory of liquid helium. It arises because of the fact that the transition in helium is not first-order, at least over an observable range of thermodynamic conditions, whereas that in the Bose-Einstein gas is. If there is to be an entropy of mixing, it would seem that some separation in ordinary space of superfluid and normal fluid, such as I have already suggested[13] would be necessary. This would be in general accord with the idea of dispersion, mentioned in Sec. 2 above. The possibility that helium II involves a dispersion has also been suggested by Semenchenko.[8,15] On the other hand, it might be possible to avoid the separation in ordinary space if the other alternative, $\bar{S}_{s,\lambda}=S_s$ and $\bar{H}_{s,\lambda}<H_s$ is the correct one. The Bose-Einstein transition is a unique one, in that the condensed state, i.e., the lowest energy level, though it apparently has an effective volume equal to zero, actually is spread out over the entire containing volume. It is, perhaps, conceivable that the lowest energy level would be affected by the molecular interactions in such a way that it was lower when most of the atoms were in excited states than when most of them were in the lowest energy level. Certain calculations[16] have been made which are based on symmetrization of free particles or Bloch-type wave functions. These indicate that if two particles are in the same energy level they are less likely to be close together than if they are in different energy levels. Depending upon whether one supposes that the repulsive or attractive forces are more important one will conclude that the mutual energy of the two particles will be relatively lowered or raised by the interatomic forces when they are in the same energy level. These conclusions are based, however, upon the general ideas of small perturbation theory.

Since the strong repulsive forces can scarcely be handled by small perturbation theory, and since they will profoundly affect the wave function, it seems to me better to approach the problem by the standard method of handling a two-particle problem, separating off the coordinates of the center of gravity, and considering then the relative radial or vibrational motion and the relative rotational motion. In the case of helium the attractive forces are relatively weak and it seems quite likely that one or two degrees above the λ point the atoms are only rarely held in any fixed position, the motion being mostly translational. This translational motion is superimposed upon a large zero-point energy; there is a potential energy well near every helium atom, but its neighbors have sufficient energy to escape from it. The unbalanced forces at the edge of the liquid, however, are sufficient to keep the average atom from escaping, so that there is a nonzero energy of evaporation. For any helium atom to go into its lowest energy level actually involves a cooperative phenomenon which

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[13] O. K. Rice, Phys. Rev. **76**, 1701 (1949); **79**, 1024 (1950).

[14] C. J. Gorter, Physica **15**, 523 (1949).

[15] V. K. Semenchenko, Doklady Akad. Nauk S.S.S.R. **74**, 335 (1950). Other writers have developed theories which involve clusters of one sort or another, e.g., H. N. V. Temperley, Proc. Phys. Soc. (London) **A65**, 619 (1952); M. Toda, Progr. Theoret. Phys. (Japan) **6**, 458 (1951). The latter assumes that the excitations in helium above 1°K consist of groups of about eight atoms in a solid-like cluster, which would involve separation in ordinary space. This is a possible type of excitation around 1°K; however, Toda assumes that the λ point occurs when the liquid consists entirely of such "molecules," and in such dense packing they would not have the statistical properties ascribed to them, so this can scarcely be a theory of the λ point. The idea that the excitation in liquid helium is connected with "molecules" is also suggested by the interesting analysis of T. Matsubara, Progr. Theoret. Phys. (Japan) **6**, 714 (1951). However, since he neglects interactions between the molecules, it would seem that the same difficulties would appear at the λ point.

[16] N. F. Mott, Phil. Mag. **40**, 61 (1949).

requires the interaction of more than one atom. Thus it takes at least two atoms to abandon their mutual translational energy for mutual vibration. Indeed, in the case of helium, it must require more than this, because the potential-energy minimum of the van der Waals attraction is hardly deep enough for there to be discrete energy levels. However, we do know that it is possible for a group of helium atoms to condense together in a lowest energy level (liquid helium at 0°K). There must be a smallest number of atoms which will do this. So in the liquid it is quite possible that a group of atoms can be firmly, though temporarily, bound together in their lowest energy level.[17] The surrounding liquid would of course be expected to alter the situation quantitatively, and the cluster would be continually exchanging atoms with neighboring portions of the liquid, either through excitation and de-excitation, or through an atom in one part of the cluster leaving while simultaneously another atom joins the group at another location. Nevertheless, the idea of low-energy clusters seems to be a reasonable speculation.

