

#### 4.1 General definitions

statistical mechanics is a probabilistic approach to equilibrium macroscopic properties of large numbers of degree of freedom.

Foundations: Liouville's theorem justifies the assumption that all accessible microstates are equally likely in an equilibrium state. (subjective assignment of prob.)

Methods: provide unbiased estimates of  $p_m(u)$  for a number of different equilibrium ensembles

Central Conclusions: In the thermodynamic limit, with large numbers of degrees of freedom, all these ensembles are in fact equivalent.

Main Question: How various systems evolve to a state of equilibrium?

## 4.2 The microcanonical ensemble

Mechanically and adiabatically isolated system (in absence of heat or work input to the system)

Fixed internal energy  $E$ , and the generalized coordinates  $\vec{x} \Rightarrow$  macrostate  $M \equiv (E, \vec{x})$

Assume that there are no other conserved quantities, so all points on this surface are mutually accessible

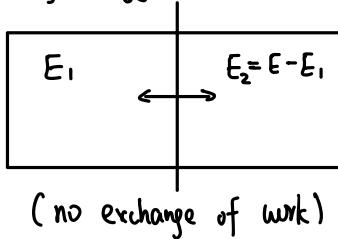
Microstates are defined by points in phase space, their time evolution governed by a Hamiltonian  $H(\mu)$ .

Hamiltonian equations conserve the total energy of a given system  
 $\Rightarrow$  all microstates are confined to the surface  $H(\mu) = E$  in phase space.

Central Postulate:  $P_{(E, \vec{x})}(M) = \frac{1}{\Omega(E, \vec{x})} \cdot \begin{cases} 1 & \text{for } H(\mu) = E \\ 0 & \text{otherwise} \end{cases}$

- (1) Boltzmann's assumption of equal a priori equilibrium prob.  
 $M \rightarrow M'$ ; volume in phase space is invariant; Jacobian of such transformation is unity; transformed prob.  $p(M') = p(M) |\partial M / \partial M'|$  is uniform on the surface of constant energy.
- (2) The normalization factor  $\Omega(E, \vec{x})$  is the area of the surface of constant energy  $E$  in phase space.  
 To avoid subtleties associated with densities that are non-zero only on a surface, define the microcanonical ensemble by requiring  $E - \Delta \leq H(\mu) \leq E + \Delta$  (uncertainty  $\Delta$ ). The normalization factor is now  $\Omega' \approx 2\Delta \Omega$   
 $\Omega$  typically depends exponentially on  $E$ , as long as  $\Delta \sim O(E^0)$  (or even  $O(E^1)$ ) ( $\Omega' - \Omega$ ) is negligible in the  $E \propto N \rightarrow \infty$  and can use  $\Omega$  or  $\Omega'$  interchangeably.
- (3) The entropy of this uniform prob. distri. is given by  
 $S(E, \vec{x}) = k_B \ln \Omega(E, \vec{x})$   
 \* For independent systems,  $\Omega_{\text{Total}} = \prod_i \Omega_i$   
 \*  $S$  is additive, as an extensive quantity  $\Rightarrow S \propto N$

exchange energy but two isolated systems



0<sup>th</sup> law: each microstate of the joint system corresponds to a pair of microstates of the two components:  $\mu = \mu_1 \otimes \mu_2$

$$\text{and } H(\mu) = H(\mu_1 \otimes \mu_2) = H(\mu_1) + H(\mu_2)$$

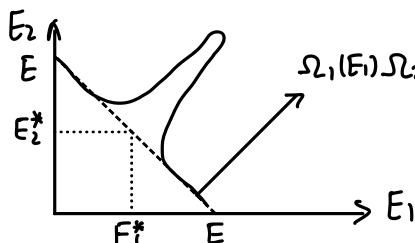
$$P_E(\mu_1 \otimes \mu_2) = \frac{1}{\Omega(E)} \cdot \begin{cases} 1 & \text{for } H(\mu_1) + H(\mu_2) = E \\ 0 & \text{otherwise} \end{cases}$$

$$\Omega(E) = \int dE_1 \Omega_1(E_1) \Omega_2(E - E_1) = \int dE_1 \exp \left[ \frac{S_1(E_1) + S_2(E - E_1)}{k_B} \right]$$

in chapter 2.6

$S_1 \propto N_1$  and  $S_2 \propto N_2$ , the integral can be approximated by saddle point method to maximum value of the integrand (at equilibrium)

$$S(E) = k_B \ln \Omega(E) \approx S_1(E_1^*) + S_2(E_2^*)$$



Maximizing  $\Omega(E)$ :  $\frac{1}{k_B} \left[ \frac{\partial S_1}{\partial E_1} \Big|_{x_1} + \frac{\partial S_2}{\partial E_2} \Big|_{x_2} \right] = 0 \quad \underline{E_2 = E - E_1} \quad \frac{\partial S_1}{\partial E_1} \Big|_{x_1} = - \frac{\partial S_2}{\partial E_2} \Big|_{x_2} \frac{\partial E_2}{\partial E_1} \Big|_{x_2} = \frac{\partial S_2}{\partial E_2} \Big|_{x_2}$

An exponentially larger number of states in the vicinity of  $(E_1^*, E_2^*)$  assumption of equal a priori prob.

$(E_1^0, E_2^0) \longrightarrow$  dynamics of evolution amongst these microstates prob. arguments

the amount of time needed to establish equilibrium provide no info.  $\longrightarrow (E_1^*, E_2^*)$

At equilibrium  $\frac{\partial S_1}{\partial E_1} \Big|_{x_1} = \frac{\partial S_2}{\partial E_2} \Big|_{x_2}$  specifies a relation between two funcs of state (empirical temp.)

Based on fundamental result of thermodynamics  $\frac{\partial S}{\partial E} \Big|_x = \frac{1}{T}$

1<sup>st</sup> law: the variation of  $S(E, \vec{x})$  with  $\vec{x}$  by changing the coordinates reversibly by  $\delta \vec{x}$ .  $dU = \vec{J} \cdot \delta \vec{x}$  and  $E' = E + \vec{J} \cdot \delta \vec{x}$

1<sup>st</sup> order change in entropy:  $\delta S = S(E + \vec{J} \cdot \delta \vec{x}, \vec{x} + \delta \vec{x}) - S(E, \vec{x}) = \left( \frac{\partial S}{\partial E} \Big|_{\vec{x}} \cdot \vec{J} + \frac{\partial S}{\partial \vec{x}} \Big|_E \right) \delta \vec{x}$

$$(* F(x+\delta x, y+\delta y) - F(x, y) = \frac{\partial F}{\partial x} \Big|_y \delta x + \frac{\partial F}{\partial y} \Big|_x \cdot \delta y)$$

