Statistical Mechanics II

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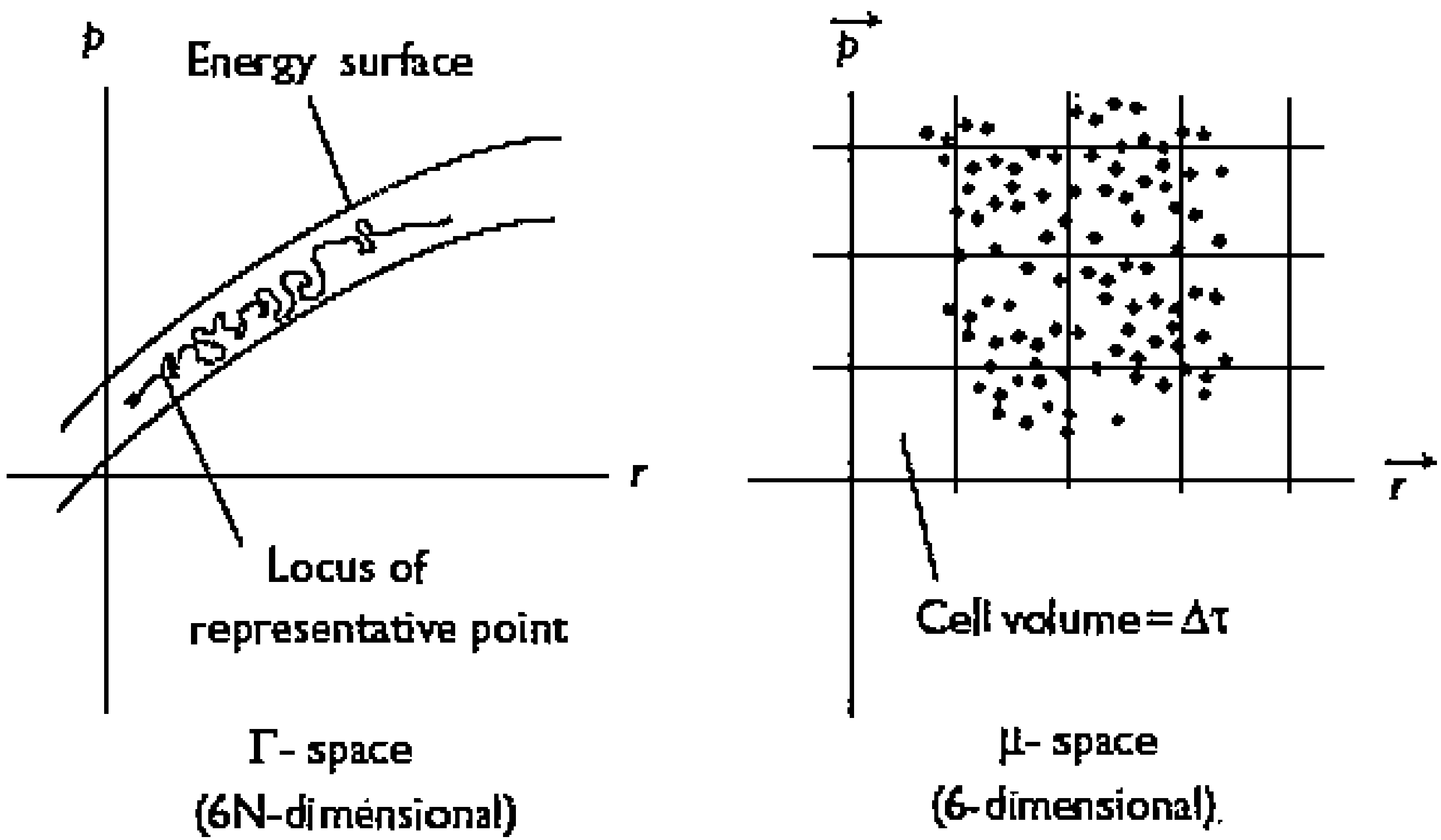
Lecture 3

Outline

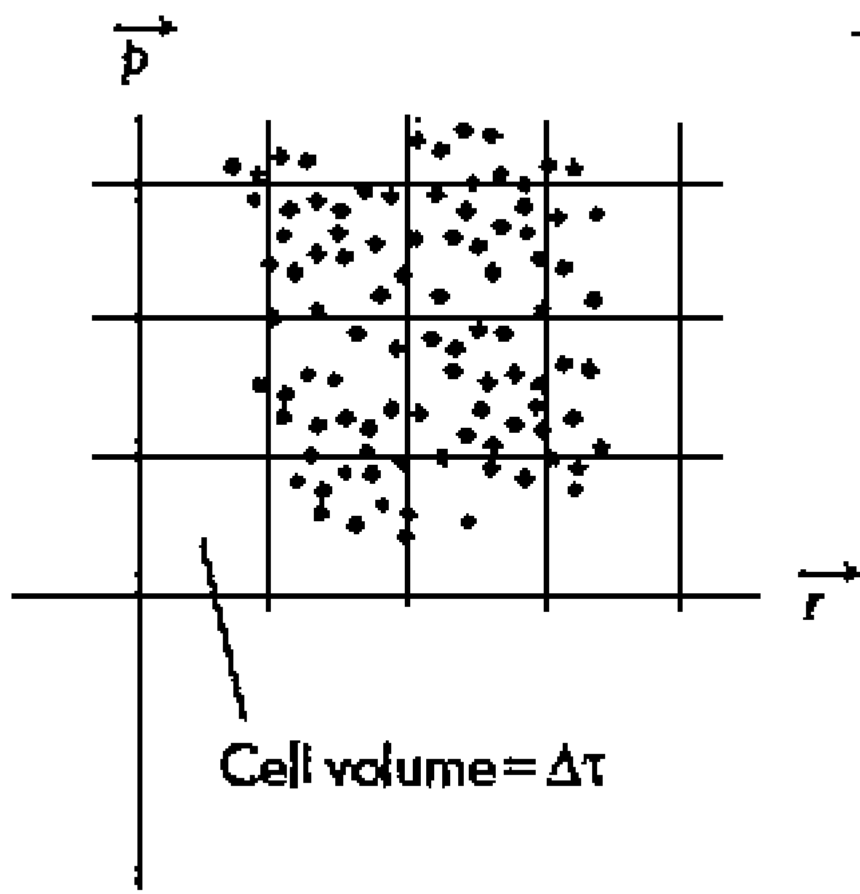
- Phase space/Description of physical systems
- The most probable distribution of quasi-independent systems
- Calculating thermal properties from distribution (classical/ breakingdown of classical/quantum harmonic oscillator/ Heat capacitor of solid/ Blackbody readiation)

Phase space



N-particle system

Distribution function



μ- space
(6-dimensional)

1. Each particle is represented by 1 points. The whole system is represented by N-points. They forms a “cloud”.

2. As time evolves, these points move and collide with each other. The distribution of cloud characterize the whole system.

$$f\left(\vec{p}, \vec{r}, t\right)$$

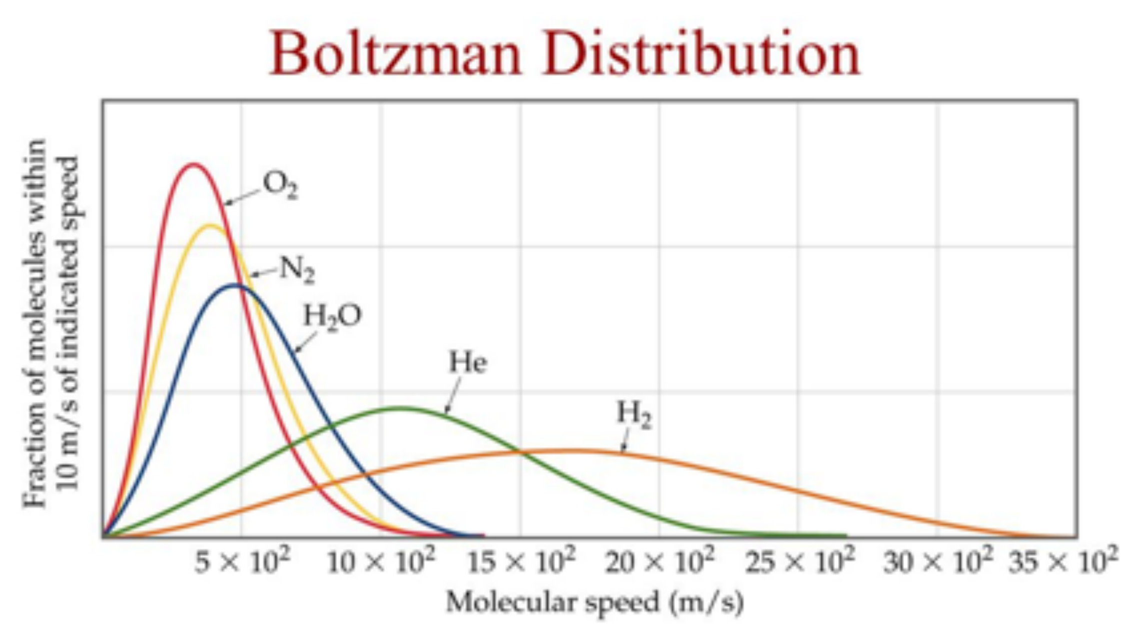
$$\begin{cases} \int f\left(\vec{p}, \vec{r}, t\right) d^3 \frac{\vec{p} d^3 \vec{r}}{h^3} = N \\ \int f\left(\vec{p}, \vec{r}, t\right) \frac{\vec{p}^2}{2m} \frac{d^3 \vec{p} d^3 \vec{r}}{h^3} = E \end{cases}$$

Distribution function for classical quasi-independent systems

if $f\left(\vec{p},\vec{r},t\right)$ is independent of $\vec{r}$

$$\int f\left(\vec{p},t\right) d^3\vec{p}\, d^3\vec{r}/h^3 = V\int f\left(\vec{p},t\right) d^3\vec{p}/h^3 = N$$

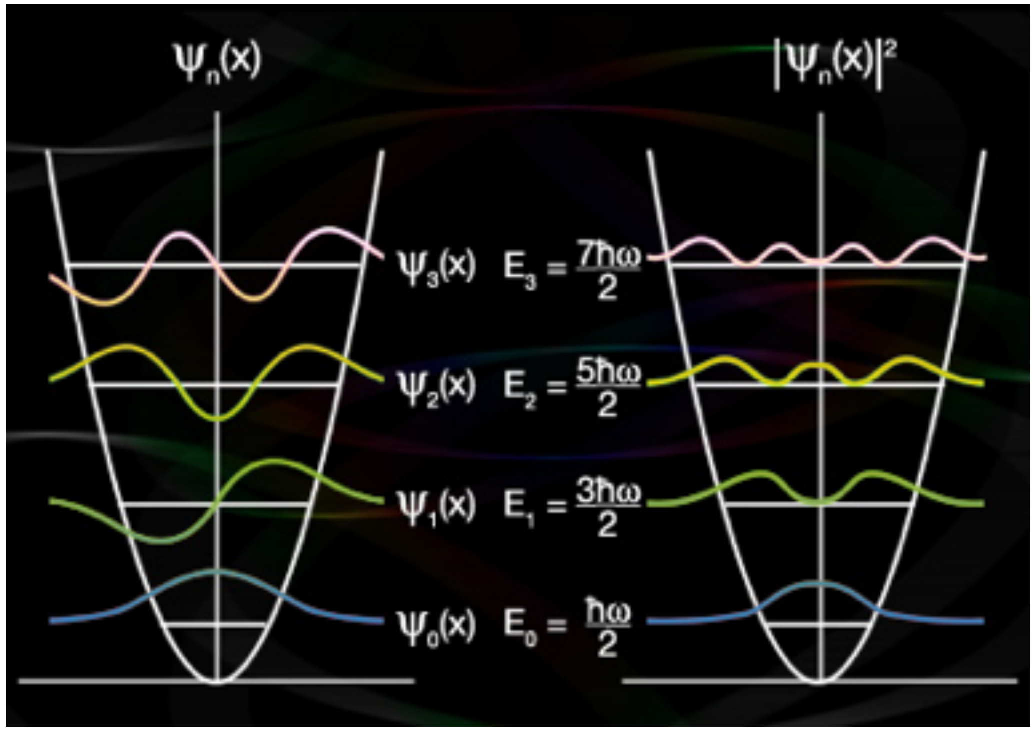
$$\begin{cases} \int f\left(\vec{p},t\right) \frac{d^3\vec{p}}{h^3} = \frac{N}{V} \\ \int f\left(\vec{p},t\right) \frac{\vec{p}^2}{2m}\frac{d^3\vec{p}}{h^3} = \frac{E}{V} \end{cases} \qquad f\left(\vec{p},t\right) = \frac{N}{V}\left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^3 e^{-\frac{\vec{p}}{2mk_BT}}$$



3 solvable cases

(1) Free particle

$$H = \frac{\vec{p}^2}{2m}$$

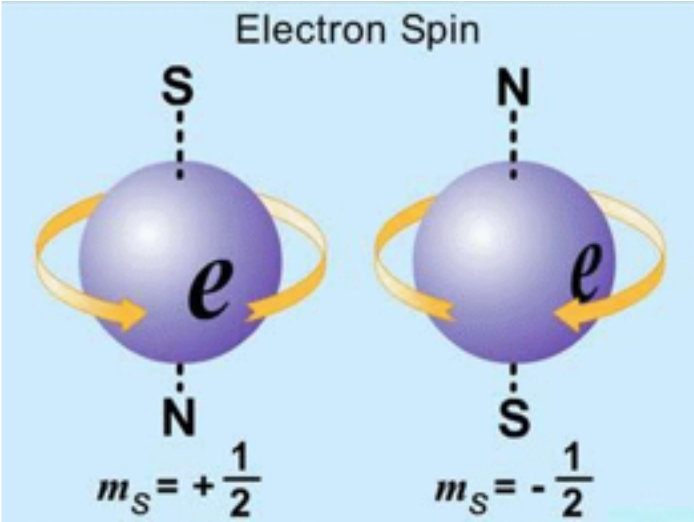


(2) Linear harmonic oscillator

$$H = \frac{\vec{p}^2}{2m} + \frac{1}{2} m\omega^2 \vec{r}^2$$

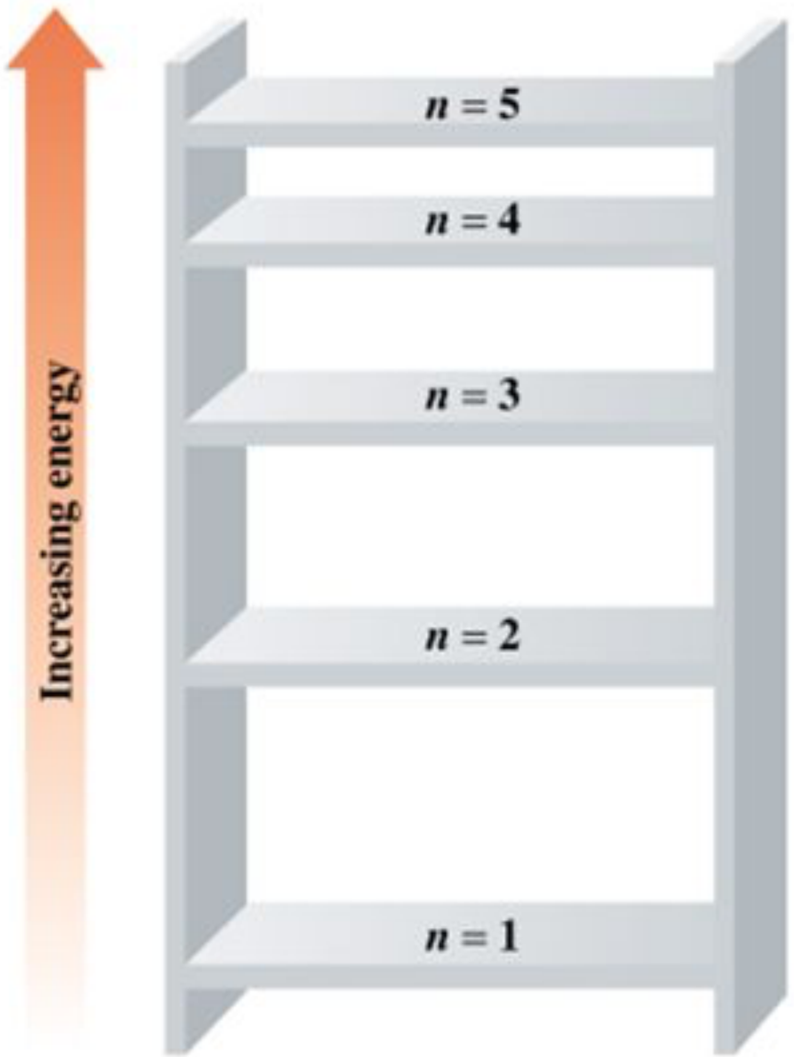
(3) Electron spin

$$H = -\vec{\mu} \cdot \vec{B} = -\mu B \cos\theta$$



The most probable distribution for classical particles

energy level	$\varepsilon_1, \varepsilon_2, \cdots, \varepsilon_\lambda, \cdots$
degeneracy	$g_1, g_2, \cdots, g_\lambda, \cdots$
occupation number	$n_1, n_2, \cdots, n_\lambda, \cdots$



$$\begin{cases} \sum_\lambda n_\lambda = N \\ \sum_\lambda \varepsilon_\lambda n_\lambda = E \end{cases}$$

