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Bose-Einstein Condensation and Liquid Helium

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The mathematical description of B.E. (Bose-Einstein) condensation is generalized so as to be applicable to a system of interacting particles. B.E. condensation is said to be present whenever the largest eigenvalue of the one-particle reduced density matrix is an extensive rather than an intensive quantity. Some transformations facilitating the practical use of this definition are given.

An argument based on first principles is given, indicating that liquid helium II in equilibrium shows B.E. condensation. For absolute zero, the argument is based on properties of the ground-state wave function derived from the assumption that there is no "long-range configurational order." A crude estimate indicates that roughly 8% of the atoms are "condensed" (note that the fraction of condensed particles need not be identified with ρ_s/ρ). Conversely, it is shown why one would not expect B.E. condensation in a solid. For finite temperatures Feynman's theory of the lambda-transition is applied: Feynman's approximations are shown to imply that our criterion of B.E. condensation is satisfied below the lambda-transition but not above it.

1. INTRODUCTION

THE analogy between liquid He^4 and an ideal Bose-Einstein gas was first recognized by London.[1,2] He suggested that the lambda-transition in liquid helium could be understood as the analog for a liquid of the transition[3,4] which occurs in an ideal B.E. (Bose-Einstein) gas at low temperatures. The fact[5] that no lambda-transition has been found in He^3 supports London's viewpoint. Further support comes from recent theoretical work[6–8] which shows in more detail how a system of interacting particles can exhibit a transition corresponding to the ideal-gas transition.

Tisza[2,9] showed that the analogy between liquid He^4 and an ideal B.E. gas is also useful in understanding the transport properties of He II. Below its transition temperature a B.E. gas in equilibrium has a characteristic property: a finite fraction of the particles occupy the lowest energy level. Tisza reasoned that the presence of these "condensed" particles would make necessary a special two-fluid hydrodynamical description for such a gas. His idea that this two-fluid description applies also to He II has been strikingly verified by many experiments.[2,10,11]

In theoretical treatments where the forces between helium atoms are taken into account, the ideal-gas analogy takes on forms differing widely from one treatment to another. For example, Matsubara[6] and Feynman[7] account for the lambda-transition by writing the partition function for liquid helium in a form similar to the corresponding expression for an ideal gas. In Bogolyubov's theory[12–14] of the superfluidity of a system of weakly repelling B.E. particles, it is the distribution of the momenta of the particles which resembles that of an ideal gas. Yet another form for the analogy has been suggested by Penrose[15]; this work will be discussed in more detail in Sec. 4 below. A further complication is that the excitation theory of superfluidity[16,17] is apparently independent of the ideal-gas analogy (though Bogolyubov's work[12] suggests that there actually is a connection).

The object of the present paper is, first, to unify the varied forms of the ideal-gas analogy mentioned above by showing how they are all closely related to a single *criterion for B.E. condensation*, applicable in either a liquid or a gas, and, secondly, to give an argument based on first principles indicating that this criterion actually is satisfied in He II. The relation between B.E. condensation and the excitation theory of superfluidity will be discussed in a later paper.

2. PRELIMINARY DEFINITIONS

We make the usual approximation of representing liquid He^4 by a system of N interacting spinless B.E. particles, each of mass m, with position and momentum vectors $\mathbf{q}_1\cdots\mathbf{q}_N$ and $\mathbf{p}_1\cdots\mathbf{p}_N$, respectively. The Hamiltonian is taken to be

$$H\equiv\sum_j p_j^2/2m+\sum_{i<j} U_{ij}. \tag{1}$$

Here U_{ij} stands for $U(|\mathbf{q}_i-\mathbf{q}_j|)$, where $U(r)$ is the interaction energy of two He^4 atoms separated by a

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[1] F. London, Nature **141**, 643 (1938); Phys. Rev. **54**, 947 (1938).

[2] F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1954), Vol. 2, especially pp. 40–58, 199–201.

[3] A. Einstein, Sitzber. preuss. Akad. Wiss. physik-math. Kl. **1924**, 261; *ibid.* **1925**, 3, 18.

[4] For bibliography, see P. T. Landsberg, Proc. Cambridge Phil. Soc. **50**, 65 (1954).

[5] E. F. Hammel in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North Holland Publishing Company, Amsterdam, 1955), Vol. 1, pp. 78–107.

[6] T. Matsubara, Progr. Theoret. Phys. Japan **6**, 714 (1951).

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

[8] G. V. Chester, Phys. Rev. **100**, 455 (1955).

[9] L. Tisza, Nature **141**, 913 (1938).

[10] V. Peshkov, J. Phys. U.S.S.R. **8**, 381 (1944); **10**, 389 (1946).

[11] E. Andronikashvili, J. Phys. U.S.S.R. **10**, 201 (1946).

[12] N. N. Bogolyubov, J. Phys. U.S.S.R. **11**, 23 (1947).

[13] N. N. Bogolyubov and D. N. Zubarev, Zhur. Eksptl. i Teort. Fiz. **28**, 129 (1955); English translation in Soviet Phys. **1**, 83 (1955).

[14] D. N. Zubarev, Zhur. Eksptl. i Teort. Fiz. **29**, 881 (1955).

[15] O. Penrose, Phil. Mag. **42**, 1373 (1951).

[16] L. D. Landau, J. Phys. U.S.S.R. **5**, 71 (1941).

[17] R. P. Feynman, Phys. Rev. **94**, 262 (1954).

distance r, and $|\mathbf{q}_i-\mathbf{q}_j|$ means the length of the vector $\mathbf{q}_i-\mathbf{q}_j$ (except when the artifice of periodic boundary conditions is used, in which case $|\mathbf{q}_i-\mathbf{q}_j|$ means the length of the shortest vector congruent to $\mathbf{q}_i-\mathbf{q}_j$). Many-body interactions are omitted from (1), but including them would make no essential difference. The interaction between the He^4 atoms and those of the container is also omitted from (1); these could be included, but it is simpler to represent the container by a closed geometrical surface, considering only configurations for which all particles are within or on this surface, and imposing a suitable boundary condition on the wave function when any particle is on the surface. This boundary condition must be chosen to make H Hermitian. We denote the volume inside the container by V, and integrations over V by $\int_V \cdots d^3\mathbf{x}$ or $\int \cdots d^3\mathbf{x}$ or $\int \cdots d\mathbf{x}$.

As always in statistical mechanics, we are concerned here with very large values of N. Therefore we can often neglect quantities (for example $N^{-\frac{1}{3}}$) which are small when N is very large. A relation holding approximately by virtue of N being very large will be written in one of the forms $A \cong B$ or $A=B+o(1)$. These mean respectively that A/B is approximately 1 and that $A-B$ is negligible compared with 1, when N is large enough. We shall also use the notation $A=e^{O(1)}$ to mean that positive upper and lower bounds are known for A, but that a relation of the form $A\cong$const has not been established. Evidently $A\cong$const>0 implies $A=e^{O(1)}$, but the example $A=2+\sin N$ shows that the converse does not hold in general. We shall use the phrase "A is finite" to mean $A=e^{O(1)}$.

