

The Time lines

384-322 BC Aristotle

1564-1642 Galileo : dialogue 1632

1643-1727 Newton principia

1736-1813 Lagrange

1805-1865 Hamilton

Coulomb

Faraday

1831-1879 Maxwell : 1865 light & EM.

$$\eta = 1 - \frac{T_L}{T_H}$$

thermodynamics

1824 S Carnot

1840s Joule

1850 Clausius

1850 Kelvin

1844-1906 Boltzmann

1839-1903 Gibbs

Einstein

1905

1915

Planck

Bohr

Heisenberg

Schrödinger

Born

Dirac

1925-1926

elementary particle theory
Gauge quantum fields
String theory

"Thermodynamics & an introduction to Thermostatistics"

2nd Ed. H. B. Callen

Date

Atomic time scale / length scale 10^{-14} s , 1 \AA

macroscopic scale $\frac{1}{100} \text{ s}$, 10^{-6} m

vibrational frequencies of hydrogen - carbon system
is 3000 cm^{-1}

$$\frac{\nu}{c} = 3000 \text{ cm}^{-1} \rightarrow \nu = 3 \times 10^8 \text{ m}^{-1} \times 3000 \frac{1}{\text{m}} \approx 10^{14} \text{ s}^{-1} \text{ (infrared)}$$

quantum
picture

electrons are even faster

consider H atom

energy

size

$$E = 13 \text{ eV}$$

$$L = 0.5 \text{ \AA}$$

$$\hbar\nu \approx 10 \text{ eV}$$

$$\nu = \frac{10 \text{ eV}}{\hbar} = \frac{10 \text{ eV}}{6 \times 10^{-34} \text{ J.s}}$$

$$= \frac{10 \times 1.6 \times 10^{-19} \text{ J}}{6 \times 10^{-34} \text{ J.s}} = 10^{15} \text{ Hz} \text{ also in the same range?}$$

classical
picture

$$\text{However } E = m \frac{L^2}{T^2} \rightarrow T = \sqrt{\frac{m L^2}{E}} = \sqrt{\frac{10^{-3} \text{ amu} \cdot 0.25 \text{ \AA}^2}{13 \text{ eV}}} = 4.3 \times 10^{-3} \sqrt{\frac{\text{amu \AA}^2}{\text{eV}}} = 10^{-2} \cdot 10^{-14} \text{ s}$$

electrons should be 2 to 3 orders faster!

Thermodynamics is for macroscopic system with many particles (10^{23})
macroscopic measurements are slow (10^{-2} s) and
coarse (10^{-3} m).

Conservation of Energy

1693 Leibniz	$\frac{1}{2}mv^2 + mgh$	mechanical point mass
	$\frac{Q_1 Q_2}{r}$	electric (as well as field engy)
1905 Einstein	$\frac{mc^2}{1 - \frac{v^2}{c^2}}$	rest mass energy

1930 Enrico Fermi proposed neutrino for energy conservation
 conservation of $E \rightarrow$ time translational invariance
 fundamental laws of physics
 are the same today, eons ago, and remote future.

1798 Rumford } heat energy
 1840's James Joule }

Callen's postulates on thermal dynamics 0-th law

} Postulate I. There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and mole number N_i of chemical components.

Existence of Equilibrium: static, independent of past history
 completely determined by extensive parameters

quiescent: not change temporarily.
 Not enough U, V, N . The N parameters characterize the system is small.

ΔU of two states

Energy difference can be measured by purely mechanical means.

Microscopic state need a large number of variables

($p_1, p_2, \dots, p_n, \dots, \bar{p}_1, \bar{p}_2, \dots, \bar{p}_n$)

first law

Quantitative definition of heat

Date

$$Q = \Delta U - W$$

\uparrow
heat flux to a system

\approx mechanical energy (work)

$$\Delta U = U_2 - U_1$$

to the system

internal
energy increase

const. N.

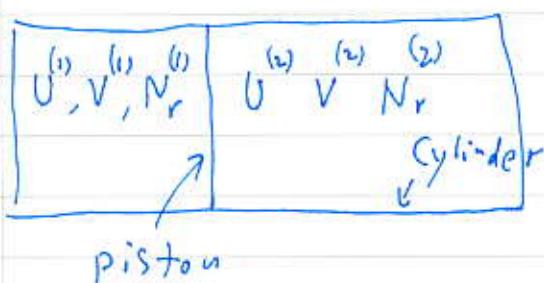
ΔU can be measured
in some adiabatic
process.

for simple system $dW = -PdV$ work done to the system is positive.

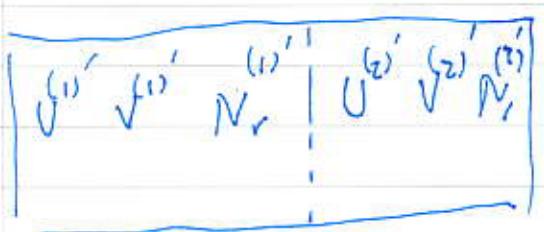
in quasi-static process (infinite slow) so that essential
the system is always
in equilibrium.

units for heat 1 calorie = 4,184 Joule

The single, all-encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system.



initial two isolated systems
a composite system.
piston is rigid, adiabatic,
no holes.



what is the new states
when internal constraints
(the piston) is removed?
i.e. piston can move
or able to transfer heat
or transfer molecules?

The Entropy Maximum Postulates

2nd law

Date _____

Postulate II. There exists a function C called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

$S(U, V, N_r, \dots)$ is known as a fundamental relation.