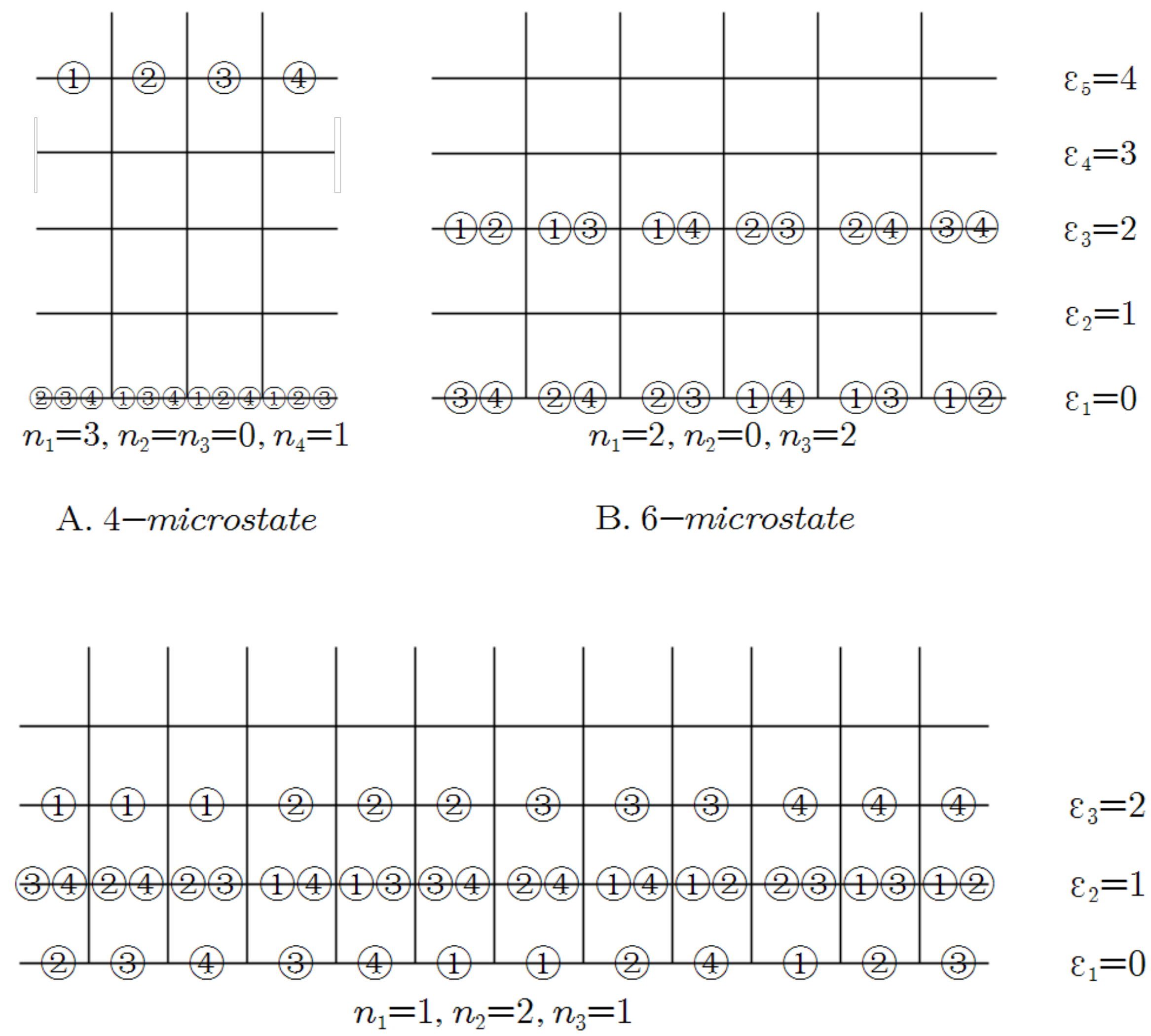
What is the most probable distribution?

The most probable distribution for classical particles

$$\begin{cases} \sum_\lambda n_\lambda = 4 \\ \sum_\lambda \varepsilon_\lambda n_\lambda = 4 \end{cases}$$

	0	1	2	3	4
A	3	0	0	0	1
B	2	0	2	0	0
C	1	2	1	0	0

	Probability
$\frac{4!}{3!1!} = 4$	$\frac{4}{22}$
$\frac{4!}{2!2!} = 6$	$\frac{6}{22}$
$\frac{4!}{1!2!1!} = 12$	$\frac{12}{22}$



A. 4−*microstate*

B. 6−*microstate*

C. 12−*microstates*

The most probable distribution for classical particles

total # of possible microstates correspond to the distribution $\{n_\lambda\}$

(a macrostate)

$$W(\{n_\lambda\}) = \frac{N!}{n_1!n_2!\cdots n_\lambda!\cdots} g_1^{n_1} g_2^{n_2} \cdots g_\lambda^{n_\lambda} \cdots$$

"ln" make it small

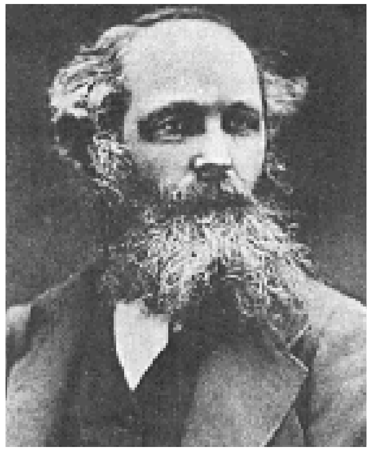
$$\mathcal{L} = \ln W(\{n_\lambda\}) - \alpha\left(\sum_\lambda g_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda n_\lambda \varepsilon_\lambda - E\right)$$

$$\ln N! = N\ln N - N \simeq N\ln N$$

$$\mathcal{L} = N\ln N - \sum_\lambda n_\lambda \ln n_\lambda + n_1 \ln g_1 - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda n_\lambda \varepsilon_\lambda - E\right)$$

$$\frac{\partial \mathcal{L}}{\partial n_\lambda} = -\ln n_\lambda + 1 + \ln g_\lambda - \alpha - \beta\varepsilon_\lambda = 0$$

$$n_\lambda = g_\lambda e^{1-\alpha g_\lambda - \beta\varepsilon_\lambda}$$



The most probable distribution

α, β are determined by

$$\begin{cases} \sum_\lambda n_\lambda = N = \sum_\lambda g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} \\ \sum_\lambda \varepsilon_\lambda n_\lambda = E = \sum_\lambda \varepsilon_\lambda g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} \end{cases}$$

Introducing function $$Z \equiv \sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}$$ partition function

$$N = e^{-\alpha} Z \qquad \alpha = \ln \frac{Z}{N}$$

$$\begin{aligned} E &= \sum_\lambda \varepsilon_\lambda g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} = \sum_\lambda -g_\lambda \frac{\partial}{\partial\beta} e^{-\alpha-\beta\varepsilon_\lambda} \\ &= -\frac{\partial}{\partial\beta} \sum_\lambda g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} = -\frac{\partial}{\partial\beta}\left[\left(e^{-\alpha}\right) Z\right] = -e^{-\alpha}\frac{\partial Z}{\partial\beta} \\ &= -\frac{N}{Z}\frac{\partial Z}{\partial\beta} = -N\frac{\partial \ln Z}{\partial\beta} \end{aligned}$$

$$\beta = \frac{1}{k_B T}$$

The most probable distribution for Bosons

$$\begin{cases} \sum_\lambda n_\lambda = 4 \\ \sum_\lambda \varepsilon_\lambda n_\lambda = 4, \quad g_\lambda = 2 \end{cases}$$

	ε_1	ε_2	ε_3	ε_4	ε_5	Boson # of microstate
A	3	0	0	0	1	$\frac{(3+2-1)!}{3!(2-1)!} \cdot \frac{(1+2-1)!}{1!(2-1)!} = 8$
B	2	0	2	0	0	$\frac{(2+2-1)!}{2!(2-1)!} \cdot \frac{(2+2-1)!}{2!(2-1)!} = 9$
C	1	2	1	0	0	$\frac{(1+1-1)!}{1!(1-1)!} \cdot \frac{(1+1-1)!}{1!(1-1)!} \cdot \frac{(2+2-1)!}{2!(2-1)!} = 3$

$\frac{(3+2-1)!}{3!(2-1)!} = 4$ ○○Δ○ ○Δ○○ ○○○Δ Δ○○○

$\frac{(2+2-1)!}{2!(2-1)!} = 3$ ○○Δ ○Δ○ Δ○○

$\frac{(1+2-1)!}{1!(2-1)!} = 2$ ○Δ Δ○

$$\begin{pmatrix} n_\lambda + g_\lambda - 1 \\ n_\lambda \end{pmatrix} = \frac{(n_\lambda + g_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!}$$

The most probable distribution for Bosons

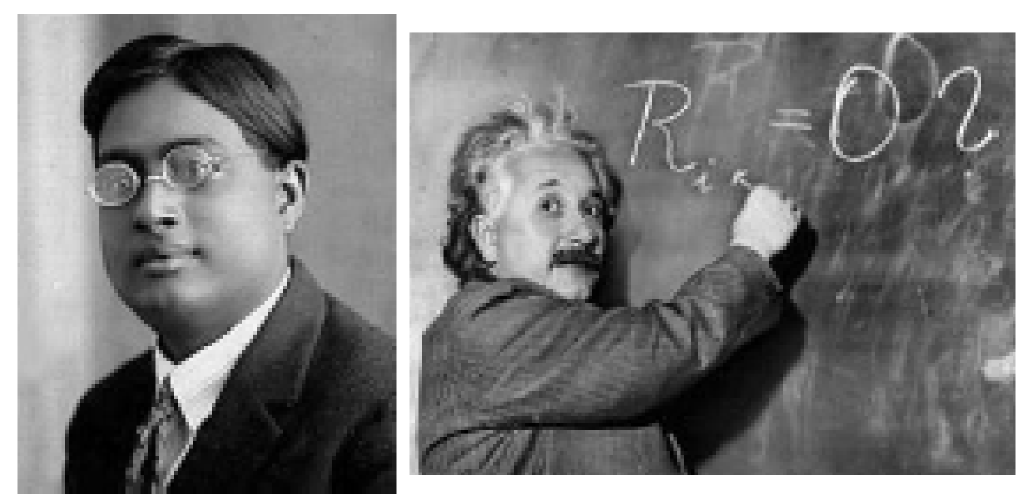
Total # of microstate for distribution $\{n_\lambda\}$ is

$$\mathcal{W}_\mathrm{B}\left(\{n_\lambda\}\right) = \prod_\lambda \begin{pmatrix} n_\lambda + g_\lambda - 1 \\ n_\lambda \end{pmatrix} = \prod_\lambda \frac{(n_\lambda + g_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!}$$

$$\begin{aligned}
\mathcal{L} &= \ln \mathcal{W}_\mathrm{B} - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= \sum_\lambda \ln \frac{(n_\lambda + g_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!} - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= (n_\lambda + g_\lambda - 1)\ln(n_\lambda + g_\lambda - 1) - n_\lambda \ln n_\lambda - (g_\lambda - 1)\ln(g_\lambda - 1) \\
&\quad -\alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial n_\lambda} &= \ln(n_\lambda + g_\lambda - 1) + 1 - \ln n_\lambda - 1 - \alpha - \beta\,\varepsilon_\lambda \\
&= \ln\left(1 + \frac{g_\lambda - 1}{n_\lambda}\right) - \alpha - \beta\,\varepsilon_\lambda = 0
\end{aligned}$$

$$n_\lambda = \frac{g_\lambda - 1}{e^{\alpha + \beta\,\varepsilon_\lambda} - 1} \overset{g_\lambda \gg 1}{\approx} \frac{g_\lambda}{e^{\alpha + \beta\,\varepsilon_\lambda} - 1}$$



Bose-Einstein distribution

The most probable distribution for Fermions

$$\begin{cases} \sum_\lambda n_\lambda = 4 \\ \sum_\lambda \varepsilon_\lambda n_\lambda = 4, \quad g_\lambda = 2 \end{cases}$$

◯ ◯ ◯ on __ __ impossible # = ◯

$\underline{◯}$ $\underline{◯}$ #=1

$\underline{◯}$ __ __ $\underline{◯}$

$$\begin{pmatrix} g_\lambda \\ n_\lambda \end{pmatrix} = \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!}$$

	ε_1	ε_2	ε_3	ε_4	ε_5	Fermion # of microstate $n_\lambda \leqslant g_\lambda$
A	3	0	0	0	1	$\frac{2!}{3!(2-3)!} \cdot \frac{2!}{1!1!} \begin{pmatrix} g_\lambda \\ n_\lambda \end{pmatrix} = 0$
B	2	0	2	0	0	$\frac{2!}{2!(2-2)!} \frac{2!}{2!(2-2)!} = 1$
C	1	2	1	0	0	$\frac{2!}{1!(2-1)!} \frac{2!}{1!(2-1)!} \frac{2!}{2!(2-2)!} = 4$

