

Statistical Mechanics II

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Lecture 7 Canonical and Giant Canonical Ensemble Theory

Outline

- Derive the distribution function of canonical ensemble from micro-canonical ensemble or maximum entropy principle
- Calculating thermodynamical property using canonical ensemble (distribution function of energy, free energy, TLS, free gas)
- Gibbs canonical ensemble (Gibbs free energy, TLS, ideal gas)
- giant canonical ensemble (Giant potential, TLS, ideal gas)

不同系综适合于不同的物理情形：正则系综适用于封闭系统（和外界不存在物质，功的交换，但是可以存在热能交换的系统，或者说和一个恒温热库相接触的一个系统）

Canonical ensemble

Derive canonical ensemble from microcanonical ensemble

$$p(\mu_S \otimes \mu_R) = \frac{1}{\Omega_{S \oplus R}(E_{\text{Tot}})} \cdot \begin{cases} 1 & \text{for } \mathcal{H}_S(\mu_S) + \mathcal{H}_R(\mu_R) = E_{\text{Tot}} \\ 0 & \text{otherwise} \end{cases}$$

$$E_{\text{Tot}} \gg E_S$$

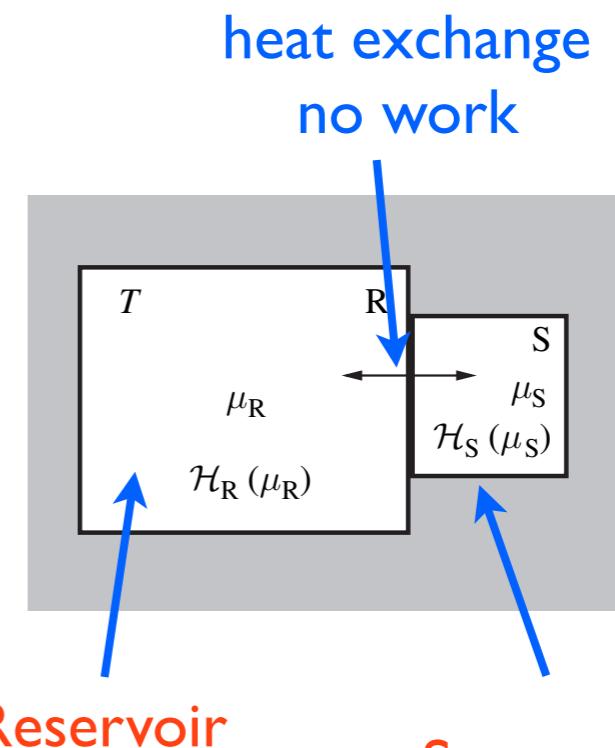
$$p(\mu_S) = \sum_{\{\mu_R\}} p(\mu_S \otimes \mu_R)$$

**the probability
of a microstate** μ_S

$$p(\mu_S) = \frac{\Omega_R(E_{\text{Tot}} - \mathcal{H}_S(\mu_S))}{\Omega_{S \oplus R}(E_{\text{Tot}})} \propto \exp \left[\frac{1}{k_B} S_R(E_{\text{Tot}} - \mathcal{H}_S(\mu_S)) \right]$$

$$E_{\text{Tot}} \gg E_S$$

$$S_R(E_{\text{Tot}} - \mathcal{H}_S(\mu_S)) \approx S_R(E_{\text{Tot}}) - \mathcal{H}_S(\mu_S) \frac{\partial S_R}{\partial E_R} = S_R(E_{\text{Tot}}) - \frac{\mathcal{H}_S(\mu_S)}{T}$$



$$p_{(T, \mathbf{x})}(\mu) = \frac{e^{-\beta \mathcal{H}(\mu)}}{Z(T, \mathbf{x})}$$

$$Z(T, \mathbf{x}) = \sum_{\{\mu\}} e^{-\beta \mathcal{H}(\mu)}$$

**Normalization
(partition function)**

$$\beta \equiv 1/k_B T$$

Canonical ensemble

What is the distribution of the system energy?
(transformation of random variable from μ to \mathcal{E})

$$p(\mathcal{E}) = \sum_{\{\mu\}} p(\mu) \delta(\mathcal{H}(\mu) - \mathcal{E}) = \frac{e^{-\beta\mathcal{E}}}{Z} \sum_{\{\mu\}} \delta(\mathcal{H}(\mu) - \mathcal{E})$$

$\Omega(\mathcal{E})$ **density of state (DoS)** number of microstates
of appropriate energy

