①

| $\Omega(E)$. Number of Microstate w/ energy E,
| $\Gamma(E)$ Number of Microstate w/ energy $\leq E$ (accumulate)
| $g(E)\Delta E$ Number of microstate between E & $E+\Delta E$
| $g(E)$ Density of states

Counting Microstate

Discrete

ex Nointeracting Spin.

N spins n spin ↓ μ magnetic moment, $\vec{B}$ field // spin.

$$E = n(-\mu B) + (N-n)\mu B.$$

$$n = \frac{N}{2} - \frac{E}{2\mu B}$$

thus total number of microstate w/ energy E

$$\Omega(n,N) = \frac{N!}{n!(N-n)!}$$

classical. ex In continuous space, $E = \frac{p^2}{2m}$, particle in 1D box length L.

~~We ask. density of state $g(E)$, and # of state (microstates)~~
~~of the system between E and $E+\Delta E$.~~
~~Define $\Gamma(E)$ be number of micros~~

To be sensible, we asked.

$$g(E)\Delta E = \Gamma(E+\Delta E) - \Gamma(E).$$

To faciliate counting, divide area by $\Delta x \Delta p$.

Hence, total number of cells.

$$\Gamma_{cl}(E) = \frac{2P_{max}L}{\Delta x \Delta p} = 2\frac{L}{\Delta x \Delta p}(2mE)^{1/2}.$$

Space restricted for the particle w/ energy E.

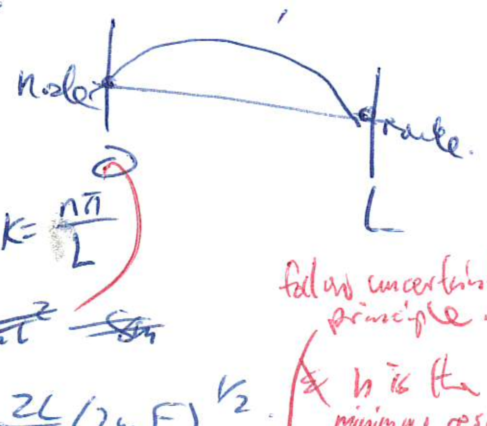
microstate of a particle is a point (x,p) in phase space (shaded area) has area: $2P_{max}L$

easier to count because energy being quantized!

Quantum. particle in 1D box L w/ mass m.

By de Broglie,

$$\lambda_n = \frac{2L}{n} \quad \underbrace{n = 1, 2, \ldots}_{\text{label \# of quantum state}}$$



&

$$p = \frac{h}{\lambda} \sim \frac{hn}{2L}. \quad \left(p = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k;\ k = \frac{n\pi}{L}\right)$$

$$E_n = \frac{P_n^2}{2m} = \frac{h^2n^2}{8mL^2} \rightarrow \cancel{n = \frac{8mL^2}{\ldots}}$$

$$n = \frac{2L}{h}(2mE)^{1/2}.$$

follow uncertainty principle.

& h is the minimum resol

So $\Gamma_q(E) = n = \frac{2L}{h}(2mE)^{1/2}$ ⟹ $\Gamma_q(E) \sim \Gamma_{cl}(E) \Rightarrow \Delta x \Delta p \sim h$

ex 1-D harmonic oscillator

classical $E = \frac{p^2}{2m} + \frac{1}{2}kx^2$ note $\omega = \sqrt{\frac{k}{m}}$.

$\hookrightarrow \frac{x^2}{\underbrace{2E/m\omega^2}_{a^2}} + \frac{p^2}{\underbrace{2mE}_{b^2}} = 1$. (ellipse) — phase space w/ area πab.

$\Rightarrow$ $\Gamma_{cl}(E) = \frac{2\pi E}{\omega \Delta x \Delta p}$.

quantum. $E_n = (n + \frac{1}{2})\hbar\omega$ $n = 1, 2, \ldots$ # of quantum state

$\Gamma_{qm}(E) = n = \frac{E}{\hbar\omega} - \frac{1}{2} \simeq \frac{E}{\hbar\omega}$ for $E >> \hbar\omega$

again. $\Delta x \Delta p \sim h$

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higher dimension, 2D.

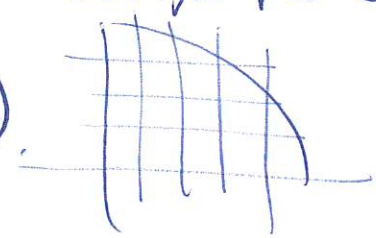
$E = \frac{1}{2m}(P_x^2 + P_y^2)$; $k_x = \frac{\pi}{L_x}n_x$ $k_y = \frac{\pi}{L_y}n_y$ $L_x = L_y = L$

$E_{n_x n_y} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2)$. ~~from here I know a single particle~~

* the minimum area associate with a single particle state is 1.

there $n^2 = n_x^2 + n_y^2$ be the radius $\Rightarrow$.

