

INTERACTION OF IMPURITIES WITH ONE ANOTHER AND WITH THE SURFACES IN AN IDEAL BOSE GAS

V. M. NABUTOVSKIĬ and V. R. BELOSLUDOV

Institute of Inorganic Chemistry, Siberian Division, USSR Academy of Sciences

Submitted October 2, 1970

Zh. Eksp. Teor. Fiz. 60, 1131-1135 (March, 1971)

The interaction between two solid immobile spheres or a plane and a sphere in an ideal Bose gas is considered. It is shown that long-range interaction arises between the spheres or between the plane and the sphere below or near the condensation point.

**I**N a system undergoing a phase transition, long-wave fluctuations begin to play an important role near the transition point, and long-range order appears below the transition point. Naturally, this should lead to a unique interaction between the impurity particles via this system even in the case when they do not interact directly. Such an interaction can lead experimentally to coagulation of impurity particles below the transition point or to their emergence at the surface.

1. INTERACTION OF SPHERES IN AN IDEAL BOSE GAS

For an asymptotically exact solution of the problem we have considered a model in which two solid (impenetrable to bosons) immobile spheres of radius  $a$  are placed in an ideal Bose gas. The distance between the spheres is  $l$  (the centers lie at the points  $y = \pm l/2$  on the  $y$  axis). We consider only the case  $l \gg a$ , and since an important contribution to the interaction at such distances can be made only by bosons with momentum  $k \lesssim l^{-1}$ , the following condition is always satisfied:

$$ka \ll 1. \tag{1}$$

The boundary conditions on the surfaces of the spheres for the wave function of the boson can be replaced by a pseudopotential, and condition (1) enables us to confine ourselves only to S-wave scattering<sup>[1]</sup>

$$V_s(\mathbf{r}) = 4\pi a \hbar^2 m^{-1} [\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)], \tag{2}$$

where  $\mathbf{r}_1 = \mathbf{r} + \frac{1}{2}\mathbf{l}$ ,  $\mathbf{r}_2 = \mathbf{r} - \frac{1}{2}\mathbf{l}$ ,  $m$  is the boson mass, and  $\hbar$  is Planck's constant.

The wave functions of the particle with wave vectors  $\mathbf{k}$  are chosen in the form

$$\psi_{\pm} = \frac{1}{2\sqrt{\pi R}} \left(1 \pm \frac{\sin kl}{kl}\right)^{-1/2} \left[ \frac{\sin kr_1}{r_1} \pm \frac{\sin kr_2}{r_2} \right] \tag{3}$$

The plus and minus signs correspond to symmetrical and antisymmetrical combinations of the S waves, and  $k$ ,  $l$ ,  $r_1$ , and  $r_2$  are the moduli of the corresponding vectors. The functions are normalized to one particle in a sphere of radius  $R$ , are orthogonal, and diagonalize the perturbation  $V_S(\mathbf{r})$ .

Let us calculate the corrections of first and second order  $E_{\pm}^{(1)}$  and  $E_{\pm}^{(2)}$  to the energy of the bosons with a perturbing potential  $V_S(\mathbf{r})$ :

$$E_{\pm}^{(1)} = \frac{2a\hbar^2 k^2}{Rm} \left(1 \mp \frac{\sin kl}{kl}\right), \tag{4}$$

$$E_{\pm}^{(2)} = \frac{4a^2\hbar^2 k^2}{Rm} \left(1 \mp \frac{\sin kl}{kl}\right) \left( \sum_{k' \neq k} \frac{k'^2 \Delta k}{k^2 - k'^2} - \frac{\pi \cos kl}{2l} \right). \tag{5}$$

The divergence at large momenta in (5) is connected with the fact that the pseudopotential (2) cannot be applied at large momenta; this divergence should be eliminated by cutting off the integrals at  $k \sim a^{-1}$ .<sup>[2]</sup>

Let us find the increment introduced in the free energy of the system by the presence of impurity particles. Since the impurities only change the spectrum of the Bose particles, it follows that

$$\begin{aligned} \Omega &= T \sum_n \ln \left[ 1 - \exp \left( -\frac{\mu - E_n^{(0)} - E_{\pm}^{(1)} - E_{\pm}^{(2)}}{T} \right) \right] \\ &+ T \sum_{n'} \ln \left[ 1 - \exp \left( -\frac{\mu - E_{n'}^{(0)} - E_{\pm}^{(1)} - E_{\pm}^{(2)}}{T} \right) \right] \\ &\approx 2T \sum_n \ln \left[ 1 - \exp \left( -\frac{\mu - E_n^{(0)}}{T} \right) \right] + \sum_{n'} \frac{E_{\pm}^{(1)} + E_{\pm}^{(2)} + E_{n'}^{(1)} + E_{n'}^{(2)}}{\exp[(\mu - E_n^{(0)})/T] - 1}, \end{aligned} \tag{6}$$

where  $n$  is the set of quantum numbers characterizing the Bose particle;  $n'$  is a set of quantum numbers on which the increments  $E_{\pm}^{(1)}$  and  $E_{\pm}^{(2)}$  depend;  $E_n^{(0)}$  is the energy of the Bose particle in the absence of impurities,  $\mu$  is the chemical potential,  $T$  is the temperature, and  $k$  is Boltzmann's constant and equals unity.