If the fundamental relation of a particular system is known all conceivable thermodynamic information about the system is ascertainable from it.

[ascertainable]

Postulate III. The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous & differentiable and is a monotonically increasing function of the energy.

$S^{(1)}$	$S^{(2)}$
1	2

total

$$S = S^{(1)} + S^{(2)}$$
 additivity

apply to single homogeneous system

$$S(\lambda U, \lambda V, \lambda N_r) = \lambda S(U, V, N_r)$$

monotonicity, differentiability $\left(\frac{\partial S}{\partial V}\right)_{U, N_r} > 0$ $\left(\frac{1}{T} = \frac{\partial S}{\partial V}\right)$ def



$S = S(U, V, N_r \dots)$ can be solved to get $U \leftarrow U(S, V, N_r \dots)$

alpha
is fixed
value

Postulate IV. The entropy of any system vanishes in the state for which

$$\left(\frac{\partial U}{\partial S}\right)_{V, N_r} = 0 \quad (\text{that is, at the zero of temperature})$$

(3rd law
of thermodynamics)

differentials

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_1, N_2 \dots N_r} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_1, N_2 \dots N_r} dV + \sum_{j=1}^r \left(\frac{\partial U}{\partial N_j}\right)_{S, V, \dots, N_r} dN_j$$

$$= T dS - P dV + \sum_{j=1}^r \mu_j dN_j$$

$$\left(\frac{\partial U}{\partial S}\right)_{V, N} \equiv T, \quad \left(\frac{\partial U}{\partial V}\right)_{S, N} \equiv -P, \quad \left(\frac{\partial U}{\partial N_j}\right)_{S, V} \equiv \mu_j$$

temperature pressure chemical potential
electro-

these three quantities as a function of S, V, N_j is also known as equations of state.

$$dW = -P dV \quad dQ = T dS \rightarrow dS = \frac{dQ}{T}$$

for quasi-static process. N fixed

"A quasi-static flux of heat into a system is associated with an increase of entropy of that system".

T, P, μ_j are intensive parameters in the sense, e.g.

$$T(2S, 2V, 2N_r) = T(S, V, N_r)$$

Definition of Temperature

Date _____

$$U = U(S, V, N_1, N_2, \dots, N_r)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_1 \dots N_r} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_1 \dots N_r} dV + \sum_j \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_1 \dots N_r} dN_j$$

$$= T dS - P dV + \sum_j \mu_j dN_j$$

$$\left(\frac{\partial U}{\partial S}\right)_{V, N_1 \dots N_r} = T \quad \text{temperature}$$

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

$$\left.\left(\frac{\partial U}{\partial V}\right)_{S, N} = -P \right.$$

are this + no
constant?

yes!

$$S = S(U, V, N_1 \dots N_r)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V, N_1 \dots N_r} dU + \left(\frac{\partial S}{\partial V}\right)_{U, N_1 \dots N_r} dV + \sum_j \left(\frac{\partial S}{\partial N_j}\right)_{U, V, N_1 \dots N_r} dN_j \quad \begin{matrix} \text{(not} \\ \text{helpful} \\ \text{to write} \\ \text{this)} \end{matrix}$$

$$\left(\frac{\partial U}{\partial S}\right)_{V, N_1 \dots N_r} \left(\frac{\partial S}{\partial U}\right)_{V, N_1 \dots N_r} = 1$$

$$\begin{matrix} \text{cancel } dU \\ 0 = dU - \left(\frac{\partial U}{\partial S}\right)_{V, N_1 \dots N_r} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_1 \dots N_r} dV \\ 0 = dU - P dV \end{matrix}$$

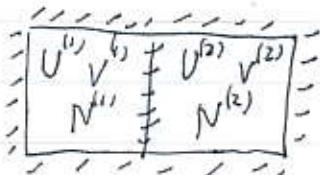
so we also have

$$\left(\frac{\partial S}{\partial V}\right)_{U, N_1 \dots N_r} = \frac{1}{T}$$

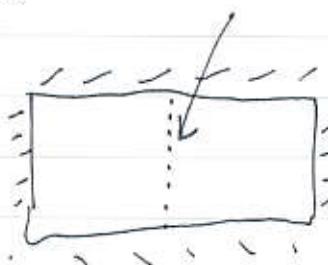
$$= T dS - P dV \quad \text{so} \quad \frac{P}{T} = \left(\frac{\partial U}{\partial V}\right)_{S, N_1 \dots N_r}$$

Thermal Equilibrium — temperature

diathermal wall



adiabatic walls



closed system

two separate, independent
simple systems with rigid, impermeable wall.

but, U, N, V
cannot change

$V^{(1)}, V^{(2)}$, do not change
 $N^{(1)}, N^{(2)}$, because of the external constraints
 (rigid wall & piston)
 impermeable

