Bose–Einstein Condensation in One- and Two-Dimensional Gases

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We show that the one- and two-dimensional ideal Bose gases undergo a phase transition if the temperature is lowered at constant pressure. At the pressure-dependent transition temperature $T_c(P)$ and in their thermodynamic limit the specific heat at constant pressure c_p and the particle density n diverge, the entropy S and specific heat at constant volume c_v fall off sharply but continuously to zero, and the fraction of particles in the ground state N_0/N jumps discontinuously from zero to one. This Bose–Einstein condensation provides a remarkable example of a transition which has most of the properties of a second-order phase transition, except that the order parameter is discontinuous. The nature of the condensed state is described in the large but finite N regime, and the width of the transition region is estimated. The effects of interactions in real one- and two-dimensional Bose systems and recent experiments on submonolayer helium films are discussed briefly.

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1. INTRODUCTION

Much theoretical work has been done recently on model one-dimensional (1D) and two-dimensional (2D) systems because they are usually more easily solved than three-dimensional (3D) models and because they have a bearing on the properties of thin films of material and laminar or chainlike 3D samples. One of the more widely discussed models is the ideal Bose gas. While the 3D ideal Bose gas has long been known[1] to have a phase transition, the 1D and 2D ideal Bose gases have always been regarded as having no phase transition at any nonzero temperature. This result is consistent with a rigorous and much more general proof[2] that there can be no Bose condensation in a wide class of 1D and 2D Bose systems.

However, one point that had not been noticed as far as we know is that the question of whether a phase transition takes place in a 1D or 2D ideal Bose gas has always been studied assuming that changes take place at constant volume (or density). We recall that the 3D ideal Bose gas undergoes a first-order phase transition when the temperature is lowered at constant pressure.[1,3] All particles go into the lowest single-particle state, the density becomes infinite everywhere, and there is a discontinuous drop in the entropy accompanied by a singularity in the specific heat at constant pressure c_p. We will show that in going from 3D to 2D or 1D the first-order transition disappears. Nevertheless, there is a sharp but continuous phase transition into the ground state at a nonzero, pressure-dependent temperature $T_c(P)$. At T_c, the particle density diverges everywhere in the system, the entropy vanishes, c_p diverges, and the specific heat at constant volume c_v vanishes. Finally, the susceptibility χ, defined as the response of the usual superfluid order parameter $\langle \psi \rangle$ to its thermodynamically conjugate field, and the number N_0 of condensed particles to which χ is proportional are also found to diverge at $T_c(P)$.

A careful consideration shows that for realistic (e.g., boxlike) boundary conditions the system can exist in states of arbitrary temperature inside the supposedly forbidden region of $T < T_c(P)$, but only in a collapsed state in which essentially all the particles are in the ground state and the volume is a subextensive variable; i.e., $V = O(N^{1/2})$. With the temperature regarded as a fixed parameter, this region is characterized by pressures exceeding a corresponding critical pressure $P_c(T)$.

In Section 2 we present a detailed calculation of the thermodynamics and susceptibility of the 2D ideal Bose gas. Results alone are presented for the 1D ideal Bose gas.

We have already emphasized in a recent paper[4] that the nature of a phase transition may crucially depend upon the constraint imposed on the system. Here we have an extreme manifestation of that effect; namely, the constant-pressure constraint shifts the transition temperature from $0°K$—its value at constant volume—to a finite temperature $T_c(P)$.

It should be noted that the fact that the collapsed state is also Bose condensed is not in contradiction with the nonexistence theorems.[2] In fact, following Widom's[5] observation that 1D and 2D ideal Bose gases that are rotating or are in a uniform gravitational field do condense, Rehr and Mermin[6] noted that a crucial assumption in the proof of these theorems is that the density be finite everywhere. Our result is thus another example in which the nonexistence theorems break down due to the occurrence of an infinite density. Furthermore, it is clear that Widom's results should follow from the general rule that Bose condensation will occur once the pressure even locally exceeds $P_c(T)$.

In Section 3 we discuss the quite unusual thermodynamics of the "condensed" phase. In particular, when boxlike boundary conditions are imposed on the system the total volume V is subextensive: $V \propto N^{1/2}$, where N is the total number of particles.

Real Bose gases cannot have infinite density and therefore cannot collapse in this way. In Section 4 we discuss the various possible effects of interactions on the above transition, drawing on the insight provided by quantum lattice gas models[7] We conclude the section with a discussion of possible interpretations of the recent experimental results of Bretz and Dash[8] on submonolayer films of helium.

In the appendix we give a detailed derivation of the thermodynamic functions of the 2D Bose gas which we think is essentially correct for both the normal and the condensed phases of the system, and also for the transition region between the two phases. The width of the transition region is calculated. Its other properties will be discussed in a future article.

A preliminary report of this work has appeared in Ref. 9.

2. THERMODYNAMICS AND SUSCEPTIBILITY OF THE TWO-DIMENSIONAL IDEAL BOSE GAS

All thermodynamic functions are expressible in terms of the following functions (Ref. 1, Section 7):

$$F_\sigma(\alpha) \equiv \sum_{s=1}^{\infty} s^{-\sigma} \exp(-s\alpha) \tag{1}$$

In particular, for the $2D$ gas we will need

$$F_0(\alpha) = [\exp(\alpha) - 1]^{-1} \tag{2}$$

$$F_1(\alpha) = -\ln[1 - \exp(-\alpha)] \tag{3}$$

and $F_2(\alpha)$, which is not an elementary function but has the following behavior (Ref. 1, Appendix):

$$F_2(\alpha) \to \tfrac{1}{6}\pi^2 + \alpha \ln \alpha \qquad \text{as} \qquad \alpha \to 0 \tag{4}$$

The particle density is given by

$$n = (2\pi)^{-2} \int d^2k\{\exp[(\hbar^2k^2/2mk_BT) + \alpha] - 1\}^{-1}$$
$$= (mk_BT/2\pi\hbar^2)F_1(\alpha) \tag{5}$$

where m is the boson mass, k_B is Boltzmann's constant, and

$$\alpha \equiv -\mu/k_BT \tag{6}$$

where μ is the chemical potential. Thus, using Eq. (3), we see that

$$\alpha = -\ln[1 - \exp(-T_0(n)/T)] \tag{7}$$

where

$$T_0(n) \equiv 2\pi\hbar^2n/mk_B \tag{8}$$

is a characteristic n-dependent temperature. The internal energy per particle is given by

$$u = n^{-1}(2\pi)^{-2} \int d^2k(\hbar^2k^2/2m)\{\exp[(\hbar^2k^2/2mk_BT) + \alpha] - 1\}^{-1}$$
$$= k_BTF_2(\alpha)/F_1(\alpha) \tag{9}$$

Using Eqs. (5) and (9) and the relation

$$P = nu \tag{10}$$

we easily show that

$$P = mk_B{}^2T^2F_2(\alpha)/2\pi^2\hbar = k_BTF_2(\alpha)/\lambda_{th}^2 \tag{11}$$

and

$$c_v/k_B = 2F_2(\alpha)/F_1(\alpha) - F_1(\alpha)/F_0(\alpha) \tag{12}$$

and

$$c_p/k_B = 2F_2(\alpha)\{[2F_2(\alpha)F_0(\alpha)/F_1(\alpha)^2] - 1\}/F_1(\alpha) \tag{13}$$

where $\lambda_{th} \equiv (2\pi\hbar^2/mk_BT)^{1/2}$ is the thermal de Broglie wavelength and c_v and c_p are the specific heats (per particle) at constant volume and pressure, respectively.

