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Equation of State of a Bose-Einstein System of Particles with Attractive Interactions*

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The equation of state in the grand canonical ensemble is calculated for a system of Bose-Einstein particles with hard-sphere repulsive interactions and weak long-range attractions. The energy levels used in this calculation are modified forms of those derived in an earlier paper. The calculation is carried out in the limit of no interactions, and attention is focused on the thermodynamic phases of the system. It is shown that the gross features of the equation of state of He^4 are reproduced. There are the phases: gas, liquid I, and liquid II. The phase transition between gas and the two liquids are first order transitions. The transition terminates in a critical point. The transition between liquid I and liquid II is the Bose-Einstein condensation. Liquid II has a negative coefficient of thermal expansion. Across the transition between liquids I and II the specific heat is discontinuous in value. In the limit of no interactions, the critical point recedes towards zero temperature, zero pressure, and infinite volume.

I. INTRODUCTION

THIS paper is the logical successor of a previous one,[1] in which the quantum mechanical energy levels of a Bose-Einstein system of particles with attractive interactions were calculated. This paper is concerned with a calculation of the thermodynamic equation of state of the same system.

The system considered, both in I and in the present investigation, consists of N Bose-Einstein particles enclosed in a box of volume Ω with periodic boundary conditions imposed on the wave functions. The particles interact among themselves with a two-body potential, which contains a hard-sphere repulsion of diameter a, plus a weak long-ranged attraction. The system is considered in the limit $N\rightarrow\infty$, $\Omega\rightarrow\infty$, with $\rho=N/\Omega$ kept finite and small: $\rho a^3\ll 1$.

It was shown in I that if the parameters of the attractive part of the potential are properly chosen, the ground state of the system is a bound state of all N particles, with a finite binding energy and a finite equilibrium density ρ_0 satisfying $\rho_0 a^3\ll 1$. The excited states can be described in terms of elementary excitations, which for low energies are phonons.

In the present investigation we calculate the partition function of the system from the energy levels obtained previously. From the partition function is derived the equation of state, which is valid for low densities and low temperatures.

The main result of this calculation is that the system exhibits three thermodynamic phases, which are called gas, liquid I, and liquid II. Liquid II is distinguished from liquid I and gas by the fact that in liquid II a finite fraction of all the particles occupy a single quantum level, whereas in the latter two phases no single level is macroscopically occupied. Furthermore, liquid II, in contradistinction to the other two phases, exhibits "superfluidity." The gas phase and the liquid I phase are distinguishable only below a certain critical temperature, and are separated by a first order transition. The gas phase and liquid II are also separated by a first order transition. The phase transition between liquid I and liquid II is a Bose-Einstein condensation, but not of first order, as would be the case in the ideal Bose gas. The specific heat of the system suffers a finite discontinuity across the Bose-Einstein condensation.

The motivation for the present work is given in Sec. II. Section III explains, in a simple and qualitative way, the results of this work in crude form. The subsequent sections describe the details of the calculation.

II. BACKGROUND AND MOTIVATION

The motivation for studying the N-body problem with Bose statistics is the desire to understand the

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* This work is supported in part by funds provided by the U. S. Atomic Energy Commission, the Office of Naval Research and the Air Force Office of Scientific Research.

[1] K. Huang, Phys. Rev. **115**, 765 (1959). Hereafter this will be referred to as I.

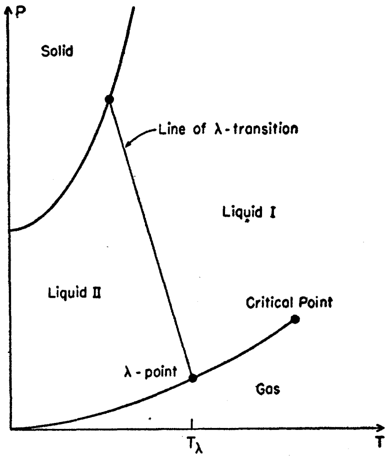

FIG. 1. The P-T diagram of He^4 (not to scale).

behavior of He^4. Some of its remarkable properties are brought out by its P-T diagram[2] (Fig. 1). In contradistinction to all other substances He^4 possesses two liquid phases, of which liquid I is ordinary in nature but liquid II is unusual. It exists down to the absolute zero of temperature and exhibits "superfluidity."[2] The specific heat measured along the vapor pressure curve is proportional to T^3 near absolute zero, and diverges logarithmically as $T \to T_\lambda$, both from above and below.[3]

From a molecular point of view, our theoretical understanding of liquid helium has been confined only to liquid II in the neighborhood of absolute zero. For this understanding we are indebted to the work of Feynman, combined with the earlier works of Tisza, London, and Landau.[2] The final picture is the following: As a consequence of the Bose statistics, the low-lying quantum states of the liquid are represented by phonon excitations, and only phonon excitations, whose energies depend linearly on their momenta. This immediately explains the T^3 behavior of the specific heat. One then takes over Tisza's two-fluid model of liquid II, and identifies the "gas" of phonons to be the normal fluid, and the rest of the system the superfluid. The superfluidity of the system is then to a large extent explained following Tisza's thermodynamic considerations and London's hydrodynamic considerations.

The nature of the λ transition remains obscure. While there seems little doubt in the correctness of London's suggestion that it is a Bose-Einstein condensation, the mathematical complexity of the problem has so far withheld a detailed understanding. This being the case, it is worthwhile to study some idealized mathematical models, in the hope that they provide insight into the actual physical problem.

One of the simplest models that has some connection with liquid helium is the hard-sphere Bose gas,[4–6] in which the particles of the gas are taken to be impenetrable spheres of diameter a. For low densities ($\rho a^3 \ll 1$) the quantum mechanical energy levels of the system have been calculated.[4] They turn out to be describable in terms of purely phonon excitations. What Feynman, Landau, London, and Tisza have achieved for liquid helium becomes immediately applicable here: The hard-sphere Bose gas, near absolute zero, exhibits superfluid properties. The equilibrium thermodynamics[5] and the transport properties[6] at higher temperatures have been studied. The thermodynamic properties may be summarized as follows:

(a) The system can exist in two phases: gas and degenerate. They are distinguished by the fact that in the former no quantum level is occupied by a finite fraction of all the particles, whereas in the latter the lowest quantum level is occupied by a finite fraction of all the particles. The transition between them is obviously the Bose-Einstein condensation. The P-T diagram of the hard-sphere Bose gas, shown in Fig. 2, is qualitatively indistinguishable from that of the ideal Bose gas.

(b) The Bose-Einstein condensation here is not a first order transition, in contradistinction to that in the ideal Bose gas. The pressure increases with volume below the transition volume. It has a discontinuous slope at the transition point, implying a finite discontinuity of the specific heat at the transition point. *Note added in proof:* This result, being nonexact, does not rule out the occurrence of singularities in a higher-order calculation.

A glance at Figs. 2 and 1 shows that the P-T diagram of the hard-sphere Bose gas bears little resemblance to that of He^4. Although it is suggestive that the λ transition in He^4 is of the same intrinsic nature as the Bose-Einstein condensation, the λ transition takes place be-

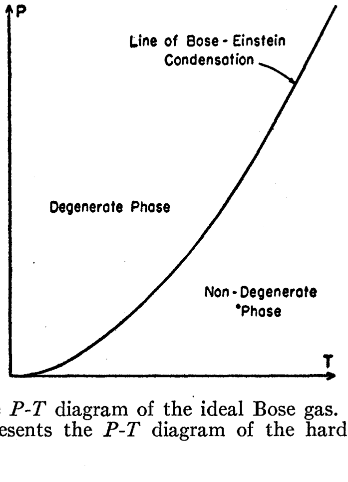

FIG. 2. The P-T diagram of the ideal Bose gas. Qualitatively this also represents the P-T diagram of the hard-sphere Bose gas.

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[2] See K. R. Atkins, *Liquid Helium* (Cambridge University Press, New York, 1959).

[3] Fairbank, Buckingham, and Kellers, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, 1957*, edited by J. R. Dillinger (The University of Wisconsin Press, Madison, 1958), p. 50.

[4] T. D. Lee, K. Huang, and C. N. Yang, Phys. Rev. **106**, 1135 (1957).

[5] T. D. Lee and C. N. Yang, Phys. Rev. **112**, 1419 (1958).

[6] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1406 (1959).

tween two *liquids*, while the gas phase makes first order transitions to liquid II and to liquid I, with the latter transition ending in a critical point. It is hence impossible to make any comparison between the hard-sphere Bose gas and He^4, as far as phase transitions are concerned. (The solid phase of He^4 may be ignored since we confine ourselves to low densities and low pressures.)

It is obvious that, just as in ordinary matter, the gas-liquid structure of He^4 arises from the attractive part of the intermolecular potential. The fact that liquid II is a bound system is evidenced by the observation that the vapor pressure curve separating liquid II and gas has a finite slope. Through the Clapeyron equation, this implies a finite latent heat, which in turn implies a finite binding energy for liquid II. The interplay between the gas-liquid condensation arising from the attraction, and the Bose-Einstein condensation arising from the Bose statistics, must be the origin of the different phases of He^4. It seems interesting, therefore, to study such an interplay of interaction and statistics in a simple mathematical model. We can make such a model by embellishing the hard-sphere Bose gas, attaching a weak long-ranged attraction to the impenetrable spheres that were the particles. This is the model studied in the present investigation.

III. QUALITATIVE EXPLANATION OF RESULTS

The main results of this work will now be explained qualitatively. It would be instructive if we first do the same thing for the hard-sphere Bose gas, which is a simpler model.

