Statistical Mechanics II

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Lecture 5 Microcanonical Ensemble Theory

Counting number of the state
Density of state

$$\omega(k) = 2\sqrt{\frac{K}{m}}|\sin\frac{ka}{2}| = 2\sqrt{\frac{K}{m}}\frac{ka}{2} \approx \nu k$$

$$\vec{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z}\right)$$

$$dn_x = (n_x + 1) - n_x = \frac{L_x}{2\pi}dk_x$$

$$\sum_{n_x} = \sum_{n_x}((n_x+1) - n_x) = \sum_{n_x}\frac{L_x dk_x}{2\pi} = \frac{L_x}{2\pi}\int dk_x$$

$$\sum_{n_x, n_y, n_z} = \frac{L_x L_y L_z}{(2\pi)^3}\int dk_x dk_y dk_z = \frac{V}{(2\pi)^3}\int d^3\vec{k}$$

$$\sum_\lambda f(\varepsilon_\lambda) = \int \frac{d^3\vec{p}d^3\vec{q}}{h^3} f(\vec{p}) = \frac{V}{h^3}\int d^3\vec{p} f(\vec{p})$$

$$\vec{p} = \hbar k = \frac{h\vec{k}}{2\pi}$$

$$\int \frac{d^3\vec{p}d^3\vec{q}}{h^3}\ f(\vec{p}) = \frac{V}{h^3}\int d^3\vec{p}\ f(\vec{p})$$

$$= \frac{V}{(2\pi)^3}\int d^3\vec{k}\ f(\hbar\vec{k})$$

$$\frac{1}{h^3}\int p_x dp_y dp_z \int dx dy dz f(\mathbf{p})$$

$$= \int 8\pi V\left(\frac{m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2} f(\varepsilon)d\varepsilon \equiv \int g(\varepsilon)f(\varepsilon)d\varepsilon$$

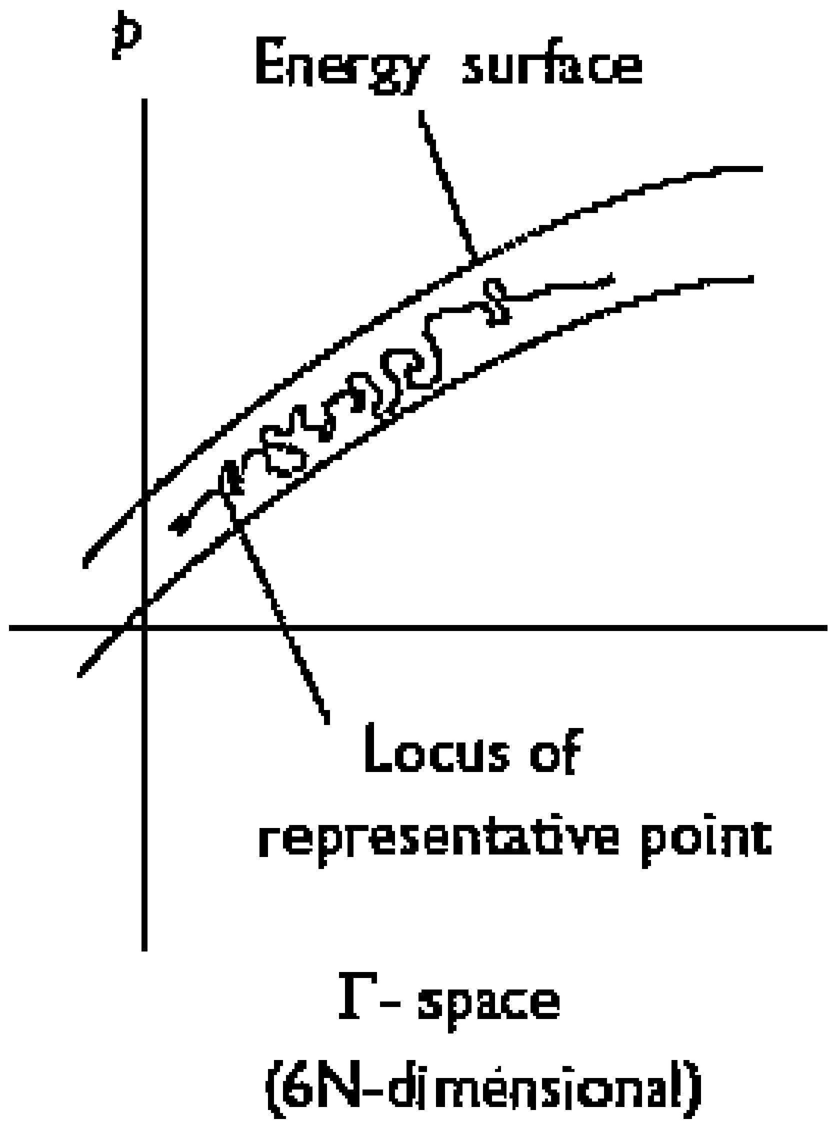
Density of state: The total number of state of the system within energy ε is Ω (ε),