Date _____

So the only variable that can change due to the removable of internal constraints (replace adiabatic wall by diathermal wall) is $U^{(1)} + U^{(2)}$ with the overall constraints

$$U^{(1)} + U^{(2)} = \text{const.} = U$$

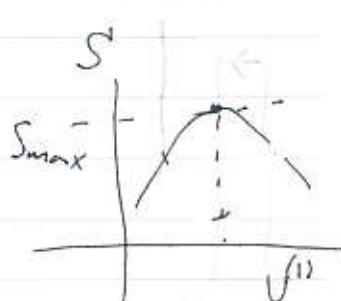
$$S = S^{(1)} + S^{(2)} = S(U, V^{(1)}, N^{(1)}) + S(U^{(2)}, V^{(2)}, N^{(2)})$$

$$dV^{(1)} = dV^{(2)} = 0 \quad \text{particle numbers}$$

$$dN^{(1)} = dN^{(2)} = 0 \quad \& \text{volume is fixed}$$

$$dS = \frac{\partial S^{(1)}}{\partial U^{(1)}} dU^{(1)} + \frac{\partial S^{(2)}}{\partial U^{(2)}} dU^{(2)}$$

$$dU^{(1)} + dU^{(2)} = 0$$



$$= \left(\frac{\partial S^{(1)}}{\partial U^{(1)}} \right)_{VN^{(2)}} - \left(\frac{\partial S^{(2)}}{\partial U^{(2)}} \right)_{V^{(1)}N^{(2)}} dU^{(1)} = 0 \quad \text{at the new equilibrium state.}$$

$$= \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} = 0 \rightarrow \frac{1}{T^{(1)}} = \frac{1}{T^{(2)}} \rightarrow T^{(1)} = T^{(2)}$$

condition of thermal equilibrium is that temperature must be the same.

Intuitive concept of temperature (heat flow from low T to high T)

Let assume $T^{(1)} > T^{(2)}$ ($T^{(1)} \approx T^{(2)}$)

initially

$$\Delta S = S_{\text{final eq}} - S_{\text{initial eq}}$$

$$\Delta S = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \Delta U^{(1)} > 0 \rightarrow \Delta U^{(1)} < 0 \quad \text{decrease!}$$

The hotter one has more energy

Units for temperature

$$dU = Tds - pdV + \mu dN$$

T energy \uparrow Kelvin [S] = joule/kelvin
IS units is joule symbol K units for energy

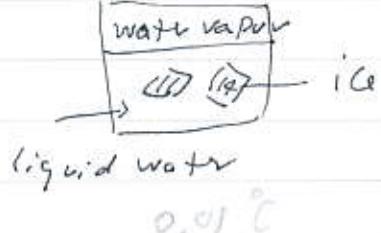
$k_B T$ is joule
then $\frac{S}{k_B}$ is dimensionless

The Kelvin scale $T=0$ is minimal possible temperature fixed by nature

$T_t = 273.16$ at the triple pts of water

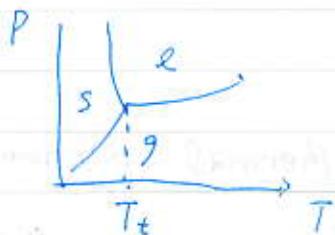
Celsius scale

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$$

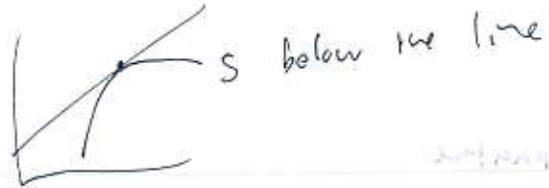


Fahrenheit scale

$$T(^{\circ}\text{F}) = \frac{9}{5} T(^{\circ}\text{C}) + 32$$



An overall feature T characterizes the equilibrium of complex systems



entanglement ent. HET

Date

concavity implies $C_V > 0$

proof: $\left(\frac{\partial^2 S}{\partial V^2}\right)_{V,N} \leq 0$ (local stability condition)

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_{V,N} = \frac{\partial}{\partial V} \left(\frac{\partial S}{\partial V} \right)_V = \left[\frac{\partial}{\partial V} \left(\frac{1}{T} \right) \right]_V = -\frac{1}{T^2} \left(\frac{\partial U}{\partial V} \right)_V$$

$$= -\frac{1}{T^2} \frac{1}{C_V} \leq 0 \quad T > 0 \rightarrow C_V > 0$$

$$\delta Q = T dS$$

thermal dynamics functions (second derivatives)

heat capacity $C_V = \left(\frac{\delta Q}{dT}\right)_{V,N} = T \left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N}$ enthalpy

$$C_P = \left(\frac{\delta Q}{dT}\right)_{P,V} = T \left(\frac{\partial S}{\partial T}\right)_{P,N} = \left(\frac{\partial H}{\partial T}\right)_{P,N} \quad H = U + PV$$

Helmholtz free energy

coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

iso thermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$C_P = C_V + \frac{T V \alpha^2}{K_T}$$

Some Formal relationships

Date

(A)

Euler equation

 U is extensivefor single species
of single systems

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

$\frac{\partial}{\partial \lambda}$ on both sides, set $\lambda = 1$

$$\frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial (\lambda S)} S + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial (\lambda V)} V + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial (\lambda N)} N \\ = U(S, V, N)$$

$$(1) \quad TS - PV + \mu N = U$$

(B)

Gibbs-Duhem relation (the intensive parameters are all independent)

differentiate (1)

$$dU = TdS + SdT - PdV - Vdp + \mu dN + Nd\mu$$

$$\text{since } dU = TdS - PdV + \mu dN$$

$$\text{we find } 0 = SdT - Vdp + Nd\mu$$

concavity of $S(U)$ see page 101(C) Maxwell's relation $U(S, V, N)$

$$\rightarrow \text{Mixed derivatives are equal} \quad \frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

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

Dynamics

Date _____

statistical mechanics \rightarrow interprets/primitively thermodynamics from atomic point of view.

classical dynamics

Newton's law $F = ma$ "principle of least action"