We can give more precise meanings to the symbols $\cong$, etc., by considering not a single system but an infinite sequence of systems with different values of N. The boundary conditions for the different members of the sequence should be the same, and should be specified on boundary surfaces of the same shape but of sizes such that N/V is independent of N. Then, if the quantities A, B, etc., are defined for each member of the sequence, $A\cong B$ means $\lim_{N\to\infty}(A/B)=1$, $A=B+o(1)$ means $\lim_{N\to\infty}(A-B)=0$, and $A=e^{O(1)}$ means that positive constants a_1, a_2, and N_1 exist such that $N>N_1$ implies that $a_1<A<a_2$.

We shall use Dirac's notation[18] for matrix elements and for eigenvalues of operators.

3. A GENERALIZED CRITERION OF B.E. CONDENSATION

It is characteristic of an ideal B.E. gas in equilibrium below its transition temperature that a finite fraction of the particles occupies the lowest single-particle energy level. Using the notation of Sec. 2, we can therefore give the following criterion of B.E. condensation[4] for an ideal gas in equilibrium:

$$\begin{aligned} \langle n_0\rangle_{\mathrm{Av}}/N &= e^{O(1)} \leftrightarrow \text{B.E. condensation,}^{19} \\ \langle n_0\rangle_{\mathrm{Av}}/N &= o(1) \leftrightarrow \text{no B.E. condensation,} \end{aligned} \tag{2}$$

where $\langle n_0\rangle_{\mathrm{Av}}$ is the average number of particles in the lowest single-particle level and the sign $\leftrightarrow$ denotes logical equivalence. This criterion has meaning for noninteracting particles only, because single-particle energy levels are not defined for interacting particles.

To generalize the criterion (2), we rewrite it in a form which has meaning even when there are interactions. This can be done by using von Neumann's statistical operator,[20] σ, whose position representative[21] $\langle q_1'\cdots q_N'|\sigma|q_1''\cdots q_N''\rangle$ is known as the density matrix.[22] We define a reduced statistical operator, σ_1, as follows[23,24]:

$$\sigma_1 = N\,\mathrm{tr}_{2\cdots N}(\sigma), \tag{3}$$

where $\mathrm{tr}_{2\cdots N}(\sigma)$ means the trace of σ taken with respect to particles $2\cdots N$ but not particle 1. For an ideal gas in equilibrium, the eigenstates of σ_1 are the single-particle stationary states, and the corresponding eigen values are the average numbers of particles in these stationary states.[25] Consequently, (2) may be rewritten as follows:

$$\begin{aligned} n_M/N &= e^{O(1)} \leftrightarrow \text{B.E. condensation,} \\ n_M/N &= o(1) \leftrightarrow \text{no B.E. condensation,} \end{aligned} \tag{4}$$

where n_M denotes the largest eigenvalue of σ_1. In this form the criterion has meaning for interacting as well as for noninteracting particles, since σ_1 is defined in either case; thus (4) provides a suitable generalization of the ideal-gas criterion (2).

According to our criterion (4), B.E. condensation cannot occur in a Fermi system, because[26] the exclusion principle implies that $0\leqslant n_M\leqslant 1$. For Bose systems, however, the only general restriction on n_M is $0\leqslant n_M\leqslant N$, a consequence of the identity $\mathrm{tr}(\sigma_1)=N$ and the fact that σ_1 is positive semidefinite.

The application of (4) is most direct when the system satisfies periodic boundary conditions and is spatially uniform (a homogeneous phase in the thermodynamic sense). For, in this case, the reduced density matrix $\langle\mathbf{q}'|\sigma_1|\mathbf{q}''\rangle$ is a function of $\mathbf{q}'-\mathbf{q}''$ only, and specifying this function is equivalent to specifying the single-particle momentum distribution. In fact, the momentum

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[18] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, London, 1947).

[19] A possible alternative to this equation is $\langle n_0\rangle_{\mathrm{Av}}/N\cong$const$>0$, but the weaker form used in (2) is easier to apply.

[20] J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, Princeton, 1955), Chap. 4.

[21] P. A. M. Dirac, reference 18, Chap. 3.

[22] P. A. M. Dirac, reference, pp. 130–135.

[23] K. Husimi, Proc. Phys. Math. Soc. Japan **22**, 264 (1940).

[24] J. de Boer, Repts. Progr. Phys. **12**, 313–316 (1949).

[25] K. Husimi, reference 23, Eq. (10.6).

[26] See, for example, P-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

representative[21] of σ_1, given by

$$\langle \mathbf{p}'|\sigma_1|\mathbf{p}''\rangle \equiv \int\int \langle \mathbf{p}'|\mathbf{q}'\rangle d\mathbf{q}'\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle d\mathbf{q}''\langle \mathbf{q}''|\mathbf{p}''\rangle$$

$$= V^{-1}\int\int \exp[i(\mathbf{p}''\cdot\mathbf{q}''-\mathbf{p}'\cdot\mathbf{q}')/\hbar] \times\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle d\mathbf{q}'d\mathbf{q}''$$

is a diagonal matrix, so that n_M is the largest diagonal element of this matrix. Now, since

$$\langle \mathbf{p}_1'\cdots\mathbf{p}_N'|\sigma|\mathbf{p}_1'\cdots\mathbf{p}_N'\rangle$$

is the probability distribution in the (discrete) momentum space of N particles,

$$\langle \mathbf{p}_1'|\sigma_1|\mathbf{p}_1'\rangle = N\sum_{\mathbf{p}_2'}\cdots\sum_{\mathbf{p}_N'}\langle \mathbf{p}_1'\cdots\mathbf{p}_N'|\sigma|\mathbf{p}_1'\cdots p_N'\rangle$$

must be the average number of particles with momentum $\mathbf{p}_1'$. [To confirm this interpretation, note that[14]

$$\langle\sum_j f(\mathbf{p}_j)\rangle_{\mathrm{Av}} = \sum_{\mathbf{p}'}\langle \mathbf{p}'|\sigma_1|\mathbf{p}'\rangle f(\mathbf{p}')$$

for arbitrary $f(\mathbf{p})$.] Therefore, according to (4), B.E. condensation is present for a spatially uniform system with periodic boundary conditions whenever a finite fraction of the particles have identical momenta. The work of Bogolybov[12] shows that this form of the criterion is satisfied in a system of weakly interacting B.E. particles at very low temperatures.

4. ALTERNATIVE FORMS OF THE CRITERION

When the system is not spatially uniform, it is more difficult to diagonalize σ_1, and some transformations of the criterion (4) are useful. The simplest of these depends on the following inequality:

$$n_M^2 \leqslant \sum_a n_a^2 \leqslant n_M \sum_a n_a = n_M N, \tag{5}$$

where the n_a's are the eigenvalues of σ_1; the fact that $\sum_a n_a = \mathrm{tr}(\sigma_1) = N$ follows from (3). We define

$$A_2 \equiv N^{-2}\int_V\int_V |\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle|^2 d^3\mathbf{q}'d^3\mathbf{q}''. \tag{6}$$

It is clear that $A_2 = N^{-2}\,\mathrm{tr}(\sigma_1^2) = N^{-2}\sum n_a^2$, and hence, by (5), that $(n_M/N)^2 \leqslant A_2 \leqslant n_M/N$. It follows that

$$A_2 = e^{O(1)} \leftrightarrow n_M/N = e^{O(1)}, \text{ while } A_2 = o(1) \leftrightarrow n_M/N = o(1).$$

The following criterion is therefore equivalent to (4):

$$\begin{aligned} A_2 &= e^{O(1)} \leftrightarrow \text{B.E. condensation,} \\ A_2 &= o(1) \leftrightarrow \text{no B.E. condensation.} \end{aligned} \tag{7}$$