From Eq. (11) we see that if the pressure P is fixed and the temperature is lowered, $F_2(\alpha)$ must grow. However, its maximum value $\pi^2/6$ occurs when $\alpha = 0$, at which point $F_1(\alpha)$ and hence the density n diverge. This occurs at a finite, pressure-dependent temperature

$$T_c(P) = [2\pi\hbar^2P/mk_B{}^2F_2(0)]^{1/2} = (12\hbar^2P/\pi mk_B{}^2)^{1/2} \tag{14}$$

Figure 1 is a sketch of the P–T diagram, where the curve

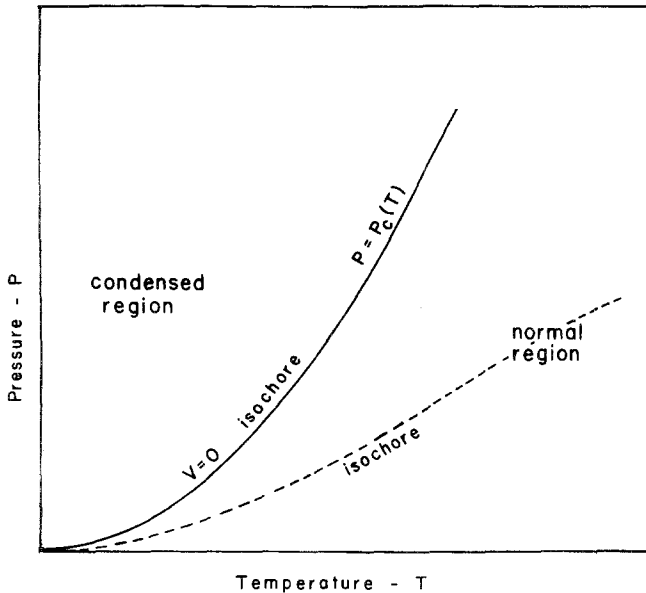$$P = \pi mk_B{}^2T^2/12\hbar^2 \equiv P_c(T) \tag{15}$$

Fig. 1. Qualitative phase diagram of the 1D or 2D ideal Bose gas in the P–T plane. Unless the effect of the boundaries is taken into account (cf. Section 3), the gas will be completely collapsed along the solid curve $P = P_c(T)$ [see Eqs. (15) and (24)] and could not exist in an equilibrium state with $P > P_c(T)$, even as a condensed phase. The dashed curve is a typical isochore. Cooling at constant volume avoids the condensed region.

separates the normal region from the condensed region. It appears as though the temperature of the system cannot be lowered below $T_c(P)$ at fixed pressure, nor can the system sustain a pressure greater than $P_c(T)$ at fixed temperature. Figure 2 is a sketch of a typical isotherm in the P–V plane. We note that $(\partial P/\partial V)_T$ vanishes as $V \to 0$.

In contrast to the above constant-pressure results, we see from Eq. (7) that if the temperature is lowered at constant density (or volume), α attains its minimum value of zero—leading to a collapse of the gas—only when $T \to 0$.

We next calculate the susceptibility in the noncondensed state. Let us define the correlation function

$$g(\mathbf{r}) \equiv \langle \psi^+(0)\psi(\mathbf{r}) \rangle \tag{16}$$

where $\psi(\mathbf{r})$ is the particle field operator. The susceptibility χ, which is a measure of the response of $\langle \psi(\mathbf{r}) \rangle$ to a thermodynamically conjugate external field, is then given by

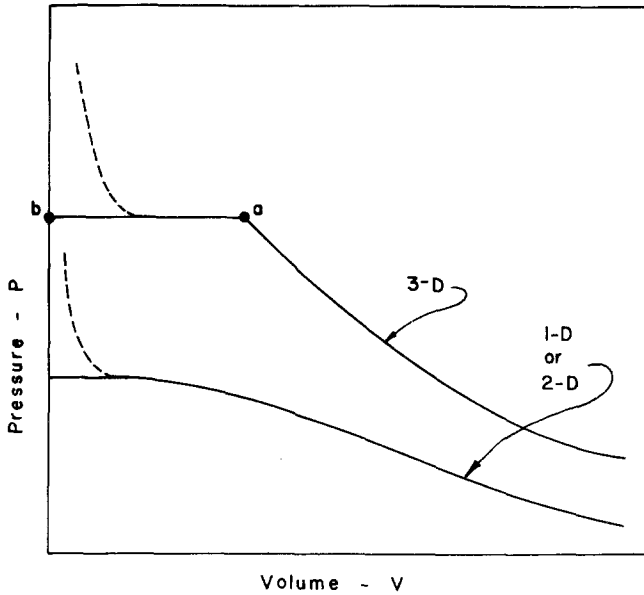$$\chi = (k_B T)^{-1} \int d\mathbf{r}\, g(\mathbf{r}) \tag{17}$$

Fig. 2. Isotherms in the P–V plane. The solid curves represent qualitatively the isotherms of the ideal gases. Along the 3D isotherm the pressure is constant from point a to b, while along the 1D or 2D isotherm $\partial P/\partial V = 0$ only at the point $V = 0$. With a small hard core a deviation from ideal behavior—indicated by the dashed curves—is expected only for small V in the 2D and 3D gases. The plateau at small V is expected to disappear completely in the 1D gas.