The quantum mechanical energy levels of the hard sphere Bose gas, in the limit of $\rho a^3 \rightarrow 0$, are labeled by a set of occupation numbers $\{n_{\mathbf{k}}\}$. The ground state energy is[7]

$$E_0(\rho)=4\pi a\rho N.$$

The low-lying excited states, in which few phonons are excited, have the energies[4]

$$E\{n_{\mathbf{k}}\}=E_0(\rho)+\sum\nolimits_{\mathbf{k}} k(k^2+16\pi a\rho)^{\frac{1}{2}} n_{\mathbf{k}},$$

where $k=|\mathbf{k}|$. This formula is valid only if

$$N^{-1}\sum_{\mathbf{k}\neq 0} n_{\mathbf{k}} \ll 1.$$

The phonons here appear as independent excitations with momenta $\mathbf{k}$ and energies $k(k^2+16\pi a\rho)^{\frac{1}{2}}$. When so many phonons are excited that their total number becomes a finite fraction of N, the energy must be replaced by the more accurate formula[5]

$$E\{n_{\mathbf{k}}\}=[1+(1-\xi)^2]E_0(\rho)+\sum\nolimits_{\mathbf{k}} k(k^2+16\pi a\rho\xi)^{\frac{1}{2}} n_{\mathbf{k}},$$

where ξ stands as an abbreviation for the fraction of particles with zero momentum:

$$\xi \equiv 1-N^{-1}\sum_{\mathbf{k}\neq 0} n_{\mathbf{k}}. \quad (0\leqslant \xi \leqslant 1)$$

If we put $\xi=1$ this formula reduces to the previous case. Thus the phonons are no longer strictly independent because ξ appears in their energies. Further, the total energy of the system, on account of the presence of the term $(1-\xi)^2$, is no longer a sum of phonon contributions. There is now a "collective" effect.

Let us now calculate the partition function of the hard-sphere Bose gas. There will exist a macroscopic parameter $\bar{\xi}$ $(0\leqslant \bar{\xi} \leqslant 1)$ which is the thermodynamic average of ξ. The Bose-Einstein condensation will be the transition separating the phase in which $\bar{\xi}=0$ (gas phase), and the phase in which $\bar{\xi}>0$ (degenerate phase). In the interest of simplicity we neglect the term $16\pi a\rho\xi$ in the phonon energy. This is a justifiable approximation if the temperature is not too low. The energy levels accordingly become

$$E\{n_{\mathbf{k}}\}=[1+(1-\xi)^2]E_0(\rho)+\sum\nolimits_{\mathbf{k}} k^2 n_{\mathbf{k}}.$$

The partition function is

$$Q_N=\sum_{\Sigma n_{\mathbf{k}}=N} \exp(-\beta E\{n_{\mathbf{k}}\}),$$

where $\beta=1/\kappa T$, κ being Boltzmann's constant. We may perform the sum-over-states in the following fashion: First choose a fixed value of ξ. Sum over all choices of $\{n_{\mathbf{k}}\}$ satisfying the condition $\sum_{\mathbf{k}\neq 0} n_{\mathbf{k}}=N(1-\xi)$. Finally sum over all values of ξ from 0 to 1. We obtain in this manner:

$$Q_N=\sum_{\xi=0}^{1} \exp\{-\beta[1+(1-\xi)^2]E_0(\rho)\}Q_{N(1-\xi)}{}^{(0)},$$

where $Q_N{}^{(0)}$ is the partition function of an ideal Bose gas of N particles. The logarithm of Q_N, in the limit $N\rightarrow\infty$, is obtained in the usual way by taking the logarithm of the largest term in the sum above. The value of ξ for the largest term is denoted by $\bar{\xi}$, which is the thermodynamic average of ξ:

$$-\beta^{-1}\ln Q_N=[1+(1-\bar{\xi})^2]E_0(\rho) +A_{N'}{}^{(0)}(\Omega,T)=A_N(\Omega,T),$$

where $A_N(\Omega,T)$ is the Helmholtz free energy of the hard-sphere Bose gas of N particles, and $A_N{}^{(0)}(\Omega,T)$ is the corresponding quantity for a modified ideal Bose gas in which the weight of the $k=0$ level is ignored; $N'\equiv N(1-\bar{\xi})$. The pressure of the system is given by $P=-\partial A_N/\partial\Omega$. In this differentiation, we need not differentiate with respect to the implicit dependence on Ω through $\bar{\xi}$, because $(\partial A/\partial\xi)=0$ when $\xi=\bar{\xi}$. At low densities $\bar{\xi}$ is determined essentially by minimizing the term $A_{N(1-\xi)}{}^{(0)}$ alone, because the other term is proportional to ρ. This of course yields for $\bar{\xi}$ its value for

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[7] We choose units such that $\hbar=1$, $2m=1$, where m is the mass of a particle.

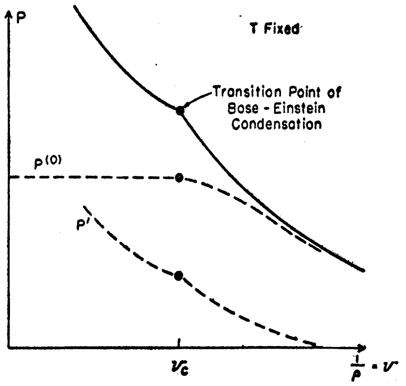

FIG. 3. Isotherm of the hard-sphere Bose gas (solid line). It is the sum of the two dotted lines. The construction is explained in the text.

the ideal Bose gas[5]:

$$\bar{\xi}=0 \quad \text{if} \quad \rho^{-1}>\rho_c^{-1},$$
$$\bar{\xi}>0 \quad \text{if} \quad \rho^{-1}<\rho_c^{-1},$$

where $\rho_c(T)$ is the transition density. With this value of $\bar{\xi}$, $A_{N'}^{(0)}$ becomes *exactly* the free energy of the true ideal Bose gas.[5] We thus obtain the pressure as a sum of two terms:

$$P=-[1+(1-\bar{\xi})^2](\partial E_0/\partial\Omega)+P^{(0)},$$

where $P^{(0)}$ is the pressure of an ideal Bose gas. Thus an isotherm is obtained by adding to an isotherm of the ideal Bose gas a curve similar in shape to the curve of $-\partial E_0/\partial\Omega$, where E_0 is the ground-state energy. A typical isotherm is sketched in Fig. 3. The "kink" in the curve arises from the derivative $\partial\bar{\xi}/\partial(1/\rho)$, which is discontinuous at $\rho=\rho_c$.

Keeping in mind the example just discussed, we can crudely explain the results of the present work with only a few arguments. This we now proceed to do.

With the addition of an attractive interaction in addition to the hard-sphere repulsion, the ground state of the system becomes a bound state over a certain range of the density ρ, with negative total energy[1] E_0. A qualitative plot of E_0/N as a function of ρ is given in Fig. 4. The pressure P_0 at absolute zero is obtained by taking the negative derivative of E_0/N with respect to ρ^{-1}. This is also shown in Fig. 4. Due to the inexactness of the calculation, the pressure becomes negative for $\rho^{-1}>\rho_0^{-1}$; but by using a limiting form of the Maxwell construction, we obtain $P_0=0$ for $\rho^{-1}>\rho_0^{-1}$.

The meaning of the Maxwell construction is the following: The state of the system at $\rho=\rho_0$ can coexist with that at $\rho=0$ because they both have the same pressure and temperature. For $\rho^{-1}>\rho_0^{-1}$ the free energy of the system is lowest if the system breaks up into two parts, one being in the state at $\rho=\rho_0$, and the other in the state at $\rho=0$. The state at $\rho=0$ is of course a vacuum. The Maxwell construction, which is usually based on a thermodynamic argument, becomes an automatic procedure if one calculates the pressure not in a canonical ensemble but in a grand canonical ensemble. Thus we already see that at absolute zero there is a first order transition of the gas-liquid type.

In order to obtain the equation of state at a finite temperature we need the excited energy levels of the system.[1] It suffices to say that they are again labeled by a set of occupation numbers $\{n_{\mathbf{k}}\}$. And, as in the hard-sphere Bose gas, the energy may be split into two terms, one depending only on the combination of the occupation numbers[8]:

$$\xi\equiv 1-N^{-1}\sum_{\mathbf{k}\neq 0} n_{\mathbf{k}},$$

and the other is the contribution from elementary excitations:

$$E\{n_{\mathbf{k}}\}=E_{1-\xi}(\rho)+\textstyle\sum_{\mathbf{k}} \omega_{\mathbf{k}} n_{\mathbf{k}},$$

where, for $\xi=1$, $E_{1-\xi}(\rho)$ reduces to the graph of Fig. 4, and where the phonon energy $\omega_{\mathbf{k}}$ approaches k^2 for large k. Again let us make the approximation $\omega_{\mathbf{k}}\cong k^2$ so that the energy levels become

$$E\{n_{\mathbf{k}}\}=E_{1-\xi}(\rho)+\textstyle\sum_{\mathbf{k}} \omega_{\mathbf{k}} n_{\mathbf{k}}.$$

In complete analogy with the hard-sphere Bose gas, we can immediately write down, for the pressure of the system, the expression

$$P=-\left(\frac{\partial E}{\partial\Omega}\right)_{1-\bar{\xi}}+P^{(0)},$$

where $P^{(0)}$ is the pressure of the ideal Bose gas, and the first term qualitatively has the same form as $P_0=-\partial E_0/\partial\Omega$ shown in Fig. 4. The first term above of course depends on the temperature through $\bar{\xi}$.

For the sake of illustration, however, let us take

$$P=-\partial E_0/\partial\Omega+P^{(0)}=P_0+P^{(0)}$$

and see what happens. A family of isotherms are shown

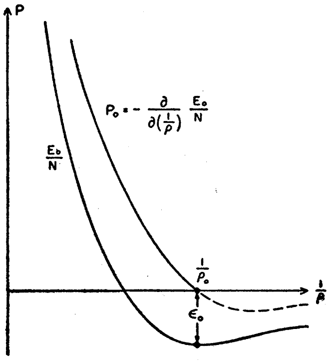

FIG. 4. Ground state energy E_0/N and isotherm at absolute zero P_0 in the present model. The dotted portion of P_0 is to be replaced by the abscissa above it, in accordance with the Maxwell construction.

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[8] This is an oversimplification. Actually the energy depends on one other combination of occupation numbers [i.e., x, see Eq. (4)]; but this suffices to bring out the qualitative features of the results.

in Fig. 5. They are obtained by graphically adding the curve P_0 to the ideal gas isotherms 1, 2, 3, 4, and then making Maxwell constructions when necessary.

