Effects of an attractive- δ -potential impurity center on Bose-Einstein condensation*

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The exact density of states for one particle in the field of an attractive δ impurity center is obtained from the system Green's function. The impurity is shown to introduce a bound state in the free-particle energy spectrum without any further modification. This result is then used to study the effects of the impurity on the thermodynamical properties of a gas of noninteracting bosons. The "Bose-Einstein phase transition" is not destroyed by the impurity, but a true condensation in position space occurs due to the existence of the bound state. The captured bosons form a cloud of well-localized particles modifying the macroscopic behavior of the gas for temperatures below a transition temperature T_c . The constantvolume specific heat, the entropy, and the pressure are evaluated as functions of the temperature and of the energy of the bound state, E_b . The transition temperature and the discontinuity of the specific heat at T_c are also obtained as a function of E_b .

I. INTRODUCTION

Very recently the problem of the existence of a phase transition in a gas of noninteracting bosons with impurity centers embedded in it has been raised by Kac and Luttinger.¹ They proved quite generally that the Bose-Einstein condensation is not destroyed by impurities with repulsive (shortrange) potential. Furthermore, it was verified that the transition temperature is increased compared to that of a completely free Bose gas, and finally that the ground-state energy of the system goes to zero in the thermodynamic limit. Unfortunately, as the authors have pointed out, it was impossible to analyze the physical details of the condensation phenomenon, due mainly to the nonspecification of the form of the particle-impurity interaction and to the formalism adopted to infer the existence of the condensation. In this paper we shall discuss the effects of an attractive δ particleimpurity interaction on the thermodynamic properties of a boson gas. With the choice of interaction potential one can evaluate the exact expression for the density of states of one particle in the impurity field of force, which in turn has allowed us to evaluate in a workable form the exact grand partition function of the system and all thermodynamical functions of interest.

In Sec. II we formulate the particle-impurity dynamical problem through Dyson's equation for the propagator in the coordinate-energy space. Because of the form of the potential the integral equation for $G(\mathbf{\vec{r}}, \mathbf{\vec{r}}', E)$ is transformed into an algebraic equation the solution of which requires a renormalization procedure on the potential strength. The single-particle density of states obtained from the trace of Q reveals just the addition of a bound state to the energy spectrum of a free particle. It is

the presence of this bound state which will modify the very essence of the condensation phenomenon, i.e., changing it from the ordinary Bose-Einstein ordering in the momentum space to a real phase separation in position space, with a fraction of the particles aggregated around the impurity and a higher density than that of the remaining particles in the gas.

A review of some results for the grand canonical ensemble needed in this paper as well as the basic one-particle partition function is dealt with in Sec. III. In Sec. IV we concentrate our attention on obtaining the logarithm of the grand partition function of a spinless Bose gas and the system's thermodynamic functions. The graphs have been evaluated with the help of the tabulated values of the Bose-Einstein function given by London.²

II. 5 POTENTIAL

The δ potential is known to be a very convenient choice for the study of the effect of localized impurities on a many-particle system. The one-dimensional 5 function is very easy to handle and all its properties are very well understood. This is not the case when one tries to generalize to dimensions larger than one. A scalar δ , δ (r) produces no effect, while a vector δ , $\delta(\vec{r})$ leads to divergences and becomes, at first sight, untractable. There is, nevertheless, a simple procedure which allows one to renormalize the potential by the introduction of an effective interaction strength. This is true in both two and three dimensions. The renormalized attractive three-dimensional 6 potential introduces a bound state in the energy spectrum of free particles and does not modify the finite-energy scattering states. This does not, we must stress, violate the completeness of the free-particle wave functions. The above result is obtained by a limiting process in which the scattering states corresponding to energies of the order $\hbar^2/2ma^2$ (where a is the range of the potential) are modified by the potential. Part of this discussion has been published' and a more detailed mathematical treatment will be presented in a future paper.

Let us now calculate the change of the density of states of a free particle in the presence of an attractive δ function of strength A . We shall follow closely the procedure followed in Ref. 3.

