

Ensemble : a collection of something

Statistical Mechanics is a probabilistic approach to macroscopic equilibrium

Macrostate  $\Leftarrow$  Microstate  $\mu$

$(E, V, N)$

$\uparrow$   
internal energy  $U$

$\nearrow$   
assign probability  $\{p_\mu\}$   
at equilibrium

\* Ensemble: a collection of systems with all possible microstates  $\mu$  that are consistent with macrostate

Different choices of macro  $\Rightarrow$  Different ensembles

They are equivalent in the T.D. limit. ( $N \rightarrow \infty$ )

$(E, V, N)$	isolated system	$\Rightarrow$ microcanonical ensemble
$(T, V, N)$	allow energy exchange	$\Rightarrow$ canonical ensemble
$(T, V, \mu)$	allow energy and particle exchange	$\Rightarrow$ grandcanonical ensemble

\* Description of Microstates

o Classical systems of  $N$  particles

$\{(\vec{p}_1, \vec{q}_1), (\vec{p}_2, \vec{q}_2), \dots, (\vec{p}_N, \vec{q}_N)\}$   $\nearrow$  phase space  
 $6N$ -dimensional space

the state of this system corresponds to a representative point in the phase space

② Quantum system  $|\psi\rangle$   $N$ -particle wavefunction

$$\Delta p_i \Delta q_i \sim h$$

③ Classical systems with discrete variables

e.g. Ising (uniformal) magnet

label as  $\sigma = \pm 1$  microstate  $\{\sigma_i\}_{i=1}^N$ ,  $2^N$  possibilities

Remark: Q.M. leaves its trace!

a factor of  $\frac{1}{N!}$  makes the entropy an extensivity

Consider an ensemble of  $N$  microstates, corresponding to  $(E, N, V)$ . Infinitesimal volume element  $d\Gamma = \prod_{i=1}^N d^3p_i d^3q_i$

Number of particles in  $d\Gamma$ :  $dN$

Define density of states (representative points)

$$\rho(p, q) = \lim_{N \rightarrow \infty} \frac{1}{N} \frac{dN}{d\Gamma} \xrightarrow{\text{normalization}} \int d\Gamma \rho(p, q) = 1$$

Observable  $O(p, q)$  e.g.  $E = \sum_{i=1}^N \frac{p_i^2}{2m_i}$

\* Ensemble Average

$$\langle O \rangle_{(t)} = \int O(p, q) \rho(p, q, t) d\Gamma$$

$$\text{Equilibrium} \quad \frac{\partial \rho(t)}{\partial t} = 0$$

How do rep. points evolve in phase space?

Hamiltonian equation  $\begin{cases} \dot{p}_i = -\frac{\partial H}{\partial q_i} \\ \dot{q}_i = \frac{\partial H}{\partial p_i} \end{cases}$

continuity equation:  $\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$

$\Rightarrow$  the total number of rep. points is conserved.

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left[ \frac{\partial}{\partial p_i} (\rho \dot{p}_i) + \frac{\partial}{\partial q_i} (\rho \dot{q}_i) \right] = 0$$

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{\infty} \left[ \rho \left( \frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right) + \dot{p}_i \frac{\partial \rho}{\partial p_i} + \dot{q}_i \frac{\partial \rho}{\partial q_i} \right] = 0$$

$\swarrow$   
 $-\frac{\partial}{\partial p_i} \left( \frac{\partial H}{\partial q_i} \right) + \frac{\partial}{\partial q_i} \left( \frac{\partial H}{\partial p_i} \right) = 0$

*Liouville theorem*

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{\infty} \left( \dot{p}_i \frac{\partial \rho}{\partial p_i} + \dot{q}_i \frac{\partial \rho}{\partial q_i} \right) = 0 \Rightarrow \frac{d\rho}{dt} = 0 \quad \text{incompressible}$$

Under Hamiltonian dynamics, density is a constant along the flow

Poisson bracket:  $\{A, B\} = \sum_{i=1}^{3N} \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right)$

$$\frac{\partial \rho}{\partial t} + \{ \rho, H \} = 0, \quad \text{Equilibrium} \quad \frac{\partial \rho_e}{\partial t} = 0 \Rightarrow \{ \rho_e, H \} = 0$$

M. E. C. E.

e.g.  $\rho_e \equiv C$  or  $\rho_e = f(H)$

\* Microcanonical Ensemble

Assumption of Equal a priori probability

Microstate  $(E, V, N)$  isolated

Microstate  $\mu$  = {all rep. points located on a constant  $E$  hypersurface}

hypersurface}

$$P_\mu = \frac{1}{\Omega} \begin{cases} 1 & \text{if } H_\mu = E \sim E \leq H \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

$\Omega(E, V, N)$  total number of microstates

o Ideal Gas  $E = \sum_{i=1}^N \frac{p_i^2}{2m_i}$

$$\Omega(E, V, N) = \frac{1}{h^{3N}} \int \prod_{i=1}^N d^3 p_i d^3 q_i [E \leq H(\mu) \leq E + \Delta E]$$

$$= \frac{V^N}{h^{3N}} \int \prod_{i=1}^N d^3 p_i [E \leq H(\mu) \leq E + \Delta E]$$

volume of a thin shell  $\sqrt{2mE}, \sqrt{2m(E+\Delta E)}$  in  $3N$ -dimensional space

$$= \frac{V^N}{h^{3N}} \cdot \text{Area} \cdot \Delta R = \frac{V^N}{h^{3N}} (\sqrt{2mE})^{3N-1} \frac{S_{3N}}{S_{3N}} \Delta R$$