It is probably not a very good approximation to consider normal modes of vibration of such a group of atoms, as in a crystal lattice; however, such an approximation may serve to give some idea of the placing of the energy levels. In a crystal lattice if all the atoms are fixed except one, that atom would vibrate with a frequency of say, ν_0. The average value of the squares of the actual frequencies obeys the relation $\langle\nu^2\rangle_{\text{Av}}=\nu_0^2$. The greater the number of atoms cooperating in the lattice the greater the spread of frequencies. Now the maximum of the sum of all the frequencies occurs when all the frequencies are equal if the frequencies are constrained in such a way that the sum of their squares has a fixed value. Thus the interaction will lower the zero-point energy, and presumably the greater the number of cooperating atoms the lower will be the zero-point energy; furthermore, this discussion would lead to the inference that the low energy atoms will occur in spatially connected groups. In any event, it seems to be unlikely that the lowest energy level for a single atom could extend spatially throughout the vessel in the case of liquid helium, because the atoms would be scattered on account of the repulsive forces. I remarked on this some years ago,[13] and it has recently been discussed with some amplification by Ziman.[18]

It is doubtful that any calculation based on the idea of lattice vibrations could have any quantitative application to liquid helium. Nevertheless it will be of interest to attempt to calculate the difference in zero-point energy between a Debye lattice and a lattice in which all the frequencies are the same and equal to $\nu_0=(\langle\nu^2\rangle_{\text{Av}})^{\frac{1}{2}}$ (i.e., the corresponding Einstein lattice). Going from an Einstein lattice to a Debye lattice involves a spread in the frequency spectrum, something like that which occurs when additional atoms are added to a cluster. The Debye characteristic temperature Θ is given by the relation[19]

$$k\Theta=(5/3)^{\frac{1}{2}}h(\langle\nu^2\rangle_{\text{Av}})^{\frac{1}{2}}=(5/3)^{\frac{1}{2}}h\nu_0; \tag{9}$$

the zero-point energy, E_D, is given by

$$E_D=(9/8)k\Theta. \tag{10}$$

The zero point of the corresponding Einstein lattice is

$$E_E=\tfrac{3}{2}h\nu_0=\tfrac{3}{2}(\tfrac{3}{5})^{\frac{1}{2}}k\Theta=1.03E_D. \tag{11}$$

Since the zero-point energy of liquid helium is 30 to 40 cal per mole,[20] the energy of the Debye lattice is around 1 cal per mole less than that of the Einstein lattice. It is of interest that the difference is of the order of magnitude of the energy content of helium at its λ point, which is about 3 cal per mole. It appears that the energy lowering arising from cooperative vibration of the atoms can easily be great enough to furnish considerable incentive for the "condensation" of atoms in their lowest energy level into considerable groups. It is to be noted that since this energy effect increases with increasing number of superfluid atoms (which would of course result in larger conglomerates) the change of $\bar{H}_s$ with temperature would be in the opposite direction to that required by the inequality (8) and noted in the next paragraph following (8).

The attractive forces between the helium atoms clearly play quite a decisive role in the picture we have just presented. If we elected to neglect specific effects of attractive forces between individual pairs of neighboring atoms, there would be no incentive to consider modes of vibration, and the idea of clusters would not present itself. It is in this way that the present discussion differs from most previous treatments. In particular, we may mention that it seems to differ in this way from the recent work of Feynman.[3]

The above discussion would seem to lend some weight to the idea that the high specific heat just above the λ point arises from the presence of superfluid globules, which have not yet coalesced into sufficiently large clusters to bring the superfluid properties into evidence. I showed that the trend of the specific heat required that there be 60 to 80 atoms in such globules.[21] My

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[17] Phonon excitations in the clusters would, of course, not be excluded, and this could occur without breaking up the cluster, but it is known that this type of excitation is not of great importance near the λ point.

