THE

PHYSICAL REVIEW

Specific Heat of the Many-Boson Gas*

ROBERT BROUT

Faculté des Sciences, Université Libre de Bruxelles, Bruxelles, Belgique

(Received 29 March 1963)

It is shown that the simple Hartree-Fock approximation to the free energy of a many-boson gas changes the Bose-Einstein condensation from a third- to a second-order transition. A term is added to the energy of the interaction system which is proportional to the specific heat of the ideal gas system. Quantitative estimates of the effect for liquid helium give an order of magnitude about 5 times too high, which shows the importance of the effect and the necessity for screening it out.

IN this article we point out that a very simple mechanism exists which changes the order of the Bose-Einstein condensation from a third- to a second-order transition. Quantitative estimates based on the potential between helium atoms leads to a specific heat in the critical region which numerically is too high as compared to experiment. The theory is too crude to reproduce the observed logarithmic singularity.[1]

The mechanism in question is simply the manner in which the Hartree-Fock theory functions in statistical mechanics. The free energy of a many-boson system in Hartree-Fock theory is

$$F = F_0 + (1/2) \sum_{kk'} [v(0) + v(k - k')] n(k) n(k'); \quad (1)$$

F_0 is the unperturbed free energy

$$= kT \sum_k \ln[1 - \exp(-\beta(\epsilon_k - \mu))];$$

$\epsilon(k)$ is the kinetic energy $= \hbar^2 k^2 / 2m$, and $v(k)$ is the Fourier transform of the interparticle potential given by

$$v(k) = (1/\Omega) \int d^3r \, v(r) \exp[i k \cdot r]. \quad (2)$$

Here Ω is the volume of the container;

$$n(k) = [\exp(\beta(\epsilon_k - \mu)) - 1]^{-1},$$

[1] M. J. Buckingham and W. M. Fairbank, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III.

$\beta = (1/kT)$, and $\mu =$ the unperturbed chemical potential. In a full Hartree-Fock theory one should replace $\epsilon(k)$ by the Hartree-Fock single-particle energy. This will not be done in this article. It introduces no new physical effects. Also, offhand it seems unjustified to include some higher order terms in v and not others, in particular, when there does not arise any particular problem of consistency.

Equation (1) gives for the energy

$$E = \partial \beta F / \partial \beta = \sum n(k) \epsilon(k)$$
$$+ \tfrac{1}{2} \sum_{kk'} [v(0) + v(k - k')] n(k) n(k')$$
$$+ \beta \sum_{kk'} [v(0) + v(k - k')] n(k') (\partial n(k) / \partial \beta). \quad (3)$$

It is the last term in Eq. (3) which is responsible for the change in the order of the transition. The specific heat of the first two terms gives rise to a third-order transition. Therefore, we consider below the last term which we denote by E'. Noting that $\sum_k (\partial n(k) / \partial \beta) = \partial N / \partial \beta = 0$, we have

$$E' = \beta \sum v(k - k') n(k') (\partial n(k) / \partial \beta), \quad (4)$$

Expanding $v(k)$ in a power series according to $v(k) = v(0) + \alpha k^2 + \cdots$ gives

$$E' = \beta \alpha \sum (k - k')^2 n(k') \partial n(k) / \partial \beta$$
$$= \beta \alpha \sum_{k'} n(k') \sum_k k^2 (\partial n(k) / \partial \beta). \quad (5)$$

The terms of order k^4 and higher in $v(k)$ do not contribute in an important way to the effect studied.

899

We now write $k^2 = (2m/\hbar^2)\epsilon(k)$ and observe that Eq. (5) can be written as

$$E' \cong (2m\alpha/\hbar^2)\beta N (dE_0/d\beta) = -T(2m\alpha/\hbar^2)N(dE_0/dT), \quad (6)$$

where $E_0 = \sum n_k \epsilon_k$. In this way we see that the Hartree-Fock energy contains a term proportional to the specific heat of the ideal gas which is continuous at the transition point. The specific heat due to E' (i.e., dE'/dT) is proportional to (dC_V^0/dT) which is discontinuous, thereby changing the order of the transition.

As is well known, the theory for $T < T_c$ (where T_c is the transition temperature) is complicated by the macroscopic value of n_0. We, therefore, take the above considerations to have meaning only for $T > T_c$, and therefore, restrict our quantitative estimate to this region.

For the potential we will take a hard-sphere repulsion plus the attractive part of the potential of de Boer and Michels.[2] For the hard-core part, since we are in Born approximation, we may use a pseudopotential method with $v_{repulsive}(\mathbf{k}) = a$. Therefore, α is due to the attraction alone and, hence, positive (i.e., $v_{attractive}(\mathbf{k}) = v_{attractive}(0) + |\alpha| k^2$). We then have

$$\alpha = \frac{4\pi}{6\Omega} \int_{r_0}^{\infty} r^4 dr \left[\frac{c}{r^{12}} - \frac{d}{r^6} \right], \quad (7)$$

where r_0 is given by $v(r_0) = 0$ and $c = 447 \times 10^{-12}$ ergÅ^{12} $d = 1.54 \times 10^{-12}$ ergÅ^6. Using the density of liquid helium of 2.2×10^{22} per cm^3 gives

$$E' = -29T(dE_0/dT). \quad (8)$$

This term gives rise to two terms in the specific heat. However, the term proportional to (dE_0/dT) is exactly canceled by the second term on the right-hand side of Eq. (3). The result is then

$$C_V = C_V^0 - 29T(dC_V^0/dT). \quad (9)$$

At $T = T_c + 0$, we have $C_V^0 = 2k/\text{atm}$,

$$dC_V^0/dT = -0.78(k/T)/\text{atm},$$

which gives

$$C_V(T = T_c + 0) = (2 + 22)k/\text{atm}, \quad (10)$$

or an enhancement by a factor of 12 over the ideal gas value. The scale of the observed values is of the order of twice ideal. It is seen that the simple Hartree-Fock modification must be an important contribution to the observed departure from ideal gas behavior, and in fact, in subsequent theory must be somewhat diminished in importance.

Work is now being done on the complete statistical mechanical theory of the problem. Indications are that simple subsets of graphs (rings and ladders) do not change the above analysis qualitatively, but may be expected to reduce the above estimate because of screening. Methods are being developed which will handle the n_0 problem for $T < T_c$ and it is hoped that this work will be completed in the near future.

I am grateful to J. de Coen for having made the calculations. It has been pointed out to me by Dr. Pierre Resibois that a similar circumstance arises in the theory of transport coefficients.[3]

[2] J. de Boer and A. Michels, Physica 5, 945 (1938).

[3] P. Resibois and J. P. Puttemans, Physica 26, 775 (1960).