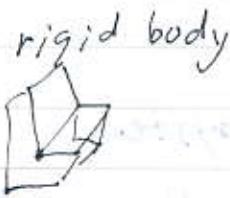
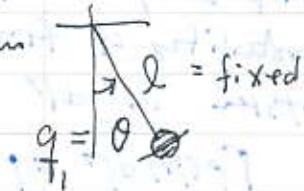
Lagrange formulation $\delta \int L dt = 0 \rightarrow$ Euler-Lagrange Eq. $\dot{q}_i = \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i}$
where $L = K - V$

Hamilton's formulation

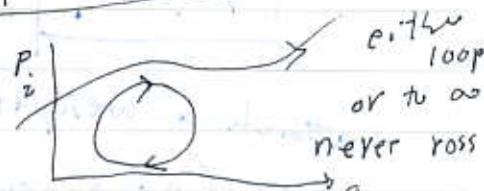
$$H(p_i, q_i) = \sum_{i=1}^n p_i \dot{q}_i - L \quad P_i = \frac{\partial L}{\partial \dot{q}_i}$$

beautify of Lagrange/Hamilton's formulation. q_1, q_2, \dots, q_5 can be any variables uniquely specify a system
(the equations are the same in any coordinate system)

pendulum



phase space (p_i, q_i)



①

Hamilton's Eq.

$$\dot{p}_i = \frac{\partial H}{\partial q_i}, \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$A(q_1, q_2, \dots, p_1, \dots, p_n)$$

Poisson brackets

$$(A, B) = \sum_i \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right)$$

No explicit t dependence

$$(p_j, H) = \dot{p}_j \quad \Rightarrow \text{also}$$

$$(A, H) = \dot{A} \quad \text{equation valid for any time}$$

$$(q_j, H) = \dot{q}_j$$

any arbitrary solution

$$(H, H) = H' = 0 \quad \text{Energy is conserved}$$

$$A_t = e^{t(H, H)} A \quad \text{function of } p, q$$

independent of

No explicit t

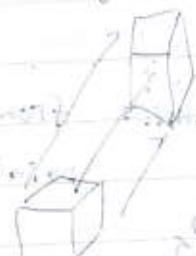
$$A_t = A(q_t, p_t) = A(q, p, t) \quad q = q_{t=0}, \quad p = p_{t=0}, \quad A = A_{t=0} = A(p, q)$$

initial conditions

$$= A(q, p, 0) + \dot{A}_{t=0} t + \ddot{A}_{t=0} \frac{t^2}{2!} + \dots = A + (A, H)t + ((A, H), H) \frac{t^2}{2!} + \dots$$

Total differential
at $t + \Delta t$ later

$$\frac{dP}{dt} = 0 = \frac{\partial P}{\partial t} + \sum_i \frac{\partial P}{\partial q_i} \frac{\partial q_i}{\partial t} + \sum_i \frac{\partial P}{\partial p_i} \frac{\partial p_i}{\partial t}$$

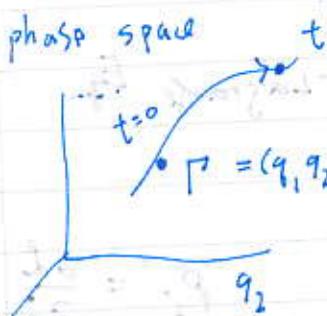


$$= \frac{\partial P}{\partial t} + \sum_i \frac{\partial H}{\partial p_i} \frac{\partial p_i}{\partial t} - \sum_i \frac{\partial H}{\partial q_i} \frac{\partial q_i}{\partial t}$$

$$= \frac{\partial P}{\partial t} + [P, H] = 0$$

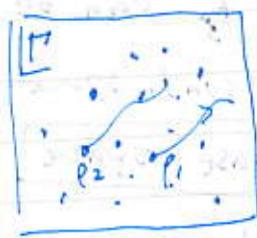
volume preserving

(2)



\therefore degrees of freedom

ensemble



distribution of points

$$P(P)$$

$$P(P) dP$$

of systems

= in phase space of systems
or probability of finding
system in dP

$$\int P(P) dP = 1$$

$$P(P) \geq 0$$

attach a weight to each system

$$\langle A \rangle = \int A(P) P(P) dP$$

ensemble average

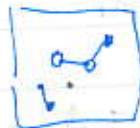
at particle time

a mechanical quantity say $t=0$.

T.S cannot be in this form

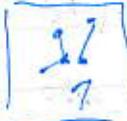
the weight is fixed to a given system

Dynamics



System 1

upper abs.
prob. p_1



System 2

upper abs.
prob. p_2

different for A
is different

say fixed t

$$\langle A \rangle_t = \int A(P, t) P(P) dP = \int dP P(P) e^{t(\cdot, H)} A(P)$$

change of variable $P \rightarrow P_t$

$$= \int A(P_t) P(P) dP$$

\checkmark Jacobian

$$= \int A(P_t) P(e^{t(\cdot, H)} P_t) \frac{dP}{dP_t} dP_t$$

$$P_t = e^{t(\cdot, H)} P$$

$$e_i \quad g_i(H) = g_i(q_1, q_2, \dots, q_n)$$

Symplectic

$$\text{property of Hamiltonian system} \xleftarrow{\text{differential}} \text{the dynamics preserved}$$

$$\omega^2 = \sum_i dp_i \wedge dq_i \quad (\omega^2)^k$$

$$dp \wedge dq = -dq \wedge dp$$

$$(\omega^2)^k = \underbrace{\omega^2 \wedge \omega^2 \wedge \dots \wedge \omega^2}_{k \text{ terms}}$$

$$(\omega^2)^5 = dp_1 \wedge dp_2 \wedge \dots \wedge dp_s \wedge dq_1 \wedge dq_2 \wedge \dots \wedge dq_s = \text{phase space volume.}$$