$\delta S = 0$  (at the most probable state)

$$\frac{\partial S}{\partial x_i} \Big|_{E, x_j \neq i} = - \frac{\partial S}{\partial E} \Big|_{\vec{x}} \cdot J_i = - \frac{J_i}{T}$$

$$\text{Therefore, } dS(E, \vec{x}) = \frac{dE}{T} - \frac{\vec{J} \cdot d\vec{x}}{T} \Rightarrow dE = TdS + \vec{J} \cdot d\vec{x}$$

heat input:  $dQ_{rev} = TdS$

2<sup>nd</sup> law: On the presence of many degrees of  $N \gg 1$ , it's unlikely to find states with energy pairs different from  $(E_1^*, E_2^*)$ :

$$\Omega_1(E_1^*, x_1) \Omega_2(E_2^*, x_2) \geq \Omega_1(E_1, x_1) \Omega_2(E_2, x_2)$$

Evolving to be more likely (and more densely populated) regions, there is an irreversible loss of info. (increase in entropy)

$$\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geq 0$$

$$\delta S = \left( \frac{\partial S_1}{\partial E_1} \Big|_{x_1} - \frac{\partial S_2}{\partial E_2} \Big|_{x_2} \right) \delta E_1 = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \delta E \geq 0$$

\* heat (energy) flows from hotter to colder body (Clausius's statement)

Stability conditions:  $(E_1^*, E_2^*)$  at maximum, second derivative of  $S_1(E_1) + S_2(E_2)$  must be negative at this point

(check section 1.9)

$$\frac{\partial^2 S_1}{\partial E_1^2} \Big|_{x_1} + \frac{\partial^2 S_2}{\partial E_2^2} \Big|_{x_2} \leq 0 \Rightarrow \frac{1}{T_1^2} \frac{\partial T_1}{\partial E_1} \Big|_{x_1} + \frac{1}{T_2^2} \frac{\partial T_2}{\partial E_2} \Big|_{x_2} \geq 0 \quad \underline{dU=0} \quad \text{condition of thermal stability, } C_x \geq 0$$

2<sup>nd</sup> order changes  $\delta^2 S = \frac{1}{2!} \frac{\partial^2 S}{\partial E^2} (\vec{J} \cdot \delta \vec{x})^2 + \frac{\partial^2 S}{\partial E \partial \vec{x}} \vec{J} (\delta \vec{x})^2 + \frac{1}{2!} \frac{\partial^2 S}{\partial \vec{x}^2} (\delta \vec{x})^2 < 0$ , as  $\delta^1 S = 0$ ,  $\delta S \leq 0$  (away from equili.)

meanwhile,  $\frac{\partial^2 S}{\partial x_i \partial x_j} \Big|_E$  be positive-definite (check section 1.9)

#### 4.3 Two-level systems

$N$  impurity atoms trapped in a solid matrix. Each can be one of two states with energy of  $0$  and  $\varepsilon$ .

(Liouville's theorem applies to Hamiltonian evolution in a continuous phase space instead of discrete one)

Occupation number  $\{n_i\}$   $H(\{n_i\}) = \varepsilon \sum_{i=1}^N n_i = EN_1$  ( $N_1 \equiv$  total number in the excited state)

Microcanonical prob.  $P(\{n_i\}) = \frac{1}{\Omega(E, N)} \delta_{\varepsilon \sum_i n_i, E}$

$$N_1 = \frac{E}{\varepsilon} \quad \& \quad \Omega(E, N) = \binom{N}{N_1} = \frac{N!}{N_1!(N-N_1)!} \Rightarrow S(E, N) = k_B \ln \frac{N!}{N_1!(N-N_1)!}$$

Simplified by Stirling's formula in the limit of  $N_1, N \gg 1$

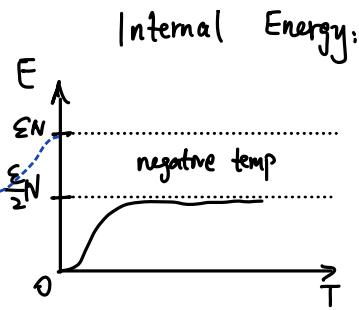
$$S(E, N) \approx k_B \left[ N \ln N - N - N_1 \ln N_1 + N_1 - (N - N_1) \ln (N - N_1) + N - N_1 \right]$$

$$= k_B N \left[ \ln N - \frac{E}{\varepsilon N} \ln \frac{E}{\varepsilon} - \left( 1 - \frac{E}{\varepsilon N} \right) \ln \left( N - \frac{E}{\varepsilon} \right) \right]$$

equilibrium temperature:

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \Big|_N = k_B N \left[ -\frac{1}{\varepsilon N} \ln \frac{E}{\varepsilon} - \frac{1}{N\varepsilon} - \left( 0 - \frac{1}{\varepsilon N} \right) \ln \left( N - \frac{E}{\varepsilon} \right) - \frac{-1}{N\varepsilon} \right] \\ &= -\frac{k_B}{\varepsilon} \ln \frac{E}{N\varepsilon - E} \end{aligned}$$

Macroscopic info for quantities:



$$E(T) = \frac{NE}{\exp(\beta E) + 1} \quad (\beta = \frac{1}{k_B T})$$

- \*  $E$  increases monotonically with  $T$
- \*  $T \rightarrow 0$ ,  $E \rightarrow 0$  and  $T \rightarrow +\infty$ ,  $E \rightarrow \frac{\varepsilon N}{2}$
- \* If  $E > \frac{\varepsilon}{2}N$ ,  $T < 0$  (negative temperature)

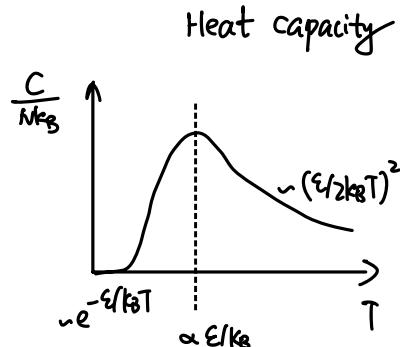
origin: decrease in number of microstates with increasing energy

tradition: two-level system has an upper-bound of energy, so increased energy leads to more order in system.

→ lose excess energy and comes to equilibrium at a positive temperature.  
In world of negative temperature, cool down by adding heat, and heated by remove it.

E.x. prepare a metastable equilibrium of negative temperature in lasers and for magnetic spins.

