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

$$n_j = d_j e^{-\alpha-\beta E_j} \tag{1}$$

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

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

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

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

The total number of particles is then

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

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

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

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

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

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

$$\sum_{j=0}^{\infty} x^j = \frac{1}{1-x} \tag{8}$$

Taking the first derivative:

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

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

And the second derivative:

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

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

We can write the coefficient in 4 as

$$(j+1)(j+2) = j(j-1)+4j+2 \tag{13}$$

and define

$$x \equiv e^{-\beta\hbar\omega} \tag{14}$$

Then we have

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

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

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

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

Plugging this back into 4 gives the result above for N.
Using $\beta=1/k_BT$, we can solve for α to get

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

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

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

For the total energy, we have

$$E=\sum_{j=0}^{\infty}n_jE_j \tag{21}$$

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

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

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

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

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

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

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

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

and

$$E \to \frac{3}{2}\hbar\omega N \tag{27}$$

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

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

$$1 + e^{-\hbar\omega/k_B T} \to 2 \tag{28}$$

$$1 - e^{-\hbar\omega/k_B T} \to \frac{\hbar\omega}{k_B T} \tag{29}$$

$$E \to 3N k_B T \tag{30}$$

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.