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

$F = \mathcal{E} - TS(\mathcal{E})$ **Helmholtz free energy**

Free energy is the key quantity
for canonical ensemble

正则系综首先要计算的是自由能，其他热力学量可以从它算出。

Distribution of energy: most likely energy and average

$$F = \mathcal{E} - TS(\mathcal{E})$$

$$Z = \sum_{\{\mu\}} e^{-\beta \mathcal{H}(\mu)} = \sum_{\mathcal{E}} e^{-\beta F(\mathcal{E})} \approx e^{-\beta F(E^*)}$$

$$F(T, \mathbf{x}) = -k_B T \ln Z(T, \mathbf{x})$$

$$\langle \mathcal{H} \rangle = \sum_{\mu} \mathcal{H}(\mu) \frac{e^{-\beta \mathcal{H}(\mu)}}{Z} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{\mu} e^{-\beta \mathcal{H}} = -\frac{\partial \ln Z}{\partial \beta}$$

most likely energy

average energy

How close is the most likely energy and average energy

这里是看正则系综的系统的能量分布（我们知道正则系综是温度恒定，能量不守恒）
可以证明，这个分布是接近高斯分布

Distribution of energy: width of the probability distribution

这里是看正则系综的系统的能量的涨落，就是方差

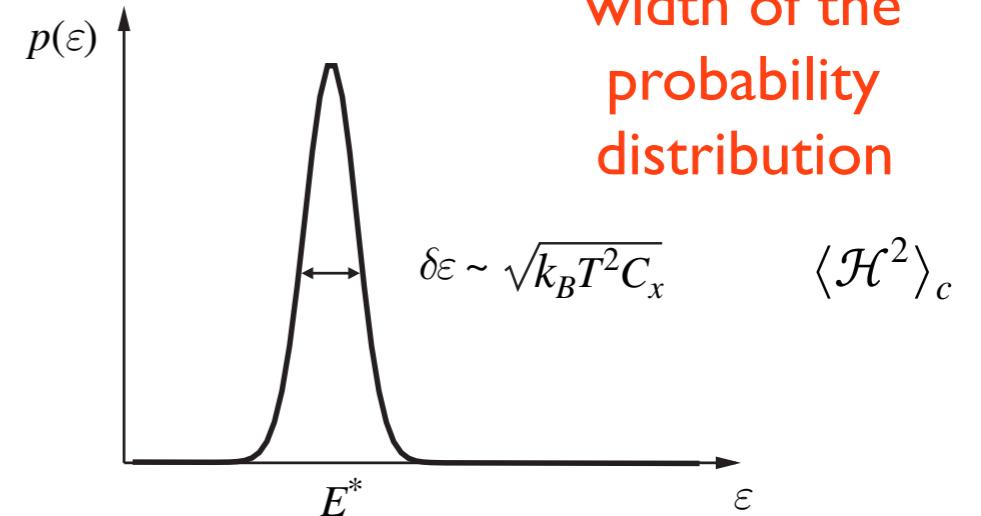
$$Z(\beta) = \sum_{\mu} e^{-\beta H(\mu)}$$

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

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

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

$$\langle \mathcal{H}^2 \rangle_c = -\frac{\partial \langle \mathcal{H} \rangle}{\partial (1/k_B T)} = k_B T^2 \left. \frac{\partial \langle \mathcal{H} \rangle}{\partial T} \right|_{\mathbf{x}}, \quad \Rightarrow \quad \langle \mathcal{H}^2 \rangle_c = k_B T^2 C_x$$



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

在反差趋向于零的时候，高斯分布的极限是Dirac函数

$$\begin{aligned} \sqrt{\langle \mathcal{H}^2 \rangle_c} &\propto N^{1/2} \\ \sqrt{\langle \mathcal{H}^2 \rangle_c} / \langle \mathcal{H} \rangle_c &\rightarrow N^{1/2} / N = 1 / \sqrt{N} \rightarrow 0 \\ p(\mathcal{E}) &\rightarrow \delta(\mathcal{E} - \langle \mathcal{H} \rangle) \end{aligned}$$

