

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

$$(0.1) \quad n_j = d_j e^{-\alpha - \beta E_j}$$

where α and β are the Lagrange multipliers and E_j is the energy of that level. For the 3-d harmonic oscillator

$$(0.2) \quad E_j = \left(j + \frac{3}{2} \right) \hbar \omega$$

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

$$(0.3) \quad d_j = \frac{1}{2} (j+1)(j+2)$$

The total number of particles is then

$$(0.4) \quad N = \frac{e^{-\alpha - 3\beta\hbar\omega/2}}{2} \sum_{j=0}^{\infty} (j+1)(j+2) e^{-\beta j\hbar\omega}$$

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

$$(0.5) \quad N = e^{-\alpha - 3\beta\hbar\omega/2} \frac{e^{3\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^3}$$

$$(0.6) \quad = e^{-\alpha} \frac{e^{3\beta\hbar\omega/2}}{(e^{\beta\hbar\omega} - 1)^3}$$

$$(0.7) \quad = e^{-\alpha} \frac{e^{-3\beta\hbar\omega/2}}{(1 - e^{-\beta\hbar\omega})^3}$$

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

$$(0.8) \quad \sum_{j=0}^{\infty} x^j = \frac{1}{1-x}$$

Taking the first derivative:

$$(0.9) \quad \frac{1}{(1-x)^2} = \sum_{j=0}^{\infty} jx^{j-1}$$

$$(0.10) \quad \frac{x}{(1-x)^2} = \sum_{j=0}^{\infty} jx^j$$

And the second derivative:

$$(0.11) \quad \frac{2}{(1-x)^3} = \sum_{j=0}^{\infty} j(j-1)x^{j-2}$$

$$(0.12) \quad \frac{2x^2}{(1-x)^3} = \sum_{j=0}^{\infty} j(j-1)x^j$$

We can write the coefficient in 0.4 as

$$(0.13) \quad (j+1)(j+2) = j(j-1) + 4j + 2$$

and define

$$(0.14) \quad x \equiv e^{-\beta\hbar\omega}$$

Then we have

(0.15)

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

$$(0.16) \quad = \frac{2x^2}{(1-x)^3} + 4 \frac{x}{(1-x)^2} + \frac{2}{1-x}$$

$$(0.17) \quad = \frac{2}{(1-x)^3} \left[x^2 + 2x(1-x) + (1-x)^2 \right]$$

$$(0.18) \quad = \frac{2}{(1-x)^3}$$

Plugging this back into 0.4 gives the result above for N .

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

$$(0.19) \quad e^{-\alpha} = N \frac{\left(1 - e^{-\hbar\omega/k_B T}\right)^3}{e^{-3\hbar\omega/2k_B T}}$$

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

$$(0.20) \quad \mu = k_B T \left[\ln N + 3 \ln \left(1 - e^{-\hbar\omega/k_B T}\right) + \frac{3\hbar\omega}{2k_B T} \right]$$

For the total energy, we have

$$(0.21) \quad E = \sum_{j=0}^{\infty} n_j E_j$$

$$(0.22) \quad = \frac{\hbar\omega}{2} e^{-\alpha} \sum_{j=0}^{\infty} (j+1)(j+2) \left(j + \frac{3}{2}\right) e^{-\beta E_j}$$

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

$$(0.23) \quad E = \frac{3\hbar\omega}{2} e^{-\alpha-3\beta\hbar\omega/2} \frac{e^{3\beta\hbar\omega} (e^{\beta\hbar\omega} + 1)}{(e^{\beta\hbar\omega} - 1)^4}$$

$$(0.24) \quad = \frac{3\hbar\omega}{2} e^{-\alpha-3\beta\hbar\omega/2} \frac{(1 + e^{-\beta\hbar\omega})}{(1 - e^{-\beta\hbar\omega})^3 (1 - e^{-\beta\hbar\omega})}$$

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

$$(0.25) \quad E = \frac{3\hbar\omega N}{2} \frac{(1 + e^{-\hbar\omega/k_B T})}{(1 - e^{-\hbar\omega/k_B T})}$$

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

$$(0.26) \quad \mu(T) \rightarrow k_B T \ln N + \frac{3}{2}\hbar\omega \rightarrow \frac{3}{2}\hbar\omega$$

and

$$(0.27) \quad E \rightarrow \frac{3}{2}\hbar\omega N$$

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

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

$$(0.28) \quad 1 + e^{-\hbar\omega/k_B T} \rightarrow 2$$

$$(0.29) \quad 1 - e^{-\hbar\omega/k_B T} \rightarrow \frac{\hbar\omega}{k_B T}$$

$$(0.30) \quad E \rightarrow 3Nk_B T$$

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.