BOSE CONDENSATION IN A FINITE VOLUME

M. Ya. AZBEL'

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences

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It is shown that the width of the transition region for Bose condensation of an ideal Bose gas is of the order $T_C N^{-1/2}$, where T_C is the condensation temperature and N is the total particle number. If the volume has a pronounced anisotropic shape the width of the transition region increases and becomes of the order $T_C^2 L_1 (T_0 L_2 L_3 n^{1/3})^{-1}$, where T_0 is the infinite-volume condensation temperature, n is the particle density and L_1, L_2, L_3 are the linear dimensions, $L_1 \gg L_2$, L_3. A method is proposed for the determination of the form of the transition. It is shown that the quantity $(\partial p/\partial V)_T$ due to the surface can be positive in the equilibrium state.

IT is known (cf. e.g.[1]) that the free energy F of an ideal Bose gas is

$$F = N\mu + T\sum_k \ln\left(1 - \exp\frac{\mu - \varepsilon_k}{T}\right), \tag{1}$$

where T is the temperature, ϵ_k are the energy levels and μ is the chemical potential, defined for given particle number N by

$$N = \sum_k \left(1 - \exp\frac{\varepsilon_k - \mu}{T}\right)^{-1}. \tag{2}$$

However, in the immediate neighborhood of the Bose condensation at the point T_0, where $(\partial p/\partial V)_T \to 0$ and the particle number fluctuations tend to infinity as $(\partial p/\partial V)_T^{-1/2}$, it is no longer legitimate to use Eq. (2), and the chemical potential vanishes and stops being a well-defined thermodynamic quantity. This can be seen from the fact that according to the definition of the thermodynamic potential

$$e^{-\Omega/T} = \sum_{N=0} \exp\left(-\frac{F_N + \mu N}{T}\right), \tag{3}$$

(2) is also a consequence of the fact that in (3) only values $N \cong \overline{N}$ are essential and the method of steepest descent is applicable, whereas near $T = T_0$ the use of the "steepest-descent" formula turns out to be not valid. (This can be seen directly computing according to (1) and (2) (i.e., separating the first term, substituting in the others an integration for the summation, etc.) and comparing it with the correct result, to be obtained below.) Therefore, for $T \cong T_0$, one should start directly from the equation for F:

$$e^{-F/T} = \sum_{\Sigma n_k = N} \exp\left(-T^{-1}\sum_k n_k\varepsilon_k\right). \tag{4}$$

We shall consider that the states are enumerated in the order of increasing energy. It is then clear that for some sufficiently large k_0 the sum over k can be terminated (when $k > k_0$ all n_k can be considered equal to zero, since the occupation probability of these states is exponentially small and their contribution to F is of the order $\exp(-\epsilon_{k_0}/T)$, which for sufficiently large k_0 becomes arbitrarily small). Then the sum (4) can be rewritten as

$$\begin{aligned} e^{-F/T} &= \sum_{n_k=0}^{\infty} \frac{1}{2\pi}\int_0^{2\pi} \exp\left(iNx - ix\sum_k n_k\right)\exp\left(-\sum_k \frac{n_k\varepsilon_k}{T}\right)dx \\ &= \frac{1}{2\pi}\int_0^{2\pi} e^{iNx}\,dx \prod_k \left[1 - \exp\left(-ix - \frac{\varepsilon_k}{T}\right)\right]^{-1} \\ &= \frac{1}{2\pi i}\oint_{|z|=1} z^{N-1}\,dz \prod_k \left[1 - \frac{1}{z}\exp\left(-\frac{\varepsilon_k}{T}\right)\right]^{-1}. \end{aligned} \tag{5}$$

Considering that the energy levels are nondegenerate (for the case of a box-potential this implies that the areas of the walls are not commensurable; it is clear that such an assumption has no effect on the results) and thus the poles in (5) are simple, we find

$$\begin{aligned} F &= -T\ln\sum_\alpha \exp\left[-\frac{N\varepsilon_\alpha}{T} - \sum_{k\neq\alpha}\ln\left(1 - \exp\frac{\varepsilon_\alpha - \varepsilon_k}{T}\right)\right] \\ &= -T\ln\sum_\alpha (-1)^\alpha \exp\left[-\frac{N\varepsilon_\alpha}{T} - \sum_{k\neq\alpha}\ln\left|1 - \exp\frac{\varepsilon_\alpha - \varepsilon_k}{T}\right|\right] \\ &\equiv -T\ln\sum_\alpha (-1)^\alpha \exp\left(-\frac{F_1(\varepsilon_\alpha)}{T}\right). \end{aligned} \tag{6}$$

If the product in (5) were infinite, one would have to prove in addition that the point z = 0 does not contribute to the integral; the truncation[1)] of the sum over k in (4) saves us the trouble of carrying through this (not too difficult) proof.

