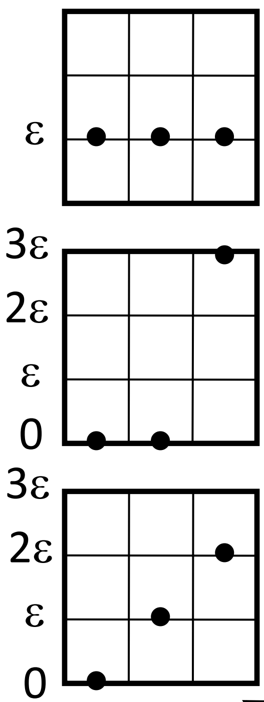
A simple example illustrating distributions, etc. in the Canonical ensemble

Consider each ensemble having one particle which can have energies of 0, ε, 2ε, 3ε, etc.

Suppose there are 3 ensemble members

and $<E>=\varepsilon$



$$W(0,3,0)=1 \qquad \frac{3!}{3!0!0!}=1$$

$$W(2,0,0,1)=3 \qquad \frac{3!}{2!1!}=3$$

$$W(1,1,1)=6 \qquad \frac{3!}{1!1!1!}=6$$

most probably weight: prob. = 6/10

20 member ensemble

- most prob. Distribution $<E>=\varepsilon$ with occurs 9.8 x 10^9 ways
- next most prob. member of distribution occurs 3.7 x 10^8 ways

10^{23} member ensemble

Distribution very strongly peaked

NVT (Canonical)

N, V, E_1	N, V, E_2	N, V, E_3	……

E_1, E_2, E_3 can differ

M ensembles

MV volume

MN particles

Energy E_1 can appear $\Omega(E_1)$ times

State	*1,*	*2,*	*3, …*
Energy	E_1,	E_2,	E_3, …
Occ #	a_1,	a_2,	a_3, …

← numbers of systems with that state

$$\Sigma a_j = M$$

$$\Sigma a_j E_j = \mathrm{E}$$

entire ensemble
has fixed E

All states consistent with constraints are equally probable

$$W(\boldsymbol{a}) = \frac{M!}{a_1!a_2!\ldots}$$

# of ways a particular distribution of a_js can be achieved (assumes objects are distinguishable)

$$P_j = \frac{\overline{a}_j}{M} = \frac{1}{M}\frac{\Sigma_a W(a)a_j(a)}{\Sigma_a W(a)} =$$

fraction of systems in j^{th} energy state when M and a_js are large, the spread in W is small and we can choose the set a_j* which maximizes $W(a)$ (under constraints)

$$P_j = \frac{a_j^*}{M}$$

$$a_j^* = e^{-\alpha'} e^{-\beta E_j}, \quad \alpha' = \alpha + 1$$

$$P_j = \frac{e^{-\beta E_j(N,V)}}{\Sigma_j e^{-\beta E_j(N,V)}}$$

$$\frac{\partial}{\partial a_j}\left[\ell n W(a) - \alpha \Sigma a_k - \beta \Sigma a_k E_k\right] = 0$$

$$Q(N,V,\beta) = \sum_j e^{-\beta E_j(N,V)} \qquad \beta = \frac{1}{k_B T}$$

$$\langle E \rangle \leftrightarrow E$$

$$\langle P \rangle \leftrightarrow P$$

association with thermodynamics

$$d\langle E\rangle = \Sigma E_j dP_j + \Sigma P_j dE_j$$

heat flow — work done on system

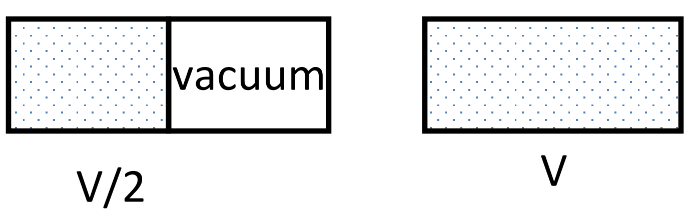
$$= \delta q_{rev} - \delta\omega_{rev}$$

change in populations without changes in energy levels

change in energies without changes in populations

$$Q = \sum_j e^{-E_j/kT} = \sum_E \Omega(N,V,E)e^{-E/kT}$$

sum over states — sum over levels



isolated system

quantum states grows
E fixed

For an isothermal process (system connected to heat bath)
remove constraint, # of accessible levels for a given E cannot <

$\Omega_2(NVE) > \Omega_1(NVE) \Rightarrow \Delta A < 0$ for spontaneous process

$$A = -kT\ell nQ \qquad \Big| \qquad \Delta A = -k_B T \ell n \frac{Q_2}{Q_1} < 0$$

$$S = k\ell n \Sigma e^{-E_j/kT} + \frac{1}{T}\frac{\Sigma E_j e^{-E_j/kT}}{\Sigma e^{-E_j/kT}} \xrightarrow[T \to 0]{} S = k\ell n\ n,$$

where n is the degeneracy of the lowest level

This is small compared to typical finite T values of S ($\propto Nk$)

In general, we choose the constant in the expression for S so that $S \to 0$ as $T \to 0$.

Can you think of a system where $S \neq 0$ in the $T \to 0$ limit?

Different ensembles

In general, in the $N \to \infty$ limit, it does not make a significant difference which ensemble we adopt

grand canonical *(V, T, μ)* *E, N* can fluctuate

$$\Xi(V,T,\mu) = \sum_N Q(N,V,T)\, e^{\mu N/kT}$$

N, P, T ensemble

$$\Delta(N,P,T) = \sum_E \sum_V \Omega(N,V,E)\, e^{-E/kT} e^{-PV/kT}$$ partition function

$$G = -kT\,\ell n \Delta$$

$$S = k\ \ell n\ \Omega(N,V,E)$$

micro canonical

$$Q(N,V,\beta) = \Sigma e^{-\beta E_j} = \sum_E \Omega(N,V,E)e^{-E/kT}$$

$$A = -kT\ell nQ$$

N V T
canonical

$$\Xi = \Sigma e^{-\beta E_j + \beta\mu N_j} = \sum_N Q,(N,V,T)e^{\mu N/kT}$$

sum over *j* for fixed *N*

grand
canonical

$$pV = kT\ell n\ [\Xi(V,T,\mu)]$$

Chapter 1 derives Ω for translational motion of non-interacting particles

$$S = Nk\ell n\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right]$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} \Rightarrow pV = NkT$$

(ideal gas law)