Stat Mech:

Lecture 1:

Fundamental principles:

Phase space

Distribution function:

Consider: System of $N \gg 1$ ($\sim 6 \times 10^{23}$) particles
Volume V

Particles have positions $\vec{q}_i$, $i = 1, \dots N$

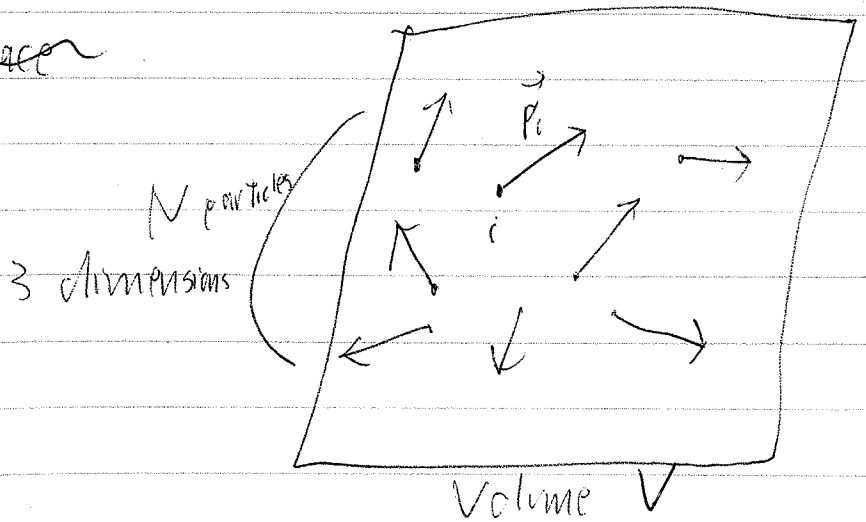
" " momentum $\vec{p}_i$, $i = 1, \dots N$

Hamiltonian (energy)

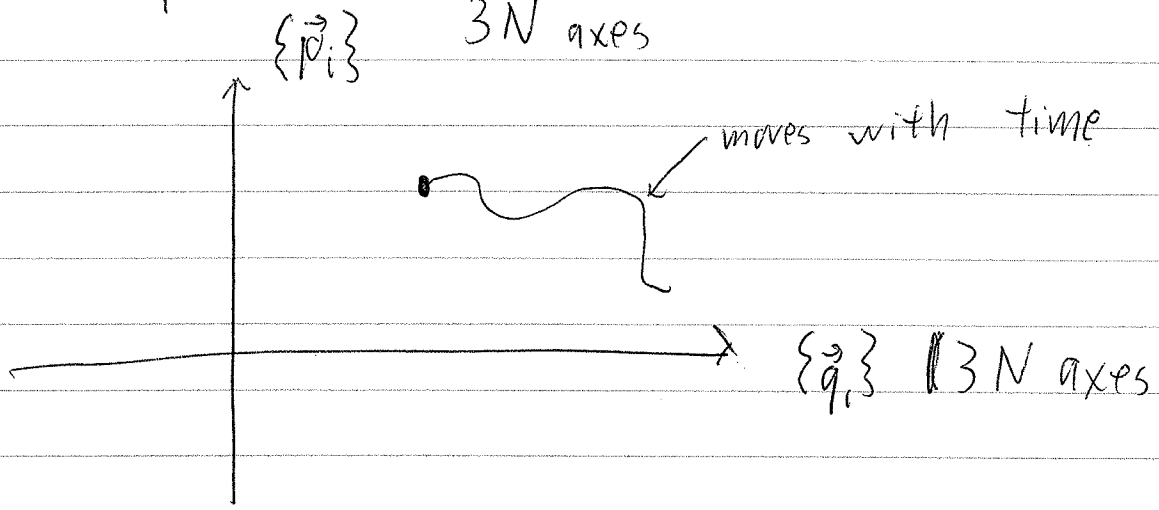
$H(\vec{p}, \vec{q})$ specified.

~~Phase space~~

Real space:



Phase space:



Ensemble Theory

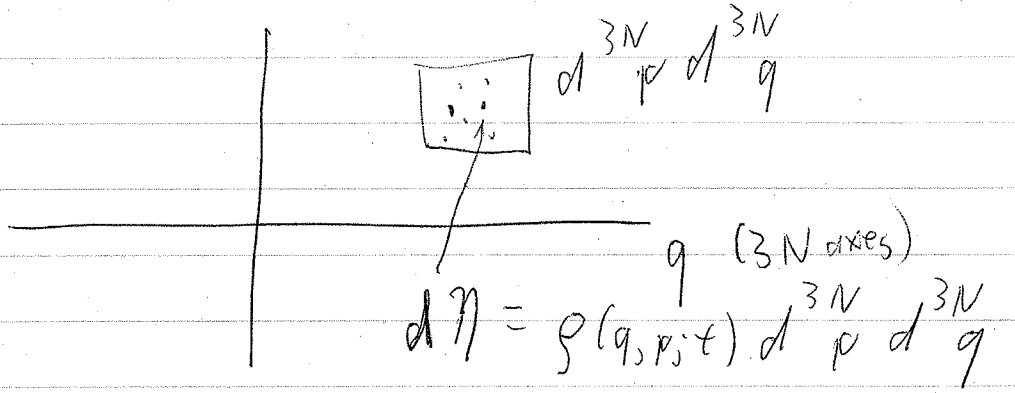
Liouville's Theorem:

Consider large # of systems in same "macrostate", evolving according to classical e.o.m.:

$$\dot{q}_i = \frac{\partial H(p,q)}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial H(p,q)}{\partial q_i}$$

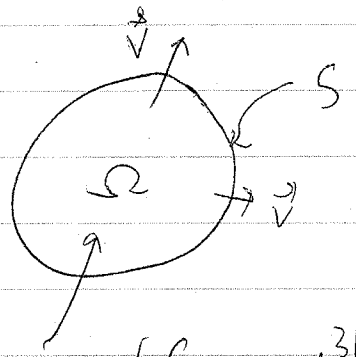
$\rho(q,p,t)$ on p (3N axes)



$$d\eta = \rho(q,p,t)\, d^{3N}p\, d^{3N}q$$

$$\Rightarrow \quad \langle f \rangle = \frac{\int f(p,q)\, \rho(p,q,t)\, d^{3N}p\, d^{3N}q}{\int \rho(p,q,t)\, d^{3N}p\, d^{3N}q}$$

