PHYSICAL REVIEW B VOLUME 12, NUMBER 9 1 NOVEMBER 1975

Bose-Einstein condensation in a two-dimensional system at constant pressure*

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(Received 8 April 1975)

Using techniques developed by Greenspoon and Pathria, a rigorous, asymptotic analysis of the onset of Bose-Einstein condensation in a finite two-dimensional system at constant pressure is carried out. Some of the results obtained by Imry, Bergman, and Gunther, who first considered this problem, are upheld while others get modified. In particular, a macroscopic occupation of the single-particle ground state at finite temperatures is indeed possible. As the critical region, $T \simeq T_c$, is approached from above, the volume of the system becomes subextensive, $V_c = O(N/\ln N)$, which is both necessary and sufficient for the onset of Bose-Einstein condensation in the system. For instance, if the system is now cooled even at constant volume $V\,(=V_c)$, the condensate fraction gradually builds up and becomes nonnegligible as T approaches $T_0 \simeq (T_c)/2$; below T_0, it grows steadily as $(1-T/T_0)$. On the other hand, if we continued to cool the system at constant P its volume, over a thermodynamically negligible range of temperatures, would reduce to values $O(N^{1/2})$ which, in turn, would be accompanied by an abrupt accumulation of practically all the particles of the system into the single-particle ground state ϵ_0. The specific heat C_P, after having passed through a maximum, would also finally reduce to subextensive values. Phase transitions of this kind may be of relevance to the physical behavior of thin helium films and helium submonolayers.

I. INTRODUCTION

It is well known that an ideal Bose system of dimensionality lower than three does not undergo Bose-Einstein condensation at finite temperatures.[1] This is true if the system is cooled at a constant particle density n $(=N/V)$ and if n is finite throughout the system.[2] Recently, Imry, Bergman, and Gunther[3] have pointed out that if the system is cooled at a constant pressure P instead, a phase transition accompanied by a macroscopic condensation of particles in the lowest single-particle state ϵ_0 does take place at a finite temperature $T_c(P)$. This is made possible by the fact that in this situation the volume of the system becomes subextensive, so that, in the thermodynamic limit, the particle density no longer remains finite. In a realistic system of bosons, interparticle interactions will certainly prevent density from becoming infinite; however, a modified form of the aforementioned transition may still take place. Such a transition would clearly be of relevance to the problem of superfluidity in thin helium films[4] and to the thermodynamic behavior of helium submonolayers.[5]

We may recall that the problem of Bose-Einstein condensation in a three-dimensional system at constant pressure has already been broached by London,[6] who demonstrated the existence of a first-order phase transition at the critical temperature

$$T_c^{(3)} = \frac{1}{k}\left[\frac{1}{\zeta(\frac{5}{2})}\left(\frac{h^2}{2\pi m}\right)^{3/2} P\right]^{2/5} . \tag{1}$$

London emphasized that in order to establish the order of the transition it is inappropriate to prescribe the volume of the system beforehand; one must instead work with pressure and temperature as independent variables of the problem. He also showed that C_P, the specific heat of the system at constant pressure, behaved very differently from C_V, the specific heat at constant volume. While C_V remained finite at all temperatures, C_P became infinite as $T \to T_c(P)$. Curiously enough, London did not examine the occurrence of such a transition in systems of dimensionality two or one. In view of the relevance that it may have for actual physical systems, such as thin films and submonolayers of superfluid helium, we have undertaken a rigorous study of this transition in a two-dimensional system (of size $L \times L$). This may be regarded as a first step towards a similar study for a three-dimensional system (of arbitrary size $L_1 \times L_2 \times L_3$)—in particular, a thin film (for which $L_3 \ll L_{1,2}$).

The most distinguishing feature of this problem is the variation of the volume of the system with temperature; we must, therefore, reckon with the quantity $(\partial V/\partial T)_P$, which makes it necessary for us to treat the system as one of *finite* size. In their study of the two-dimensional problem, Imry *et al.* also argued for the necessity of subjecting the system to Dirichlet boundary conditions $(\Psi_S = 0)$, so that the condensate could also make a contribution

$$P_0 = N_0 \epsilon_0 / V \sim N_0 h^2 / m V^2 \quad (V = L^2) \tag{2}$$

towards the total pressure of the system and thus help in keeping it fixed at the given value P even when T is less than the critical temperature $T_c^{(2)}$, where

$$T_c^{(2)} = \frac{1}{k}\left(\frac{1}{\zeta(2)}\,\frac{h^2}{2\pi m}\,P\right)^{1/2} ; \tag{3}$$

clearly, this is not possible in the case of a system which, right from the beginning, is treated as infinite.

It follows from Eqs. (2) and (3) that for N_0 to be a significant fraction of N and for P_0 to be a significant fraction of P the volume of the system must be *subextensive*:

$$V \sim (h^2/mkT_c^{(2)})N^{1/2} . \tag{4}$$

This would result in an abrupt accumulation of practically all the particles of the system into the single-particle state ϵ_0 over an infinitesimally small range of temperatures around $T = T_c^{(2)}$. At the same time, the specific heat C_P would show a singular behavior, marked by an infinitely large value at $T = T_c^{(2)}$ and a vanishingly small value for practically all $T < T_c^{(2)}$.

