Finally, the mean occupation number is

$$\langle n \rangle = \frac{e^{-\xi}}{1 - e^{-\xi}} = \frac{1}{1 - e^{-\xi}} = \frac{1}{e^{\beta \hbar \omega - 1}} \,, \tag{30}$$

which is the same result we found by the first approach.

HW Problem. Schroeder problem 6.17, p. 231.

HW Problem. Schroeder problem 6.18, p. 231.

HW Problem. Schroeder problem 6.19, p. 231.

Exercise.

   (a) Using methods similar to those used in the last example, show that the mean value of the energy of any system in thermal contact with a reservoir having temperature T is:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \,. \tag{31}$$

   (b) Show that for a single harmonic oscillator in thermal contact with a reservoir,

$$\langle E \rangle = \left(\langle n \rangle + \frac{1}{2} \right) \hbar \omega \,. \tag{35}$$

[EOC, Wed. 3/15/2006, #28]

Reading assignment. Schroeder, section **6.4**.

   It's essentially trivial to extend the derivative trick to find mean values of higher powers of the energy:

$$\langle E^m \rangle = \frac{\sum_n E_n^m e^{-\beta E_n}}{Z} \,. \tag{40}$$

First we take the mth derivative of the partition function:

$$\frac{\partial^m}{\partial \beta^m} Z = \frac{\partial^m}{\partial \beta^m} \sum_n e^{-\beta E_n}$$

$$= (-1)^m \underbrace{\sum_n E_n^m e^{-\beta E_n}}_{Z \langle E^m \rangle} \,. \tag{41}$$

Then we solve for the average value, obtaining

$$\langle E^m \rangle = \frac{(-1)^m}{Z} \frac{\partial^m Z}{\partial \beta^m} \,. \tag{42}$$

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0.1.2   The equipartition theorem

Classical statistical mechanics

All of the statistical mechanics we've done so far has been applied to quantum-mechanical systems. We even quantized the ideal gas in order to be able to count the number of discrete microstates corresponding to any given macrostate. The reason we've limited ourselves to quantum systems is principally that some of the treatment of classical systems suffers from a need to make what appear, in a purely classical analysis, to be ad hoc adjustments in order to make the classical results agree with the classical limits for quantum-mechanical systems.

The ideal gas is a good example. We found its multiplicity to be

$$\Omega = \frac{\epsilon_p}{(2mU)^{1/2}} \frac{V^N (2\pi mU)^{3N/2}}{N! \, h^{3N}} \frac{2}{\Gamma\left(\frac{3N}{2}\right)}, \tag{43}$$

which includes two odd-looking features for a classical system. One is the presence of Planck's constant, and the other is the division by $N!$ to account for indistinguishability of the particles. That indistinguishability is only an issue in quantum mechanics, where the many-particle wave function must be appropriately symmetrized for the type of identical particles being described. A purely classical derivation of the entropy of the ideal gas would miss the contributions that arise from these two features of the multiplicity, and fixing that up either requires some unsatisfying hand waving, or it requires a quantum-mechanical calculation, such as we did.

Nevertheless, it is useful to be able to apply statistical mechanics to classical systems, and the customary way to do that is through use of the Hamiltonian formulation of classical mechanics. The state of a classical system is completely specified in the Hamiltonian formalism by the generalized coordinates and momenta of all the particles. The Hamiltonian function of the system depends on each of them:

$$\mathcal{H} = \mathcal{H}(q_1, q_2, \ldots, q_{3N}, p_1, p_2, \ldots, p_{3N}), \tag{44}$$

where we've assumed there are exactly $6N$ coordinates and momenta for N particles, which is typical of three-dimensional systems, but not universal. It's convenient to abbreviate the list of coordinates as simply q, taken to represent the typically $3N$-dimensional vector of generalized coordinates of all the particles. Similarly, we'll denote the typically $3N$-dimensional vector of generalized momenta of all the particles by p. Then the Hamiltonian is a considerably easier to write:

$$\mathcal{H} = \mathcal{H}(q, p). \tag{45}$$

The space defined by all of the coordinates and momenta, generally of dimension $6N$, is referred to as *phase space.*

The time development of the system is controlled by the Hamiltonian through Hamilton's equations of motion:

$$\dot{q}_i(t) = \frac{\partial H(q,p)}{\partial p_i} \quad \text{and} \quad \dot{p}_i(t) = -\frac{\partial H(q,p)}{\partial q_i}, \tag{46}$$

of which there are $2N$ for an N-particle system.

