

## STATISTICAL MECHANICS IN QUANTUM THEORY: 3-D HARMONIC OSCILLATOR

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.37.

Here's another example of working out the energy of a collection of particles. This time we'll look at the 3-d harmonic oscillator and consider distinguishable particles only. In this case, the number of particles  $n_j$  in energy level  $j$  is

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

where  $\alpha$  and  $\beta$  are the Lagrange multipliers and  $E_j$  is the energy of that level. For the 3-d harmonic oscillator

$$E_j = \left( j + \frac{3}{2} \right) \hbar \omega \quad (2)$$

and  $j$  is the sum of the three quantum numbers  $j = j_x + j_y + j_z$  in the three rectangular coordinates. The degeneracy of state  $j$  was worked out to be

$$d_j = \frac{1}{2} (j+1)(j+2) \quad (3)$$

The total number of particles is then

$$N = \frac{e^{-\alpha - 3\beta\hbar\omega/2}}{2} \sum_{j=0}^{\infty} (j+1)(j+2) e^{-\beta j\hbar\omega} \quad (4)$$

The sum can be evaluated directly in Maple, giving the result

$$N = e^{-\alpha - 3\beta\hbar\omega/2} \frac{e^{3\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^3} \quad (5)$$

$$= e^{-\alpha} \frac{e^{3\beta\hbar\omega/2}}{(e^{\beta\hbar\omega} - 1)^3} \quad (6)$$

$$= e^{-\alpha} \frac{e^{-3\beta\hbar\omega/2}}{(1 - e^{-\beta\hbar\omega})^3} \quad (7)$$

However, to see how this is done using the method suggested by Griffiths, we start with the geometric series

$$\sum_{j=0}^{\infty} x^j = \frac{1}{1-x} \quad (8)$$

Taking the first derivative:

$$\frac{1}{(1-x)^2} = \sum_{j=0}^{\infty} jx^{j-1} \quad (9)$$

$$\frac{x}{(1-x)^2} = \sum_{j=0}^{\infty} jx^j \quad (10)$$

And the second derivative:

$$\frac{2}{(1-x)^3} = \sum_{j=0}^{\infty} j(j-1)x^{j-2} \quad (11)$$

$$\frac{2x^2}{(1-x)^3} = \sum_{j=0}^{\infty} j(j-1)x^j \quad (12)$$

We can write the coefficient in 4 as

$$(j+1)(j+2) = j(j-1) + 4j + 2 \quad (13)$$

and define

$$x \equiv e^{-\beta\hbar\omega} \quad (14)$$

Then we have

$$\sum_{j=0}^{\infty} (j+1)(j+2)e^{-\beta j\hbar\omega} = \sum_{j=0}^{\infty} j(j-1)x^j + 4 \sum_{j=0}^{\infty} jx^j + 2 \sum_{j=0}^{\infty} jx^{j-1} \quad (15)$$

$$= \frac{2x^2}{(1-x)^3} + 4 \frac{x}{(1-x)^2} + \frac{2}{1-x} \quad (16)$$

$$= \frac{2}{(1-x)^3} \left[ x^2 + 2x(1-x) + (1-x)^2 \right] \quad (17)$$

$$= \frac{2}{(1-x)^3} \quad (18)$$

Plugging this back into 4 gives the result above for  $N$ .

Using  $\beta = 1/k_B T$ , we can solve for  $\alpha$  to get

$$e^{-\alpha} = N \frac{\left(1 - e^{-\hbar\omega/k_B T}\right)^3}{e^{-3\hbar\omega/2k_B T}} \quad (19)$$

In terms of the chemical potential, we have  $\mu = -\alpha k_B T$  so

$$\mu = k_B T \left[ \ln N + 3 \ln \left(1 - e^{-\hbar\omega/k_B T}\right) + \frac{3\hbar\omega}{2k_B T} \right] \quad (20)$$

For the total energy, we have

$$E = \sum_{j=0}^{\infty} n_j E_j \quad (21)$$

$$= \frac{\hbar\omega}{2} e^{-\alpha} \sum_{j=0}^{\infty} (j+1)(j+2) \left(j + \frac{3}{2}\right) e^{-\beta E_j} \quad (22)$$

This sum can be done in a similar way to the previous one (though we need another derivative of the geometric series). However, I can be lazy and get Maple to do the work, giving the result

$$E = \frac{3\hbar\omega}{2} e^{-\alpha - 3\beta\hbar\omega/2} \frac{e^{3\beta\hbar\omega} (e^{\beta\hbar\omega} + 1)}{(e^{\beta\hbar\omega} - 1)^4} \quad (23)$$

$$= \frac{3\hbar\omega}{2} e^{-\alpha - 3\beta\hbar\omega/2} \frac{(1 + e^{-\beta\hbar\omega})}{(1 - e^{-\beta\hbar\omega})^3 (1 - e^{-\beta\hbar\omega})} \quad (24)$$

Substituting for  $e^{-\alpha}$  and  $\beta$  from above, we get

$$E = \frac{3\hbar\omega N}{2} \frac{(1 + e^{-\hbar\omega/k_B T})}{(1 - e^{-\hbar\omega/k_B T})} \quad (25)$$

In the limit of very low temperatures  $k_B T \ll \hbar\omega$  and

$$\mu(T) \rightarrow k_B T \ln N + \frac{3}{2}\hbar\omega \rightarrow \frac{3}{2}\hbar\omega \quad (26)$$

and

$$E \rightarrow \frac{3}{2}\hbar\omega N \quad (27)$$

Thus all particles settle into the ground state, although even at absolute zero the energy is not zero.

At the other extreme, where  $k_B T \gg \hbar\omega$

$$1 + e^{-\hbar\omega/k_B T} \rightarrow 2 \quad (28)$$

$$1 - e^{-\hbar\omega/k_B T} \rightarrow \frac{\hbar\omega}{k_B T} \quad (29)$$

$$E \rightarrow 3Nk_B T \quad (30)$$

The equipartition theorem from classical statistical mechanics says that at thermal equilibrium, each degree of freedom in the system contributes  $\frac{1}{2}k_B T$  to the total energy. In the 3-d harmonic oscillator, each particle has 3 translational degrees of freedom and 3 vibrational degrees of freedom making a total of 6, giving the energy above.