We shall be interested, in this section, in the change of the density of states produced by the impurity

$$
\Delta \rho(E) = (-1/\pi) \operatorname{Im} \int d^3r \left[G(\vec{r}, \vec{r}, E) - G_0(\vec{r}, \vec{r}, E) \right].
$$

In order to obtain G , we first write down Dyson's equation for the exact one-particle Green's function, 4

$$
G(\mathbf{\tilde{r}}, \mathbf{\tilde{r}'}, E) = G_0(\mathbf{\tilde{r}}, \mathbf{\tilde{r}'}, E) + \int d^3 r'' G_0(\mathbf{\tilde{r}}, \mathbf{\tilde{r}''}, E)
$$

× $A\delta(\mathbf{\tilde{r}''})G(\mathbf{\tilde{r}''}, \mathbf{\tilde{r}'}, E)$. (2.1)

Here G_0 is the free-particle Green's function

$$
G_0(\mathbf{\bar{r}}, \mathbf{\bar{r}'}, E) = \frac{1}{(2\pi\hbar)^3} \int d^3p \; \frac{e^{(i/\hbar)} \mathbf{\bar{r}} \cdot (\mathbf{\bar{r}} - \mathbf{\bar{r}'})}{E - E_{\mathbf{\bar{p}}} + i\eta}, \qquad (2.2)
$$

where $E_{\overline{p}} = p^2/2m$ and $\eta \rightarrow 0$, positively. Both G and $G_{\rm o}$ satisfy the boundary condition of vanishing at infinity.

Dyson's equation may be solved formally for G,

$$
G(\mathbf{\tilde{r}}, \mathbf{\tilde{r}'}, E) = G_0(\mathbf{\tilde{r}}, \mathbf{\tilde{r}'}, E) + \frac{AG_0(\mathbf{\tilde{r}}, 0, E)G_0(0, \mathbf{\tilde{r}'}, E)}{1 - AG_0(0, 0, E)}.
$$
\n(2.3)

Since we shall be interested in the trace of G , we look to the change in the diagonal part of ΔG ,

$$
\Delta G(\vec{\mathbf{r}}, \vec{\mathbf{r}}, E) = \frac{G_0(\vec{\mathbf{r}}, 0, E)G_0(0, \vec{\mathbf{r}}, E)}{1/A - G_0(0, 0, E)}.
$$
 (2.4)

The denominator of ΔG is not well defined since $G₀(0, 0, E)$ diverges. We shall treat it as a limit process, namely,

$$
\frac{1}{A} - G_0(0, 0, E) \equiv \lim_{\substack{A \to 0 \\ K \to \infty}} \left[\frac{1}{A} + \frac{1}{(2\pi\hbar)^3} \int_0^K \frac{d^3 p}{E_{\vec{p}}}\right]
$$

$$
-P \int \frac{dE_{\vec{p}} E N(E_{\vec{p}})}{E_{\vec{p}}(E - E_{\vec{p}})} + i\pi N(E), \tag{2.5}
$$

where the limit is made to be equal to α^{-1} , a positive and finite quantity, P is the principal value of

the integral and

$$
N(E) = \frac{1}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}
$$
 (2.6)

is the free one-particle density of states per unit of volume. Using the renormalized interaction strength α , we can rewrite

$$
\Delta G(\mathbf{\bar{r}}, \mathbf{\bar{r}}, E)
$$

=
$$
\frac{G_0(\mathbf{\bar{r}}, 0, E)G_0(0, \mathbf{\bar{r}}, E)}{(1/\alpha) - P \int dE_{\mathbf{\bar{p}}}[E N(E_{\mathbf{\bar{p}}})/E_{\mathbf{\bar{p}}}(E - E_{\mathbf{\bar{p}}})] + i\pi N(E)}
$$

(2.7)

The calculation of $\rho(E)$ is carried out for the two situations $E > 0$ and $E < 0$. For that purpose we write down the expression for $G_0(\tilde{r}, o, E)$,

$$
G_0(\vec{r}, 0, E) = -G_0(0, \vec{r}, E) = \frac{1}{(2\pi\hbar)^3} \frac{4\pi^2 m \,\hbar}{r} \, e^{\,i/\hbar \, r(2m E)^{\,1/2}}
$$
\n
$$
\text{for } E > 0 \,. \tag{2.8}
$$