Equation of continuity:



$$\partial_t \left(\int \rho \underbrace{d^{3N}p\, d^{3N}q}_{d\Omega} \right) = -\int dS\, \rho \vec{v} \cdot d\vec{S}$$

$$\vec{v} \equiv (\dot{p}_i, \dot{q}_i), \quad i = 1, \dots 3N$$

$$\int d\vec{S} \cdot (\rho \vec{v}) = \int d\Omega\, \vec{\nabla} \cdot (\rho \vec{v})$$

$$\vec{\nabla} = \left(\frac{\partial}{\partial q_i}, \frac{\partial}{\partial p_i} \right), \quad i = 1, \dots 3N$$

$$\Rightarrow \int d\Omega \left(\partial_t \rho + \vec{\nabla} \cdot (\rho \vec{v}) \right) = 0$$

True for <u>any</u> Ω

$$\Rightarrow \partial_t \rho + \vec{\nabla} \cdot (\rho \vec{v}) = 0$$

$$\partial_t \rho + \rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \partial_{p_i} \rho = 0$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\Rightarrow \partial_t \rho + \rho\left(\frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial p_i \partial q_i}\right) + \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} = 0$$

$$\Rightarrow \partial_t \rho + \rho \cdot 0 + \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} = 0$$

In equilibrium, $\partial_t \rho = 0$

$$\Rightarrow \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} = \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i}$$

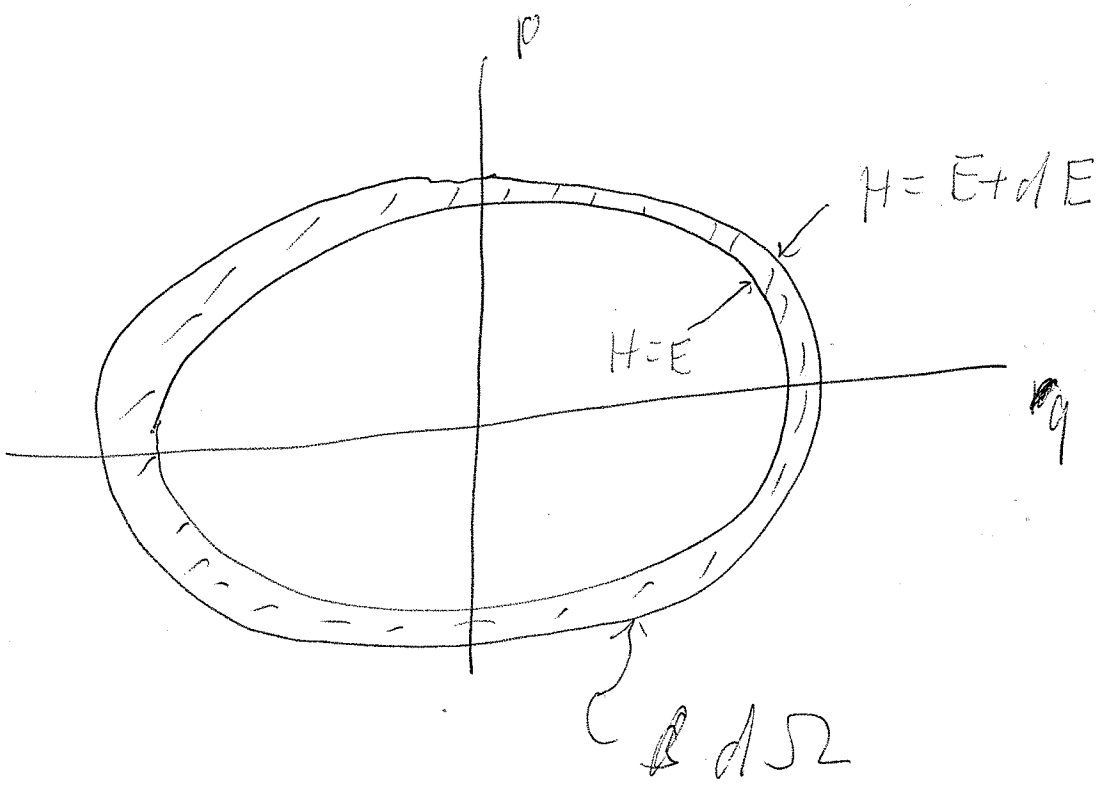
Solution: $\boxed{\rho = f(H(p,q))}$

$$LHS = \frac{\partial H}{\partial p_i} f' \frac{\partial H}{\partial q_i}$$

$$RHS = \frac{\partial H}{\partial q_i} f' \frac{\partial H}{\partial p_i} = LHS \checkmark$$

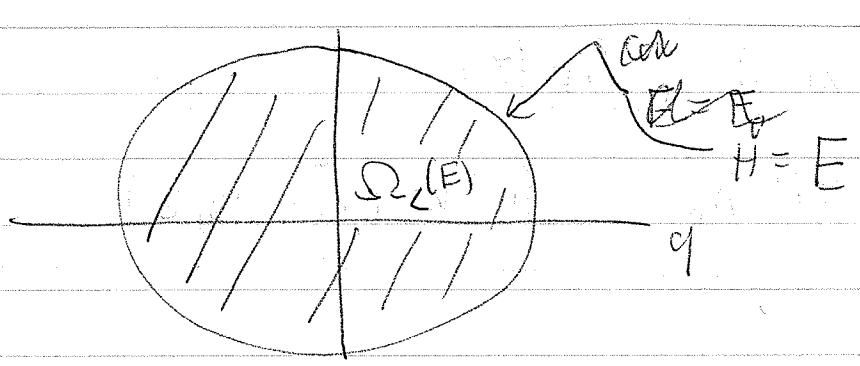
"Microcanonical ensemble:"

$$f(H) = \begin{cases} \frac{1}{d\Omega}\text{th} & , \quad E < H < E + dE \\ 0 & , \quad \text{all other } H\text{'s} \end{cases}$$



(1.5 pt)

Can also define $\Omega_<(E_0)$ (don't confuse with $\Omega(E)$)



Clearly, $\delta\Omega(E, dE) = \Omega_<(E+dE) - \Omega_<(E)$

$$= \frac{d\Omega_<}{dE} dE \equiv \Omega(E)\, dE$$

↑ Definition

Like a surface area, but not quite

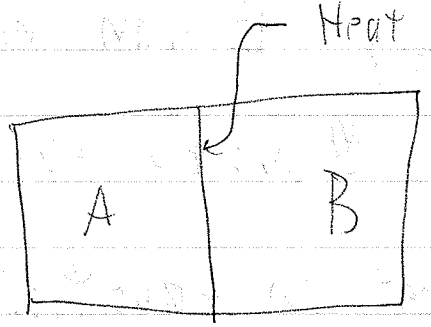
$$\boxed{\Omega(E) = \frac{d\,\Omega_<(E)}{dE}}\ ;\ \Omega_<(E) = \text{phase space volume with } H(p,q) < E$$

~~Now, I'll show that this $\Omega(E)$ satisfies all microcanonical properties~~ ($\frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V}$ etc.)