Note also that the Hamiltonian (really its negative) can be obtained from the Lagrangian via a Legendre transformation that replaces all the generalized velocities by the corresponding generalized momenta as independent variables:

$$\mathcal{L}(q,\dot{q},t) - \sum_i p_i \dot{q}_i = -\mathcal{H}(q,p,t), \tag{47}$$

where the generalized momentum conjugate to the generalized coordinate q_i is

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}. \tag{48}$$

The equipartition theorem

We won't need to make use of much of Hamiltonian mechanics in order to derive the equipartition theorem. It mostly suffices to recall that the Hamiltonian function plays the role of the energy of the system, and the coordinates and momenta determine the state, as well as the Hamiltonian. The probability distribution for the states of a classical system in thermal contact with a reservoir looks much like its quantum-mechanical analog:

$$\mathcal{P}(q,p) = \frac{e^{-\beta \mathcal{H}(q,p)}}{\mathcal{I}}, \tag{49}$$

where the normalization constant is

$$\mathcal{I} = \int e^{-\beta \mathcal{H}(q,p)} \, d^{3N}q \, d^{3N}p. \tag{50}$$

The integral is taken over all values of the coordinates and momenta allowed for the system. If the system is in a box, the coordinates will be restricted to lie within the box, but the momenta can still have unlimited values. Because of the complication I mentioned above, that the classical expressions must be tweaked to match the classical limits of their quantum-mechanical analogs, the classical partition function is not simply the integral $\mathcal{I}$, but $\mathcal{I}/(h^{3N}N!)$. Fortunately, we won't have to worry about that, since we only need the probability distribution.

Take note that the function $\mathcal{P}(q,p)$ is not a probability, but a probability density. The normalization integral $\mathcal{I}$ acquires dimensions through the phase-space volume element $d^{3N}q \, d^{3N}p$, so the probability distribution function has dimensions of inverse phase-space volume. This means its interpretation is that $\mathcal{P}(q,p) \, d^{3N}q \, d^{3N}p$ is the probability that the phase space

coordinates and momenta lie within the volume element $d^{3N}q\, d^{3N}p$ about the values specified by q and p.

Now, as I mentioned when we first encountered the equipartition theorem, the important coordinates and momenta are those appearing quadratically in the Hamiltonian function. For a system of identical three-dimensional harmonic oscillators, the Hamiltonian looks like:

$$\mathcal{H}(q,p) = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{K}{2} q_i^2 \right) , \qquad (51)$$

where K is the spring constant. Both the coordinates q_i and the momenta p_i appear quadratically.

For a system of noninteracting diatomic molecules, all the energy is kinetic, but it can be decomposed into contributions from the linear motion of the center of mass of each of the molecules and from the rotational motion of each. The rotational coordinates for each molecule can be taken to be the polar and azimuthal angles the bond axis makes with respect to a set of Cartesian axes attached to the molecule and aligned some common set of axes:
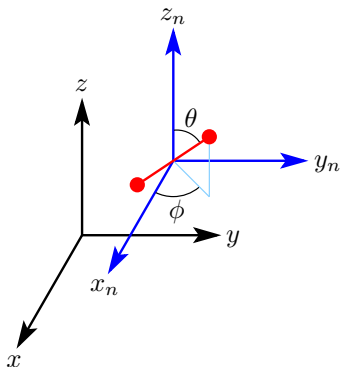
For molecule i, we'll denote the polar angle by θ_i and the azimuthal angle by ϕ_i. The generalized momenta conjugate to these will be denoted by p_{ϕ_i} and p_{θ_i}, respectively. Then one can show that the Hamiltonian function of the system is

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{j=1}^{N} \frac{1}{2I} \left(p_{\theta_j}^2 + \frac{p_{\phi_j}^2}{\sin^2 \theta_j} \right) , \qquad (52)$$

where I is the moment of inertia of the molecule for rotation about an axis perpendicular to the bond and passing through the center of mass of the molecule. The center-of-mass momentum components p_i appear quadratically, as do the generalized momenta for the rotational motion. Notice that the last term also contains $\sin^2 \theta_j$, which is not quadratic, so that coordinate will not contribute to the energy in the equipartition

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theorem. Also, it will not interfere with the quadratic dependence on p_{ϕ_j}, as our derivation will show.

Notice also that this Hamiltonian contains no contributions from rotation of the molecule about the bond axis or vibration of the atoms along the bond axis. We argued in our original discussion on the equipartition theorem that the moment of inertia for rotation about the bond axis is so tiny that its minimum quantum excitation energy, proportional to the inverse of the moment of inertia, is too large for excitation to occur at any temperature below the decomposition temperature of the molecules. As well, we argued that the vibrational quantum of excitation for common diatomic molecules is large enough to require temperatures well above room temperature to excite vibrations.

With these two examples in mind, we'll embark on our derivation of the equipartition theorem. The strategy will be to single out one of the quadratic coordinates or momenta for special treatment, showing that regardless of the dependence of the Hamiltonian on the other coordinates and momenta, the energy of the system will contain a contribution $kT/2$ arising from the selected coordinate or momentum. Let x denote the coordinate or momentum of interest, and let X denote all the other coordinates and momenta, say $M = 6N - 1$ in number. Then the Hamiltonian function can be decomposed into two parts, one proportional to x^2 and one independent of x:

$$\mathcal{H}(q, p) = \mathcal{H}(x, X) = A(X)x^2 + B(X), \qquad (53)$$

where A and B are functions of the other coordinates and momenta. For example, for the diatomic molecular ideal gas the function $A(X)$ multiplying the generalized momentum component $x = p_{\phi_i}$ is

$$A(X) = \frac{1}{2I \sin^2 \theta_i}, \qquad (54)$$

and the function $B(X)$ consists of all the other terms in the Hamiltonian.