Another form of the criterion depends on inequalities satisfied by

$$A_1 \equiv (NV)^{-1}\int_V\int |\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle| d^3\mathbf{q}'d^3\mathbf{q}''. \tag{8}$$

Unlike A_2, this quantity has no simple interpretation in terms of the eigenvalues of σ_1/N, but it is easier to use. An upper bound for A_1 comes from the fact that $(A_1N/V)^2$, the square of the mean value of the function $|\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle|$, cannot exceed $A_2(N/V)^2$, the mean value of the square of this function; therefore we have

$$A_1^2 \leqslant A_2. \tag{9}$$

To find a lower bound for A_1, we use the fact that σ_1 is positive semidefinite (this follows intuitively from the probability interpretation of the eigenvalues of σ_1/N; alternatively it can be proved rigorously from (3) and the fact that σ is positive semidefinite). Since σ_1 has no negative eigenvalues, its square root is Hermitian. Applying the Schwartz inequality to the two state vectors $\sigma_1^{\frac{1}{2}}|\mathbf{q}'\rangle$ and $\sigma_1^{\frac{1}{2}}|\mathbf{q}''\rangle$, we obtain

$$|\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle| \leqslant [\langle \mathbf{q}'|\sigma_1|\mathbf{q}'\rangle\langle \mathbf{q}''|\sigma_1|\mathbf{q}''\rangle]^{\frac{1}{2}} \leqslant \alpha N/V, \tag{10}$$

where $\alpha N/V$ is any upper bound of $\langle \mathbf{q}'|\sigma_1|\mathbf{q}'\rangle$. Combining (6), (8), and (10), we find

$$A_2 \leqslant \alpha A_1. \tag{11}$$

For any physical system, α can be chosen independent of N; for $\langle \mathbf{q}'|\sigma_1|\mathbf{q}'\rangle$ is the average number density at the point $\mathbf{q}'$ and cannot become indefinitely large. For example, in a liquid at thermal equilibrium, $\langle \mathbf{q}'|\sigma_1|\mathbf{q}'\rangle$ is approximately N/V except near the boundary, so that α can be chosen just greater than 1. Treating α as finite, and combining (7) with (9) and (11), we obtain

$$\begin{aligned} A_1 &= e^{O(1)} \leftrightarrow \text{B.E. condensation,} \\ A_1 &= o(1) \leftrightarrow \text{no B.E. condensation.} \end{aligned} \tag{12}$$

A third form of the criterion is valuable when the reduced density matrix $\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle$ has the asymptotic form $\Psi(\mathbf{q}')\Psi^*(\mathbf{q}'')$ for large $|\mathbf{q}'-\mathbf{q}''|$ (Ψ^* is the complex conjugate of Ψ). Some consequences of assuming this asymptotic relation for He II were discussed by Penrose.[15] Here we formulate the assumption as follows:

$$|\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle - \Psi(\mathbf{q}')\Psi^*(\mathbf{q}'')| \leqslant (N/V)\gamma(|\mathbf{q}'-\mathbf{q}''|), \tag{13}$$

where the (non-negative) function $\gamma(r)$ is independent of N and satisfies

$$\lim_{r\to\infty}\gamma(r) = 0. \tag{14}$$

To use (13), we need the following lemma:

$$\Gamma(\mathbf{x}) \equiv V^{-1}\int \gamma(|\mathbf{x}'-\mathbf{x}|)d^3\mathbf{x}' = o(1). \tag{15}$$

Proof.—Let ϵ be an arbitrary positive number. Then, by (14), there exists a number R (depending on ϵ) such that

$$0 \leqslant \gamma(r) < \tfrac{1}{2}\epsilon \quad \text{if} \quad r > R. \tag{16}$$

We also have

$$0 \leqslant \gamma(r) < \gamma_M + \tfrac{1}{2}\epsilon \quad \text{if} \quad 0 \leqslant r \leqslant R,$$

where γ_M is the maximum of the function $\gamma(r)$. Using (16) in (15) we obtain $0 \leqslant \Gamma(\mathbf{x}) < \frac{1}{2}\epsilon + V^{-1}\gamma_M V_R(\mathbf{x})$, where $V_R(\mathbf{x})$ is the volume of $\mathbf{x}'$-space for which $|\mathbf{x}'-\mathbf{x}| \leqslant R$. Since $V_R(\mathbf{x}) \leqslant 4\pi R^3/3$, we can ensure that $0 \leqslant \Gamma < \epsilon$ by choosing $V > 8\pi\gamma_M R^3/3\epsilon$. By the definition of a limit, this implies $\lim_{V\to\infty}\Gamma = 0$; that is, (15) is true.

We can now obtain a criterion of B.E. condensation, using the relation

$$(NV)^{-1}\int\int |\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle - \Psi(\mathbf{q}')\Psi^*(\mathbf{q}'')|\,d\mathbf{q}'d\mathbf{q}'' = o(1), \tag{17}$$

which follows from (13) and (15). Combining this with (8) with the help of the elementary inequality $-|u-v| \leqslant |u|-|v| \leqslant |u-v|$ gives

$$A_1 = (NV)^{-1}\left[\int |\Psi(\mathbf{x})|\,d^3\mathbf{x}\right]^2 + o(1). \tag{18}$$

Using (12), we obtain the criterion, valid whenever (13) holds:

$$\begin{aligned} V^{-1}\int |\Psi|\,d^3\mathbf{x} &= e^{O(1)} \leftrightarrow \text{B.E. condensation,} \\ V^{-1}\int |\Psi|\,d^3\mathbf{x} &= o(1) \leftrightarrow \text{no B.E. condensation.} \end{aligned} \tag{19}$$

The function Ψ has a simple interpretation when B.E. condensation is present: we can show that $\Psi(\mathbf{x})$ is a good approximation to the eigenfunction of the matrix $\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle$ corresponding to the eigenvalue n_M, and also that its normalization is

$$n_\Psi \equiv \int |\Psi(\mathbf{x})|^2 d^3\mathbf{x} \cong n_M. \tag{20}$$

We note first that all eigenvalues of the matrix

$$N^{-1}\langle \mathbf{q}'|\tau|\mathbf{q}''\rangle \equiv N^{-1}[\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle - \Psi(\mathbf{q}')\Psi^*(\mathbf{q}'')]$$

are $o(1)$, since, by (17), (8), and (12), a system whose reduced density matrix was τ would not show B.E. condensation. It follows that

$$\begin{aligned} f\{\varphi(\mathbf{x})\} &\equiv N^{-1}\int\int \varphi^*(\mathbf{q}')\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle\varphi(\mathbf{q}'')\,d\mathbf{q}'d\mathbf{q}'' \\ &= |(\varphi,\Psi)|^2/N + o(1), \end{aligned} \tag{21}$$

where φ is an arbitrary normalized function and

$$(\varphi,\Psi) \equiv \int \varphi^*(\mathbf{x})\Psi(\mathbf{x})\,d^3\mathbf{x}.$$