To do this, define microcanonical ensemble:

ensemble of systems with $E < H(p,q) < E+dE$

Now, consider 2 part, macro system again:

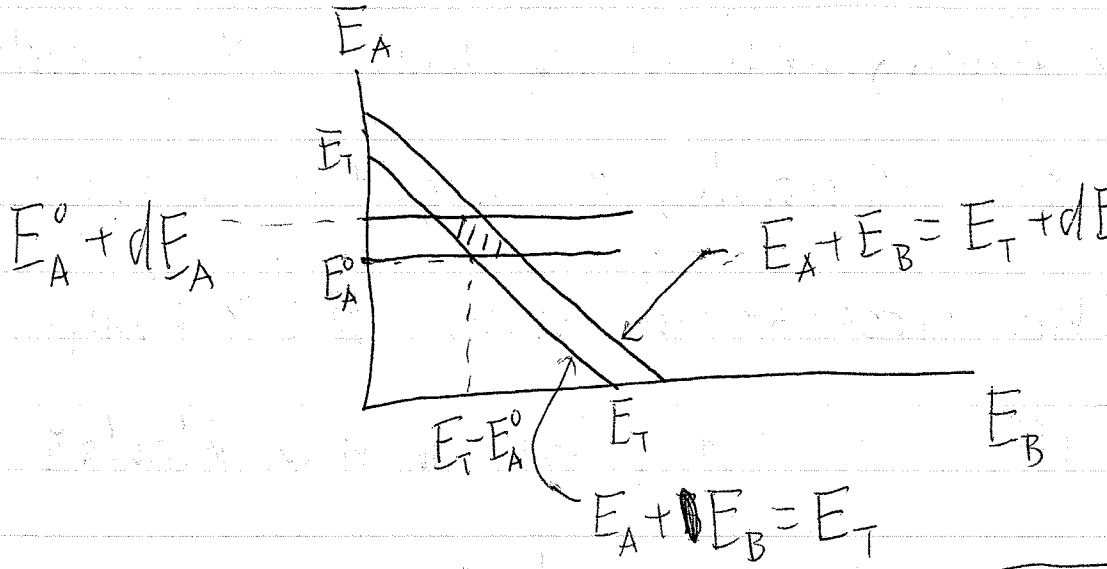


$$E_A + E_B = E_T$$

Total system has $E_T < H_{Total}(p,q) < E_T + dE_T$

~~Microcanonical ensemble~~

Seek $P(E_A^0)\,dE_A$ = prob that $E_A^0 < E_A < E_A^0 + dE_A$



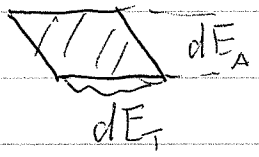
replace $E_A' \to E_A^0$, $E_B \to E_T - E_A^0$

$$P(E_A^0)\,dE_A = \frac{\delta\Omega_T^{VII}}{\delta\Omega_T(E_T, dE_T)} = \frac{\int_{VII} dE_A'\, dE_B\, \Omega_A(E_A')\,\Omega_B(E_B)}{\Omega_T(E_T)\,dE_T}$$

$$P(E_A^0)\,dE_A = \frac{\Omega_A(E_A^0)\,\Omega_B(E_T - E_A^0)}{\Omega_T(E_T)\,dE_T} \int_{//} dE_A'\,dE_B$$

$\int_{//}$ = Area in $E \times E$ space (Not phase space) of //

Area $\square$ = base × height



$\Rightarrow$ Area $= dE_T\,dE_A$

$$\Rightarrow P(E_A^0)\,\cancel{dE_A} = \frac{\Omega_A(E_A^0)\,\Omega_B(E_T - E_A^0)\,\cancel{dE_A}\,\cancel{dE_T}}{\Omega_T(E_T)\,\cancel{dE_T}}$$

$$\Rightarrow \boxed{P(E_A^0) = \frac{\Omega_A(E_A^0)\,\Omega_B(E_T - E_A^0)}{\Omega_T(E_T)}}$$

This is where we started. (page 1.8 of notes)

$\Omega(N, V, E)$: completely determines all macroscopic properties of system (e.g., pressure P, temperature T, ...)

~~Definiti~~

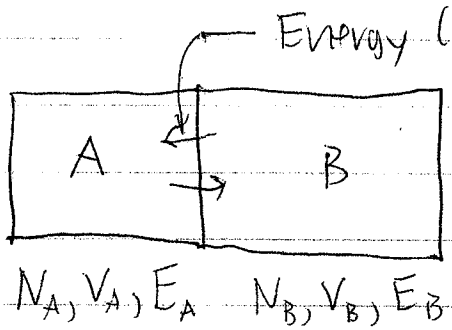
Quantum mechanically:

$$E = \sum_i n_i \epsilon_i \qquad (1)$$

$$N = \sum_i n_i \qquad (2)$$

$\Omega(N, E, V)$ = # of quantum states satisfying (1) and (2) ~~consistent with~~

Definition of temperature:



$E_A + E_B = E_T = \text{constant} \qquad (3)$

$V_{A,B}$, $N_{A,B}$ fixed (immovable, impermeable wall)