In this paper we wish to report the results of a rigorous asymptotic analysis of this problem carried out by using techniques developed earlier by Pathria[7] and by Greenspoon and Pathria.[8] While some of the conclusions arrived at by Imry *et al.*[3] (in particular, the macroscopic occupation of the single-particle state ϵ_0 at finite temperatures below T_c) are upheld, others are found to require modifications. First of all, we find that the variety of finite-size corrections appearing in the basic expressions for the total number of particles N and the total pressure P of the system is such that the condensate pressure P_0 does not play a dominant role in the critical region $T \simeq T_c$. Equally important is the role played by the finite-size effect on the density of states of the system which arises from the specific choice of the boundary conditions. The two effects together determine the precise nature of the physical behavior of the system in the critical region. Of course, for temperatures below T_c, the condensate pressure P_0 does play a dominant role in this problem.

We shall also demonstrate that as $T \to T_c$ from above and the volume of the system becomes "somewhat" subextensive, i.e.,

$$V \to V_c \sim (h^2/mkT_c)(N/\ln N), \tag{5}$$

cf. Eq. (4), the system has actually shrunk enough for the onset of Bose-Einstein condensation even at constant V. Thus, if the system is cooled below T_c at a constant volume, $V = V_c$, the condensate fraction gradually increases and becomes $O(1)$ when $T < T_0$ where $T_0 \simeq \frac{1}{2}T_c$. Below T_0, the condensate fraction varies as $(1 - T/T_0)$. Clearly, the process of condensation in this case is spread over a finite range of temperatures between zero and T_0, rather than being concentrated at a single temperature T_c. Apparently, this will simulate more faithfully the superfluid behavior met with in actual physical systems.

II. FORMULATION OF THE PROBLEM

We consider a Bose system of noninteracting particles with mean occupation numbers $\langle n_i\rangle$ for the single-particle energy states ϵ_i. The total number of particles N and the total pressure P of the system are then given by

$$N = \sum_i \langle n_i\rangle \tag{6}$$

and

$$P = -\sum_i \langle n_i\rangle \frac{\partial\epsilon_i}{\partial V} , \tag{7}$$

where

$$\langle n_i\rangle = (e^{\alpha+\epsilon_i/kT} - 1)^{-1} \tag{8}$$

and

$$\alpha = -(\mu/kT) , \tag{9}$$

μ being the chemical potential of the system; the derivatives $(\partial\epsilon_i/\partial V)$ appearing in Eq. (7) are determined by the energy spectrum of the single-particle states. For a two-dimensional system of side L (and "volume" $V = L^2$), the energy spectrum *under Dirichlet boundary conditions* is given by

$$\epsilon(l_1, l_2) = \frac{h^2}{8mL^2}(l_1^2 + l_2^2) \propto \frac{1}{V} \quad (l_{1,2} = 1, 2, 3, \ldots). \tag{10}$$

It follows that $(\partial\epsilon_i/\partial V) = -(\epsilon_i/V)$ and hence

$$P = \sum_i \langle n_i\rangle \frac{\epsilon_i}{V} = \frac{U}{V} , \tag{11}$$

U being the total energy of the system.

For the evaluation of the sums in Eqs. (6) and (11) we first of all note that if the summand $f(l_1, l_2)$ is an *even* function of the quantum numbers l_1 and l_2 then[7]

$$\sum_{l_{1,2}=1}^{\infty} f(l_1, l_2) = \frac{1}{4}\left[\sum_{l_{1,2}=-\infty}^{\infty} f(l_1, l_2) - \left(\sum_{l_1=-\infty}^{\infty} f(l_1, 0) + \sum_{l_2=-\infty}^{\infty} f(0, l_2)\right) + f(0, 0)\right] \tag{12}$$

or, alternatively,

$$S_D^{(2)}(L) = \tfrac{1}{4}[S_P^{(2)}(2L) - 2S_P^{(1)}(2L) + f(0, 0)], \tag{13}$$

where $S_D^{(m)}$ denotes an m-dimensional sum under Dirichlet boundary conditions, while $S_P^{(m)}$ denotes a similar sum under periodic boundary conditions, the energy spectrum in the latter case being

$$\epsilon(l_1, l_2) = (h^2/2mL^2)(l_1^2 + l_2^2) \quad (l_{1,2} = 0, \pm 1, \pm 2, \ldots). \tag{14}$$

The sums $S_p^{(m)}$ may be evaluated by using the method of Greenspoon and Pathria,[8] whence Eq. (6) becomes (for $L \gg \lambda$)

$$N = \frac{L^2}{\lambda^2}\left(g_1(\alpha) + 2 \sum_{q_{1,2}=-\infty}^{\infty}{}' K_0[2y(q_1^2+q_2^2)^{1/2}] - \frac{\lambda}{L}[g_{1/2}(\alpha) + 2\pi^{1/2}\alpha^{-1/2} g_0(2y)] + \frac{\lambda^2}{4L^2} g_0(\alpha)\right), \tag{15}$$

where $\lambda\ [=h/(2\pi mkT)^{1/2}]$ is the mean thermal wavelength of the particles, $g_n(\delta)$ are the Bose-Einstein functions[9]

$$g_n(\delta) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}\,dx}{e^{x+\delta} - 1}, \tag{16}$$

and $K_0(z)$ is a modified Bessel function, while the *thermogeometric parameter* y (which, in our formulation, plays the role of a scaling variable) is given by[7,10]

$$y = 2\pi^{1/2}\alpha^{1/2}(L/\lambda) = L/\xi\ ; \tag{17}$$

here, $\xi\ [=\lambda/(2\pi^{1/2}\alpha^{1/2})]$ is the *correlation length* of the bulk system. Note that the sum Σ' in Eq. (15) excludes the term with $q_1 = q_2 = 0$.