Solid Angle

Spherical Coordinates

$$I = \int dx_1 \dots dx_d e^{-\sum_{i=1}^d x_i^2} = (\int dx e^{-x^2})^d = \pi^{\frac{d}{2}}$$

$$= S_d \cdot \int r^{d-1} e^{-r^2} dr = S_d \cdot \frac{1}{2} \int_0^\infty dy y^{\frac{d}{2}-1} e^{-y} = \frac{1}{2} \Gamma(\frac{d}{2}) S_d$$

$$\Rightarrow S_d = \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})}$$

so  $\Omega(E, V, N) = \frac{V^N}{h^{3N}} \underbrace{(2mE)^{\frac{3N-1}{2}}}_{\text{Radius}^{3N-1}} \cdot \underbrace{\frac{2\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2})}}_{\substack{3N\text{-d solid} \\ \text{angle } S_{3N}}} \underbrace{\left(\frac{m}{2E}\right)^{\frac{1}{2}} \Delta E}_{\Delta R}$

$$= \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2})} \frac{\Delta}{E}$$

$$\Rightarrow \Omega \sim E^{\frac{3N}{2}}$$

Sum of Exponentials: consider  $I = \sum_{i=1}^M e^{N\phi_i} \quad N \rightarrow \infty$

$$I \stackrel{N \rightarrow \infty}{\approx} e^{N\phi_{\max}}, \quad e^{N\phi_{\max}} \leq I \leq M e^{N\phi_{\max}}$$

$$\phi_{\max} \leq \frac{\ln I}{N} \leq \phi_{\max} + \left(\frac{\ln M}{N}\right) \rightarrow \ll 0$$

Saddle point integration

$$I = \int dx e^{N\phi(x)} \quad N \rightarrow \infty$$



if  $x = x_m$   $\phi(x)$  maximized,  $\nearrow \phi'(x_m) = 0, \phi''(x_m) < 0$ , Expand near  $x = x_m$ :

$$\phi(x) \approx \phi(x_m) - \frac{1}{2} |\phi''(x_m)| (x - x_m)^2 \dots$$

$$I = \int dx e^{N[\phi(x_m) - \frac{1}{2} |\phi''(x_m)| (x - x_m)^2]}$$

$$= e^{N\phi(x_m)} \int dx e^{-\frac{N}{2} |\phi''| (x - x_m)^2}$$

$$= e^{N\phi(x_m)} \sqrt{\frac{2\pi}{N|\phi''|_{x=x_m}}}$$

Higher order correction:

$$I \cong \int dx e^{N[\phi(x_m) - \frac{1}{2} |\phi''| (x - x_m)^2 + \frac{1}{3!} \phi^{(3)} (x - x_m)^3 + \frac{1}{4!} \phi^{(4)} (x - x_m)^4]}$$

$$= e^{N\phi(x_m)} \int dx e^{-\frac{N}{2} |\phi''| (x - x_m)^2} \cdot e^{N[\frac{1}{3!} \phi^{(3)} (x - x_m)^3 + \frac{1}{4!} \phi^{(4)} (x - x_m)^4]}$$

$$= e^{N\phi(x_m)} \int dx e^{-\frac{N}{2} |\phi''| (x - x_m)^2} \left[ 1 + \frac{\frac{N}{3!} \phi^{(3)} (x - x_m)^3 + \frac{N}{4!} \phi^{(4)} (x - x_m)^4}{\sqrt{\frac{2\pi}{N|\phi''|}}} \right]$$

$\quad \quad \quad 0 \quad \quad \quad O(\frac{1}{N})$

$$\frac{\ln I}{N} = \phi(x_m) - \frac{1}{2N} \ln \frac{N|\phi''|}{2\pi} + O(\frac{1}{N^2})$$

Stirling's Approximation for  $N!$ ,  $N \rightarrow \infty$

$$N! = \Gamma(N+1) = \int_0^\infty t^N e^{-t} dt = \int_0^\infty e^{N(\ln t - \frac{t}{N})} dt$$

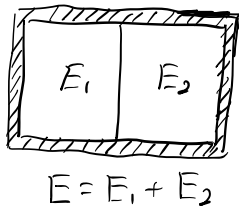
$$\phi'(t_m) = 0 \Rightarrow t_m = N, \quad \phi''(t_m) = -\frac{1}{N^2}, \quad \phi(t_m) = \ln N - 1$$

$$N! = e^{N(\ln N - 1)} \int dx e^{-\frac{1}{2N} (x - x_m)^2}$$

$$= e^{N \ln N - N} \sqrt{2\pi N}$$

$$\text{or } \ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N)$$

$$\Omega(E, V, N)$$



total # of microstates

$$\Omega(E) = \int dE_1 \Omega_1(E_1) \Omega_2(E - E_1)$$

$$\approx \Omega(E_1^*) \Omega_2(E - E_1^*) \quad E_1^* \text{ maximize } \Omega_1 \cdot \Omega_2$$

extraction:  $\frac{d\Omega_1}{dE} \Omega_2 - \frac{d\Omega_2}{dE} \Omega_1 = 0 \Rightarrow \frac{1}{\Omega_1} \frac{d\Omega_1}{dE} = \frac{1}{\Omega_2} \frac{d\Omega_2}{dE}$