Assume: Interaction Range $\ll L_{A,B}$

$\Rightarrow$ A, B <u>independent</u> except for (3)

$$\Rightarrow P(E_A, E_B) = \frac{\Omega_A(E_A)\,\Omega_B(E_B)}{\Omega_T(E_T)}$$

Most probable E_A:

$$\frac{dP}{dE_A} = \frac{1}{\Omega_T}\left[\left(\frac{\partial \Omega_A(E_A)}{\partial E_A}\right)_{N_A, V_A} \Omega_B(E_B) + \left(\frac{\partial \Omega(E_B)}{\partial E_B}\right)_{N_B, V_B}\left(\frac{dE_B}{dE_A}\right)\right] = 0$$

$$\frac{dE_B}{dE_A} = -1$$

$$\Rightarrow \frac{1}{\Omega_A(E_A)}\left(\frac{\partial \Omega_A}{\partial E_A}\right)_{N_A, V_A} = \frac{1}{\Omega_B(E_B)}\left(\frac{\partial \Omega_B}{\partial E_B}\right)_{N, V}$$

$$\Rightarrow \boxed{\left(\frac{\partial \ln \Omega_A(E)}{\partial E_A}\right)_{N_A, V_A} = \left(\frac{\partial \ln \Omega_B(E_B)}{\partial E_B}\right)_{N_B, V_B}}$$

condition for equilibrium

Suppose out of equilibrium, which way will energy (heat) spontaneously flow?

Consider case $\left(\frac{\partial \ln \Omega_A(E_A)}{\partial E_A}\right)_{N_A,V_A} > \left(\frac{\partial \ln \Omega_B(E_B)}{\partial E_B}\right)_{N_B,V_B}$

$$\Rightarrow \frac{dP}{dE_A} = \frac{\Omega_A(E_A)\Omega_B(E_B)}{\Omega_i(E_T)}\left[\left(\frac{\partial \ln \Omega_A(E_A)}{\partial E_A}\right)_{N_A,V_A} - \left(\frac{\partial \ln \Omega_B(E_B)}{\partial E_B}\right)_{N_B,V_B}\right] > 0$$

$\Rightarrow P \uparrow$ when $E_A \uparrow$

$\Rightarrow$ Energy flows spontaneously from B to A

(fundamental postulate of thermodynamics)

$\Rightarrow$ B is "hotter" than A

$\Rightarrow \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \uparrow \Rightarrow$ "temperature" $\downarrow$

$\Rightarrow$ Define temperature: $\boxed{\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \equiv \frac{1}{k_B T}}$

k_B: Boltzmann constant (arbitrary)

Measured by Ideal gas thermometer

Zeroeth law of thermodynamics:

Heat spontaneously flows from high T to low T

~~Pressure: let V_A, V_B change:~~

~~$\frac{\partial \ln \Omega}{\partial V_A}$~~

Entropy: define $S = k_B \ln \Omega$

$$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_{N,V} = T$$

$$\Rightarrow (dE)_{N,V} = T\,dS \equiv đQ \quad \text{(heat)}$$

1st law of thermodynamics:

Energy (including heat) is conserved.

Other thermodynamic quantities

Pressure P (Force/Area),

chemical potential μ (Energy/particle)

$$d(\ln\Omega) = \left(\frac{\partial \ln\Omega}{\partial E}\right)_{N,V} dE + \left(\frac{\partial \ln\Omega}{\partial V}\right)_{N,E} dV + \left(\frac{\partial \ln\Omega}{\partial N}\right)_{V,E} dN$$

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

$$\Rightarrow \quad dE = T\, d(k_B \ln\Omega) - k_B T \left(\frac{\partial \ln\Omega}{\partial V}\right)_{N,E} dV - k_B T \left(\frac{\partial \ln\Omega}{\partial N}\right)_{V,E} dN$$

$$\equiv T\,dS - P\,dV + \mu\,dN$$

$\Rightarrow$ Entropy: $S \equiv k_B \ln\Omega$

Pressure: $P = k_B T \left(\frac{\partial \ln\Omega}{\partial V}\right)_{N,E}$ (simple mechanical work)

chemical potential: $\mu = -k_B T \left(\frac{\partial \ln\Omega}{\partial N}\right)_{V,E}$

Heat: $dQ = T\,dS$ reversible processes only

Specific heats:

$$C_V = \left(\frac{dQ}{dT}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$$

$$C_P = \left(\frac{dQ}{dT}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

Can you calculate $\Omega(N, V, E)$?

Rare Example: Classical Ideal gas

N identical, <u>indistinguishable</u> particles, mass m, volume V

<u>Non-interacting</u>: <u>Always</u> good approximation as $\frac{N}{V} \to 0$ $\left(r_{int} << \left(\frac{V}{N}\right)^{1/3} = r_{inter-particle}\right)$

Dependence of $\Omega(N, V, E)$ on V:

Each particle equally likely to be <u>anywhere</u> in volume V

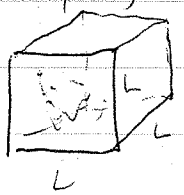
$$\Rightarrow \Omega_{\not<} \propto \int d^{3N}x = V^N \Rightarrow \boxed{\Omega = V^N f(E, N)}$$

Pressure follows at once:

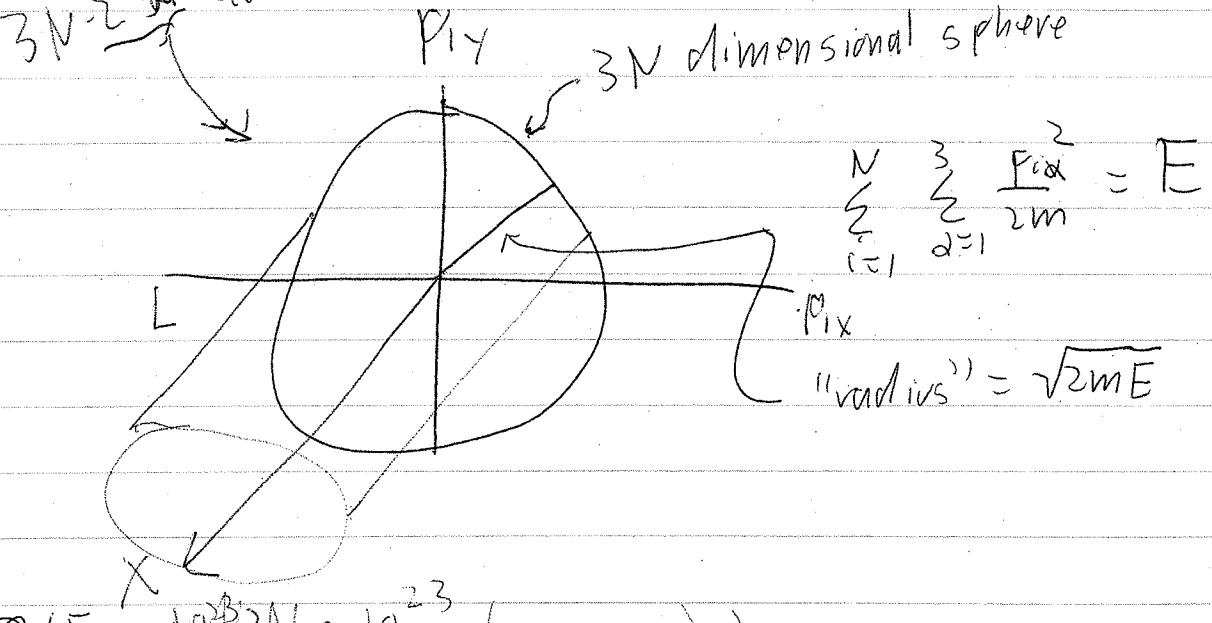
$$P = k_B T \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} = \frac{N k_B T}{V}$$: Boyle's law