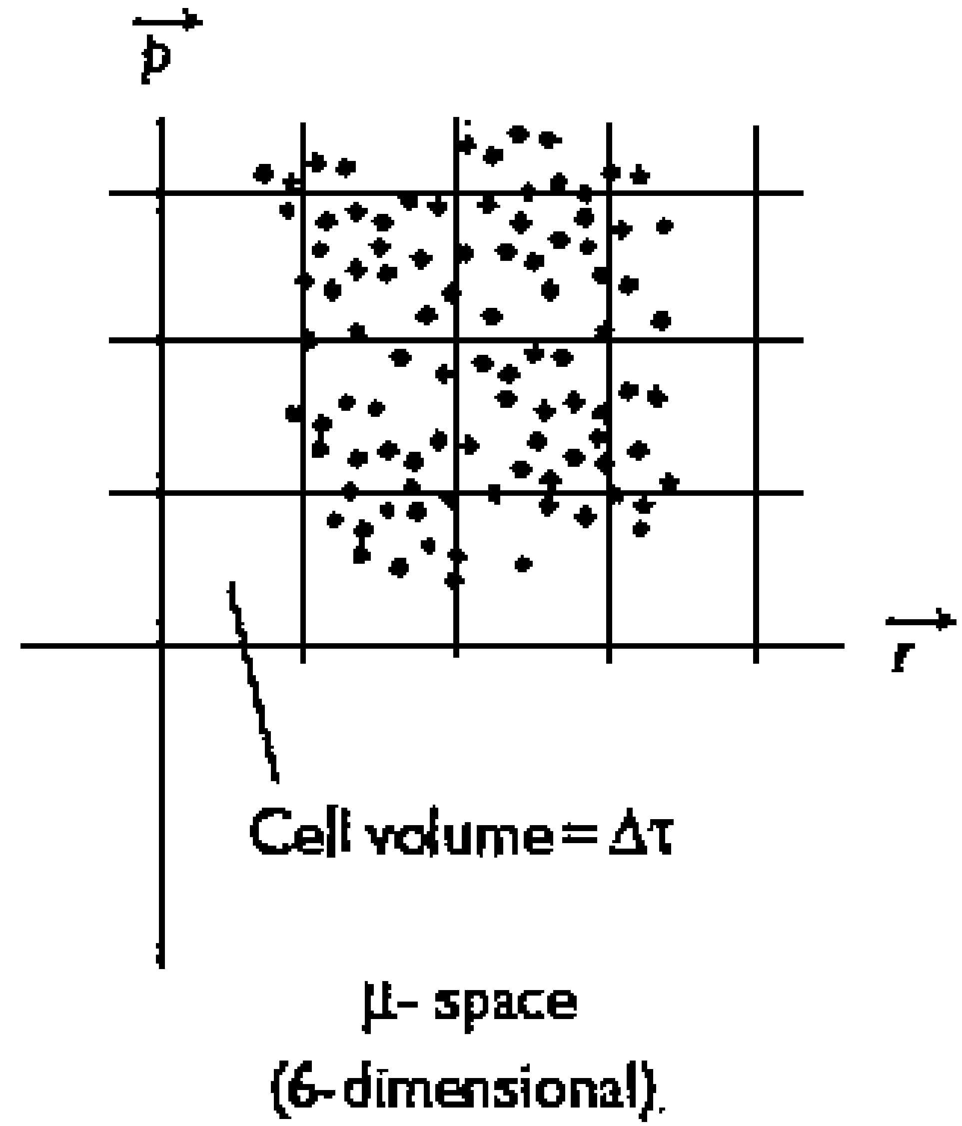
$$g(\varepsilon) = d\Omega(\varepsilon)/d\varepsilon$$

Outline

- Phase space of N-particle system and ensemble theory
- The most probable distribution of micro-canonical ensemble
- 3 laws of thermodynamics from micro-canonical ensemble theory
- Calculating thermal properties from the distribution i.e. from the number of microstate.

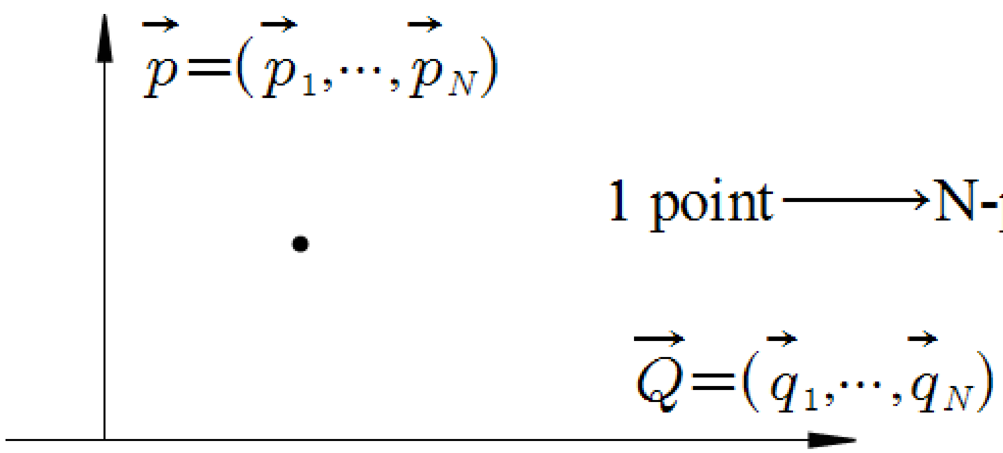
Phase space





N-particle system

General definition: Density function of N-particle system



1 point $\longrightarrow$ N-particles system

density function

$$\int \rho\left(\vec{Q},\vec{P},t\right) d\Gamma \equiv 1$$

$\rho\left(\vec{Q},\vec{P},t\right)$ (interacting system)

$$O = \langle O\left(\vec{Q},\vec{P}\right)\rangle = \int \frac{d^{3N}\vec{Q}d^{3N}\vec{P}}{h^{6N}} O\left(\vec{Q},\vec{P}\right) \rho\left(\vec{Q},\vec{P},t\right)$$

$\boxed{\text{Microstate}}$ $\quad \Gamma = \prod_{\alpha} \{q_\alpha, p_\alpha\}_{\alpha=1}^{N}$ $\quad$ 6N-dim

$\downarrow$

$\boxed{\text{Macrostates}}$ $\quad (P, V, T, S, E)$ $\quad$ a few-dim

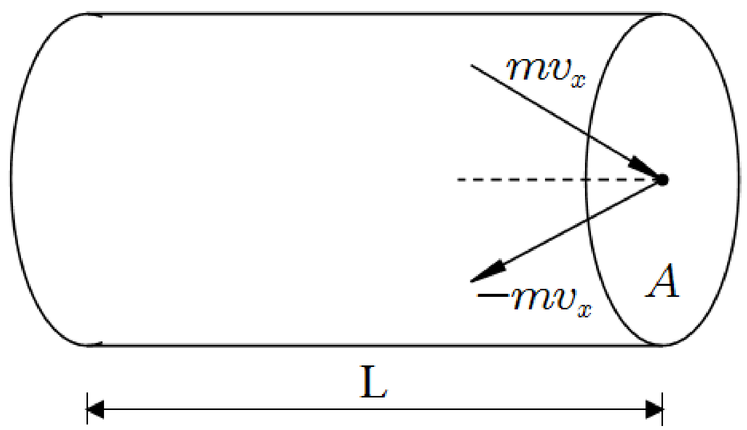
Ensemble theory

- Assuming a distribution of many copies of the same system (ensemble) in accessible phase space (determined by the connection between the system with the environments). The macroscopic properties of the system is just the average values of such ensemble.