Negative temperature  $\not\rightarrow$  Universe



$$C = \frac{dE}{dT} = \frac{dE}{d\beta} \frac{d\beta}{dT} = - \frac{N\varepsilon}{(\exp(\beta\varepsilon) + 1)^2} \exp(\beta\varepsilon) \cdot \varepsilon \cdot \left(-\frac{1}{k_B T^2}\right)$$

$$= N k_B \left(\frac{\varepsilon}{k_B T}\right)^2 \exp\left(\frac{\varepsilon}{k_B T}\right) \left[\exp\left(\frac{\varepsilon}{k_B T}\right) + 1\right]^{-2}$$

- \*  $T \rightarrow 0, C_m \rightarrow 0; T \rightarrow +\infty, C_m \rightarrow 0$
- \*  $T \rightarrow 0, C_m \sim \exp(-\varepsilon/k_B T)$ : all systems with an energy gap separating the ground state and lowest excited state.
- \*  $T \rightarrow +\infty, C_m \sim (\varepsilon/2k_B T)^2$ : saturation effect; common to system with a maximum in the number of states as a func. of energy.
- \* The maximum  $C_m$  is at characteristic temperature of  $T_E \propto \varepsilon/k_B$   
(since it is a type of Lambert W func.; no analytical solution)

Microscopic info:

(1) Complete joint prob. distri.:  $P(\{n_i\}) = \frac{1}{\Omega(E, N)} \delta_{\sum_{i=1}^N n_i, E}$

(2) unconditional prob. for exciting a particular impurity

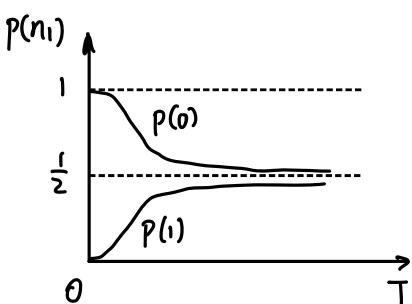
$$P(n_i) = \sum_{\{n_2, \dots, n_N\}} P(\{n_i\}) = \frac{\Omega(E-n_i\varepsilon, N-1)}{\Omega(E, N)} \leftarrow n_i \text{ is in an excited status.}$$

$$P(n_i=0) = \frac{\Omega(E, N-1)}{\Omega(E, N)} = \frac{(N-1)! / [N_i! (N-1-N_i)!]}{N! / [N_i! (N-N_i)!]} = \frac{N-N_i}{N} = 1 - \frac{N_i}{N}$$

$$P(n_i=1) = 1 - P(n_i=0) = \frac{N_i}{N} \quad \& \quad N_i = \frac{E}{\varepsilon} \quad \& \quad E(T) = \frac{N\varepsilon}{\exp(\beta\varepsilon) + 1} \quad (\beta = \frac{1}{k_B T})$$

$$\Rightarrow P(0) = 1 - \frac{E}{\varepsilon N} = 1 - \frac{N\varepsilon}{\varepsilon N [\exp(\beta\varepsilon) + 1]} = \frac{\exp(-\beta\varepsilon)}{\exp(\beta\varepsilon) + 1} = \frac{1}{1 + \exp(-\beta\varepsilon)}$$

$$P(1) = \frac{1}{\exp(\beta\varepsilon) + 1} = \frac{\exp(-\beta\varepsilon)}{1 + \exp(-\beta\varepsilon)} \quad (\beta = \frac{1}{k_B T})$$



## 4.4 The ideal gas

microstates of a gas of  $N$  particles correspond to points  $\mathcal{M} = \{\vec{p}_i, \vec{q}_i\}$  in  $6N$ -dimensional phase space

(ignore gas-gas interaction)

$$\mathcal{H} = \sum_{i=1}^N \left[ \frac{\vec{p}_i^2}{2m_i} + U(\vec{q}_i) \right] \quad U(\vec{q}_i): \text{potential imposed by a box of volume } V$$

A microcanonical ensemble is specified by its energy, volume and number of particles

$$M \equiv (N, V, E)$$

generalized solid angle:

$$S_d = \frac{A}{r^2} = \frac{\text{surface area}}{\text{radius of sphere}}$$

The joint PDF :

$$P(M) = \frac{1}{\Omega(E, V, N)} \cdot \begin{cases} 1 & \text{for } \vec{q}_i \in \text{box, and } \sum_i \vec{p}_i^2 / 2m_i = E (\pm \Delta E) \\ 0 & \text{otherwise} \end{cases}$$

\* coordinates of the particles must be within the box

momenta are constraint to the surface of (hyper-)sphere  $\sum_{i=1}^N \vec{p}_i^2 = 2mE$

$\Rightarrow$  phase space =  $V^N$  (coordinates)  $\cdot$  surface area ( $3N$ -dimensional sphere,  $R = \sqrt{2mE}$ )

(if accept in the energy interval  $E \pm \Delta E$ ; thickness of (hyper-)sphere is  $\Delta R = d(\sqrt{2mE})/dE \cdot \Delta E \cdot 2 = \sqrt{2m/E} \Delta E$ )

$A_d = S_d R^{d-1} \Rightarrow$  How to calculate  $d$ -dimensional solid angle

Sol: consider product of  $d$  Gaussian integrals:

$$I_d = \left( \int_{-\infty}^{+\infty} dx_i e^{-x_i^2} \right)^d = \pi^{d/2}$$

$$= \prod_{i=1}^d dx_i \exp(-x_i^2)$$

$$= \int dV_d \exp(-x_i^2) \quad \text{and} \quad dV_d = S_d R^{d-1} dR$$

$$= \int_0^{+\infty} dR S_d R^{d-1} e^{-R^2} \quad \text{and} \quad \text{let } R = \sqrt{y}, \quad dR = \frac{1}{2} y^{-\frac{1}{2}} dy$$

$$= \frac{S_d}{2} \int_0^{+\infty} dy y^{d/2-1} e^{-y} \quad \text{and} \quad \Gamma(z) = \int_0^{+\infty} t^{z-1} e^{-t} dt = (z-1)! \quad (\text{in chapter 2})$$

$$= \frac{S_d}{2} \left( \frac{d}{2} - 1 \right) !$$

$$\Rightarrow S_d = \frac{2\pi^{d/2}}{(d/2 - 1)!}$$

$$\Omega(E, V, N) = V^N \cdot \frac{2\pi^{3N/2}}{(3N/2 - 1)!} (2mE)^{(3N-1)/2} \Delta R$$

volume of  $\vec{x}$      $S_d$      $R^{d-1}$     thickness  
volume of  $\vec{p}$

$$\Omega(E, V, N) \approx V^N \cdot \frac{3N\pi^{3N/2}}{(3N/2)!} (2m)^{3N/2} E^{(3N-2)/2} \Delta E \approx V^N \frac{(2m\pi E)^{3N/2}}{(3N/2)!} \cdot \frac{3N\Delta E}{E}$$

Entropy (in large  $N$  limit)

for distinct particles

$$\begin{aligned} S(E, V, N) &= k_B \ln \Omega(E, V, N) \approx k_B N \left( \ln V + \frac{3}{2} \ln (2m\pi E) - \frac{3}{2} \ln \frac{3N}{2} + \frac{3}{2} \right) + k_B \ln \frac{3N\Delta E}{E} \\ &= N k_B \ln \left[ V \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + k_B \ln \left( \frac{3\Delta E}{E} \right) \quad (\varepsilon = \frac{E}{N}) \\ &\approx N k_B \ln \left[ V \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] \quad \boxed{\varepsilon \sim \Delta E} \end{aligned}$$