Liouville's theorem

$$(f\dot{q}_1)_{q_1} \rightarrow | \quad q_1 \quad q_1 + \Delta q_1 \quad | \rightarrow (f\dot{q}_1)_{q_1 + \Delta q_1}$$

$$P(q_1, q_2, \dots, p_1, \dots, p_s)$$

Gibbs picture of ensembles
probability of find. the
system.

$$F_1 = \text{flux in } f\dot{q}_1 \underbrace{\Delta q_2 \Delta q_3 \dots}_{\text{surface perpendicular to axis } q_1} \Delta p_s$$

use
contin
mechan
analog
compar
elem
Eq in

$$F_2 = \text{flux out } (f\dot{q}_1)_{q_1 + \Delta q_1} \Delta q_2 \Delta q_3 \dots \Delta p_s$$

not need to
in compressible
fluid.

$$\bar{f} = (f\dot{q}_1 + \frac{\partial f}{\partial q_1} \Delta q_1)$$

define

$$\frac{\partial f}{\partial t} \Delta q_1 \Delta q_2 \dots \Delta p_s = F_1 - F_2 = \bar{f} \left(\frac{\partial \dot{q}_1}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right) \Delta q_1 \Delta q_2 \dots \Delta p_s$$

$$\frac{\partial f}{\partial t} = \sum_j -\dot{q}_j \frac{\partial f}{\partial q_j} - \dot{p}_j \frac{\partial f}{\partial p_j} + f \left(\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right)$$

partial derivative

$$= \sum_j -\frac{\partial H}{\partial p_j} \frac{\partial f}{\partial q_j} + \frac{\partial H}{\partial q_j} \frac{\partial f}{\partial p_j} + f \left(\frac{\partial^2 H}{\partial q_j \partial p_j} + \frac{\partial^2 (-H)}{\partial p_j \partial q_j} \right) \approx 0$$

$$= (H, f)$$

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial x} (f\dot{x}) = 0 \text{ generates to } 2N - \text{dim}$$

Balescu

$\tilde{\Gamma}_t$ remains to Γ

$$\frac{\partial \tilde{\Gamma}_t}{\partial \Gamma_t} = 1$$

$$\langle A \rangle_t = \int A(\Gamma) \rho(e^{-t(\cdot, H)} \tilde{\Gamma}) d\tilde{\Gamma}$$

$$= \int A(\Gamma) e^{-t(\cdot, H)} \rho(\Gamma) d\Gamma = \int A(\Gamma) \rho(\cdot) d\Gamma$$

$$\rho(t) = e^{-t(\cdot, H)} \rho(0)$$

$$\frac{\partial \rho}{\partial t} = -(\cdot, H) \rho = (H, \rho)$$

Liouville eq

$$\rho(\Gamma)$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \Gamma} \cdot (\rho \dot{\Gamma}) = 0 \quad \text{incompressible}$$

$$\frac{\partial \rho}{\partial t} + \cancel{\rho \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma}} + \dot{\Gamma} \cdot \frac{\partial \rho}{\partial \Gamma} = 0$$

$$\frac{\partial \rho}{\partial t} + \sum q_i \frac{\partial \rho}{\partial p_i} + \sum p_i \frac{\partial \rho}{\partial q_i} = 0 \Rightarrow \frac{D\rho}{dt} = 0$$

$$\frac{\partial \rho}{\partial t} + \sum \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \sum \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} = 0$$

$$\frac{\partial \rho}{\partial t} + (H, \rho) = 0 \rightarrow \frac{\partial \rho}{\partial t} = -(H, \rho)$$

Hilbert space $(\varphi, \psi) = (\varphi, \psi)^* = \langle \varphi | \psi \rangle$

$$(\varphi, \psi) = (\varphi, \psi)^*$$

$$(\varphi, \psi + \chi) = (\varphi, \psi) + (\varphi, \chi)$$

Hilbert space $A(\cdot, \cdot) = \langle \cdot, A \cdot \rangle$

$A\varphi = \lambda\varphi$ where λ is called eigenvalue of A for φ .

Quantum dynamics

State $\Psi(q_1, q_2, \dots, q_s)$ wave function

$$\rho_j = \frac{\hbar}{i} \frac{\partial}{\partial q_j}$$

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

$$H\left(+ \frac{\hbar^2}{2} \frac{\partial^2}{\partial q^2}, \dots, q_1, q_2, \dots, q_s \right)$$

given $\Psi(t=0)$ we can predict $\Psi(t)$ for any t

$$Ap \quad \rho^2 = \rho$$

$$\langle A \rangle_{QM} = \langle \Psi(t) | A | \Psi(t) \rangle = \int dq_1 dq_2 \dots dq_s \Psi^* A \Psi = \text{Tr}(A |\Psi\rangle \langle \Psi|)$$

Heisenberg picture

$$= \langle \Psi(0) | e^{i\frac{Ht}{\hbar}} A e^{-i\frac{Ht}{\hbar}} | \Psi(0) \rangle = \langle \Psi(0) | \hat{A}(t) | \Psi(0) \rangle$$

$$\hat{A}(t) = e^{i\frac{Ht}{\hbar}} A e^{-i\frac{Ht}{\hbar}} | \Psi(0) \rangle = e^{i\frac{Ht}{\hbar}} | \Psi(t) \rangle$$