For $E > 0$ the integrations are straight-forward. leading in the limit of arbitrary large volume to

$$
\times A\delta(\mathbf{\tilde{r}}'')G(\mathbf{\tilde{r}}'',\mathbf{\tilde{r}}',E). \qquad \rho(E)=\rho_0(E)=VN(E); \qquad (2.9)
$$

 (2.1) i.e., the density of scattering states is unaffected. For $E < 0$

$$
G_0(\bar{\mathbf{r}},0,E) = -\frac{1}{(2\pi\hbar)^3} \frac{4\pi^2 m \,\hbar}{r} \, e^{-r(2m|E|)^{1/2}/\hbar} \quad (2.10)
$$

and the change on the density of states is given by

$$
\Delta \rho(E) = \frac{\pi}{2} \frac{N(E)}{E} \delta \left(\frac{1}{\alpha} - P \int dE \frac{E}{\rho} \frac{|E| N(E \frac{\epsilon}{\rho})}{E \frac{\epsilon}{\rho} (|E| + E \frac{\epsilon}{\rho})} \right)
$$

$$
= \delta \left\{ E + \left[4\pi \left(\frac{\hbar^2}{2m} \right)^{3/2} \frac{1}{\alpha} \right]^2 \right\}. \tag{2.11}
$$

Therefore, the one-particle density of states can be written in the thermodynamic limit as

$$
\rho(E) = \frac{Vm}{2\pi^2\hbar^3} (2mE)^{1/2} + \delta \left\{ E + \left[4\pi \left(\frac{\hbar^2}{2m} \right)^{3/2} \frac{1}{\alpha} \right]^2 \right\}.
$$
\n(2.12)

At this point we may state that in this work, and to make it physically sound, we shall be looking only for finite negative energies. This implies that the δ potential may be understood as, for instance, the limit of a spherical square well with just one bound energy kept fixed in the entire limit process. It is easy to verify that in the limit of the square well with $V_0 \rightarrow \infty$ and $a \rightarrow 0$, such that $V_0 a^2$ remains finite, only one bound-state energy can remain finite, all others going to $-\infty$. This is the reason why we keep just one finite bound state.

III. THERMODYNAMIC FUNCTIONS

We start from the known equation for the logarithm of the grand partition function Z for an ideal quantum gas which contains the thermodynamic information about the system,⁵

$$
\ln Z\left(\beta, V, \mu\right) = -\epsilon \sum_j \ln\left(1 - \epsilon e^{\beta \left(\mu - E_j\right)}\right),\tag{3.1}
$$

where β^{-1} = kT is the product of the Boltzmann constant k times the absolute temperature T . V is the system volume, μ is the chemical potential, ϵ takes the value of $(+1)$ for particles obeying Bose-Einstein statistics and (-1) for Fermi-Dirac statistics, and, finally, E_t is the *j*th single-particlestate energy. We shall recall here the restriction upon the chemical potential for boson systems. In order to avoid negative average occupation number of the single-particle state *j* we must have $\mu < E$. for all *j*, which is tantamount to $\mu < E$ _{minimum}.

The evaluation of the sum over all single-particle states j can be carried out in a simplified way after the use of Me11in transform representation for the logarithm function, $\frac{6}{3}$ that is,

$$
\ln(1 - \epsilon e^{\beta(\mu - E_j)}) = \frac{1}{2\pi i} \int_{c - i\infty}^{c + i\infty} \pi [\cos(\pi t)]^{\epsilon' t^{-1}} \csc(\pi t)
$$

$$
\times e^{\beta(\mu - E_j)} dt, \qquad (3.2)
$$

which allows us to rewrite the expression for $\ln Z$ as follows:

$$
\ln Z = \frac{-\epsilon}{2\pi i} \int_{c - i\infty}^{c + i\infty} \pi [\cos(\pi t)]^{\epsilon' t^{-1}} \csc(\pi t) e^{\beta t \mu}
$$
\nwhere\n
$$
\times \sum_{j} e^{-\beta t E_{j}} dt,
$$
\n(3.3)\n
$$
E_{b} = -\left[4\pi\right]
$$

where $\epsilon' = \frac{1}{2}(\epsilon + 1)$, $0 < c < 1$, and we have interchanged the order of integration and summation.