In the region of interest ($\alpha \ll 1$), we may write

$$g_1(\alpha) = -\ln(1 - e^{-\alpha}) \simeq -\ln\alpha; \quad g_{1/2}(\alpha) \simeq \pi^{1/2}\alpha^{-1/2}\ . \tag{18}$$

No such approximation is permissible for the functions $K_0[2y(q_1^2 + q_2^2)^{1/2}]$ and $g_0(2y)$ because the parameter y varies drastically over the transition region. We, therefore, retain the relation

$$g_0(2y) = (e^{2y} - 1)^{-1} \tag{19}$$

and write

$$g_{1/2}(\alpha) + 2\pi^{1/2}\alpha^{-1/2} g_0(2y) \simeq \pi^{1/2}\alpha^{-1/2}\coth y. \tag{20}$$

The primed summation in Eq. (15) can be reduced to a more appropriate form by using a method owing to Fetter, Hohenberg, and Pincus,[11] with the result (valid for *all* y)

$$\sum_{q_{1,2}=-\infty}^{\infty}{}' K_0[2y(q_1^2+q_2^2)^{1/2}] = \frac{\pi}{2y^2} + \lim_{\epsilon\to 0}[S(\epsilon) - \tfrac{1}{2}E_1(\epsilon)] - \frac{y^2}{2\pi}\sum_{q_{1,2}=-\infty}^{\infty}{}'\left(\frac{1}{(q_1^2+q_2^2)[y^2+\pi^2(q_1^2+q_2^2)]}\right), \tag{21}$$

where

$$S(\epsilon) = \frac{1}{2\pi}\sum_{q_{1,2}=-\infty}^{\infty}{}' \frac{\exp[-(\pi^2\epsilon/y^2)(q_1^2+q_2^2)]}{q_1^2+q_2^2} \tag{22}$$

and

$$E_1(\epsilon) = \int_1^\infty t^{-1} e^{-\epsilon t}\,dt\ . \tag{23}$$

The behavior of the function $S(\epsilon)$, for $\epsilon \ll 1$, can be obtained by using a result owing to Glasser,[12,13] whereby

$$S(\epsilon) = -\tfrac{1}{2}\ln\epsilon + \tfrac{1}{2}\gamma - \tfrac{1}{2}\ln\frac{[\Gamma(\frac{1}{4})]^4}{4\pi y^2} + O(\epsilon), \tag{24}$$

γ being the Euler constant. Under the same condition,

$$E_1(\epsilon) = -\ln\epsilon - \gamma + O(\epsilon)\ . \tag{25}$$

We thus have,

$$\lim_{\epsilon\to 0}[S(\epsilon) - \tfrac{1}{2}E_1(\epsilon)] = \gamma - \tfrac{1}{2}\ln\frac{[\Gamma(\frac{1}{4})]^4}{4\pi y^2}\ . \tag{26}$$

At the same time the last summation in Eq. (21) can be written

$$\sum_{q_{1,2}=-\infty}^{\infty}{}'(\ldots) = \frac{2\pi^2}{3y^2} - \frac{2\pi^2\coth y}{y^3} + \frac{2\pi^2}{y^4} + 4\sum_{q_{1,2}=1}^{\infty}(\ldots)\ . \tag{27}$$

In view of Eqs. (26) and (27), Eq. (21) takes the form

$$\sum_{q_{1,2}=-\infty}^{\infty}{}' K_0[2y(q_1^2+q_2^2)^{1/2}] = \tfrac{1}{2}\ln\frac{4\pi y^2}{[\Gamma(\frac{1}{4})]^4} + \gamma - \frac{\pi}{3} + \frac{\pi\coth y}{y} - \frac{\pi}{2y^2} - \frac{2y^2}{\pi}S_1(y^2), \tag{28}$$

where

$$S_1(y^2) = \sum_{q_{1,2}=1}^{\infty}(q_1^2+q_2^2)^{-1}[y^2+\pi^2(q_1^2+q_2^2)]^{-1}\ . \tag{29}$$

Substituting Eqs. (18), (20), and (28) into (15), we finally obtain

$$N = \frac{x}{4\pi}\left(\ln x + C - \frac{4y^2}{\pi}S_1(y^2)\right), \tag{30}$$

where x is another parameter, defined by

$$x = y^2/\alpha = 4\pi(L/\lambda)^2\ , \tag{31}$$

while

$$C = \ln\frac{4\pi}{[\Gamma(\frac{1}{4})]^4} + 2\gamma - \frac{2\pi}{3} = -3.56103\ . \tag{32}$$

Note that x is a measure of the "volume" of the system.