at large N limit, canonical ensemble is equivalent to microcanonical ensemble

Comparison of two ensemble ME and CE

Table 4.1 *Comparison of canonical and microcanonical ensembles*

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

Canonical ensemble fit the cases of
most experiments



Standard procedure

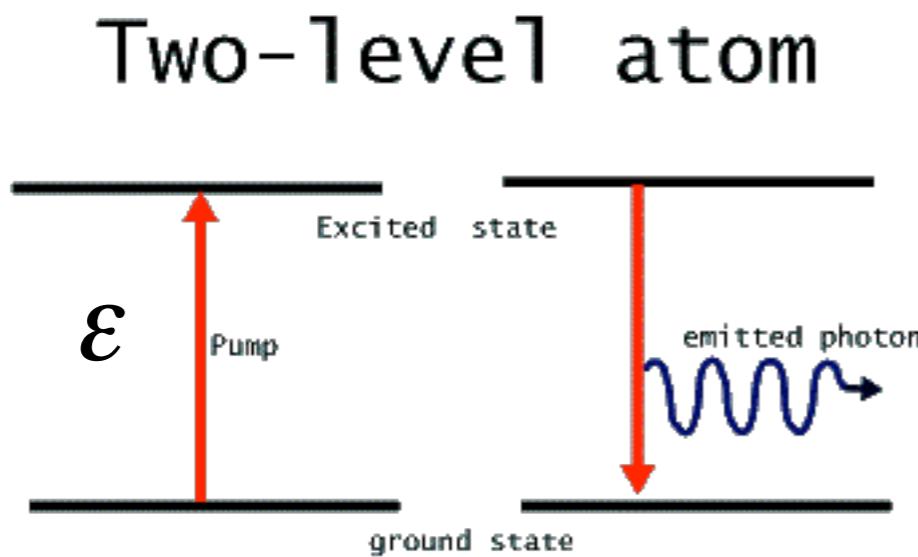
- 1) Calculating partition function from all possible configurations $Z(\beta) = \sum e^{-\beta H(\mu)}$
应用正则系综的时候，先求配分函数
- 2) Using partition function to get free energy and other physical quantities.

$$F(T, N) = -k_B T \ln Z : \quad S = - \left. \frac{\partial F}{\partial T} \right|_N$$
$$E = - \left. \frac{\partial \ln Z}{\partial \beta} \right.$$

求配分函数后求自由能，在从热力学关系
求其他热力学函数

- $dF = -SdT - PdV + \mu dN$
- 3) single particle probability distribution can also be obtained from the N – particle distribution

Examples: two-level-system



N: total number of atoms

T: temperature

$E = N_1 \epsilon$ is unknown!

应用正则系综：求两能级系统的热力学性质，
现在的外界条件是温度恒定

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

$$= (1 + e^{-\beta \epsilon})^N,$$

$$F(T, N) = -k_B T \ln Z = -N k_B T \ln [1 + e^{-\epsilon/(k_B T)}]$$

$$S = - \frac{\partial F}{\partial T} \Big|_N = \underbrace{N k_B \ln [1 + e^{-\epsilon/(k_B T)}]}_{-F/T} + N k_B T \left(\frac{\epsilon}{k_B T^2} \right) \frac{e^{-\epsilon/(k_B T)}}{1 + e^{-\epsilon/(k_B T)}}.$$

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

$$p = \prod_i p_i \quad p_i(n_i) = \frac{e^{-\beta \epsilon n_i}}{1 + e^{-\beta \epsilon}}$$

much easier
than using ME!

Examples: ideal gas

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

for microstates
 $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$

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

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

求配分函数

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

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

求自由能

$$dF = -SdT - PdV + \mu dN$$

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

求熵和其他热力学量

Examples: ideal gas (cont.)

$$Z(T, V, N) = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}$$

应用正则系综的时候，先求配分函数

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

求配分函数后求自由能，在从热力学关系
求其他热力学函数

$$E = -\frac{\partial \ln Z}{\partial \beta} \quad E = 3Nk_B T/2.$$

$$P = -\left. \frac{\partial F}{\partial V} \right|_{T,N} = \frac{Nk_B T}{V}, \quad \Rightarrow \quad PV = Nk_B T,$$

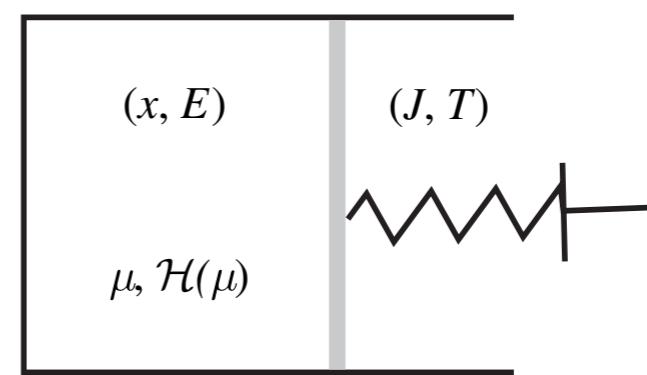
$$\mu = \left. \frac{\partial F}{\partial N} \right|_{T,V} = \frac{F}{N} + k_B T = \frac{E - TS + PV}{N} = k_B T \ln(n\lambda^3)$$

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

The Gibbs canonical ensemble

Internal energy changed by addition of both heat and **work!**

$$p(\mu_S, \mathbf{x}) = \exp[-\beta \mathcal{H}(\mu_S) + \beta \mathbf{J} \cdot \mathbf{x}] / \mathcal{Z}(T, N, \mathbf{J}),$$



$$\begin{aligned} \mathcal{Z}(N, T, \mathbf{J}) &= \sum_{\mu_S, \mathbf{x}} e^{\beta \mathbf{J} \cdot \mathbf{x} - \beta \mathcal{H}(\mu_S)} \\ \langle \mathbf{x} \rangle &= k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mathbf{J}} \end{aligned}$$

$$G = E - TS - \mathbf{x} \cdot \mathbf{J}$$

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

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

$$\text{enthalpy } H \equiv E - \mathbf{x} \cdot \mathbf{J}$$

$$C_J = \partial H / \partial T$$

不同系综适合于不同的物理情形：
吉布斯正则系综适用于封闭系统（和外界不存在物质交换，但是存在热能，功的交换的系统，即与一个恒温热库相接触，且在恒定外力作用下的系统）