The arbitrary function $\varphi(\mathbf{x})$ in (21) can be written in the form $\varphi(\mathbf{x}) = n_\Psi^{-\frac{1}{2}}[a\Psi(\mathbf{x}) + b\Phi(\mathbf{x})]$, where Φ is chosen to make $(\Psi,\Phi) = 0$ and $(\Phi,\Phi) = n_\Psi$, and where (since φ is normalized) $|a|^2 + |b|^2 = 1$. Inserting this expression for φ into (21) gives

$$f\{\varphi\} = |a|^2 n_\Psi/N + o(1) = (1-|b|^2)n_\Psi/N + o(1).$$

Now, the maximum value of $f\{\varphi\}$ is n_M/N, and it is attained when φ equals φ_M, the normalized eigenfunction of $\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle$ corresponding to the eigenvalue n_M. The last expression for $f\{\varphi\}$ shows that this maximum is $n_\Psi/N + o(1)$ and is attained with $|b| = o(1)$. It follows that $n_M \cong n_\Psi$ in agreement with (20), and also that

$$\int |a n_\Psi^{-\frac{1}{2}}\Psi(\mathbf{x}) - \varphi_M(\mathbf{x})|^2 d^3\mathbf{x} = |b|^2 = o(1). \tag{22}$$

This equation tells us that $\Psi(\mathbf{x})$ is to a good approximation proportional to $\varphi_M(\mathbf{x})$. In view of these results, we may call Ψ the *wave function of the condensed particles*, and n_Ψ/N the *fraction of condensed particles.*

5. GROUND STATE OF A B.E. FLUID

In this section we derive some general properties of the ground-state wave function. These will be needed in Sec. 6.

Let us define the ground-state wave function $\psi(\mathbf{x}_1\cdots\mathbf{x}_N)$ to be the real symmetric function which minimizes the expression

$$\int\cdots\int[\hbar^2\sum_j(\nabla_j\psi)^2/2m + \sum_{i<j}U_{ij}\psi^2]\,d\mathbf{x}_1\cdots d\mathbf{x}_N, \tag{23}$$

while at the same time satisfying the boundary conditions and the normalization condition. The Euler equation of this variation problem shows that ψ satisfies Schrödinger's equation for the Hamiltonian (1). Now, the function $|\psi|$ also conforms to the above definition, and so it too satisfies Schrödinger's equation. The first derivative of $|\psi|$ must therefore be continuous wherever the potential energy is finite. This is possible only if ψ does not change sign. We may therefore take ψ to be non-negative. Suppose now that ψ_1 and ψ_2 are two different non-negative functions conforming to the above definition. Then, since Schrödinger's equation is linear, $\psi_1 - \psi_2$ also conforms to the definition, and (by the result just proved) does not change sign; but this contradicts the original assumption that both ψ_1 and ψ_2 are normalized. Hence the above definition yields a unique, non-negative function[27] ψ.

For a fluid phase, we can obtain further information if we assume [28] that there is *no long-range configurational*

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[27] These properties of the ground-state wave function are fairly well known [see, for example, R. P. Feynman, Phys. Rev. **91**, 1301 (1953)], but the authors have seen no proof in the literature. A proof for the special case $N=1$ (to which no symmetry requirements apply) is given by R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Verlag Julius Springer, Berlin, 1931), Vol. 1, Chap. 6, Secs. 6, 7.

[28] A similar principle is often used in the classical theory of liquids—for example by J. E. Mayer and E. W. Montroll, J. Chem. Phys. **9**, 2 (1941). Its use here amounts to assuming that

order. By this we mean that there is a finite "range of order" R with the following property: for any two concentric spheres S_1 and S_2 with radii R_1 and R_1+R, respectively, the relative probabilities of the various possible configurations of particles inside S_1 are approximately[29] independent of the situation outside S_2. By the "situation" outside S_2, we mean here the number of particles ouside S_2, their positions, and the position of the part of the boundary surface outside S_2.

This assumption implies that, if the configuration of the particles inside S_1 is altered while everything else remains the same, then the probability density in configuration space changes by a factor approximately independent of the situation outside S_2. Hence, if the point $\mathbf{x}_i$ is inside S_1, then $\nabla_i \log\psi$ is approximately independent of the situation outside S_2. This is true for any choice of S_1 provided S_1 encloses $\mathbf{x}_i$, and in particular it is true when R_1 is vanishingly small. Therefore, $\nabla_i \log\psi$ is independent of the situation outside a sphere $S(\mathbf{x}_i)$ with center $\mathbf{x}_i$ and radius R.

Setting $i=1$ in this result and integrating shows that ψ can be written in the form

$$\psi(\mathbf{x}_1\cdots\mathbf{x}_N)=\theta(\mathbf{x}_2\cdots\mathbf{x}_N)\chi(\mathbf{x}_1;\mathbf{x}_2\cdots\mathbf{x}_N), \qquad (24)$$

where the functions θ and χ are symmetric in $\mathbf{x}_2\cdots\mathbf{x}_N$, and χ is approximately[30] independent of the situation outside $S(\mathbf{x}_1)$.

The function θ in (24) has a simple physical meaning. To find this, we write the Schrödinger equation satisfied by ψ in the form

$$-(\hbar^2/2m)\sum_j[\nabla_j^2 \log\psi+(\nabla_j \log\psi)^2]+\sum_{i<j} U_{ij}=\text{const.} \qquad (25)$$

Taking the gradient with respect to x_i $(i\neq 1)$ and substituting from (24), we obtain after some rearrangement

$$\begin{aligned}\nabla_i\{-(\hbar^2/2m)\textstyle\sum_j{}'[\nabla_j^2 \log\theta+(\nabla_j \log\theta)^2]+\sum_j{}'' U_{ij}\}\\ =(\hbar^2/2m)\textstyle\sum_j[\nabla_j^2+2(\nabla_j \log\theta)\cdot\nabla_j]\nabla_i \log\chi\\ +(\hbar^2/m)\textstyle\sum_j(\nabla_j \log\chi)\cdot\nabla_j\nabla_i \log\psi-\nabla_i U_{1i},\end{aligned} \qquad (26)$$

where $\sum_j{}'$ means a sum with the $j=1$ term omitted, and $\sum_j{}''$ means a sum with the $j=1$ and $j=i$ terms omitted. Since the left member of (26) does not contain $\mathbf{x}_1$, the right member must be independent of $\mathbf{x}_1$. To evaluate the right member, we may therefore choose $\mathbf{x}_1$ to make $|\mathbf{x}_i-\mathbf{x}_1|>2R$. The properties of χ then imply that $\nabla_i \log\chi\simeq 0$, so that the first sum vanishes approximately; they also imply that the summand in the second sum is negligible unless $|\mathbf{x}_j-\mathbf{x}_1|\leqslant R$. The argument preceding (24) shows, however, that $\nabla_i \log\psi$ is independent of $\mathbf{x}_j$ unless $|\mathbf{x}_j-\mathbf{x}_i|\leqslant R$. Since $|\mathbf{x}_j-\mathbf{x}_1|$ and $|\mathbf{x}_j-\mathbf{x}_i|$ cannot both be less than R (because $|\mathbf{x}_1-\mathbf{x}_i|>2R$), the summand in the second sum is always negligible. The term $\nabla_i U_{1i}$ also vanishes, because the interaction has a short range. Thus the entire right member of (26) vanishes approximately.[31] The expression in curly brackets is therefore approximately independent of $\mathbf{x}_i$ for $i=2\cdots N$. This means that $\theta(\mathbf{x}_2\cdots\mathbf{x}_N)$ approximately satisfies an equation, analogous to (25), which is equivalent to Schrödinger's equation for a system of $N-1$ particles. Since θ is non-negative, it must therefore have the form

$$\theta(\mathbf{x}_2\cdots\mathbf{x}_N)\simeq c\vartheta(\mathbf{x}_2\cdots\mathbf{x}_N), \qquad (27)$$

where c is a constant and ϑ is the normalized ground-state wave function for $N-1$ particles.