The advantage of writing $\ln Z$ in this way is the appearance of the always-desirable separation of the statistics effects from the quantum-mechanical problem. Therefore, the consequences of finite size, geometry, and dimensionality of the container of the gas, as well as the presence of external fields on the bulk properties of the system, are solely incorporated in the single-particle partition function Z , (β) ,

$$
Z_1(\beta) = \sum_j e^{-\beta E_j} = \int_{-\infty}^{\infty} \rho(E) e^{-\beta E} dE, \qquad (3.4)
$$

where $\rho(E)$ is the density-of-states function. The energy range has been taken from $-\infty$ to $+\infty$ to include all possible bound states that might exist. There is no convergence problem at the lower limit due to the conditions imposed on $\rho(E)$. Effects of the statistics obeyed by the particles are taken into account by the term $\epsilon[\cos(\pi t)]^{\epsilon'}$; the remaining terms together with the integration in the complex t plane are responsible for transforming the single-particle function into a (many-particle) thermodynamic expression.

It is also known from the theory of the grand canonical ensemble that other thermodynamic functions of the system can be calculated from $\ln Z$ using the following expressions':

$$
N = (\beta)^{-1} \frac{\partial \ln Z}{\partial \mu} \bigg|_{T, V}, \text{ average particle number}
$$
\n(3.5)

$$
E = \mu N - \frac{\partial \ln Z}{\partial \beta} \bigg|_{\mu, \gamma}, \quad \text{energy} \tag{3.6}
$$

$$
S = \frac{\partial (\beta^{-1} \ln Z)}{\partial T} \bigg|_{\mu, \gamma}, \quad \text{entropy} \tag{3.7}
$$

$$
S = \frac{\partial (\beta^{-1} \ln Z)}{\partial T} \bigg|_{\mu, \nu}, \quad \text{entropy} \tag{3.7}
$$

$$
P = \beta^{-1} \frac{\partial \ln Z}{\partial V} \bigg|_{\mu, T}, \quad \text{pressure.} \tag{3.8}
$$

To proceed further in the detailed analysis of the effects due to the presence of impurities (with attractive δ -function potential) on the macroscopic behavior of a quantum gas, in particular a boson gas, the first step to be taken is the evaluation of $Z_1(\beta)$. By combining Eqs. (2.12) and (3.4) we obtain after a straightforward calculation

$$
Z_1(\beta) = V \left(\frac{m}{2\pi\hbar^2 \beta}\right)^{3/2} + e^{\beta |E_b|}, \tag{3.9}
$$

where

$$
E_b = - \left[\ 4\pi \left(\frac{\hbar^{\,2}}{2m} \right)^{\,3 \,/\, 2} \, \frac{1}{\alpha} \, \right]^{\,2}
$$

Clearly, the first term comes from the excited states and the last one from the bound state.

The problem of an ideal Bose gas with an analogous density of states, which can be obtained from Eq. (2.12), shifting it rigidly to the right along the energy axis until the δ term sits on the origin, is discussed by London. Therefore, the single-particle partition functions satisfy the simple relationship

$$
Z_1(\beta)_{\text{London}} = e^{-\beta |E_b|} Z_1(\beta). \tag{3.10}
$$

Consequently, a11 mathematical calculations presented here are essentially the same as London's calculations; for instance, his equations can be obtained from ours if we set μ = μ_London – $|E_b|$ and call $|E_b| = \Delta$, the width of the gap in the spectrum.

Furthermore, we expect that the properties which are related to energy differences will have the same form in both cases, e.g., the heat capacities. However, there are some basic differences which are worthy of mention at this stage. First,

the existence of an energy gap in the spectral density functions is due to different mechanisms; in one case, the presence of interaction with the external field of the impurity is responsible —which, by the way, appeared as an exact result as shown in Sec. II. In the other case the gap in the energy spectrum is introduced somewhat phenomenologically to take care of interparticle interaction. A second major difference is related to the wave functions of the lowest energy states. In the present problem the wave function' of the bound state

$$
\psi(\vec{r}) = \left(\frac{\hbar^2}{m\alpha}\right)^{1/2} \frac{\exp(-2\pi\hbar^2|\vec{r}|/m\alpha)}{|\vec{r}|}
$$

is centered at the impurity and well localized in space, by contrast to the zero-momentum wave function, which spreads over the entire available volume of the system. These distinct physical situations will manifest themselves on a large scale when the conditions for the macroscopic occupation of the lower-energy states occur, making the thermodynamical behavior of these systems sufficiently different to motivate the discussion presented here.