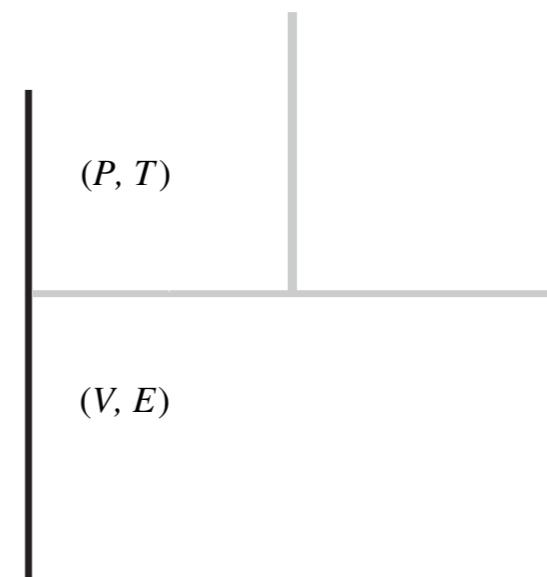
推导与一般正则系综一样，只不过能量的形式有点改变而已

Examples: ideal gas in isobaric ensemble

additional term compared with free ideal gas

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

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



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

$$dG = -SdT + VdP + \mu dN$$

$$V = \left. \frac{\partial G}{\partial P} \right|_{T,N} = \frac{N k_B T}{P}, \quad \Rightarrow \quad PV = N k_B T.$$

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

$$C_P = dH/dT = 5/2 N k_B$$

应用Gibbs正则系综的时候，先求配分函数
 求配分函数后求Gibbs自由能，在从热力学关系
 求其他热力学函数

Examples: spin in a magnetic field

所有可能的微观态求和

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

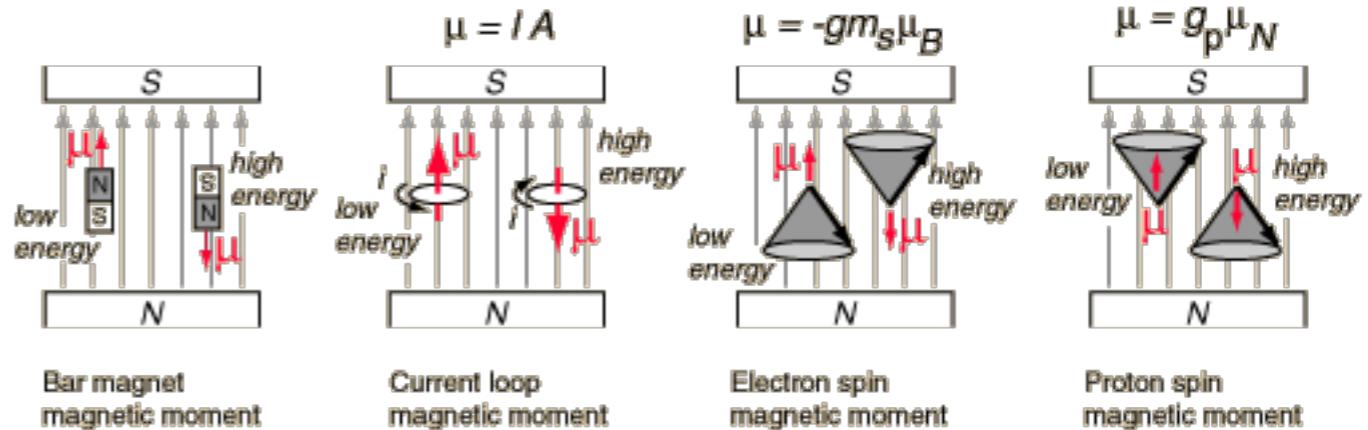
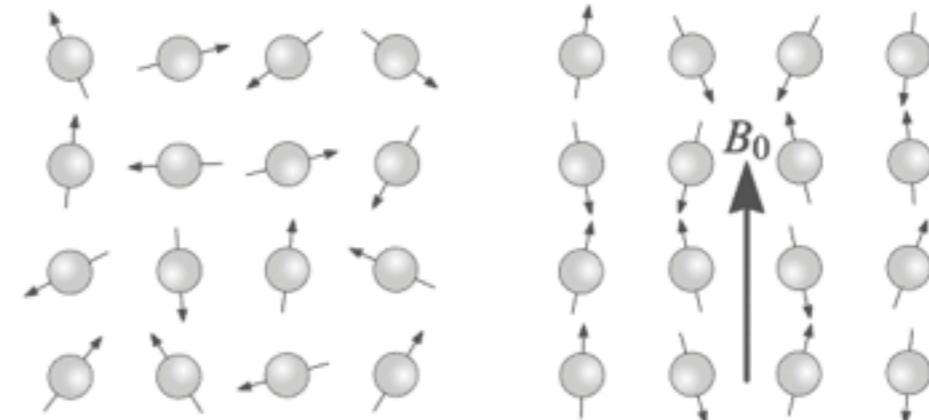
$$M = \mu_0 \sum_{i=1}^N \sigma_i \quad \text{Ising spins}$$