The transition line of the Bose-Einstein condensation divides the P–ρ^{-1} plane into two parts. If a point lies to the right of this line, it represents a state for which $\xi=0$. Otherwise $\xi>0$. This is true throughout the P–ρ^{-1} plane except in the area under the line $OPABCDEQR$. A point lying within this area represents a system composed of two parts in thermodynamic equilibrium with each other. For example, at α the two parts are respectively in states P ($\xi>0$) and Q ($\xi=0$), and at β they are B ($\xi=0$) and D ($\xi=0$). The area under $OPABCDEQR$ therefore represents the transition region of first order transitions. The area below AE has to do with those first order transitions between $\xi=0$ and $\xi>0$ states, while that above AE has to do with those first order transitions between $\xi=0$ and $\xi=0$ states. To use a terminology suggestive of He^4, the former are transitions between gas and liquid II, while the latter are between gas and liquid I. The transition region for the gas-liquid I transitions end in a critical point C, above which one can no longer distinguish gas and liquid.

The transition line of Bose-Einstein condensation meets the transition area of first order transitions at point A. It can be seen graphically that below point A this transition area *necessarily* contains the line of Bose-Einstein condensation, so that the latter never "comes out" again. Once inside the said transition area, the line of Bose-Einstein condensation is no longer meaningful because, as we have said, a point there represent a mixture of two states each of which are states lying on the boundary line $OPABCDEQR$. Above point A the line of Bose-Einstein condensation divides liquids I and II. We may therefore call it the line of λ-transition.

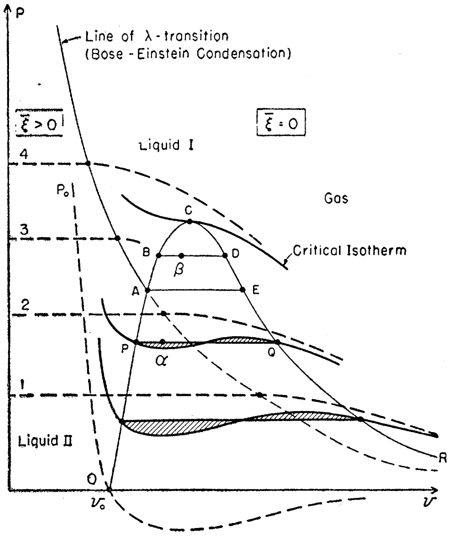

FIG. 5. Qualitative isotherms in the present model. They are obtained by adding curve P_0 to the various isotherms of the ideal Bose gas 1, 2, 3, 4. The construction is explained in the text.

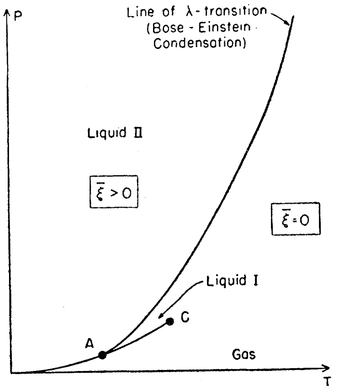

FIG. 6. P-T diagram of the present model.

It is easy to construct qualitatively the P-T diagram. This is shown in Fig. 6 and we see that it now reproduces the features of the P-T diagram of He^4 (Fig. 1), with the exception of the solid phase.

These, qualitatively, are the results of the present investigation.

IV. DEFINITION OF THE MODEL

The starting point of this investigation is Eq. (57) of I for the energy levels of a system of Bose-Einstein particles with hard-sphere repulsive interactions plus weak long-range attractive interactions. The Fourier transform of the interparticle potential is

$$\begin{aligned} v_{\mathbf{k}} &= 8\pi a \quad \text{if} \quad |\mathbf{k}|>k_0 \\ &= -8\pi b \quad \text{if} \quad |\mathbf{k}|<k_0. \end{aligned} \tag{1}$$

The parameters characterizing the potential are a, b, and k_0:

a = scattering length (diameter) of hard sphere;
b = total scattering length of the potential at zero energy; (2)
$k_0 \sim$ (range of the attractive part of potential)$^{-1}$.

There is only one other parameter for this N-body problem, namely the particle density ρ.

An energy eigenvalue of the N-body system, according to Eq. (57) of I, is labeled by a set of occupation numbers $\{n_{\mathbf{k}}\}$, where $\mathbf{k}$ is a vector in the momentum lattice space with lattice constant $L=\Omega^{\frac{1}{3}}$. Each $n_{\mathbf{k}}$ is 0 or a positive integer, and the set $\{n_{\mathbf{k}}\}$ satisfies the condition

$$\textstyle\sum_{\mathbf{k}} n_{\mathbf{k}}=N. \tag{3}$$

The energy eigenvalue corresponding to $\{n_{\mathbf{k}}\}$ is $E\{n_{\mathbf{k}}\}$, given by the formula[7]

$$\begin{aligned} (1/N)&E\{n_{\mathbf{k}}\} \\ &= -4\pi b\rho+4\pi a\rho\{g(\xi,x)+(128/15)(\rho a^3/\pi)^{\frac{1}{2}} \\ &\times F(\sigma)[f(\xi,x)]^{\frac{5}{2}}\}+(1/N)\sum_{k>k_0} k[k^2+16\pi a\rho f(\xi,x)]^{\frac{1}{2}}n_{\mathbf{k}} \\ &\qquad +(1/N)\sum_{0<k<k_0} k[k^2+16\pi a'(\rho)\rho h(\xi,x)]^{\frac{1}{2}}n_{\mathbf{k}}, \end{aligned} \tag{4}$$

where[9]

$$\xi \equiv 1 - N^{-1} \sum_{\mathbf{k}\neq 0} n_{\mathbf{k}} \qquad (0 \leqslant \xi \leqslant 1), \quad (5)$$

$$x \equiv \Big[\sum_{0<k<k_0} n_{\mathbf{k}}\Big] \Big/ \Big[\sum_{k\neq 0} n_{\mathbf{k}}\Big] \qquad (0 \leqslant x \leqslant 1), \quad (6)$$

$$f(\xi,x) \equiv \xi + (1-\xi)x \qquad (0 \leqslant f \leqslant 1), \quad (7)$$

$$g(\xi,x) \equiv (1-\xi)^2[(1+b/a)(1-x)^2 - b/a]$$

$$\cong (1-\xi)^2[(1-x)^2 - b/a], \quad (8)$$

$$\sigma \equiv k_0[16\pi a\rho f(\xi,x)]^{-\frac{1}{2}}, \quad (9)$$

$$F(\sigma) \equiv (15/2)[\tfrac{1}{3}(1+\sigma^2)^{\frac{3}{2}} - \tfrac{1}{5}(1+\sigma^2)^{\frac{5}{2}} + \tfrac{1}{6}\sigma^3 + \tfrac{1}{5}\sigma^5]. \quad (10)$$

The quantity $a'(\rho)$ is given in Eq. (50) of I. We shall not need it here. The quantity $h(\xi,x)$ has not been calculated but will not be needed. We know, however, that $h=1$ when $\xi=1$, and in general $h \leqslant 1$.

The formula (4) is valid under the following restrictions:

(a) $\rho a^3 \ll 1$, $k_0 a \ll 1$, $b/a \ll 1$.

(b) The set $\{n_{\mathbf{k}}\}$ is such that $n_{\mathbf{k}}$ changes negligibly when k changes by k_0.

(c) The set $\{n_{\mathbf{k}}\}$ is such that the levels with large k are not appreciably occupied (low excitations).

(d) Except n_0, no other $n_{\mathbf{k}}$ is a finite fraction of N.

The ground energy is obtained by setting $n_0 = N$ and all other $n_{\mathbf{k}} = 0$:

$$E_0/N = -4\pi b\rho + 4\pi a\rho(128/15)(\rho a^3/\pi)^{\frac{1}{2}} F(\nu), \quad (11)$$

where $\nu = k_0(16\pi a\rho)^{-\frac{1}{2}}$. If one plots this as a function of ρ^{-1}, the energy is everywhere positive if $(b/a) < 2k_0 a/\pi$. It becomes negative for a range of ρ^{-1} if

$$b/a > (2/\pi)k_0 a. \quad (12)$$

This condition is the condition for binding.[10] We shall assume this to be the case, so that E_0/N is qualitatively the curve in Fig. 4. The equilibrium density ρ_0 and binding energy per particle ϵ_0 are then given by

$$a^3\rho_0 \cong \frac{k_0 a}{32}\left(\frac{b}{a} - \frac{2}{\pi}k_0 a\right),$$
$$\epsilon_0 \cong -(64\pi a\rho_0)\rho_0 a^3/k_0 a. \quad (13)$$

We can make ρ_0 as small as we please by making $(b/a) - (2k_0 a/\pi)$ as close to zero as we please. Thus we expect that the interesting phenomenon of condensation can be made to occur at as low a density as we please.

In the calculations to follow, we shall be interested primarily in the phase transitions of the system. The detailed form of the excitation spectrum of elementary excitations, important for the specific heat and for superfluid properties near absolute zero, is not expected to make any *qualitative* difference in the nature of the phase transitions. Accordingly, we replace this spectrum by k^2, the spectrum of a free particle, in order to simplify the calculations. The energy levels then become

$$\frac{1}{N}E\{n_{\mathbf{k}}\} = 4\pi a\rho\left\{-\frac{b}{a}[1+(1-\xi)^2] + (1-f)^2 + \frac{128}{15}\left(\frac{\rho a^3}{\pi}\right)^{\frac{1}{2}} f^{\frac{5}{2}} F(\sigma)\right\} + \frac{1}{N}\sum_{\mathbf{k}\neq 0} k^2 n_{\mathbf{k}}, \quad (14)$$

where $f \equiv f(\xi,x)$ is defined in (7). We have used the fact that

$$(1-f) = (1-\xi)(1-x), \quad (15)$$

which easily follows from (7). According to the remarks following (13), we may confine the calculation to as low a density as we please. This enables us to simplify $F(\sigma)$ by expanding $f^{\frac{5}{2}}F(\sigma)$ about $\rho = 0$:

$$f^{\frac{5}{2}}F(\sigma) = \tfrac{15}{16} f^2 v^{\frac{1}{2}} \times [1 + \tfrac{1}{2}(f/v) - (11/48)(f/v)^2 + \cdots], \quad (16)$$

where v is a dimensionless volume defined by

$$v \equiv [16\pi a^3\rho/(k_0 a)^2]^{-\frac{1}{2}}. \quad (17)$$

The final form of the energy eigenvalues is

$$\frac{1}{N}E\{n_{\mathbf{k}}\} = \left(\frac{4\pi}{a}\right)^2 \left(\frac{k_0 a}{4\pi}\right)^3 \times \left\{\left(\frac{\pi}{k_0 a}\right)\left[(1-f)^2 - \frac{b}{a} - \frac{b}{a}(1-\xi)^2\right]\frac{1}{v} + \frac{2f^2}{v}\left(1 + \frac{f}{2v}\right)\right\} + \frac{1}{N}\sum_{k\neq 0} k^2 n_{\mathbf{k}}, \quad (18)$$

where v is defined by (17).