A simple illustration of (24) is provided by a type of approximation to $\psi(\mathbf{x}_1\cdots\mathbf{x}_N)$ used by various authors[32,33,13]:

$$\psi(\mathbf{x}_1\cdots\mathbf{x}_N)\propto\Big[\prod_j \mu(\mathbf{x}_j)\Big]\prod_{i<j} \omega(|\mathbf{x}_i-\mathbf{x}_j|), \qquad (28)$$

where $\omega(r)\to 1$ when r is large. In this approximation, (24) can be satisfied by taking

$$\theta(\mathbf{x}_2\cdots\mathbf{x}_N)\propto\Big[\prod_i{}' \mu(\mathbf{x}_i)\Big]\prod_{i<j}{}' \omega(|\mathbf{x}_i-\mathbf{x}_j|), \qquad (29)$$

$$\chi(\mathbf{x}_1;\mathbf{x}_2\cdots\mathbf{x}_N)=\mu(\mathbf{x}_1)\prod_i{}' \omega(|\mathbf{x}_i-\mathbf{x}_1|), \qquad (30)$$

where Π' means a product with all $i=1$f actors omitted. It is clear that (29) is consistent with (27), and that, if R is large enough, χ as defined in (30) is approximately independent of the positions of the particles outside $S(\mathbf{x}_1)$.

6. LIQUID HELIUM-4 AT ABSOLUTE ZERO

At absolute zero, the density matrix is given by

$$\langle \mathbf{q}_1'\cdots\mathbf{q}_N'|\sigma|\mathbf{q}_1''\cdots\mathbf{q}_N''\rangle=\psi(\mathbf{q}_1'\cdots\mathbf{q}_N')\psi(\mathbf{q}_1''\cdots\mathbf{q}_N''),$$

since the ground-state wave function ψ is real and normalized. The reduced density matrix is therefore

$$\langle \mathbf{q}'|\sigma_1|\mathbf{q}''\rangle=N\int\cdots\int\psi(\mathbf{q}',\mathfrak{x})\psi(\mathbf{q}'',\mathfrak{x})d\mathfrak{x}, \qquad (31)$$

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the probability density in configuration space is qualitatively similar to the corresponding probability density for a classical liquid. The importance of this principle for the ground state of a quantum liquid was noted by A. Bijl, Physica **7**, 869 (1940).

[29] The meaning of the word "approximately" is purposely left vague, since it would complicate the discussion too much to attempt a rigorous formulation. As we see it, a rigorous formulation would have to depend on a limit operation $R\to\infty$: that is, it would assume that the approximation of statistical independence could be made arbitrarily good by choosing R large enough.

[30] If the theory were formulated more rigorously (see reference 29), the corresponding property of χ might be $\nabla_j\chi(\mathbf{x}_1;\mathbf{x}_2\cdots\mathbf{x}_N)\leqslant K(|\mathbf{x}_j-\mathbf{x}_1|)$ where $K(r)\to 0$ in a suitable way as $r\to\infty$.

[31] Only a rigorous treatment can completely justify the implicit assumption that the sum of N negligible terms is itself negligible. The present methods can, however, be used to show that the contribution of a given j value to the sums in the right member of (26) is negligible compared with its contribution to the sums in the left (with a finite number of exceptions, for which $|\mathbf{x}_j-\mathbf{x}_1|\leqslant R$ and the contributions on both sides are negligible).

[32] A. Bijl, reference 28.

[33] R. B. Dingle, Phil. Mag. **40**, 573 (1949).

where $\mathfrak{x}$ and $d\mathfrak{x}$ are abbreviations for $\mathbf{x}_2\cdots\mathbf{x}_N$ and $d^3\mathbf{x}_2\cdots d^3\mathbf{x}_N$, respectively. For a preliminary discussion of (31), we use a crude approximation to ψ suggested by Feynman[7]:

$$\psi(\mathbf{x}_1\cdots\mathbf{x}_N)\simeq(\Omega_N)^{-\frac{1}{2}}F_N(\mathbf{x}_1\cdots\mathbf{x}_N), \tag{32}$$

where Ω_N is a normalizing constant, and $F_N(\mathbf{x}_1\cdots\mathbf{x}_N)$ by definition takes the value 1 whenever $\mathbf{x}_1\cdots\mathbf{x}_N$ is a possible configuration for the centers of N hard spheres of diameter d and the value 0 for all other configurations. Here $d\simeq 2.6$A is the diameter of a He^4 atom. The approximation amounts to using (28) with $\mu=1$ and with $\omega(r)=0$ for $r<d$ and $\omega=1$ for $r\geqslant d$.

The normalization integral corresponding to (32) shows that $\Omega_N/N!$ is the configurational partition function for a classical system of N noninteracting hard spheres. Moreover, the integral in (31) is now closely related to the pair distribution function for $N+1$ hard spheres, defined as follows[24]:

$$n_2(\mathbf{q}',\mathbf{q}'')\equiv(N+1)N\int\cdots\int F_{N+1}(\mathbf{q}',\mathbf{q}'',\mathfrak{x})d\mathfrak{x}/\Omega_{N+1}. \tag{33}$$

Under the approximation (32), the integrand in (31) is $1/\Omega_N$ times that in (33) when $|\mathbf{q}'-\mathbf{q}''|\geqslant d$, so that

$$\langle\mathbf{q}'|\sigma_1|\mathbf{q}''\rangle=z^{-1}n_2(\mathbf{q}',\mathbf{q}'')\quad\text{if}\quad|\mathbf{q}'-\mathbf{q}''|\geqslant d. \tag{34}$$

Here $z\equiv(N+1)\Omega_N/\Omega_{N+1}$ is the activity of the hard-sphere system. The physical meaning of n_2 shows that, for large $|\mathbf{q}'-\mathbf{q}''|$, n_2 tends to $(N/V)^2$. Hence (13) can be satisfied by taking $\Psi\cong\text{const}\cong z^{-\frac{1}{2}}N/V$ (except, possibly, near the boundary). Hence, by (19), B.E. condensation is present; moreover, by (20) and the discussion following (20), the fraction of condensed particles is

$$n_M/N\cong n_\Psi/N\cong\Psi^2V/N\cong N/Vz. \tag{35}$$

The right member of (35) can be calculated from the virial series for hard spheres.[34] Taking the density of He II to be 0.28 times the density at closest packing, we obtain the result 0.08. Thus, Feynman's approximation (32) implies that B.E. condensation is present in He II at absolute zero and that the fraction of condensed particles is about 8%.

The above discussion makes it plausible that a treatment based on the true wave function will also indicate the presence of B. E. condensation. To supply such a treatment, we first substitute from (24) and (27) into (31). This yields

$$\langle\mathbf{q}'|\sigma_1|\mathbf{q}''\rangle=c^2N\langle\chi(\mathbf{q}';\mathfrak{x})\chi(\mathbf{q}'';\mathfrak{x})\rangle_\vartheta, \tag{36}$$

where, for any function $f(\mathfrak{x})$

$$\langle f\rangle_\vartheta\equiv\langle f(\mathfrak{x})\rangle_\vartheta\equiv\int\cdots\int f(\mathfrak{x})\vartheta^2(\mathfrak{x})d\mathfrak{x} \tag{37}$$

is the expectation value of $f(\mathfrak{x})$ in the ground state of a liquid of $N-1$ particles whose configuration is $\mathfrak{x}\equiv\mathbf{x}_2\cdots\mathbf{x}_N$.