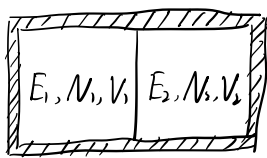
$$\Rightarrow \frac{d \ln \Omega_1}{dE} = \frac{d \ln \Omega_2}{dE} = \frac{1}{k_B T}$$

Recall  $\frac{\partial S}{\partial E} = \frac{1}{T}$ , Identify  $S(E, V, N) = k_B \ln \Omega(E, V, N)$

Entropy of Ideal Gas

$$\begin{aligned} S(E, V, N) &= N k_B \ln \left[ V \left( \frac{2\pi m E}{h^2} \right)^{\frac{3}{2}} \right] - k_B \ln \left( \frac{3N}{2} - 1 \right)! + \ln \left( \frac{\Delta E}{E} \right) \xrightarrow{0} \\ &= N k_B \ln \left[ V \left( \frac{4\pi m E}{3N h^2} \right)^{\frac{3}{2}} \right] + \frac{3}{2} N k_B \end{aligned}$$

Mixing entropy



initially at temp  $T$

two distinct gases, mix irreversible  $\Delta S > 0$

Ini.  $S = S_1 + S_2 = N_1 k_B \ln \left[ V_1 \left( \frac{4\pi m E_1}{3N_1 h^2} \right)^{\frac{3}{2}} \right] + N_2 k_B \ln \left[ V_2 \left( \frac{4\pi m E_2}{3N_2 h^2} \right)^{\frac{3}{2}} \right] + \frac{3}{2} N k_B$

Fin.  $S_f = N_1 k_B \ln \left[ V \left( \frac{4\pi m E_1}{3N_1 h^2} \right)^{\frac{3}{2}} \right] + N_2 k_B \ln \left[ V \left( \frac{4\pi m E_2}{3N_2 h^2} \right)^{\frac{3}{2}} \right] + \frac{3}{2} N k_B$

$$S_f - S_i = N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2} > 0 \quad \checkmark$$

But what about same gas?

Micro: if  $\frac{N_1}{V_1} = \frac{N_2}{V_2}$ ,  $S_f - S_i > 0$ , the actual particles <sup>(switched)</sup> changed

but macroscopically nothing happens,  $\Delta S = 0 \Rightarrow$  Gibbs Paradox

Resolution: particles are identical, overturned  $\Omega$  by  $N!$

$$\Omega = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}) N!} \frac{\Delta}{E}, \quad S = N k_B \ln \left[ \frac{V}{N} \left( \frac{4\pi m E}{3N h^2} \right)^{\frac{3}{2}} \right] + \frac{5}{2} N k_B$$

$$\Delta S = \left( N k_B \ln \left[ \frac{V}{N} \left( \frac{4\pi m E}{3N h^2} \right)^{\frac{3}{2}} \right] + \frac{5}{2} N k_B \right) - \left( N_1 k_B \ln \left[ \frac{V_1}{N_1} \left( \frac{4\pi m E}{3N_1 h^2} \right)^{\frac{3}{2}} \right] + N_2 k_B \ln \left[ \frac{V_2}{N_2} \left( \frac{4\pi m E}{3N_2 h^2} \right)^{\frac{3}{2}} \right] + \frac{5}{2} N k_B \right)$$

=

\* phase space measure for identical particles

$$d\Gamma = \frac{\prod_{i=1}^N d^3 p_i d^3 q_i}{h^{3N} N!}$$

Q. M. wavefunction must be (anti-)symmetrized

\* Properties of Ideal Gas from M.E.

$$dS = \frac{dE}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N} = \frac{3}{2} N k_B \cdot \frac{1}{E} \Rightarrow E = \frac{3}{2} N k_B T$$

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E, N} = N k_B \cdot \frac{1}{V} \Rightarrow pV = N k_B T$$

$$-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{E, V} = \frac{5}{2} k_B + k_B \ln \left[ \frac{V}{N} \left( \frac{4\pi m E}{3N h^2} \right)^{\frac{3}{2}} \right] - \frac{5}{2} k_B$$

$$= k_B \ln \left[ \frac{V}{N} \left( \frac{4\pi m E}{3N h^2} \right)^{\frac{3}{2}} \right]$$

$$(E = \frac{3}{2} N k_B T) \quad \mu = k_B T \ln \left[ \frac{N}{V} \left( \frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} \right]$$

$$\downarrow \quad \downarrow \quad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{thermal de-Broie wavelength}$$

$$\Rightarrow \frac{\mu}{k_B T} = \ln(n \lambda_T^3)$$

$n \lambda_T^3$  otherwise QM effect important  
 $< 1$  QM effect negligible  
 classical particle average distance  $\sim n^{-1/3}$