Independent of $f(E,N) \Rightarrow$ Valid for all gases (monoatomic, diatomic, hairy) at low density.

Calculating $f(E,N)$ for simple, monoatomic gas: 10^{23} other p's



$3N-2$



10^{23} $3N \sim 10^{23}$ (x, y, z)'s

(c) Volume of $3N$-dimensional sphere:

~~$\Omega(E,V,N) =$~~ of radius R:

For our $\{\vec{p}\}$ sphere

$$V_p = C(N) R^{3N} = C(N)(2mE)^{3N/2}$$

$$\Rightarrow \Omega_{\angle}(E,V,N) = V_p \text{ ``}V_x\text{''} = C(N)(2mE)^{3N/2} V^N$$

``V_x'' = ?

$$\Rightarrow \Omega_{\angle}(E,V,N) = C(N)(2mE)^{3N/2} V^N$$

$$\Rightarrow \boxed{\Omega(E,V,N) = \left(\frac{\partial \Omega_{\angle}}{\partial E}\right)_{N,V} = C(N)\frac{3N}{2}(2mE)^{\frac{3N}{2}-1} V^N}$$

neglect ($N \gg 1$)

$$\Rightarrow \frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = \frac{\left(\frac{3N}{2}-1\right)}{E} = \frac{3N}{2E}$$

$$\Rightarrow \boxed{E = \frac{3}{2} N k_B T} \Rightarrow \frac{E}{\text{particle}} = ?$$

$$\Rightarrow \frac{E}{\text{independent momentum}} = ?$$

$$S = k_B \ln \Omega = \left(\frac{3N}{2} - 1\right) \ln E + N \ln V + f(N)$$

(neglect the -1)

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

$$\Rightarrow S = \frac{3N}{2} \ln T + N \ln V + f_2(N)$$

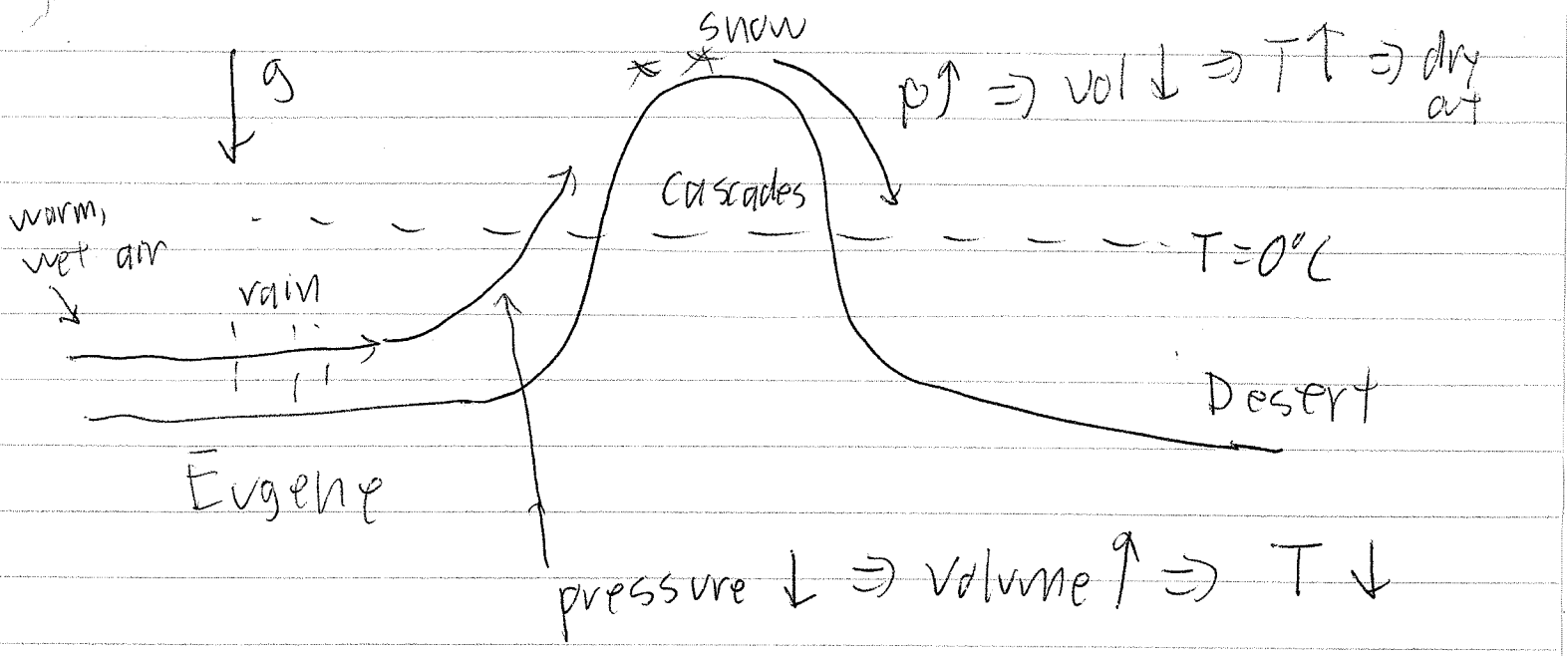
~~Part~~

Consider a process where particles are conserved $\Rightarrow dN = ?$

$$\Rightarrow \Delta S = ~~\Delta N~~ ?$$

$$\Rightarrow T^{3/2} V = \text{constant}$$

Oregon weather



Lecture 2 1/10/96

A Little Thermodynamics

Recall: $S = k_B \ln \Omega$ Entropy

Pressure: $P = k_B T \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} = T\left(\frac{\partial S}{\partial V}\right)_{N,E}$