One can see that the essential contribution to the sum (6) near the transition temperature (cf. infra) comes from $\epsilon_\alpha \ll T$. This means that one can select an m such that $\epsilon_\alpha \ll \epsilon_m \ll T$, and transform $F_1(\epsilon_\alpha)$ in the first approximation (the accent denotes the omission of the term with $k = \alpha$):

$$\begin{aligned} T^{-1}F_1(\varepsilon_\alpha) - \frac{N\varepsilon_\alpha}{T} &= \sum_{k=0}^{\alpha-1}\ln\left(\exp\frac{\varepsilon_\alpha - \varepsilon_k}{T} - 1\right) \\ &+ \sum_{k=\alpha+1}^{\infty}\ln\left(1 - \exp\frac{\varepsilon_\alpha - \varepsilon_k}{T}\right) = \sum_{k=0}^{m}{}'\ln\left|\frac{\varepsilon_\alpha - \varepsilon_k}{T}\right| \\ &+ \sum_{k=m+1}^{\infty}\ln\left[1 - \exp\left(-\frac{\varepsilon_k}{T}\right) - \frac{\varepsilon_\alpha}{T}\exp\left(-\frac{\varepsilon_k}{T}\right)\right] \\ &= \sum_{k=0}^{m}{}'\ln\left|\frac{\varepsilon_\alpha - \varepsilon_k}{T}\right| + \sum_{k=m+1}^{\infty}\ln\left[1 - \exp\left(-\frac{\varepsilon_k}{T}\right)\right] \end{aligned}$$

[1)] I am indebted to A. P. Kazantsev for proposing such a "truncation".

$$-\frac{\varepsilon_\alpha}{T}\sum_{k=m+1}^{\infty}\left[\exp\left(+\frac{\varepsilon_k}{T}\right)-1\right]^{-1}.$$

Writing $\sum\limits_{k=m+1}^{\infty}$ as $\sum\limits_{k=0}^{\infty} - \sum\limits_{k=0}^{m}$ and expanding the terms of the second sum with respect to $\epsilon_k/T \ll 1$, we obtain

$$\frac{\mathcal{F}_1(\varepsilon_\alpha)-N\varepsilon_\alpha}{T}\approx\frac{F_0(T)}{T}+\frac{N-N_0(T)}{T}\varepsilon_\alpha+\sum_{k=1}^{m}{}'\left[\ln\left|1-\frac{\varepsilon_\alpha}{\varepsilon_k}\right|+\frac{\varepsilon_\alpha}{\varepsilon_k}\right]$$

$$\approx\frac{F_0(T)}{T}-\frac{N_0(T)}{T}\varepsilon_\alpha+\sum_{k=1}^{\infty}{}'\left[\ln\left|1-\frac{\varepsilon_\alpha}{\varepsilon_k}\right|+\frac{\varepsilon_\alpha}{\varepsilon_k}\right],$$

so that

$$\mathcal{F}_1(\varepsilon_\alpha)=F_0(T)+(N-N_0(T))\varepsilon_\alpha+\sum_{k=1}^{\infty}{}'\left(\ln\left|1-\frac{\varepsilon_\alpha}{\varepsilon_k}\right|+\frac{\varepsilon_\alpha}{\varepsilon_k}\right),\quad(7)$$

where

$$F_0(T)=T\sum_{k=1}^{\infty}\left[1-\exp\left(-\frac{\varepsilon_k}{T}\right)\right],\quad N_0(T)=\sum_{k=1}^{\infty}\left[\exp\frac{\varepsilon_k}{T}-1\right]^{-1}.\quad(8)$$

Comparing (6), (7), and (8) one can see that everything is determined by the quantity

$$\xi=\frac{N-N_0(T)}{T}(\varepsilon_1-\varepsilon_0)\sim\frac{N(\varepsilon_1-\varepsilon_0)}{T_0}\tau,\quad(9)$$

$$N_0(T_0)=N,\quad\tau=(T_0-T)/T_0.\quad(10)$$

(ϵ_0 is the ground state energy).

Not too close to the phase transition point T_0, when $\xi \gg 1$, only the first term is important in the sum (6), and

$$F(T)\approx\mathcal{F}_1(\varepsilon_0)=N\varepsilon_0+T\sum_{k=1}^{\infty}\ln\left[\frac{\varepsilon_k-\varepsilon_0}{T}-1\right].\quad(11)$$

(We stress that this result does not coincide with the result which follows from Eqs. (1) and (2).) For $-\xi \gg 1$ the free energy can be computed making use of Eq. (5) and in the definition of the integral considering the exterior of the unit circle, using the method of steepest descent to compute it. It is easy to see that this method of calculation is equivalent to the use of Eqs. (1) and (2).