$$\sigma_i = \pm 1$$

no interaction
between spins $(\mathcal{H} = 0)$

$$p(\{\sigma_i\}) = \frac{1}{\mathcal{Z}} \exp \left[\beta B \mu_0 \sum_{i=1}^N \sigma_i \right]$$

$$\mathcal{Z}(N, T, B) = [2 \cosh(\beta \mu_0 B)]^N$$



求配分函数

Examples: spin in a magnetic field (cont.)

Gibbs free energy 吉布斯自由能

$$G = -k_B T \ln \mathcal{Z} = -Nk_B T \ln [2 \cosh(\beta\mu_0 B)] \quad \text{求其他热力学量}$$

magnetization 磁化强度

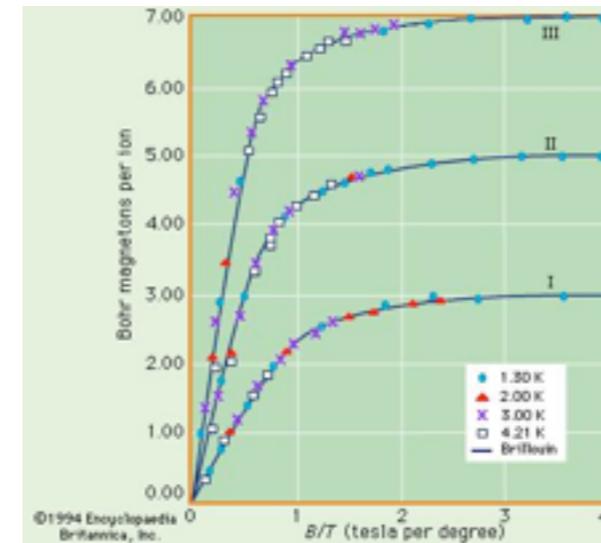
$$M = -\frac{\partial G}{\partial B} = N\mu_0 \tanh(\beta\mu_0 B)$$

magnetic susceptibility 磁化率

$$\chi(T) = \left. \frac{\partial M}{\partial B} \right|_{B=0} = \frac{N\mu_0^2}{k_B T}$$

Heat capacity 热容

$$C_B = -B \partial M / \partial T.$$



Grand Canonical ensemble (for open systems)

巨正则系综适用于开放系统，就是与外界存在物质，热，功交还的系统

probability distribution of a microstate

$$p(\mu_S) = \exp[\beta\mu N(\mu_S) - \beta\mathcal{H}(\mu_S)] / Q.$$

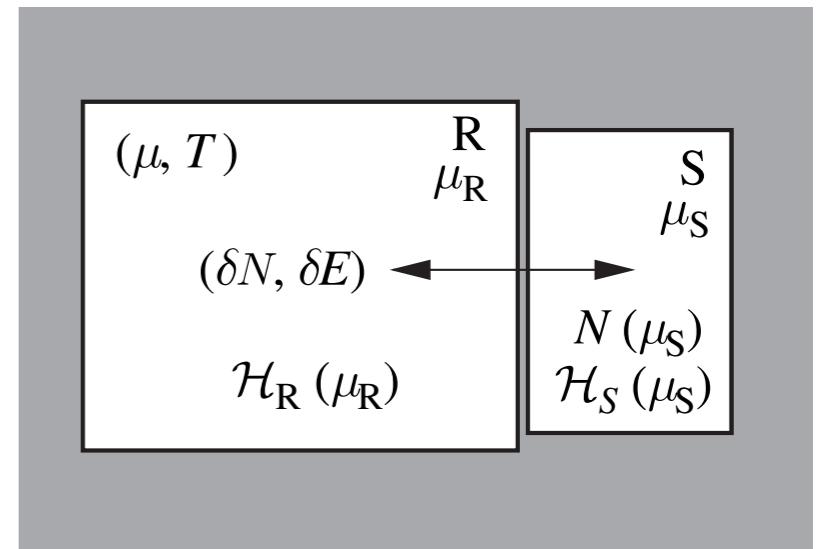
grand partition function 巨配分函数

$$Q(T, \mu, \mathbf{x}) = \sum_{\mu_S}^{\infty} e^{\beta\mu N(\mu_S) - \beta\mathcal{H}(\mu_S)}.$$

$$Q(T, \mu, \mathbf{x}) = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{(\mu_S|N)} e^{-\beta\mathcal{H}_N(\mu_S)}.$$

probability of finding system with particle number N is

$$p(N) = \frac{e^{\beta\mu N} Z(T, N, \mathbf{x})}{Q(T, \mu, \mathbf{x})}. \quad \text{系统存在粒子数为 } N \text{ 的状态的概率}$$