At this point we wish to emphasize the fact that our final expression for N is such that it passes smoothly from the region with $y^2 > 0$ to the region with $y^2 < 0$. This is important because, under Dirichlet boundary conditions, one must ultimately deal with the region of negative y^2—in particular, with the limiting situation when $y^2 \simeq -2\pi^2$. In this connection, we observe that the zero-temperature limit of the chemical potential μ of the system is given by ϵ_0, which is equal to $\epsilon(1,1) = h^2/4mL^2$; accordingly, the limiting value of α is $-h^2/4mL^2kT = -\frac{1}{2}\pi(\lambda/L)^2$ and, by Eq. (17), the corresponding value of y^2 is $-2\pi^2$. The relevance of this limit is highlighted by the fact that the ground-state occupation number N_0 is given by

$$N_0 = \frac{1}{e^{\alpha+\beta\epsilon(1,1)} - 1} \simeq \frac{1}{\alpha + \beta\epsilon(1,1)} = \frac{x}{y^2 + 2\pi^2} . \tag{33}$$

Clearly, for a macroscopic occupation of the ground state, y^2 must be very close to $-2\pi^2$; in fact, we must have for this purpose

$$y^2 = -2\pi^2 + O(x/N). \tag{34}$$

In passing we note that N_0 is also given directly by the first term of the sum $S_1(y^2)$ in Eq. (30).

Following a similar procedure we obtain for the pressure of the system

$$P = \frac{kT}{\lambda^2}\left\{\frac{\pi^2}{6} - \frac{1}{2}\zeta\left(\frac{3}{2}\right)\frac{\lambda}{L} - \alpha \times \left[\ln\frac{y^2}{\alpha} + C + 1 - \frac{4y^2}{\pi}S_1(y^2)\right]\right\} . \tag{35}$$

Using Eqs. (30) and (31), this becomes

$$P = \frac{8\pi^2 mk^2T^2}{h^2}\left(\frac{\pi}{24} - \frac{\zeta(\frac{3}{2})}{4\pi^{1/2}x^{1/2}} - \frac{Ny^2}{x^2} - \frac{y^2}{4\pi x}\right). \tag{36}$$

We note that the first term in Eq. (36) represents the *bulk* behavior of the system, the second term arises from the modification of the density of states of the system owing to its finite size (and depends crucially on the choice of the boundary conditions[14,15]), while the last two terms arise explicitly from the discreteness of the single-particle states. The pressure P_0 exerted by the condensate can be extracted from the third term by letting $y^2 \to -2\pi^2$; we obtain, as expected,

$$P_0 = N_0\frac{16\pi^4 mk^2T^2}{h^2x^2} = N_0\frac{h^2}{4mL^4} = N_0\frac{\epsilon_0}{V} . \tag{37}$$

III. CRITICAL BEHAVIOR

For studying the critical behavior of the system we must first of all determine the manner in which the parameters x and y^2 vary as the system is cooled at constant N and P. From Eq. (30) we obtain

$$\left(\frac{dy^2}{dx}\right)_N = \left(\frac{N}{x^2} + \frac{1}{4\pi x}\right)\frac{1}{S_2(y^2)} > 0 , \tag{38}$$

where

$$S_2(y^2) = \frac{1}{\pi^2}\frac{d}{dy^2}[y^2S_1(y^2)] = \sum_{q_{1,2}=1}^{\infty}[y^2 + \pi^2(q_1^2 + q_2^2)]^{-2} . \tag{39}$$

Equation (36) now gives

$$\left(\frac{\partial P}{\partial T}\right)_N = 2\frac{P}{T} + \frac{8\pi^2mk^2T^2}{h^2}\left(\frac{\partial x}{\partial T}\right)_N\left[\frac{\zeta(\frac{3}{2})}{8\pi^{1/2}x^{3/2}} + y^2\left(\frac{2N}{x^3} + \frac{1}{4\pi x^2}\right) - \left(\frac{N}{x^2} + \frac{1}{4\pi x}\right)^2\frac{1}{S_2(y^2)}\right]. \tag{40}$$

The constancy of P, therefore, implies that

$$\left(\frac{\partial x}{\partial T}\right)_{N,P} = \frac{h^2P}{4\pi^2mk^2T^3}\left[\left(\frac{N}{x^2} + \frac{1}{4\pi x}\right)^2\frac{1}{S_2(y^2)} - \frac{\zeta(\frac{3}{2})}{8\pi^{1/2}x^{3/2}} - y^2\left(\frac{2N}{x^3} + \frac{1}{4\pi x^2}\right)\right]^{-1}. \tag{41}$$

Now, thermodynamics requires that $(\partial x/\partial T)_{N,P}$ be non-negative, see Eqs. (31) and (53); accordingly, we must have

$$\left(\frac{N}{x^2} + \frac{1}{4\pi x}\right)^2 > S_2(y^2) \times \left[\frac{\zeta(\frac{3}{2})}{8\pi^{1/2}x^{3/2}} + y^2\left(\frac{2N}{x^3} + \frac{1}{4\pi x^2}\right)\right]. \tag{42}$$

The foregoing inequality forces us to consider temperatures above the critical point separately from those below the critical point. The former correspond to $y^2 \gg 1$, the latter to $y^2 \simeq -2\pi^2$.