In studying (36) it will be convenient to look on $\mathbf{q}'$ and $\mathbf{q}''$ as parameters and to treat $\chi'\equiv\chi(\mathbf{q}';\mathfrak{x})$ and $\chi''\equiv\chi(\mathbf{q}'';\mathfrak{x})$ as variables depending on the configuration $\mathfrak{x}$ of a liquid of $N-1$ particles. The correlation coefficient[35] of χ' and χ'' is defined by

$$\rho(\mathbf{q}',\mathbf{q}'')\equiv\frac{\langle\chi'\chi''\rangle_\vartheta-\langle\chi'\rangle_\vartheta\langle\chi''\rangle_\vartheta}{[\langle\chi'^2\rangle_\vartheta-\langle\chi'\rangle_\vartheta{}^2]^{\frac{1}{2}}[\langle\chi''^2\rangle_\vartheta-\langle\chi''\rangle_\vartheta{}^2]^{\frac{1}{2}}}. \tag{38}$$

Now, it was shown in Sec. 5 that χ' is independent of the "situation" outside $S(\mathbf{q}')$ and that χ'' is independent of the situation outside $S(\mathbf{q}'')$. By applying the principle of no long-range configurational order, given in Sec. 5, to the ground state of a liquid of $N-1$ particles, with the sphere S_1 chosen large enough to enclose both $S(\mathbf{q}')$ and $S(\mathbf{q}'')$, we find that $\rho(\mathbf{q}',\mathbf{q}'')$ is independent of V for large enough V. By applying the same principle with S_1 this time taken to coincide with $S(\mathbf{q}')$, we find that χ' and χ'' are approximately statistically independent if $S(\mathbf{q}'')$ is entirely outside S_2; that is, $\rho(\mathbf{q}',\mathbf{q}'')$ approximately vanishes if $|\mathbf{q}'-\mathbf{q}''|>3R$.

We can now show that (13) holds, with

$$\Psi(\mathbf{q}')=cN^{\frac{1}{2}}\langle\chi'\rangle_\vartheta. \tag{39}$$

For, substituting (36) and (39) into the left member of (13) gives $c^2N[\langle\chi'\chi''\rangle_\vartheta-\langle\chi'\rangle_\vartheta\langle\chi''\rangle_\vartheta]$, which, by (38), is less than $c^2N\rho(\mathbf{q}',\mathbf{q}'')[\langle\chi'^2\rangle_\vartheta\langle\chi''^2\rangle_\vartheta]^{\frac{1}{2}}$. Setting $\mathbf{q}'=\mathbf{q}''$ in (36) shows that this last expression equals $\rho(\mathbf{q}',\mathbf{q}'')\times[\langle\mathbf{q}'|\sigma_1|\mathbf{q}'\rangle\langle\mathbf{q}''|\sigma_1|\mathbf{q}''\rangle]^{\frac{1}{2}}$. Therefore, by (10) and the properties of $\rho(\mathbf{q}',\mathbf{q}'')$ given above, (13) can be satisfied by making $\gamma(|\mathbf{q}'-\mathbf{q}''|)\geqslant\alpha\rho(\mathbf{q}',\mathbf{q}'')$ for every $\mathbf{q}'$ and $\mathbf{q}''$.

If the distance from $\mathbf{q}'$ to the boundary exceeds $2R$, then $\langle\chi'\rangle_\vartheta$ and $\langle\chi'^2\rangle_\vartheta$ are (approximately) positive constants independent of N and $\mathbf{q}'$. For we may take the sphere S_1 defined in Sec. 5 to be $S(\mathbf{q}')$; then the relative probabilities for the various configurations of particles inside $S(\mathbf{q}')$—on which alone χ' depends—are independent of N and the relative positions of S_2 and the boundary. It follows that $V^{-1}\int_V\langle\chi'\rangle_\vartheta d^3\mathbf{q}'\cong\text{const}>0$ and also, by (36), that $c^2N\cong\text{const}>0$ since $\langle\mathbf{q}'|\sigma_1|\mathbf{q}'\rangle\cong N/V$ if $\mathbf{q}'$ is far from the boundary. Applying the criterion (19) to the Ψ defined in (39), we conclude that B.E. condensation is present in liquid He^4 at absolute zero.

The above discussion would not lead one to expect B.E. condensation in a solid, because the assumption of no long-range configurational order is valid for a fluid phase only. In fact, it can be argued that a solid does *not* show B.E. condensation, at least for $T=0$°K. We assume that a solid at $T=0$°K is a perfect crystal

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[34] M. N. Roxenbluth and A. W. Rosenbluth, J. Chem. Phys. **22**, 881 (1954).

[35] H. Cramer, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, 1946), p. 277.

—i.e., that there exists a set of lattice sites such that ψ is small unless one particle is near each lattice site.[36] In the expression (31) for the reduced density matrix, therefore, the integrand will be appreciable only if every one of the points $\mathbf{x}_2\cdots\mathbf{x}_N$ is near a separate lattice site, while both $\mathbf{q}'$ and $\mathbf{q}''$ are near the remaining site. When $|\mathbf{q}'-\mathbf{q}''|$ is large, this last condition cannot be fulfilled, so that $\langle\mathbf{q}'|\sigma_1|\mathbf{q}''\rangle$ will tend to 0 for large $|\mathbf{q}'-\mathbf{q}''|$. This indicates that the function Ψ of (13) will be 0, so that, by (20), there is no B.E. condensation in a solid at absolute zero.

Our result that B.E. condensation occurs in liquid He^4 at $T=0°$K must now be extended to nonzero temperatures. (The need for such an extension is illustrated by the example of a two-dimensional B.E. gas, which[4] shows B.E. condensation at $T=0°$K but not for $T\neq 0°$K.) This will be done in the next section.

7. B.E. CONDENSATION AND THE LAMBDA-TRANSITION

Feynman,[7] and also Matsubara,[6] have studied the lambda-transition in liquid helium by expressing the partition function in the form

$$Z=\sum_{\{m_l\}}[\prod_l (m_l!l^{m_l})]^{-1}\,\mathrm{tr}(Pe^{-\beta H}),\tag{40}$$

where the sum is over all partitions of the number N (that is, over all sets $\{m_l\}$ of non-negative integers satisfying $\sum_l m_l=N$), P is any permutation containing m_l cycles[37] of length l ($l=1\cdots N$), and $\beta\equiv 1/kT$ with $k\equiv$Boltzmann's constant. Evaluating (40) with the help of approximations for $\mathrm{tr}(Pe^{-\beta H})$, they showed how it could exhibit a transition, which they identified with the lambda-transition. In the present section, we shall show that Feynman's approximations also imply that the criterion (4) of B.E. condensation is satisfied for He II in equilibrium.