Heisenberg Eq. of motion

the Heisenberg picture wave function

$$\begin{aligned} \dot{\hat{A}}(t) &= e^{i\frac{Ht}{\hbar}} \left(i\frac{H}{\hbar} A \right) e^{-i\frac{Ht}{\hbar}} - e^{i\frac{Ht}{\hbar}} A \frac{iH}{\hbar} e^{-i\frac{Ht}{\hbar}} \\ &= \frac{i}{\hbar} (A H - H A(t)) = \frac{i}{\hbar} [\hat{A}(t), H] \end{aligned}$$

$$= (\hat{A}(t), H)$$

$$(A, B) = \frac{i}{\hbar} (AB - BA)$$

$$\rightarrow \dot{A} = (A, H)$$

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

$$\frac{Dp}{Dt} = \frac{\partial p}{\partial t} + \dot{q} \frac{\partial p}{\partial q} + \dot{p} \frac{\partial p}{\partial p} = 0$$

Books to read: Balescu: chapter 1, 2, 4

K Huang: chapter 1, 6, 8

Plischke & Bergersen: chapter 1, 2

Toda Rubo Saito: chapter 1, 2

Richard C Tolman: the principles of Stat Mech

$$J = \begin{pmatrix} 0 & -I \\ I & 0 \end{pmatrix}$$

canonical transform

0) $\dot{x} = J \frac{\partial H}{\partial \dot{x}} \Rightarrow \dot{P} = J \frac{\partial K}{\partial P}$ $K = H + \dots$
 $x = \begin{pmatrix} P \\ Q \end{pmatrix}$ $P = \begin{pmatrix} P \\ Q \end{pmatrix}$ $P dq - H = \dot{P} dQ - K + \frac{dF}{dt}$
 $\Gamma = \Gamma(x, t)$

1) $\omega^2 = \sum dq \wedge dP$ $\omega^2 = \Omega^2$
 $\Omega^2 = \sum dQ \wedge dP$

2) $M^T J M = J$ $(M)_{ij} = \frac{\partial \Gamma_i}{\partial x_j}$ $\det(M) = 1$

3) $(Q_i, P_j)_x = \delta_{ij}$
 $(Q_i, Q_j)_x = 0$ $\rightarrow (A, B) = \left(\frac{\partial A}{\partial x} \right)^T J \frac{\partial B}{\partial x}$
 $(P_i, P_j)_x = 0$

4) $\Gamma = \Gamma(x) = e^{\alpha(\cdot, \Theta)} \Gamma_0$ is a canonical transform

set of all canonical transforms form a group

Poisson bracket is invariant
under canonical transformation

classical Poisson bracket

$$(A, B) = \sum_j \frac{\partial A}{\partial q_j} \frac{\partial B}{\partial p_j} - \frac{\partial B}{\partial q_j} \frac{\partial A}{\partial p_j}$$

↑
arbitrary functions of canonical variables p, q

Quantum version

$$(A, B) = \frac{1}{i\hbar} [A, B]$$

↑
operators in Hilbert space

common properties of Poisson bracket

① antisymmetric

$$(A, B) = -(B, A)$$

② linear

$$(A+B, c) = (A, c) + (B, c)$$

③ Jacob identity

$$((A, B), c) + ((B, c), A) + ((c, A), B) = 0$$

④ Leibnitz rule

$$(AB, c) = A(B, c) + (A, c)B$$

c 's action is like
a differential operator

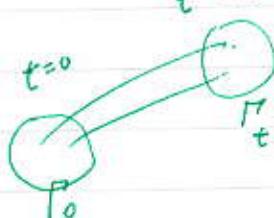
$$(q_j, p_k) = \delta_{jk} \quad \text{true in both classical \& quantum mechanics}$$

1. should that the Jacobian of the transform

$$\Gamma_0 \rightarrow \Gamma_t$$

$t = t$ for first t is 1.

$$D = \det \left(\frac{\partial \mathbf{x}_j(t)}{\partial \mathbf{x}_i(0)} \right)$$



$$D(t) = 1 \quad \text{compare } D(t)$$

$$\mathbf{x} = (q \dots p \dots)$$

$$2. \text{ show } \frac{d \langle A \rangle}{dt} = \langle \frac{d A}{dt} \rangle \quad \langle A \rangle = \int A \rho d\Gamma$$

where we assume term ten is zero!

Density Matrix

a pure state.

for a single quantum state $\rho = |\psi\rangle\langle\psi|$ can be used instead of $|\psi\rangle$ to represent a stateLet $|\psi_i\rangle$ be arbitrary orthonormal states

$$\rho = \sum_i w_i |\psi_i\rangle\langle\psi_i| \quad \leftarrow \text{Spectral decomposition of } \rho$$

$w_i \geq 0, \sum_i w_i = 1$

Schroedinger
representant
objekt

$$\text{Tr}(\rho) = 1. \quad \leftarrow \text{state arises}$$

$$\langle A \rangle = \text{Tr}(\rho A) = \sum_i w_i \text{Tr}(|\psi_i\rangle\langle\psi_i| A) = \sum_i w_i \langle\psi_i| A |\psi_i\rangle$$