热库提供热能和粒子源，
具有恒定温度和化学势

Entropy and grand potential

Entropy from information theory 熵

$$\begin{aligned} S &= -k_B \sum_{\mu_s} p(\mu_s) \ln p(\mu_s) = -k_B \sum_{\mu_s} \frac{e^{\beta \mu N(\mu_s) - \beta H(\mu_s)}}{Q} \ln \left(\frac{e^{\beta \mu N(\mu_s) - \beta H(\mu_s)}}{Q} \right) \\ &= -k_B \sum_{\mu} \frac{e^{\beta \mu N(\mu_s) - \beta H(\mu_s)}}{Q} [\beta \mu N(\mu_s) - \beta H(\mu_s) - \ln Q] \\ &= -\sum_{\mu} \frac{p(\mu_s) [\mu N(\mu_s) - H(\mu_s)]}{T} + \sum_{\mu} p(\mu) \ln Q = \frac{\langle H \rangle - \mu \langle N \rangle}{T} + k_B \ln Q \end{aligned}$$

$$-k_B \ln Q = \langle H \rangle - \mu \langle N \rangle - TS = E - \mu N - TS = \mathcal{G}(T, \mu, V) \text{ 巨势}$$

$$\mathcal{G}(T, \mu, \mathbf{x}) = E - TS - \mu N = -k_B T \ln \mathcal{Q}$$

$$d\mathcal{G} = -SdT - Nd\mu + \mathbf{J} \cdot d\mathbf{x}, \quad \text{热力学关系}$$

entropy 熵	particle number 粒子数	generalized force 广义力
$-S = \frac{\partial \mathcal{G}}{\partial T} \Big _{\mu, \mathbf{x}}$	$N = -\frac{\partial \mathcal{G}}{\partial \mu} \Big _{T, \mathbf{x}}$	$J_i = \frac{\partial \mathcal{G}}{\partial x_i} \Big _{T, \mu}$

巨势能够与巨配分函数直接联系起来所以我们先计算了巨配分函数，再算巨势，在然后由热力学关系算其他热力学量

GCE: ideal gas in an open systems

$$\begin{aligned}
 \mathcal{Q}(T, \mu, V) &= \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{1}{N!} \int \left(\prod_{i=1}^N \frac{d^3 \vec{q}_i d^3 \vec{p}_i}{h^3} \right) \exp \left[-\beta \sum_i \frac{p_i^2}{2m} \right] \\
 &= \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} \left(\frac{V}{\lambda^3} \right)^N \quad \left(\text{with } \lambda = \frac{h}{\sqrt{2\pi m k_B T}} \right) \\
 &= \exp \left[e^{\beta\mu} \frac{V}{\lambda^3} \right], \quad \text{巨配分函数}
 \end{aligned}$$

$$\mathcal{G}(T, \mu, V) = -k_B T \ln \mathcal{Q} = -k_B T e^{\beta\mu} \frac{V}{\lambda^3}. \quad \text{巨势}$$

$$d\mathcal{G} = -SdT - Nd\mu - PdV \quad \text{热力学关系}$$

$$P = -\frac{\mathcal{G}}{V} = -\left. \frac{\partial \mathcal{G}}{\partial V} \right|_{\mu, T} = k_B T \frac{e^{\beta\mu}}{\lambda^3}. \quad \text{压强, 由此得状态方程}$$

$$N = -\left. \frac{\partial \mathcal{G}}{\partial \mu} \right|_{T, V} = \frac{e^{\beta\mu} V}{\lambda^3}. \quad \text{粒子数}$$

Summary

- Derive the distribution function of canonical ensemble from micro-canonical ensemble or maximum entropy principle
- Calculating thermodynamical property using canonical ensemble (distribution function of energy, free energy, TLS, free gas)
- Gibbs canonical ensemble (Gibbs free energy, TLS, ideal gas)
- giant canonical ensemble (Giant potential, TLS, ideal gas)

Exercise I: microcanonical ensemble

12.1 A perfect crystal has N lattice sites and M interstitial locations. An energy Δ is required to remove an atom from a site and place it in an interstitial, when the number of displaced atoms, n , is much smaller than N or M .

