

STATISTICAL MECHANICS IN QUANTUM THEORY: BOSE CONDENSATION

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.29.

We've seen the distribution of particles for the most probable state in the cases of distinguishable particles and fermions so to complete the set we need to look at bosons. Following the same technique as in the other two cases, we start with the total number of states for bosons:

$$S_b(\{n_j\}) = \prod_{j=1}^m \binom{n_j + d_j - 1}{n_j} \quad (1)$$

Taking the log of this and using Lagrange multipliers to add in the constraints, we get the function

$$G = \ln S_b + \alpha \left(N - \sum_{j=1}^{\infty} n_j \right) + \beta \left(E - \sum_{j=1}^{\infty} n_j E_j \right) \quad (2)$$

$$= \sum_{j=1}^{\infty} [\ln(n_j + d_j - 1)! - \ln n_j! - \ln(d_j - 1)! - \alpha n_j - \beta n_j E_j] + \alpha N + \beta E \quad (3)$$

Using Stirling's approximation again we get

$$G \approx \sum_{j=1}^{\infty} [(n_j + d_j - 1) \ln(n_j + d_j - 1) - (n_j + d_j - 1) - n_j \ln n_j + n_j - \ln(d_j - 1)! - \alpha n_j - \beta n_j E_j] + \quad (4)$$

We can now take the derivative to get n_j :

$$\frac{\partial G}{\partial n_j} = \ln(n_j + d_j - 1) - \ln n_j - \alpha - \beta E_j = 0 \quad (5)$$

$$n_j = (n_j + d_j - 1) e^{-\alpha - \beta E_j} \quad (6)$$

$$n_j = \frac{(d_j - 1) e^{-\alpha - \beta E_j}}{1 - e^{-\alpha - \beta E_j}} \quad (7)$$

$$= \frac{d_j - 1}{e^{\alpha + \beta E_j} - 1} \quad (8)$$

Since $d_j \gg 1$ (usually), we can safely drop the -1 in the numerator to get the number distribution for bosons:

$$n_j = \frac{d_j}{e^{\alpha + \beta E_j} - 1} \quad (9)$$

At this stage, we can try to find α and β by evaluating the total number of particles and the total energy for a particular potential, such as the infinite square well. Using the same technique as before, we get

$$N = \int_0^\infty \frac{d(k)}{e^{\alpha + \beta E_j} - 1} dk \quad (10)$$

$$= \frac{V}{2\pi^2} \int_0^\infty \frac{k^2}{e^{\alpha + \hbar^2 k^2 \beta / 2m} - 1} dk \quad (11)$$

This integral does not appear to have a closed form, even if we try to find some special functions. If we use the same definitions for α and β as before, we get

$$N = \frac{V}{2\pi^2} \int_0^\infty \frac{k^2}{e^{(\hbar^2 k^2 / 2m - \mu) / k_B T} - 1} dk \quad (12)$$

We can use this formula to derive a few conclusions. First, since the integrand is the product of two quantities (number at energy level k and degeneracy), the integrand must always be non-negative. This means that the exponent in the denominator must be non-negative, so

$$\mu < \frac{\hbar^2 k^2}{2m} \quad (13)$$

for all possible values of k . Since μ is a constant for given values of N , V and T , it must be less than the minimum energy in the system.

For the ideal gas, the minimum energy is zero, so $\mu < 0$ for all values of N , V and T . If N and V are fixed, then from 12, the integral must

remain constant as T is varied. This means that, for a given value of k , $(\hbar^2 k^2 / 2m - \mu) / k_B T$ must remain constant as T varies. In particular, as T decreases, $\hbar^2 k^2 / 2m - \mu$ must also decrease and since $\mu < 0$, this means that μ must increase towards zero.

The condition is, for a function $A(k)$:

$$\frac{\hbar^2 k^2}{2m} - A(k) k_B T = \mu(T) \quad (14)$$

That is, A depends only on k and μ depends only on T . Since the LHS must always be less than zero, there is a critical temperature T_c where the LHS becomes zero, which occurs at

$$T_c = \frac{\hbar^2 k^2}{2mA(k)k_B} \quad (15)$$

Of course, we can't use this formula to determine T_c because we don't know $A(k)$. However, we can try to do the integral above in the special case where $\mu = 0$. That is, we have

$$\frac{2\pi^2 N}{V} = \int_0^\infty \frac{k^2}{e^{\hbar^2 k^2 / 2mk_B T_c} - 1} dk \quad (16)$$

Using Maple, the integral comes out to

$$\int_0^\infty \frac{k^2}{e^{\hbar^2 k^2 / 2mk_B T_c} - 1} dk = (mk_B T_c)^{3/2} \frac{\sqrt{\pi}}{\sqrt{2}\hbar^3} \zeta\left(\frac{3}{2}\right) \quad (17)$$

where ζ is the Riemann zeta function. Solving for T_c we get

$$T_c = \frac{2\pi\hbar^2}{mk_B} \left(\frac{N}{V\zeta\left(\frac{3}{2}\right)} \right)^{2/3} \quad (18)$$

For liquid ^4He the mass density is 150 kg m^{-3} which gives it a number density of

$$\frac{N}{V} = \frac{150}{6.645 \times 10^{-27}} = 2.2573 \times 10^{28} \text{ m}^{-3} \quad (19)$$

Plugging in the numbers then gives

$$T_c = 3.21 \text{ K} \quad (20)$$

The experimental value is $T_c = 2.17 \text{ K}$ and at this point, helium becomes a superfluid. The phenomenon that occurs at the critical temperature is

known as *Bose condensation*. The ideal gas model cannot, of course, explain superfluidity, but it's interesting that we can predict the existence of a critical temperature even in this simple model.

PINGBACKS

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