CHM 421/621
Statistical Mechanics

Lecture 3

Introduction and Review

Lecture Plan

An example application of Statistical Mechanics (ctd.):
Calculation of average energy

A familiar example

Classical microstates - set of instantaneous coordinates and velocities.

System: Consider a system of *N* particles moving independently of each other and inside a closed container of volume *V.* The container (and hence the particles) is assumed to be in thermal contact with a reservoir at temperature *T*.

Model:

$$H(\{\mathbf{r}_i(t), \mathbf{p}_i(t)\}) = \sum_{i=1}^{N} \frac{1}{2m} p_i^2$$

$\mathbf{p}_i$ Momentum of i^{th} particle
$\mathbf{r}_i$ Position of i^{th} particle

Probability distribution:

$$\rho(\{\mathbf{r}_i, \mathbf{p}_i\}) = \frac{1}{Q(N,V,T)} \exp\left(-\beta H(\{\mathbf{r}_i, \mathbf{p}_i\})\right)$$

$$\beta = \frac{1}{k_B T}$$

A familiar example

Probability distribution:

$$\rho(\{\mathbf{r}_i, \mathbf{p}_i\}) = \frac{1}{Q(N,V,T)} \exp\left(-\beta H(\{\mathbf{r}_i, \mathbf{p}_i\})\right)$$

Meaning:
The probability of finding the system in a microstate with the momenta of the particles between $\mathbf{p}_i$ and $\mathbf{p}_i$ + d$\mathbf{p}_i$ and their positions between $\mathbf{r}_i$ and $\mathbf{r}_i$ + d$\mathbf{r}_i$ is given by

$$\rho\left(\{\mathbf{r}_i, \mathbf{p}_i\}\right) d^{3N} r_i d^{3N} p_i$$

=> $$\int \rho\left(\{\mathbf{r}_i, \mathbf{p}_i\}\right) d^{3N} r_i d^{3N} p_i = 1$$

So what is $Q(N,V,T)$?

A familiar example

$$Q(N,V,T) = AV^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

Here *A* is a constant to ensure the correct dimensions. We will show later that

$$A = \frac{1}{h^{3N}}$$

$$\boxed{Q(N,V,T) = \left(\frac{V}{\Lambda^3}\right)^N}$$

With $$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

In this case, the normalisation equation becomes

$$\frac{1}{h^{3N}} \int \rho\left(\{\mathbf{r}_i, \mathbf{p}_i\}\right) d^{3N} r_i d^{3N} p_i = 1$$

Average Energy

Calculate

$$U = \langle H \rangle = \frac{1}{h^{3N}} \int d\mathbf{r} \int d\mathbf{p}\ H(\{\mathbf{r}_i, \mathbf{p}_i\})\ \rho(\{\mathbf{r}_i, \mathbf{p}_i\})$$

Answer

$$U = \frac{3}{2} N k_B T$$

Average Energy

$$U = \langle H \rangle = \frac{1}{h^{3N}} \int d\mathbf{r} \int d\mathbf{p} \; H(\{\mathbf{r}_i, \mathbf{p}_i\}) \; \rho(\{\mathbf{r}_i, \mathbf{p}_i\})$$

$$= \frac{1}{Qh^{3N}} \int d\mathbf{r} \int d\mathbf{p} \; \left(\sum_{i=1}^{N} \frac{p_i^2}{2m} \right) \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} \right)$$

$$= \frac{1}{Qh^{3N}} \left(\prod_{i=1}^{N} \int_V d\mathbf{r}_i \right) \int d\mathbf{p} \; \left(\sum_{i=1}^{N} \frac{p_i^2}{2m} \right) \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} \right)$$

$$= \frac{1}{Qh^{3N}} V^N \int d\mathbf{p} \; \left(\sum_{i=1}^{N} \frac{p_i^2}{2m} \right) \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} \right)$$

Average Energy

$$= \frac{1}{Qh^{3N}} V^N \sum_{j=1}^{N} \int d\mathbf{p} \; \frac{p_j^2}{2m} \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)$$

Since all p_j are being integrated over each integral in the sum is identical

$$= \frac{N}{Qh^{3N}} V^N \int d\mathbf{p} \; \frac{p_1^2}{2m} \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)$$

$$= \frac{N}{Qh^{3N}} V^N \left(\int \prod_{i=1}^{N} d\mathbf{p}_i \; \frac{p_1^2}{2m} \exp\left(-\beta \frac{p_i^2}{2m}\right)\right)$$

Average Energy

$$= \frac{N}{Qh^{3N}} V^N \prod_{i=2}^{N} \left(\int d\mathbf{p}_i \, \exp\left(-\beta \frac{p_i^2}{2m}\right)\right) \int d\mathbf{p}_1 \frac{p_1^2}{2m} \exp\left(-\beta \frac{p_1^2}{2m}\right)$$

$$= \frac{N}{Qh^{3N}} V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3(N-1)}{2}} (2m)^{\frac{3}{2}} \int d\mathbf{y} \; y^2 \exp\left(-\beta y^2\right)$$

where we have substituted $\mathbf{y} = \frac{\mathbf{p}}{\sqrt{2m}}$

Average Energy

Now

$$\int d\mathbf{y}\ y^2 \exp\left(-\beta y^2\right)$$

$$= \sum_{\nu=1}^{3} \left(\prod_{\mu\neq\nu} \int dy_\mu\ \exp\left(-\beta y_\mu^2\right) \right) \int dy_\nu\ y_\nu^2 \exp\left(-\beta y_\nu^2\right)$$

$$= \sum_{\nu=1}^{3} \frac{\pi}{\beta} \int dy_\nu\ y_\nu^2 \exp\left(-\beta y_\nu^2\right)$$

$$= \frac{3\pi}{\beta} \int dy_1\ y_1^2 \exp\left(-\beta y_1^2\right) \quad = \frac{3}{2\beta} \left(\frac{\pi}{\beta}\right)^{\frac{3}{2}}$$

Using this formula in the previous equations and setting $Q = \left(\frac{V}{\Lambda^3}\right)^N$ we get …

Average Energy

$$U = N\ \Lambda^{3N} \left(\frac{2\pi m}{\beta\hbar^2}\right)^{\frac{3N}{2}} \frac{3}{2\beta}$$

$$= \boxed{\frac{3}{2} N k_B T}$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Using

$$\beta = \frac{1}{k_B T}$$

Which is the desired result!