[18] J. M. Ziman, Phil. Mag. **44**, 548 (1953).

[19] See O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941).

[20] F. London, J. Phys. Chem. **43**, 49 (1939).

[21] There is perhaps other evidence for globules of superfluid above the λ point, namely, the absorption and dispersion of sound just above the λ point. A. B. Pippard, Phil. Mag. **42**, 1209 (1951), has explained this in terms of fluctuations involving large regions composed of helium II; it seems probable that this is equivalent to small regions of pure superfluid and, indeed, H. Satô, Busseiron Kenkyû **35**, 15 (1951), has attempted to explain the same phenomenon on the basis of my original theory. However, Satô found that to obtain agreement it was necessary to assume only five atoms in the globules, which is entirely too low to explain the specific heat data, and there appeared to be other quantitative discrepancies.

theory, however, could not tell much about the transition itself. It now appears likely that the transition may be described in much the same terms as we described a second-order transition at the end of Sec. 2. The globules need not be spherical clusters but could be rod-like or filament-like, or of irregular shape. Since the energy decreases with increasing cluster size, a point could be reached as the temperature is lowered (or, isothermally, as the pressure is lowered) where, rather suddenly, a much larger size of globule, or perhaps a network which extends for a long distance in at least one direction, becomes stable. If such a network is practically macroscopic in one direction, the superfluid properties would be expected to come into evidence when it appears. As the temperature (or pressure) is lowered, these extended networks would rapidly fill the liquid volume, and so grow at the expense of smaller clusters, which now have less free volume, and at the same time also grow at the expense of the normal fluid.

The formation of extended networks corresponds to the appearance of long-range order in the ordinary type of order-disorder transition. There is, of course, a considerable resemblance between our description of the helium transition, and the usual type of order-disorder process. The effective attraction of two neighboring atoms of superfluid is an essential element. A lattice approximation, however, would scarcely be applicable, and the situation also differs from that of the Ising lattice, for example, in that the interactions are not additive, the interactions depending on how many are already in the low-energy group.[22] The latter difference is quite important, for according to the picture given here, the apparent attraction between the superfluid atoms will actually effectively exist only between a certain minimum number of them, and will become stronger rather rapidly for a while as more are added to the group; then after a certain number are present the attraction will approach an asymptotic value. It is this fact which is responsible for the appearance of definite clusters. In spite of these differences, it is interesting that the specific heat of an Ising lattice with a simple cubic arrangement, according to calculations of Wakefield[23] closely parallels that of liquid helium, except very close to the transition point, where the specific heat of the Ising lattice probably becomes infinite.

In my earlier paper I estimated that only 4 or 5 percent of the helium was in the form of superfluid at the λ point. This seems rather a small fraction of locally ordered material to bring about the onset of long-distance order. For example, the quasi-chemical approximation for the simple cubic lattice gives 14 percent local order at the transition point, while Wakefield's calculations, judging from the specific heat curves, indicate even more. This point, therefore, may merit some elaboration.

Let us derive an expression for the molal heat capacity at constant pressure C_p on the basis of the two-fluid hypothesis. We will use the subscript n to denote normal fluid, the subscript s to denote superfluid. Mole fractions will be designated by x.