IV. BOSE GAS

We will now particularize Eq. (3.3) for a boson system ($\epsilon = \epsilon' = 1$):

$$
\ln Z = \frac{1}{2} i \int_{c-i\infty}^{c+i\infty} \cot(\pi t) t^{-1} e^{\beta t \mu} \times (V\lambda^{-3} t^{-3/2} + e^{\beta t |E_b|}) dt, \qquad (4.1)
$$

where we have used Eq. (3.9) and $\lambda = (2\pi\hbar^2\beta/m)^{1/2}$ is the thermal de Broglie wavelength; from now on as a notational convenience we will drop the bars of the modulus $|E_h|$. The evaluation of $\ln Z$ is finally complete if we close the straight-line contour with the arc of a circle, such that the integrand satisfies all the conditions for the application of the residue theorem. The requirement for the vanishing of the integral taken along the arc in the limit of infinite radius is assured by the restriction on the chemical potential of the boson system. Hence

$$
\ln Z = V \lambda^{-3} \sum_{n=1}^{\infty} \frac{e^{n \beta \mu}}{n^{5/2}} + \sum_{n=1}^{\infty} \frac{e^{n \beta (\mu + E_b)}}{n}
$$
 (4.2)

$$
= V\lambda^{-3}F_{5/2}(-\beta\mu) + F_1[-\beta(\mu + E_b)], \qquad (4.2')
$$

where $F_{\sigma}(\xi)$ are the so-called Bose-Einstein functions.²

We also observe that $\ln Z$ for the free Bose gas (absence of impurity) is recovered from Eq. (4.2') if we set $E_b = 0$ and let μ run again from $-\infty$ up to zero. This is the general procedure to be followed in all forthcoming equations in order to obtain the corresponding free-case limits.

Using Eq. (3.6) in combination with Eq. $(4.2')$ we obtain for the average particle number

$$
N = V\lambda^{-3}F_{3/2}(-\beta\mu) + (e^{-\beta(\mu+E_b)} - 1)^{-1} = N_{\text{out}} + N_b,
$$
\n(4.3)

where N_b is the average number of bosons captured by the impurity and N_{out} is the average number of the remaining particles in the gas. As usual, this equation determines the chemical potential as function of the temperature, particle density, and strength of the binding energy (Fig. 1). In deriving Eq. (4.3) we have made use of the following property of the Bose-Einstein function $F_a(\xi)$:

$$
\frac{d}{d\alpha} F_{\sigma}(\xi) = -F_{\sigma-1}(\xi) . \qquad (4.4)
$$

The monotonically decreasing character of the $F_{\sigma}(\xi)$'s (which are also bounded for $\sigma > 1$) together with the upper-limit value of the chemical potential determine the maximum number of particles which can be accomodated outside the bound state, i.e.,

$$
N_{\rm out} = N = V (m k T_c / 2 \pi \hbar^2)^{3/2} F_{3/2} (E_b / k T_c). \qquad (4.5)
$$

The above equation defines a critical temperature $T_c(E_b)$. We see immediately that $T_c(E_b)$ is always larger than $T_c(0)$, the free-Bose-gas critical temperature, as a direct consequence of the steadydecreasing behavior of $F_{3/2}$. Moreover, the deriviative of T_c with respect to the binding energy diverges at $E_b = 0$, indicating that the "turning on" of the bound state introduces abrupt changes in the properties of the system (see Fig. 2).

The expression for the average number of par-

FIG. 1. Chemical potential for the Bose gas with the 5-function impurity vs temperature for different values of E_b . The curve branches for $T > T_c$ are obtained from Eq. (4.7). $T_c(0) = (2\pi\hbar^2/mk)[N/VF_{3/2}(0)]^{2/3}$ is the critical temperature for the ideal Bose gas.