A. Region of $T > T_c$

To study this region we note that, in view of Eqs. (28) and (39),

$$S_1(y^2) = (\pi/4y^2)(\ln y^2 + C) + O(1/y^4) \tag{43}$$

and hence

$$S_2(y^2) = (1/4\pi y^2) - O(1/y^4) , \tag{44}$$

with C as given by Eq. (32). Substituting Eq. (44) into (42), we obtain the asymptotic condition

$$N^2 > \frac{\zeta(\frac{3}{2})x^{5/2}}{32\pi^{3/2}y^2}\left[1 - O\left(\frac{1}{y^2}\right)\right], \tag{45}$$

which restricts us to temperatures above a critical value T_c where T_c is determined by the relationship

$$\xi_c = [32\pi^{3/2}/\zeta(\tfrac{3}{2})]N^2 \quad (\xi = x^{5/2}/y^2) . \tag{46}$$

At this stage we also recall Eq. (30) which, in view of Eq. (43), takes the form

$$N = (x/4\pi)\ln(x/y^2) \quad (y^2 \gg 1) . \tag{47}$$

Equations (46) and (47) together determine the *critical parameters* x_c and y_c^2.

One readily sees that

$$x_c \sim \frac{8\pi N}{\ln N}, \quad y_c^2 \sim \frac{4\pi\zeta(\frac{3}{2})(2N)^{1/2}}{\ln^{5/2} N} \tag{48}$$

and

$$V_c \sim \left(\frac{\pi h^2}{3mP}\right)^{1/2} \frac{N}{\ln N} \; . \tag{49}$$

The corresponding *critical temperature* T_c can be determined by using Eq. (36), whence

$$T_c^2 = \frac{3h^2 P}{\pi^3 m k^2}\left(1 - \frac{6\zeta(\frac{3}{2})}{\pi^{3/2} x_c^{1/2}} - \frac{24Ny_c^2}{\pi x_c^2} - \frac{6y_c^2}{\pi^2 x_c}\right)^{-1} . \tag{50}$$

Using Eq. (46), this gives

$$t_c = \frac{T_c - T_c(\infty)}{T_c(\infty)} \simeq \frac{3\zeta(\frac{3}{2})}{\pi^{3/2} x_c^{1/2}}\left(1 + \frac{x_c}{8\pi N} + \frac{x_c^2}{32\pi^2 N^2}\right)$$

$$\sim \frac{3}{2\pi^2}\,\zeta\left(\frac{3}{2}\right)(2N)^{-1/2}\ln^{1/2} N \; ; \tag{51}$$

here, $T_c(\infty)$ denotes the bulk value of T_c and is given by Eq. (3). For the amount of condensate present at $T = T_c$ we have, see Eq. (33),

$$(N_0)_c \simeq (x_c/y_c^2) \sim [1/\zeta(\tfrac{3}{2})](2N)^{1/2}\ln^{3/2} N, \tag{52}$$

which is not macroscopic in magnitude.

For the specific heat at constant pressure we have

$$C_P = \left(\frac{\partial}{\partial T}(U + PV)\right)_{N,P} = 2P\left(\frac{\partial V}{\partial T}\right)_{N,P}$$

$$= \frac{P\lambda^2}{2\pi}\left[\left(\frac{\partial x}{\partial T}\right)_{N,P} - \frac{x}{T}\right], \tag{53}$$

where $(\partial x/\partial T)_{N,P}$ is given by Eq. (41). We observe that, for temperatures close to T_c,

$$C_P/Nk = O(N^{1/2}/\ln^{3/2} N), \tag{54}$$

which diverges in the thermodynamic limit. The exact nature of this divergence, as $T \to T_c$, can be studied by introducing the *shifted temperature deviation*[16]

$$\mathring{t} = t - t_c \, , \tag{55}$$

where

$$t = \frac{T - T_c(\infty)}{T_c(\infty)} \simeq \frac{3\zeta(\frac{3}{2})}{\pi^{3/2} x^{1/2}} + \frac{12Ny^2}{\pi x^2} + \frac{3y^2}{\pi^2 x}, \tag{56}$$

and expressing the limiting behavior of C_P, namely,

$$\frac{C_P}{k} \sim \frac{\pi}{576}\,\frac{x_c^4}{y_c^2 N^2}\,\frac{\xi_c}{\xi - \xi_c} \quad \left(\xi = \frac{x^{5/2}}{y^2}\right), \tag{57}$$

in terms of $\mathring{t}$. We obtain

$$\frac{C_P}{k} \sim \left(\frac{2\pi^2}{3}\right)^{3/2}\left[\zeta\left(\frac{3}{2}\right)\right]^{-1/2} \frac{(2N)^{5/4}}{\ln^{7/4} N}\,\mathring{t}^{-1/2} . \tag{58}$$

It will be noted that, for Eq. (58) to yield a result of the same order in N as Eq. (54), $\mathring{t}$ must be $O(N^{-1/2}\ln^{-1/2} N)$, which may be compared with expression (51) for t_c.