- (a) How many ways are there of removing n atoms from N sites?
- (b) How many ways are there of placing n atoms on M interstitials?
- (c) Use the microcanonical ensemble to calculate the entropy as a function of total energy E , and define the temperature.
- (d) Show that the average number of displaced atoms n at temperature T is given by

$$\frac{n^2}{(N-n)(M-n)} = e^{-\Delta/kT}.$$

Obtain n for $\Delta \gg kT$, and $\Delta \ll kT$.

- (e) Use this model for defects in a solid. Set $N = M$, and $\Delta = 1 \text{ eV}$, find the defect concentration at $T = 1,000$ and 300 K .

12.1

(a)

The number of ways to choose the n atoms to remove from N sites is

$$N! / [n! (N - n)!]$$

(b)

The number of ways to choose the n interstitials out of M is

$$M! / [n! (M - n)!]$$

(c)

The total energy is $E = n\Delta$. The phase space volume is

$$\Gamma(n) = \frac{N!M!}{n! (N - n)! n! (M - n)!}$$

Using the Stirling approximation, we obtain the entropy

$$\frac{S}{k} = \ln \Gamma(n) = n \ln \frac{N}{n} - (N - n) \ln \left(1 - \frac{n}{N}\right) + n \ln \frac{M}{n} - (M - n) \ln \left(1 - \frac{n}{M}\right)$$

The temperature is defined through

$$\frac{1}{kT} = \frac{1}{k} \frac{\partial S}{\partial E} = \frac{1}{\Delta} \frac{\partial \ln \Gamma(n)}{\partial n}$$

This gives

$$\frac{\Delta}{kT} = \frac{\partial}{\partial n} \ln \Gamma(n) = \ln \left(\frac{N}{n} - 1\right) + \ln \left(\frac{M}{n} - 1\right)$$

(d)

The previous equation can be rewritten as

$$\frac{n^2}{(N - n)(M - n)} = \exp \left(-\frac{\Delta}{kT}\right)$$

The low- and high-temperature limits are

$$\begin{aligned} n &\approx \sqrt{NM} \exp(-\Delta/2kT) & (kT \ll \Delta) \\ \frac{1}{n} &\approx \frac{1}{N} + \frac{1}{M} & (kT \gg \Delta) \end{aligned}$$

(e)

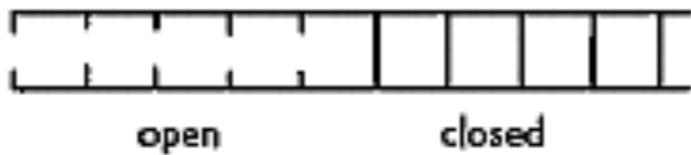
$$\frac{n}{N} \approx \exp(-\Delta/2kT)$$

For $T = 300$ K: $n/N \approx e^{-20} = 2 \times 10^{-9}$.

For $T = 1000$ K: $n/N \approx e^{-6} = 2.5 \times 10^{-3}$.

Exercise 2: canonical ensemble

12.4 The unwinding of a double-stranded DNA molecule is like unzipping a zipper. The DNA has N links, each of which can be in one of two states: a closed state with energy 0, and an open state with energy Δ . A link can open only if all the links to its left are already open, as illustrated in the sketch.



- (a) Show that the partition function of the DNA chain is

$$Q_N = \frac{1 - e^{-(N+1)\Delta/kT}}{1 - e^{-\Delta/kT}}.$$

- (b) Find the average number of open links in the low-temperature limit $kT \ll \Delta$.

12.4

(a)

The possible states are labeled by the number of open links $n = 0, 1, 2, \dots, N$. The energy with n open links is $E_n = n\Delta$. The partition function is

$$Q_N = \sum_{n=0}^N e^{-\beta n\Delta} = \frac{1 - e^{-\beta(\bar{N}+1)\Delta}}{1 - e^{-\beta\Delta}}$$

(b)

The average number of open links is

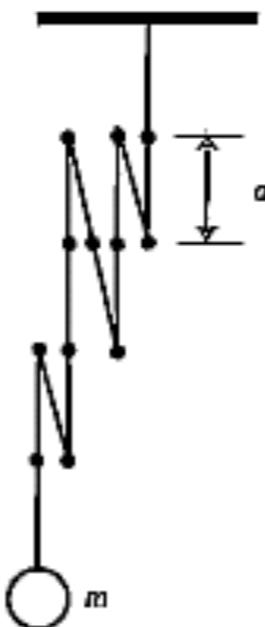
$$\bar{n} = -\frac{1}{\Delta} \frac{\partial \ln Q_N}{\partial \beta} = \frac{e^{-\beta\Delta}}{1 - e^{-\beta\Delta}} - \frac{(N+1)e^{-\beta(\bar{N}+1)\Delta}}{1 - e^{-\beta(\bar{N}+1)\Delta}}$$

The second term is negligible for large N . At low temperatures $\beta\Delta \gg 1$ we have

$$\bar{n} \approx e^{-\beta\Delta}$$

Exercise 2: canonical ensemble

12.3 A chain made of N segments of equal length a hangs from the ceiling. A mass m is attached to the other end under gravity. Each segment can be in either of two states, up or down, as illustrated in the sketch.