Classical limit  $T \rightarrow \infty$

$$\frac{\mu}{k_B T} = \ln(n \lambda_T^3) \xrightarrow{T \rightarrow \infty} -\infty$$

$\mu < 0$  ! Classical ideal gas

$\mu \rightarrow -\infty$ , faster than  $k_B T$

\* Maxwell-Boltzmann distribution

$$P(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N; \vec{q}_1, \vec{q}_2, \dots, \vec{q}_N) = \frac{1}{\Omega(E, V, N)}$$

joint probability distribution

prob of particle #1 being at  $\vec{p}_1$   $P(\vec{p}_1) = ?$

$$P(\vec{p}_1) = \int d^3 q_1 \prod_{i=2}^N \int d^3 \vec{p}_i d^3 \vec{q}_i P(p, q) \quad \text{ignore } N! \& h^{3N}$$

$$= \frac{V}{\Omega(E, V, N)} \int \prod_{i=2}^N d^3 p_i d^3 q_i$$

$$= \frac{V \Omega(E - \frac{\vec{p}_1^2}{2m}, V, N-1)}{\Omega(E, V, N)}$$

$$= \frac{V \cancel{V^{N-1}}}{V^N} \cdot \frac{[2\pi m (E - \frac{\vec{p}_1^2}{2m})]^{\frac{3(N-1)}{2}}}{(2\pi m E)^{\frac{3N}{2}}} \cdot \frac{(\frac{3N}{2} - 1)!}{(\frac{3(N-1)}{2} - 1)!}$$

$$= (2\pi m E)^{-\frac{3}{2}} (1 - \frac{\vec{p}_1^2}{2mE})^{\frac{3N}{2}} \cdot (\frac{3N}{2})^{\frac{3}{2}}$$

$$= (\frac{3N}{4\pi m E})^{\frac{3}{2}} \exp(-\frac{3N \vec{p}_1^2}{4mE})$$

$$= (2\pi m k_B T)^{-\frac{3}{2}} e^{-\frac{\vec{p}_1^2}{2m k_B T}}$$

\* Ising magnet (two states system)

$$\sigma = \pm 1, \quad \{\sigma_i\}_{i=1}^N, \quad H = -\mu B \sigma = \begin{cases} \epsilon_+ = -\mu B \\ \epsilon_- = \mu B \end{cases}$$

# of microstates  $\Omega(E, N)$      $n_+$ : # of  $\sigma_i = +1$ ,  $n_-$ , ... -

$$\Omega(E, N) = \frac{N!}{n_+! n_-!} \quad S(E, N) = k_B \ln \Omega = k_B (N \ln N - n_+ \ln n_+ - n_- \ln n_-)$$

$$\text{but } \begin{cases} n_+ + n_- = N \\ \epsilon_+ n_+ + \epsilon_- n_- = E \end{cases} \quad n_{\pm} = \frac{1}{2} \left( N \mp \frac{E}{\mu_0 B} \right)$$

$$\frac{\partial}{\partial E} (n_+ \ln n_+) = (\ln n_+ + 1) \frac{\partial n_+}{\partial E}$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = -k_B [(\ln n_+ + 1) \frac{\partial n_+}{\partial E} + (\ln n_- + 1) \frac{\partial n_-}{\partial E}]$$

$$= k_B \ln \frac{n_+}{n_-} \cdot \frac{1}{2\mu_0 B} \Rightarrow \frac{1}{k_B T} = \frac{1}{2\mu_0 B} \ln \frac{n_+}{n_-}$$

$$\frac{n_-}{n_+} = \exp\left(-\frac{2\mu_0 B}{k_B T}\right) \quad p(n_+) = \frac{e^{-\frac{\mu_0 B}{k_B T}}}{e^{-\frac{\mu_0 B}{k_B T}} + e^{\frac{\mu_0 B}{k_B T}}} \xrightarrow{L \rightarrow Z} p(n_-) = \frac{e^{-\frac{\mu_0 B}{k_B T}}}{e^{-\frac{\mu_0 B}{k_B T}} + e^{\frac{\mu_0 B}{k_B T}}}$$

Ergodic Hypothesis  $\langle O \rangle = \int d\Gamma O(p, q) \rho_{HE}(p, q)$

\* Canonical Ensemble  $= \lim_{T \rightarrow \infty} \frac{1}{T} \int dt O(p(t), q(t))$

Macrostate  $(T, V, N) \Rightarrow$  allow energy exchange

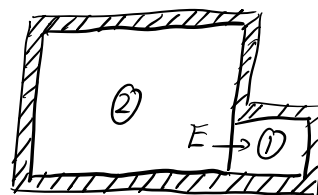
total energy of 1+2 fixed  $\Rightarrow$  M.E.

$$E_T = E_1 + E_2$$

° Prob of system 1 in a particular

state  $|n\rangle$  with energy  $E_n$ .