FIG. 2. Reduced critical temperature $T_c/T_c(0)$ as a function of the reduced binding energy $E_h/kT_c(0)$ obtained from Eg. (4.5).

tieles can be rewritten in a more convenient form after using the definition for T_c :

$$
N = N \left(\frac{T}{T_c}\right)^{3/2} \frac{F_{3/2}(-\beta \mu)}{F_{3/2}(E_b/kT_c)} + (e^{-\beta(\mu + E_b)} - 1)^{-1}.
$$
\n(4.6)

Now for $T>T_c$, we can neglect the contribution N_b to the total average number of particles and the chemical potential is determined by the relation

$$
F_{3/2}(-\beta \mu) = (T_c/T)^{3/2} F_{3/2} (E_b/kT_c), \quad T > T_c.
$$
\n(4.7)

If, on the other hand, $T < T_c$, the first term in Eq. (4.6) will be only a fraction of N and consequently the last one has to make up for the rest of the particles, implying that $|\mu| \simeq E_{b}$ (see Fig. 1). Therefore

$$
N_b = N \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \frac{F_{3/2}(\beta E_b)}{F_{3/2}(E_b/kT_c)} \right], \quad T < T_c \,.
$$
\n(4.8)

comparing the above equation for the number of condensed bosons with that of a free boson gas, both systems with the same particle density and temperature T lower than $T_c(0)$, we see once more an enhancement effect created by the existence of the bound state (see Fig. 8). By contrast to both free gas and London's system there will now be a true condensation in *position space*. The impurity behaves as a nucleation center and some bosons will "condense," forming a cloud of localized particles around it with increasing density as the temperature goes to zero.

FIG. 3. Average occupation number of the bound state as a function of the temperature for different values of the binding energy E_b .

It has been shown⁷⁻⁹ that the existence of the Bose condensation in infinite systems of one and two dimensions is related to the occurrence of unbounded particle density somewhere in the system. Equation (4.8) shows that this behavior is also present here. For $T < T_c$ the particle density around the impurity becomes infinite in the thermodynamic limit. This fact is responsible for the change in the nature of the condensate.

The other particles which remain in the gas are essentially unaffected by the presence of the impurity center and by which degeneracy state can be inferred from the relation between the average interparticle distance l and the small thermal wavelength:

$$
\lambda / l = (N_{\text{out}} / V)^{1/3} \lambda = F_{3/2}^{1/3} (E_b / kT), \quad T < T_c. \tag{4.9}
$$

The average particle density $\rho \sim N_b / \alpha^3$ at the condensation region can also be changed by a combined variation of temperature and binding energy as, for instance, along the interrupted dotted line \overline{OP} in Fig. 4. At $T = 0$ all particles are trapped at the impurity site with a minimum spreading. As the temperature increases some particles will gain sufficient energy to evaporate from the cloud, which simultaneously is swelling in size. This situation will continue until all particles have departed and no vestige of the particle lump is left; i.e., we have reached point P . In more poetic language, we can describe this situation as a blooming flower which loses its petals as it grows.

The 6 potential acts as an ideal source/sink of particles, which allows for the nondegenerate behavior of the remainder gas. If one considers a saturation effect of the potential due to a repulsion interaction between the particles, the density

around the impurity will now be bounded. In this situation the number of impurities in the system will play a more decisive role in determining the degeneracy state of the gas. Two ranges of strength of $E_{\,b}$ naturally arise; for strong bindin energies the particles in the gas always form a classical system, even at extremely low temperatures. On the other hand, in the weakly-boundstate limit the gas will be classical only at high and low temperatures, having a degenerate behavior at intermediate temperatures.