Properties of the ideal gas:

$$\text{from } Tds = dE + pdV - \mu dN, \quad \frac{1}{T} = \frac{\partial S}{\partial E} \Big|_{V,N} = Nk_B \frac{3}{2} \frac{1}{E}, \quad , \quad \frac{P}{T} = \frac{\partial S}{\partial V} \Big|_{E,N} = \frac{Nk_B}{V}$$

Internal energy:  $E = \frac{3}{2} N k_B T$ ;  $E$  is only a func. of  $T$

Heat capacity:  $C_V = \left. \frac{\partial Q}{\partial T} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{3}{2} N k_B$ ;  $C_V$  is a constant

Eqn. of state:  $pV = Nk_B T$

unconditional prob. of finding a particle of mom.  $\vec{p}_i$  in the gas

$$p(\vec{p}_i) = \int d^3 \vec{q}_i \prod_{i=1}^N d^3 \vec{q}_i d^3 \vec{p}_i p(\{\vec{p}_i, \vec{q}_i\}) \quad \& \quad P(u) = \begin{cases} 1 & u \in \Omega(E, V, N) \\ 0 & \text{otherwise} \end{cases} \dots$$

$$= \frac{V \Omega(E - \vec{p}_i^2/2m, V, N-1)}{\Omega(E, V, N)} \quad (\Delta_R \text{ almost the same})$$

$$= V \frac{V^{N-1} \pi^{3(N-1)/2} (2mE - \vec{p}_i^2)^{(3N-4)/2}}{(3(N-1)/2 - 1)!} \cdot \frac{(3N/2 - 1)!}{V^N \pi^{3N/2} (2mE)^{(3N-1)/2}}$$

$$= \left(1 - \frac{\vec{p}_i^2}{2mE}\right)^{3N/2-2} \left(\frac{1}{2\pi mE}\right)^{3/2} \frac{(3N/2 - 1)!}{(3(N-1)/2 - 1)!}$$

\*  $\ln(3N/2 - 1)! = (\frac{3}{2}N - 1) \ln(\frac{3}{2}N - 1) - \frac{3}{2}N + 1 \dots \textcircled{1}$

$\ln(3(N-1)/2 - 1)! = (\frac{3}{2}N - \frac{5}{2}) \ln(\frac{3}{2}N - \frac{5}{2}) - \frac{3}{2}N + \frac{5}{2} \dots \textcircled{2}$

$$\textcircled{1} - \textcircled{2}: \quad \left(\frac{3}{2}N - 1\right) \ln \frac{\frac{3}{2}N - 1}{\frac{3}{2}N - \frac{5}{2}} + \frac{3}{2} \ln \left(\frac{3}{2}N - \frac{5}{2}\right) - \frac{3}{2} \xrightarrow[N \rightarrow \infty]{(E \rightarrow \infty)} \frac{3}{2} \ln \left(\frac{3}{2}N\right)$$

\*  $\ln \left(1 - \frac{\vec{p}_i^2}{2mE}\right)^{3N/2-2} = \left(\frac{3N}{2} - 2\right) \ln \left(1 - \frac{\vec{p}_i^2}{2mE}\right) \xrightarrow[N \rightarrow \infty]{(E \rightarrow \infty)} \frac{3N}{2} \cdot \left(-\frac{\vec{p}_i^2}{2mE}\right)$

\*  $E = \frac{3}{2} N k_B T$

$$P(\vec{p}_i) = \exp\left(-\frac{3}{2}N \frac{\vec{p}_i^2}{3Nk_B T}\right) \cdot \left(\frac{1}{3\pi N m k_B T}\right)^{\frac{3}{2}} \left(\frac{3}{2}N\right)^{\frac{3}{2}}$$

$$= \left(\frac{1}{2\pi m k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{\vec{p}_i^2}{2m k_B T}\right)$$

#### 4.5 Mixing entropy and the Gibbs paradox

Entropy of ideal gas in 4.4 is not extensive.  $(E, V, N) \rightarrow (\lambda E, \lambda V, \lambda N)$ ;  $S \rightarrow \lambda(S + Nk_B \ln \lambda)$

Additional term comes from the contribution of  $V^N$  of the coordinates to the available phase space.

Mixing entropy of two gases:

$V_1, N_1$ gas 1	$V_2, N_2$ gas 2
same T	

two distinct gas

$$S_i = S_1 + S_2 = N_1 k_B (\ln V_1 + \sigma_1) + N_2 k_B (\ln V_2 + \sigma_2)$$

$$\text{and } \sigma_\alpha = \ln \left( \frac{4\pi e M_\alpha E_\alpha}{3N_\alpha} \right)^{\frac{3}{2}} \quad \frac{E_\alpha / N_\alpha = \frac{3}{2} k_B T}{\text{momentum contribution}} \quad \sigma_\alpha = \frac{3}{2} \ln (2\pi e m_\alpha k_B T)$$

Temperature is unchanged by mixing

$$* \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T; \quad E_f = E_1 + E_2 = \frac{3}{2} (N_1 + N_2) k_B T = \frac{3}{2} N_f k_B T_f \Rightarrow T_f = T$$

$$S_f = N_1 k_B \ln(V_1 + V_2) + N_2 k_B \ln(V_1 + V_2) + k_B(N_1 \sigma_1 + N_2 \sigma_2)$$

no change in contribution from the momenta, which only depends on Temp.

$$\Delta S_{\text{mixing}} = S_f - S_i = N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2} = -Nk_B \left[ \frac{N_1}{N} \ln \frac{V_1}{V} + \frac{N_2}{N} \ln \frac{V_2}{V} \right]$$

solely from the contribution of the coordinates

Generalizing to the mixing  
of many components at  
the same temperature.

$$\Delta S_{\text{mix}} = -Nk_B \sum_\alpha \left( \frac{N_\alpha}{N} \right) \ln \left( \frac{V_\alpha}{V} \right)$$

Gibbs paradox:

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same T

two identical gas with same density

$$N_1/V_1 = N_2/V_2$$

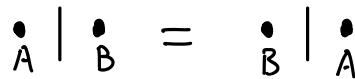
modified volume in phase space:

modified entropy:

Exchange of distinct particles leads to 2 configurations



Exchange of identical particles leads to only 1 configuration.