The most probable distribution for Fermions

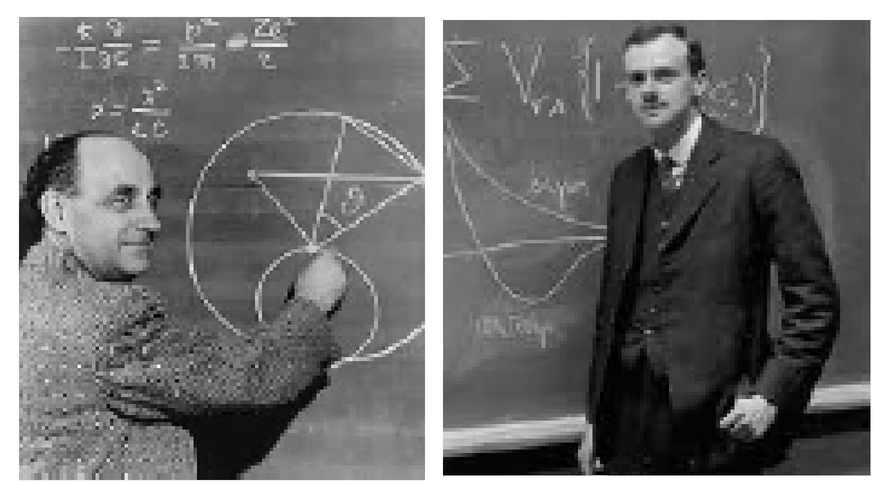
Total # of microstate for distribution $\{n_\lambda\}$ is

$$W_F\left(\{n_\lambda\}\right) = \prod_\lambda \begin{pmatrix} g_\lambda \\ n_\lambda \end{pmatrix} = \prod_\lambda \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!}$$

$$\begin{aligned}
\mathcal{L} &= \ln W_F - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= \sum_\lambda \ln \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!} - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= \sum_\lambda g_\lambda \ln g_\lambda - \sum_\lambda n_\lambda \ln n_\lambda - \sum_\lambda (g_\lambda - n_\lambda) \ln (g_\lambda - n_\lambda) \\
&\quad - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)
\end{aligned}$$

$$0 = \frac{\partial \mathcal{L}}{\partial n_\lambda} = -\ln n_\lambda + 1 + \ln (g_\lambda - n_\lambda) + 1 - \alpha - \beta\,\varepsilon_\lambda$$

$$n_\lambda = \frac{g_\lambda}{e^{\alpha + \beta\,\varepsilon_\lambda} + 1}$$



Fermi-Dirac distribution

The most probable distribution

	$W(\{n_\lambda\})$	most probable distribution	
localized particles (Classical Mechanics)	$W_C(\{n_\lambda\}) = \frac{N!}{\prod_\lambda n_\lambda!} g_\lambda^{n_\lambda}$	$n_\lambda = g_\lambda e^{-\alpha-\beta\varepsilon_\lambda}$ can be numbered	Heat capacity of solid Equal Partition Theorem Spin - System (magnetization)
delocalized particles (Quantum Mechanics) indistinguishable particles	$W_B(\{n_\lambda\}) = \prod_\lambda \frac{(n_\lambda + g_\lambda - 1)!}{n_\lambda!(g_\lambda - 1)!}$	$n_\lambda = \frac{g_\lambda}{e^{\alpha+\beta\varepsilon_\lambda} - 1}$ can not be numbered	Breaking down of Equal Partion Theorem Heat capacity of solid (QM) Black - body Radiation Bose - Einstein condensation
	$W_F(\{n_\lambda\}) = \prod_\lambda \frac{g_\lambda}{n_\lambda!(g_\lambda - n_\lambda)!}$	$n_\lambda = \frac{g_\lambda}{e^{\alpha+\beta\varepsilon_\lambda} + 1}$	Pauli exclusion principle Fermi - Liquid Superconductivity

http://demonstrations.wolfram.com/BoseEinsteinFermiDiracAndMaxwellBoltzmannStatistics/

Summary 1

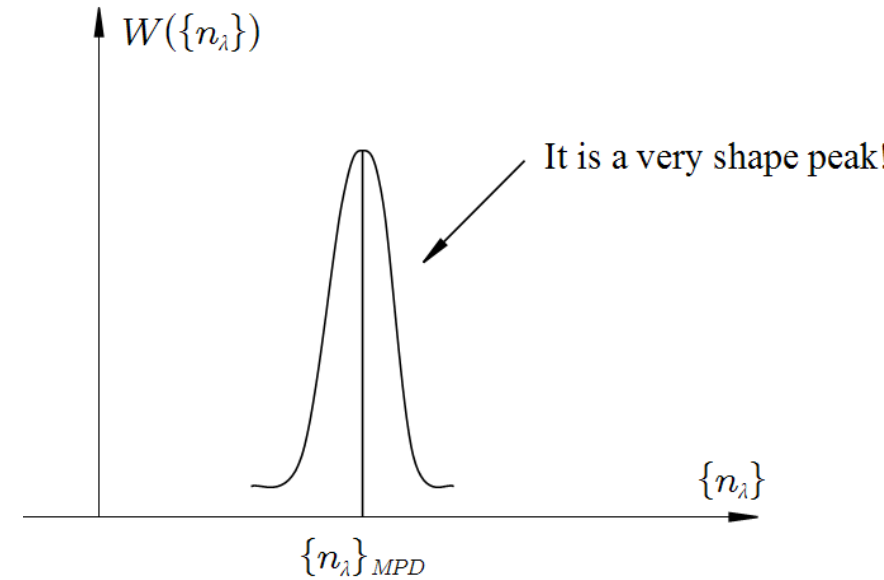
- Phase space/Description of physical systems
- The most probable distribution of quasi-independent systems

The most probable distribution (MPD) ≈ real distribution

$$W_C(\{n_\lambda\}) = \frac{N!}{\prod\limits_\lambda n_\lambda!} g_\lambda^{n_\lambda}$$

$$\mathcal{L} = \ln W_C(\{n_\lambda\}) - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)$$

$$= -\sum_\lambda n_\lambda \ln n_\lambda + n_\lambda \ln g_\lambda - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)$$



$$\frac{\partial \mathcal{L}}{\partial n_\lambda} = -\ln n_\lambda - 1 + \ln g_\lambda - \alpha - \beta\varepsilon_\lambda = 0$$

$$n_\lambda = g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} \qquad \frac{\partial^2 \mathcal{L}}{\partial n_\lambda^2} = -\frac{1}{n_\lambda} < 0$$

$$\ln W_C(\{n\}) = \ln W_C(\{n_\lambda\}_{MPD}) + \sum_\lambda \frac{\delta \mathcal{L}}{\delta n_\lambda}\delta n_\lambda - \sum_\lambda \frac{1}{n_\lambda}(\delta n_\lambda)^2$$

$$I = \frac{W_C(\{n_\lambda\})}{W_C(\{n_\lambda\}_{MPD})} = e^{\sum\limits_\lambda \left(\frac{\delta n_\lambda}{n_\lambda}\right)^2 n_\lambda} \qquad \frac{\delta n_\lambda}{n_\lambda} \sim 10^{-6}$$

$$\begin{aligned} I &= e^{-\sum\limits_\lambda (10^{-6})^2 n_\lambda} = e^{-(10^{-6})^2 \sum\limits_\lambda n_\lambda} \\ &= e^{-10^{-12}N} = e^{-10^{-12}10^{20}} = e^{-10^8} \sim 0 \end{aligned}$$

Breakingdown of CSM

Breakingdown of Classical SM

CSM $\quad n_\lambda = g_\lambda e^{-\alpha-\beta\varepsilon_\lambda}$ $\quad$ QSM $\quad n_\lambda = \dfrac{g_\lambda}{e^{\alpha+\beta\varepsilon_\lambda} \pm 1}$

If $e^\alpha \gg 1$ (i.e. $\frac{n_\lambda}{g_\lambda} = \frac{1}{e^{\alpha+\beta\varepsilon_\lambda}\pm 1} \ll 1$) then we can ignore ± 1

$$
\begin{aligned}
W_{BE}\left(\{n_\lambda\}\right) &= \prod_\lambda \frac{(g_\lambda + n_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!} \\
&= \prod_\lambda \frac{(g_\lambda + n_\lambda - 1)\,(g_\lambda + n_\lambda - 2)\cdots(g_\lambda)}{n_\lambda!} \\
&= \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}\left[1 + \frac{n_\lambda - 1}{g_\lambda}\right]\left[1 + \frac{n_\lambda - 2}{g_\lambda}\right]\cdots\left[1 + \frac{0}{g_\lambda}\right] \\
&\backsimeq \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}
\end{aligned}
$$

Breakingdown of CSM

$$W_{FD}(\{n_\lambda\}) = \prod_\lambda \begin{pmatrix} g_\lambda \\ n_\lambda \end{pmatrix} = \prod_\lambda \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!}$$

$$= \prod_\lambda \frac{g_\lambda\,(g_\lambda - 1)\cdots(g_\lambda - n_\lambda + 1)}{n_\lambda!}$$

$$= \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}\,[1]\left[1 - \frac{1}{g_\lambda}\right]\cdots\left[1 - \frac{(n_\lambda - 1)}{g_\lambda}\right]$$

$$\simeq \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}$$

$$W_{MB} = \frac{N!}{n_1!\cdots n_\lambda!\cdots}\, g_\lambda^{n_\lambda}$$

$$= N!\prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}$$

$$W_{BE} \simeq W_{FD} \simeq \frac{1}{N!} W_{MB}$$

$\frac{1}{N!}$ is a constant.

$\frac{\delta \ln W}{\delta n}$ give same results give the same MB distribution.

But it will affect the value of entropy.

Breakingdown of CSM

$$N = \sum_\lambda n_\lambda = \sum_\lambda g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} = e^{-\alpha} Z$$

$$e^\alpha = \frac{Z}{N} = \frac{\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}{N}$$

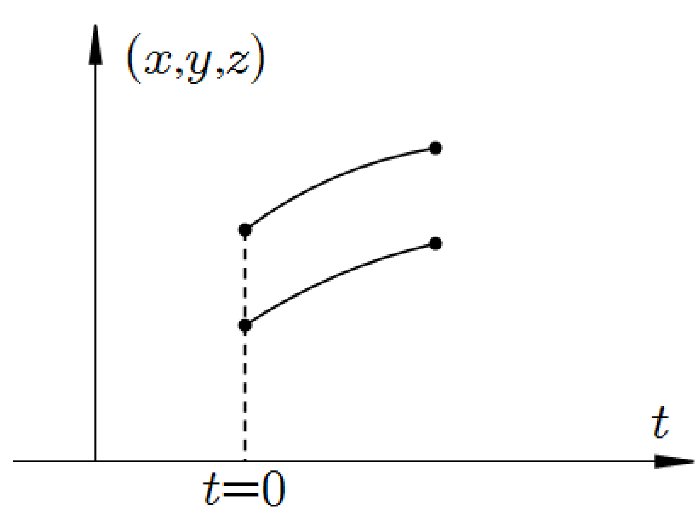
$$\begin{aligned} Z &= \int \frac{d^3\vec{q}\,d^3\vec{p}}{h^3} e^{-\beta\varepsilon} \\ &= \frac{V}{h^3} \prod_{i=1}^{3} dp_i e^{-\beta\frac{p_i^2}{2m}} \\ &= \frac{V}{h^3} (2\pi m k_B T)^{\frac{3}{2}} \end{aligned}$$

$$e^\alpha = \frac{Z}{N} = \frac{V}{N}\left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^3 = \frac{V}{N}\frac{1}{\lambda_T^3}$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \qquad \frac{V}{N} = d^3$$

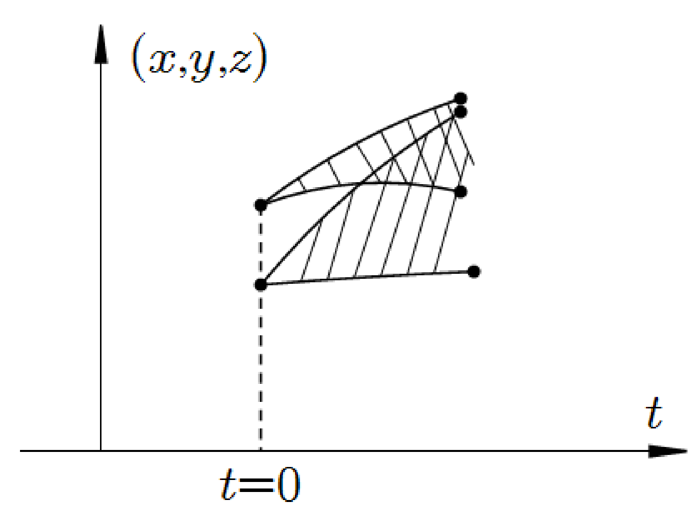
If $e^\alpha = \left(\frac{d}{\lambda_T}\right)^3 \gg 1$

particles are not overlap and distinguishable.

