CHM 421/621 Statistical Mechanics

Lecture 18 Uncertainty and Entropy

Formalisms of Statistical Mechanics

Lecture Plan

Formalisms of Statistical Mechanics

Basic Postulates

Postulate 1:
The physical properties of a macroscopic system depend only on the average behaviour of all the atoms in that system.

Or

All macroscopic properties of a system are averages of some microscopic behaviour within the system

Formalisms of Statistical Mechanics

Basic Postulates

Postulate 2:
All micro states of a system that have the same energy are assumed to be equally probable.

Also called the postulate of equal *a priori* probability.

Formalisms of Statistical Mechanics

Basic Postulates

Justification:

In a closed system we can show that the energy does not change during dynamics

Classically,

$$\begin{aligned}\frac{dH}{dt} &= \frac{\partial H}{\partial t} + \sum_{i=1}^{N} \frac{\partial H}{\partial p_i}\dot{p}_i + \frac{\partial H}{\partial q_i}\dot{q}_i \\ &= \frac{\partial H}{\partial t} + \sum_{i=1}^{N} -\dot{q}_i\dot{p}_i + \dot{p}_i\dot{q}_i = 0\end{aligned}$$

Where $H(p_i,q_i)$ is the system Hamiltonian without explicit time-dependence.

Quantum mechanically the same holds for <H> through Ehrenfest theorem.

Formalisms of Statistical Mechanics

Probability distribution

The 2nd postulate means that if we know the total number of allowed microstates in a closed system we can determine the probability of each.

Let this number be $\Omega(U, V, N)$

Then the probability of each is $1/\Omega(U, V, N)$.

Let us perform such a counting operation.

Formalisms of Statistical Mechanics

Counting microstates in an ideal gas

Consider a system with *N* non-interacting atoms moving freely in a closed container of volume *V* and having a total energy *U.*

The Hamiltonian is given by

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

The number of microstates with energy *U* is given by

$$\Omega(U, V, N) = \frac{1}{N!} \times \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p \; \delta\left(\sum_{j=1}^{N} p_j^2/2m - U \right)$$

Accounts for indistinguishability of atoms

Phase-space Quantisation

Formalisms of Statistical Mechanics

Counting microstates in an ideal gas

Integrating over the spatial coordinates and by a transformation of variables we can write

$$\Omega(U,V,N) = \frac{1}{N!} \times \left(\frac{V(2m)^{\frac{3}{2}}}{h^3} \right)^N \int d^{3N}y \; \delta \left(\sum_{j=1}^{N} y_j^2 - U \right)$$

This is just an integral over the surface of a 3N-dimensional sphere of radius $\sqrt{U}$

We can show that (See these links for a nice explanation)

$$\Omega(U,V,N) = \frac{1}{N! \; \Gamma(\frac{3N}{2})} \left(\frac{V(2m\pi)^{\frac{3}{2}}}{h^3} \right)^N U^{\frac{3N-1}{2}}$$

$$\boxed{\approx \frac{1}{N! \; (\frac{3N}{2})!} \left[\frac{V}{h^3} (2\pi m U)^{\frac{3}{2}} \right]^N} \quad (N \to \infty)$$

Formalisms of Statistical Mechanics

Counting microstates in an ideal gas

So for large number of atoms we have

$$\Omega(U,V,N) = \frac{1}{N!\,(\frac{3N}{2})!}\left[\frac{V}{h^3}\,(2\pi m U)^{\frac{3}{2}}\right]^N$$

What is the uncertainty in the distribution?

$$\begin{aligned} H &= \ln\,\Omega(U,V,N) \\ &= N\,\ln\,\left[\frac{V}{h^3}\left(\frac{4\pi m U}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}\,N - \ln\,N! \end{aligned}$$

To simplify we can use Stirling's approximation (see *Atkins* or *McQuarrie*, for example).

$$\ln\,N! \approx N\,\ln\,N - N \qquad (N \to \infty)$$