total # of microstates 1+2 is:



$$\Omega(E_T) = \sum_n \overset{\hookrightarrow 1, |n\rangle}{\Omega_1(E_n)} \Omega_2(E_T - E_n)$$

$$= \sum_n 1 \cdot \Omega_2(E_T - E_n)$$

$E_n \ll E_T$ , expand around  $E_T$

$$\ln \Omega_2(E_T - E_n) = \ln \Omega_2(E_T) + \frac{\partial \ln \Omega_2}{\partial E} \cdot (-E_n)$$

$$= \ln \Omega_2(E_T) - \beta E_n \quad \underbrace{\beta}_{\frac{1}{k_B T}}$$

$$\Rightarrow \Omega(E_T) = \sum_n \Omega_2(E_T) e^{-\beta E_n}$$

$$= \Omega_2(E_T) \sum_n e^{-\beta E_n}$$

$$P(E_n) = \frac{\Omega_2(E_T) e^{-\beta E_n}}{\Omega_2(E_T) \sum_n e^{-\beta E_n}} = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{1}{Z} e^{-\beta E_n}$$

where  $Z = \sum_n e^{-\beta E_n}$ , partition function

Prob of system 1 having energy  $E = E_n$

rarely used  
for calculation  
in practice

$$P(E) = \frac{1}{Z} g e^{-\beta E} = \frac{\Omega(E) e^{-\beta E}}{Z}$$

$\Omega(E)$ : # of microstate  
with energy  $E$

$$\sum_n e^{-\beta E_n} = \sum_E e^{-\beta E} \sum_n \delta_{E_n E} \Omega(E) \sim E^N$$

in multi-body quantum system.  
 $E_n$  is dense, so when  $n$  is  
big,  $\Omega(E_n)$  grows with  $n$

Physical Meaning of  $Z$ ?

$$Z = \sum_E \Omega(E) e^{-\beta E} = \sum_E e^{\frac{S(E)}{k_B}} e^{-\beta E}$$

$$= \sum_E e^{-\beta(E - TS(E))} = \sum_E e^{-\beta F}$$

$$\approx e^{-\beta F(E^*)} \quad E^* \text{ minimize } F(E)$$

$$\text{suggest } F \sim -\frac{1}{\beta} \ln Z = -k_B T \ln Z$$

## Thermodynamic Quantities

$$\begin{aligned}\langle E \rangle &= \sum_n E_n P(E_n) = \frac{1}{Z} \sum_n E_n e^{-\beta E_n} \\ &= \frac{1}{Z} \left( - \frac{\partial}{\partial \beta} \right) \sum_n e^{-\beta E_n} = \frac{1}{Z} - \frac{\partial}{\partial \beta} Z = - \frac{\partial}{\partial \beta} \ln Z\end{aligned}$$

$$F = E - TS \quad df = -SdT - pdV + \mu dN$$

$$\Rightarrow F = E + T \frac{\partial F}{\partial T}, \quad E = F - T \frac{\partial F}{\partial T} = \frac{\partial(\frac{F}{T})}{\partial(\frac{1}{T})} = \frac{\partial(\beta F)}{\partial \beta}$$

$$F = -\frac{1}{\beta} \ln Z, \quad p = - \frac{\partial F}{\partial V} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}, \quad \mu = \frac{\partial F}{\partial N} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial N}$$

$$S = -\frac{\partial F}{\partial T} = \frac{\partial(k_B T \ln Z)}{\partial T} = k_B (\ln Z + T \frac{\partial \ln Z}{\partial T}) = k_B (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z) = k_B \ln Z - \frac{E}{T}$$

$$P(E_n) = \frac{1}{Z} e^{-\beta E_n}, \quad \ln P(E_n) = -\beta E_n - \ln Z$$

$$\begin{aligned}\sum_n P(E_n) \ln P(E_n) &= -\beta \underbrace{\sum_n E_n P(E_n)}_E - \underbrace{\sum_n P(E_n)}_1 \ln Z \\ &= -\beta E - \ln Z = -\beta E + \beta F = \frac{1}{k_B T} \cdot (-TS) = -\frac{S}{k_B}\end{aligned}$$

$$\Rightarrow S = -k_B \sum_n P(E_n) \ln P(E_n)$$

$$I = - \sum_x p(x) \ln p(x) \quad \text{information (Shannon) entropy}$$

Eg. 1 Ideal gas

$$E = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

summation  $\rightarrow$  integration  
 $k_B T \gg \Delta E$

compute partition function:

$$\begin{aligned}Z &= \frac{1}{N! h^{3N}} \int \prod_{i=1}^N d^3 \vec{p}_i d^3 \vec{q}_i e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}} \\ &= \frac{V^N}{N! h^{3N}} \int \prod_{i=1}^N d^3 \vec{p}_i e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}} = \frac{V^N}{N! h^{3N}} \left( \int d^3 p e^{-\frac{\beta}{2m} p^2} \right)^{3N}\end{aligned}$$

$$= \frac{V^N}{N! h^{3N}} (2\pi m k_B T)^{\frac{3N}{2}} = \frac{V^N}{N! \lambda_T^{3N}} \quad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$\ln Z = N \ln \frac{V}{\lambda_T^3} - \ln N! \quad Z = \frac{V^N}{N!} \left( \frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}}$$

$$= N \ln \left[ V \left( \frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} \right] - \ln N!$$