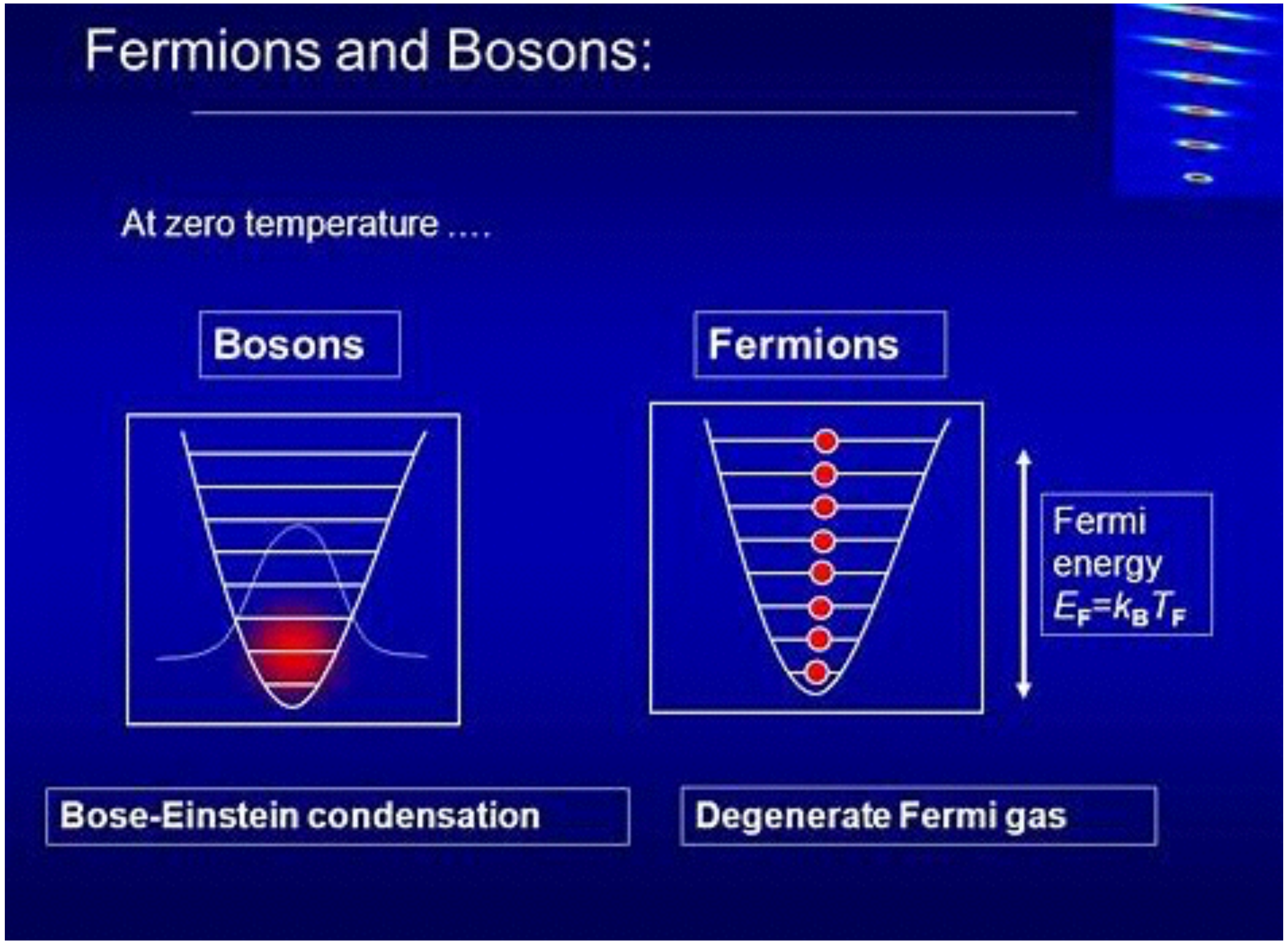


If $e^\alpha \sim 1$ or $\ll 1$

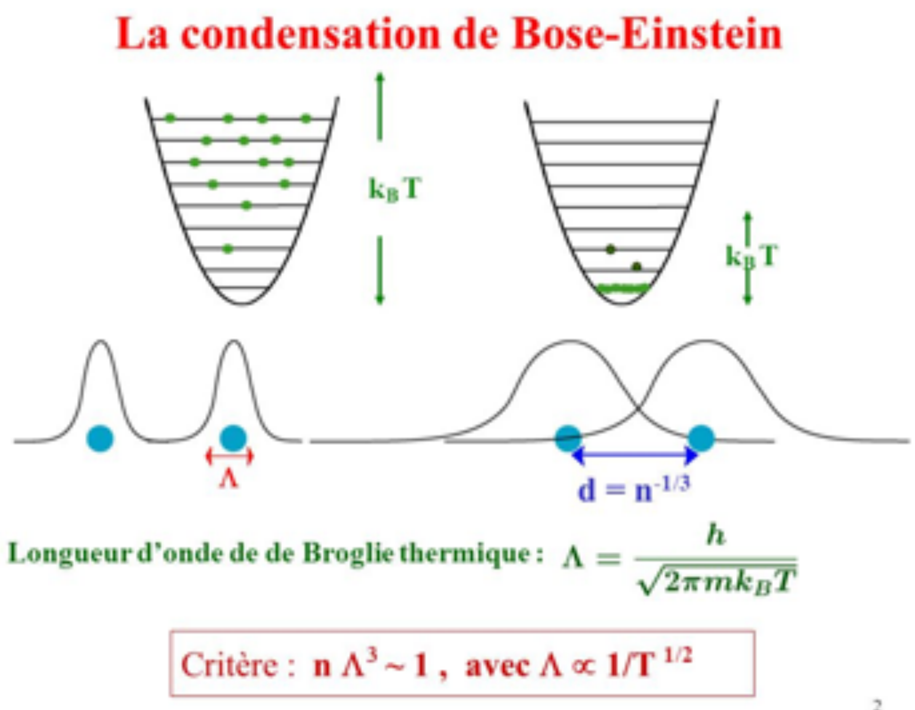
particles are indistinguishible.

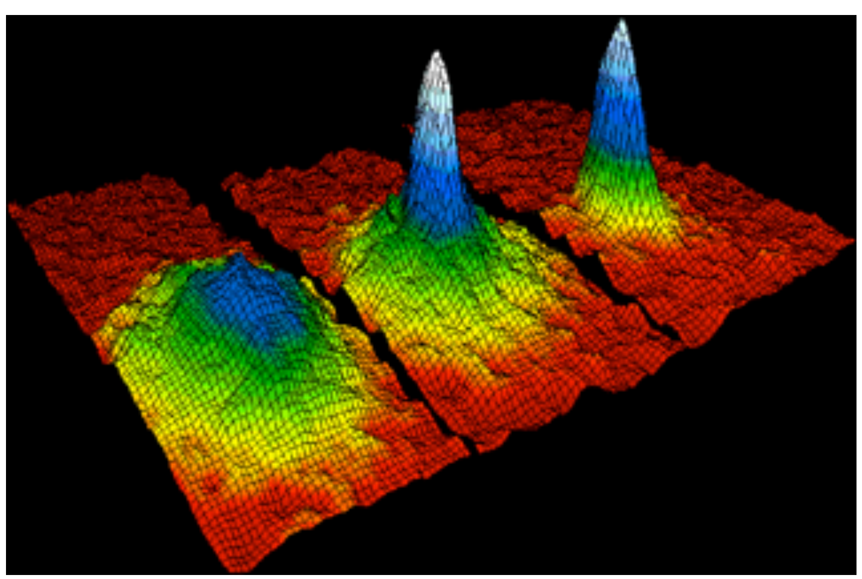


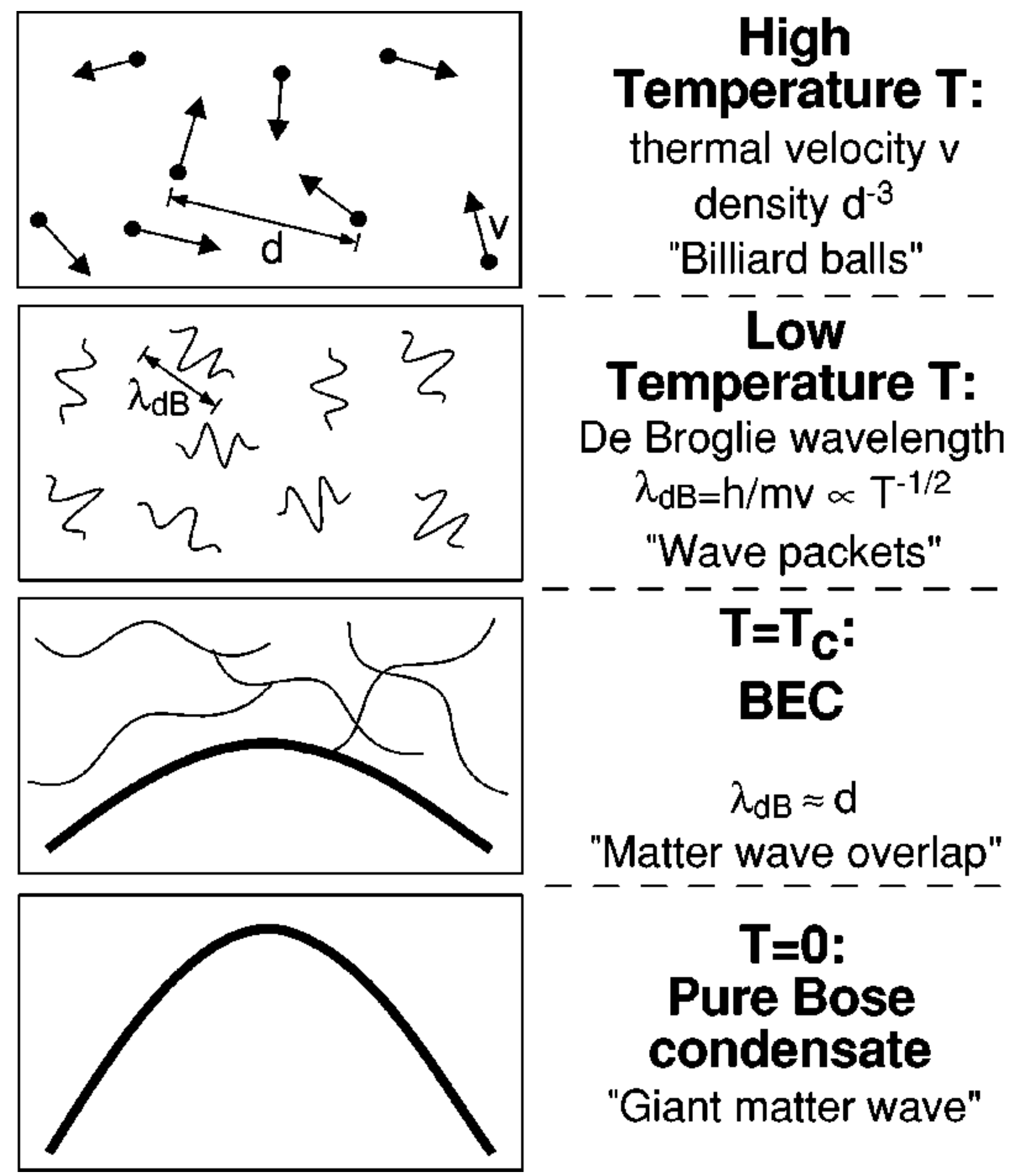
Degenerated quantum gas



Bose-Einstein condensate



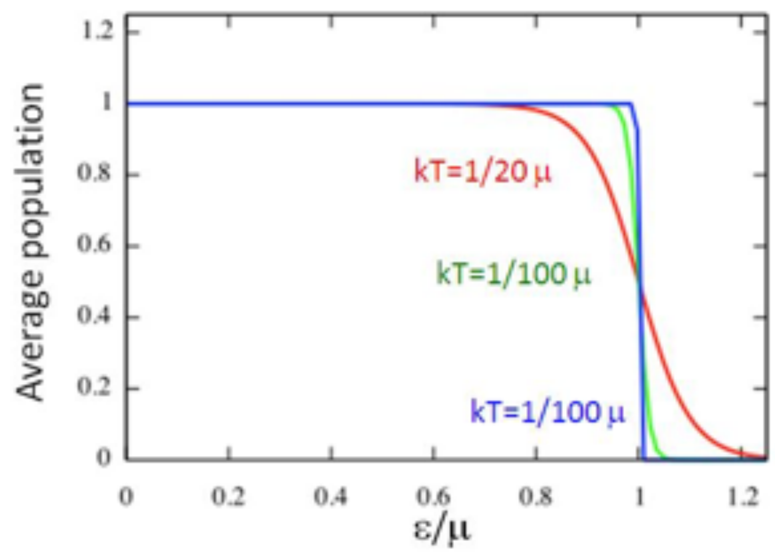


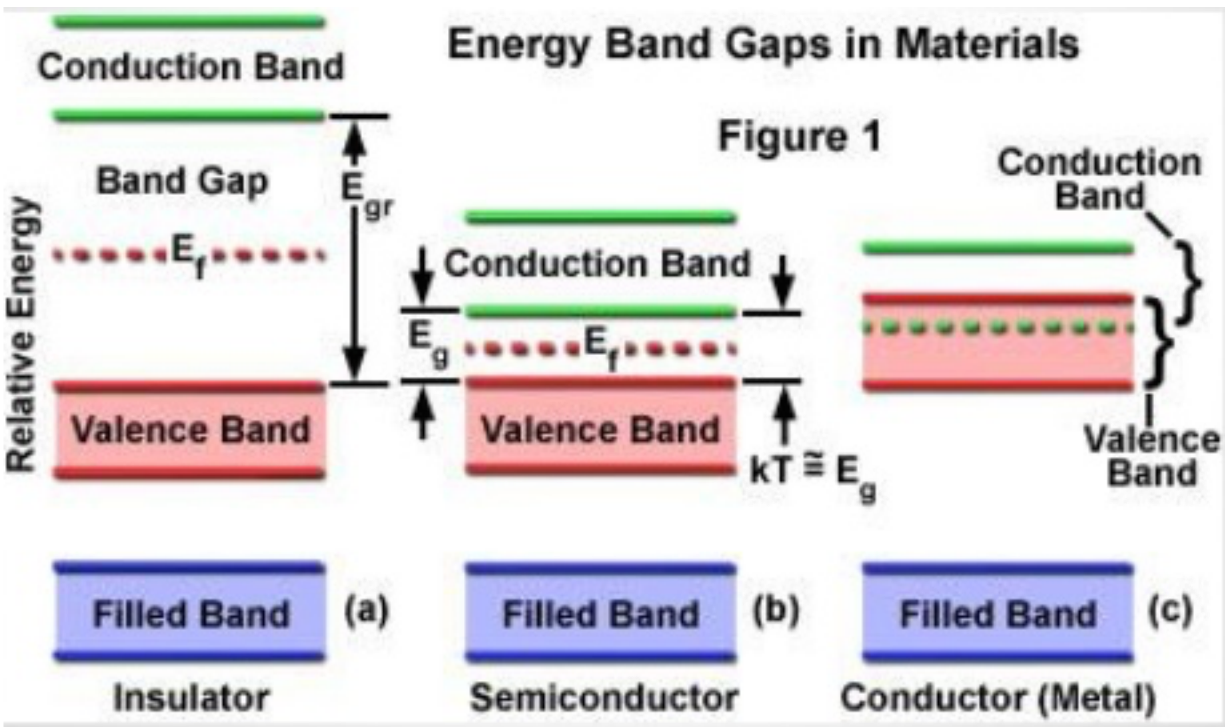


https://en.wikipedia.org/wiki/Bose–Einstein_condensate

Degenerated Fermi gas

$$\langle n_i \rangle = \frac{1}{1+e^{\beta(\varepsilon_i-\mu)}}$$





Thermal properties of classical noninteracting system

$$\begin{cases} \sum_\lambda n_\lambda = N = \sum_\lambda g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} \\ \sum_\lambda \varepsilon_\lambda n_\lambda = E = \sum_\lambda \varepsilon_\lambda g_\lambda e^{-\alpha-\beta\varepsilon_\lambda} \end{cases}$$

Introducing function $Z = \sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}$ partition function

$$\frac{E}{N} = \frac{\sum_\lambda \varepsilon_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}{\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}} = \frac{-\frac{\partial}{\partial\beta}\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}{\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}} = \frac{-\frac{\partial}{\partial\beta}Z}{\mathcal{Z}} = -\frac{\partial \ln \mathcal{Z}}{\partial\beta}$$

$$f(\varepsilon_\lambda) = \frac{1}{\mathcal{Z}} e^{-\beta\varepsilon_\lambda} \qquad \sum_\lambda f(\varepsilon_\lambda) = 1$$

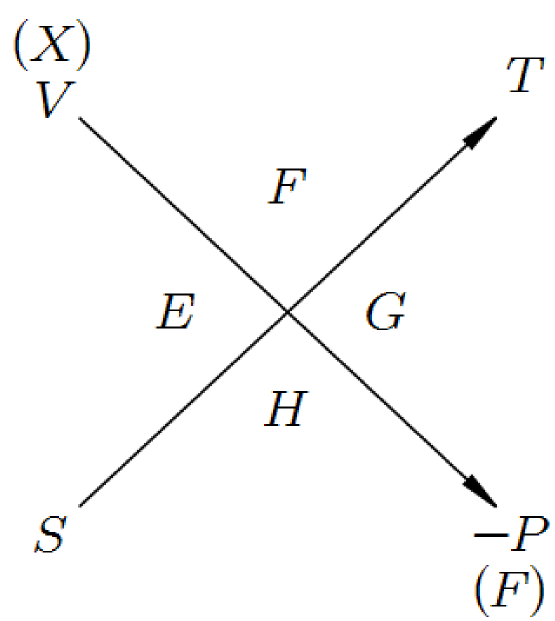
$$\frac{\mathcal{S}}{N} = -k_B \sum_\lambda f(\varepsilon_\lambda) \ln f(\varepsilon_\lambda) = -k_B \sum_\lambda f(\varepsilon_\lambda) \ln \frac{e^{-\beta\varepsilon_\lambda}}{\mathcal{Z}}$$

$$= -k_B \sum_\lambda f(\varepsilon_\lambda)(-\beta\varepsilon_\lambda) + k_B \sum_\lambda f(\varepsilon_\lambda) \ln \mathcal{Z} = k_B\beta \sum_\lambda f(\varepsilon_\lambda)\varepsilon_\lambda + k_B \ln \mathcal{Z}$$

$$= \frac{E/N}{T} + k_B \ln \mathcal{Z} \qquad -k_B T \ln \mathcal{Z} = \frac{E}{N} - \frac{T\mathcal{S}}{N} \equiv \frac{\mathcal{F}}{N}$$