Different macroscopic environmental constraints $\longrightarrow$ different types of ensembles

Constratints	Fixed Variables	Ensemble
Isolated	E, N	Microcanonical Ensemble
Thermal Contact	N	Canonical Ensemble
Particle Diffusion		Grandcanonical Ensemble

Ergodic hypothesis



$$P = \frac{F}{A} = \frac{1}{V}\frac{2}{3}\overline{\frac{1}{2}mv^2}$$

microstate average
(sampling)

Average over time
(what you measured)

$$\langle O \rangle_T = \frac{1}{T_0}\int_0^{T_0} O\left(\Gamma\left(t\right)\right) dt$$

Ensemble average

$$\langle O \rangle_E = \int \rho\left(\Gamma, t\right) O\left(\Gamma\right) d\Gamma$$

time average $\approx$ microstates average $\approx$ ensemble average

$\boxed{\text{Ergodic hypothesis}}$

$$\langle O \rangle_T = \langle O \rangle_E$$

Different ensemble

	Isolated system	Closed system		Open system
Ensemble	Microcannonical	Cannonical	Gibbs Cannonical	Grand Cannonical
δQ	$\times$	$\surd$	$\surd$	$\surd$
δW	$\times$	$\times$	$\surd$	$\surd$
δN	$\times$	$\times$	$\times$	$\surd$
Conserved quantities	(E, N, V)	(T, N, V)	(T, N, P)	(T, μ, V)
$\rho\left(\vec{Q}, \vec{P}, t\right)$	$\frac{1}{\Omega(E,N,V)}$	$\frac{1}{\mathcal{Z}} e^{-\beta H(\mu_s)}$	$\frac{1}{\mathcal{Z}} e^{\beta \vec{J}\cdot\vec{x} - \beta H(\mu_s)}$	$\frac{1}{\Omega} e^{\beta\mu N - \beta H(\mu_s)}$
1st thermal quantity obtained to connect microstate and macrostate	$S = k_B \ln \Omega$ entropy	$F = -k_B T \ln \mathcal{Z}$ free energy	$G = -k_B T \ln \mathcal{Z}$ Gibbs free energy	$g = -k_B T \ln \Omega$ Giant potential
Other quantities	$dE = TdS - PdV$ $+JdX + \mu dN$ E $\left.\frac{dE}{dS}\right\|_X = \frac{1}{T}$ $\left.\frac{dE}{dX}\right\|_S = J$ $\left.\frac{dS}{dX}\right\|_E = -\frac{J}{T}$	$dF = -SdT - PdV$ $+JdX + \mu dN$ $F = E - TS$ $S = -\left.\frac{dF}{dT}\right\|_V$ $P = -\frac{dF}{dV}$ $J = \frac{dF}{dX}$	$dG = -SdT + PdV$ $-XdJ + \mu dN$ $G = E - TS - JX$ $P = \frac{dG}{dV}$ $X = -\frac{dG}{dJ}$ $\mu = \frac{dG}{dN}$	$dg = -SdT + JdX$ $-Nd\mu - PdV$ $g = E - TS - \mu N$ $N = -\frac{dg}{d\mu}$

Microcanonical ensemble (ME)

- (macrostates) An ensemble consists of many copies of isolated system with fixed energy E
- (microstates) Each systems has many different microstates corresponding the fixed E macrostate. Each microstate are equally probable.

$\delta N = 0$	No particle exchange
$\delta W = 0$	No work done
$\delta Q = 0$	No heat exchange
Macrostate (N, E, V)	

Equal probability distribution

Isolated System

$\delta N = 0$	No particle exchange
$\delta W = 0$	No work done
$\delta Q = 0$	No heat exchange
Macrostate (N, E, V)	

$$L = -\int \rho \ln \rho \, d\Gamma - \alpha \left[\int \rho \, d\Gamma - 1 \right]$$

$$0 = \frac{\delta L}{\delta \rho} = -\ln \rho - 1 - \alpha = 0$$

$$\rho = e^{-1-\alpha} = const$$

$$\rho\left(E, \vec{X}\right)(\Gamma) = \begin{cases} \frac{1}{\Omega\left(E, \vec{X}\right)} & \text{for } H(\Gamma) = E \\ 0 & \text{for } H(\Gamma) \neq E \end{cases}$$

Information entropy and entropy of statistical mechanics

The entropy of statistical mechanics and the information entropy of information theory are basically the same thing.

$$S = -\sum_{i=1}^{M} p(i) \ln p(i)$$ (information theory)

$$S(E,\boldsymbol{x}) = -k_B \sum_i \frac{1}{\Omega} \ln \frac{1}{\Omega} = k_B \left(\sum_i \frac{1}{\Omega} \right) \ln \Omega = k_B \ln \Omega$$

$$S(E, \mathbf{x}) = k_B \ln \Omega(E, \mathbf{x})$$ (statistical mechanics)