The molal enthalpy is given by

$$H = x_n \bar{H}_n + x_s \bar{H}_s. \tag{12}$$

To obtain C_p we differentiate this expression, remembering that $dx_s = -dx_n$, and that $x_n(\partial\bar{H}_n/\partial x_n)_T + x_s(\partial\bar{H}_s/\partial x_n)_T = 0$:

$$C_p = (\bar{H}_s - \bar{H}_n)dx_s/dT + x_n(\partial\bar{H}_n/\partial T)_{x_s} + x_s(\partial\bar{H}_s/\partial T)_{x_s}. \tag{13}$$

We have taken x_s and T as the variables, and p is, of course, always assumed constant. This is the situation, practically, when helium is heated under its own vapor pressure. If there were no superfluid, we should have $C_p = \partial\bar{H}_n/\partial T$. Therefore, subtracting this from Eq. (13), and noting that $1 - x_n = x_s$, we find for the "anomalous" part of the specific heat,

$$C_{p,a} = (\bar{H}_s - \bar{H}_n)dx_s/dT + x_s[(\partial\bar{H}_s/\partial T)_{x_s} - (\partial\bar{H}_n/\partial T)_{x_s}]. \tag{14}$$

Since x_s is small above the λ point, since $(\partial\bar{H}_s/\partial T)_{x_s}$, i.e., the specific heat of superfluid at constant mole fraction, should presumably be zero and even $(\partial\bar{H}_n/\partial T)_{x_s}$, roughly the "nonanomalous" part of the specific heat, is relatively small, we may write, approximately

$$C_{p,a} = (\bar{H}_s - \bar{H}_n)dx_s/dT. \tag{15}$$

Hence x_s at the λ point, T_λ, will be given by

$$-x_{s,\lambda} = \int_{T_\lambda}^{\infty} [C_{p,a}/(\bar{H}_s - \bar{H}_n)]dT. \tag{16}$$

On the basis of the assumption that the normal part of the specific heat was 2.2 cal deg^{-1} mole^{-1}, I estimated that $C_{p,a} = 3.0 \exp[(T_\lambda - T)/0.05]$. Substituting this in Eq. (16) and assuming that $\bar{H}_n - \bar{H}_s$ is approximately equal to the enthalpy of the liquid at the λ point, which is about 3.0 cal mole^{-1}, one finds $x_{s,\lambda} = 0.05$.

The difficulty may well lie with the estimate of the normal value of C_p, hence of $C_{p,a}$. If we examine the specific heat curves for the order-disorder case[23] we notice that they drop rapidly near the transition point, then tail off very slowly at higher temperatures. This corresponds to a decrease in the average size of the clusters as the temperature increases. The temperature coefficient for the number of clusters of any given size depends on the difference between the energy of the entire cluster and the energy of the same number of atoms without local order. This energy difference is

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[22] I. Prigogine and J. Philippot, Physica **19**, 508 (1953) have considered the λ transition to be an order-disorder phenomenon in a treatment which is based on a discussion of fluctuations, and which apparently takes no direct account of the two-fluid hypothesis. See also H. Fröhlich, Physica 4, 639 (1937).

[23] A. J. Wakefield, Proc. Cambridge Phil. Soc. **47**, 419, 799 (1951).

approximately proportional to the size of the cluster. Thus the number of small clusters will fall off much less rapidly with increasing temperature than the number of large clusters, and as the small clusters remain after the large ones disappear the specific heat decreases less rapidly. Thus, we should not really expect a simple exponential falling off of $C_{p,a}$ with T, and this suggests that our normal specific heat should have been taken somewhat lower than 2.2 cal deg^{-1} mole^{-1}. If $C_{p,a}$ were an average of 0.2 to 0.3 greater over a range of 1 to 1.5 degrees, this would make a considerable difference in the percentage of superfluid at the λ point.