Free energy

Thermal properties of classical noninteracting system



(1) Ideal gas

$$d\mathcal{F} = -P dV - \mathcal{S} dT + F dX$$

$$\mathcal{S} = -\frac{\partial \mathcal{F}}{\partial T}\bigg|_V \qquad P = -\frac{\partial \mathcal{F}}{\partial V}\bigg|_T \qquad F = \frac{\partial \mathcal{F}}{\partial X}\bigg|_{V,T}$$

$$\mathcal{Z} = N \int e^{-\beta \frac{\vec{p}^2}{2m}} \frac{d^3\vec{q} d^3\vec{p}}{h^3} = N V \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}$$

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

$$P = -\frac{\partial \mathcal{F}}{\partial V}\bigg|_T = N k_B T \frac{\partial \ln V}{\partial V} = \frac{N k_B T}{V}$$

$$PV = N k_B T$$

$$\frac{\mathcal{S}}{N} = -\frac{\partial \mathcal{F}}{\partial T}\bigg|_V = k_B \ln V \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} - \frac{3}{2} k_B$$

Thermal properties of classical noninteracting system

$$\frac{E}{N} = -\frac{\frac{\partial}{\partial\beta} Z(\beta)}{Z(\beta)} = -\frac{\partial}{\partial\beta} \ln Z(\beta) = -\frac{\partial}{\partial\beta} \ln\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V$$

$$= -\frac{\partial}{\partial\beta}\left[\ln\left(\frac{1}{\beta^{3/2}}\right) + \ln\left(\frac{2\pi m}{h^2}\right)^{3/2} V\right] = \frac{3}{2\beta}$$

From experiment $\qquad \dfrac{E}{N} = \dfrac{3}{2} k_B T \Rightarrow \beta = \dfrac{1}{k_B T}$

$$C_V = \left.\frac{dE}{dT}\right|_V = \frac{3}{2} N k_B$$

Derivation of thermodynamics

$$dE = \frac{3}{2} N k_B dT$$

$$\mathcal{S}(V, T)$$

$$\frac{d\mathcal{S}}{N k_B} = d \ln V + \frac{3}{2} d \ln T = \frac{dV}{V} + \frac{3}{2}\frac{dT}{T} = \frac{dV}{V} + \frac{3}{2}\frac{dE}{E}$$

$$\frac{dV}{V} = \frac{PdV}{N k_B T}$$

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

$$\frac{d\mathcal{S}}{N k_B} = \frac{PdV}{N k_B T} + \frac{dE}{N k_B T}$$

$$d\mathcal{S} = \frac{PdV + dE}{T} = \frac{dQ}{T}$$

$$\boxed{dQ = T d\mathcal{S}}$$

Derivation of thermodynamics

$$E = \sum_{\lambda} \varepsilon_{\lambda} n_{\lambda}$$

$$dE = \sum_{\lambda} [(d\varepsilon_{\lambda}) n_{\lambda} + \varepsilon_{\lambda}(dn_{\lambda})]$$

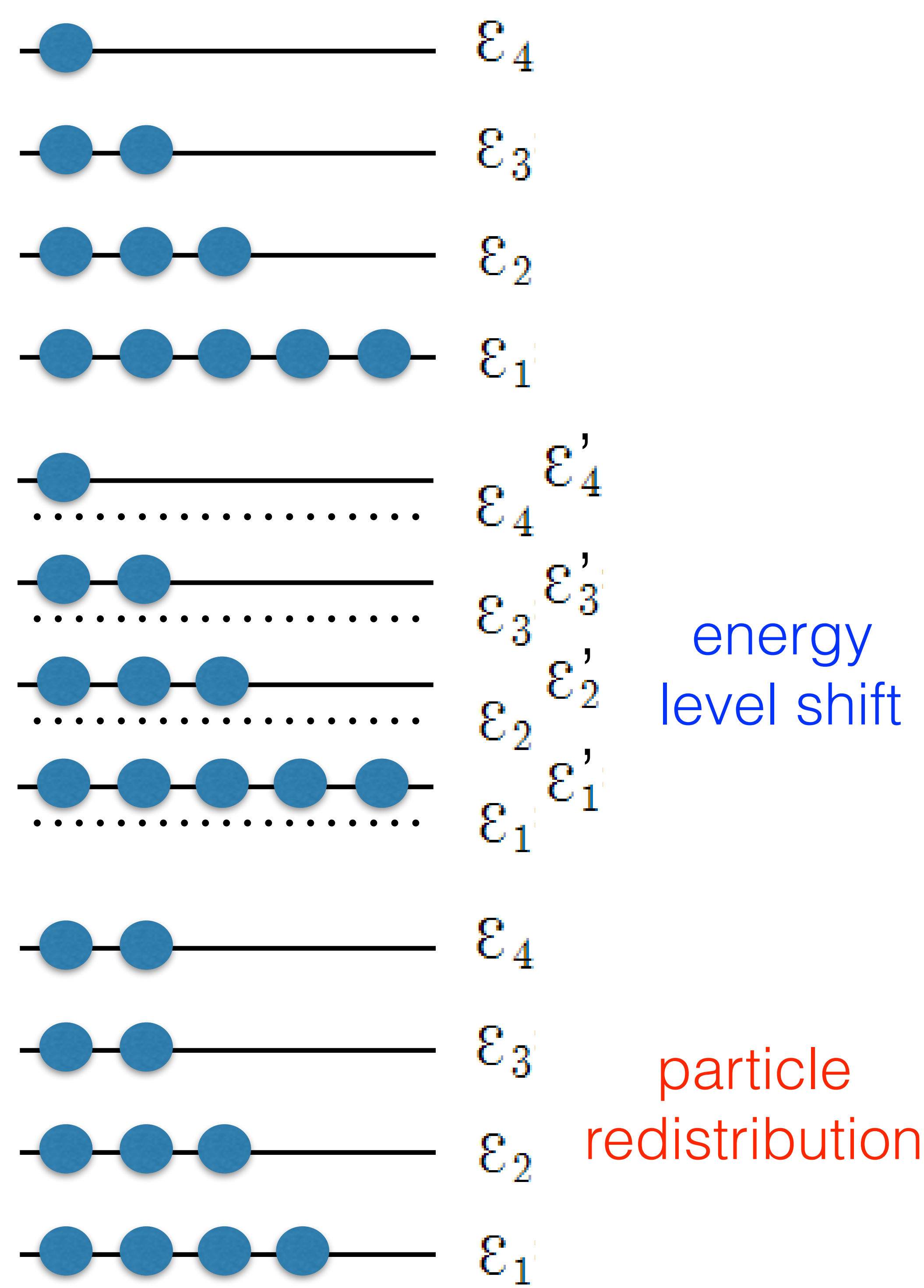
$$dE = J_i dx_i + TdS$$

$$\text{đ}W = \sum_i J_i dx_i$$

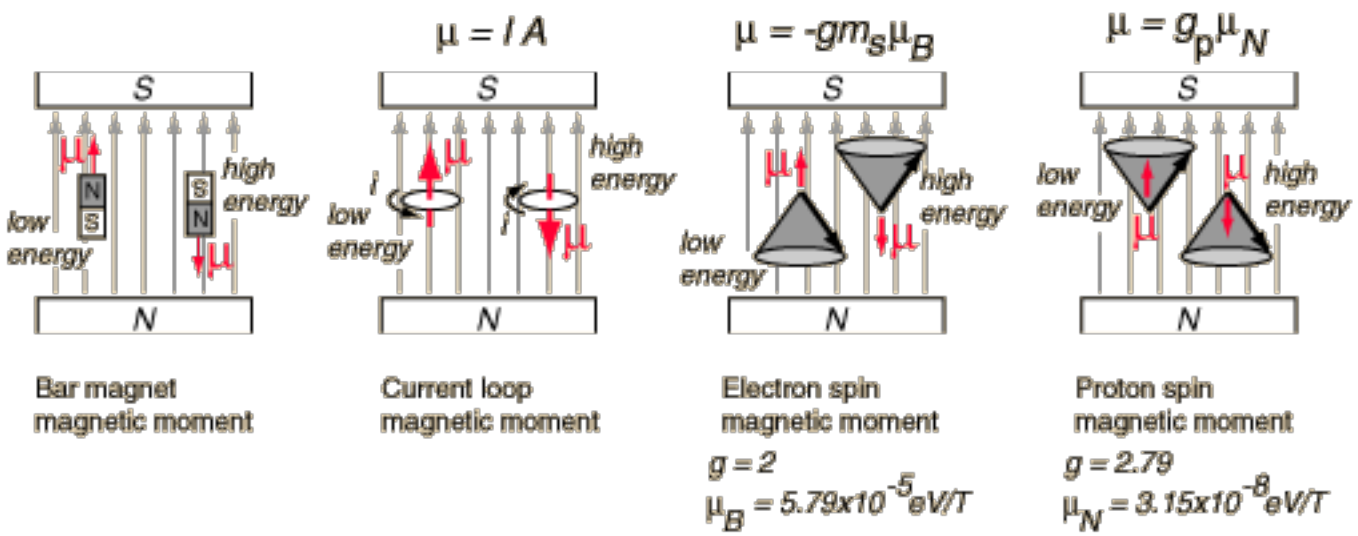
work

$$dQ = TdS$$

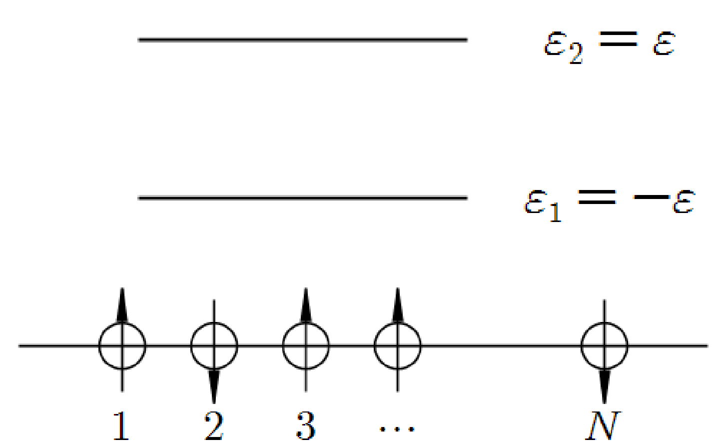
heat



Thermal properties of classical noninteracting system



Two Level System



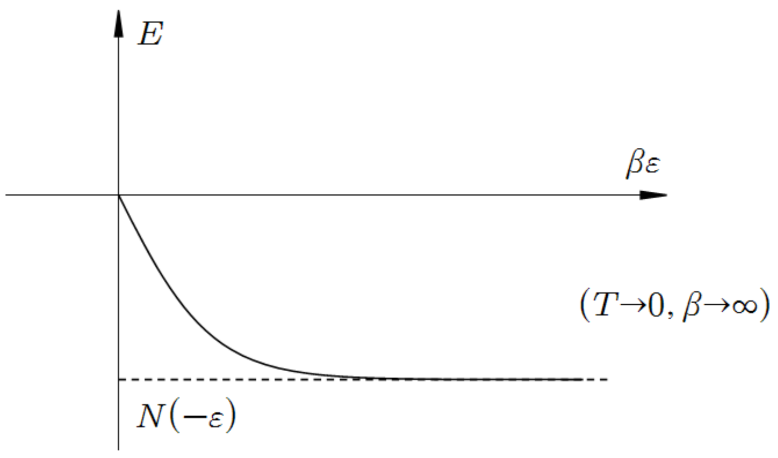
$$\mathcal{Z} = 2\cosh\beta\,\varepsilon \qquad \frac{\mathcal{F}}{N} = -k_B T \ln\mathcal{Z}$$

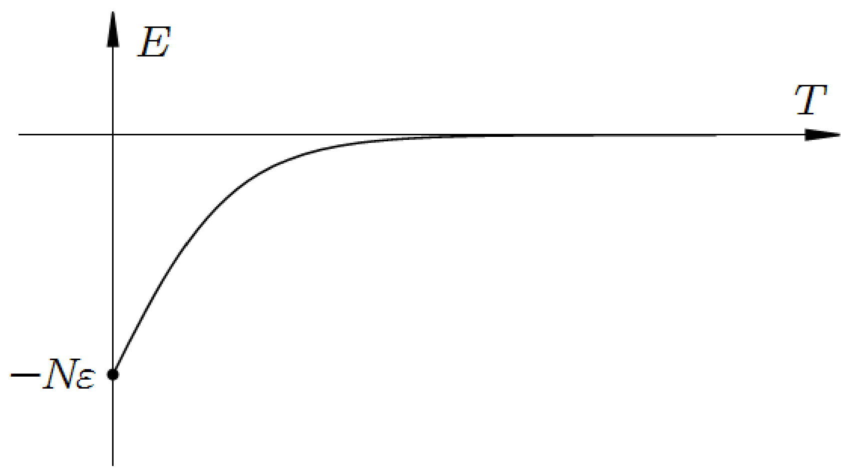
$$\frac{E}{N} = -\frac{\partial\ln\mathcal{Z}}{\partial\beta} = -\frac{\partial\ln 2\cos\beta\,\varepsilon}{\partial\beta} = -\frac{2\sinh\beta\,\varepsilon}{2\cosh\beta\,\varepsilon}\varepsilon = -\varepsilon\tanh\beta\,\varepsilon$$

$$E = -N\varepsilon\tanh\beta\,\varepsilon$$

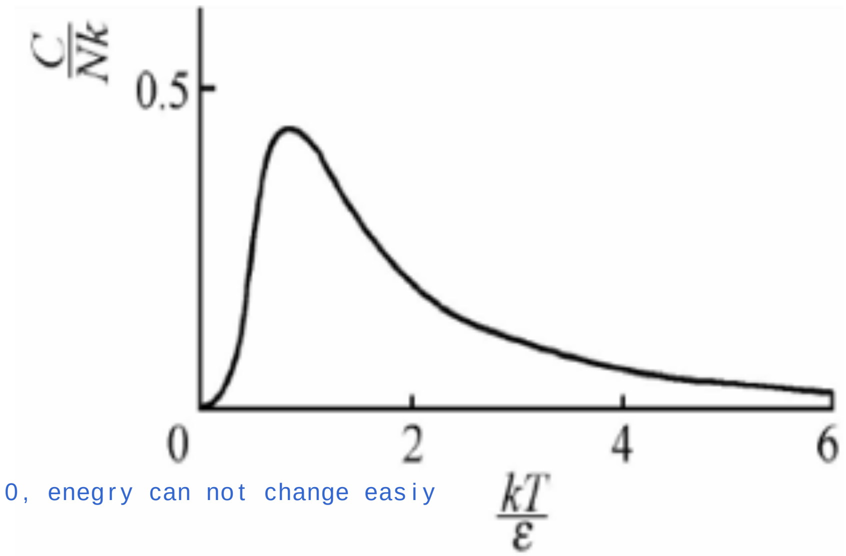
Thermal properties of classical noninteracting system