We shall use the energy levels (18) for the calculation of the partition function of the system. According to the restrictions on the validity of (18), this partition function gives valid results for low densities and low temperatures. Therefore the effects that we are looking for, e.g., phase transitions, must be such that they can exist in the limit of zero density and temperature. We shall find this to be the case. This is not surprising, because both the formation of a bound state and the Bose-Einstein condensation can occur in that limit.

We shall also find that restriction (b) is satisfied when $k_0 \to 0$. The only misgiving one might have concerning the use of (18) in the partition function is that it does not include all possible energy eigenvalues of the system. Specifically, it left out those states in which an $n_{\mathbf{k}}$ other than n_0 is a finite fraction of N. Such misgivings may be partly dissipated by the following plausibility arguments:

(a) Such states have small statistical weights so that

---

[9] In I, $F(\sigma)$ was misprinted as $F(\nu)$. There it should have been $F(\nu f^{-\frac{1}{2}})$.

[10] In I this condition was misquoted. It was wrong by a factor of 2.

they cannot be of importance in the equilibrium thermodynamics;

(b) Our calculation is self-consistent, in that we shall find no tendency for any level other than $\mathbf{k}=0$ to be macroscopically occupied, under thermal equilibrium.

In any event, our model is that the partition function shall be calculated from (18).

Finally, it is convenient to introduce the following dimensionless variables and parameters:

$$\begin{aligned}
&r=b/a,\\
&s=k_0a/4\pi,\\
&v=k_0a/(16\pi\rho a^3)^{\frac{1}{2}} \text{ (dimensionless specific volume)},\\
&\theta=\kappa T/k_0^2 \qquad \text{(dimensionless temperature)}.
\end{aligned}\tag{19}$$

In the above, κ is Boltzmann's constant, and T the absolute temperature. We require

$$0<r\ll1,\quad 0<s\ll1,\quad (r/8s)-1>0.\tag{20}$$

The last condition is the same as (12), the condition for binding. From (19) we have

$$\begin{aligned}
(\rho a^3/\pi)^{\frac{1}{2}}&=s/v,\\
\kappa T&=(4\pi s/a)^2\theta.
\end{aligned}\tag{21}$$

Thus, if for fixed a we let $r\rightarrow0$, $s\rightarrow0$, then any finite value of v^{-1} would be a low density, and any finite value of θ would be a low temperature. In terms of these dimensionless parameters we can write

$$E\{n_{\mathbf{k}}\}=E'(f,\xi)+\sum_{k\neq0}k^2n_{\mathbf{k}},$$

where

$$\frac{1}{N}E'(f,\xi)=\left(\frac{4\pi}{a}\right)^2s^3\left\{\frac{1}{4sv}[(1-f)^2-r-r(1-\xi)^2]+\frac{2f^2}{v}\left(1+\frac{f}{2v}\right)\right\}.\tag{22}$$

V. THE PARTITION FUNCTION

The thermodynamic properties of the system shall be calculated in the grand canonical ensemble. In an exact calculation of any physical problem, the results in the grand canonical ensemble must agree with those in the canonical ensemble. In an inexact calculation, such as ours, this is not necessarily so, but the grand ensemble usually leads to more physical results. The well-known relation between the two is the following: To obtain the equation of state in the grand canonical ensemble, make Maxwell constructions, whenever necessary, in the equation of state in the canonical ensemble. Therefore it is sufficient to calculate the canonical partition function.

The canonical partition function is

$$\begin{aligned}
\exp(-\beta A_N)&=\sum_{\Sigma n_{\mathbf{k}}=N}\exp(-\beta E\{n_{\mathbf{k}}\})\\
&=\sum_{\Sigma n_{\mathbf{k}}=N}\{\exp[-\beta E'(f,\xi)]\exp[-\beta\sum_{\mathbf{k}}k^2n_{\mathbf{k}}]\},
\end{aligned}$$

where $\beta=(\kappa T)^{-1}$, κ being Boltzmann's constant, and T the absolute temperature. We perform the partition sum as follows: First we pick a fixed set of values f, ξ, and sum over all sets of occupation numbers $\{n_{\mathbf{k}}\}$ satisfying the two conditions

$$\sum_{\mathbf{k}\neq0}n_{\mathbf{k}}=(1-\xi)N,\quad\text{and}\quad\sum_{0<k<k_0}n_{\mathbf{k}}=x(1-\xi)N.$$

These are equivalent to the conditions

$$\sum_{k>k_0}n_{\mathbf{k}}=(1-\xi)(1-x)N=(1-f)N,\tag{23a}$$

$$\sum_{0<k<k_0}n_{\mathbf{k}}=x(1-\xi)N=(f-\xi)N.\tag{23b}$$

After this is done we sum over all values of f and ξ, whose ranges are $0\leqslant\xi\leqslant f$, $0\leqslant f\leqslant1$. To obtain A_N, the Helmholtz free energy of the system, we shall need the logarithm of the partition function. In the limit $N\rightarrow\infty$ this is obtained by retaining only one term in the sum over f and ξ, namely the largest term in that sum. The values of f, ξ corresponding to this term is denoted by $\bar{f}$, $\bar{\xi}$. They are interpreted to be the thermodynamic averages of f, ξ.

We obtain, in the way just described:

$$A_N/N=\mathrm{Min}_{f,\xi}\{E'(f,\xi)/N-Z(f,\xi)\},\tag{24}$$

where the symbol $\mathrm{Min}_{f,\xi}\{\ \}$ denotes the smallest value of the quantity in the bracket $\{\ \}$, in the range $0\leqslant\xi\leqslant f$, $0\leqslant f\leqslant1$. The quantity $Z(f,\xi)$ is defined by

$$Z(f,\xi)\equiv-(N\beta)^{-1}\sum_{\{nk\}}{}'\exp(-\beta\sum_{\mathbf{k}}k^2n_{\mathbf{k}}),\tag{25}$$

where the sum $\sum'$ is subject to the conditions (23a) and (23b).

In Appendix A, it is shown that the minimization with respect to ξ can be immediately carried out, giving the result

$$\begin{aligned}
\bar{\xi}&=0 &&\text{if }\ \bar{f}<f_c\quad\text{(nondegenerate region)}\\
&=\bar{f}-f_c &&\text{if }\ \bar{f}>f_c\quad\text{(degenerate region)},
\end{aligned}\tag{26}$$

where

$$f_c(\theta,v)=16sv\int_0^1dt\,t^{\frac{1}{2}}(e^{t/\theta}-1)^{-1}.\tag{27}$$

Since $\bar{\xi}$ is the average fraction of particles with zero momentum, (26) expresses the Bose-Einstein condensation. In the θ–v plane, the transition region of the Bose-Einstein condensation is the locus of $\bar{f}(\theta,v)-f_c(\theta,v)=0$.

It is also shown in Appendix A that the free energy can be expressed through the following groups of formulas. Let

$$\begin{aligned}
A_N/N&=(4\pi/a)^2s^3\mathcal{A}(\theta,v)\\
P&=(4\pi/a)^2(\pi/a^3)s^5\mathcal{P}(\theta,v).
\end{aligned}\tag{28}$$

The dimensionless quantities $\mathcal{A}(\theta,v)$ and $\mathcal{P}(\theta,v)$ shall from now on be referred to, respectively, as the free energy and the pressure. They are given by:

$$\mathcal{P}(\theta,v)=-[\partial\mathcal{A}(\theta,v)/\partial v]_\theta \qquad \text{(equation of state)}, \tag{29}$$

$$\mathcal{A}(\theta,v)=\text{Min}_f\{\mathcal{A}_f(\theta,v)\}\ (0\leqslant f\leqslant 1)\ \text{(free energy)}, \tag{30}$$

$$\mathcal{A}_f(\theta,v)=\mathcal{E}_f(\theta,v)+\mathcal{H}_f(\theta,v)+\mathcal{L}_f(\theta,v), \tag{31}$$

$$\begin{aligned}\mathcal{E}_f(\theta,v)&=\left[-\frac{r}{2s}+\frac{1}{4s}(1-f)^2+2f^2\left(1+\frac{f}{2v}\right)\right]\frac{1}{v}\\&\quad+\begin{cases}0 & \text{if } f<f_c\\ (r/4sv)(f-f_c)(2+f_c-f) & \text{if } f>f_c,\end{cases}\end{aligned} \tag{32}$$

$$\mathcal{H}_f(\theta,v)=16v\theta\int_1^\infty dt\, t^{\frac{1}{2}}\ln(1-\zeta e^{-t/\theta}) +(\theta/s)(1-f)\ln\zeta, \tag{33a}$$

$$1-f=16sv\int_1^\infty dt\, t^{\frac{1}{2}}(\zeta^{-1}e^{t/\theta}-1)^{-1}\quad (0\leqslant\zeta\leqslant e^{1/\theta}), \tag{33b}$$

$$\mathcal{L}_f(\theta,v)=16v\theta\int_0^1 dt\, t^{\frac{1}{2}}\ln(1-ze^{-t/\theta})+(\theta/s)f\ln z \quad \text{if}\quad f<f_c, \tag{34a}$$

$$f=16sv\int_0^1 dt\, t^{\frac{1}{2}}(z^{-1}e^{t/\theta}-1)^{-1}\quad(0\leqslant z\leqslant 1) \quad \text{if}\quad f<f_c, \tag{34b}$$

$$\mathcal{L}_f(\theta,v)=\mathcal{L}_{f_c}(\theta,v)=16v\theta\int_0^1 dt\, t^{\frac{1}{2}}\ln(1-e^{-t/\theta}) \quad \text{if}\quad f>f_c. \tag{34c}$$

The designation of the functions $\mathcal{E}_f$, $\mathcal{H}_f$, $\mathcal{L}_f$ are suggestive of the fact that $\mathcal{E}_f$ is qualitatively similar to the ground state energy, $\mathcal{H}_f$ is the contribution from excited particles with high momentum ($k>k_0$), and $\mathcal{L}_f$ is the contribution from excited particles of low momentum $0<k<k_0$.