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As an intermediary step in the calculation of the heat capacity at constant volume we evaluate the

system energy E . We obtain after a direct calculation

$$
E = \frac{3}{2} (Nk) T \left(\frac{T}{T_c}\right)^{3/2} \frac{F_{5/2}(-\beta \mu)}{F_{3/2}(E_b/kT_c)} - E_b N_b,
$$
\n(4.10)

which gives a finite ground-state energy for the system instead of zero, as for the free Bose gas. Of course it is the possibility of a macroscopic occupation of the bound state which will make it relevant to the thermodynamics of the system,

$$
C_{V} = \frac{\partial E}{\partial T}\Big|_{V} = \frac{15}{4} N k \left(\frac{T}{T_c}\right)^{3/2} \frac{F_{5/2}(-\beta\mu)}{F_{3/2}(E_b/kT_c)} - \frac{3}{2} T(Nk) \left(\frac{T}{T_c}\right)^{3/2} \frac{F_{3/2}(-\beta\mu)}{F_{3/2}(E_b/kT_c)} \frac{\partial (-\beta\mu)}{\partial T}\Big|_{V} - E_b \frac{\partial}{\partial T} N_b, \tag{4.11}
$$

where we have made use again of Eq. (4.4). For all $T < T_c$ the chemical potential has its maximum value $-\mu = E_h$; hence

$$
\frac{\partial \left(-\beta \mu\right)}{\partial \mu}\bigg|_{\gamma} = -E_b / kT^2 \tag{4.12}
$$

and a simple expression for $C_{\mathbf{v}}$ is obtained:

FIG. 4. Schematic plotting for degeneracy state of the gas as a function of T and E_b . The full curve $E_b(T)$ starting at $T_c(0)$ divides the quadrant of the E_bT plane into two regions. In the unprimed region there is no condensation phenomenon and in the primed region the condensation is present. The broken curves are obtained choosing arbitrarily the ratio λ/l equal to 10^{-1} and 1 in Eq. (4.9) for $T < T_c$ and in Eq. (4.5) for $T > T_c$. A, classical region for the gas; B, region of mild degeneracy; C, degenerate region for the gas. A', classical region for the noncondensed particles in the gas; B', region of mild degeneracy for the particles in the depleted gas; C', degenerate region for the depleted gas. The particle density in the unprimed region is higher than in the corresponding primed region.

$$
C_V = \frac{15}{4} (Nk) \left(\frac{T}{T_c}\right)^{3/2} \frac{F_{5/2} (E_b/kT)}{F_{3/2} (E_b/kT_c)} + \frac{(Nk) (E_b/kT)}{F_{3/2} (E_b/kT_c)}
$$

$$
\times \left(\frac{T}{T_c}\right)^{3/2} \left[3F_{3/2} \left(\frac{E_b}{kT}\right) + \left(\frac{E_b}{kT}\right) F_{1/2} \left(\frac{E_b}{kT}\right)\right],
$$

$$
T < T_c \tag{4.13}
$$

By taking the derivative of Eq. (4.7) with respect to $-\beta \mu$ we obtain

$$
\frac{\partial (\rho - \beta \mu)}{\partial T} \bigg|_{V} = (3/2T) \frac{F_{3/2}(-\beta \mu)}{F_{1/2}(-\beta \mu)},
$$
\n(4.14)

other branch of the heat capacity,

which is then put back in Eq. (4.11) to give the
other branch of the heat capacity,

$$
C_V = \frac{3}{2} (Nk) \left(\frac{5}{2} \frac{F_{5/2}(-\beta \mu)}{F_{3/2}(-\beta \mu)} - \frac{3}{2} \frac{F_{3/2}(-\beta \mu)}{F_{1/2}(-\beta \mu)} \right), \quad T > T_c
$$
(4.15)

where we have neglected the changing of average occupation number of the bound state with the temperature. μ can be eliminated from $C_v(T>T_c)$ with the help of Eq. (4.7). The Dulong-Petit value for C_v is obtained from Eq. (4.15) after approximating $F_{\alpha}(\xi)$ for larger values of ξ ,

$$
F_{\sigma}(\xi) \cong e^{-\xi} \quad \text{for } \xi \gg 1 \; . \tag{4.16}
$$

The low-temperature behavior of C_{v} , on the other hand, will differ from the $T^{3/2}$ law for the free Bose gas, as can be seen from Eqs. (4.13) and (4.16),

$$
C_V \simeq \frac{Nke^{-E_b/kT}}{F_{3/2}(E_b/kT_c)} \left(\frac{E_b}{kT}\right)^{1/2} \left(\frac{E_b}{kT_c}\right)^{3/2}.
$$
 (4.17)