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} \frac{1}{\beta} = \frac{3N}{2} k_B T$$

$$p = \frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial V} = k_B T \frac{N}{V} \Rightarrow pV = N k_B T$$

$$S = k_B (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z) = k_B \ln Z + \frac{E}{T}$$

$$= N k_B \left( \ln \left[ \frac{V}{N} \left( \frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right)$$

$$\mu = - \frac{1}{\beta} \frac{\partial \ln Z}{\partial N} = - k_B T \ln \left[ \frac{V}{N} \left( \frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} \right] = k_B T \ln (n \lambda_T^3)$$

Eg - 2 Two-level system

Ising magnet  $\sigma_i = \pm 1$ ,  $\{\sigma_i\}_{i=1}^N$ , Energy  $\varepsilon_i = -\mu_B \sigma_i \begin{cases} \varepsilon_+ = -\mu_B \\ \varepsilon_- = \mu_B \end{cases}$

total energy  $E = \sum_{i=1}^N \varepsilon_i$

$$Z = \sum_{\{\varepsilon_i\}} e^{-\beta \sum_{i=1}^N \varepsilon_i} = \sum_{\{\sigma_i\}} e^{\beta \mu_B \sum_{i=1}^N \sigma_i} = \sum_{\{\sigma_i = \pm 1\}} \prod_i e^{\beta \mu_B \sigma_i}$$

$$= \left( \sum_{\sigma_1 = \pm 1} e^{\beta \mu_B \sigma_1} \right) \left( \sum_{\sigma_2 = \pm 1} e^{\beta \mu_B \sigma_2} \right) \dots \left( \sum_{\sigma_N = \pm 1} e^{\beta \mu_B \sigma_N} \right)$$

$$= \left( \sum_{\sigma_i = \pm 1} e^{\beta \mu_B \sigma_i} \right)^N$$

$$= [2 \cosh(\beta \mu_B)]^N, \quad \ln Z = N \ln [2 \cosh(\beta \mu_B)]$$

$$E = - \frac{\partial}{\partial \beta} \ln Z = -N \mu_B \tanh(\beta \mu_B)$$

$$= -N \mu_B \cdot \frac{e^{\beta \mu_B} - e^{-\beta \mu_B}}{e^{\beta \mu_B} + e^{-\beta \mu_B}}$$



$$= N \cdot \frac{(-\mu B)e^{-\beta \mu B} + \mu B e^{\beta \mu B}}{e^{-\beta \mu B} + e^{\beta \mu B}}$$

$$= N \langle \epsilon \rangle \rightarrow \text{average energy of a single spin}$$

Remark: both examples are about non-interacting d.f.

$$\text{total energy } E = \sum_{i=1}^N \epsilon_i$$

$$Z = \sum_{\{\epsilon_i\}} e^{-\beta \sum_{i=1}^N \epsilon_i} = \prod_{i=1}^N \sum_{\{\epsilon_i\}} e^{-\beta \epsilon_i} = z^N$$

$$* \text{caution identical particle } Z = \frac{1}{N!} z^N$$

Fluctuation:

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$$

$$\langle E^2 \rangle = \frac{1}{Z} \sum_s E_s^2 e^{-\beta E_s} = \frac{1}{Z} \sum_s \frac{\partial^2}{\partial \beta^2} e^{-\beta E_s} = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z$$

$$\begin{aligned} \sigma_E^2 &= \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z - \left( \frac{1}{Z} \frac{\partial}{\partial \beta} \ln Z \right)^2 \\ &= \frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial E}{\partial \beta} = k_B T^2 C_V \propto N \Rightarrow \sigma_E \sim \sqrt{N} \end{aligned}$$

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \rightarrow P(E) \text{ narrowly peaks at } \langle E \rangle \text{ in L.T.D.}$$

$$\langle E^n \rangle_c = \langle E^n \rangle - \langle E \rangle^n = (-1)^n \frac{\partial^n}{\partial \beta^n} \ln Z \sim N$$

cumulant


Central Limit Theorem

$p(x_i)$   $i=1, 2, \dots, N$  identically independent distribution  
drawn out of  $p(x)$

$$X = \sum_{i=1}^N x_i \quad \langle X^n \rangle_c = N \langle x^n \rangle_c$$

$$Y = \frac{1}{N} X, \quad P(Y) = \frac{1}{\sqrt{2\pi \frac{1}{N} \langle x^2 \rangle_c}} \exp\left[-\frac{(y - \langle x \rangle)^2}{2 \cdot \frac{1}{N} \langle x^2 \rangle_c}\right]$$

$$p(E) = \frac{1}{Z} \Omega(E) e^{-\beta E} = \frac{1}{Z} e^{-\beta F(E)} \quad \text{if } N \rightarrow \infty \Rightarrow$$

$$\frac{1}{\sqrt{2\pi k_B T^2 C_V}} \exp\left[-\frac{(E-E^*)^2}{2k_B T^2 C_V}\right] \quad \begin{array}{c} \Delta E \text{ is} \\ \text{narrow} \sim O(\sqrt{N}) \end{array}$$