At this point we would like to remark that if one ignores the finite-size effects arising from the modification of the density of states of the system and takes into account only those that arise explicitly from the discreteness of the low-lying quantum states one recovers precisely the results obtained earlier by Imry *et al.* for $T > T_c(\infty)$. For instance, one then obtains from Eq. (56)

$$y^2/x^2 \sim \pi t/12N \tag{59}$$

whence one gets, with the help of Eq. (30),

$$x \sim \frac{4\pi N}{|\ln t|}, \quad y^2 \sim \frac{4\pi^3 N t}{3|\ln t|^2} . \tag{60}$$

One is then led to the following results:

$$\frac{C_P}{k} \sim \frac{\pi}{576}\,\frac{x^4}{y^2 N^2} \sim \frac{\pi^2 N}{3t\,|\ln t|^2}, \tag{61}$$

$$V = \lambda^2\,\frac{x}{4\pi} \sim \left(\frac{\pi h^2}{12mP}\right)^{1/2}\frac{N}{|\ln t|}, \tag{62}$$

$$N_0 \simeq \frac{x}{y^2} \sim \frac{3|\ln t|}{\pi^2 t}, \tag{63}$$

and

$$\frac{C_V}{k} \simeq \frac{\pi}{12}\,x \sim \frac{\pi^2 N}{3|\ln t|} . \tag{64}$$

As t decreases and becomes $O(\ln N/N)$ one obtains the limiting forms

$$\begin{aligned} &x = O(N/\ln N), \quad y^2 = O(1/\ln N), \\ &N_0 = O(N), \quad C_P/k = O(N^2/\ln^3 N), \\ &V/\lambda_c^2 = O(N/\ln N), \quad \text{and} \quad C_V/k = O(N/\ln N). \end{aligned} \tag{65}$$

A comparison of these results with the ones obtained in the preceding paragraphs shows that the inclusion of the density-of-states effects causes significant modifications in the results obtained by Imry *et al.* for the critical behavior of the system.

B. Region of $T < T_c'$

To study this region we put

$$y^2 = -2\pi^2 + \epsilon \quad (\epsilon \simeq x/N_0 \simeq x/N \ll 1). \tag{66}$$

In this case

$$S_2(y^2) = 1/\epsilon^2 + O(1) \simeq N^2/x^2 . \tag{67}$$

Substituting Eqs. (66) and (67) into Eq. (42) we obtain the asymptotic condition

$$N > \frac{\zeta(\frac{3}{2})}{32\pi^{5/2}} x^{3/2} \left[1 - O(1/x^{1/2}) \right] , \tag{68}$$

which restricts us to temperatures below a critical value T_c' where T_c' is determined by the relationship

$$x_c' = [32\pi^{5/2} N/\zeta(\tfrac{3}{2})]^{2/3} ; \tag{69}$$

accordingly,

$$y_c^{2\prime} \simeq -2\pi^2 + [32\pi^{5/2}/\zeta(\tfrac{3}{2})]^{2/3} N^{-1/3} . \tag{70}$$

Equation (30) now takes the form

$$N = N_0 + \frac{x}{4\pi} \left(\ln x + C - \frac{2}{\pi} + \frac{8\eta}{\pi} \right) , \tag{71}$$

where

$$\eta = \sum_{q_{1,2}=1}^{\infty}{}' (q_1^2 + q_2^2)^{-1} (q_1^2 + q_2^2 - 2)^{-1} = 0.24341 ; \tag{72}$$

note that the summation Σ' in Eq. (72) excludes the term with $q_1 = q_2 = 1$. It follows that

$$V_c' = \lambda_c^2 O(N^{2/3}), \quad (N_0)_c' = N - O(N^{2/3} \ln N), \tag{73}$$

which means that practically all the particles of the system are in the state ϵ_0. From Eqs. (3) and (36) we now obtain

$$\frac{T}{T_c(\infty)} \simeq \left(1 - \frac{6\zeta(\frac{3}{2})}{\pi^{3/2} x^{1/2}} + \frac{48\pi N}{x^2} \right)^{-1/2} , \tag{74}$$

whence

$$t_c' = \frac{T_c' - T_c(\infty)}{T_c(\infty)} \simeq \frac{9}{32\pi} \left(\frac{2\zeta(\frac{3}{2})}{\pi} \right)^{4/3} N^{-1/3} . \tag{75}$$

For T close to $T_c(\infty)$, we may write

$$t = \frac{T - T_c(\infty)}{T_c(\infty)} \simeq \frac{1}{3} t_c' \left[4 \left(\frac{x_c'}{x} \right)^{1/2} - \left(\frac{x_c'}{x} \right)^2 \right] \tag{76}$$

and

$$\mathring{t} = t - t_c' \simeq \frac{1}{3} t_c' \left[4 \left(\frac{x_c'}{x} \right)^{1/2} - \left(\frac{x_c'}{x} \right)^2 - 3 \right] \leq 0. \tag{77}$$

We may also define a variable ζ where

$$\zeta = (x - x_c')/x_c' \leq 0 . \tag{78}$$

For $|\mathring{t}|$ and $|\zeta| \ll 1$, we obtain

$$|\zeta| \simeq \frac{(128)^{1/3} \pi^{7/6}}{3[\zeta(\frac{3}{2})]^{2/3}} N^{1/6} |\mathring{t}|^{1/2} . \tag{79}$$