Other thermodynamic functions may be obtained from the free energy as follows:

$$\begin{aligned}&\mathcal{S}(\theta,v)=-[\partial\mathcal{A}(\theta,v)/\partial\theta]_v && \text{(entropy)},\\&\mathcal{U}(\theta,v)=\mathcal{A}(\theta,v)+\theta\mathcal{S}(\theta,v) && \text{(internal energy)},\\&\mathcal{C}(\theta,v)=-\theta[\partial^2\mathcal{A}(\theta,v)/\partial\theta^2]_v && \text{(specific heat)}.\end{aligned} \tag{35}$$

VI. THE EQUATION OF STATE

1. Some General Properties

To obtain the equation of state from the free energy, it is necessary to know some of the properties of $\bar{f}(\theta,r)$, the value of f which minimizes $\mathcal{A}_f(\theta,v)$. These are studied in Appendix B. The results may be summarized as follows:

(a) The transition region of the Bose-Einstein condensation, given by $\bar{f}(\theta,v)-f_c(\theta,v)=0$, is a narrow ribbon in the θ–v plane which deviates from the transition line of the ideal Bose gas by an amount of the order of s. Let the transition volume, as the transition region is approached from large volumes, be $v_c(\theta)$, then $v_c(\theta)\cong v_0(\theta)$ where

$$v_0(\theta)=[8\pi^{\frac{1}{2}}(2.612)]^{-1}\theta^{-\frac{3}{2}} \tag{36}$$

is the transition volume of the ideal Bose gas. A more accurate formula for $v_c(\theta)$ is given in Appendix B. For fixed θ the transition region ends when $v=v_c-\delta$, where the width $\delta(\theta)$ of the transition region, of order rsv_0, is also given in Appendix B. The two phases separated by the Bose-Einstein condensation can be characterized as follows:

$$\begin{aligned}&\bar{f}<f_c(\theta,v),\ \text{or}\ v>v_c(\theta)\ \text{(nondegenerate region)},\\&\bar{f}>f_c(\theta,v),\ \text{or}\ v<v_c(\theta)-\delta(\theta)\ \text{(degenerate region)}.\end{aligned} \tag{37}$$

(b) The function $\bar{f}(\theta,v)$ is determined by the condition

$$\left[\frac{\partial\mathcal{A}_f(\theta,v)}{\partial f}\right]_{f=\bar{f}}=0, \tag{38}$$

both for $\bar{f}>f_c$ and $\bar{f}<f_c$, but not in the transition region $\bar{f}=f_c$. This immediately enables us to write, outside of the transition region:

$$\mathcal{P}(\theta,v)=-\left\{\left[\frac{\partial\mathcal{A}_f(\theta,v)}{\partial v}\right]_{\theta,f}\right\}_{f=\bar{f}}. \tag{39}$$

Using (39), we may calculate the equation of state more explicitly. The results are as follows:

$$\mathcal{P}(\theta,v)=\mathcal{P}_E(\theta,v)+\mathcal{P}_H(\theta,v)+\mathcal{P}_L(\theta,v). \tag{40}$$

$$\begin{aligned}\mathcal{P}_E(\theta,v)&=\frac{1}{v^2}\left[-\frac{r}{2s}+\frac{1}{4s}(1-\bar{f})^2+2\bar{f}^2\left(1+\frac{\bar{f}}{v}\right)\right]\\&\quad+\begin{cases}0 & \text{if } v>v_c\\ (r/2sv^2)[\bar{f}-\frac{1}{2}(\bar{f}^2-f_c^2)] & \text{if } v<v_c-\delta.\end{cases}\end{aligned} \tag{41}$$

$$\mathcal{P}_H(\theta,v)=-16\theta\int_1^\infty dt\, t^{\frac{1}{2}}\ln(1-\zeta e^{-t/\theta}), \tag{42a}$$

$$1-\bar{f}=16sv\int_1^\infty dt\, t^{\frac{1}{2}}(\zeta^{-1}e^{t/\theta}-1)^{-1},\ (0\leqslant\zeta\leqslant e^{1/\theta}). \tag{42b}$$

$$\mathcal{P}_L(\theta,v)=-16\theta\int_0^1 dt\, t^{\frac{1}{2}}\ln(1-ze^{-t/\theta})\quad \text{if}\quad v>v_c, \tag{43a}$$

$$\bar{f}=16sv\int_0^1 dt\, t^{\frac{1}{2}}(z^{-1}e^{t/\theta}-1)^{-1}\quad \text{if}\quad v>v_c. \tag{43b}$$

$$\mathcal{P}_L(\theta,v)=-16\theta\int_0^1 dt\, t^{\frac{1}{2}}\ln(1-e^{-t/\theta})\quad \text{if}\ v<v_c-\delta. \tag{43c}$$

In the transition region, when v lies in the narrow interval between $v_c-\delta$ and v_c, the pressure can be worked out by setting $f=f_c$ in $\mathcal{A}_f(\theta,v)$ and then differentiating with respect to v. However we shall not be interested in that.

To the formulas (40)–(43), we must append the instruction to make Maxwell constructions whenever necessary. With this prescription, (40)–(43) yield the equation of state in the grand canonical ensemble.

The three terms $\mathcal{P}_E$, $\mathcal{P}_H$, and $\mathcal{P}_L$ are in one-to-one correspondence with the three terms $\mathcal{E}_f$, $\mathcal{H}_f$, and $\mathcal{L}_f$ of (31). $\mathcal{P}_E$ is qualitatively similar to $-\partial E_0/\partial\Omega$. Its values on both sides of the transition region differ by the amount

$$\begin{aligned}\mathcal{P}(v=v_c-\delta)-\mathcal{P}(v=v_c)&=(r/2s)(f_c/v_c^2)\\&\cong rs64\pi(2.612)^2\theta^3\int_0^{1/\theta}dx\,x^{\frac{1}{2}}(e^x-1)^{-1}.\end{aligned}\tag{44}$$

The last approximation is valid for $\theta\ll1$. Its slopes $\partial\mathcal{P}/\partial v$ also differ on both sides of the transition region by an amount of order s^3. There are no discontinuities in $\mathcal{P}_H$ and $\mathcal{P}_L$. Thus, due to $\mathcal{P}_E$, the total pressure is discontinuous both in value and in slope across the transition region. In physical terms, there is a drop in pressure when particles are taken out of the $\mathbf{k}=0$ level. This is the opposite behavior to the hard-sphere gas, in which the pressure rises instead.[5]

2. Lowest Order Approximation

We are interested in studying the equation of state in the region where phase transitions occur. We know that there is a Bose-Einstein condensation at all temperatures, and that there is a first order transition of the gas-liquid type at absolute zero. What we want to find out is what happens to these transitions at finite temperatures. The energy levels (4) on which this model is based are the results of a perturbation calculation in which the interaction between particles must be considered vanishing small. Accordingly, any phase transition that appears in this model must appear at very low temperatures (note that this means $\kappa T\ll1$, but not necessarily $\theta\ll1$), where the pressure of the ideal Bose gas is vanishingly small—so small, in fact, that it can be significantly changed by the interactions. Since the pressure of the ideal Bose gas actually goes to zero at absolute zero, it is not *a priori* ruled out that an arbitrarily small interaction can produce significant effects, at sufficiently low temperatures. Such an effect is indeed what we seek.

It is shown in Appendix B that $\bar{f}$ deviates from the corresponding quantity of the ideal gas only by an amount of the order of s—a result that is hardly surprising. To investigate the equation of state to the lowest order in the interactions, it is sufficient to put

$$\begin{aligned}\bar{f}&=f_0,\\v_c&=v_0,\\\delta&=0.\end{aligned}\tag{47}$$

Any corrections to the results so obtained would be of a higher order. Doing this, we find that $\mathcal{P}_H+\mathcal{P}_L$ becomes identical with the pressure $\mathcal{P}^{(0)}$ of the ideal gas:

$$\begin{aligned}\mathcal{P}^{(0)}(\theta,v)&=8\pi^{\frac{1}{2}}\theta^{\frac{5}{2}}g_{\frac{5}{2}}(z)\quad\text{if}\quad v>v_0\\&=8\pi^{\frac{1}{2}}\theta^{\frac{5}{2}}g_{\frac{5}{2}}(1)\quad\text{if}\quad v<v_0,\end{aligned}\tag{48}$$

where v_0 is given by (36), $g_n(z)\equiv\sum_{l=1}^{\infty}l^{-n}z^l$, and z is the root of the equation

$$g_{\frac{3}{2}}(z)/g_{\frac{3}{2}}(1)=v_0/v.\tag{49}$$

Some numbers of relevance are: $g_{\frac{5}{2}}(1)=1.341$, $g_{\frac{3}{2}}(1)=2.612$. Some of the isotherms of the ideal Bose gas are qualitatively shown in Fig. 5.