By all means the most interesting feature of $C_{\mathbf{v}}$ is the finite discontinuity at T_c (see Figs. 5 and 6). Let us examine now the entropy. Using Eq. (3.7) after a little algebra we obtain

FIG. 5. Specific heat at constant volume as a function of temperature for an arbitrary value of the binding energy E_b .

$$
S = \frac{5}{2} k \lambda^{-3} V F_{5/2}(-\beta \mu) - k (\beta \mu) \lambda^{-3} V F_{3/2}(-\beta \mu)
$$

- $k \beta (\mu + E_b) N_b + k \ln(1 + N_b)$. (4.18)

We notice the vanishing contribution of the last two terms in the thermodynamic limit. Again we have to study the two branches of S. For $T < T_c$ we substitute $\mu = -E_b$ and use Eq. (4.8), which gives us the right value for N_b in

$$
S = \frac{5}{2} k \lambda^{-3} V F_{5/2} (\beta E_b) + k (\beta E_b) \lambda^{-3} F_{3/2} (\beta E_b)
$$

+ k ln (1 + N_b). (4.19)

Now for $T > T_c$

$$
S = \frac{5}{2} k \lambda^{-3} V F_{5/2}(-\beta \mu) - k (\beta \mu) \lambda^{-3} F_{3/2}(-\beta \mu) .
$$
\n(4.20)

FIG. 6. Binding energy dependence of the specificheat gap at $T = T_c$ given by $(\Delta C_v / Nk)_{T=T_c} = (\frac{9}{4})[F_{3/2}(E_b / k)]$ kT_c / F_1 _{/2} (E_b/kT_c)] + $(E_b/kT_c)^2$ [F_1 _{/2} (E_b/kT_c) / F_3 _{/2} (E_b/kT_c) kT_c] +3(E_b/kT_c).

When writing the above expression we have dropped the negligible contribution from the last two terms of the general expression given by Eq. (4.18).

Finally we derive the expression for the pressure using Eq. (3.8),

$$
P = \beta^{-1} \left. \frac{\partial \ln Z}{\partial V} \right|_{\mu, T} = \beta^{-1} \lambda^{-3} F_{5/2}(-\beta \mu) \,. \tag{4.21}
$$

This expression is identical to that of the free Bose gas, except for the new upper limit of the chemical potential. The two branches for the pressure are

$$
P = \beta^{-1} \lambda^{-3} F_{5/2} (E_b / kT), \quad T < T_c \tag{4.22}
$$

$$
P = \beta^{-1} \lambda^{-3} F_{5/2}(-\mu / kT), \quad T > T_c.
$$
 (4.23)

Therefore, the presence of the bound state has not destroyed the volume-independent relationship of the pressure below the critical temperature. It has, however, made it lower compared to the free Bose gas.

As in the case for the heat capacity and entropy, the μ dependence of the pressure for $T>T_c$ can be eliminated by means of Eq. (4.7). One can do it in the way suggested by London, i.e., developing the F_o 's in terms of $F_{3/2}$ or numerically, as we have done when it applied in all figures presented in this paper.

V. DISCUSSION

The effect of a δ attractive potential on the Bose gas can be calculated exactly, this being the main reason for the model interaction proposed. The most interesting results seem to be (a) the discontinuity of the specific heat at the transition temperature, which could be expected if one just recalls London's work where a similar result is obtained in a different context; (b) the classical behavior of the gas in a region of temperature, for which the pure boson system would be degenerate. This behavior is probably existent for any system of weakly interacting bosons in the presence of impurities which trap particles from the system in some way. In spite of the fact that real bosons are expected to exhibit a repulsive interaction of sufficiently close distances, a cluster formation around the impurity (such as positive ion clusters in liquid He) may lead to a similar phenomenon, namely, the transition to a classical gas with a smaller density than the original Bose system plus a cluster of bosons around the impurities. (c) The attractive δ function does not inhibit condensation, but induces a spatial condensation around it. This result can be understood from the fact that the δ

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potential possesses only one bound state in the limit discussed previously in Sec. II, and thus the density of states corresponding to negative energies is integrable, being a function δ in energy.

It has been shown' that short-range repulsive impurities do not prevent condensation. In our case an attractive δ potential, i.e., an extremely shor attractive potential, does not prevent it either.

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