It then follows that

$$\chi = N_0/k_\mathrm{B}T \tag{18}$$

where N_0 is the number of particles in the lowest single-particle state and is given by the usual Bose population function

$$N_0 = [\exp(-\mu/k_\mathrm{B}T) - 1]^{-1} = [\exp(\alpha) - 1]^{-1} \tag{19}$$

Let us now define the variable

$$\epsilon \equiv T/T_c(P) - 1 \tag{20}$$

Usings Eqs. (4) and (11), we find that

$$\alpha \to -\pi^2\epsilon/(3 \ln \epsilon) \qquad \text{as} \qquad T \to T_c(P)^+ \tag{21}$$

Therefore, as $T \to T_c(P)^+$

$$
\begin{aligned}
&n \to -(3mP/\pi^3\hbar^2)^{1/2} \ln \epsilon, \qquad c_p \to \pi^2 k_\mathrm{B}/3\epsilon(\ln \epsilon)^2 \\
&c_v \to -\pi^2 k_\mathrm{B}/(3 \ln \epsilon), \qquad\qquad \chi \to -3(\ln \epsilon)/\pi^2 k_\mathrm{B}T_c\epsilon
\end{aligned}
\tag{22}
$$

As $T \to 0$, with n and hence $T_0(n)$ held constant,

$$c_p \to (\pi^4 k_B/9)(T/T_0)^3 \exp(T_0/T)$$
$$c_v \to (\pi^2 k_B/3)(T/T_0), \qquad \chi \to (k_B T)^{-1} \exp(T_0/T) \tag{23}$$

A similar analysis for the 1D ideal Bose gas leads to the following results. At fixed pressure, there exists a collapse temperature given by

$$T_c(P) = [32\pi\hbar^2 P^2/m\zeta(3/2)^2]^{1/3} \tag{24}$$

where $\zeta(x)$ is the Riemann zeta function. As $T \to T_c(P)^+$, with $\epsilon \equiv T/T_c(P) - 1$,

$$n \to \text{const} \times (mP/\hbar^2)^{1/3}/\epsilon^{1/2}, \qquad c_p \to \text{const} \times k_B/\epsilon^2$$
$$c_v \to \text{const} \times k_B \epsilon, \qquad\qquad \chi \to \text{const}/k_B T_c \epsilon^2 \tag{25}$$

At a fixed linear density n, there again exists a characteristic temperature T_0, given by

$$T_0(n) \equiv 2\pi\hbar^2 n^2/mk_B \tag{26}$$

such that as $T \to 0$

$$c_p \to \text{const} \times k_B(T_0/T),$$
$$c_v \to \text{const} \times k_B(T/T_0)^{1/2} \tag{27}$$
$$\chi \to \text{const} \times T_0/k_B T^2$$

3. THE CONDENSED PHASE OF THE 2D BOSE GAS

From the results of Section 2 one might be tempted to conclude that the 2D ideal Bose gas cannot exist in states with a pressure greater than $P_c(T)$. However, those results were obtained by working in the thermodynamic limit and replacing all sums over single-particle states by integrals. It turns out, as might have been expected, that this is not a valid procedure for $P > P_c(T)$. In the appendix we show that a correct procedure is to treat the ground-state term in these sums exactly, while still using a slightly modified integration approximation for the sum on all the other states. It is also essential to defer taking the thermodynamic limit until the end of the calculation.

The equations for N and P thus become [see Eqs. (A.34) and (A.18) in the appendix]

$$N = N_0 + VF_1(\beta\epsilon_1 + \alpha)/\lambda_{th}^2 \tag{5'}$$

$$P = (N_0\epsilon_0/V) + [k_B T F_2(\beta\epsilon_1 + \alpha)/\lambda_{th}^2] + [\epsilon_1 F_1(\beta\epsilon_1 + \alpha)/\lambda_{th}^2] \tag{11'}$$

where $\beta \equiv 1/k_B T$,

$$N_0 \equiv 1/[\exp(\beta\epsilon_0 + \alpha) - 1]$$

is the occupation number of the ground state, and ϵ_0 and ϵ_1 are the energies of the single-particle ground state and the first excited state, respectively. The exact value of ϵ_1 is not important, however, except perhaps in a small transition region around $P_c(T)$ (see the appendix). Similarly, the last term in (11')

is important only in the transition region. Below $P_c(T)$, Eqs. (5′) and (11′) have solutions where $\alpha = O(1)$ and $N_0 = O(1)$, and therefore ϵ_1, as well as the first term on the rhs of both equations, can all be neglected. Above $P_c(T)$, the only role of ϵ_1 is to keep the arguments of F_1 and F_2 from falling below $O(1/V)$, as we shall presently see. When this is secured, the last term of (11′) is at most of order $O(\ln V/V)$, and is thus again negligible compared to the second term.

Since the second term on the rhs of Eq. (11′) is bounded by $P_c(T)$, the only way we can hope to satisfy this equation when $P > P_c(T)$ is through a significant contribution of the other terms. The first term represents the ground-state contribution to the pressure and is therefore strongly dependent upon the boundary conditions at the walls of the box. If periodic boundary conditions are imposed upon the single-particle states, $\epsilon_0 = 0$ and the first term vanishes. If, on the other hand, the wave function must vanish at the walls, we get

$$\epsilon_0 = O(\hbar^2/mV) \neq 0 \qquad (28)$$

This rather unusual situation—in which results depend upon the boundary conditions—forces us to consider carefully what boundary condition is appropriate.

The boundary condition is really a mathematical artifice used to circumvent the need to consider explicitly the forces exerted by the walls that keep the particles inside the box. If the walls could be represented by a truly infinite potential barrier, the zero boundary condition would be rigorously correct. Even for realistic walls, it appears to be much better justified than the periodic boundary condition. We therefore use it to calculate the first terms on the rhs of Eqs. (5′) and (11′).

In order to solve Eq. (11′) for α when $P > P_c(T)$, assuming for the moment that we can neglect the last term, we must have

$$N_0\epsilon_0/V = O(1) \qquad (29)$$

Therefore, since $\epsilon_0 = O(1/V)$, we find

$$N_0 \cong (\epsilon_0/k_B T + \alpha)^{-1} = O(V^2) \qquad (30)$$

This equation requires α to be negative and of order $O(1/V)$, so as to cancel most of $\beta\epsilon_0$, hence the importance of ϵ_1 in (5′) and (11′). Consequently, using Eq. (3) and the fact that $\epsilon_1 - \epsilon_0 = O(1/V)$, the second term on the rhs of Eq. (5′) becomes

$$VF_1(\epsilon_1/k_B T + \alpha)/\lambda_{\text{th}}^{2} = O(V \ln V) \ll N_0 \qquad (31)$$

and we can indeed neglect it. We thus have

$$N \cong N_0 = O(V^2) \qquad (32)$$

i.e., all the particles (except for a negligible number) go into the condensate and the system collapses to a volume which is subextensive:

$$V = O(N^{1/2}) \tag{33}$$

The total pressure can thus be written as

$$P = NP_0 + P_c(T) \tag{34}$$

where

$$P_0 = -\partial \epsilon_0 / \partial V = \epsilon_0 / V \tag{35}$$

is the pressure of a single particle in the lowest state and depends only on the volume and the shape of the box, but not on the temperature.