(2) Two Level System





$$C_V = \frac{dE}{dT} = N k_B (\beta \varepsilon)^2 \frac{1}{\cosh^2 \beta \varepsilon}$$



at 0, enegry can not change easiy

Thermal properties of classical noninteracting system

(3) Harmonic Oscillator

Why here are 6 freedom degree

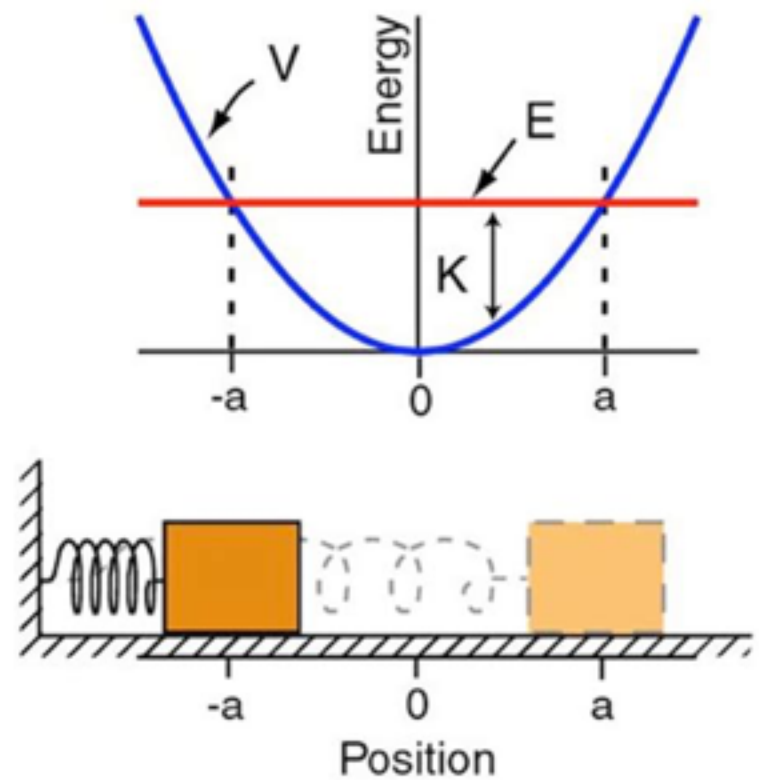
$$H\left(\{\vec{q}_i, \vec{p}_i\}\right) = \sum_{i=1}^{N}\left[\frac{\vec{p}_i^2}{2m} + \frac{1}{2}m\omega^2\vec{q}_i^2\right] \qquad n_\lambda = g_\lambda e^{-\beta\varepsilon_\lambda} \qquad \lambda = (\vec{q}, \vec{p})$$

$$\mathcal{Z} = \frac{1}{h^3}\int e^{-\beta\left(\frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega^2\vec{q}^2\right)} d^3\vec{q}\, d^3\vec{p}$$

$$f\left(\vec{q}, \vec{p}\right) = \frac{N}{Z} e^{-\beta\left(\frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega^2\vec{q}^2\right)}$$

$$\int e^{-\beta\frac{1}{2}m\omega^2 q^2} dq = \sqrt{\frac{\pi}{\frac{1}{2}m\omega^2\beta}}$$

$$\int e^{-\beta\frac{p^2}{2m}} dp = \sqrt{\frac{\pi}{\frac{1}{2m}\beta}}$$



$$\frac{E}{N} = -\frac{\partial \ln \mathcal{Z}}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln\frac{1}{\beta^3} = \frac{3\partial\ln\beta}{\partial\beta} = \frac{3}{\beta} = 3k_B T$$

Thermal properties of classical noninteracting system

$$\mathcal{Z} = \frac{1}{h^3}\left(\sqrt{\frac{\pi}{\frac{1}{2m}\beta}}\sqrt{\frac{\pi}{\frac{1}{2}m\omega^2\beta}}\right)^3 = \frac{1}{h^6}\left(\frac{4\pi}{\omega^2\beta}\right)^{\frac{3}{2}} = \frac{1}{(\hbar\omega)^3\,\beta^3} = \left(\frac{k_B T}{\hbar\omega}\right)^3$$

$$\mathcal{F} = -k_B T \ln\left(\frac{1}{(\hbar\omega)^3\,\beta^3}\right) = -k_B T \ln\left(\frac{k_B T}{\hbar\omega}\right)^3$$

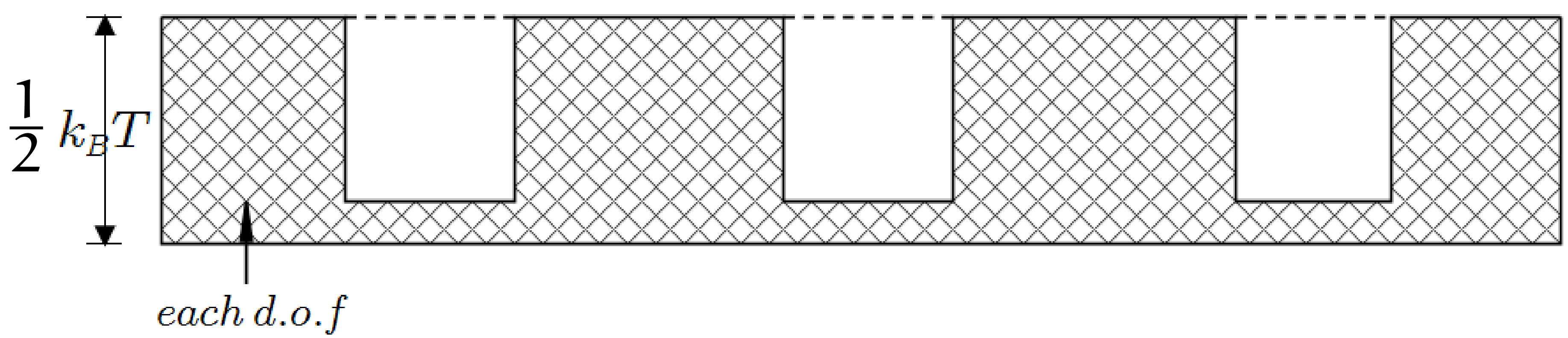
$$\mathcal{F} = -k_B T \ln\left(\frac{1}{(\hbar\omega)^3\,\beta^3}\right) = -k_B T \ln\left(\frac{k_B T}{\hbar\omega}\right)^3$$

$$\frac{\mathcal{S}}{N} = -\frac{\partial\mathcal{F}}{\partial T} = k_B \ln\left(\frac{k_B T}{\hbar\omega}\right)^3 + 3k_B T\frac{1}{T} = k_B \ln\left(\frac{k_B T}{\hbar\omega}\right)^3 + 3k_B$$

Equal-partition theorem

$$\int e^{-\beta c p^2} dp \sim \sqrt{\frac{\pi}{\beta c}}$$
$$\int e^{-\beta c q^2} dq \sim \sqrt{\frac{\pi}{\beta c}}$$

$\Longrightarrow$ Contribute $\frac{1}{2} k_B T$ energy per degree of freedom.



The above physical picture are based on two assumptions:

1. energy can continously change. & the lowest energy of all d.o.f are all zero.
2. Energy can transfered from one to another.

Homework

PROBLEM 1: For a many particles system with Hamiltonian,

$$H = \sum_{i=1}^{N} \varepsilon s_i \qquad s_i = -1, 0, 1$$

(a) Calculate the partition function for classical case

$$Z = \sum_{s_i=-1,0,1} e^{-\beta \varepsilon s_i}$$

(b) From the partition function Z, calculate the total energy E, heat capacity C, entropy S of this system.

PROBLEM 2: For a 2D many particles system with Hamiltonian,

$$H = \sum_{i=1}^{N} c|\vec{p}_i|$$

(a) Calculate the partition function for classical case

$$Z = \int \frac{d^2\vec{q}\, d^2\vec{p}}{h^2} e^{-\beta c|\vec{p}|}$$

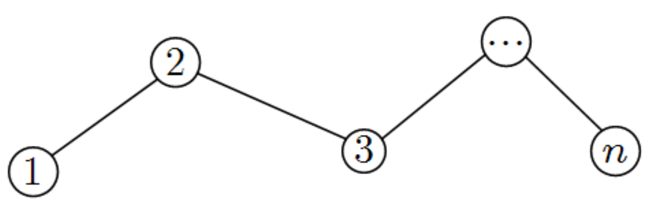
(b) From the partition function Z, calculate the energy E, heat capacity C, entropy S and pressure P of this system.

Breakingdown of CSM

Equipartition of energy

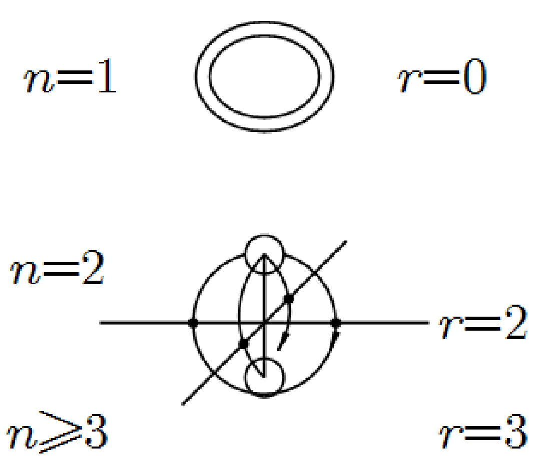
Each degree of freedom will contribute $\frac{N}{2}k_B T$ to energy of the system.

N-atom molecular gas



$$N_{d.o.f} = 3n + m = 3 + r + 2m$$

r=rotating d.o.f.

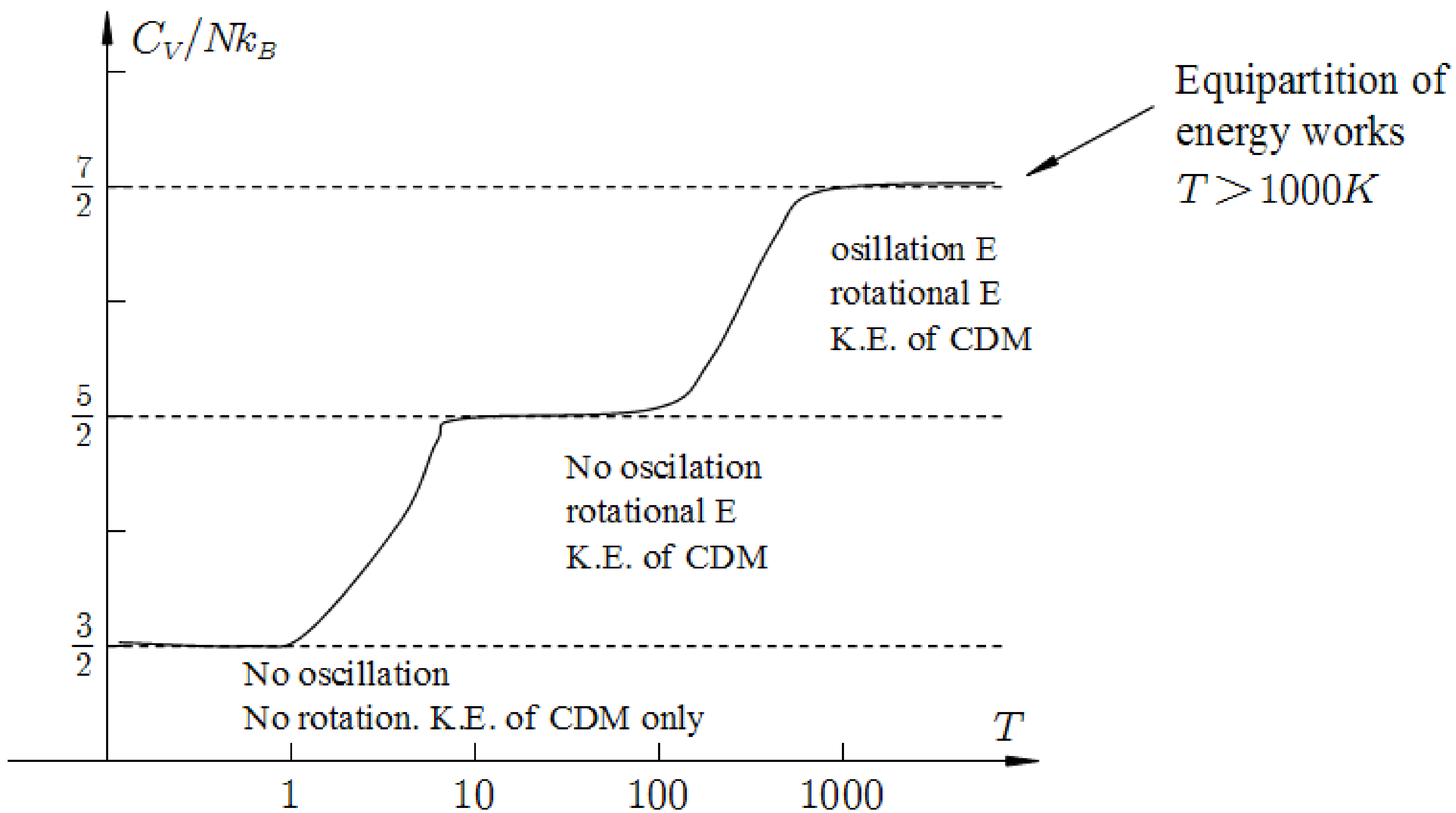


$$m = 3n - 3 - r$$

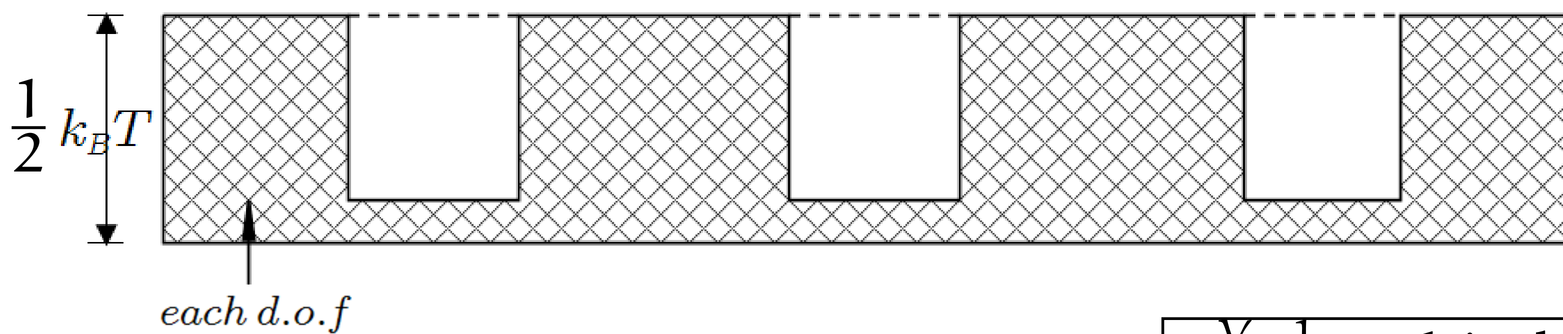
2m=oscillating d.o.f.