The specific heat at constant pressure then behaves as

$$\frac{C_P}{k} \simeq \frac{16\pi^5 N}{9[\zeta(\frac{3}{2})]^2} \left[\left(\frac{x_c'}{x} \right)^3 - \left(\frac{x_c'}{x} \right)^{3/2} \right]^{-1} , \tag{80}$$

$$\simeq \frac{32\pi^5 N}{27[\zeta(\frac{3}{2})]^2} |\zeta|^{-1} \simeq \frac{(256)^{1/3} \pi^{23/6}}{9[\zeta(\frac{3}{2})]^{4/3}} N^{5/6} |\dot{t}|^{-1/2} . \tag{81}$$

The same result follows by observing that, in this limit,

$$\frac{C_P}{k} \simeq \frac{\pi}{12} x_c' \left(\frac{\partial \zeta}{\partial \dot{t}} \right) . \tag{82}$$

Equations (58) and (81) describe, asymptotically, the nature of the singularity in C_P.

As T decreases below $T_c(\infty)$ we encounter a rather broad range of temperatures in which $x \ll x_c'$. The (x, T) relationship in this range is given by, see Eq. (74),

$$\frac{T}{T_c(\infty)} \simeq \left(1 + \frac{48\pi N}{x^2} \right)^{-1/2} , \tag{83}$$

whence

$$x \simeq (48\pi N)^{1/2} T [T_c^2(\infty) - T^2]^{-1/2} \tag{84}$$

and

$$V \simeq (N h^2/4mP)^{1/2} T_c(\infty) [T_c^2(\infty) - T^2]^{-1/2} . \tag{85}$$

As $T \to 0$, $V \to V_0 = (N h^2/4mP)^{1/2}$, which is precisely the volume required, in this limit, to maintain the system at constant pressure P; see Eq. (37). The specific heat at constant pressure is now given by

$$C_P/k \simeq (\tfrac{1}{3}\pi^3 N)^{1/2} T\, T_c^2(\infty) [T_c^2(\infty) - T^2]^{-3/2} \tag{86}$$

and the condensate fraction by

$$N_0/N = 1 - O(N^{-1/2} \ln N). \tag{87}$$

Results (83)–(87) apply in that range of temperatures in which the finite-size effects arising from the modification of the density of states of the system are not as important as the ones arising explicitly from the discreteness of the low-lying quantum states, viz., $|t| \gg N^{-1/3}$. Accordingly, they correspond to the treatment of Imry *et al.* for temperatures below $T_c(\infty)$, with the difference that in their case the validity of these results is supposed to extend right up to the limit $|t| \to 0$. One then obtains

$$V \propto N^{1/2} |t|^{-1/2} \tag{88}$$

and

$$C_P \propto N^{1/2} |t|^{-3/2} , \tag{89}$$

which may be compared with our rigorous results (73) and (81), respectively.

An awkward feature of the foregoing results is that the temperature regions A and B somewhat overlap; see Eqs. (51) and (75) for t_c and t_c' whereby $t_c' > t_c$. This means that if we approach the region of overlap from above we encounter a somewhat different behavior of the system than if we approach this region from below. Hopefully, a more refined treatment of the problem will overcome this difficulty. Nevertheless, since the width of the region of overlap is thermodynamically negligible, the main results obtained in this section may provide a correct asymptotic picture of the situation actually obtained in the system.

IV. COOLING THE SYSTEM AT CONSTANT VOLUME V_c

We have seen that the system under study, when cooled at *constant pressure* P from above, reaches a stage (as $T \to T_c$) where its volume becomes "somewhat" subextensive, i.e.,

$$V \to V_c = \lambda_c^2 (x_c/4\pi) = \lambda_c^2\, O(N/\ln N).$$

Still, at this stage, the amount of condensation in the single-particle ground state ϵ_0 is not macroscopic. We shall now show that, for a macroscopic occupation of the state ϵ_0, a further reduction in V is not necessary; the system may, if desired, be cooled at *constant volume* V_c. Under this constraint, we would have

$$x = 4\pi V_c/\lambda^2 = x_c(T/T_c) \tag{90}$$

and

$$\left(\frac{\partial x}{\partial T}\right)_{N,V_c} = \frac{x_c}{T_c} = \text{const} \quad (\text{for all } T < T_c). \tag{91}$$

The parameter y^2, as a function of T, will now be determined by Eqs. (30) and (90).

Since a macroscopic occupation of the ground state requires that y^2 be close to $-2\pi^2$, see Eq. (34), it appears advisable that we first locate the temperature range in which $|y^2|$ becomes $O(1)$. We find that this occurs in a very small neighborhood of the temperature T_0 at which $y^2 = 0$, i.e., where y^2 passes from positive to negative values. We get

$$T_0 = (x_0/x_c)\, T_c\,, \tag{92}$$

where x_0 is the solution of the equation

$$N = (x_0/4\pi)(\ln x_0 + C). \tag{93}$$

Clearly,

$$x_0 \sim 4\pi N/\ln N\,. \tag{94}$$

Recalling Eq. (48), we find that

$$T_0/T_c = x_0/x_c \simeq \tfrac{1}{2}\,. \tag{95}$$

The amount of condensate present at $T = T_0$ turns out to be

$$(N_0)_0 = x_0/2\pi^2 \sim (2/\pi)(N/\ln N). \tag{96}$$

Comparing this with Eq. (52), we find that, as T decreases from T_c to T_0, the condensate fraction f $(=N_0/N)$ builds up considerably. Thermodynamically, however, it still remains negligible:

$$f_0 = O(1/\ln N). \tag{97}$$

For further analysis we set $y^2 = -2\pi^2 + \epsilon$, with $\epsilon = O(1/\ln N)$; this would make $f = x/(N\epsilon) = O(1)$. Equation (30) then gives

$$\epsilon(T) = \frac{4\pi(T/T_0)}{4\pi(N/x_0) - (T/T_0)[\ln(x_0 T/T_0) + C - 2/\pi + (8/\pi)\eta} = \frac{x_0}{N}\,\frac{T/T_0}{1 - (T/T_0) + O(1/\ln N)}\,, \tag{98}$$

which gives explicitly the dependence of ϵ, or of y^2, on T. The condensate fraction is then given by

$$f(T) = 1 - \frac{x_0}{4\pi N}\,\frac{T}{T_0}\left[\ln\left(x_0 \frac{T}{T_0}\right) - 3.57781\right] \tag{99}$$

$$= \left(1 - \frac{T}{T_0}\right) + O\left(\frac{1}{\ln N}\right) \quad (0 < T < T_0). \tag{100}$$

Thus, in the present case, the condensate builds up steadily as T decreases over the finite range of temperatures from T_0 to 0, and not abruptly around T_c. Nevertheless, a macroscopic growth of the condensate *does* take place at finite temperatures.

The foregoing result is in sharp contrast with the one obtained by cooling the system at constant volume, L^2, right from the beginning. In that case, one would have from Eq. (30)

$$f(T) = 1 - \frac{L^2}{N\lambda^2}\left[\ln\left(4\pi\frac{L^2}{\lambda^2}\right) + C - \frac{2}{\pi} - \frac{4y^2}{\pi} S_1'(y^2)\right], \tag{101}$$

where $S_1'(y^2)$ denotes the sum $S_1(y^2)$ *minus* the term with $q_1 = q_2 = 1$. As $y^2 \to -2\pi^2$, the last term in the square brackets tends to the constant value $8\eta/\pi = 0.61984$. In the thermodynamic limit, therefore, the asymptotic behavior of the condensate fraction $f(T)$ is essentially determined by the relationship

$$(L^2/\lambda^2)\ln(L^2/\lambda^2) = (1 - f)\, N. \tag{102}$$

It follows that for a macroscopic buildup of the condensate in this case we require that

$$\lambda^2 \sim L^2 (\ln N/N)\,,$$

that is,

$$T \sim \frac{h^2}{mk}\frac{N}{V}\frac{1}{\ln N} \sim \frac{1}{\ln N}, \tag{103}$$

which, in the thermodynamic limit, tends to zero. In our problem, however, the volume of the system, as a result of prior cooling at constant pressure, itself reduced from the original value $V \sim O(N)$ to the critical value $V_c \sim O(N/\ln N)$. No wonder that a further cooling of the system, even at constant volume, resulted in Bose-Einstein condensation at finite temperatures!

In the end we consider the specific heat of the system at temperatures below T_c. Naturally, in this case, we must consider C_V, at $V = V_c$, rather than C_P. We obtain

$$(C_V)_{V=V_c} = \left(\frac{\partial U}{\partial T}\right)_{N, V_c} = V_c\left(\frac{\partial P}{\partial T}\right)_{V_c}, \tag{104}$$

where $(\partial P/\partial T)_{V_c}$ may be obtained from the relations, see Eqs. (36) and (38),

$$P = \frac{8\pi^2 mk^2 T_c^2}{h^2}\left[\frac{\pi}{24}\left(\frac{T}{T_c}\right)^2 - \frac{\zeta(\frac{3}{2})}{4\pi^{1/2}x_c^{1/2}} \times \left(\frac{T}{T_c}\right)^{3/2} - \frac{y^2}{4\pi x_c}\frac{T}{T_c} - \frac{Ny^2}{x_c^2}\right] \tag{105}$$

and

$$\left(\frac{\partial y^2}{\partial T}\right)_{V_c} = \frac{1}{T_c}\left[\frac{N}{x_c}\left(\frac{T_c}{T}\right)^2 + \frac{1}{4\pi}\frac{T_c}{T}\right]\frac{1}{S_2(y^2)}. \tag{106}$$

We obtain

$$\frac{1}{k}(C_V)_{V=V_c} = x_c\left[\frac{\pi}{12}\frac{T}{T_c} - \frac{3\zeta(\frac{3}{2})}{8\pi^{1/2}x_c^{1/2}}\left(\frac{T}{T_c}\right)^{1/2}\right] - \frac{y^2}{4\pi} - \left[\frac{N}{x_c}\frac{T_c}{T} + \frac{1}{4\pi}\right]^2\frac{1}{S_2(y^2)}. \tag{107}$$

The asymptotic behavior of C_V is essentially determined by the first two terms of Eq. (107); of these, the first one represents the bulk behavior (with $V = V_c$), while the second one represents the correction arising from the finite-size effect on the density of states of the system.

ACKNOWLEDGMENT

We are thankful to Dr. Nelson Lima Teixeira for helpful discussions during the course of this work.

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*Work supported in part by the National Research Council of Canada.

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