Even though the volume is subextensive in the condensed phase, it can still be rather large. As a function of pressure it has the following form:

$$V \sim \{N/[P - P_c(T)]\}^{1/2} \tag{36}$$

Close to the transition point one may also express this equation in an alternative form:

$$V \sim \{N/[T_c(P) - T]\}^{1/2} \tag{37}$$

These expressions are valid for the condensed phase except inside a very small transition region around $P_c(T)$ over which the system changes from the normal to the condensed state. The size of this region of course goes to zero in the thermodynamic limit. A similar behavior is exhibited by the entropy, which in the condensed phase is proportional to V [see Eq. (A.40)]. In Fig. 3 we have sketched qualitatively some of the interesting thermodynamic quantities as functions of T at a fixed P.

An interesting result that emerges from these calculations is that, although all the usual extensive thermodynamic quantities tend continuously to zero (on the scale of N) as the condensation point is approached from the normal phase and remain zero in the condensed phase, the occupation number N_0 of the lowest state undergoes a jump from essentially zero to essentially N. Thus, although the transition is certainly not of the first order in the usual sense, the order parameter which characterizes it does undergo a discontinuous change. This result reminds us of the puzzling property of thin films of superfluid helium, namely that the superfluid density ρ_s appears to be discontinuous at the transition point[10,11] in contrast to the transition in bulk helium, where ρ_s goes to zero continuously at the lambda point.

4. EFFECTS OF INTERACTIONS

The interactions between He atoms in real ^{4}He fluid consist of a repulsive, short-range potential (which we will replace by a hard core, for simplicity)
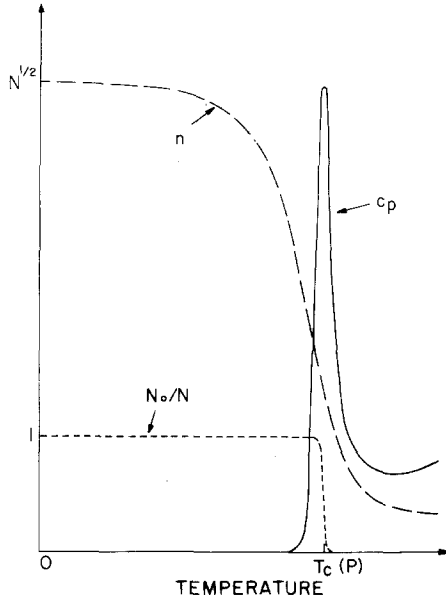
Fig. 3. Qualitative graph of some thermodynamic quantities as functions of T at constant P. Shown are the particle density n, the fraction of particles in the ground state N_0/N, and the heat capacity per particle c_p. We assume a large but finite total N.

and a long-range attractive tail.[1] Each of these parts plays an essential and distinct role in determining the properties of real ^{4}He fluid.

We begin by discussing the effect of the hard core. In one dimension even a small hard core has a catastrophic effect on the transition since the particles cannot move past each other. Indeed, the 1D Bose gas with a repulsive delta-function interaction is equivalent to an ideal 1D Fermi gas[12] and thus does not exhibit any of the characteristics of the transition. A 1D Bose gas with a finite-size hard core is not expected to be radically different.

The effect of the hard core is not as dramatic in two and three dimensions. In both cases we expect the hard core to become important only when the density is so high that the interparticle distance is of the order of the hard-core diameter. At such a high density (or small volume) there should be a sharp rise in the pressure (see Fig. 2). We therefore expect that for low pressures the phase transition will be retained in three but destroyed in two dimensions. Nevertheless, an inspection of Eqs. (22) reveals that a remnant of the transition may still occur even in two dimensions: As $\epsilon \to 0$ the density increases logarithmically while c_p increases more rapidly—as $[\epsilon(\ln \epsilon)^2]^{-1}$. But the deviations from ideal gas behavior begin only when the density is so high that the hard core interferes with the free motion of the particles. For

low pressures this begins to occur only for very small values of ϵ. Our discussion does not preclude the possibility of a large peak developing in c_p as a function of ϵ long before deviations from ideal gas behavior become important.

The addition of an attractive part to the hard core will assist in the constant-pressure transition. Thus, the collapse at constant pressure of the 3D gas is expected to become a phase transition in which the density increases discontinuously to a noninfinite value as the temperature is lowered. One would also expect that at least for weak enough interactions N_0 would increase discontinuously. This conclusion should be valid at pressures so low that the volume per particle V/N around the point where the transition takes place in the absence of interactions is much greater than the hard-core volume v_c. This conclusion is also in agreement with the phase transition of ^{4}He at low pressures, where the system makes a transition directly from the gas phase to a superfluid liquid (Ref. 1, Section 1). Our qualitative reasoning does not tell us what will happen in two dimensions except that there is now a chance for a transition to take place. Whatever may be the case, Bose condensation is ruled out because the density is bounded.

We get more definite conclusions using the quantum lattice gas (QLG) model[7] for the interacting system, of which a very clear discussion is found in Ref. 13. In the simplest version of a QLG with a hard core and no attractive interaction the corresponding magnetic model is a ferromagnetic, nearest-neighbor, isotropic X–Y model and is represented by the Hamiltonian of Eq. (38) below with $J_\parallel = 0$. This model is believed to have a transition in three dimensions but was proved by Mermin and Wagner[14] not to have spontaneous magnetization in the x or y directions (corresponding to Bose condensation in the QLG) in one and two dimensions. This result merely confirms our previous conclusion, namely that the presence of a hard core and the nonexistence theorems of Ref. 2 rule out Bose condensation. The question of whether one can have $\langle \sigma^z \rangle \neq 0$, corresponding to a transition into the liquid state, is related to the magnitude of the attractive part of the interaction, as discussed below.

The situation changes markedly when the attractive part of the interaction is introduced. A Heisenberg–Ising model is obtained, with the Hamiltonian

$$H = -\sum_{(ij)} [J_\parallel \sigma_i^z \sigma_j^z + J_1(\sigma_i^x \sigma_j^x + \sigma_i^y \sigma_j^y)] - h \sum_i \sigma_i^z \tag{38}$$

where $\sum_{(ij)}$ signifies a sum over nearest-neighbor spins, the σ_i^α are Pauli spin operators, h represents an external magnetic field and is related to the chemical potential, and $J_\parallel$ and J_1 are both positive and related to the strength of the attractive forces and to the hard core size, respectively.