The average value of the energy is obtained from the Hamiltonian and the probability distribution in just the same way we calculated the average for a quantum-mechanical system, but now the sum is replaced by an integral:

$$
\begin{aligned}
\langle E \rangle &= \frac{\displaystyle\int \mathcal{H}(x, X)e^{-\beta\mathcal{H}}\, dx\, d^M X}{\displaystyle\int e^{-\beta\mathcal{H}}\, dx\, d^M X} \\[2mm]
&= \frac{\displaystyle\int [A(X)x^2 + B(X)]e^{-\beta\mathcal{H}}\, dx\, d^M X}{\displaystyle\int e^{-\beta\mathcal{H}}\, dx\, d^M X} \\[2mm]
&= \left\langle Ax^2 \right\rangle + \langle B \rangle ,
\end{aligned}
\qquad (55)
$$

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where the first term is the contribution due to x^2. If we look more closely at that contribution, we find

$$
\begin{aligned}
\langle Ax^2 \rangle &= \frac{\displaystyle\int A(X)x^2 e^{-\beta[A(X)x^2 + B(X)]}\, dx\, d^M X}{\displaystyle\int e^{-\beta[A(X)x^2 + B(X)]}\, dx\, d^M X} \\[2ex]
&= \frac{\displaystyle\int A(X)e^{-\beta B(X)}\left(\int x^2 e^{-\beta A(X)x^2}\, dx\right) d^M X}{\displaystyle\int e^{-\beta B(X)}\left(\int e^{-\beta A(X)x^2}\, dx\right) d^M X}\,.
\end{aligned}
\tag{56}
$$

In the denominator, we have the integral of a Gaussian:

$$
\int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx = \left(\frac{\pi}{\alpha}\right)^{1/2},
\tag{57}
$$

and the integral in the numerator can be obtained from the integral of the Gaussian via the differentiation trick we've used previously for obtaining sums of series:

$$
\begin{aligned}
\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}\, dx &= -\frac{\partial}{\partial \alpha}\int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx \\[2ex]
&= -\frac{\partial}{\partial \alpha}\left(\frac{\pi}{\alpha}\right)^{1/2} \\[2ex]
&= \frac{\sqrt{\pi}}{2}\alpha^{-3/2}\,.
\end{aligned}
\tag{58}
$$

Here $\alpha = \beta A(X)$, so the mean value of Ax^2 is

$$
\begin{aligned}
\langle Ax^2 \rangle &= \frac{\displaystyle\int Ae^{-\beta B}\frac{\sqrt{\pi}}{2}(\beta A)^{-3/2}\, d^M X}{\displaystyle\int \sqrt{\pi}(\beta A)^{-1/2}e^{-\beta B}\, d^M X} \\[2ex]
&= \frac{1}{2\beta}\frac{\displaystyle\int A^{-1/2}e^{-\beta B}\, d^M X}{\displaystyle\int A^{-1/2}e^{-\beta B}\, d^M X} \\[2ex]
&= \frac{1}{2\beta} \\[2ex]
&= \frac{kT}{2}\,.
\end{aligned}
\tag{59}
$$

Thus *any* quadratic coordinate or momentum contributes $\frac{1}{2}kT$ to the mean value of the energy. Since any other term in the Hamiltonian that contains

a quadratic coordinate or momentum makes a similar contribution, the equipartition theorem follows immediately.

As an example, recall the classical harmonic crystal, consisting of N atoms and having Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{K}{2} q_i^2 \right), \tag{60}$$

which has two quadratic terms for each dimension and each particle. Thus, the equipartition theorem gives the mean total energy of the system as:

$$\langle E \rangle = U = 3NkT. \tag{61}$$

Recall that this is a classical result, so it does not take into account the quantum freeze-out of degrees of freedom at low temperatures. Thus, it is useful as a quick way to find the energy of a system in a temperature range in which the behavior is classical. That occurs, of course, when kT is significantly larger than the quantum excitation energy.

For the diatomic gas of N molecules, we saw that the Hamiltonian could be written in the form

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{j=1}^{N} \frac{1}{2I} \left(p_{\theta_j}^2 + \frac{p_{\phi_j}^2}{\sin^2 \theta_j} \right), \tag{62}$$

which has three translational quadratic terms per molecule and two rotational quadratic terms per molecule. The energy given by the equipartition theorem is then

$$U = \frac{5}{2} NkT. \tag{63}$$

Recall also that for point particles (no rotational degrees of freedom) the energy is

$$U = \frac{3}{2} NkT, \tag{64}$$

which is just what the equipartition theorem gives if only the translational quadratic terms are present in the Hamiltonian.

HW Problem. Schroeder problem 6.32, pp. 240–241.