E. T. Jaynes

$$\boxed{\Omega(E) = e^{\frac{S(E)}{k_B}}}$$

Entropy of isolated system

$$\Gamma = \Gamma_1 \otimes \Gamma_2$$

$$H(\Gamma) = H(\Gamma_1) + H(\Gamma_2)$$

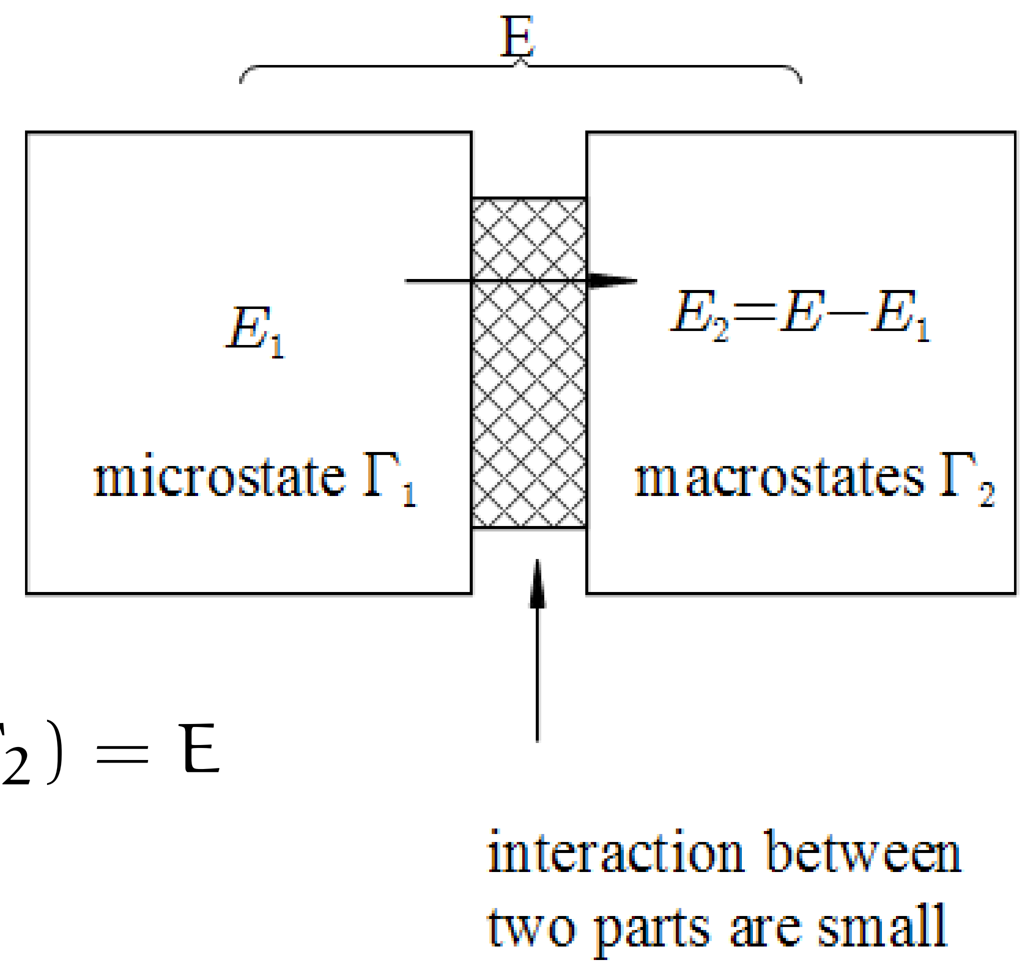
i.e. $E = E_1 + E_2$

$$\rho_E(\Gamma) = \rho_E(\Gamma_1 \otimes \Gamma_2)$$

$$= \begin{cases} \frac{1}{\Omega(E)} & \text{for } H(\Gamma_1) + H(\Gamma_2) = E \\ 0 & \text{otherwise} \end{cases}$$

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

$$= \int e^{S(E_1)/k_B} e^{S(E-E_1)/k_B} dE_1$$



The 2nd law of thermodynamics

$$\int e^{S(E)/k_B} dE \sim e^{S(E*)/k_B}$$

Rule of large number

$$\begin{aligned}\Omega(E) &= \int \exp\left[\frac{S_1(E_1)+S_2(E-E_1)}{k_B}\right] dE_1 \\ &= \exp\left[\frac{S_1\left(E_1^*\right)+S_2\left(E-E_1^*\right)}{k_B}\right]\end{aligned}$$

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

$$S_1(E_1^*) + S_2(E_2^*) \geqslant S_1(E_1) + S_2(E_2)$$

The 2nd law: The system is determined by the state where entropy is maximized.

The 0-th law of thermodynamics

$$
\begin{aligned}
0 &= \left.\frac{\partial\left[S_1(E_1)+S_2(E-E_1)\right]}{\partial E_1}\right|_{E_1=E_1^*} \\
&= \left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1=E_1^*} + \left.\frac{\partial S_2(E_2)}{\partial E_2}\frac{\partial E_2}{\partial E_1}\right|_{E_1=E_1^*} \qquad (E_2 = E - E_1^*) \\
&= \left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1=E_1^*} - \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2=E_2^*}
\end{aligned}
$$

$$
\text{i.e.} \quad \left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1^*,\vec{X}_1} = \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2^*,\vec{X}_2}
$$

$$
\left.\frac{\partial S_i}{\partial E_i}\right|_{E_i^*,\vec{X}_i} = \frac{1}{T_i} \qquad\qquad T_1 = T_2
$$

The 0-th law: When two contacted system are at equilibrium, they should have the same temperature.

The 1st law of thermodynamics

$$
\begin{aligned}
\delta S &= \delta S\left(E + \vec{J}\cdot\delta\vec{X}, \vec{X} + \delta\vec{X}\right) \\
&= \left.\frac{\partial S}{\partial E}\right|_{\vec{X}} \vec{J}\cdot\delta\vec{X} + \left.\frac{\partial S}{\partial \vec{X}}\right|_{E} \cdot\delta\vec{X} \\
&= \left(\left.\frac{\partial S}{\partial E}\right|_{\vec{X}} \vec{J} + \left.\frac{\partial S}{\partial \vec{X}}\right|_{E}\right)\delta\vec{X}
\end{aligned}
$$

$$\frac{\delta S}{\delta \vec{X}} = 0$$

$$0 = \left.\frac{\partial S}{\partial E}\right|_{\vec{X}} \cdot \vec{J} + \left.\frac{\partial S}{\partial \vec{X}}\right|_{E}$$

$$\left.\frac{\partial S}{\partial \vec{X}}\right|_{E} = -\frac{\vec{J}}{T}$$

$$dS\left(E, \vec{X}\right) = \left.\frac{\partial S\left(E, \vec{X}\right)}{\partial E}\right|_{\vec{X}} dE + \left.\frac{\partial S\left(E, \vec{X}\right)}{\partial \vec{X}}\right|_{T} d\vec{X} = \frac{1}{T}dE - \frac{\vec{J}\cdot d\vec{X}}{T}$$

$$dE = TdS + \vec{J}\cdot d\vec{X}$$

$$\boxed{\text{The 1st law: Energy conservation.}}$$

The stability of an isolated system

$$
\begin{aligned}
\frac{\partial^2 S(E)}{\partial E_1} &= \frac{\partial}{\partial E_1}\left[\frac{\partial}{\partial E_1}\left(S_1(E_1) + S_2(E - E_1)\right)\right] \\
&= \frac{\partial}{\partial E_1}\left(\frac{\partial S_1(E_1)}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right) \\
&= \frac{\partial^2 S_1(E_1)}{\partial E_1^2} + \frac{\partial S_2(E_2)}{\partial E_2^2} \leqslant 0
\end{aligned}
$$

$$
\frac{\partial}{\partial E_i}\frac{\partial S_i}{\partial E_i} = \frac{\partial}{\partial E_i}\left(\frac{1}{T_i}\right) = -\frac{1}{T_i^2}\frac{\partial T_i}{\partial E_i} = -\frac{1}{T_i^2}\frac{1}{C_{\vec{X}}}
$$