We expanded the potential  $\Omega$  in (6) in powers of  $E_{\pm}^{(1)}$  and  $E_{\pm}^{(2)}$ . If we substitute expressions (4) and (5) in (6), then we obtain two increments to  $\Omega$ , one of which,  $\Delta\Omega_1$ , does not depend on  $l$  and is connected with scattering by isolated spheres, and the other,  $\Delta\Omega_2$ , depends on  $l$  and is connected with the interaction of the spheres. We are interested in  $\Delta\Omega_2$ . Recognizing that the additions to all the potentials in terms of their variables are the same:  $(\Delta F)_T, V, N = (\Delta\Omega)_T, V, \mu$ <sup>[2]</sup>, we obtain

an expression for the increment to the free energy of the system, connected with the interaction of the spheres:

$$\Delta F_2 = -\frac{a^2}{\pi l^2 m} \int_0^{\infty} \frac{p \sin(2pl/\hbar) dp}{\exp[(p^2/2m - \mu(T))/T] - 1} \tag{7}$$

where

$$\mu(T) = -1.2T_0 \tau^2 \tag{8}$$

<sup>2)</sup>It can be shown, by solving the exact problem of scattering by a sphere, that such a cutoff does not change the character of the singularities.

<sup>1)</sup>The corrections due to the  $l'$  waves with  $l' \neq 0$  are smaller by a factor  $(a/l)2^{l'-1}$  than  $E_{\pm}^{(2)}$ .

is the chemical potential of an ideal Bose gas with density  $n$  near the condensation point  $T_0$ , and  $\tau = (T - T_0)/T_0^{[2]}$ . We see that (7) does not contain divergent parts, i.e., there is no need to use cutoff for its calculation.

The integral in (7) is investigated in the Appendix. Above the condensation point ( $\tau > 0$ )

$$\Delta F_2 = \begin{cases} -\frac{2a^2 T}{\sqrt{\pi} l^2} \exp\left(-\frac{2l}{r_c}\right) & \text{for } l \gg \lambda_T \\ -\frac{4.8\sqrt{2}a^2 T}{\pi \lambda_T l} & \text{for } l \ll \lambda_T \end{cases}, \quad (9)$$

where  $r_c = h/\sqrt{2m\mu(T)}$  is the correlation radius and  $\lambda_T = h/\sqrt{2mT}$  is the thermal length of the wave.

We see that on approaching the condensation point there arises an attraction force between the spheres  $\sim l^{-3}$  (for  $l \gg \lambda_T$ ) and  $\sim l^{-2}$  (for  $l \ll \lambda_T$ ). Below the condensation point ( $\mu = 0$ ), by separating from the integral (7) the term connected with the condensate, we obtain for the free energy

$$\Delta F_2 = \begin{cases} -\frac{4}{3} \frac{\pi^3 \hbar^2 a^2 n}{ml} \left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] - \frac{2a^2 T}{\sqrt{\pi} l^2} & \text{for } l \gg \lambda_T \\ -\frac{4}{3} \frac{\pi^3 \hbar^2 a^2 n}{ml} \left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] - \frac{4.8\sqrt{2}a^2 T}{\pi \lambda_T l} & \text{for } l \ll \lambda_T \end{cases} \quad (10)$$

The first term in the expressions of (10) is connected with the presence of the condensate and leads to an attraction force  $\sim l^{-2}$ . The ratio of this term to the second is  $\sim \lambda_T^2 n l \tau$  (when  $l \gg \lambda_T$ ) and  $\sim \lambda_T^3 n \tau$  (when  $l \ll \lambda_T$ ), so that the first term plays the principal role only at very large distances  $l \sim 1/\lambda_T^2 n \tau$  (at  $l \gg \lambda_T$ ). If  $T \rightarrow 0$ , the principal role is played by the condensate term.

