1 Average kinetic energy and potential energy

Consider a system of N particles with energy:

$$E(\{x_i\},\{p_i\}) = \frac{1}{2m}\sum_{i=1}^{3N} p_i^2 + V(\{x_i\})\,. \tag{1}$$

where the first term is the kinetic and the second the potential energy.

In the canonical ensemble (constant NVT), the partition function is

$$\begin{aligned} Z &= \int dx_1 \ldots \int dx_{3N} \int dp_1 \ldots \int dp_{3N}\, e^{-\beta E(\{x_i\},\{p_i\})} \\ &= \int \prod_{i=1}^{3N} dx_i dp_i\, e^{-\beta E(\{x_i\},\{p_i\})}\,, \end{aligned} \tag{2}$$

where $\beta = 1/(k_B T)$ and we have simplified the integral notation in the last expression.

The average kinetic energy is given by

$$\langle K\rangle = \frac{1}{2m}\sum_{i=1}^{3N}\langle p_i^2\rangle\,. \tag{3}$$

Let us see what is the contribution of the kinetic degree of freedom k to the total kinetic energy:

$$\begin{aligned} \frac{1}{2m}\langle p_k^2\rangle &= \frac{1}{2m}\frac{\int \prod_{i=1}^{3N} dx_i dp_i\, p_k^2\, e^{-\beta E(\{x_i\},\{p_i\})}}{\int \prod_{i=1}^{3N} dx_i dp_i\, e^{-\beta E(\{x_i\},\{p_i\})}} \\ &= \frac{1}{2m}\frac{\int dp_k\, p_k^2\, e^{-\beta p_k^2/2m}}{\int dp_k\, e^{-\beta p_k^2/2m}} \\ &= \frac{1}{\beta}\frac{\int dp\, p^2\, e^{-p^2}}{\int dp\, e^{-p^2}} \\ &= \frac{k_B T}{2}\,. \end{aligned} \tag{4}$$

This is the so-called "equipartition theorem of (kinetic) energy" which states that each momentum coordinate has on average $k_B T/2$ of kinetic energy in the canonical ensemble.

Since each momentum component contributes $k_B T/2$ to the kinetic energy, the total average becomes:

$$\boxed{\langle K\rangle = \frac{3}{2} N k_B T}\,. \tag{5}$$

In a molecular dynamics simulation, one can therefore use the kinetic energy to access the average temperature of the system as

$$T = \frac{2}{3Nk_B}\langle K\rangle\,, \tag{6}$$

where the average is then a time average over the trajectory of the particles.

If the potential is also a quadratic function of $\{x_i\}$ as in the case of $3N$ independent harmonic oscillators:

$$\boxed{V(\{x_i\}) = \sum_{i=1}^{3N} \frac{1}{2} k x_i^2}\,, \tag{7}$$

then, using the same derivation as done for the kinetic component, you have

$$\frac{1}{2} k \langle x_i^2 \rangle = \frac{k_B T}{2}\,, \tag{8}$$

and the total potential becomes

$$\boxed{\langle V \rangle = \frac{3}{2} N k_B T}\,. \tag{9}$$

More generally, one can formulate the "equipartition theorem" by saying that the average value of every independent quadratic term in the energy contributes equally to the energy with $k_B T/2$. If all terms in the energy are quadratic, the mean energy is then spread equally over all degrees of freedom.

2 Coupled harmonic oscillators

It is possible to show that the average kinetic and potential contributions to the energy are equal also for particles coupled by springs as in the example of Assignment 4. The simplest way to demonstrate this is to note that the oscillators can be decoupled by defining a coordinate transformation to the normal modes of the system. In these new variables, the energy can be written as a kinetic term and a potential of independent oscillators. You should have seen something similar in Solid State Physics when discussing the harmonic approximation of a solid.

The second route is via the virial theorem and is derived below.

2.1 Virial theorem

Consider a potential $V(\{x_i\})$. The virial for a given k is defined as

$$\frac{\partial V}{\partial x_k} x_k = -f_k x_k\,, \tag{10}$$

where f_k is the force acting on x_k. The average of this quantity is easily computed as

$$\begin{aligned} \left\langle \frac{\partial V}{\partial x_k} x_k \right\rangle &= \frac{\int \prod_{i=1}^{3N} dx_i dp_i \, \frac{\partial V}{\partial x_k} x_k \, e^{-\beta E(\{x_i\},\{p_i\})}}{\int \prod_{i=1}^{3N} dx_i dp_i \, e^{-\beta E(\{x_i\},\{p_i\})}} \\ &= \frac{\int \prod_{i=1}^{3N} dx_i \, \frac{\partial V}{\partial x_k} x_k \, e^{-\beta V(\{x_i\})}}{\int \prod_{i=1}^{3N} dx_i \, e^{-\beta V(\{x_i\})}}\,. \end{aligned} \tag{11}$$

We have

$$\begin{aligned}\frac{\partial V}{\partial x_k} x_k \, e^{-\beta V(\{x_i\})} &= -\frac{1}{\beta} x_k \frac{\partial}{\partial x_k} \, e^{-\beta V(\{x_i\})} \\ &= -\frac{1}{\beta}\left[\frac{\partial}{\partial x_k}\left(x_k \, e^{-\beta V(\{x_i\})}\right) - e^{-\beta V(\{x_i\})}\right] , \end{aligned} \tag{12}$$

and, consequently,

$$\begin{aligned}\int dx_k \frac{\partial V}{\partial x_k} x_k \, e^{-\beta V(\{x_i\})} &= -\frac{1}{\beta}\left[x_k \, e^{-\beta V(\{x_i\})}\Big|_{-\infty}^{\infty} - \int dx_k \, e^{-\beta V(\{x_i\})}\right] \\ &= \frac{1}{\beta}\int dx_k \, e^{-\beta V(\{x_i\})} , \end{aligned} \tag{13}$$

where we have assumed that the surface term goes to zero, namely, that $V(\{x_i\})$ goes to the same value at the boundary of the system. Therefore, we obtain the "virial theorem":

$$\left\langle \frac{\partial V}{\partial x_k} x_k \right\rangle = \boxed{-\langle f_k x_k \rangle = k_B T} . \tag{14}$$

If we sum over all coordinates, we obtain

$$\sum_{i=1}^{3N} \left\langle \frac{\partial V}{\partial x_i} x_i \right\rangle = 3N k_B T \, . \tag{15}$$

Let us now assume that $V(\{x_i\})$ is a homogeneous function of order n, namely,

$$\boxed{V(\{\lambda x_i\}) = \lambda^n V(\{x_i\})} , \tag{16}$$

where every coordinate on the left hand side is multiplied by λ. Then, we have that

$$\left.\frac{\partial V(\{\lambda x_i\})}{\partial \lambda}\right|_{\lambda=1} = \sum_{i=1}^{3N} \frac{\partial V}{\partial x_i} x_i = n V(\{x_i\}) \tag{17}$$

Using Eq. 15, we obtain

$$3N k_B T = n \left\langle V(\{x_i\}) \right\rangle \, , \tag{18}$$

or, equivalently,

$$\boxed{2 \left\langle K \right\rangle = n \left\langle V \right\rangle} . \tag{19}$$

For the coupled harmonic oscillators, $n = 2$ and, therefore, $\langle K \rangle = \langle V \rangle$.