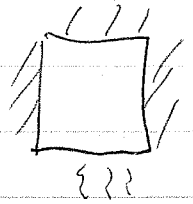
Chemical Potential $\mu = -k_B T \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V,E} = -T\left(\frac{\partial S}{\partial N}\right)_{V,E}$

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

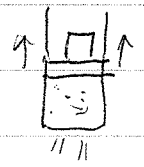
$$dE = T\,dS - P\,dV + \mu\,dN$$

Heat capacities:

constant Volume: $C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_{V,N}$



Constant Pressure $C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$



Other Useful Thermodynamic Functions

Enthalpy $H \equiv E + PV$

$$\Rightarrow dH = dE + P\,dV + V\,dP = T\,dS + V\,dP + \mu\,dN$$

$$\Rightarrow \left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N} = C_P$$

Useful; often easier to fix P than V

Free Energy F (Pathria's "A")

$$F \equiv E - TS$$

$$\Rightarrow dF = dE - TdS - SdT$$

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

F: Easy to calculate in canonical ensemble

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \qquad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -P$$

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$$

Useful, because easier to fix T than E

Also useful because they relate thermodynamic derivatives

Example:

$$dF = -SdT - PdV$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial V \partial T}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$\Rightarrow$ know equation of state $P(V,T)$

$\Rightarrow$ know $\left(\frac{\partial S}{\partial V}\right)_T$

What's this good for?

Relation between specific heats:

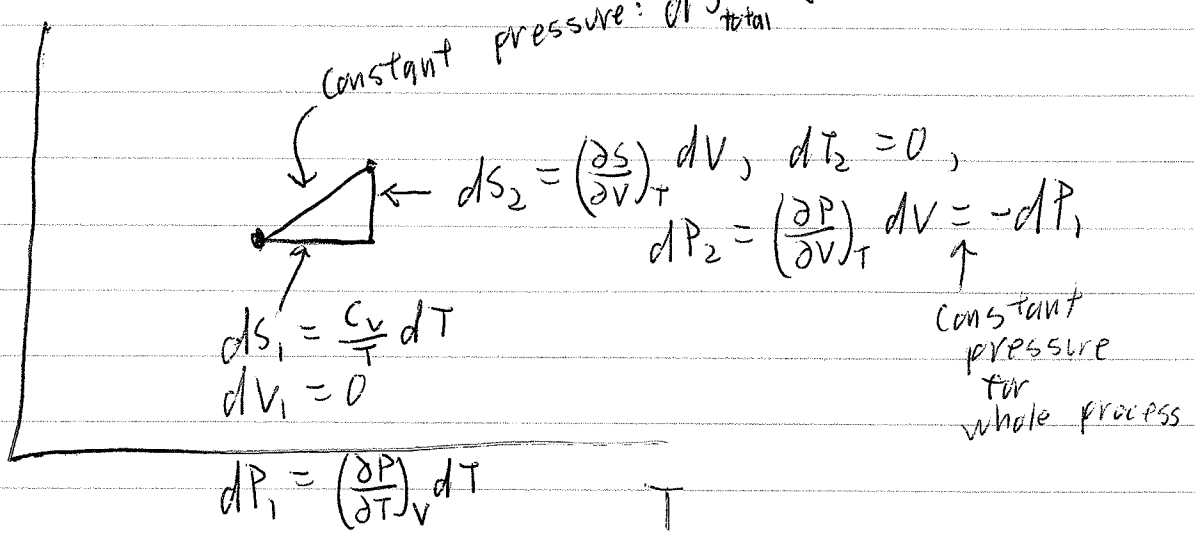
Constant pressure: $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$

" volume: $C_v = T\left(\frac{\partial S}{\partial T}\right)_v$

Calculating C_p from C_v, equation of state:

2 step process:

$dS_{total} = \left(\frac{\partial S}{\partial T}\right)_p dT = \frac{C_p}{T} dT$



Step 1: Constant volume

Step 2: Constant temperature

$dS_{total} = dS_1 + dS_2 = \left(\frac{\partial S}{\partial V}\right)_T dV + \frac{C_v}{T} dT = \frac{C_p}{T} dT$

$\Rightarrow$ $\boxed{C_p = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + C_v = C_v + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p}$ (1)

Using $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Thermodynamics involves many manipulations of these quantities, using relations like

If $x = f(y,z)$, then

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Proof: $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$

set $dx = 0$

$$\Rightarrow \left(\partial y\right)_x = -\frac{\left(\partial z\right)_x \left(\frac{\partial x}{\partial z}\right)_y}{\left(\frac{\partial x}{\partial y}\right)_z}$$

$$\Rightarrow \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z$$

$$\Rightarrow \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

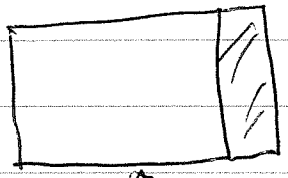
Using this, can show, e.g.

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = \left(\frac{\partial S}{\partial V}\right)_{N,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} \quad \left(\text{because } -\left(\frac{\partial E}{\partial V}\right)_{N,S}\left(\frac{\partial V}{\partial S}\right)_{N,E}\left(\frac{\partial S}{\partial E}\right)_{N,V} = 1\right)$$

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = -\left(\frac{\partial S}{\partial N}\right)_{V,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} \quad \left(\text{" } -\left(\frac{\partial E}{\partial N}\right)_{S,V}\left(\frac{\partial N}{\partial S}\right)_{E,V}\left(\frac{\partial S}{\partial E}\right)_{N,V} = 1\right)$$

E.g., Adiabatic law

Expand without heating:



↑ Insulating walls $\Rightarrow \not{d}Q = 0 \Rightarrow dS = 0$

$\Rightarrow$ entropy S = constant

Important for: Sound propagation

Sound wave goes by <u>too</u> <u>fast</u> for heat exchange

$\Rightarrow$ Sound speed $c = \sqrt{V\left(\frac{\partial P}{\partial V}\right)_S}$

↖ adiabatic sound speed

Newton thought:

