CHM 421/621
Statistical Mechanics

Lecture 19 Microcanonical Ensemble

Formalisms of Statistical Mechanics

Lecture Plan

Basic Postulates

Counting microstates in an ideal gas

Boltzmann equation for entropy

Microcanonical Ensemble

Canonical Ensemble

Formalisms of Statistical Mechanics

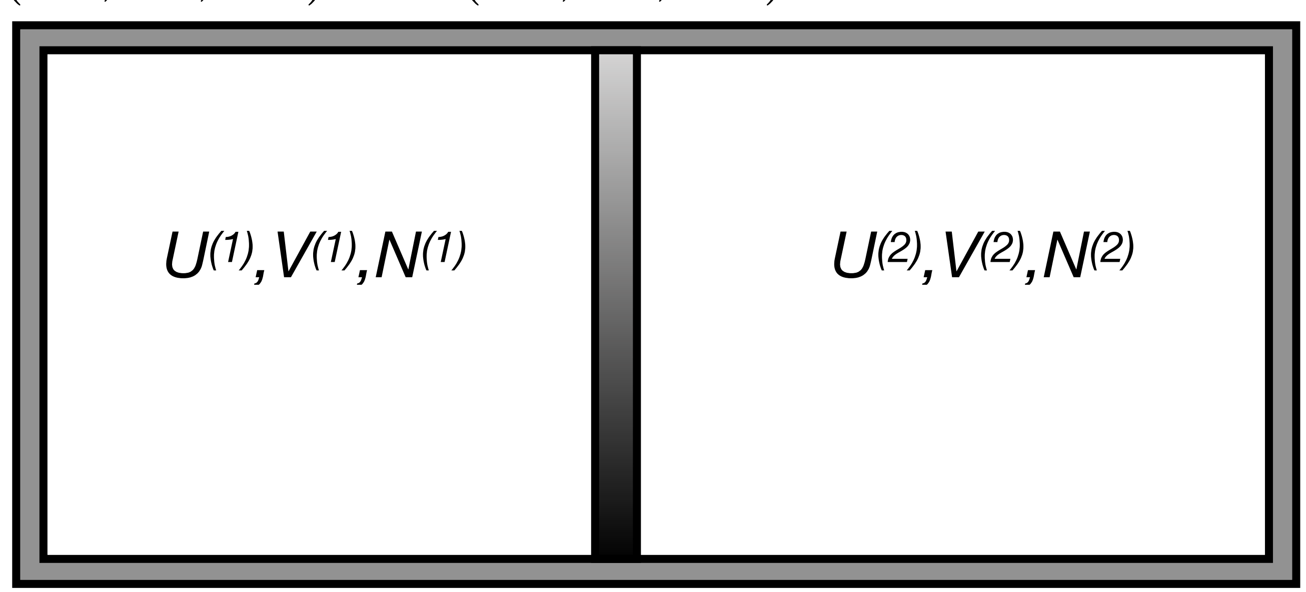
Uncertainty and Entropy

$$H(U,V,N) = N\ \ln\ \left[\frac{V}{h^3}\left(\frac{4\pi mU}{3N}\right)^{\frac{3}{2}}\right] + \frac{3}{2}\ N - \ln\ N!$$

1. *H* is a monotonically increasing function of *U.*
2. *H* is extensive. => *H(2N) = 2 H(N).* (in the large *N* limit)
3. Uncertainty for a composite system.

$$\Omega_{tot}(U_1, U_2, N_1, N_2, V_1, V_2) = \Omega(U_1, V_1, N_1) \times \Omega(U_2, V_2, N_2)$$

$$\implies H_{tot} = H_1 + H_2$$



If wall is removed what is the change in uncertainty?

$$H - H_1 - H_2 = ?$$

Formalisms of Statistical Mechanics

Uncertainty and Entropy

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

$$N = N_1 + N_2$$
$$V = V_1 + V_2$$
$$U = U_1 + U_2$$

$$H - H_1 - H_2 =$$
$$= \ln\left(\frac{V^N}{V_1^{N_1} V_2^{N_2}}\right) + \frac{3}{2}\ln\left(\frac{U^N}{U_1^{N_1} U_2^{N_2}}\right) + \Delta C(N)$$

Determine change in uncertainty if $U_1 = U_2 = U/2$, $N_1=N_2=N/2$, $V_1=V_2=V/2$.

Show that uncertainty will necessarily increase when relaxing internal constraints.

Formalisms of Statistical Mechanics

Boltzmann equation for entropy

Inspired by the similarity between uncertainty and the thermodynamic definition of entropy Boltzmann (and Planck) proposed

$$S \equiv k_B \ln \Omega \left(U, V, N\right)$$

$$k_B = 1.38 \times 10^{-23} J/K$$

Note that this means maximising entropy is the same as maximising uncertainty.

Formalisms of Statistical Mechanics

Boltzmann equation for entropy

For a monatomic ideal gas

$$S = \frac{S}{N} = k_B \ln V + \frac{3}{2} k_B \ln U + C$$

$$\frac{P}{T} = ?$$

$$\frac{1}{T} = ?$$

$$C_V = ?$$