Breakingdown of CSM

$$(\,2\ atom\ molecule \qquad r = 2 \longrightarrow m = 1\,)$$

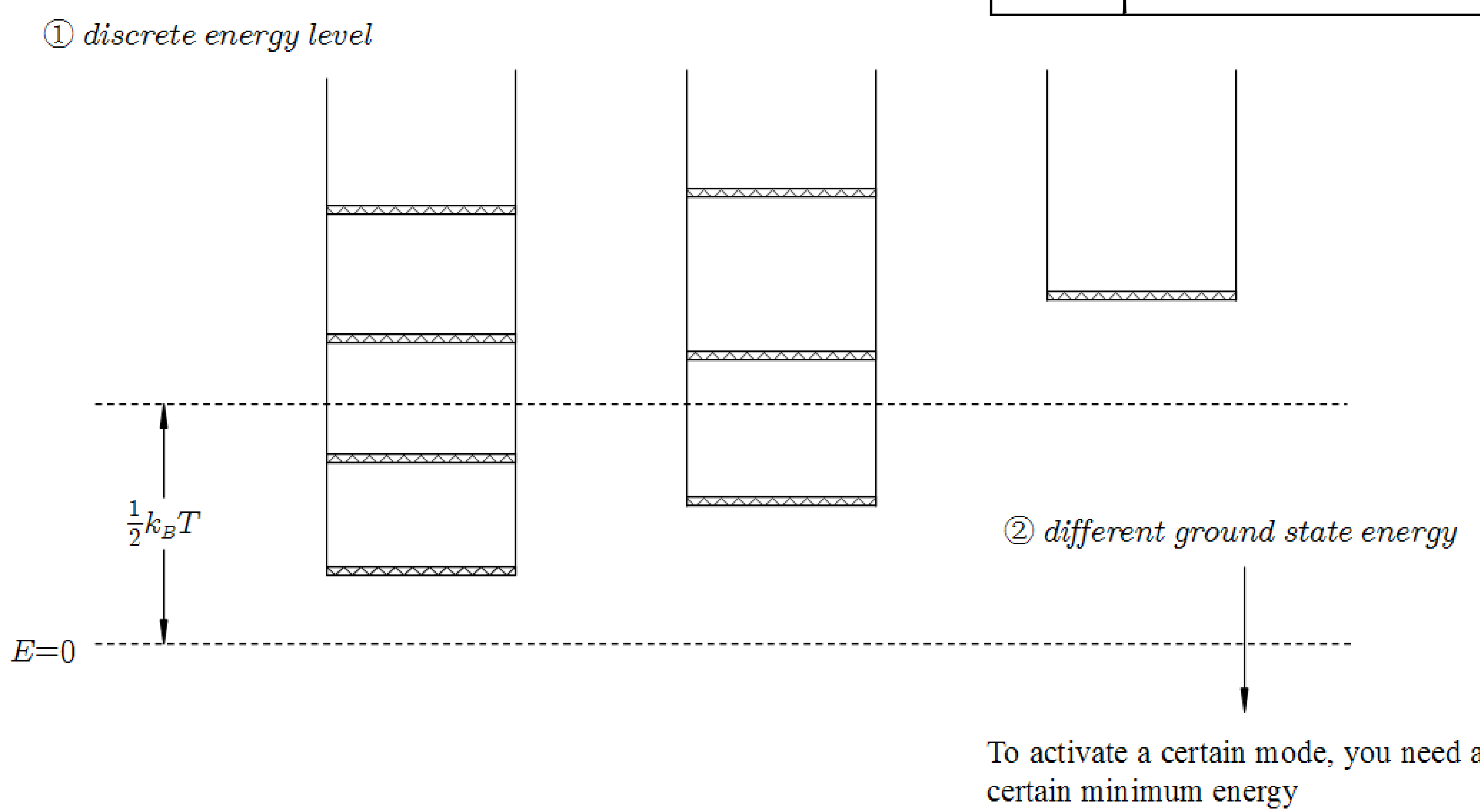


Breakingdown of CSM



CSM

$$\boxed{\frac{V}{N}\frac{1}{\lambda_T^3} \sim 1 \text{ is the criteria.}}$$



Quasi-classical approach of SM

$$H_{vib}^{QM} = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$Z_{vib}^{QM} = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

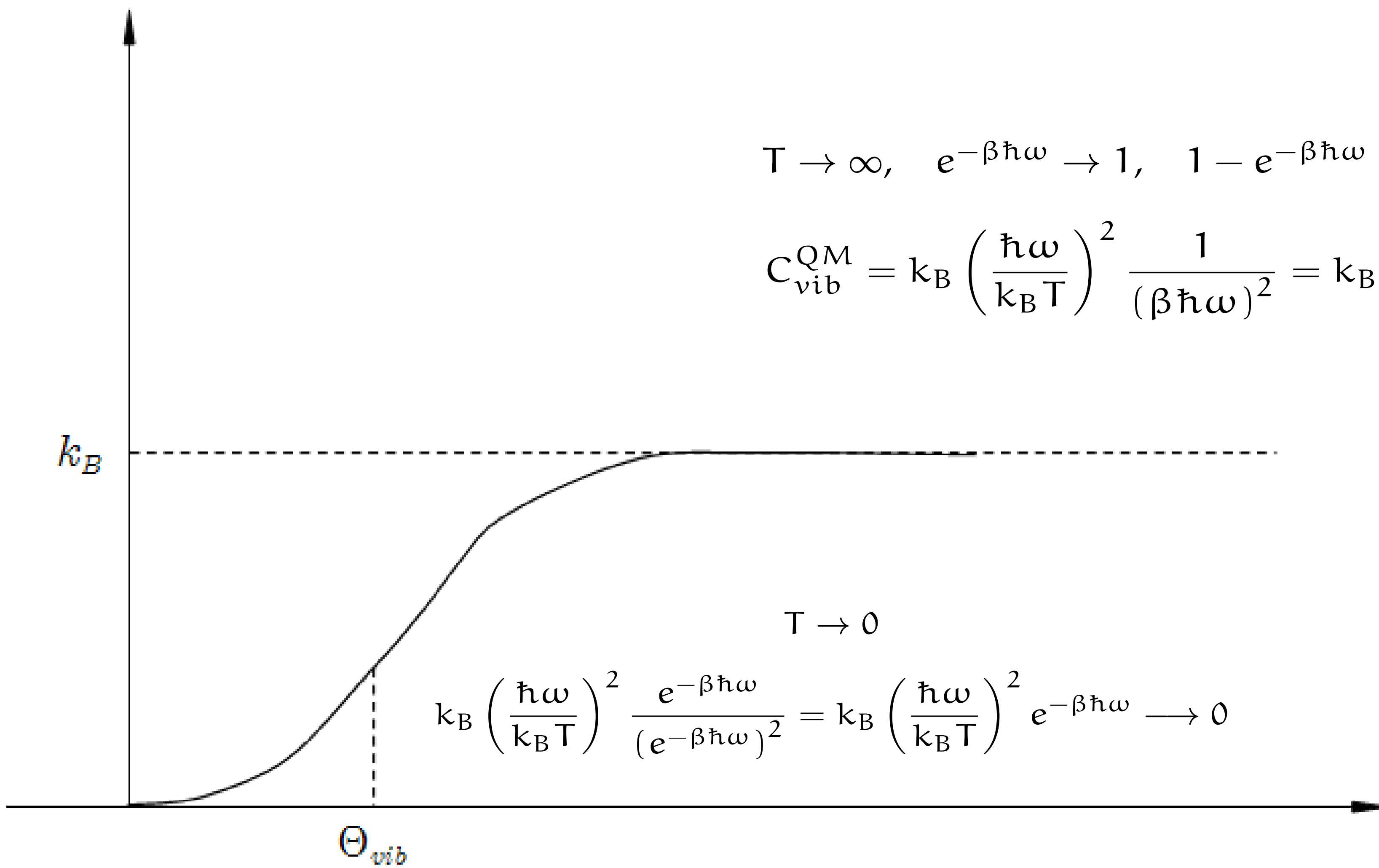
$$E_{vib}^{QM} = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = -\frac{\partial}{\partial\beta}\left[-\frac{1}{2}\beta\hbar\omega - \ln\left(1-e^{-\beta\hbar\omega}\right)\right]$$

$$= \frac{1}{2}\hbar\omega + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$n(\omega) = \frac{1}{e^{\beta\hbar\omega}-1}$$

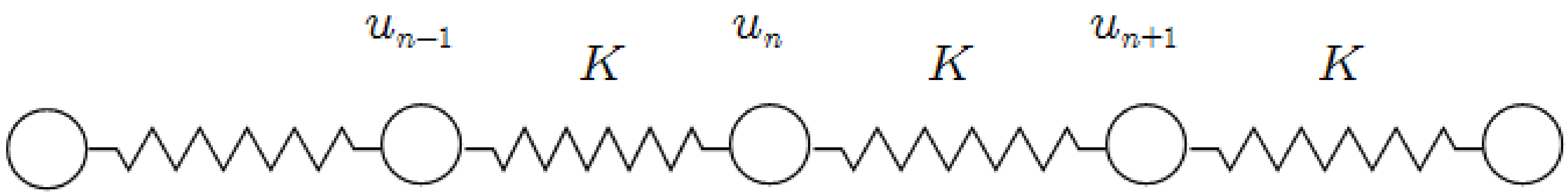
$$C_{vib}^{QM} = \frac{dE_{vib}^{QM}}{dT} = k_B\left(\frac{\hbar\omega}{k_B T}\right)\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}$$

Quasi-classical approach of SM



$k_B\Theta_{vib} = \hbar\omega \qquad \Theta_{vib} \sim 10^3 — 10^4 \mathrm{K}$

Heat capacity of solid



$$\omega(k) = 2\sqrt{\frac{k}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

1 harmonic oscillator $\quad C_{vib} = k_B\left(\frac{\hbar\omega}{k_B T}\right)\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}$

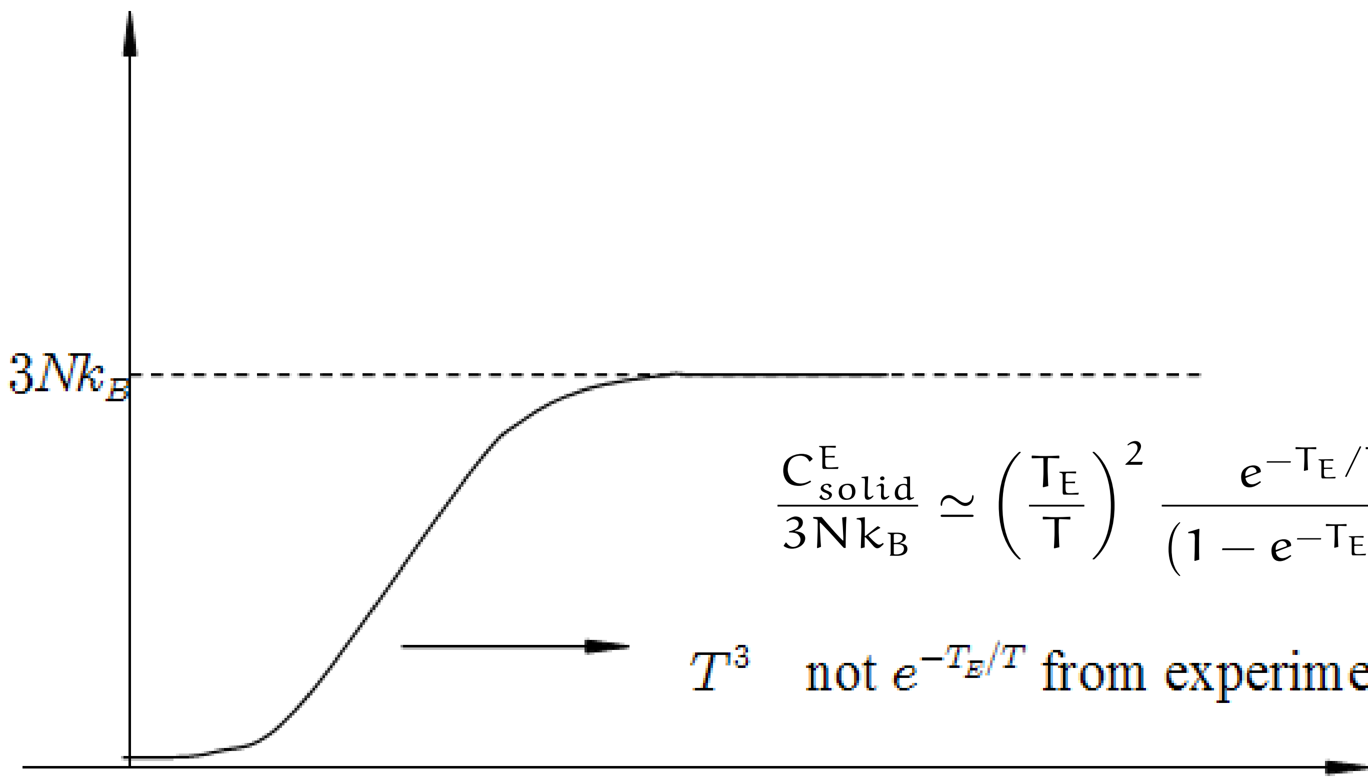
N-harmonic oscillator $\quad C_{solid} = \sum_{\vec{k}} k_B\left(\frac{\hbar\omega}{k_B T}\right)^2\frac{e^{-\beta\hbar\omega_k}}{(1-e^{-\beta\hbar\omega_k})^2}$

Einstein model (All harmonic oscillators have the same frequency)

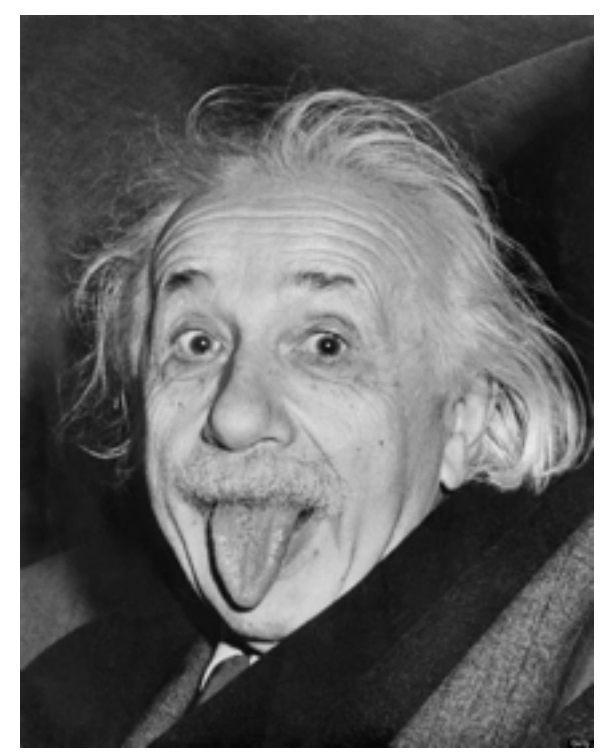
$\omega_k \equiv \omega_E \quad$ const $\hbar\omega_E = k_B T_E$ $\quad$ Einstein model

$$C^E_{solid} = N k_B\left(\frac{\hbar\omega_E}{k_B T}\right)^2\frac{e^{-\beta\hbar\omega_E}}{(1-e^{-\beta\hbar\omega_E})^2}$$

Heat capacity of solid



$$\frac{C^{E}_{\text{solid}}}{3Nk_B} \simeq \left(\frac{T_E}{T}\right)^2 \frac{e^{-T_E/T}}{\left(1-e^{-T_E/T}\right)^2} \sim e^{-T_E/T}$$



Heat capacity of solid

Debye model

$$C_{solid} = \sum_{\vec{k}} k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\beta\hbar\omega_k}}{(1 - e^{-\beta\hbar\omega_k})^2}$$