Indistinguishable from microscopical ensemble with energy  $[E^* - \frac{\Delta}{2}, E^* + \frac{\Delta}{2}]$

$$Z = \int dE e^{-\beta F(E)} = e^{-\beta F(E)^*} \cdot \sqrt{2\pi k_B T^2 C_V}$$

$$\Rightarrow \ln Z = -\beta F(E^*) + \ln \sqrt{2\pi k_B T^2 C_V}, \quad F = F^* - \frac{1}{\beta} \ln \sqrt{2\pi k_B T^2 C_V} \quad O(\ln N)$$

Different Representation of Entropy

Microcanonical:  $S_{M.E.} = k_B \ln \Omega(E^*)$

Canonical:  $S_{C.E.} = -k_B \sum_{E_n} p(E_n) \ln p(E_n)$

$$F = E - TS \Rightarrow S_{C.E.} = \frac{\langle E \rangle - F}{T} = \frac{E^* - F^* + \frac{1}{\beta} \ln \sqrt{2\pi k_B T^2 C_V}}{T}$$

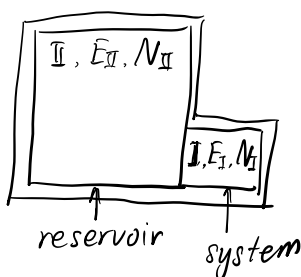
$$e^{-\beta F^*} = \Omega(E^*) e^{-\beta E^*} \quad S_{C.E.} = S_{M.E.}(E^*) + \left( \frac{k_B}{2} \ln(2\pi k_B T^2 C_V) \right) \sim O(\ln N)$$

$\ln \frac{\Delta}{E}$

M. E is equivalent to C.E.

Grand Canonical Ensemble

Macrostate  $(T, V, \mu)$  allow both energy and particle exchange



$$\begin{cases} E_I^{(N_I)} + E_{\bar{I}}^{(N_{\bar{I}})} = E \\ N_I + N_{\bar{I}} = N \end{cases} \quad \text{fixed}$$

prob of system at a particular state  $|n\rangle$ ,  
with energy  $(E_I^{(N_I)}, N_I)$

total # of microstates of 1+2

$$\Omega(E, V, N) = \sum_{N_1, E_1^{(N_1)}} \underbrace{\Omega_1(E_1^{(N_1)}, V, N_1)}_{=1, \ln} \Omega_2(E - E_1^{(N_1)}, V, N - N_1)$$

Expand

$$\ln \Omega_2(E - E_1^{(N_1)}, V, N - N_1) \cong \ln \Omega_2(E, V, N) - \underbrace{\frac{\partial \ln \Omega_2}{\partial E}}_{\beta} E_1^{(N_1)} - \underbrace{\frac{\partial \ln \Omega_2}{\partial N}}_{-\beta \mu} N_1$$

$$\Omega_2(E - E_1^{(N_1)}, V, N - N_1) = \Omega_2(E, V, N) e^{-\beta E_1^{(N_1)} + \beta \mu N_1}$$

so:

$$\Omega(E, N, V) = \sum_{N_1} \sum_{E_1^{(N_1)}} \Omega_2(E, N, V) e^{-\beta(E_1^{(N_1)} - \mu N_1)}$$

$$p(E_1^{(N_1)}, N_1) = \frac{\Omega_2(E, N, V) e^{-\beta(E_1^{(N_1)} - \mu N_1)}}{\sum_{N_1} \sum_{E_1^{(N_1)}} \Omega_2(E, N, V) e^{-\beta(E_1^{(N_1)} - \mu N_1)}}$$

M.E. prob  
distribution

$$P(E_N, N) = \frac{1}{Q} e^{-\beta(E_N - \mu N)}, \quad Q = \sum_{E_N, N} e^{-\beta(E_N - \mu N)}$$

\* Note:  $\alpha = -\beta \mu \Rightarrow e^{-\beta E - \alpha N}$   $\alpha, \beta$  are independent variables  
since  $\mu, T$  are independent

$e^{\beta \mu} \equiv z$  fugacity 逸度

$$Q = \sum_N e^{\beta \mu N} \left( \sum_{E_N} e^{-\beta E_N} \right) = \sum_N e^{\beta \mu N} \underline{Z(T, V, N)}$$

canonical partition function

$$\begin{aligned} Q &\cong e^{\beta \mu N^*} Z(T, V, N^*) = e^{\beta \mu N^*} \cdot e^{-\beta F^*} & \psi = F - \mu N = -pV \\ &= e^{-\beta(F^* - \mu N^*)} = e^{-\beta \psi^*} & \psi = -k_B T \ln Q \end{aligned}$$

Thermodynamic quantities  $d\psi = -SdT - p dV - N d\mu$

$$\langle E \rangle = - \left( \frac{\partial}{\partial \beta} \ln Q \right)_{\alpha \leftrightarrow \alpha}$$

$$\langle N \rangle = - \left( \frac{\partial}{\partial \alpha} \ln Q \right)_{\beta} = \left( \frac{\partial}{\partial (\beta \mu)} \ln Q \right)_{\beta}$$