$c = \sqrt{V\left(\frac{\partial P}{\partial V}\right)_T}$: isothermal sound speed

differ by ~ 20%

Calculating $\left(\frac{\partial P}{\partial V}\right)_S$:

(1) $$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1$$

(2) $$\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = -1$$

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take ratio $\frac{(1)}{(2)}$:

$$\frac{\left(\frac{\partial T}{\partial P}\right)_S}{\left(\frac{\partial T}{\partial V}\right)_S} \quad \frac{\left(\frac{\partial P}{\partial S}\right)_T}{\left(\frac{\partial V}{\partial S}\right)_T} \quad \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V} = 1$$

$$\| \qquad \| \qquad \|$$

$$\left(\frac{\partial V}{\partial P}\right)_S \quad \left(\frac{\partial P}{\partial V}\right)_T \quad \frac{(C_P \cancel{T})}{(C_V \cancel{T})}$$

$$\Rightarrow \boxed{\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T \frac{C_V}{C_P} \quad (2)}$$

$\Rightarrow$ Measure C_V, $P(V,T)$; use (1) to calculate C_P,

(2) to calculate $\left(\frac{\partial V}{\partial P}\right)_S$

Can also use to derive adiabatic law for arbitrary ideal gas (as you'll see).

3 Laws of thermodynamics:

1) Closed system $\Rightarrow$ $dS = 0$ (no heat in or out)
$dV = 0$ (walls don't move)
$dN = 0$ (walls impermeable)

$\Rightarrow$ $dE = 0$; Energy conserved in closed system
1st law of thermodynamics. (1)

2) Closed system, out of equilibrium: seeks largest $\Omega \Rightarrow$ largest $S = k \ln \Omega$

$\Rightarrow$ S always increases in closed system

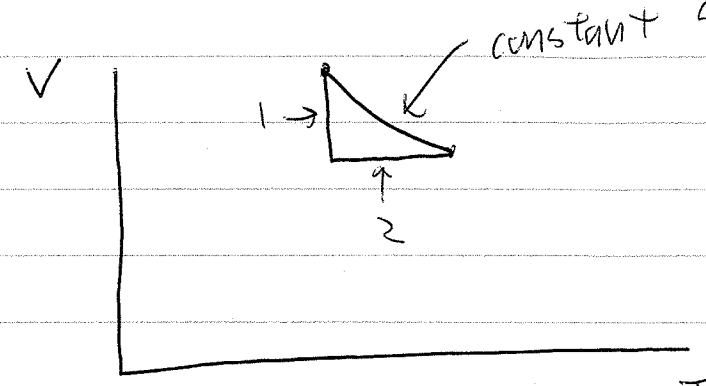
3) as $T \to 0$, system finds (quantum) ground state $\Rightarrow \Omega = 1 \Rightarrow$

$S = 0$ at $T = 0$

Adiabatic heating and cooling:

Air conditioning, refrigerators, weather:

$\left(\frac{\partial T}{\partial V}\right)_S$:



$$dP = \left(\frac{\partial P}{\partial V}\right)_S dV = \frac{dV}{\left(\frac{\partial V}{\partial P}\right)_S} = \frac{C_P}{C_V}\left(\frac{\partial P}{\partial V}\right)_T dV$$

$$= \underbrace{\left(\frac{\partial P}{\partial V}\right)_T dV}_{\text{step 1}} + \underbrace{\left(\frac{\partial P}{\partial T}\right)_V dT}_{\text{step 2}}$$

Divide by $dV \Rightarrow$ $\frac{C_P}{C_V}\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_S$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{C_P - C_V}{C_P}\right)\frac{\left(\frac{\partial P}{\partial V}\right)_T}{\left(\frac{\partial P}{\partial T}\right)_V}}$$

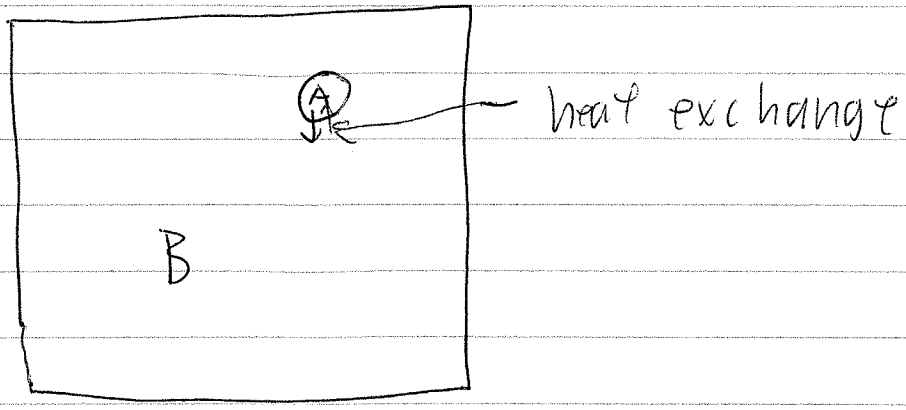
$C_P > C_V$

$\left(\frac{\partial P}{\partial V}\right)_T < 0$

$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S < 0$

$\Rightarrow$ Compress $\rightarrow$ heating; expand $\Rightarrow$ cooling

Canonical Ensemble:



B much bigger than A; B = "heat bath"

$N_A \ll N_B$

$V_A \ll V_B$

$E_A \ll E_B$

Together, in <u>microcanonical</u> ensemble: $E_A + E_B = E_T$ fixed

Question: What is probability that A is in some <u>particular</u> quantum state i, energy E_i?

$$P_i(E_i) = \frac{\Omega_B(E_T - E_i)\left[\Omega_A(E_i; i) = 1\right]}{\Omega_T(E_T)}$$

$$= \frac{\Omega_B(E_T - E_i)}{\Omega_T(E_T)}$$

~~[illegible], [illegible], V_A, [illegible]~~

Probability of states close by in energy

$$\frac{dP_i}{dE_i} = -\frac{1}{\Omega_T}\frac{\partial \Omega_B}{\partial E_B} = -\frac{\Omega_B}{\Omega_T}\left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)$$

$$= -\frac{P_i}{k_B T_B} \quad (1)$$

↑ definition of temperature.