The equation of state to lowest order is given by

$$\mathcal{P}(\theta,v)=\mathcal{P}^{(0)}(\theta,v)+\mathcal{P}'(\theta,v),\tag{50}$$

where

$$\begin{aligned}\mathcal{P}'(\theta,v)=&-\frac{2}{v^2}\left[\frac{r}{4s}-f_0^2-\frac{1}{4s}(1-f_0)^2\right]+\frac{2f_0^3}{v^3}\\&+\begin{cases}0 & \text{if}\quad v>v_0\\(r/2sv^2)[f_0-\frac{1}{2}(f_0^2-f_c^2)] & \text{if}\quad v<v_0\end{cases}\end{aligned}\tag{51}$$

where v_0 is given by (36), f_c by (27), and f_0 by the following:

$$\begin{aligned}f_0&\equiv\langle N^{-1}\sum_{k<k_0}n_{\mathbf{k}}\rangle_{\text{ideal gas}}\\&=\begin{cases}16sv\int_0^1 dt\,t^{\frac{1}{2}}(z^{-1}e^{t/\theta}-1)^{-1} & \text{if}\quad v>v_0\\1-16sv\int_1^{\infty}dt\,t^{\frac{1}{2}}(e^{t/\theta}-1)^{-1} & \text{if}\quad v<v_0\end{cases}\end{aligned}\tag{52}$$

with z given by (49). According to (52) and (49) f_0 is, for fixed θ, a monotonically decreasing function of v. It is a linear decreasing function of v for $v<v_0$. At $v=v_0$ both f_0 and $\partial f_0/\partial v$ are continuous. For $v>v_0$, f_0 decreases slower than a linear function, and approaches an asymptote as $v\to\infty$:

$$f_0\underset{v\to\infty}{\longrightarrow}2\pi^{-\frac{1}{2}}\int_0^{1/\theta}dx\,x^{\frac{1}{2}}e^{-x}.\tag{53}$$

At $\theta=0$, $\mathcal{P}'$ is, apart from a constant factor, identical with $-\partial E_0/\partial\Omega$, shown qualitatively in Fig. 4. At small but finite θ, $\mathcal{P}'$ is still qualitatively the same, except that at $v=v_0$ it has a discontinuity both in value and in slope. At some finite θ, $\mathcal{P}'$ becomes a monotonically decreasing function of v, and no longer possess a minimum. It is now clear that the discussions in Sec. III embody the qualitative features of this model.

The isotherms according to (50) are similar to those illustrated in Fig. 5 and Fig. 6, and the interpretation of the various phases is the same as that discussed in Sec. III. More accurately, the shape of the gas-liquid

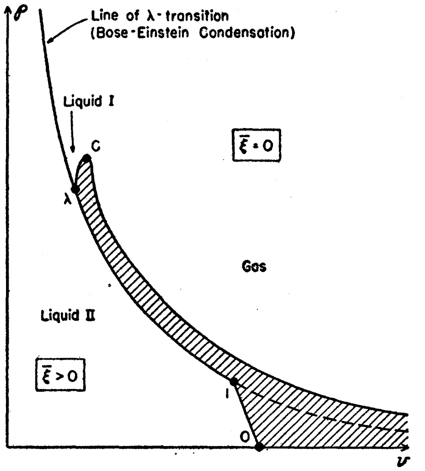

FIG. 7. Transition region in the $\mathcal{P}$-v plane of the present model. The coefficient of thermal expansion is negative for liquid II, positive for liquid I. The reason is given in Appendix C.

transition region is that shown in Fig. 7, and some relevant calculations are given in Appendix C. The temperatures and volumes of the points on the diagrams are as follows:

$$\begin{array}{lll} \text{point 0:} & \theta=0, & v=\tfrac{3}{2}[(r/8s)-1]^{-1}, \\ \text{point 1:} & \theta_1\sim-(\ln s)^{-1}, & v_1\sim s^{-1}(-\ln s)^{\frac{3}{2}}, \\ \lambda\text{-point }(\lambda): & \theta_\lambda\sim 1, & v_\lambda\sim s^{-1}, \\ \text{critical point }(c): & \theta_{\text{crit}}\sim 1, & v_{\text{crit}}\sim s^{-1}. \end{array} \qquad (54)$$

As shown in Fig. 6, liquid II has a negative coefficient of thermal expansion, while liquid I has a positive coefficient. The reasons for these, including a physical one, are contained in the calculations of Appendix C. The limit of no interaction is to be approached by first letting $r\to 0^+$, $s\to 0^+$, $(r/8s)-1\to 0^+$ and then letting $a\to 0^+$. Referring to the definitions of θ and v in (19) in terms of the conventional absolute temperature and particle density, we see that in that limit the transition region (a) collapses towards the transition line of the ideal Bose gas, and (b) recedes towards zero temperature, zero pressure, and infinite volume. As explained earlier, this makes the calculation self-consistent.

Since $\bar{f}\cong f_0$, it is clear that the average occupation number $\langle n_{\mathbf{k}}\rangle$ deviates negligibly from that of the ideal Bose gas. Therefore the assumption restriction in the use of energy levels (4), that $n_{\mathbf{k}}$ changes negligibly when k changes by k_0, is satisfied when $k_0\to 0$.

The specific heat can be calculated to the same approximation used here. It has a finite discontinuity across the transition region.

APPENDIX A. CALCULATION OF THE PARTITION FUNCTION

We shall calculate $Z(f,\xi)$ defined in (25). Clearly we can write

$$Z(f,\xi)=-(N\beta)^{-1}\ln\Big[\sum_{\{n_{\mathbf{k}}\}}{}^{(a)}\exp\Big(-\beta\sum_{0<k<k_0}k^2n_{\mathbf{k}}\Big)\Big] -(N\beta)^{-1}\ln\Big[\sum_{\{n_{\mathbf{k}}\}}{}^{(b)}\exp\Big(-\beta\sum_{k>k_0}k^2n_{\mathbf{k}}\Big)\Big],$$

where the sum $\sum^{(a)}$ is subject to (23a), and $\sum^{(b)}$ to (23b). Let

$$B_\alpha\equiv-(N\beta)^{-1}\ln\Big[\sum_{\{n_{\mathbf{k}}\}}{}^{(1)}\exp\Big(-\beta\sum_{0<k<k_0}k^2n_{\mathbf{k}}\Big)\Big], \qquad (A1)$$

where the sum $\sum^{(1)}$ is subject to

$$\sum_{0<k<k_0}n_{\mathbf{k}}=N\alpha,$$

and let

$$C_\alpha\equiv-(N\beta)^{-1}\ln\Big[\sum_{\{n_{\mathbf{k}}\}}{}^{(2)}\exp\Big(-\beta\sum_{k>k_0}k^2n_{\mathbf{k}}\Big)\Big], \qquad (A2)$$

where the sum $\sum^{(2)}$ is subject to

$$\sum_{k>k_0}n_{\mathbf{k}}=N\alpha.$$

Then we may write

$$Z(f,\xi)=B_{f-\xi}+C_{1-f}. \qquad (A3)$$

In the limit $N\to\infty$, B_α and C_α can be calculated by the method of saddle-point integration. Introducing the dimensionless functions

$$\begin{aligned}\mathcal{B}_y(\theta,v)&\equiv(\mathcal{A}/4\pi)^2s^{-3}B_y,\\ \mathcal{C}_f(\theta,v)&\equiv(\mathcal{A}/4\pi)^2s^{-3}C_f,\end{aligned} \qquad (A4)$$

where

$$y\equiv f-\xi \quad (0\leqslant y\leqslant f), \qquad (A5)$$

we obtain

$$\begin{aligned}\mathcal{B}_y(\theta,v)&=16v\theta\int_0^1 dt\, t^{\frac{1}{2}}\ln(1-ze^{-t/\theta})+(\theta/s)y\ln z\\ y&=16sv\int_0^1 dt\, t^{\frac{1}{2}}(z^{-1}e^{t/\theta}-1)^{-1}, \quad (0\leqslant z\leqslant 1),\end{aligned} \qquad (A6)$$

and

$$\begin{aligned}\mathcal{C}_f(\theta,v)&=16v\theta\int_1^\infty dt\, t^{\frac{1}{2}}\ln(1-\zeta e^{-t/\theta})\\ &\qquad+(\theta/s)(1-f)\ln\zeta \qquad (A7)\\ 1-f&=16sv\int_1^\infty dt\, t^{\frac{1}{2}}(\zeta^{-1}e^{t/\theta}-1), \quad (0\leqslant\zeta\leqslant e^{1/\theta}),\end{aligned}$$

where z, ζ are to be eliminated between each set of equations above. The second equations in (A6) and (A7) are the saddle-point conditions; namely $\partial\mathcal{B}/\partial z=0$, $\partial\mathcal{C}/\partial\zeta=0$, respectively.

Writing $\xi=f-y$, we recast the Helmholtz free energy (24) in the following form:

$$A_N/N=\text{Min}_{f,y}\Big\{\frac{1}{4sv}(1-f)^2-\frac{r}{4sv}+\frac{2f^2}{v}\Big(1+\frac{f}{2v}\Big) -\frac{r}{4sv}(1-f+y)^2+(4\pi/a)^2s^3[\mathcal{C}_f(\theta,v)+\mathcal{B}_y(\theta,v)]\Big\}, \qquad (A8)$$

where $\mathrm{Min}_{f,y}\{\ \}$ denotes the smallest value of the curly bracket in the range $0 \leqslant y \leqslant f$, $0 \leqslant f \leqslant 1$.

It is now possible to carry out the minimization with respect to y. For this we need to study the properties of $\mathcal{B}_y(\theta,v)$. The second equation of (A6) determines z as a monotonically increasing function of y. For different sets of values (θ,v), we obtain a family of z-y curves shown qualitatively in Fig. 8. Let

$$v_f(\theta) \equiv (16s/f) \int_0^1 dt\, t^{\frac{1}{2}} (e^{t/\theta}-1)^{-1}, \tag{A9}$$

the meaning of which is clear from Fig. 8. It is also clear from Fig. 8 that the range of y is $0 \leqslant y \leqslant f$ if $v > v_f(\theta)$, and $0 \leqslant y \leqslant f_c(\theta,v)$ if $v < v_f(\theta)$, where

$$f_c(\theta,v) \equiv 16sv \int_0^1 dt\, t^{\frac{1}{2}} (e^{t/\theta}-1)^{-1}. \tag{A10}$$

Equivalently the ranges of y are, for given θ, v, and f,

$$\begin{aligned} &0 \leqslant y \leqslant f \quad \text{if} \quad f < f_c, \\ &0 \leqslant y \leqslant f_c \quad \text{if} \quad f > f_c, \end{aligned} \tag{A11}$$

where $f_c \equiv f_c(\theta,v)$.