E.g. Ideal gas

$$Z(T, V, N) = \frac{1}{N!} \left( \frac{V}{\lambda_T^3} \right)^N, \quad Q = \sum_{N=0}^{\infty} \frac{e^{\beta \mu}}{N!} \left( \frac{V}{\lambda_T^3} \right)^N = \exp \left( z \frac{V}{\lambda_T^3} \right)$$

$$\ln Q = z \frac{V}{\lambda_T^3} \quad \psi = -k_B T z \frac{V}{\lambda_T^3}, \quad p = k_B T \frac{z}{\lambda_T^3}$$

$$z = e^{\beta \mu} \Rightarrow N = \frac{\partial}{\partial (\beta \mu)} \ln Q = z \frac{V}{\lambda_T^3} \Rightarrow p = k_B T N / V$$

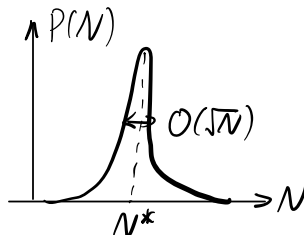
$$N = z \frac{V}{\lambda_T^3} \Rightarrow e^{\beta \mu} = n \lambda_T^3 \Rightarrow \beta \mu = \ln(n \lambda_T^3)$$

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln Q = -z V \frac{\partial}{\partial \beta} (\lambda_T^{-3}) = \frac{3}{2} \frac{z V}{\lambda_T^3} \frac{1}{\beta} = \frac{3}{2} N k_B T$$

\* Fluctuation around  $\langle E \rangle, \langle N \rangle$  in G.C.E.

$$\langle N^2 \rangle_c = \langle N^2 \rangle - \langle N \rangle^2 = \frac{\partial^2}{\partial (\beta \mu)^2} \ln Q \Big|_{\beta} = \frac{\partial N}{\partial (\beta \mu)} \Big|_{\beta} = k_B T \left( \frac{\partial N}{\partial \mu} \right)_T \sim N$$

$$\frac{\sqrt{\langle N^2 \rangle_c}}{\langle N \rangle} \sim \frac{1}{\sqrt{N}}$$



$$\left( \frac{\partial N}{\partial \mu} \right)_T ? \Rightarrow \left( \frac{\partial \mu}{\partial N} \right)_T ? \quad d\mu = -s dT + v dp,$$

$$\left( \frac{\partial \mu}{\partial N} \right)_{T, V} = \left( \frac{\partial \mu}{\partial p} \right)_{T, N} \left( \frac{\partial p}{\partial N} \right)_{T, V} = v \left( \frac{\partial p}{\partial N} \right)_{T, V}$$

$$= - \left( \frac{V}{N} \right)^2 \left( \frac{\partial p}{\partial V} \right)_{T, N}$$

$$\langle N^2 \rangle_c = k_B T - \left( \frac{V}{N} \right)^2 \left( \frac{\partial v}{\partial p} \right)_{T, N} = k_B T \frac{N^2}{V} \kappa_T$$

near critical point  $\kappa_T \rightarrow \infty$   
 $\langle N^2 \rangle_c \rightarrow \infty$   
 "critical opalescence"

$$\langle E^2 \rangle_c = \frac{\partial^2}{\partial \beta^2} \ln Q = - \left( \frac{\partial E}{\partial \beta} \right)_{\alpha, V} = k_B T^2 \left( \frac{\partial E}{\partial T} \right)_{\alpha, V}$$

$$= k_B T^2 C_V + k_B T \left( \frac{\partial E}{\partial N} \right)^2 \langle N^2 \rangle_c \sim N$$

## Conclusion on Ensemble Theory.

	Macrostates	Probability	Partition Function	Thermodynamic Function
Microcanonical	$(E, V, N)$	$\frac{1}{\Omega(E, V, N)}$	$\sum_{\mu} \delta_{E, H_{\mu}}$	$S = k_B \ln \Omega, dS = \frac{dE}{T} + \frac{p}{T} dV - \frac{\mu}{T} dN$
Canonical	$(T, V, N)$	$\frac{1}{Z} e^{-\beta E}$	$Z = \sum_n e^{-\beta E_n}$	$F = -k_B T \ln Z, dF = -S dT + p dV + \mu dN$
Grandcanonical	$(T, V, \mu)$	$\frac{1}{Q} e^{-\beta(E_s - \mu N)}$	$Q = \sum_N \sum_s e^{-\beta(E_s - \mu N)}$	$\psi = -k_B T \ln Q, d\psi = -S dT + p dV - N d\mu$

Canonical  $\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$ , Grandcanonical  $\langle E \rangle = -\left(\frac{\partial}{\partial \beta}\right)_{\alpha} \ln Q$ ,  $\langle N \rangle = -\left(\frac{\partial}{\partial \alpha}\right)_{\beta} \ln Q$ ,  $\alpha = -\beta \mu$

Equivalence of Ensembles in Thermodynamic Limit

$$\frac{\langle E \rangle_c}{\langle E \rangle} \sim O\left(\frac{1}{\sqrt{N}}\right), \quad \frac{\langle N \rangle_c}{\langle N \rangle} \sim O\left(\frac{1}{\sqrt{N}}\right)$$