Now, if $E_B \gg E_A$, T_B won't change much as we change E_i ⇒ in limit $\frac{B}{A} \to \infty$, T_B doesn't change at all (def'n. of "heat bath")

⇒ Integrate (1); get $P_i = \frac{e^{-\beta E_i}}{Z}$, $\beta \equiv \frac{1}{k_B T}$

Z = constant (independent of i), normalization

Choose Z such that $\sum_i P_i(E_i) = 1$

$$\Rightarrow \frac{\sum_i e^{-\beta E_i}}{Z} = 1 \Rightarrow \boxed{Z = \sum_i e^{-\beta E_i}}$$

Classically: $\boxed{Z = \int d^{3N}p \, d^{3N}q \, e^{-\beta H(p,q)}}$

Z: Partition function

Determines all of statistical mechanics

$$Z = \begin{cases} \int d^{3N}p\, d^{3N}q\, e^{-\beta E(p,q)} & \text{Classical} \\ \sum_i e^{-\beta E_i} & \text{Quantum} \end{cases}$$

Normalization factor.

Amazingly, can determine all thermodynamic properties from Z.

~~$P(E,T) = \frac{e^{-\beta E(p,q)}}{Z}$~~

$$P(p,q,T) = \frac{e^{-E(p,q)/k_B T}}{Z}$$

Canonical distribution

Amazing results!

Example: Any classical system

(Not necessarily ideal gas,

but can even have strong interactions)

velocity distribution:

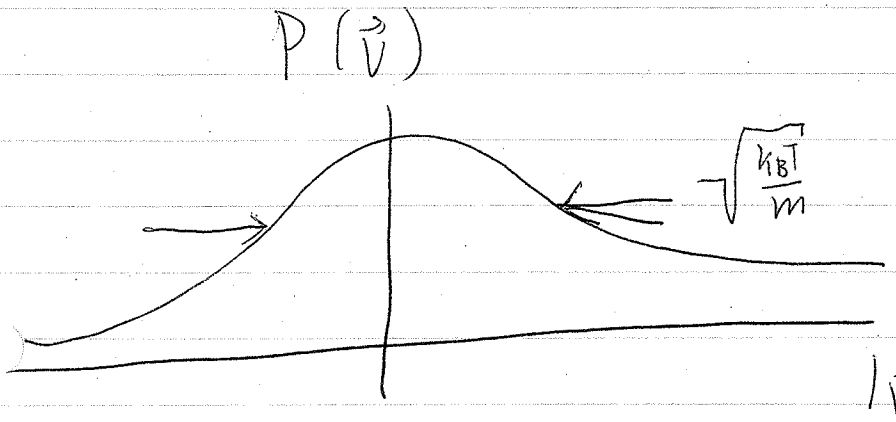
$$H = \sum_i \frac{p_i^2}{2m} + U(\{q_i\})$$

Any potential

$$P(\vec{v}_i) = \frac{\int d^d q_i \; e^{-\frac{m v_i^2}{2k_BT}} \left(\int \prod_{j\neq i} dp_j \; e^{-\frac{p_j^2}{2mk_BT}}\right)}{\int \prod_j dp_j \; e^{-\frac{p_j^2}{2mk_BT}} \int \prod_i dq_i \; e^{-\beta U(q_i)}}$$

$$P(\vec{v}_i) = e^{-\frac{m|\vec{v}_i|^2}{2k_BT}} \left(\int \prod_{j\neq i} dp_j \; e^{-\frac{\beta p_j^2}{2m}}\right) \int \prod_i dq_i \; e^{-\beta U(q_i)}$$

$$= \frac{e^{-\frac{m|\vec{v}_i|^2}{2k_BT}}}{\sqrt{2\pi k_BT/m}}$$: Maxwellian velocity distribution



Works for solids, liquids, gases, glass, magnets ...

$$\langle |\vec{v}_i|^2 \rangle = \frac{3}{2} \frac{k_B T}{m}$$

$$\langle |F_{\alpha}^{\text{ext}}|^2 \rangle = \frac{m k_B T}{2} : \text{Equipartition theorem}$$

General: If ~~$H(x, \{y_i\})$~~

$$H(x, \{y_i\}) = \frac{1}{2} a x^2 + f(\{y_i\})$$

then $\langle x^2 \rangle = \frac{k_B T}{a} \Rightarrow \langle E \rangle = \langle \frac{1}{2} a x^2 \rangle = \frac{k_B T}{2a}$

Back to thermodynamics

$$Z = \sum_i e^{-\beta E_i}, \quad \beta = \frac{1}{k_B T}$$

Deriving thermodynamic quantities from this:

$$\langle E \rangle = \sum_i P(E_i) E_i = \frac{\sum_i e^{-\beta E_i} E_i}{Z}$$

$$= -\frac{\partial}{\partial \beta} (\ln Z) = -\frac{\sum_i \frac{\partial}{\partial \beta} (e^{-\beta E_i})}{Z} = \frac{\sum_i e^{-\beta E_i} E_i}{Z} \checkmark$$

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

Closing loopholes in derivation of thermodynamics from Z

$$Z = \sum_i e^{-E_i/k_B T}$$

a. For $T \to 0$, $T \ll \frac{E_1 - E_0}{k_B} = \frac{\Delta E}{k_B}$ (very low temperature)

$$\Rightarrow \quad Z \to e^{-E_0/k_B T}\left(1 + O\left(e^{-\frac{\Delta E}{k_B T}}\right)\right) = e^{-\beta E_0}\left(1 + O(e^{-\beta \Delta E})\right)$$

Last time, showed

$$S = k_B\left[\ln Z - \beta\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V}\right] + f(N,V)$$

Want to show: $f(N,V) = 0$

Consider $T \to 0$; $S \to 0$ (Nernst's Thm)

$$\Rightarrow \quad f(N,V) = \lim_{T\to 0} k_B\left[\beta\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V} - \ln Z\right]$$

$$= k_B \lim_{\beta \to \infty}\left[\beta\left(\frac{\partial}{\partial \beta}(-\beta E_0)\right)_{N,V} - (-\beta E_0)\right]$$

$$= k_B$$

$$= \lim_{T\to 0} k_B\left[\frac{1}{k_B T}\left(\frac{\partial \ln Z}{\partial T}\right)_{N,V}\frac{dT}{d\beta} - \ln Z\right]$$

$$\frac{dT}{d\beta} = -\frac{1}{k_B \beta^2} = -k_B T^2 \quad \Rightarrow f(N,V) = -\lim_{T\to 0}\left[k_B T\left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} + k_B \ln Z\right]$$