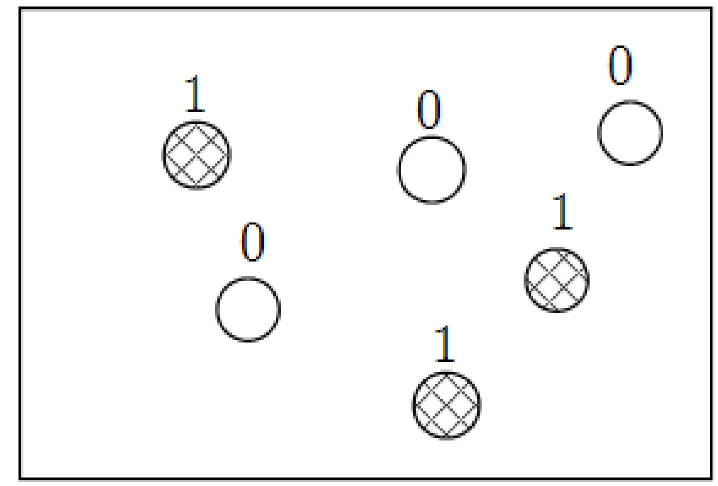
$$
\frac{\partial^2 S}{\partial E_1^2} = -\frac{1}{T_1^2}\frac{1}{C_{\vec{X}_1}} - \frac{1}{T_2^2}\frac{1}{C_{\vec{X}_2}} \quad = -\frac{1}{T^2}\left(\frac{1}{C_{\vec{X}_1}} + \frac{1}{C_{\vec{X}_2}}\right) \leqslant 0
$$

So $\frac{1}{C_{\vec{X}_1}} + \frac{1}{C_{\vec{X}_2}} \leqslant 0$, i.e. $C_{X_i} \geqslant 0$. (Stability condition)

Two level systems

$n_i = 1$ excited state energy is ϵ.

$n_i = 0$ ground state energy is zero.



N impurity atoms

$$H(\{n_i\}) = \epsilon \sum_{i=1}^{N} n_i \equiv \epsilon N_1$$

$$\rho_E(\{n_i\}) = \frac{1}{\Omega(E,N)} \delta\left(\sum_i \epsilon n_i - E\right)$$

$$\Omega(E,N) = \left(\begin{array}{c} N \\ N_1 \end{array}\right) = \frac{N!}{N_1!(N-N_1)!}$$

$$\begin{aligned}
S(E,N) &= k_B \ln \Omega(E,N) = k_B \ln \frac{N!}{N_1!(N-N_1)!} \\
&= k_B [\ln N! - \ln N_1! - \ln (N-N_1)!] \\
&= k_B [N \ln N - N_1 \ln N_1 - (N-N_1) \ln (N-N_1)] \\
&= k_B [[N_1 + (N-N_1)] \ln N - N_1 \ln N_1 - (N-N_1) \ln (N-N_1)] \\
&= -N k_B \left[\frac{N_1}{N} \ln \frac{N_1}{N} + \frac{N-N_1}{N} \ln \frac{N-N_1}{N}\right] \\
&= -N k_B \left[\left(\frac{E}{N\epsilon}\right) \ln \left(\frac{E}{N\epsilon}\right) + \left(1-\frac{E}{N\epsilon}\right) \ln \left(1-\frac{E}{N\epsilon}\right)\right] \\
&= -N k_B [x \ln x + (1-x) \ln (1-x)]
\end{aligned}$$

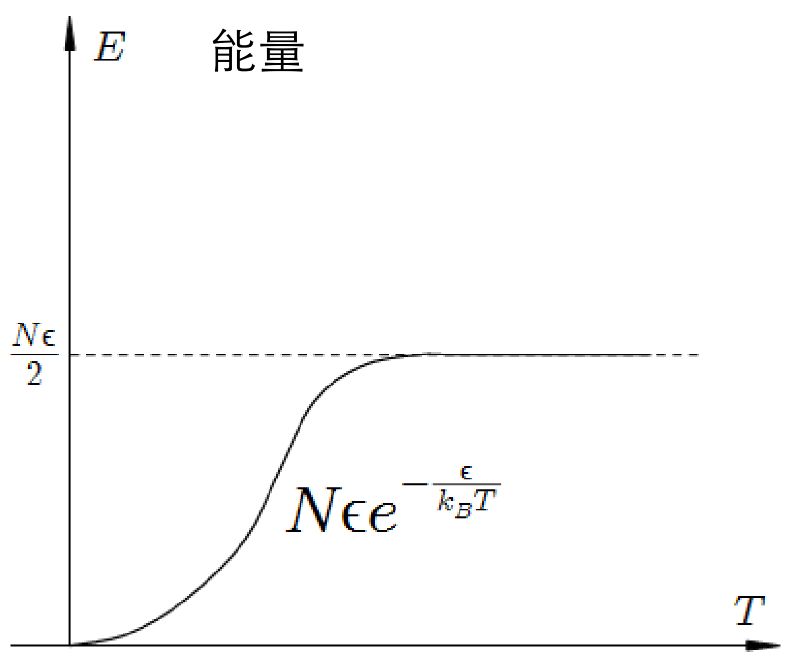
$$\begin{aligned}
\frac{\partial S(E,N)}{\partial E} &= \frac{\partial S(E,N)}{\partial x} \frac{1}{N\epsilon} \\
&= \frac{-N k_B}{N\epsilon} \frac{\partial}{\partial x} [x \ln x + (1-x) \ln (1-x)] \\
&= -\frac{k_B}{\epsilon} [\ln x + 1 - \ln (1-x) + 1] \\
&= -\frac{k_B}{\epsilon} \ln \left(\frac{x}{1-x}\right) \\
&= -\frac{k_B}{\epsilon} \ln \frac{E}{N\epsilon - E} = -\frac{k_B}{\epsilon} \ln \frac{1}{\frac{N\epsilon}{E} - 1} \\
&= \frac{k_B}{\epsilon} \ln \left(\frac{N\epsilon}{E} - 1\right)
\end{aligned}$$