$\Gamma(E) = \frac{1}{4}\pi n^2 = \pi \frac{L^2}{h^2}(2mE)$. $L^2 = V$



3D. $E = \frac{1}{2m}(\underbrace{P_x^2 + P_y^2 + P_z^2}_{R^2})$ $K_x = \frac{\pi n_x}{L_x}$ $K_y = \frac{\pi n_y}{L_y}$ $K_z = \frac{\pi n_z}{L_z}$

now. $= \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$ $L_x = L_y = L_z = L$.

$\Gamma(E) = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right)$

$\Gamma(E) = \frac{4\pi}{3}\frac{V}{h^3}(2mE)^{3/2}$. $V = L^3$

ex

In general N-D $\Gamma(K) \sim K^D$ & generalized phonon excitation spectrum $\omega(\vec{k}) \sim k^b \Rightarrow$ $\Gamma(\omega) \sim \omega^{\frac{D}{b}}$, $g(\omega) = \frac{d\Gamma(\omega)}{d\omega} \sim \omega^{\frac{D}{b}-1}$

ex. Two noninteracting particles (m) in ~~single b~~ 1D box length L. total energy.

quantum #/quantum state

$$E_{n_1,n_2} = \frac{h^2}{8mL^2}(n_1^2+n_2^2)$$

they are ~~not same~~ indistinguishable.

i.e. $(n_1=2, n_2=1)$ equivalent to $(n_1=1, n_2=2)$

Must Obey Bose / Fermi statistics

i.e. • Bose: ~~th~~ any particle may be in same ~~state~~ single particle quantum state

• Fermi two particle may not in same single-particle state.

i.e. $(n_1, n_2) = (1,1)$ $(2,2)$, $(3,3)$ etc are excluded!

GT P.200

Remark: Can approximate by semi-classical limit (ie number of single particle state Γ $\gg$ number of particle N.)

then $$\frac{(N+\Gamma-1)!}{N!\,(\Gamma-1)!}$$

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ex For N particles (distinguishable) in 3D box

the number of microstates w/ energy $\leq E$ is given by computing the positive parts of a 3N dimensional hypersphere w/ $R = \frac{2L}{h}(2mE)^{1/2}$

note $E = \sum_{\substack{i=1,\dots,N\\ j=1,2,3}} \frac{p_{ij}^2}{2m} = \sum_{ij} \frac{h^2}{8mL^2}(n_{ij}^2)$

~~$V_n(R)$~~ For n-dim hypersphere:

$$V_n(R) = \int_{x_1^2+\dots+x_n^2<R^2} dx_1 dx_2 \cdots dx_n$$

define volume of positive part of n-d sphere of Radius R:

$$V_n(R) = \frac{2\pi^{n/2}}{n\,\Gamma(n/2)}R^n \rightarrow \Gamma_n(R) = \left(\frac{1}{2}\right)^n V_n(R)$$

For $n = 3N$ & $R = \frac{2L}{h}(2mE)^{1/2}$

$$\Gamma(E,V,N) = \left(\frac{1}{2}\right)^{3N} \frac{2\pi^{3N/2}}{3N(3N/2-1)!} R^{3N} = \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}$$

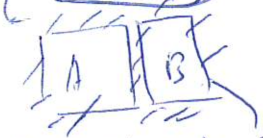
Correction: $\Gamma_c(E,V,N) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{[illegible]}$

Microcanonical Ensemble

	Macrostate	Prob. dist.	Thermo
Microcanonical	E, V, N	$P_s = \frac{1}{\Omega}$	$S(E,V,N) = k\ln\Omega$
Canonical	T, V, N	$P_s = e^{-\beta E_s}/Z$	$F(T,V,N) = -kT\ln Z$
Grand canonical	T, V, μ	$P_s = e^{-\beta(E_s-\mu N_s)}/Z_G$	$\Omega_G(T,V,\mu) = -kT\ln Z_G$

assume ~~the~~ accessing these microstates are equally likely.

ex (initially)

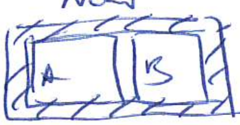


$\Omega_A(E_A, V_A, N_A)$ $\Omega_B(E_B, V_B, N_B)$

$$\Omega = \Omega_A(E_A, V_A, N_A)\,\Omega_B(E_B, V_B, N_B)$$

$$\boxed{S = k\ln\Omega} \Rightarrow S = S_A + S_B \text{ additive}$$

Now



E_A, E_B vary
$E = E_A + E_B$ fixed

# of accessible state now?

$\Omega_A(E_A)$ w/ $\Omega_B(E - E_A)$

$$\Omega(E) = \sum_{E_A} \Omega_A(E_A)\,\Omega_B(E - E_A)$$

$$P_A(E_A) = \frac{\Omega_A(E_A)\,\Omega_B(E - E_A)}{\Omega(E)}$$

(valid due to weak interaction btw system)
so microstates of each system unchanged
(at thermodynamic limit $N, V \to \infty$ & $\rho = \frac{N}{V}$ = constant
so fraction of particle at boundary $\to 0$