- (a) Show that the partition function at temperature T is given by

$$Q_N = (1 + e^{-mg a / kT})^N.$$

- (b) Find the entropy of the chain.
(c) Find the internal energy, and determine the length of the chain.
(d) Show that the chain obeys Hooke's law, namely, a small force pulling on the chain increases its length proportionately. Find the proportionality constant.

12.3

(a)

Assume that a link can be up or down independently. The partition function is the product of the partition functions of the individual links. The possible energies are 0 and mga . Thus $Q_N = [1 + \exp(-\beta mga)]^N$. We have ignored the fact that the energy of the n th link depends on its height, and therefore on the states of the preceding links. We have also ignored is the restriction that the links cannot go above the ceiling.

(b)

$$U = -\frac{\partial \ln Q_N}{\partial \beta} = \frac{Nmga}{\exp(\beta mga) + 1}$$

The length of the chain is $L = (N - N')a$, where $N' = U/(mga)$ is the number of up links. Thus

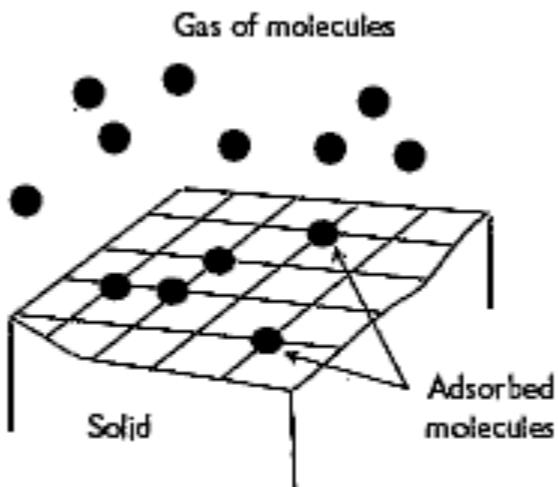
$$L = \frac{Na}{1 + \exp(-\beta mga)}$$

(c)

Since $U = mga[N - (L/a)]$, the force constant is mg .

Exercise 3: grand canonical ensemble

13.3 Gas molecules can adsorb on the surface of a solid at N possible adsorption sites. Each site has binding energy ϵ , and can accommodate at most one molecule. The adsorbed molecules are in equilibrium with a gas surrounding the solid (see sketch). We can treat the system of adsorbed molecules in a grand canonical ensemble with temperature T and chemical potential μ .



- If there are M adsorbed molecules, what is the energy $E(M)$ of the system? What is the degeneracy $\Gamma(M)$ of the energy?
- Write down the grand partition function of the system as a sum over M . Determine the thermal average \bar{M} as the value that maximized the summand.
- Suppose the gas surrounding the solid has pressure P . Calculate \bar{M} using the ideal-gas expression for μ .
- Find $\overline{M^2} - \bar{M}^2$.

13.3

(a)

$$E(M) = -\epsilon M$$

$$\Gamma(M) = \binom{N}{M}$$

(b)

The grand partition function of the adsorbed gas is

$$Q(z, T) = \sum_{M=0}^N \binom{N}{M} (ze^{\beta\epsilon})^M = (1 + ze^{\beta\epsilon})^N$$

where $z = e^{\beta\mu}$. The average fraction of occupied sites can be obtained either by maximizing the summand using the Stirling approximation:

$$\ln \left[\binom{N}{M} (ze^{\beta\epsilon})^M \right] \approx M \ln (ze^{\beta\epsilon}) + N \ln N - M \ln M - (N - M) \ln (N - M)$$

or by calculating the grand canonical average:

$$\frac{\bar{M}}{N} = \frac{z}{N} \frac{\partial}{\partial z} \ln Q = \frac{1}{z^{-1} e^{-\beta\epsilon} + 1}$$

(c)

The chemical potential for an ideal gas is given in Prob.3.2: $\mu = kT \ln(n\lambda^3)$, where $\lambda = \sqrt{2\pi\hbar^2\beta/m}$, and $n = \beta P$. In equilibrium, the chemical potential of the adsorbed gas must equal that of the surrounding gas. Thus

$$\frac{\bar{M}}{N} = \frac{\lambda^3 \beta P}{e^{-\beta\epsilon} + \lambda^3 \beta P}$$

(d)

$$\overline{M^2} - \bar{M}^2 = z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} \ln Q = \frac{ze^{-\beta\epsilon}}{(e^{-\beta\epsilon} + z)^2}$$