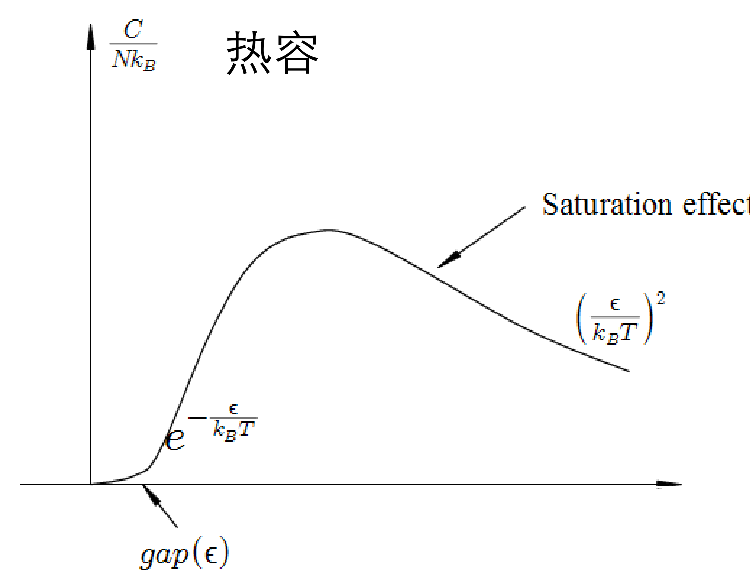
Energy and heat capacity of TLS

$$\frac{N_1}{N} = \frac{N_1\epsilon}{N\epsilon} = \frac{E}{N\epsilon}, \quad \frac{N-N_1}{N} = 1 - \frac{E}{N\epsilon}$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = \frac{1}{N\epsilon}\frac{\partial S}{\partial (E/N\epsilon)}, x = \frac{E}{N\epsilon}.$$

$$\frac{N\epsilon}{E} - 1 = e^{\frac{\epsilon}{k_B T}} \qquad E = \frac{N\epsilon}{e^{\frac{\epsilon}{k_B T}}+1} = N\left[\epsilon\frac{e^{\frac{-\epsilon}{k_B T}}}{e^{\frac{-\epsilon}{k_B T}}+1} + 0\frac{1}{e^{\frac{-\epsilon}{k_B T}}+1}\right]$$





$$C = \frac{dE}{dT} = Nk_B\left(\frac{\epsilon}{k_B T}\right)^2 \frac{e^{\frac{\epsilon}{k_B T}}}{\left(e^{\frac{\epsilon}{k_B T}}+1\right)^2}$$

The distribution of 1 TLS

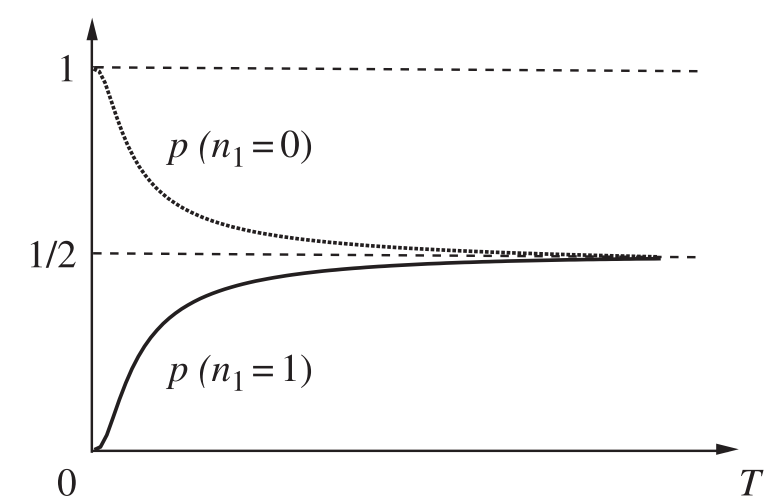
$$P(n_1) = \sum_{\{n_2, n_3, \cdots, n_N\}} \rho(\{n_1, n_2, \cdots, n_N\}) \quad = \frac{\Omega(E - n_1, N-1)}{\Omega(E, N)}$$

$$P(n_1 = 0) = \frac{\Omega(E, N-1)}{\Omega(E, N)} = \frac{\frac{(N-1)!}{N_1!(N-N_1-1)!}}{\frac{N!}{N_1!(N-N_1)!}}$$

$$= \frac{N - N_1}{N} = 1 - \frac{N_1}{N} = 1 - \frac{E}{N\epsilon} \quad = \frac{N - N_1}{N} = 1 - \frac{N_1}{N} = 1 - \frac{E}{N\epsilon}$$

$$P(n_1 = 0) \quad = \quad \frac{1}{e^{\frac{-\epsilon}{k_B T}} + 1}$$

$$P(n_1 = 1) \quad = \quad \frac{e^{\frac{-\epsilon}{k_B T}}}{e^{\frac{-\epsilon}{k_B T}} + 1} = \frac{1}{e^{\frac{\epsilon}{k_B T}} + 1} = 1 - P(n_1 = 0)$$