QM angle

$$\dot{\rho} = \sum_i w_i \left(\frac{\partial}{\partial t} |\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\psi_i| \frac{\partial}{\partial t} \right)$$

$$= \sum_i w_i \left(\frac{i}{\hbar} H |\psi_i\rangle\langle\psi_i| + |\psi_i\rangle \left(-\frac{i}{\hbar} \right) \langle\psi_i| H \right)$$

$$= \frac{i}{\hbar} (H\rho - \rho H) = (H, \rho) \quad \leftarrow \begin{array}{l} \text{Quantum Liouville eq.} \\ \text{or von Neumann eq.} \end{array}$$

General solution of $\dot{\rho} = (H, \rho) = -i\hbar \rho$

$$\rho(t) = e^{-i\hbar t} \rho(0) = e^{-\frac{iHt}{\hbar}} \rho(0) e^{\frac{iHt}{\hbar}}$$

$$i\hbar \dot{\rho} = [H, \rho]$$

32 relation between classical & quantum description

$$b \rho(p, q) \quad \hat{P}$$

Date

Wigner's Distribution function

$$\text{1D: } \rho_w(p, q) = \int_{-\infty}^{\infty} dr e^{-ipr/\hbar} \langle x | \hat{P} | x' \rangle$$

$$q = \frac{x+x'}{2}$$

$$r = x - x'$$

$$\text{then } \langle A \rangle = \text{Tr}(\hat{\rho} \hat{A})$$

$$= \frac{1}{\hbar} \int d\mathbf{p} dq \ A_w(q, p) \rho_w(q, p)$$

$$\rho(p, q) = \frac{1}{(2\pi\hbar)^3} \int_{-\infty}^{\infty} \rho_w(q, p) dq dp + O(\hbar^2)$$

$$\Delta q \Delta p \gg \hbar$$

	classical	quantum
state	a point in phase space $\Gamma = \begin{pmatrix} p_1 \\ p_2 \\ q_1 \\ q_2 \\ \vdots \\ q_n \end{pmatrix}$	wave func $\psi \rightarrow \psi(q_1, q_2, \dots, q_n)$
operator	$A(\Gamma)$	hermitian op \hat{A}
distrn	$\rho(\Gamma)$ Liouville eq.	$\hat{\rho}$ related by Wigner transf & $\hbar \rightarrow 0$ von Neumann eq
avg	$\int d\Gamma A(\Gamma)$	$\text{tr}(\hat{A} \hat{\rho})$
input math object	$(A, B) = \sum \dots$ Poisson brackets	$\frac{i}{\hbar} [\hat{A}, \hat{B}]$

macroscopic
classical observables

$$\bar{A} = \frac{1}{T} \int_0^T A(p_1, p_2, \dots, q_1, q_2, \dots, q_M) dt$$

T large $T \rightarrow \infty$
time avg



when $T \rightarrow \infty$ the system approaches eq.

\bar{A} because indep't of T

\bar{A} can be computed on a computer by MD.

typical microscopy time scale 10^{-14} s

$$T \approx 10^6 \sim 10^9 \times 10^{-14} \text{ s} \simeq \text{ns} = 10^6 \text{ s}$$

statistical mechanics method bypasses the explicit average process. replace it by ensemble average

$$\langle A \rangle = \int \dots \int dp_1 dp_2 \dots dp_s dq_1 dq_2 \dots dq_s P(p_1, p_2, \dots, q_1, q_2, \dots, q_s) A(p, q)$$

$$\bar{A} = \langle A \rangle$$

$$\int \dots \int dp \dots dq P(\dots) = 1$$

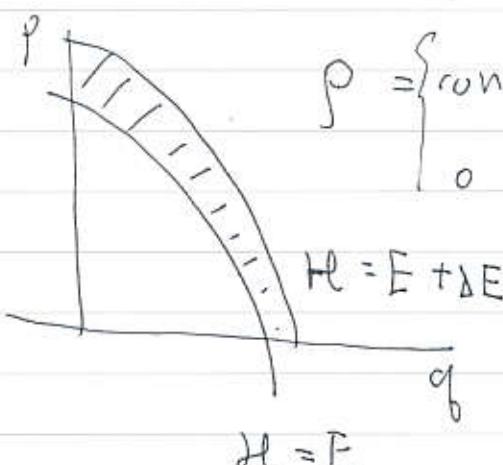
time avg equal ensemble avg

Ergodic hypothesis: Yes $\bar{A} = \langle A \rangle$

microcanonical ensemble

$$\frac{\partial P}{\partial t} = 0 \quad (\text{H.P.})$$

Liouville's



$$P = \begin{cases} \text{const} & E < H < E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

$$\text{otherwise } P \propto \delta(H - E)$$

$$S(E, V, N) \propto \log(\text{phase space volume})$$

Boltzmann's Principle

\rightarrow K we get by Planck give it a 2% accurate value in study of black body radiation
(if we use only T , to more temperature from $T_{\text{K}} = 1$)
Date

$$S = k_B \ln \Omega$$

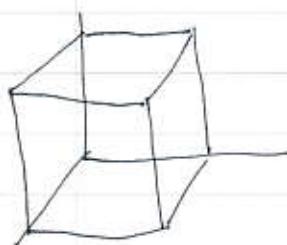
Number of microscopic states consistent with the macroscopic constraints

↑ natural log (base e) simplicity i.e., assumes that each quantum Boltzmann's constant $k_B = 1.38065 \times 10^{-23} \text{ J/K}$ microstate are equal probable. i.e. instantaneous.

when a system is in a unique ground state $\Omega = 1$, $S = 0$
This is the 3rd law of thermodynamics

Example.