$N!$  permutations leads to indistinguishable microstates

$$\Omega(N, V, E) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(3N/2 - 1)!} (2mE)^{(3N-1)/2} \Delta_R$$

$$S(N, V, E) = k_B [N \ln V - N \ln N + N] + Nk_B \sigma = Nk_B \left[ \ln \frac{eV}{N} + \sigma \right]$$

\*  $V \rightarrow V/N$ ; modified S is extensive.

$$\text{Mixing of distinct gas: } \Delta S_{\text{mix}} = S_f - S_i = N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2} - \left( N_1 k_B \ln \frac{V_1}{V_1} + N_2 k_B \ln \frac{V_2}{V_2} \right)$$

$$= -Nk_B \left[ \frac{N_1}{N} \ln \frac{V_1}{V} + \frac{N_2}{N} \ln \frac{V_2}{V} \right] \quad (\text{exactly as obtained before})$$

"Mixing" of identical gas  
(with  $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1+N_2}{V_1+V_2}$ )

$$\Delta S_{\text{mix}} = S_f - S_i = (N_1 + N_2) k_B \ln \frac{V_1 + V_2}{N_1 + N_2} - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2} = 0$$

Note: After considering the permutation of identical particles into account.

coordinate volume in final state:  $\sqrt{N_1+N_2} / N_1! N_2!$  for distinct particles

$\sqrt{N_1+N_2} / (N_1+N_2)!$  for identical particles

Additional comments for the microcanonical entropy:

1. In the example of two-level impurities in a solid matrix (Section 4.3), there is no need for the additional factor of  $N!$ , as the defects can be distinguished by the locations.

2. The corrected formula for the ideal gas entropy does not affect the computations of energy  $(\partial S / \partial E)_{N,V}$  and pressure  $(\partial S / \partial V)_{N,E}$ . But essential for obtaining an intensive chemical potential

$$\frac{\mu}{T} = -\left. \frac{\partial S}{\partial N} \right|_{E,V} = -k_B \left( \ln \frac{eV}{N} + \sigma \right) - N k_B \left( -\frac{1}{N} - \frac{3}{2} \frac{1}{N} \right) = -k_B \ln \left[ \frac{N}{V} \left( \frac{4\pi e M E}{3N} \right)^{\frac{3}{2}} \right]$$

$$* S_\alpha = N_\alpha k_B \left( \ln \frac{eV_\alpha}{N_\alpha} + \sigma_\alpha \right) \text{ with } \sigma_\alpha = \ln \left( \frac{4\pi e M_\alpha E_\alpha}{3N_\alpha} \right)^{\frac{3}{2}}$$

3. Additional postulate of classical statistical mechanics: indistinguishability.

Description of identical particles in QM requires proper symmetrization of wave func. Its microstates naturally yield the  $N!$  factor.

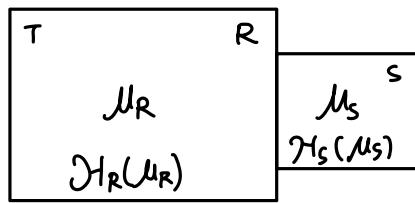
4. Problems of arbitrary constant that appears in changing the units of measurement for  $\vec{q}$  and  $\vec{p}$ . The volume of phase space involves products  $\vec{p}\vec{q}$  (coordinates \* conjugate momenta), with unit  $(\text{action})^N$   
In QM, action  $\propto$  Plank constant ( $\hbar$ )

phase space for identical particles

$$d\Gamma_N = \frac{1}{\hbar^{3N} N!} \prod_{i=1}^N d^3 \vec{p}_i d^3 \vec{q}_i$$

#### 4.6 The canonical ensemble

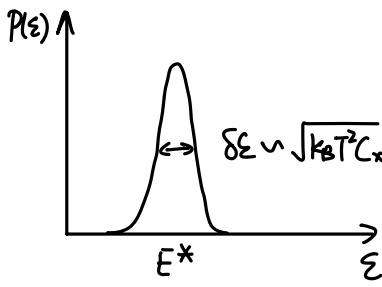
$M \equiv (T, \vec{x})$ , allowing the input heat into the system, but no external work.



System S maintains the same temperature through contact with reservoir R. The temperature doesn't change with reservoir R which is very large.

Similar to two-level system  $\Rightarrow$   
and ideal gas  
(a portion of the system in equili.  
with the rest of it)

Question: Is  $E$  of system S well defined? (By changing variable from  $\mu$  to  $H(\mu)$ )



Combined system  $R \oplus S$  belongs to a microcanonical ensemble of energy  $E_{\text{tot}} \gg E_S$ , so the joint probability of microstates  $(M_R \otimes M_S)$  is

$$P(M_S \otimes M_R) = \frac{1}{\Omega_{S \oplus R}(E_{\text{tot}})} \cdot \begin{cases} 1, & \text{for } H_S(M_S) + H_R(M_R) = E_{\text{tot}} \\ 0, & \text{otherwise} \end{cases}$$

Unconditional prob. for microstates of S

$$P(M_S) = \sum_{\{M_R\}} P(M_S \otimes M_R) = \frac{\Omega_R(E_{\text{tot}} - H_S(M_S))}{\Omega_{S \oplus R}(E_{\text{tot}})} \propto \exp \left[ \frac{1}{k_B} S_R(E_{\text{tot}} - H_S(M_S)) \right]$$

By assumption:  $E_{\text{tot}} \gg E_S$ , do Taylor expansion at  $E_{\text{tot}}$

$$S_R(E_{\text{tot}} - H_S(M_S)) \approx S_R(E_{\text{tot}}) - H_S(M_S) \frac{\partial S_R}{\partial E_R} = S_R(E_{\text{tot}}) - \frac{H_S(M_S)}{T}$$

Normalized prob. (Partition func)

$$P_{(T, \vec{x})}(\mu) = \frac{e^{-\beta H(\mu)}}{Z(T, \vec{x})} \quad \text{with } Z(T, \vec{x}) = \sum_{\{M\}} e^{-\beta H(M)}, \quad \beta = \frac{1}{k_B T}$$

\* Unbiased estimates obtained (as section 2.7) by constraining the average energy.

$$P(E) = \sum_{\{M\}} P(M) \delta(H(M) - E) = \frac{e^{-\beta E}}{Z} \sum_{\{M\}} \delta(H(M) - E)$$

Restricted sum is the number  $\Omega(E)$  of microstates of appropriate energy.

$$P(E) = \frac{\Omega(E) e^{-\beta E}}{Z} = \frac{1}{Z} \exp \left[ \frac{S(E)}{k_B} - \frac{E}{k_B T} \right] = \frac{1}{Z} \exp \left[ -\frac{F(E)}{k_B T} \right]$$

\* Helmholtz free energy:  $F = E - TS(E)$

\*  $P(E)$  is sharply peaked at a most probable energy  $E^*$ , minimizing  $F(E)$   
(Using section 2.6 for summing over integrals)

$$Z = \sum_{\{M\}} e^{-\beta H(M)} = \sum_E e^{-\beta F(E)} \approx e^{-\beta F(E^*)} \quad \dots (1) \text{ at most probable energy}$$

Average energy:

$$\langle H \rangle = \sum_M H(M) \frac{e^{-\beta H(M)}}{Z} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_M e^{-\beta H} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \quad \dots (2)$$

In thermodynamics, similarly  $E = F + TS = F - T \frac{\partial F}{\partial T} \Big|_{\vec{x}} = -T^2 \frac{\partial}{\partial T} \left( \frac{F}{T} \right) = \frac{\partial (\beta F)}{\partial \beta}$