The statistical operator for thermal equilibrium is

$$\sigma=(N!Z)^{-1}\sum_P Pe^{-\beta H},\tag{41}$$

where the sum is over all permutations P of the N particles. Feynman's path integral[7] for the density matrix shows that the position representative of (41) is non-negative. Therefore the corresponding reduced density matrix, calculated according to (3), is also non-negative, so that the quantity defined in (8) is now given by

$$A_1=(N!ZV)^{-1}\sum_P\int\int d\mathbf{q}'_1 d\mathbf{q}_1''\langle\mathbf{q}_1'|\mathrm{tr}_{2\ldots N}Pe^{-\beta H}|\mathbf{q}_1''\rangle.\tag{42}$$

All permutations corresponding to a given partition $\{m_l\}$ and also having particle No. 1 in a cycle of given length L contribute equal terms to the above sum, since a suitable relabeling of the particles $2\cdots N$ will turn any one such term into any other. Collecting together, for each $\{m_l\}$ and L, the $(L/N)N!/\prod_l(m_l!l^{m_l})$ equal terms, we can write A_1 as a sum over L and $\{m_l\}$, obtaining

$$A_1=N^{-1}\sum_L L\langle m_L A_{1,L}\{m_l\}\rangle.\tag{43}$$

Here we have defined, for any function $f\equiv f\{m_l\}$ depending on the set of numbers $\{m_l\}$, a quantity

$$\langle f\rangle\equiv Z^{-1}\sum_{\{m_l\}}[\prod_l(m_l!l^{m_l})]^{-1}f\{m_l\}\,\mathrm{tr}(Pe^{-\beta H}),\tag{44}$$

where P is any permutation corresponding to the partition $\{m_l\}$. We have also defined

$$A_{1,L}\{m_l\}\equiv\frac{\int\int d\mathbf{q}_1'd\mathbf{q}_1''\langle\mathbf{q}_1'|\mathrm{tr}_{2\ldots N}Pe^{-\beta H}|\mathbf{q}_1''\rangle}{V\,\mathrm{tr}(Pe^{-\beta H})},\tag{45}$$

where P is any permutation which corresponds to the partition $\{m_l\}$ and also has particle No. 1 in a cycle of length L.

To use (43), we introduce two approximations due to Feynman.[7,38] The first is

$$\begin{aligned}\langle\mathbf{q}_1'\cdots\mathbf{q}_N'|Pe^{-\beta H}|\mathbf{q}_1''\cdots\mathbf{q}_N''\rangle\\ \simeq K\lambda^{-3N}\phi(\mathbf{q}_1'\cdots\mathbf{q}_N')\phi(\mathbf{q}_1''\cdots\mathbf{q}_N'')\\ \times\exp[-(\pi/\lambda^2)\textstyle\sum_j(\mathbf{q}_j'-\mathbf{q}_{Pj}'')^2],\end{aligned}\tag{46}$$

where K is a constant, λ means $h(2\pi m'kT)^{-\frac{1}{2}}$ with m' an effective mass, and $\phi(\mathbf{x}_1\cdots\mathbf{x}_N)$ is a normalized non-negative symmetric function which reduces to the ground-state wave function when $T\to 0°$K. (We deviate slightly from Feynman's usage: he does not take ϕ to be normalized.) Feynman's other approximation is used in evaluating integrals over configuration space involving (46); it is to replace the factor containing ϕ by its value averaged over the region of integration and to replace each factor $\exp[-\pi(\mathbf{x}_i-\mathbf{x}_j)^2/\lambda^2]$ by

$$G(\mathbf{x}_i-\mathbf{x}_j)\equiv p(|\mathbf{x}_i-\mathbf{x}_j|)\exp[-\pi(\mathbf{x}_i-\mathbf{x}_j)^2/\lambda^2],\tag{47}$$

where $p(0)\equiv 1$ and $p(r)$ for $r>0$ is the radial distribution function, tending to 1 as $r\to\infty$.

Using these approximations in (45), we obtain

$$A_{1,L}\{m_L\}\simeq A_{1,\infty}\delta_L/f_L,\tag{48}$$

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[36] For equilibrium at a temperature $T\neq 0°$K, a few atoms will be in interstitial positions far from their proper lattice sites. The fraction of interstitial atoms will be $e^{-W/kT}$, where W is the energy required to excite one atom from a lattice to an interstitial site. This fraction tends to 0 as T tends to 0°K.

[37] For the definition of a cycle, see R. P. Feynman, reference 7, or H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 538.

[38] For a critical discussion of these approximations, see G. V. Chester, Phys. Rev. **93**, 1412 (1954).

where (with $\mathfrak{x}$ standing, as before, for $\mathbf{x}_2\cdots\mathbf{x}_N$)

$$A_{1,\infty}\equiv V^{-1}\int\cdots\int\phi(\mathbf{q}',\mathfrak{x})\phi(\mathbf{q}'',\mathfrak{x})d\mathbf{q}'d\mathbf{q}''d\mathfrak{x},\tag{49}$$

$$\delta_L\equiv V^{-1}\int\cdots\int\prod_{j=1}^{L}G(\mathbf{x}_{j+1}-\mathbf{x}_j)d\mathbf{x}_1\cdots d\mathbf{x}_{L+1},\tag{50}$$

$$f_L\equiv\int\cdots\int G(\mathbf{x}_1-\mathbf{x}_L)\prod_{j=2}^{L}G(\mathbf{x}_j-\mathbf{x}_{j-1})d\mathbf{x}_1\cdots d\mathbf{x}_L.\tag{51}$$

[For $L=1$ we interpret (51) as $f_1\equiv V$.]

To find the order of magnitude of $A_{1,\infty}$, we replace ϕ in (49) by the ground-state wave function ψ (since ϕ is qualitatively similar to ψ and both are normalized). Then, by (31) and (8), $A_{1,\infty}$ roughly equals the value of A_1 for $T=0°K$; this is finite, by (12) and the result of Sec. 6. Feynman[7] has suggested using the approximation (32) for ϕ as well as for ψ; this leads, by (18) and (35), to the rough estimate $A_{1,\infty}\simeq 0.08$.

We estimate δ_L by replacing the integrals over $d\mathbf{x}_2\cdots d\mathbf{x}_{L+1}$ in (50) by the corresponding infinite integrals. This gives $\delta_L\simeq\delta_1{}^L$, which, when combined with (48) and (43), yields

$$A_1/A_{1,\infty}\simeq N^{-1}\textstyle\sum_L L\langle m_L\rangle\delta_1{}^L/f_L.\tag{52}$$

To study (52), we note that Feynman's approximations (46) and (47) also imply[7] $\operatorname{tr}(Pe^{-\beta H})\simeq K\lambda^{-3N}\times\prod_l(f_l{}^{m_l})$. Substituting this into (40) and (44) yields

$$\langle Lm_L/f_L\rangle=Q_{N-L}/Q_N,\tag{53}$$

where

$$Q_M\equiv\sum_{\{ml\}}\prod_l(f_l/l)^{m_l}/m_l!,\tag{54}$$

the sum being over all partitions of the arbitrary integer M. Equation (54) is just Mayer's expression[39] for the configurational partition function of an imperfect gas of M particles with cluster integrals $b_l=f_l/lV$. Therefore if $z\equiv Q_{N-1}/Q_N\cong\text{const}$ is the activity of this imperfect gas when it contains N particles, the approximation $Q_{N-L}/Q_N\cong z^L$ will hold provided $L\ll N$.

Using this approximation with (53) and (52), we obtain

$$A_1/A_{1,\infty}\simeq N^{-1}\sum_{L=1}^{N}(z\delta_1)^L\simeq N^{-1}(1-z\delta_1)^{-1}=o(1)\tag{55}$$

provided that $z\delta_1\cong\text{const}<1$. Feynman's work[7] shows that this condition holds above the transition temperature; therefore, since $A_{1,\infty}=e^{O(1)}$ and (12) holds, there is no B.E. condensation in HeI.