In one dimension, phase transitions cannot occur. In two dimensions two cases are distinguishable:

(a) Strong attraction: $J_{\parallel} > J_{\perp}$. Here we expect a phase transition to a state with nonzero $\langle \sigma^z \rangle$ but with no Bose condensation.[4]

(b) Weak attraction: $J_{\parallel} < J_{\perp}$. Here no definite statement can be made.[5]

We conclude with a brief statement of four as yet unanswered questions raised by this paper.

(a) Is there a phase transition in a 2D Bose fluid with a hard-core and weak attraction?

(b) While in three dimensions the phase transition at constant P is always first order, with or without interactions, the phase transition in two dimensions is of a different kind in the ideal gas but might become an ordinary first-order transition in the presence of attractive interactions.

(c) In the case of the first-order transition in the 3D ideal gas, we do not know whether phase separation actually occurs: This depends upon the surface tension, which may be absent in the ideal gas but will reappear when attractive interactions are present.

(d) Bretz and Dash[8] obtained a peak in the specific heat of submonolayer ^{4}He films at a finite temperature. This result was attributed[15] to inhomogeneities of the substrate, which produce nonuniform potentials that can also bring about an incipient Bose condensation similar to the one we have been discussing and a consequent peak in the specific heat. Were these experiments performed under constant lateral pressure, such a peak could be related to the one that we find. Even if this is not really the case, such behavior would still be obtained if the system broke up into a series of droplets due to attractive interactions[6] and/or substrate inhomogeneities.[15] In that case each droplet would be, effectively, under something like a constant pressure.

Further investigation is necessary in order to determine whether there is any connection between the transition we have found in a 2D Bose gas and the superfluid-to-normal transition observed in the somewhat thicker helium films where superflow and third sound can occur. We have mentioned in Section 3 the fact that in these films the transition seems to be accompanied by a jump in ρ_s even though none of the usual extensive properties such as

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[4] This phase transition is not ruled out by the theorem of Ref. 14. We expect it to occur since the case $J_{\parallel} > J_{\perp}$ should be qualitatively similar to an Ising model. We also note that while the usual spin wave argument does rule out spontaneous magnetization in the isotropic case, it allows for a finite $\langle \sigma^z \rangle$ in this case.

[5] We know that in the ground state $\langle \sigma^z \rangle$ vanishes while $\langle \sigma^x \rangle$ and/or $\langle \sigma^y \rangle$ do not vanish. Mermin and Wagner [14] showed that $\langle \sigma^x \rangle = \langle \sigma^y \rangle = 0$ for nonzero temperatures. Hence, since higher temperatures usually lead to a smaller order parameter, we might expect that $\langle \sigma^z \rangle = 0$ for all temperatures. Nevertheless, the rigorous nonexistence theorems do not rule out a transition into a state of nonzero $\langle \sigma^z \rangle$ at a finite temperature.

[6] Both the effective mass and the strength of the attractive interaction for adsorbed He atoms will be different from those in the gas. A larger ratio $J_{\parallel}/J_{\perp}$ seems reasonable.

volume and entropy have any discontinuity. The jump in N_0 at the condensation point of the 2D Bose gas and the lack of any jump in other extensive quantities could be connected with the above-mentioned experimental observation on helium films. But even if there is no connection (and this might well be the case, since a superfluid helium film is very different from a 2D ideal Bose gas), our model at least provides an example of a system where a superfluid transition with such properties is possible. Therefore one should not immediately rule out the possibility that the observed onset of superfluidity in thin helium films is in fact a phase transition, rather than a threshold of some strong attenuation mechanism.[10,16–18]

We finally note that our results were derived using the grand canonical ensemble, as is usually the practice in the theory of Bose–Einstein condensation. If another ensemble, for example, the canonical one, were used, the mathematics would be greatly complicated. Ordinarily, a change in the statistical ensemble used should not essentially alter the values of average quantities but may affect only the fluctuations around the average. It is an interesting open question whether this will be the case here, or whether more drastic changes will follow, for this rather unusual system.

APPENDIX. STATISTICAL MECHANICS OF THE 2D IDEAL BOSE GAS

Our starting point is the grand-canonical partition function Z_G given by

$$Z_G = \text{Tr} \exp(-\beta \hat{H} - \alpha \hat{N}) = \prod_k [1 - \exp(-\beta \epsilon_k - \alpha)]^{-1} \quad \text{(A.1)}$$

where $\epsilon_k = \hbar^2 k^2/2m$, and where $\hat{H}$ and $\hat{N}$ are the Hamiltonian and particle number operators, respectively. The internal energy U is given by

$$U = -\partial(\ln Z_G)/\partial\beta = \sum_k \epsilon_k/[\exp(\beta\epsilon_k + \alpha) - 1]^{-1} \quad \text{(A.2)}$$

and the pressure is given by

$$P \equiv \left\langle -\frac{\partial \hat{H}}{\partial V} \right\rangle = \frac{1}{\beta}\frac{\partial \ln Z_G}{\partial V} = -\sum_k \frac{\partial\epsilon_k/\partial V}{\exp(\beta\epsilon_k + \alpha) - 1} \quad \text{(A.3)}$$

If the volume of the system is varied without changing the shape (i.e., the ratios of all linear dimensions to each other are kept fixed), we find that $\epsilon_k \sim 1/V$. Therefore

$$\partial\epsilon_k/\partial V = -\epsilon_k/V \quad \text{(A.4)}$$

and we can write

$$P = U/V \quad \text{(A.5)}$$

This is an exact result. One might be tempted to use another well-known relationship to calculate P, namely

$$P = (k_{\mathrm{B}}T/V) \ln Z_G \tag{A.6}$$

This is not exact, because (A.6) is derived under the assumption that $\ln Z_G$ is an extensive quantity. But the ground-state term in $\ln Z_G$ is not·extensive, nor may it be discarded here, as we shall see later. [See the discussion following Eq. (A.18).]