① & ②  $F(T, \vec{x}) = -k_B T \ln Z(T, \vec{x})$

How close are the most probable energy ( $E^*$ ) and the average energy ( $\langle \mathcal{H} \rangle$ )

$\Rightarrow$  the width of the prob. distri.  $p(\varepsilon)$  by computing the variance  $\langle \mathcal{H}^2 \rangle_c$

from characteristic func.  
(with  $\beta$  replacing  $i\kappa$ )

$$-\frac{\partial \mathcal{Z}}{\partial \beta} = \sum_{\mu} \mathcal{H} e^{-\beta \mathcal{H}} \quad \text{and} \quad -\frac{\partial^2 \mathcal{Z}}{\partial \beta^2} = \sum_{\mu} \mathcal{H}^2 e^{-\beta \mathcal{H}}$$

$$\text{Cumulants of } \mathcal{H}, \langle \mathcal{H} \rangle_c, \quad \langle \mathcal{H} \rangle_c = \frac{1}{\mathcal{Z}} \sum_{\mu} \mathcal{H} e^{-\beta \mathcal{H}} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} = \frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

$$\langle \mathcal{H}^2 \rangle_c, \quad \langle \mathcal{H}^2 \rangle_c = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{1}{\mathcal{Z}} \sum_{\mu} \mathcal{H}^2 e^{-\beta \mathcal{H}} - \frac{1}{\mathcal{Z}} \left( \sum_{\mu} \mathcal{H} e^{-\beta \mathcal{H}} \right)^2 = \frac{\partial^2 \ln \mathcal{Z}}{\partial \beta^2} = -\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta}$$

$$\text{More generally, } \langle \mathcal{H}^n \rangle_c, \quad \langle \mathcal{H}^n \rangle_c = (-1)^n \frac{\partial^n \ln \mathcal{Z}}{\partial \beta^n} \propto N, \text{ as } \mathcal{Z} = \mathcal{Z}(N, \vec{\alpha}, T)$$

$$\langle \mathcal{H}^2 \rangle_c = -\frac{\partial \langle \mathcal{H} \rangle}{\partial (1/k_B T)} = k_B T^2 \frac{\partial \langle \mathcal{H} \rangle}{\partial T} \Big|_X \Rightarrow \langle \mathcal{H}^2 \rangle_c = k_B T^2 C_X \quad (\text{variance})$$

$$* \sqrt{\langle \mathcal{H}^2 \rangle_c} \propto N^{1/2};$$

relative error  $\sqrt{\langle \mathcal{H}^2 \rangle_c} / \langle \mathcal{H} \rangle_c$  in thermodynamic limit,  $\propto N^{-1/2}$

PDF for energy in a canonical ensemble

$$p(\varepsilon) = \frac{1}{\mathcal{Z}} e^{-\beta F(\varepsilon)} \approx \frac{1}{\sqrt{2\pi k_B T^2 C_X}} \exp\left[-\frac{(\varepsilon - \langle \mathcal{H} \rangle)^2}{2k_B T^2 C_X}\right]$$

\* The mean and most likely energies interchangeably

\* Distribution is sufficiently sharp to make unambiguous internal energy in canonical ensemble in thermodynamic limit ( $N \rightarrow \infty$ )

\* Care about whether  $C_X$  is divergent in continuous phase transition.

(Use eqn in Section 2.7 and  $\mathcal{Z} \approx e^{-\beta F(E^*)}$ )

$$S = -k_B \langle \ln p(\mu) \rangle = -k_B \langle (-\beta \mathcal{H} - \ln \mathcal{Z}) \rangle = (E - F)/T$$

For finite system, canonical and microcanonical properties are distinct.

For infinite system, thermodynamics limit ( $N \rightarrow \infty$ ), the prob. of canonical ensemble is so sharply peaked around the average energy. Two ensembles are indistinguishable.

Ensemble	Macrostate	$p(\mu)$	Normalization
Microcanonical	$(E, \vec{\alpha})$	$\delta_{\Delta}(\mathcal{H}(\mu) - E) / \Omega$	$S(E, \vec{\alpha}) = k_B \ln \Omega$
Canonical	$(T, \vec{\alpha})$	$\exp(-\beta \mathcal{H}(\mu)) / \mathcal{Z}$	$F(T, \vec{\alpha}) = -k_B T \ln \mathcal{Z}$

## 4.7 Canonical examples

Re-examine Section 4.3 and 4.4

① Two-level systems:

$N$  impurities; macrostate  $M \equiv (T, N)$ ; microstates  $\mathcal{M} = \{n_i\}$

$$(1) \quad H = \epsilon \sum_{i=1}^N n_i, \quad P(\{n_i\}) = \frac{1}{Z} \exp \left[ -\beta \epsilon \sum_{i=1}^N n_i \right]$$

$$(2) \quad Z(T, N) = \sum_{\{n_i\}} \exp \left[ -\beta \epsilon \sum_{i=1}^N n_i \right] = \left( \sum_{n_1=0}^1 e^{-\beta \epsilon n_1} \right) \cdots \left( \sum_{n_N=0}^1 e^{-\beta \epsilon n_N} \right) = (1 + e^{-\beta \epsilon})^N$$

$$(3) \quad F(T, N) = -k_B T \ln Z = -N k_B T \ln [1 + e^{-\epsilon/(k_B T)}] \quad \leftarrow \text{thermodynamic limit}$$

$$(4) \quad S = -\frac{\partial F}{\partial T} \Big|_N = N k_B \ln [1 + e^{-\epsilon/(k_B T)}] + \frac{N\epsilon}{T} \frac{e^{-\epsilon/(k_B T)}}{1 + e^{-\epsilon/(k_B T)}}$$

$$(5) \quad E = F + TS = \frac{N\epsilon}{1 + e^{\epsilon/(k_B T)}} \quad \text{or} \quad = -\frac{\partial \ln Z}{\partial \beta} = \frac{N\epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}}$$

Joint prob. is in the form of

a product  $P = \prod_{i=1}^N p_i$ . The excitation

$$p_i(n_i) = \frac{e^{-\beta \epsilon n_i}}{1 + e^{-\beta \epsilon}} \quad \sim \text{similar to } P(n_i) \text{ in Section 4.3}$$

of different impurities are indepe. \* In thermodynamic limit ( $N \rightarrow \infty$ ), canonical and microcanonical ensembles describe the same physics, both at macro or micro levels.  
of each other  $\Rightarrow$  uncond. prob.

