(from pp 238-240)

First, we take an energy with a quadratic position or momentum component named q. For simplicity's sake, we treat this as the only degree of freedom in the system. The system is in equilibrium with a reservoir at temperature T. Each value of q corresponds to a separate independent state, which are discretely spaced by very small intervals of delta_q.

$$E = c q^2$$

Note:

The equipartition theorem tells us that, for a system in equilibrium at temperature T, the average energy of each quadratic degree of freedom is 1/2kT, where k is Boltzmann's constant.

What we mean when we say "degree of freedom" is essentially the number of independent position or momentum coordinates needed to describe a system. In this specific context, "degrees of freedom" refer to any quadratic energy terms which are needed to describe the motion of an atom or molecule through a given system.

For example, if we take a monoatomic gas, only translational motion is required to describe their behavior. So in this case, we'd say each monoatomic molecule has 3 degrees of freedom (each referring to the translational kinetic energy in all three orthogonal directions). Alternatively, if we take a diatomic molecule, then the molecule can also rotate about axes (not including the axis along the length of the molecule for quantum mechanical reasons). Additionally, diatomic molecules can also vibrate since the atoms are bound together and can be perturbed such that they oscillate around an equilibrium position. This together with the rotational degrees of freedom gives them a total of 7 total degrees of freedom.

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta c q^2}$$

We take the partition function and plug in our energy function. This gives us the sum of all Boltzmann factors. Importantly, the quantity Z is a "constant" in that it does not depend on any particular state q (it does however depend on temperature). The partition function essentially counts how many states are accessible to the atom, weighting each one in proportion to its probability (pp. 225).

$$\beta = \frac{1}{kT}$$

Beta was defined at equal to kT on pp. 229.

$$Z = \frac{1}{\Delta q} \sum_q e^{-\beta c q^2} \Delta q$$

We can multiply the partition function by delta_q over delta_q, keeping the numerator term in the sum while bringing the denominator outside to get this.

The sum can now be interpreted as the area under a bar graph whose height it determined by the Boltzmann factor (pp. 225).

So long as delta_q is small, we can approximate the bar graph with a smooth curve and turn the sum into an integral.

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta c q^2} dq$$

$$x = \sqrt{\beta c}\, q \quad (\text{change of variables})$$

$$dx = \sqrt{\beta c}\, dq$$

$$\frac{1}{\sqrt{\beta c}} dx = dq$$

$$Z = \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx$$

The integral term in this expression is equal to the square root of pi. The proof of this is in Appendix B, pp. 384. Using this, we are able to write the following.

$$Z = \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \sqrt{\pi} \qquad C = \frac{1}{\Delta q} \sqrt{\frac{\pi}{c}}$$

$$= C \beta^{-1/2}$$

With this, we can use formula 6.25 to get the average energy.

$$\overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{(C\beta^{-1/2})} \frac{\partial}{\partial \beta}\left(C\beta^{-1/2}\right) = -\frac{1}{C\beta^{-1/2}} \cdot -\frac{1}{2} C \beta^{-3/2}$$

$$= \frac{\beta^{1/2}}{2 \beta^{3/2}} = \frac{1}{2\beta} = \frac{1}{2} kT$$

Interestingly, since we saw how both q and c from the original energy function canceled out to give us the final definition of the average energy per degree of freedom, this same proof should hold for any number of degrees of freedom, with any number of constants.

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