## 2. INTERACTION OF A SPHERE WITH THE SURFACE

As the model of the surface we consider an infinite plane impenetrable to bosons. The problem reduces to the same as before; the only difference is that we must choose in (3) only the antisymmetrical function  $\psi$ . In this case the first-order correction to  $\Omega$  differs from zero. Using expressions (4) and (6), we obtain for the increment to the free interaction energy of the surface with the sphere

$$\Delta F = -\frac{2a}{\pi m l} \int_0^\infty \frac{p \sin(2pl/\hbar) dp}{\exp[(p^2/2m - \mu)/T] - 1}, \quad (11)$$

where  $l_1$  is the distance between the sphere and the plane. Expression (11) is investigated in analogy with expression (7). For  $T \geq T_0$  we obtain

$$\Delta F = \begin{cases} -\frac{4aT}{\sqrt{\pi} l_1} \exp\left(-\frac{2l_1}{r_c}\right) & \text{for } l_1 \gg \lambda_T \\ -\frac{9.6\sqrt{\pi} a T}{\sqrt{2} \lambda_T} & \text{for } l_1 \ll \lambda_T \end{cases} \quad (12)$$

and for  $T \leq T_0$

$$\Delta F = \begin{cases} -\frac{8}{3} \frac{\pi^3 \hbar^2 a n}{m} \left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] - \frac{4aT}{\sqrt{\pi} l_1} & \text{for } l_1 \gg \lambda_T \\ -\frac{8}{3} \frac{\pi^3 \hbar^2 a n}{m} \left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] - \frac{9.6\sqrt{2} a T}{\pi \lambda_T} & \text{for } l_1 \ll \lambda_T \end{cases} \quad (13)$$

We see that on approaching the transition point the impurities will be concentrated from a layer  $\sim r_c$  into a layer  $\sim \lambda_T$ .

Although an ideal Bose gas does not correspond to any real system, one can hope that the main features of the considered phenomenon are retained also for real systems such as liquid helium, the critical point of a liquid, and the critical point of lamination of solutions.

The idea of the general character of the interaction near critical points was expressed by A. Z. Patashinskiĭ, to whom the authors express their gratitude.

## APPENDIX

To investigate the integral (7) we introduce the convenient variables

$$x = \frac{p}{(2mT)^{1/2}}, \quad \mu' = -\frac{\mu(T)}{T}, \quad \rho = \frac{2^{3/2} l}{\lambda_T}, \quad c = \frac{\pi l^2}{a^2 T}.$$

Then

$$\begin{aligned} c\Delta F_2 &= 2 \int_0^\infty \frac{x dx \sin x \rho}{\exp(x + \mu') - 1} = \text{Im} \sum_{n=0}^\infty \int_0^\infty k dk \exp\left[+ik\rho - (k^2 + \mu')(n+1)\right] \\ &= \frac{\sqrt{\pi}}{2} \rho \sum_{n=0}^\infty \exp\left[-\mu'(n+1) - \frac{\rho^2}{4(n+1)}\right] (n+1)^{-1/2}. \end{aligned} \quad (A.1)$$

For  $\rho \gg 1$ , using the Poisson summation formula, (A.1) can be represented in the form

$$c\Delta F_2 = I_0 + \sum_{n=1}^\infty I_n, \quad (A.2)$$

where

$$\begin{aligned} I_0 &= \frac{\sqrt{\pi} \rho}{2} \int_0^\infty \exp\left[-\mu'(x+1) - \frac{\rho^2}{4(x+1)}\right] (x+1)^{-1/2} dx, \\ I_n &= \frac{\sqrt{\pi} \rho}{2} \int_0^\infty \exp\left[2\pi n x i - \mu'(x+1) - \frac{\rho^2}{4(x+1)}\right] (x+1)^{-1/2} dx. \end{aligned}$$

It is easy to show that  $I_n/I_0 \sim e^{-\rho}$ . Retaining the first term in (2) and making the substitution  $(x+1) = y^{-1}$ , we obtain

$$I_0 = \rho \sqrt{\pi} \int_0^1 \exp\left(-\frac{\mu'}{y^2} - \frac{\rho^2 y^2}{4}\right) dy. \quad (A.3)$$

The main contribution to (3) is made by  $\rho' \ll 1$  and  $\mu' \ll 1$ , and therefore the integral can be extended to infinity, and can then be found in the tables. As a result

$$c\Delta F_2 \approx 2\sqrt{\pi} \exp(-2\rho\sqrt{\mu'}).$$

When  $\rho \ll 1$  and  $\mu' \ll 1$ , the main contribution to (1) is made by small  $x$ :

$$c\Delta F_2 = 2 \int_0^\infty \frac{x dx \sin x \rho}{e^{x+\mu'} - 1} \approx 2\rho \int_0^\infty \frac{x^2 dx}{e^x - 1} = 4.8\rho. \quad (A.4)$$

<sup>1</sup> Kerson Huang, *Statistical Mechanics*, Wiley, 1963.

<sup>2</sup> L. D. Landau and E. M. Lifshitz, *Statisticheskaya fizika (Statistical Physics)*, Nauka, 1964 [Addison-Wesley].