4. PROPERTIES OF He^3 AND OF He^3-He^4 SOLUTIONS

Although there has been little mention thus far in the discussion of the Bose-Einstein statistics, it is easily shown that this type of statistics actually plays a most important role in determining the possibility of the occurrence of clusters. We will discuss this in terms of the rotational states of pairs. Since such pairs are in close contact with other atoms and interact with them in such a way that angular momentum will not be conserved, it is clear that this procedure involves an approximation. There seems little doubt, however, that we touch in this way on the essence of the matter. If a cluster of atoms is to be in its lowest state, it would appear that, in terms of the above approximation, any pair should be in its lowest possible rotational state.[24] In the case of an atom with no nuclear spin no complication can result, since the state of zero relative angular momentum is allowed. He^3, however, has a nuclear spin of $\frac{1}{2}$ and obeys the Fermi statistics, that is, the wave function of a pair of atoms is antisymmetrical. The situation is similar to that which occurs with H_2, which results in the distinction between *ortho-* and *para-*hydrogen. With any pair of atoms there is only one chance in four that their nuclear spins will have the proper relation, so as to allow them to have no mutual angular momentum. In any group of atoms, a large fraction of the adjacent pairs must have an angular momentum with respect to each other, and, in view of the small mass, this will be associated with a considerable energy. Because of the small depth of the potential-energy well in which any He^3 atom is vibrating, this energy would be expected to be sufficient to cause "dissociation" by rotation. Thus we do not expect a group of He^3 atoms to be bound together in a low-energy cluster.

It is interesting to speculate on the effect of a He^3 atom if introduced into a cluster of He^4 superfluid. Since there are no symmetry requirements, in a pair consisting of a He^3 and a He^4 atom, there would be no bar to the He^3 atom going into a state of zero angular momentum. On account of its smaller mass, however, it would be expected to have a higher zero-point energy than the He^4 atoms. Indeed, its zero-point energy would be greater than it would be in pure He^3, since He^3 has a considerably lower density than He^4. It is probable that an He^3 atom could not be accommodated in the potential energy wells available in He^4. Indeed, London and I[25] thought that He^3 could not liquify at all, on account of its higher zero-point energy. This was not a good prediction, as it proved possible to circumvent this high zero-point energy by forming a liquid of lower density. However, it is not to be expected that a single He^3 could ordinarily cause a sufficient lowering of density in its neighborhood to enable it to fit into a superfluid cluster. Certainly if it did so, and probably in any event, it would tend to disrupt the cooperative action of the atoms in the cluster, and so effectively raise the energy more than if it were dissolved in normal fluid. Thus we may have found some basis for Taconis' hypothesis,[26] that He^3 is not soluble in superfluid, but only in normal fluid, although it has recently been suggested[27] that the abnormally high vapor pressure of He^3 from solutions of He^4 is only what is to be expected from a mixture of ideal gases, one obeying Einstein-Bose and the other Fermi-Dirac statistics. In other words, it is supposed that in the explanation of this phenomenon, the liquid forces could be neglected entirely. On the other hand, Morrow[28] has shown that Taconis' assumption, combined with rather usual ideas about nonideal solutions, can account for many of the experimental results.

Note added in proof.—Since this paper went to press, L. Guttman and J. R. Arnold, Phys. Rev. **92**, 547 (1953), have presented evidence that He^6 participates only slightly in the superfluidity of He^4. This may be because of the effect of a particle of higher mass on the zero-point energy of a cluster of superfluid. A particle of infinite mass, introduced into a linear array of atoms, would effectively cut the array into two pieces, thus increasing the zero-point energy. Introduction of an He^6 atom into a superfluid cluster of He^4 would have a considerably smaller, but nevertheless similar, effect, and might increase the zero-point energy sufficiently so that He^6 would tend to be expelled from the superfluid.

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[24] See E. G. D. Cohen, quoted by I. Prigogine and J. Philippot, Physica **18**, 747 (1952).

[25] F. London and O. K. Rice, Phys. Rev. **73**, 1188 (1948).

[26] Taconis, Beenakher, Nier, and Aldrich, Phys. Rev. **75**, 1966 (1949).

[27] C. V. Heer and J. G. Daunt, Phys. Rev. **81**, 447 (1951); Daunt, Tseng, and Heer, Phys. Rev. **86**, 911 (1952); A. Harasima, J. Phys. Soc. Japan **6**, 271 (1951).

[28] J. C. Morrow, Phys. Rev. **84**, 502 (1951).