In what follows, we will assume that β, i.e., T, is finite, i.e., of order one. Using (A.4) or (A.5), we can write P in the form

$$P = \frac{1}{V} \sum_{k} \frac{\epsilon_k}{\exp(\beta\epsilon_k + \alpha) - 1} \tag{A.7}$$

In Fig. 4 we show a schematic graph of the summand of this equation,

$$\beta\epsilon/[\exp(\beta\epsilon + \alpha) - 1] \tag{A.8}$$

as a function of ϵ, assuming that α is slightly negative, so that

$$\beta\epsilon_0 + \alpha = o(1/V) \tag{A.9}$$

where ϵ_0 is the energy of the single-particle ground state. We will see later that this assumption begins to hold when the condensation point is approached
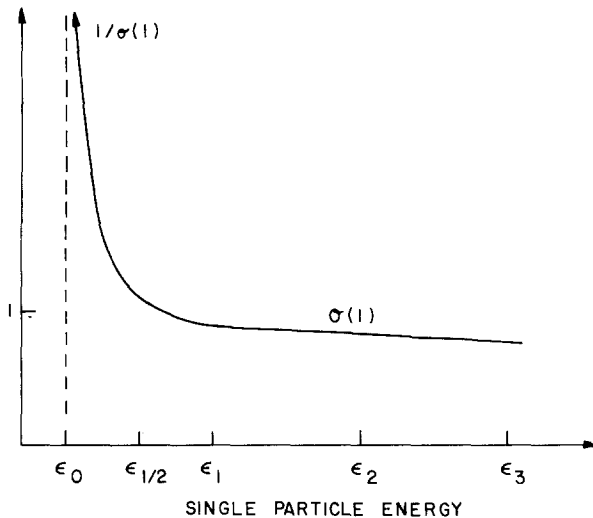

Fig. 4. Qualitative graph of the function. $\beta\epsilon[\exp(\beta\epsilon + \alpha) - 1]$ vs. the single-particle energy ϵ for $\beta\epsilon_0 + \alpha = o(1/V)$. This function shoots up to large values, i.e., of order $1/o(1)$, only in a region of order $o(1/V)$ around ϵ_0. The same graph also describes qualitatively the function (A.30), the summand of (A.37), and most other summands which might appear in such a sum on single-particle states.

closely enough from the normal phase, and continues to hold in both the transition region and in the condensed phase. We assume zero boundary conditions for the single-particle wave functions, so that

$$\epsilon_0 = O(1/V) \neq 0 \tag{A.10}$$

It is clear from Fig. 4 that, except for a neighborhood of ϵ_0 that is of order $o(1/V)$, (A.8) is perfectly smooth and finite, and is moreover a monotonic decreasing function of ϵ. It is also concave upward.

The last properties result from the fact that α is slightly negative. Hence, the derivative of (A.8) with respect to ϵ is

$$[e^{\beta\epsilon+\alpha}(1 - \beta\epsilon) - 1]/(e^{\beta\epsilon+\alpha} - 1)^2 \tag{A.11}$$

Since

$$1 - \beta\epsilon < e^{-\beta\epsilon} \tag{A.12}$$

the numerator of (A.11) satisfies

$$e^{\beta\epsilon+\alpha}(1 - \beta\epsilon) - 1 < e^\alpha - 1 < 0 \tag{A.13}$$

That the second derivative is positive, and the function (A.8) therefore always concave upward, follows from the following considerations:

$$\frac{d}{d\epsilon}\left[\frac{e^{\beta\epsilon+\alpha}(1 - \beta\epsilon) - 1}{(e^{\beta\epsilon+\alpha} - 1)^2}\right] = \frac{\beta e^{\beta\epsilon+\alpha}}{(e^{\beta\epsilon+\alpha} - 1)^3}[\beta\epsilon(e^{\beta\epsilon+\alpha} + 1) - 2(e^{\beta\epsilon+\alpha} - 1)]$$

The square brackets on the r.h.s. can be developed as follows:

$$\beta\epsilon\left[2 + (\beta\epsilon + \alpha) + \frac{(\beta\epsilon + \alpha)^2}{2!} + \cdots\right] - 2\left[\beta\epsilon + \alpha + \frac{(\beta\epsilon + \alpha)^2}{2!} + \cdots\right]$$

$$= \left[(\beta\epsilon + \alpha)^2 + \frac{(\beta\epsilon + \alpha)^3}{2!} + \frac{(\beta\epsilon + \alpha)^4}{3!} + \cdots\right]$$

$$- \alpha\left[\beta\epsilon + \alpha + \frac{(\beta\epsilon + \alpha)^2}{2!} + \cdots\right]$$

$$- 2\alpha - 2\left[\frac{(\beta\epsilon + \alpha)^2}{2!} + \frac{(\beta\epsilon + \alpha)^3}{3!} + \cdots\right]$$

$$> -\alpha\left[\beta\epsilon + \alpha + \frac{(\beta\epsilon + \alpha)^2}{2!} + \cdots\right] - 2\alpha$$

$$= -\alpha(e^{\beta\epsilon+\alpha} - 1) - 2\alpha > 0$$

because α is negative.

It is now reasonable to expect that we might be able to approximate the sum in (A.7) for $\epsilon_k \neq \epsilon_0$ by an integral. In order to make this statement more precise, we will specialize to the case where the ϵ_k are nondegenerate and

equally spaced in energy. Since (A.8) is a decreasing function, a lower bound to the sum is given by the integral of (A.8) from ϵ_1 to infinity:

$$\int_{\epsilon_1}^{\infty} \frac{Vg\epsilon \, d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} < \sum_{\epsilon_k \neq \epsilon_0} \frac{\epsilon_k}{\exp(\beta\epsilon_k + \alpha) - 1}$$

where $1/Vg$ is the level spacing, which is of order $O(1/V)$. Because (A.8) is also concave upward, an upper bound to the sum is given by a similar integral from $\epsilon_{1/2}$ to infinity, where $\epsilon_{1/2}$ is halfway between ϵ_0 and ϵ_1. We can thus write

$$\int_{\epsilon_1}^{\infty} \frac{Vg\epsilon \, d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} < \sum_{\epsilon_k \neq \epsilon_0} \frac{\epsilon_k}{\exp(\beta\epsilon_k + \alpha) - 1}$$

$$< \int_{\epsilon_{1/2}}^{\infty} \frac{Vg\epsilon \, d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} \qquad (A.14)$$

The integrals in (A.14) are of order $O(V)$ each, and they differ by less than

$$\tfrac{1}{2}\epsilon_{1/2}/[\exp(\beta\epsilon_{1/2} + \alpha) - 1] = O(1) \qquad (A.15)$$

We can therefore write

$$\frac{1}{V} \sum_{\epsilon_k \neq \epsilon_0} \frac{\epsilon_k}{\exp(\beta\epsilon_k + \alpha) - 1} = \int_{\epsilon_1}^{\infty} \frac{g\epsilon \, d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} + O\left(\frac{1}{V}\right) \quad (A.16)$$

Actually, the precise values of ϵ_k will depend on the shape of the box, and they will usually be neither equally spaced nor nondegenerate. The average level spacing will, however, be independent of ϵ and of the precise shape of the box, and we expect that (A.16) will continue to hold even then, with $1/Vg$ now standing for the average level spacing. It is not easy to prove this rigorously, and we do not attempt to provide such a proof here.[7]