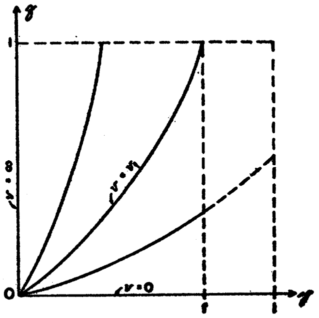

FIG. 8. Graphical aid for the analysis of (A6) and (A8).

Now $\mathcal{B}_y(\theta,v)$ is a monotonically decreasing function of y after elimination of the dependence on z. This is because along one of the z-y curves $\partial\mathcal{B}_y/\partial y = (\theta/s)\ln z \leqslant 0$. Therefore, for given values of θ, v, and f, the minimum value of $\mathcal{B}_y(\theta,v)$ occurs at the maximum allowable value of y. In (A8), the only other term depending on y is $-(1-f+y)^2$ which assume its smallest value also at the maximum allowable y. Denoting by $\bar{y}$ the value of y which for given θ, v, and f minimizes (A8), we have

$$\begin{aligned} \bar{y} &= f \quad \text{if} \quad f < f_c \\ &= f_c \quad \text{if} \quad f > f_c. \end{aligned} \tag{A12}$$

In terms of $\bar{\xi} \equiv \bar{f} - \bar{y}$ this means that

$$\begin{aligned} \bar{\xi} &= 0 && \text{if} \quad \bar{\xi} < f_c \quad \text{(system nondegenerate)} \\ &= \bar{f} - f_c && \text{if} \quad \bar{f} > f_c \quad \text{(system degenerate)}, \end{aligned} \tag{A13}$$

where $\bar{f}$ is the value of f which minimizes (A8). Equation (A13) expresses the Bose-Einstein condensation. At the end of the calculation, where we would have determined $\bar{f}$, the transition region of Bose-Einstein condensation, as a relation between θ and v, will be defined by $\bar{f} - f_c = 0$. This gives a physical meaning to f_c.

From here on it is straightforward to obtain the results (28)–(34).

APPENDIX B. BOSE-EINSTEIN CONDENSATION

We define $\bar{f}$ to be the value of f which, for given θ and v, minimizes $\mathcal{A}_f(\theta,v)$ of (30). Thus $\bar{f}$ is the thermodynamic average of f. Its physical significance lies in the fact (see Appendix A) that

$$\begin{aligned} &\bar{f} < f_c \text{ defines the nondegenerate region } (\bar{\xi}=0), \\ &\bar{f} > f_c \text{ defines the degenerate region } (\bar{\xi}>0), \end{aligned} \tag{B1}$$

where f_c is defined by (27) or (A10). The transition region of the Bose-Einstein condensation is therefore the region in the θ-v plane which satisfies

$$\bar{f}(\theta,v) - f_c(\theta,v) = 0. \tag{B2}$$

From (7), we may also interpret $\bar{f}$ to be the thermodynamic average of the fraction of particles with momenta smaller than k_0 (including the momentum 0):

$$\bar{f} = \langle N^{-1} \sum_{k<k_0} n_{\mathbf{k}} \rangle. \tag{B3}$$

Therefore to study the Bose-Einstein condensation we must first study $\bar{f}$.

According to (30), $\mathcal{A}_f(\theta,v)$ is made up of three terms. They are qualitatively sketched in Fig. 9 as functions of f, with some fixed finite values of θ and v. Referring to Fig. 9, we see that $\bar{f}$ is never equal to 0 or 1 for finite θ, v, because $\partial\mathcal{L}_f/\partial f$, $\partial\mathcal{H}_f/\partial f$ diverge at $f=0$, $f=1$, respectively. Except at $f=f_c$, where $\mathcal{E}_f$ has a discontinuous slope, both $\mathcal{A}_f$ and $\partial\mathcal{A}_f/\partial f$ are continuous functions of f. Therefore $\bar{f}$ satisfies the equation

$$(\partial\mathcal{A}_f/\partial f)_{f=\bar{f}} = 0 \text{ except when } \bar{f} = f_c. \tag{B4}$$

If, for fixed θ, $\bar{f}=f_c$ holds only at an isolated value of v, then (B4) must be generally valid by continuity. However, it is possible that for fixed θ, $\bar{f}=f_c$ holds over a

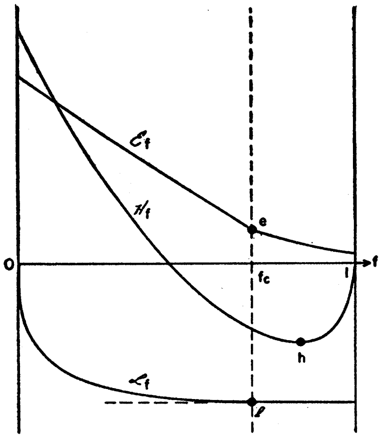

FIG. 9. Qualitative plots of the three terms whose sum is $\mathcal{A}_f$. $\bar{f}$ is the value of f at the lowest point of $\mathcal{A}_f$.

finite interval of v. In that case (B4) is invalid over that interval. We shall find that the latter is the case.

Since $0 \leqslant \bar{f} \leqslant 1$, the Bose-Einstein condensation can occur only if $f_c(\theta,v)<1$. The locus of $f_c(\theta,v)=1$ is a line in the θ-v plane:

$$vg(\theta)=1, \tag{B5}$$

where

$$g(\theta)=16s\int_0^1 dt\, t^{\frac{1}{2}}(e^{t/\theta}-1)^{-1}. \tag{B6}$$

It divides the θ-v plane into an upper part and a lower part (with θ chosen as the ordinate and v the abscissa). The Bose-Einstein transition occurs somewhere in the lower part.

Assuming $f_c<1$ and referring to Fig. 9, we see that in the neighborhood of $f=f_c$ the function $\mathcal{L}_f$ is a constant. Therefore it is of no relevance to the determination of $\bar{f}$ in this neighborhood. The function $\mathcal{E}_f$ has a discontinuous slope at $f=f_c$:

$$\begin{aligned}\operatorname*{Lim}_{\epsilon\to 0}\left(\frac{\partial \mathcal{E}_f}{\partial f}\right)_{f=f_c-\epsilon} &= -\frac{1}{2s}\left[\frac{1}{v}-K(\theta)\right],\\ \operatorname*{Lim}_{\epsilon\to 0}\left(\frac{\partial \mathcal{E}_f}{\partial f}\right)_{f=f_c+\epsilon} &= -\frac{1}{2s}\left[\frac{1-r}{v}-K(\theta)\right],\end{aligned} \tag{B7}$$

where

$$K(\theta)=g(\theta)\{1+8s[1+\tfrac{3}{4}g(\theta)]\}. \tag{B8}$$

Let us keep θ fixed and imagine that v is so chosen that $\bar{f}$ is less than f_c. If we now decrease v, $\bar{f}$ would move closer to f_c, becomes equal to f_c, and finally becomes less than f_c. During such a variation of v, the shape of the curve $\mathcal{A}_f=\mathcal{E}_f+\mathcal{K}_f+\mathcal{L}_f$ in the neighborhood of f_c goes through the following changes: When $\bar{f}\to f_c$ from above it looks like __/. This occurs when $v=v_c$. Then it looks like \/, finally it looks like __. This occurs when $v=v_c-\delta$. The width of the Bose-Einstein transition region is δ. It will be shown that $\delta\sim rsv_0$.

We call v_c the transition volume of the Bose-Einstein condensation. It is given, for fixed θ, by solving the equation

$$\left(\frac{\partial \mathcal{K}_f}{\partial f}\right)_{f=f_c}+\operatorname*{Lim}_{\epsilon\to 0}\left(\frac{\partial \mathcal{E}_f}{\partial f}\right)_{f=f_c-\epsilon}=0, \tag{B9}$$

which yields

$$v_c^{-1}=v_0^{-1}-16s[1-\alpha(\theta)] \times\int_1^\infty dt\frac{t^{\frac{1}{2}}e^{-t/\theta}}{[1-\alpha(\theta)e^{-t/\theta}][1-e^{-t/\theta}]}, \tag{B10}$$

where v_0 is the transition volume of the ideal Bose gas given by (36) and where $\alpha(\theta)$ is the root of the equation

$$\theta\ln\alpha=-8s\int_1^\infty dt\, t^{\frac{1}{2}}(\alpha^{-1}e^{t/\theta}-1)^{-1} +4sg(\theta)[1+\tfrac{3}{4}g(\theta)]. \tag{B11}$$

When $s\to 0$ the second term is negligible compared to the first. For finite θ we write $\alpha=1-\delta\alpha$ and find to first order in s that

$$\delta\alpha\cong 8(s/\theta)\int_1^\infty dt\, t^{\frac{1}{2}}(e^{t/\theta}-1)^{-1}. \tag{B12}$$

Substituting this into (B10) yields

$$v_c/v_0\cong 1-sJ(\theta), \tag{B13}$$

where

$$J(\theta)=\frac{16\theta^{\frac{1}{2}}}{\pi^{\frac{1}{2}}(2.612)}\int_{1/\theta}^\infty dt\frac{t^{\frac{1}{2}}e^{-t}}{1-e^{-t}}\times\int_{1/\theta}^\infty dt\frac{t^{\frac{1}{2}}e^{-t}}{(1-e^{-t})^2}. \tag{B14}$$

The width of the transition region is small of second order:

$$\delta/v_0\cong 32rsJ(\theta). \tag{B15}$$

In summary, the transition region of the Bose-Einstein condensation may be represented in the θ-v plane by a very narrow ribbon close to the transition line of the ideal Bose gas. The distance between them is of the order of s. The width of the ribbon is of order rs. The line of Bose-Einstein condensation separates the two phases characterized as follows:

$$\begin{aligned}&\text{Nondegenerate phase: } \bar{f}<f_c,\ \xi=0, && v>v_c,\\ &\text{Degenerate phase: } \bar{f}>f_c,\ \xi=\bar{f}-f_c, && v<v_c-\delta.\end{aligned} \tag{B16}$$