In the region $\xi \sim 1$ it can be seen from (6) that the free energy varies rapidly with temperature; the characteristic interval τ is defined by (9) and obviously depends essentially on the shape of the volume, particularly on its anisotropy. For the case of a volume the dimensions of which are of the same order in all directions, a substantial change occurs in a region $\tau \sim N^{-1/3}$, where there is a jump in the derivative of the heat capacity. Such a width of the transition region is caused, as for all transitions, by the finiteness of the particle number, i.e., by surface effects, for which the relative contribution is exactly of the order $N^{-1/3}$.

The anisotropy widens the transition region, lowering $\epsilon_1-\epsilon_0$ which is of course determined by the largest dimension and leads to the estimate given in the abstract. As is clear from (10), (8) there exist several "transition temperatures," corresponding to the condensation of bosons with quantum numbers corresponding to the different linear dimensions. Thus for a potential box with $L_1 \gg L_2 \gg L_3$ and

$$\varepsilon=\frac{\hbar^2}{2m}\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right)$$

we get first a condensation into the state with $n_3 = 1$, then with $n_2 = 1$, and finally, with $n_1 = 1$. (This fact was first pointed out by Sonin[2].)

Equations (10) and (8) allow us, naturally, to compute the dependence of the condensation temperature on the linear dimensions of a strongly anisotropic system. In the different limiting cases such a problem has been investigated in detail in a series of papers.[3] The starting point of these papers were essentially Eqs. (1) and (2). For the determination of the transition temperature up to terms of the order of the width of the transition region (but only with this accuracy!) Eqs. (1) and (2) are applicable. This is clear both from the preceding consideration, and from the fact that the average occupation numbers are by definition

$$\bar{n}_k=\sum_{\Sigma n_j=N}n_k\exp\frac{F-E}{T}=-Te^{F/T}\frac{\partial}{\partial\varepsilon_k}\sum_{\Sigma n_j=N}e^{-E/F}=\frac{\partial F}{\partial\varepsilon_k}.\quad(12)$$

Substituting into (12) the expression F(T) from (11) we find

$$\bar{n}_k=\left(\exp\frac{\varepsilon_k-\varepsilon_0}{T}-1\right)^{-1},\quad k\neq 0;\quad \bar{n}_0=N-\sum_{k=1}^{\infty}\bar{n}_k.\quad(13)$$

It is easy to see that in the "quasi-two-dimensional" case ($L_1 \gg L_2 \sim L_3$, n is the boson density) the Bose condensation temperature is

$$T_c(L_3)=T_c(\infty)\left[1+a\frac{\ln(n^{1/3}L_1)}{n^{1/3}L_3}\right]^{-1},\quad a\sim 1,\quad(14)$$

and in the "quasi-one-dimensional" case

$$T_c(L_2)=\frac{T_c(\infty)}{1+bn^{-1/6}L_1^{1/2}/L_2}\qquad b\sim 1.\quad(15)$$

In conclusion we call attention to one peculiar circumstance. It is well known that a condition for thermodynamic equilibrium (albeit a metastable one) is the negative character of $(\partial p/\partial V)_T$; a state with $(\partial p/\partial V)_T > 0$ is absolutely unstable with respect to phase separation. However, if $(\partial p/\partial V)_T > 0$ as a consequence of level quantization (owing to the presence of a surface) the phase separation cannot change anything. Moreover, under these circumstances $(\partial p/\partial V)_T$ is not a single-valued quantity and depends on the mode in which the surface area varies when the volume changes. It is simplest to demonstrate this general feature on the example of black-body radiation in a bounded volume (L_1, L_2, L_3), when

$$F=\Omega=T\sum_k\ln\left[1-\exp\left(-\frac{\varepsilon_k}{T}\right)\right]^{-1},$$

$$\left(\frac{\partial p}{\partial V}\right)_T=-\left(\frac{\partial^2F}{\partial V^2}\right)_T=-\sum\frac{\partial^2\varepsilon_k/\partial V^2}{\exp(\varepsilon_k/T)-1}$$

$$+\frac{1}{T}\sum\left(\frac{\partial\varepsilon_k}{\partial V}\right)^2\frac{\exp(\varepsilon_k/T)}{[\exp(\varepsilon_k/T)-1]^2},$$

and if, for instance $\delta L_1/L_1 = \delta L_2/L_2 = \delta L_3/L_3$, we have

$$\left(\frac{\partial p}{\partial V}\right)_T=\frac{-6E+4T\partial E/\partial T}{V^2}=\frac{2\pi^2T^4}{3V\hbar^3c^2}>0.$$

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