Equation (A.16) is further transformed by defining $x \equiv \epsilon - \epsilon_1$. We thus find

$$\int_{\epsilon_1}^{\infty} \frac{g\epsilon \, d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} = \int_{0}^{\infty} \frac{g(x + \epsilon_1) \, dx}{\exp(\beta x + \beta\epsilon_1 + \alpha) - 1}$$

$$= \frac{k_B T}{\lambda_{th}^2} F_2(\beta\epsilon_1 + \alpha) + \frac{\epsilon_1}{\lambda_{th}^2} F_1(\beta\epsilon_1 + \alpha) \qquad (A.17)$$

---

[7] In the event that future investigations will prove the error estimate of Eq. (A.16) to be overly optimistic [due to an unforeseen dependence on details of the level distribution which will lead to, e.g., an $O(V^{-1/2})$ error], our only result that will be affected is the estimate of the transition region. All the rest of the discussion, including that of the importance of the first term on the right-hand side of Eq. (A.18), will remain valid.

We can thus write (A.7) in the following form:

$$P = \frac{\epsilon_0/V}{\exp(\beta\epsilon_0 + \alpha) - 1} + \frac{k_\mathrm{B}T}{\lambda_\mathrm{th}^2} F_2(\beta\epsilon_1 + \alpha)$$

$$+ \frac{\epsilon_1}{\lambda_\mathrm{th}^2} F_1(\beta\epsilon_1 + \alpha) + O\left(\frac{1}{V}\right) \tag{A.18}$$

Note that the first term on the rhs is the pressure exerted by particles in the ground state. We have already discussed this term in Section 3 [see Eq. (28) and the discussion thereof]. But we would now like to point out that this term is not reproduced by the incorrect equation (A.6). This explains why it was essential to use the correct expression (A.3) for P. The problems with (A.6) arise due to the fact that the condensed state we are considering has a subextensive volume.

Although we have derived Eq. (A.18) under the assumption (A.9), it is easy to argue that it is still valid even when (A.9) is not satisfied, i.e., when

$$\beta\epsilon_0 + \alpha \geqslant O(1/V) \tag{A.19}$$

This is because (A.8) is now finite even at ϵ_0. We can therefore use the integration approximation for the entire sum and the error thus incurred is still only $O(1/V)$, though one has to argue more carefully to derive this result since (A.8) may now have a region with a positive slope for small ϵ. For this case the first term in (A.18) is of the same order as the error, i.e., $O(1/V)$.

The third term in (A.18) is also of order $O(1/V)$ when α is large. But when α is small this term combines with the second term to give a result which is independent of the precise value of ϵ_1 in all the significant orders:

$$\frac{k_\mathrm{B}T}{\lambda_\mathrm{th}^2} F_2(\beta\epsilon_1 + \alpha) + \frac{\epsilon_1}{\lambda_\mathrm{th}^2} F_1(\beta\epsilon_1 + \alpha)$$

$$\simeq \frac{k_\mathrm{B}T}{\lambda_\mathrm{th}^2} F_2(0) + \frac{k_\mathrm{B}T}{\lambda_\mathrm{th}^2} (\beta\epsilon_1 + \alpha) \ln(\beta\epsilon_1 + \alpha)$$

$$- \frac{\epsilon_1}{\lambda_\mathrm{th}^2} \ln(\beta\epsilon_1 + \alpha) + O(\beta\epsilon_1 + \alpha)$$

$$= \frac{k_\mathrm{B}T}{\lambda_\mathrm{th}^2} F_2(0) + \frac{k_\mathrm{B}T\alpha}{\lambda_\mathrm{th}^2} \ln(\beta\epsilon_1 + \alpha) + O(\beta\epsilon_1 + \alpha) \tag{A.20}$$

If $\alpha > O(1/V)$, we can neglect ϵ_1, and if $\alpha \leqslant O(1/V)$, we can write

$$\ln(\beta\epsilon_1 + \alpha) = -\ln V + O(1) \tag{A.21}$$

which is again independent of the precise value of ϵ_1. This result is of importance if we wish to investigate the transition region between the normal and

the condensed phases around $P_c(T)$. From (A.18) and (A.20) we find that, for small α,

$$\Delta P \equiv P - P_c(T) \simeq \frac{\epsilon_0 N_0}{V} + \frac{k_B T \alpha}{\lambda_{th}^2} \ln(\beta\epsilon_1 + \alpha) \tag{A.22}$$

In the condensed phase

$$\frac{\epsilon_0 N_0}{V} = O(1) \gg \frac{k_B T \alpha}{\lambda_{th}^2} \ln(\beta\epsilon_1 + \alpha) = O\left(\frac{\ln V}{V}\right) \tag{A.23}$$

while in the normal phase

$$\frac{\epsilon_0 N_0}{V} = O\left(\frac{1}{V^2}\right) \ll \frac{k_B T \alpha}{\lambda_{th}^2} \ln(\beta\epsilon_1 + \alpha) = O(1) \tag{A.24}$$

The transition region is reached when both terms on the rhs of (A.22) are equal. This leads to the following relationships:

$$\beta\epsilon_0 + \alpha = O(1/V \ln V) \tag{A.25}$$

$$N_0 = O(V \ln V) \tag{A.26}$$

$$\alpha = -\beta\epsilon_0 + O(1/V \ln V) = -O(1/V) \tag{A.27}$$

The exact equations for the edge of the transition region ΔP_c and for $\beta\epsilon_0 + \alpha$ at that point are

$$\beta\epsilon_0 + \alpha = -\lambda_{th}^2/[V \ln \beta(\epsilon_1 - \epsilon_0)] \tag{A.28}$$

$$\Delta P_c = -2\epsilon_0[\ln \beta(\epsilon_1 - \epsilon_0)]/\lambda_{th}^2 = O(\ln V/V) \tag{A.28a}$$

The other quantity we are interested in calculating is

$$N = \sum_k \{1/[\exp(\beta\epsilon_k + \alpha) - 1]\} \tag{A.29}$$

The summand here is always a monotonic decreasing function of ϵ_k, and is also concave upward. Moreover, if we consider the function

$$(1/V)/[\exp(\beta\epsilon + \alpha) - 1] \tag{A.30}$$

under the assumption (A.9), we find that it has a form qualitatively described by Fig. 4 for small ϵ. We can thus again sandwich the sum for $\epsilon_k \neq \epsilon_0$ between two inequalities if we assume a constant level spacing:

$$\int_{\epsilon_1}^{\infty} \frac{Vg\,d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} < \sum_{\epsilon_k \neq \epsilon_0} \frac{1}{\exp(\beta\epsilon_k + \alpha) - 1}$$

$$< \int_{\epsilon_{1/2}}^{\infty} \frac{Vg\,d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} \tag{A.31}$$