This is a convenient place to give more details concerning the function $\bar{f}(\theta,v)$ outside of the transition region of the Bose-Einstein condensation. For $v<v_c-\delta$ or $v>v_c$, we can use (B4), combined with (31)–(34) to obtain the equations that $\bar{f}$ satisfies:

$$\begin{aligned}&-\frac{1-\bar{f}}{2sv}+\frac{4\bar{f}}{v}\left(1+\frac{3}{4}\frac{\bar{f}}{v}\right)-\frac{\theta}{s}\ln\frac{\zeta}{z}=0,\\ &\bar{f}=16sv\int_0^1 dt\, t^{\frac{1}{2}}(z^{-1}e^{t/\theta}-1)^{-1}, \quad \text{if } \bar{f}<f_c\\ &1-\bar{f}=16sv\int_1^\infty dt\, t^{\frac{1}{2}}(\zeta^{-1}e^{t/\theta}-1)^{-1},\end{aligned} \tag{B17}$$

$$\left.\begin{aligned}&-\frac{1-\bar{f}}{2sv}+\frac{4\bar{f}}{v}\left(1+\frac{3}{4}\frac{\bar{f}}{v}\right)-\frac{\theta}{s}\ln\zeta=0,\\ &1-\bar{f}=16sv\int_1^\infty dt\, t^{\frac{1}{2}}(\zeta^{-1}e^{t/\theta}-1)^{-1}\end{aligned}\right\}\quad \text{if } \bar{f}>f_c. \tag{B18}$$

In the equations above, ζ and z are to be eliminated to yield $\bar{f}$ as an explicit function of θ and v. The following observations can be made:

(a) $\bar{f}$ is a continuous monotonically decreasing function of v, for given θ.

(b) $\bar{f}=1$ when $v=0$ or $\theta=0$.

(c) $$\bar{f}\xrightarrow[v\to\infty]{}2\pi^{-\frac{1}{2}}(2.612)\int_0^{1/\theta}dt\, t^{\frac{1}{2}}e^{-t}.$$

(d) $$\zeta/z\xrightarrow[s\to 0]{}1+O(s),$$

$$\zeta\xrightarrow[s\to 0]{}1+O(s).$$

From these it is easily verified that

$$\bar{f}\xrightarrow[s\to 0]{}f_0+O(s), \tag{B19}$$

where f_0 is the $\bar{f}$ for the ideal Bose gas, given in (52).

APPENDIX C. EQUATION OF STATE

We shall study $\mathcal{P}'(\theta,v)$, defined by (51). We shall first study it for $v<v_0$, and then for $v>v_0$.

For $v<v_0$, let us first consider $\theta\ll 1$. We may use the following approximation for f_0:

$$f_0\cong 1-16s\theta e^{-1/\theta}v \quad \text{if} \quad v<v_0 \quad \text{and} \quad \theta\ll 1. \tag{C1}$$

Since $v<v_0$, $(1-f_0)<2\pi^{-\frac{1}{2}}(2.612)^{-1}\theta^{-\frac{1}{2}}e^{-1/\theta}$. Hence f_0 differs very little from unity. Substituting (C1) into (51), and keeping only terms to the lowest order of s, we obtain:

$$\mathcal{P}'(\theta,v)\cong -\frac{2}{v^2}\left[\left(\frac{r}{8s}-1\right)+48s\theta e^{-1/\theta}\right]+\frac{2}{v^3}-\frac{64s\theta e^{-1/\theta}}{v}$$

$$\text{if} \quad v<v_0 \quad \text{and} \quad \theta\ll 1. \tag{C2}$$

For fixed θ the minimum of this function occurs at

$$v_{\min}=\tfrac{3}{2}[(r/8s-1)+48s\theta e^{-1/\theta}]^{-1}. \tag{C3}$$

Thus, as θ increases, $v_{\min}$ decreases, though extremely slowly. This is the origin of the negative sign of the coefficient of thermal expansion. The function $v_{\min}$ is sketched in Fig. 10.

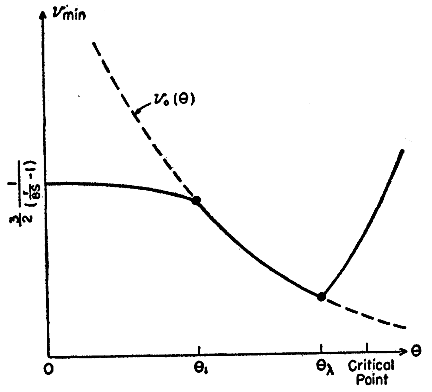

FIG. 10. Plot of $v_{\min}$ against θ, where $v_{\min}$ is the volume at which the smallest value of $\mathcal{P}'(\theta,v)$ occurs, for fixed θ. The slope of this curve furnishes a qualitative picture of the coefficient of thermal expansion.

When θ increases, v_0 also decreases, and it does so much faster than $v_{\min}$. At $\theta=\theta_1$ the two become equal. Above that temperature (C3) is no longer applicable. For θ_1 we have

$$\tfrac{2}{3}[(r/8s-1)+48s\theta_1 e^{-1/\theta_1}]=8\pi^{\frac{1}{2}}(2.612)s\theta_1^{\frac{3}{2}}, \tag{C4}$$

the solution to which is

$$\theta_1\sim -(\ln s)^{-1} \quad \text{as} \quad s\to 0. \tag{C5}$$

Thus $\theta_1\ll 1$. This corresponds to point 1 of Fig. 7. For $v<v_0$, we need not consider $\mathcal{P}'(\theta,v)$ at higher temperatures (unless we want more quantitative information about the equation of state).

For $v>v_0$, it is necessary to study $\mathcal{P}'(\theta,v)$ at all θ. When $\theta\ll 1$, the curve $\mathcal{P}'(\theta,v)$ as a function of v has no minimum at all. It is everywhere negative and monotonically decreases until $v=v_0$, at which point $\mathcal{P}'(\theta,v)$ abruptly rises as (C2) takes over. Thus, for $\theta>\theta_1$, the entire curve $\mathcal{P}'(\theta,v)$, for fixed θ, is V-shaped at $v=v_0$. This is the lowest point of the curve. Hence $v_{\min}$ "gets stuck" at v_0 for an extended range of θ above θ_1. This is shown in Fig. 10.

When θ is sufficiently large, a minimum will begin to appear in $\mathcal{P}'(\theta,v)$ for $v>v_0$. This first happens when $\theta=\theta_\lambda$. At that temperature the V-shape flattens out on the right side to become an L. This corresponds to the λ-point in Fig. 7. We can determine θ_λ by the condition

$$\lim_{\epsilon\to 0}(\partial\mathcal{P}'/\partial v)_{v=v_0+\epsilon}=0. \tag{C6}$$

Differentiation of (51) combined with (52) yields, for $v>v_0$,

$$\frac{\partial\mathcal{P}'}{\partial v}=\frac{4}{v^3}\left[\frac{r}{4s}-\frac{1}{4s}(1-f_0)\right]$$

$$+\frac{4}{v^3}\left[\frac{1}{4s}(1-f_0)-f_0-\frac{6f_0^2}{v}\right]L(\theta,v), \tag{C7}$$

where

$$L(\theta,v)=\int_0^{1/\theta}dx\frac{x^{\frac{1}{2}}ze^{-x}}{(1-ze^{-x})^2}\Big/$$

$$\int_0^{\infty}dx\frac{x^{\frac{1}{2}}ze^{-x}}{(1-ze^{-x})^2}\xrightarrow[v\to v_0+]{}1, \tag{C8}$$

with z given by (49). We obtain θ_λ to be the root of

$$\int_0^{1/\theta_\lambda}dx\, x^{\frac{1}{2}}(e^x-1)^{-1}=\pi^{\frac{1}{2}}(2.612)(r/8s). \tag{C9}$$

Since $(r/8s)\sim 1$, (C9) gives

$$\theta_\lambda\sim 1. \tag{C10}$$

When $\theta>\theta_\lambda$, $v_{\min}$ rapidly increases to infinity. Hence the temperature θ_{crit} of the critical isotherm is not far above θ_λ. The critical temperature is therefore also of the order of 1. Figure 10 shows $v_{\min}$ as a function of θ.

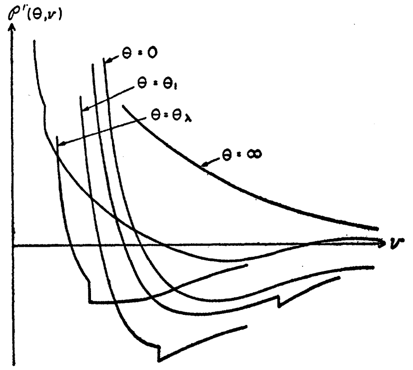

FIG. 11. Qualitative plot of the function $\mathcal{P}'(\theta,v)$.

Its slope may be regarded as a qualitative picture of the coefficient of thermal expansion. We see that this coefficient is negative for $v_{\min} < v_0$ and positive when $v_{\min} > v_0$.

With the above, we can now qualitatively sketch $\mathcal{P}'(\theta,v)$, as is done in Fig. 11. Adding these curves to the isotherms of the ideal Bose gas gives the isotherms in the present model. It is easy to see that the transition regions are as shown in Fig. 7.

It may be noted that the negative sign of the coefficient of thermal expansion for $v < v_0$ (degenerate phase) originates with the decrease of f_0 with increasing temperature. Since f_0 is the average fraction of particles with momentum less than k_0, the decrease of f_0 is largely due to particles leaving the level $\mathbf{k} = 0$. Thus the negative coefficient of thermal expansion and the abrupt rise of pressure at $v = v_0$ share the same origin. They can both be understood physically in the following terms: When attractive forces predominate, Bose particles can achieve a lower energy by occupying momentum states as different from one another as possible. In other words, *a spatial attraction leads to a momentum space repulsion.* Being in different momentum states makes the expectation value of the interparticle distance small (a consequence of the symmetry of the wave function), so that greater advantage is taken of the attraction.[11] The spreading out in momentum space clearly leads to higher pressure, while the concomitant decrease in interparticle separation leads to smaller volume.

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[11] Compare the discussion in K. Huang and C. N. Yang, Phys. Rev. **105**, 767 (1957), for the opposite case of repulsive interactions.