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

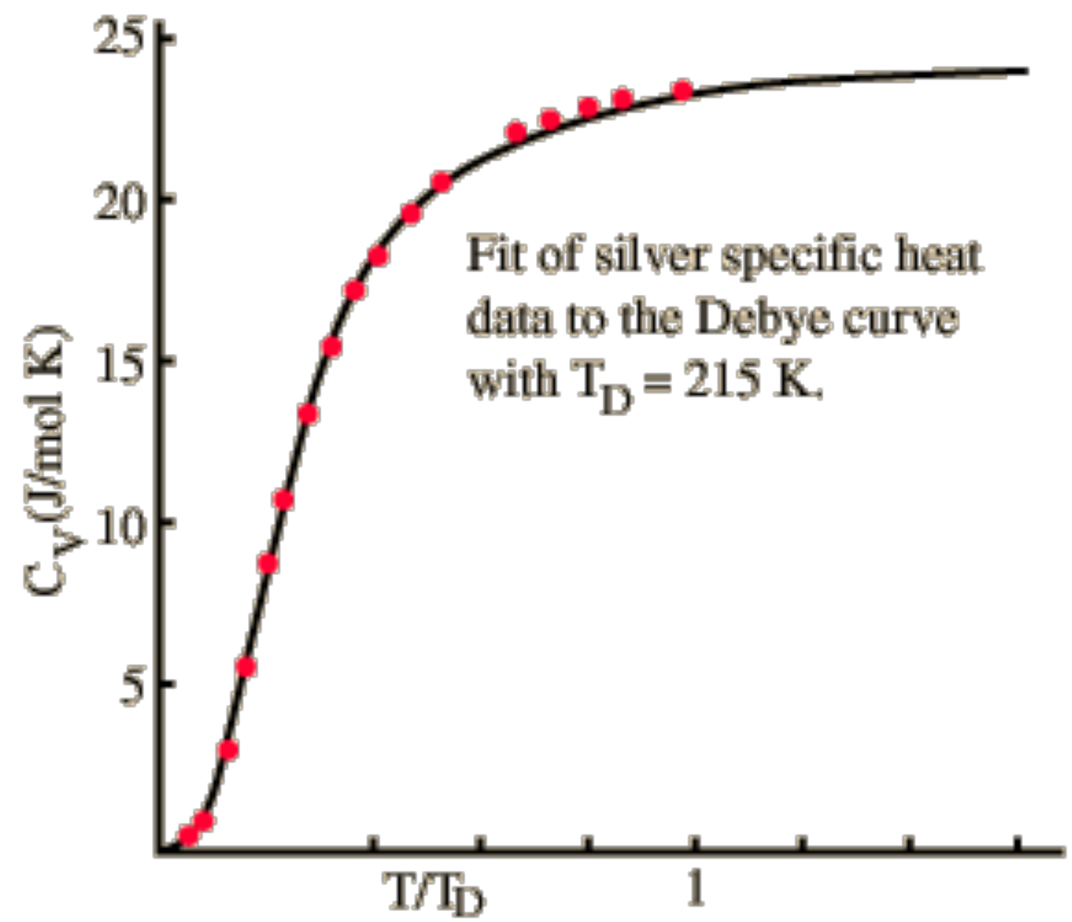
$$\sum_{n_x, n_y, n_z} = \frac{L_x L_y L_z}{(2\pi)^3} \int dk_x dk_y dk_z = \frac{V}{(2\pi)^3} \int d^3\vec{k}$$

$$\begin{aligned}
E_{solid} &= E_0 + \sum_{\vec{k}} \frac{\hbar\omega_{\vec{k}}}{e^{\beta\hbar\omega\vec{k}} - 1} \\
&= E_0 + \frac{3V}{(2\pi)^3} \int 4\pi k^2 dk \frac{\hbar\nu k}{e^{\beta\hbar\nu k} - 1} \\
&= E_0 + \frac{3V}{2\pi^2} \left(\frac{k_B T}{\hbar\nu}\right)^3 k_B T \int_0^\infty \frac{x^3 dx}{e^x - 1} \\
&= E_0 + \frac{\pi^2}{10} V \left(\frac{k_B T}{\hbar\nu}\right)^3 k_B T
\end{aligned}$$

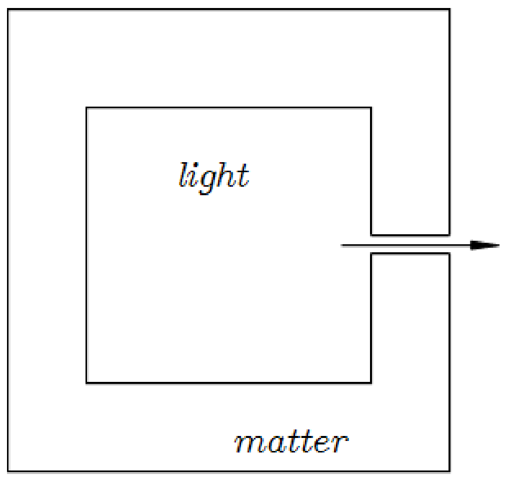
$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

Heat capacity of solid

$$C^{D}_{solid} = \frac{dE}{dT} = \frac{2\pi^2 \nu}{5}\left(\frac{k_B T}{\hbar \nu}\right)^3 k_B \propto \left(\frac{T}{T_D}\right)^3$$



Blackbody radiation



phonon $\longrightarrow$ *photon*

collective motion of atoms

collective motion of Electric − magnetic field

$$H = \frac{1}{2}\sum_{\vec{k},\alpha}\left[|\tilde{P}_{\vec{k},\alpha}|^2 + \omega_\alpha\left(\vec{k}\right)|\tilde{u}_\alpha\left(\vec{k}\right)|^2\right]$$

$$\omega_\alpha\left(\vec{k}\right) = ck$$

c light of speed

$\alpha = \pm$ only 2 polarization

$$Z = \prod_{\vec{k},\alpha}\frac{e^{-\beta\hbar ck/2}}{1 - e^{-\beta\hbar ck/2}}$$

$$F = -k_B T \ln \mathcal{Z} = k_B T\left[\frac{\beta\hbar ck}{2} + \ln\left(1 - e^{-\beta\hbar ck}\right)\right]$$

$$= 2V\int\frac{d^3\vec{k}}{(2\pi)^3}\left[\frac{\hbar ck}{2} + k_B T\ln\left(1 - e^{-\beta\hbar ck}\right)\right]$$

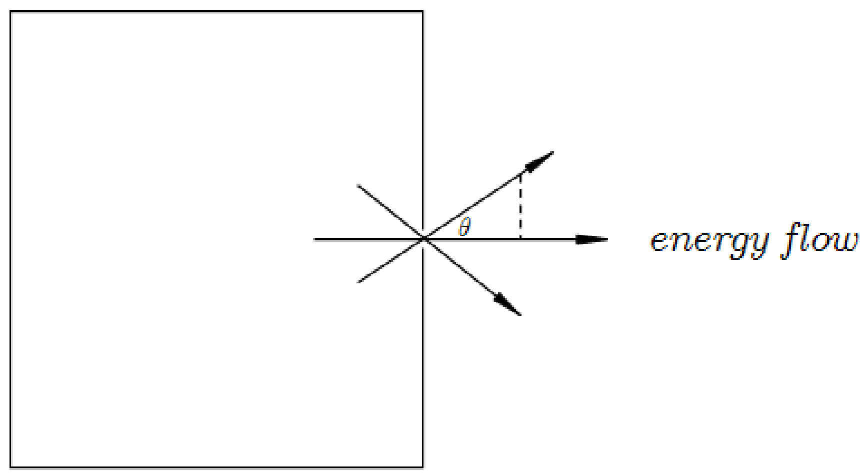
$$P = -\frac{\partial F}{\partial V}$$

$$= -\int\frac{d^3k}{(2\pi)^3}\left[\hbar ck + 2k_B T\ln\left(1 - e^{-\beta\hbar ck}\right)\right]$$

$$= P_0 + \frac{k_B T}{\pi^2}\int_0^\infty dk\,\frac{k^3}{3}\,\frac{\beta\hbar c e^{-\beta\hbar ck}}{1 - e^{-\beta\hbar ck}}$$

$$= P_0 + \frac{1}{3}\frac{E}{V}$$

Blackbody radiation



$$\frac{E}{V} = \frac{\pi^2}{15}\left(\frac{k_B T}{\hbar c}\right)^3 k_B T$$

$$\phi = \langle C_\perp \rangle \frac{E}{V}$$

$$\langle C_\perp \rangle = C \frac{1}{4\pi} \int_0^{2\pi} 2\pi \sin\theta d\theta \,(\cos\theta) = \frac{C}{4}$$

energy flow

radiation power

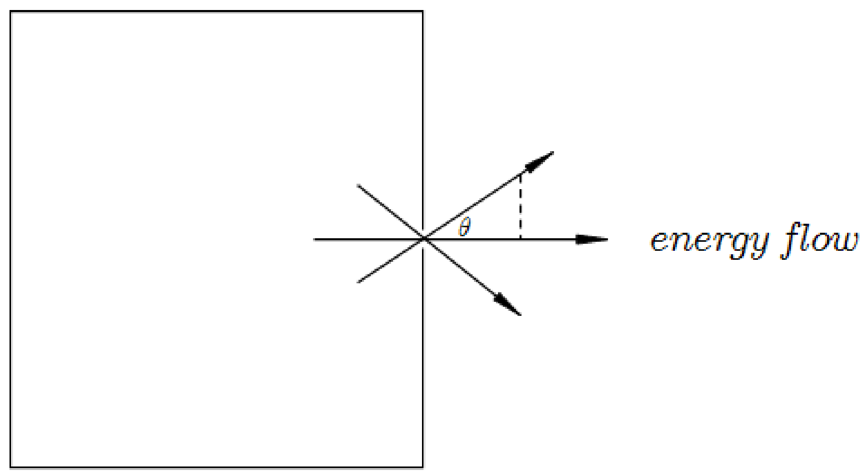
$$\phi = \frac{C}{4}\frac{E}{V} = \frac{C}{4}\frac{\pi^2}{15}\left(\frac{k_B T}{\hbar C}\right)^3 k_B T = \frac{\pi^2}{60}\frac{k_B^4}{\hbar^3 C^2} \equiv \sigma T^4$$

$$\sigma \simeq 5.67 \times 10^{-8} \mathrm{W m^{-2} K^{-4}}$$

$$P_{net} = P_{emit} - P_{absorb} = A\sigma\left(T^4 - T_0^4\right)$$

$$T = 37°\mathrm{C}, \quad T_0 = 20°\mathrm{C}, \quad A = 2\mathrm{m}^2, \quad P_{net} = 100\mathrm{W}.$$

Blackbody radiation



$$\frac{E}{V} = \frac{\pi^2}{15}\left(\frac{k_B T}{\hbar c}\right)^3 k_B T$$

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$$\phi = \frac{C}{4}\frac{E}{V} = \frac{C}{4}\frac{\pi^2}{15}\left(\frac{k_B T}{\hbar C}\right)^3 k_B T = \frac{\pi^2}{60}\frac{k_B^4}{\hbar^3 C^2} \equiv \sigma T^4$$

energy flow
radiation power

$$\sigma \simeq 5.67 \times 10^{-8} \mathrm{W m^{-2} K^{-4}}$$

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$$T = 37°\mathrm{C}, \quad T_0 = 20°\mathrm{C}, \quad A = 2\mathrm{m}^2, \quad P_{net} = 100\mathrm{W}.$$

Blackbody radiation

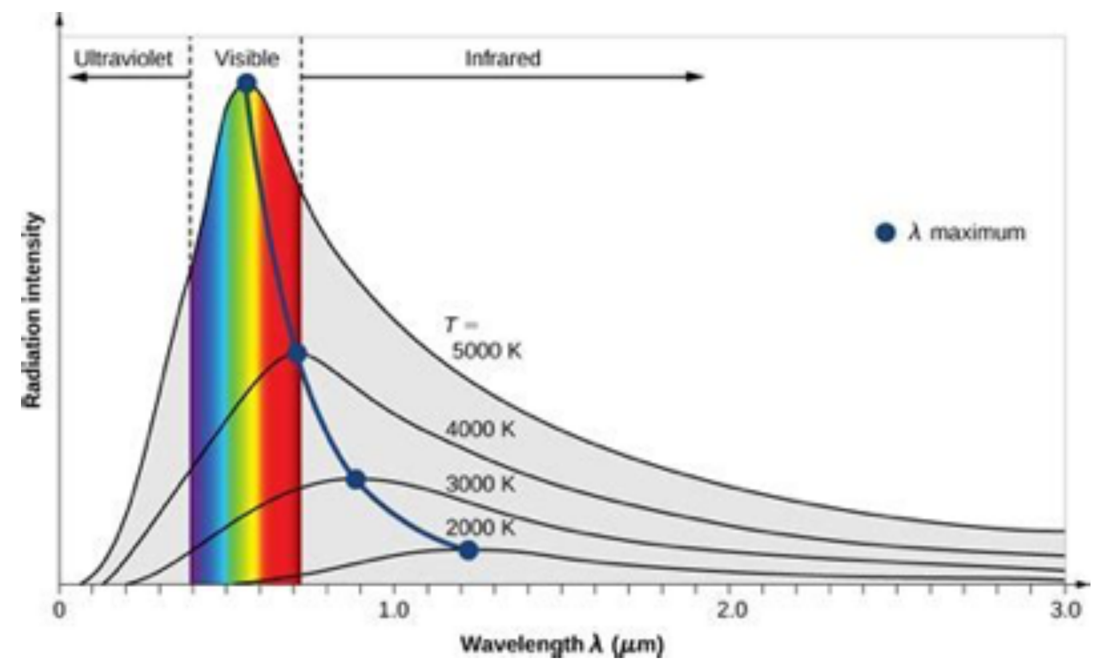
energy flow per unit area per unit time for certain k.

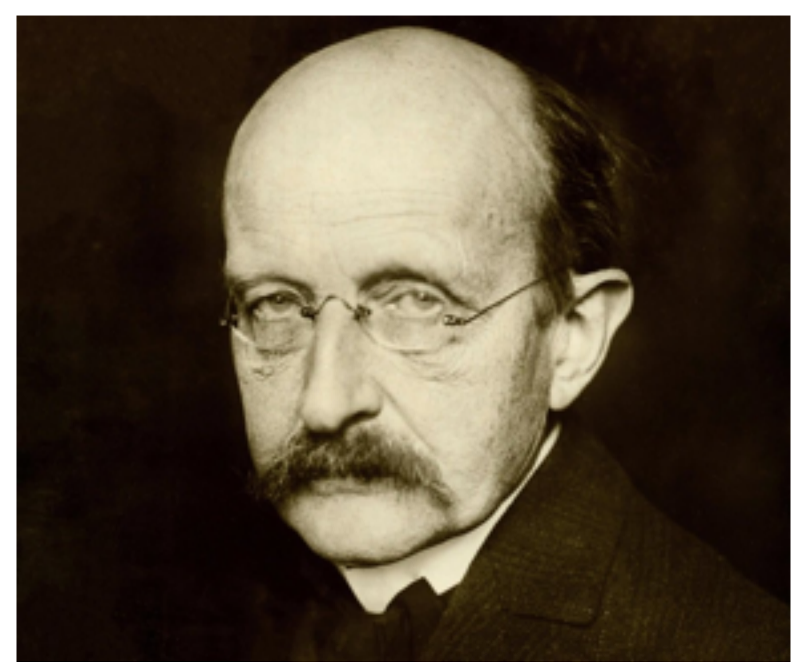
$$I(k,T) = \frac{c}{4}\varepsilon(k,T) = \frac{\hbar c^2}{4\pi^2}\frac{k^3}{e^{\beta\hbar c k}-1}$$

$$\xrightarrow{\beta\hbar c k \ll 1} \quad \frac{\hbar c^2}{4\pi^2}\frac{k^3}{\beta\hbar c k} \sim \frac{c k_B T}{4\pi^2}k^2$$

$$\xrightarrow{\beta\hbar c k \gg 1} \quad \frac{\hbar c^2}{4\pi^2}k^3 e^{-\beta\hbar c k}$$

$$k^*(T) \sim \frac{k_B T}{\hbar c} \Longrightarrow \lambda_{max} \approx \frac{b}{T}$$





Summary

- Phase space/Description of physical systems
- The most probable distribution of quasi-independent systems
- Calculating thermal properties from distribution (classical/ breakingdown of classical/quantum harmonic oscillator/ Heat capacitor of solid/ Blackbody readiation)