The integrals differ by less than

$$\tfrac{1}{2}/[\exp(\beta\epsilon_{1/2} + \alpha) - 1] = O(V) \tag{A.32}$$

and we can write

$$\sum_{\epsilon_k \neq \epsilon_0} \frac{1}{\exp(\beta\epsilon_k + \alpha) - 1}$$

$$= \int_{\epsilon_1}^{\infty} \frac{Vg\, d\epsilon}{\exp(\beta\epsilon + \alpha) - 1} + O(V)$$

$$= \int_0^{\infty} \frac{Vg\, dx}{\exp(\beta x + \beta\epsilon_1 + \alpha) - 1} + O(V) = \frac{V}{\lambda_{\text{th}}^2} F_1(\beta\epsilon_1 + \alpha) + O(V)$$

$$\cong -\frac{V}{\lambda_{\text{th}}^2} \ln(\beta\epsilon_1 + \alpha) + O(V) = O(V \ln V) + O(V) \tag{A.33}$$

Therefore the error is less than the leading term by $O(1/\ln V)$ when (A.9) is valid, and we can write

$$N \cong N_0 + (V/\lambda_{\text{th}}^2)F_1(\beta\epsilon_1 + \alpha) \tag{A.34}$$

It is easily verified that this equation is valid even when (A.9) is not satisfied.

This equation supplies us with another way of defining the transition region: Since the first term on the rhs is negligible in the normal phase while the second term is negligible in the condensed phase, we set

$$N_0 = (V/\lambda_{\text{th}}^2)F_1(\beta\epsilon_1 + \alpha) = -(V/\lambda_{\text{th}}^2) \ln(\beta\epsilon_1 + \alpha) \tag{A.35}$$

at the edge of the transition region. This equation is exactly the same as (A.28), which was derived in a different way, starting from ΔP. We also learn from this that at ΔP_c

$$N_0 = N/2 = O(V \ln V) \tag{A.36}$$

By making for

$$\ln Z_G = -\sum_k \ln[1 - \exp(-\beta\epsilon_k - \alpha)] \tag{A.37}$$

considerations similar to those made for P and N, we find that

$$\ln Z_G = -\ln[1 - \exp(-\beta\epsilon_0 - \alpha)]$$
$$+ (V/\lambda_{\text{th}}^2)F_2(\beta\epsilon_1 + \alpha) + O(\ln V) \tag{A.38}$$

when (A.9) is satisfied. It looks as though both the ground-state term and the $V(\beta\epsilon_1 + \alpha) \ln(\beta\epsilon_1 + \alpha)$ part of VF_2 are then of order $O(\ln V)$, i.e., the same as the error. Nevertheless, if these terms are kept and the whole expression is differentiated with respect to either β, α, or V, one gets the right expressions for U, N, and P, respectively! This occurs just because $\ln Z_G$ is not a homogeneous function of V. Thus, different parts of $\ln Z_G$ behave differently when they are differentiated, some of them gaining in importance more than others. This also explains why one cannot assume that $\ln Z_G$ is extensive. The whole question of identifying the most important contribution to any thermodynamic quantity becomes tricky. We have (hopefully) not made any mistakes

so far because we never differentiated an approximate expression: Integration approximations for discrete sums were always made only after differentiating.

Using the same caution, we calculate the entropy S from the exact relation

$$S = k_B \ln Z_G + (U/T) + N k_B \alpha \tag{A.39}$$

Substituting for the three terms on the rhs from (A.38), (A.5), (A.18), and (A.34), we get

$$\frac{S}{k_B} = -\ln(\beta \epsilon_0 + \alpha) + \frac{2V}{\lambda_{th}^2} F_2(\beta \epsilon_1 + \alpha)$$

$$+ 1 + \frac{V(\beta \epsilon_1 + \alpha)}{\lambda_{th}^2} F_1(\beta \epsilon_1 + \alpha) + O(\ln V) \tag{A.40}$$

The first and third terms are always no greater than the error in this expression and may be neglected. When $T \to T_c(P)$ or $P \to P_c(T)$ in the normal phase, S obviously tends to zero (on the scale of N) because $\beta \epsilon_1 + \alpha \to O(1/V)$ and $V \to O(N^{1/2})$. In the condensed phase the only significant term in (A.40) is the second one, which is of order $O(N^{1/2})$.

By taking all the necessary precautions that we have outlined above, we can calculate c_v and c_p for the condensed phase outside the transition region between the two phases. The results are

$$c_v/k_B = (2V/N\lambda_{th}^2)[F_2(\beta \epsilon_1 + \alpha) + \beta(\epsilon_1 - \epsilon_0)F_1(\beta \epsilon_1 + \alpha)]$$
$$+ O(1/N)$$
$$= (2V/N\lambda_{th}^2)F_2(0) + O(1/N) = O(N^{-1/2}) + O(N^{-1}) \tag{A.41}$$

$$c_p/k_B = [2PV^2 F_2(0)/\epsilon_0 \lambda_{th}^2 N](\beta \epsilon_0 + \alpha)$$
$$\times [1 + (V/\lambda_{th}^2)(\beta \epsilon_0 + \alpha)F_1(\beta \epsilon_1 + \alpha) + O(1/V)]$$
$$= O(1/N^{1/2}) + O(\log N/N) + O(1/N) \tag{A.42}$$

We note that in c_p, as in P, we also get the first correction to the leading order correctly.

Using (A.22), (A.23), and the fact that $N_0 = N$, we can write

$$\Delta P = N\epsilon_0 V(1/V^2) \tag{A.43}$$

$$V = (N\epsilon_0 V/\Delta P)^{1/2} \tag{A.44}$$

$$V^2/\epsilon_0 = V^3/\epsilon_0 V = (\epsilon_0 V)^{1/2}(N/\Delta P)^{3/2} \tag{A.45}$$

Substituting the last result into (A.42) we get

$$c_p/k_B = 2PF_2(0)(\epsilon_0 V)^{1/2}/N\lambda_{th}^2(\Delta P)^{3/2} \tag{A.46}$$

This would increase to infinity as P approaches $P_c(T)$ from above, except that when the edge of the transition region [see Eq. (A.28a)] is reached, (A.46) ceases to be valid. Instead of increasing to infinity, c_p then rounds off at a value that depends upon N.

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