- If one take the most probable value of E_A $\tilde{E}_A$, then

$$\Omega(E) \simeq \Omega_A(\hat{E}_A)\,\Omega(E - \hat{E}_A) \Rightarrow S = k\ln\Omega = S_A + S_B$$

For ~~continuous energy as var~~ energy as continuous variable.

$$S = k\ln(g(E)\Delta E) \underset{\text{equivalent}}{\equiv} S = k\ln\Gamma(E)$$

Early we have $\Gamma(E) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!}$

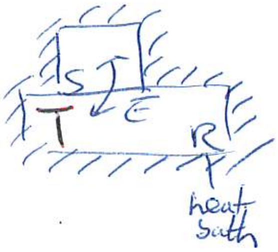
Stirling's approximation $\Rightarrow$, $\ln\Gamma(E,V,N) = N\ln\frac{V}{N} + \frac{3}{2}N\ln\frac{mE}{3N\pi\hbar^2} + \frac{5}{2}N$

then, for ideal gas. $\because$ noninteracting.

$$S(E,V,N) = Nk\left(\ln\frac{V}{N} + \frac{3}{2}\ln\frac{mE}{3N\pi\hbar^2} + \frac{5}{2}\right)$$

work out as exercise

Canonical Ensemble



S + R composite system which has equally likely accessible state.

S has E_s, R has $\cancel{E_R}\, E_b$ } $E_b = E - E_s$, $\underline{E_s \ll E_b \Rightarrow E_s \ll E}$

Because ~~E_s~~ of these a given microstate of system s, heat bath can be in $\underline{\text{any one}}$ of a large number of microstates. ~~w/o varying~~

Probability P_s that sys. in S w/ E_s:

$$P_s \simeq \frac{\Omega_b(E-E_s)}{\sum_s \Omega_b(E-E_s)}$$

As $E_s \uparrow$ $\Omega_b(E-E_s)\downarrow$ & $P_s \downarrow$ clearly b/c larger E_s lesser energy available to heat bath.

(can simplify: $\Omega_b(E-E_s) = \Omega_b(E_b)$ for $E >> E_s$ and no Σ_s involve.

thus, $\ln P_s = C + \ln \Omega_b(E_b)$

$$\ln P_s \approx C + \ln \Omega_b(E) - E_s \left.\frac{\partial \ln \Omega_b(E_b)}{\partial E_b}\right|_{E_b = E}$$

$$= C + \ln \Omega_b(E) - \frac{E_s}{kT}$$

$S = k \ln \Omega$, $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$, $\frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E}$

$\Rightarrow$ ~~$P_s = \frac{1}{Z} e^{-\frac{E_s}{T}}$~~

$$\boxed{P_s = \frac{e^{-\frac{E_s}{kT}}}{Z}}$$

$$\boxed{Z = \sum_s e^{-\frac{E_s}{kT}}}$$

applied to system in equilibrium at "T"

| Boltzmann distribution

Thermal Properties:

$$\boxed{\langle E \rangle = \sum_s P_s E_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s}} \quad \text{def.}$$

by generating function:

$$\boxed{\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z.}$$

operation

$$\boxed{C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{kT^2}\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2\right] = \frac{1}{kT^2}\left[\langle E^2 \rangle - \langle E \rangle^2\right]}$$

Proof

$\bar{p} = -\sum_s \Pi_s P_s$ $-\Pi_s = \left(\frac{dE_s}{dV}\right)_{T,N}$

$$\boxed{\bar{p} = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}}$$

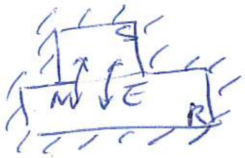
$$\boxed{S = -k \sum_s P_s \ln P_s}$$

$F = E - TS$

$$\boxed{F = -kT \ln Z}$$

$dE = \sum_s E_s dP_s - \bar{p}\,dV$

Grand Canonical Ensemble



In equilibrium at T & μ w/ V fixed

$$P_s = \frac{1 \times \Omega_R(E-E_s, N-N_s)}{\sum_s \Omega_R(E-E_s, N-N_s)} \quad \text{where } E_s \ll E,\ N_s \ll N$$

ln

$$P_s = \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)}$$

$$Z_G = \sum_s e^{-\beta(E_s - \mu N_s)}$$

W $\boxed{\Omega_G = -kT \ln Z_G}$ $\quad \Omega_G = F - \mu N$ (Landau Potential)

Entropy is Not a Measure of Disorder

Entropy is a measure of uncertainty or lack of information!

& phase transition from low to high density macrostate is driven by entropy!

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ex
- low density suitcase consistent w/ disorder.
  (small amount ~~p~~ articles vs suitcase vol.)
- high density suitcase: random ~~org~~ packing won't close suitcase.
  but many ways to organize articles
  s.t. suitcase can be closed!
  thus has higher entropy.

ex crystal has higher entropy than liquid