Preliminary

Surface of a d-dimensional super sphere

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

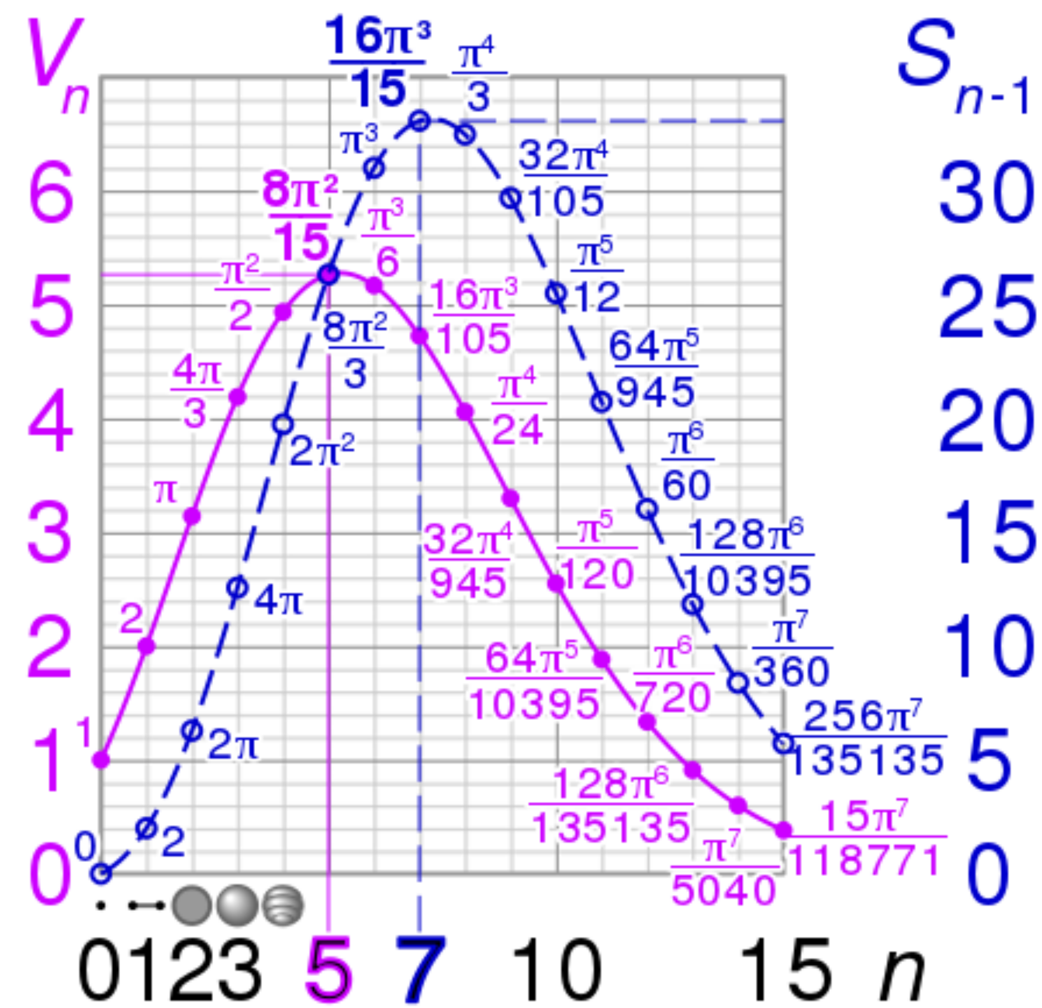
Proof: d-dimensional super sphere

$$R^2 = \sum_{i=1}^{d} x_i^2$$

$$I_d = \int \prod_{i=1}^{d} e^{-x_i^2} dx_i = S_d \int_0^\infty R^{d-1} e^{-R^2} dR$$

$$= \frac{S_d}{2} \int_0^\infty y^{\frac{d}{2}-1} e^{y} dy = \frac{S_d}{2} \left(\frac{d}{2}-1\right)! = \pi^{\frac{d}{2}}$$

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



Ideal gas

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

Constant E space= 3N dim sphere surface $\frac{R^2}{2m} = E, \qquad R = \sqrt{2mE}$

$$\Omega(E,V,N) = \int \frac{d^3\vec{q}_i d^3\vec{p}_i}{h^{3N}} \delta\left(\sum_i \frac{\vec{p}_i^2}{2m} - E\right) = \frac{V^N}{h^{3N}} S_{3N} \cdot R^{3N-1} dR$$

$$= \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(3N/2-1)!} (2mE)^{\frac{3N-1}{2}} dR$$

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

$$\frac{1}{T} = \frac{\partial S}{\partial E} = N k_B \frac{3}{2}\frac{1}{E} \longrightarrow \overset{\text{能量}}{E = \frac{3}{2} N k_B T} \longrightarrow \overset{\text{热容}}{C_V = \frac{\partial E}{\partial T} = \frac{3}{2} N k_B}$$

$$dE = TdS - PdV \xrightarrow{dE=0} \frac{P}{T} = \left.\frac{dS}{dV}\right|_E = \frac{N k_B}{V} \longrightarrow \underset{\text{状态方程}}{PV = N k_B T}$$

Ideal gas: distribution

从N个粒子的概率分布计算单粒子的分布函数：
把其他N-1个粒子的变量积掉

Distribution function of single particle

$$
\begin{aligned}
P(\vec{p}_1) &= \int d^3\vec{q}_1 \int \prod_{i=1}^{N} d\vec{q}_i d\vec{p}_i\, \rho\left(\{\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2, \cdots, \vec{q}_N, \vec{p}_N\}\right) \\
&= V \frac{\Omega\left(N-1, E-\frac{\vec{p}_1^2}{2m}, V\right)}{\Omega(N, E, V)} \\
&= \frac{V \frac{V^{N-1}}{h^{3(N-1)}} S_{3N}\left(2m\left(E-\frac{\vec{p}_1^2}{2m}\right)\right)^{[3(N-1)-1]/2} \Delta R^{\frac{1}{V}\frac{2}{3}\overline{\frac{1}{2}mv^2}}}{\frac{V^{3N}}{h^{3N}} S_{3(N-1)}\,(2mE)^{(3N-1)/2}\,\Delta R} \\
&= \left(1-\frac{\vec{p}_1^2}{2m}\right)^{\frac{3N}{2}-2} \frac{1}{\pi^{\frac{3}{2}}(2mE)^{\frac{3}{2}}} \frac{\left(\frac{3N}{2}-1\right)!}{\left(\frac{3(N-1)}{2}-1\right)!} \\
&= \left(1-\frac{\vec{p}_1^2}{2m}\right)^{\frac{3N}{2}-2} \frac{\left(\frac{3N}{2}-1\right)^{\left(\frac{3N}{2}-1\right)}}{(2\pi mE)^{\frac{3}{2}}\left(\frac{3N}{2}-1-\frac{3}{2}\right)^{\left(\frac{3N}{2}-1-\frac{3}{2}\right)}} \\
&\cong \left(1-\frac{\vec{p}_1^2}{2mE}\right)^{\frac{3N}{2}-2} \frac{1}{(2\pi mE)^{\frac{3}{2}}} \left(\frac{3N}{2}\right)^{\frac{3}{2}} \\
&\cong \left(1-\frac{\vec{p}_1^2}{2m(3N/2)k_B T}\right)^{\frac{3N}{2}} \left(\frac{3N}{4\pi mE}\right)^{\frac{3}{2}} \\
&\cong \left(\frac{3N}{4\pi m(3N/2)k_B T}\right)^{\frac{3}{2}} e^{-\frac{\vec{p}_1^2}{2mk_B T}} \\
&= \left(\frac{1}{2\pi mk_B T}\right)^{\frac{3}{2}} e^{-\frac{\vec{p}_1^2}{2mk_B T}}
\end{aligned}
$$

unconditional probability

$$\frac{1}{\Omega(E,V,N)}$$

$$E = 3Nk_B T/2$$

$$\lim_{N\to\infty}\left(1-\frac{x}{N}\right)^N = e^{-x}$$

Maxwell-Boltzman distribution

Mixing entropy

Problem: Ideal gas entropy is NOT extensive!