② Ideal gas:

Canonical macrostate  $M \equiv (T, V, N)$ ;

(1) joint PDF for microstates  $\mathcal{M} \equiv \{\vec{p}_i, \vec{q}_i\}$

$$P(\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{Z} \exp \left[ -\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \in \text{box} \\ 0 & \text{otherwise} \end{cases}$$

(2) As phase space  $\equiv \frac{1}{h^{3N} N!} \prod_{i=1}^N d^3 \vec{q}_i d^3 \vec{p}_i$

$$\begin{aligned} Z(T, V, N) &= \int \frac{1}{N!} \prod_{i=1}^N \frac{d^3 \vec{q}_i d^3 \vec{p}_i}{h^3} \exp \left[ -\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \right] \\ &= \frac{V^N}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} = \frac{1}{N!} \left( \frac{V}{\lambda(T)^3} \right)^N \end{aligned}$$

Thermal wavelength where  $\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$  (a characteristic length associated with action  $h$ )

\* This length scale controls the onset of quantum mechanical effects in ideal gas.

$$(3) \quad F = -k_B T \ln Z = -N k_B T \ln V + N k_B T \ln N - N k_B T - \frac{3N}{2} k_B T / n \left( \frac{2\pi m k_B T}{h^2} \right)$$

$$= -N k_B T \left[ \ln \left( \frac{V_0}{N} \right) + \frac{3}{2} \ln \left( \frac{2\pi m k_B T}{h^2} \right) \right]$$

$$(4) \quad \text{As } dF = -SdT - pdV + \mu dN$$

$$-S = \left. \frac{\partial F}{\partial T} \right|_{V,N} = -N k_B \left[ \ln \left( \frac{V_0}{N} \right) + \frac{3}{2} \ln \left( \frac{2\pi m k_B T}{h^2} \right) \right] - N k_B T \frac{3}{2T} = \frac{F-E}{T}$$

$$(5) \Rightarrow E = \frac{3}{2} N k_B T$$

$$(6) \quad P = - \left. \frac{\partial F}{\partial V} \right|_{T,N} = + N k_B T \frac{1}{V} \Rightarrow PV = N k_B T$$

$$(7) \quad \mu = \left. \frac{\partial F}{\partial N} \right|_{T,V} = \frac{F}{N} + k_B T = \frac{E - TS + PV}{N} = k_B T / n(n\lambda^3)$$

$$(8) \quad P(\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{Z} \exp \left[ -\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \in \text{box} \\ 0 & \text{otherwise} \end{cases}.$$

the momenta of  $N$  particles are taken from independent Maxwell-Boltzmann distributions, consistent with  $P(\vec{p}_i) = \left( \frac{1}{2\pi m k_B T} \right)^{\frac{3}{2}} \exp \left( -\frac{\vec{p}_i^2}{2m k_B T} \right)$

## 4.8 The Gibbs canonical ensemble

The internal energy changes by the addition of both heat and work. Macrostate  $M \equiv (T, \vec{J})$

Thermodynamic coordinates  $\vec{x}$  appear as additional random variables

At constant force through external elements. Including the work done against the forces, the energy of the combined system is  $H - \vec{J} \cdot \vec{x}$  (As the internal and external coordinates  $\vec{x}$  have the opposite signs)

Microstates of combined system  
with canonical prob.

$$P(\vec{\mu}_S, \vec{x}) = \exp[-\beta H(\vec{\mu}_S) + \beta \vec{J} \cdot \vec{x}] / \mathcal{Z}(T, N, \vec{J})$$

Gibbs partition func

$$\mathcal{Z}(T, N, \vec{J}) = \sum_{\vec{\mu}_S, \vec{x}} e^{\beta \vec{J} \cdot \vec{x} - \beta H(\vec{\mu}_S)} \quad (\text{no chemical work})$$

Expectation of the coordinates

$$\langle \vec{x} \rangle = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \vec{J}} \quad \text{with thermodynamic identity} \quad \vec{x} = - \frac{\partial G}{\partial \vec{J}}$$

$$\Rightarrow G(N, T, \vec{J}) = -k_B T \ln \mathcal{Z}$$

Gibbs free energy:  $G = E - TS - \vec{x} \cdot \vec{J}$  (or maximize the prob. w.r.t.  $\vec{x}$ )

Enthalpy:  $H = E - \vec{x} \cdot \vec{J}$

$$-\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \langle H - \vec{x} \cdot \vec{J} \rangle = H$$

Heat capacity at constant force (including work done against the external force)

$$C_J = \frac{\partial H}{\partial T}$$

Examples using Gibbs canonical ens.

(1) ideal gas in the isobaric ensemble maintained at P ①

Macrostate:  $M \equiv (T, P, N)$ ; microstate  $m = \{\vec{p}_i, \vec{q}_i\}$  with volume V

$$P(\{\vec{p}_i, \vec{q}_i\}, V) = \frac{1}{\mathcal{Z}} \exp\left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m} - \beta PV\right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \in \text{box of volume } V \\ 0 & \text{otherwise} \end{cases}$$

$$\begin{aligned} \mathcal{Z}(T, P, N) &= \int_0^\infty dV e^{-\beta PV} \int \frac{1}{N!} \prod_{i=1}^N \frac{d^3 p_i d^3 q_i}{h^3} \exp\left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m}\right] \\ &= \int_0^\infty dV V^N e^{-\beta PV} \frac{1}{N! \lambda(T)^{3N}} = \frac{1}{(\beta P)^{N+1} \lambda(T)^{3N}} \end{aligned}$$

$$\textcircled{3} \quad G = -k_B T \ln \mathcal{Z} \approx N k_B T \left[ \ln P - \frac{5}{2} \ln k_B T + \frac{3}{2} \ln \left( \frac{\hbar^2}{2 \pi m} \right) \right]$$

ignore non-extensive contributions:  $\frac{\ln P}{N} \rightarrow 0$  and  $\frac{\ln k_B T}{N} \rightarrow 0$  as  $N \rightarrow \infty$

$$\textcircled{4} \quad \text{from } dG = -SdT + Vdp + \mu dN$$

$$V = \frac{\partial G}{\partial P}_{T,N} = \frac{N k_B T}{P} \Rightarrow PV = N k_B T$$

$$\textcircled{5} \quad \text{enthalpy } H = \langle E + PV \rangle$$

$$H = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{5}{2} N k_B T \Rightarrow C_P = \frac{\partial H}{\partial T} = \frac{5}{2} N k_B$$

(2) Spins in an external magnetic field  $\vec{B}$

$$\mathcal{Z}(N, T, B) = \text{tr} [\exp(-\beta H + \beta \vec{B} \cdot \vec{M})]$$

\*  $\vec{M}$  net magnetization

\* tr the sum over all spins of freedom (in QM formalism, are restricted to discrete values)

spin of  $1/2$ :  $\ell_s = \frac{1}{2}$

projections along fields:  $m_s = \pm \frac{1}{2}$

Microstates of  $N$  spins : the set of Ising variables  $\{\sigma_i = \pm 1\}$

$M = M_0 \sum_{i=1}^N \sigma_i$ , where  $M_0$  is a microscopic magnetic moment

① Assume no interactions between spins ( $H=0$ )

$$P(\{\sigma_i\}) = \frac{1}{8} \exp \left[ \beta B M_0 \sum_{i=1}^N \sigma_i \right]$$

$$\textcircled{2} \quad \mathcal{Z}(N, T, B) = \sum_{\{\sigma_i\}} \exp \left[ \beta B M_0 \sum_{i=1}^N \sigma_i \right] = \left( \exp[\beta B M_0] + \exp[-\beta B M_0] \right)^N$$

$$= [2 \cosh(\beta B M_0)]^N \quad \sim \text{similar to two-level system}$$

$$\textcircled{3} \quad G = -k_B T \ln \mathcal{Z} = -N k_B T \ln [2 \cosh(\beta B M_0)]$$