This argument fails below the transition temperature, where $z\delta_1\cong 1$. To study this case, we combine (52) with the identity $1=N^{-1}\sum_L L\langle m_L\rangle$ [which follows from (40) and (44)] and use (53); this gives

$$1-A_1/A_{1,\infty}\simeq N^{-1}\textstyle\sum_L(f_L-\delta_1{}^L)Q_{N-L}/Q_N.\tag{56}$$

Feynman[7] estimates that, unless L is a small integer,

$$f_L\simeq(L^{-\frac{3}{2}}V\Delta+1)\delta_1{}^L,\tag{57}$$

where

$$\Delta\equiv\left[3\delta_1\Big/8\pi^2\int_0^\infty G(r)r^4dr\right]^{\frac{3}{2}}.$$

Therefore, although the approximation $Q_{N-L}/Q_N\simeq z^L$ is no longer legitimate in (52), it is still legitimate in (56), according to (57), a convergent series results even though $z\delta_1\cong 1$:

$$1-A_1/A_{1,\infty}\cong\text{const}+N^{-1}\sum_{L=1}^{\infty}V\Delta L^{-\frac{3}{2}}\cong\text{const},\tag{58}$$

where the first "const" takes care of the error due to the failure of (57) for small L. Feynman's work[7] shows that the right-hand side of (58) is less than 1 below the transition. Hence $A_1/A_{1,\infty}\cong\text{const}>0$, and, by (12), B.E. condensation does occur in He II.

The deductions we have made from Feynman's approximations can be paraphrased as follows: the quantity $\langle A_{1,L}\{m_l\}\rangle$ is very small if $L\ll(V\Delta)^{\frac{2}{3}}$ (where Δ is finite), and equals the finite quantity $A_{1,\infty}$ if $L\gg(V\Delta)^{\frac{2}{3}}$. Hence, by (43), $A_1/A_{1,\infty}$ equals the contribution of large L values to the sum $N^{-1}\sum L\langle m_L\rangle$; that is, it equals the fraction of particles in large cycles. Above the lambda-transition this fraction is negligible, so that, by (12), there is no B.E. condensation; below the transition this fraction is finite, so that B.E. condensation is present.

8. DISCUSSION

Equation (4) provides a mathematical definition of B.E. condensation, applicable for a system of interacting particles as well as for an ideal gas. Physically, the definition means that B.E. condensation is present whenever a finite fraction—n_M/N— of the particles occupies one single-particle quantum state, φ_M. The definitions of n_M and φ_M are given in Sec. 3 and Sec. 4, respectively. Even for an ideal gas, our definition is more general than the usual one, since here φ_M is not necessarily the lowest single-particle energy level. The close relation between our definition of B.E. condensation and London's suggested[1,2] "condensation in momentum space" is illustrated in the last paragraph of Sec. 3 above, where it is shown that under suitable conditions φ_M actually is an eigenstate of momentum.

The reasoning of Secs. 5, 6, and 7 indicates that liquid helium II satisfies our criterion of B.E. condensation. For $T=0°K$ the only physical assumption used is that a quantum liquid—as distinct from a solid—lacks long-range configurational order (though the mathematical treatment of this assumption is not yet

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[39] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), pp. 277–282.

completely rigorous). For $T>0°\text{K}$, some fairly crude approximations, taken from Feynman's theory of the lambda-transition, have to be introduced. This part of the theory is therefore open to improvement—possibly in the form of a more rigorous proof that Feynman's implied criterion for B.E. condensation [the importance of long cycles in the sum (40) for the partition function] is equivalent to our criterion (4) at thermal equilibrium. Despite these imperfections, however, our analysis would appear to strengthen materially the case put forward previously by London[1,2] and Tisza[9] for the importance of B.E. condensation in the theory of liquid helium.

We have not considered here how B.E. condensation is related to superfluidity and to the excitation theory[16,17] of liquid helium. This will be done in another paper, where some of the results already obtained by Bogolyubov[12] for weakly repelling B.E. particles will be extended[40] to the case of interacting He^4 atoms.

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[40] A brief account of this work was given at the National Science Foundation Conference on Low-Temperature Physics and Chemistry, Baton Rouge, Louisiana, December, 1955 (unpublished).

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Spectral Diffusion in Magnetic Resonance*

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Electron spin-spin interaction is discussed for the case of strong hyperfine broadening. The hyperfine interaction is represented by a resonance spectrum of width $\Delta\omega$ and the electron interactions, which are taken to be dipolar, are treated by time-dependent perturbation theory. A characteristic relaxation time for electron spins, $\tau_s=\Delta\omega/\Delta^2$, is found, where Δ is a measure of the strength of the dipolar interaction. The time-dependent theory suggests a modification of the Bloch equations to give a phenomenological description of systems of this kind. Spin-spin relaxation is represented by a term which gives diffusion of spin excitation through the resonance spectrum. Slow passage, rapid passage, and free relaxation are considered by using the modified equations.

I. INTRODUCTION

THE Bloch equations[1] have given a satisfactory description of saturation effects involving F centers in alkali halides.[2] One of the reasons for this success is that the dipolar interaction between F-center electrons is extremely weak compared with the lattice interaction.[3] The effects of spin-spin interaction have not been observed in room temperature studies. Although the interaction is quite weak, it should be detectable at liquid helium temperatures.

The purpose of this note is to consider the form expected for such an interaction. In the first part a treatment of dipolar interaction is developed in terms of time-dependent perturbation theory. The results of this treatment are applied to a macroscopic description of the interaction in terms of a modification of the Bloch equations. In the final section, these equations are applied in an examination of slow passage, rapid passage, and free relaxation.

II. MICROSCOPIC THEORY

We consider a system suggested by the interaction between F-center electrons in alkali halides. The interaction between electron spins is taken to be dipolar. There is a contact-type hyperfine interaction between electron and nuclear magnetic moments.[4] For simplicity electron spin-orbit coupling is neglected. The magnetic Hamiltonian in an external field $\mathbf{H}_0$ is given by

$$\mathcal{H}=\sum_i g\beta\mathbf{s}_i\cdot\mathbf{H}_0-\frac{16\pi}{3}\sum_{il}\beta\mu_l|\psi_i(\mathbf{r}_l)|^2\mathbf{s}_i\cdot\mathbf{I}_l/I_l$$
$$+\tfrac{1}{2}\sum_{ij}g\beta\mathbf{s}_i\cdot\left[\frac{g\beta\mathbf{s}_j}{r_{ij}^3}-\frac{3g\beta\mathbf{r}_{ij}(\mathbf{r}_{ij}\cdot\mathbf{s}_j)}{r_{ij}^3}\right]. \quad (2.1)$$

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[1] F. Bloch, Phys. Rev. **70**, 460 (1946).

[2] A. M. Portis, Phys. Rev. **91**, 1071 (1953). The identification of T_2 in this reference with the mean dipolar field is in error. As established in the present treatment, T_2 should equal T_1 for F centers in KCl at room temperature. This yields a corrected value of 8×10^{-6} sec for T_1.

[3] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[4] Kip, Kittel, Levy, and Portis, Phys. Rev. **91**, 1066 (1953).