$$S(E, V, N) = Nk_B \ln \left[V \left(\frac{4\pi e m E}{3N} \right)^{3/2} \right]$$

上面得到的理想气体的熵有缺陷:
因为这样的熵不是广延量，E，V，N扩大
一个倍数，熵不是扩大相应倍数

$$(E, V, N) \to (\lambda E, \lambda V, \lambda N) \qquad S \to \lambda(S + Nk_B \ln \lambda)$$

Reason: It is due to volume term.

$$S(E,V,N) = Nk_B \ln V + Nk_B \ln \left(\frac{4\pi e m E}{3N} \right) = Nk_B \ln V + Nk_B \sigma$$

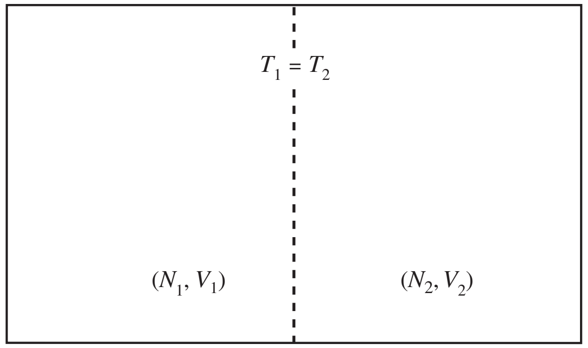
Solution: Multiplying a factor 1/N! since particles are identical.

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

$$S = k_B \ln \Omega = k_B [N \ln V - N \ln N + N \ln e] + Nk_B \sigma = Nk_B \left[\ln \frac{eV}{N} + \sigma \right]$$

Mixing entropy

Mixture of two isolated gas



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

$$\sigma_\alpha = \ln\left(\frac{4\pi e m_\alpha}{3} \cdot \frac{E_\alpha}{N_\alpha}\right)^{3/2}$$

contribution from momentum

$$\frac{3}{2}k_B T_f = \frac{E_1 + E_2}{N_1 + N_2} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2}k_B T.$$

Temperature is unchanged.

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

contribution from momentum
satisfies the extensive condition

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

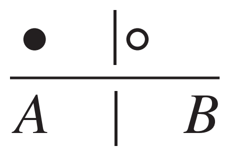
Gibbs paradox

$N_1/V_1 = N_2/V_2.$

no changes physically
but mixed entropy from above is nonzero!

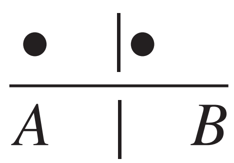
$$\frac{\bullet \quad |\circ}{A \quad | \quad B} \quad \text{and} \quad \frac{\circ \quad | \quad \bullet}{A \quad | \quad B}$$

Identical particles

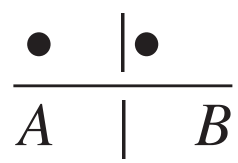


and

distinct particles



and



identical particles

Over-count the phase space of N identical particles by the number of possible permutation

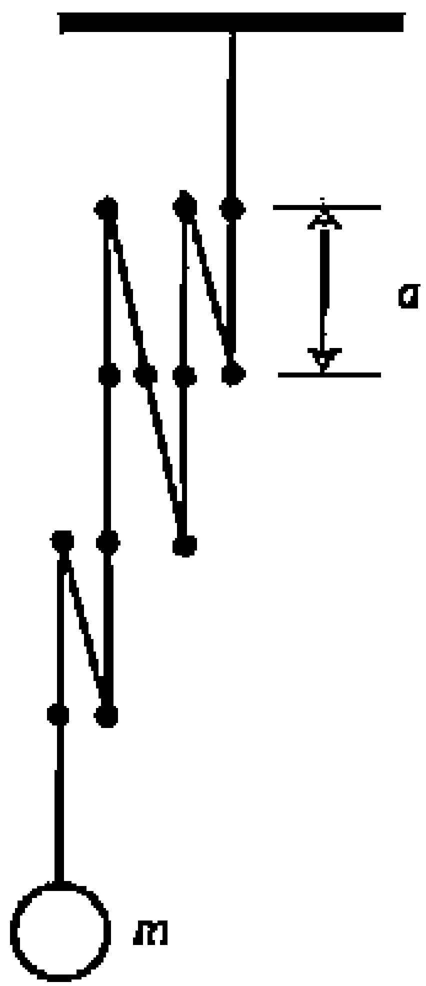
$$\Omega(N, E, V) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(3N/2-1)!} (2mE)^{(3N-1)/2} \Delta_R$$

$$S = k_B \ln \Omega = k_B[N \ln V - N \ln N + N \ln \mathrm{e}] + Nk_B\sigma = Nk_B \left[\ln \frac{\mathrm{e}V}{N} + \sigma \right]$$

In classical mechanics, particle are distinguishable, only in QM, particles are identical.

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

Homework 3



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

1) The ceiling is chosen as the reference point of the poetical energy, if the mass is L away from the ceiling, what is the entropy of this system?
2) If the temperature of the system is T, what is the length of L as a function of T?
3) What is the free energy of the system at T?

Homework 3

Relativistic particles: N *indistinguishable* relativistic particles move in *one dimension* subject to a Hamiltonian

$$\mathcal{H}\left(\{p_i, q_i\}\right) = \sum_{i=1}^{N} \left[c|p_i| + U(q_i)\right],$$

with $U(q_i) = 0$ for $0 \leq q_i \leq L$, and $U(q_i) = \infty$ otherwise. Consider a *microcanonical* ensemble of total energy E.

(a) Compute the contribution of the coordinates q_i to the available volume in phase space $\Omega(E, L, N)$.

(b) Compute the contribution of the momenta p_i to $\Omega(E, L, N)$.
(*Hint*. The volume of the hyperpyramid defined by $\sum_{i=1}^{d} x_i \leq R$, and $x_i \geq 0$, in d dimensions is $R^d/d!$.)

(c) Compute the entropy $S(E, L, N)$.

(d) Calculate the one-dimensional pressure P.

(e) Obtain the heat capacities C_L and C_P.

(f) What is the probability $p(p_1)$ of finding a particle with momentum p_1?

Summary

- Phase space of N-particle system and ensemble theory
- The most probable distribution of micro-canonical ensemble
- 3 laws of thermodynamics from micro-canonical ensemble theory
- Calculating thermal properties from the distribution i.e. from the number of microstate.