④ Average magnetization:

$$M = \langle M \rangle = -\frac{\partial G}{\partial B} = N M_0 \tanh(\beta B M_0)$$

⑤ Expanding average magnetization for small  $B$

$\Rightarrow$  Curie law for magnetic susceptibility of non-interacting spins

$$\chi(T) = \left. \frac{\partial M}{\partial B} \right|_{B=0} = \left. \frac{N M_0^2}{k_B T} \operatorname{sech}^2(B \beta M_0) \right|_{B=0} = \frac{N M_0^2}{k_B T}$$

$$(* \operatorname{sech}(x) = 2/(e^x + e^{-x}))$$

⑥ Enthalpy:  $H = \langle E - BM \rangle = -BM$ , and

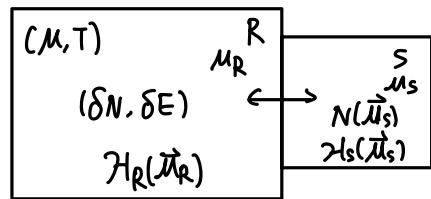
$$C_B = -B \frac{\partial M}{\partial T}$$

#### 4.9 The grand canonical ensemble

(In section 4.b)

In thermodynamics limit ( $N \rightarrow \infty$ ), microcanonical ensemble  $\stackrel{\triangle}{=}$  canonical ensemble (easier to compute in can. ens.)

Allow chemical work (by fixing  $\mu$  instead of  $N$ ), but no mechanical work. Macrostates  $M \equiv (T, \mu, \vec{x})$



Microstates  $\mu_S$  contains an infinite number of particles  $N(\vec{\mu}_S)$   
system  $S$  can be maintained at constant chemical potential ( $\mu$ ) through  
contact with a reservoir  $R$ , at  $T$  and  $\mu$ .

By summing over all states of reservoir (similar as the one in Section 4.b)

$$\textcircled{1} \quad p(\vec{\mu}_S) = \exp [\beta \mu N(\vec{\mu}_S) - \beta H(\vec{\mu}_S)] / Q$$

$$\textcircled{2} \quad \text{Grand Partition func. } Q(T, \mu, \vec{x}) = \sum_{\vec{\mu}_S} e^{\beta \mu N(\vec{\mu}_S) - \beta H(\vec{\mu}_S)} = \boxed{\sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{(\vec{\mu}_S|N)} e^{-\beta H_N(\vec{\mu}_S)}}$$

summation by grouping all microstates with a given num. of particles  
\* restricted sums are just the  $N$ -particle partitn funcs.

$$\textcircled{3} \quad \text{unconditional prob. of finding } N \text{ particles in the system} \quad \text{As each term in } Q \text{ is total weight of all microstates of } N \text{ particles.}$$

$$P(N) = \frac{e^{\beta \mu N} Z(T, N, \vec{x})}{Q(T, \mu, \vec{x})}$$

$$\textcircled{4} \quad \text{Average number of particles in the system} \quad \langle N \rangle = \frac{1}{Q} \frac{\partial}{\partial (\beta \mu)} Q = \frac{\partial (\ln Q)}{\partial (\beta \mu)}$$

$$\textcircled{5} \quad \text{number fluctuations (var)} \quad \langle N^2 \rangle_c = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{Q} \frac{\partial^2}{\partial (\beta \mu)^2} \ln Q - \left( \frac{\partial}{\partial (\beta \mu)} \ln Q \right)^2 = \frac{\partial^2 (\ln Q)}{\partial (\beta \mu)^2} = \frac{\partial \langle N \rangle}{\partial (\beta \mu)}$$

\*  $\langle N^2 \rangle_c \propto N$ ; relative number fluctuation  $\sqrt{\langle N^2 \rangle_c / \langle N \rangle} \propto N^{-1/2} \rightarrow 0$  ( $N \rightarrow \infty$ )  
in thermodynamic limit. Similar to Section 4.b

$\textcircled{6}$  The sharpness of the distribution for  $N$ , the sum in grand partition func can be approximated by its largest term at  $N = N^* \approx \langle N \rangle$

$$Q(T, \mu, \vec{x}) = \lim_{N \rightarrow \infty} \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, N, \vec{x}) = e^{\beta \mu N^*} Z(T, N^*, \vec{x}) = e^{\beta \mu N^* - \beta F}$$

$$= e^{-\beta(-\mu N^* + E - TS)} = e^{-\beta G}$$

$$\text{Grand potential } G(T, \vec{x}, \mu) = E - TS - \mu N^* = -k_B T \ln Q$$

$$\text{Thermodynamic info: } dG = -SdT - Nd\mu + \vec{J} \cdot d\vec{x} \quad \text{as} \quad -S = \frac{\partial G}{\partial T} \Big|_{\vec{x}, \mu}, \quad N = \frac{\partial G}{\partial \mu} \Big|_{T, \vec{x}}, \quad J_i = \frac{\partial G}{\partial x_i} \Big|_{T, \mu, \vec{x}_{j \neq i}}$$

Example: ideal gas of non-interacting particles in the grand canonical ensemble.

Macrostates:  $M \equiv (T, \mu, V)$

Microstates:  $\{\vec{p}_i, \vec{q}_i\}$  infinite number of particle

① Grand partition func.  $Q(T, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{N!} \int \prod_{i=1}^N \frac{d^3 \vec{p}_i d^3 \vec{q}_i}{h^3} \exp\left(-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}\right)$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{N!} \left(\frac{V}{\lambda^3}\right)^N \quad \text{w.r.t. } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$
$$= \exp\left[e^{\beta \mu} \frac{V}{\lambda^3}\right]$$

② Grand potential  $G(T, \mu, V) = -k_B T \ln Q = -k_B T e^{\beta \mu} \frac{V}{\lambda^3}$

③ Gas pressure  
 $P = -\frac{\partial G}{\partial V} = -\left.\frac{\partial S}{\partial V}\right|_{T, \mu} = k_B T \frac{e^{\beta \mu}}{\lambda^3}$

④ Particle number  $N = -\left.\frac{\partial G}{\partial \mu}\right|_{T, V} = \frac{V e^{\beta \mu}}{\lambda^3}$

⑤ Eqn. of state  $P = k_B T N / V$

⑥ Chemical potential  $\mu = k_B T \ln\left(\frac{\lambda^3 N}{V}\right) = k_B T \ln\left(\frac{\lambda^3 P}{k_B T}\right)$