

The equipartition theorem

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1 Introduction

We'll derive one of my favorite theorems from equilibrium statistical mechanics. Then, we'll apply it to a variety of thermodynamic systems.

2 The setup

Consider an ensemble of particles which achieve thermal equilibrium at temperature T and individually have energy

$$E = E(q_1, \dots, q_n, p_1, \dots, p_n)$$

where q_i, p_i are generalized positions and momenta. Assume we may decompose the energy stored by a particular mode (position or momenta) as such:

$$E = u_i(q_i) + E', \quad (1)$$

where E' is not a function of q_i . Also assume a power-law dependence for the potential

$$u_i(q_i) = \alpha_i q_i^n. \quad (2)$$

We will show that the total energy is, on average, *equipartitioned* into each of the active modes q_i , and in particular

$$\langle u_i \rangle = \frac{1}{n} k_B T,$$

where $\langle \cdot \rangle$ denotes an expected value.

3 Derivation

From Boltzmann statistics, we know the probability that a particle has energy E obeys

$$P(E) \propto e^{-\beta E},$$

where $\beta = \frac{1}{k_B T}$. By definition,

$$\begin{aligned}\langle u_i \rangle &= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} u_i(q_i) P(q_i) dq_1 \cdots dq_n dp_1 \cdots dp_n \\ &= \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} u_i(q_i) e^{-\beta E} dq_1 \cdots dq_n dp_1 \cdots dp_n}{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta E} dq_1 \cdots dq_n dp_1 \cdots dp_n}.\end{aligned}$$

We can simplify this monster by applying assumptions (1) and (2):

$$\langle u_i \rangle = \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} u_i(q_i) e^{-\beta E'} e^{-\beta u_i(q_i)} dq_1 \cdots dq_n dp_1 \cdots dp_n}{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta E'} e^{-\beta u_i(q_i)} dq_1 \cdots dq_n dp_1 \cdots dp_n}.$$

Since E' is not a function of q_i , we may untangle the integrals and cancel all the waste:

$$\begin{aligned}\langle u_i \rangle &= \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta E'} dq_1 \cdots dq_n dp_1 \cdots dp_n}{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta E'} dq_1 \cdots dq_n dp_1 \cdots dp_n} \frac{\int_{-\infty}^{\infty} u_i(q_i) e^{-\beta u_i(q_i)} dq_i}{\int_{-\infty}^{\infty} e^{-\beta u_i(q_i)} dq_i} \\ &= \frac{\int_{-\infty}^{\infty} u_i(q_i) e^{-\beta u_i(q_i)} dq_i}{\int_{-\infty}^{\infty} e^{-\beta u_i(q_i)} dq_i}.\end{aligned}$$

One can use integration by parts to relate the numerator to the denominator. Alternatively, note that since the region of integration $(-\infty, \infty)$ is fixed, Feynman's rule yields

$$\frac{d}{d\beta} \int_{-\infty}^{\infty} e^{-\beta u_i} dq_i = \int_{-\infty}^{\infty} \frac{\partial}{\partial \beta} e^{-\beta u_i} dq_i = - \int_{-\infty}^{\infty} u_i e^{-\beta u_i} dq_i,$$

so

$$\begin{aligned}\langle u_i \rangle &= - \frac{\frac{d}{d\beta} \int_{-\infty}^{\infty} e^{-\beta u_i(q_i)} dq_i}{\int_{-\infty}^{\infty} e^{-\beta u_i(q_i)} dq_i} \\ &= - \frac{d}{d\beta} \log \left(\int_{-\infty}^{\infty} e^{-\beta u_i(q_i)} dq_i \right) \\ &= - \frac{d}{d\beta} \log \left(\int_{-\infty}^{\infty} e^{-\beta \alpha_i q_i^n} dq_i \right) \\ &= - \frac{d}{d\beta} \log \left(\frac{1}{(\alpha_1 \beta)^n} \int_{-\infty}^{\infty} e^{-x^n} dx \right).\end{aligned}$$

To finish, simply note that by properties of logarithms

$$\begin{aligned}\langle u_i \rangle &= - \frac{d}{d\beta} \left(- \frac{1}{n} \log \beta - \frac{1}{n} \log \alpha_1 + \log \int_{-\infty}^{\infty} e^{-x^n} dx \right) \\ &= \frac{1}{n\beta} = \frac{1}{n} k_B T,\end{aligned}$$

as desired. Energy is split evenly into all active modes, on average.

4 Basic applications

Consider an ideal, monatomic gas at equilibrium with temperature T , and isolate one gas particle. There are three active modes which may store energy: the three principal directions of translation. Since kinetic energy is quadratic with momentum, we have

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \left\langle \frac{1}{2}mv_y^2 \right\rangle = \left\langle \frac{1}{2}mv_z^2 \right\rangle = \frac{1}{2}k_B T$$

for a total kinetic energy of

$$\langle K_{\text{mono}} \rangle = \frac{3}{2}k_B T.$$

If the gas is diatomic, there are now two new rotational modes corresponding to the two possible principal rotations. Note that the rotational mode corresponding to the molecule spinning along the bond axis has negligible moment of inertia, and thus stores negligible energy. Then we have

$$\langle K_{\text{dia}} \rangle = \frac{5}{2}k_B T.$$

Technically, the vibrational modes matter too, but these only get activated at very low temperature. For a polyatomic gas, all the rotational modes matter, and then

$$\langle K_{\text{poly}} \rangle = 3k_B T.$$

We also have the rms speed to be

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{k_B T}{m}}.$$

Now consider a molecule of air in the atmosphere. Since the gravitational potential is linear, the average gravitational potential energy is $k_B T$ and the average kinetic energy is $\frac{3}{2}k_B T$. Then the average ratio of kinetic energy to potential energy of a molecule is $\frac{3}{2}$, which can also be proved in a more cumbersome way with dynamics.