classical Ideal gas

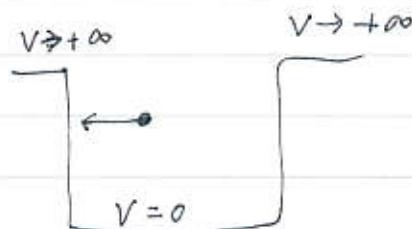


$$-\infty < p_j < +\infty$$

$$0 \leq q_1, q_2, \dots, q_{3N} < L, \quad \text{volume } V = L^3$$

$$H(p_1, p_2, \dots, q_1, q_2, \dots) = \sum_{j=1}^{3N} \frac{p_j^2}{2m} + V(q_1, \dots, q_{3N})$$

effect of walls + weak interaction



$$l \propto \frac{1}{N \cdot \sigma^2}$$

$$\text{air at room } T, \quad \sigma \approx 1 \text{ \AA} \quad \frac{N}{V} \approx 10^{25} \text{ m}^{-3}$$

$$l \propto 10^{-8} \text{ m} \approx 100 \text{ \AA}$$

tutorial 1 Sat 20 Jan 07

Date _____

2.6-4:

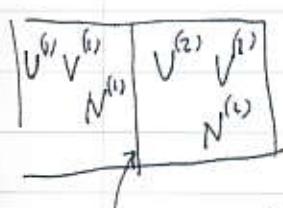
$$\frac{1}{T^{(1)}} = \frac{3}{2} R N^{(1)} / V^{(1)} \quad \text{mole number}$$

$$\frac{1}{T^{(2)}} = \frac{5}{2} R N^{(2)} / V^{(2)} \quad \left. \begin{array}{l} \text{equation} \\ \text{of state} \end{array} \right\}$$

$$V^{(1)} = \frac{3}{2} N^{(1)} R T$$

$$\left. \begin{array}{l} \text{Eq. of states} \\ \frac{1}{T} = \frac{\partial S}{\partial U} \\ P = -\frac{\partial U}{\partial V} |_{S,N} \\ M = \frac{\partial U}{\partial N} |_{S,V} \end{array} \right\}$$

$$R = 8.314 \text{ J/(mole.K)}$$



diathermal wall

$$N^{(1)} = 2$$

$$N^{(2)} = 3$$

$$T^{(1)} = 250 \text{ K}$$

$$T^{(2)} = 350 \text{ K}$$

compute the entropy

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{V^{(1)}} = \frac{\partial S^{(1)}}{\partial U^{(1)}} \quad \left. \begin{array}{l} S^{(1)}(U^{(1)}, V^{(1)}, N^{(1)}) \\ V^{(1)}, N^{(1)} \end{array} \right\}$$

Fixed value and N , in the problem

$$S^{(1)} = \int \frac{3}{2} R \frac{N^{(1)}}{V^{(1)}} dV^{(1)} = \frac{3}{2} R N^{(1)} \ln \frac{V^{(1)}}{V_0^{(1)}} + \text{const}$$

$$\text{Similarly } S^{(2)} = \frac{5}{2} R N^{(2)} \ln \frac{V^{(2)}}{V_0^{(2)}}$$

$$S = S^{(1)} + S^{(2)} = \frac{3}{2} R N^{(1)} \ln \frac{V^{(1)}}{V_0^{(1)}} + \frac{5}{2} R N^{(2)} \ln \frac{V^{(2)}}{V_0^{(2)}}$$

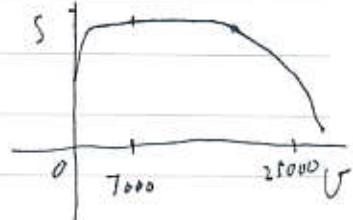
$$U = U^{(1)} + U^{(2)} = \text{const} = \frac{3}{2} N^{(1)} R T^{(1)} + \frac{5}{2} N^{(2)} R T^{(2)}$$

$$= \left(\frac{3}{2} \cdot 2 + \frac{5}{2} \cdot 3 \right) 250 \text{ K} \times 8.314 \text{ J/(mole.K)}$$

$$= 3 \times (250 + \frac{5}{2} \cdot 350) \times 8.314 = 28059.75 \text{ J}$$

S is concave

$$S = \frac{3}{2} R N^{(1)} \ln \frac{U}{U_0^{(1)}} + \frac{5}{2} R N^{(2)} \ln \left(\frac{U - U^{(1)}}{U_0^{(2)}} \right)$$



find maximum of S

$$\frac{\partial S}{\partial V^{(1)}} = 0 \Rightarrow \frac{3}{2} R N^{(1)} \frac{1}{U^{(1)}} + \frac{5}{2} R N^{(2)} \frac{(-1)}{(U - U^{(1)})}$$

$$\frac{3 N^{(1)}}{U^{(1)}} = \frac{5 N^{(2)}}{U - U^{(1)}} \rightarrow \frac{6}{U^{(1)}} = \frac{15}{U - U^{(1)}}$$

$$2(U - U^{(1)}) = 5 U^{(1)} \rightarrow 2U = 7U^{(1)}$$

$$U_{eq}^{(1)} = \frac{2}{7} U = \frac{2}{7} \times 28059.75 \text{ J} = 8017.07 \text{ J}$$

$$U_{eq}^{(2)} = U - U^{(1)} = \underline{\frac{5}{7} U} = 5726.48 \text{ J} = 20042.68 \text{ J}$$

$$T_{eq} = T_{eq}^{(1)} = T_{eq}^{(2)} = \frac{U_{eq}^{(1)}}{\frac{3}{2} R N^{(1)}} = \frac{8017.07 \text{ J}}{\frac{3}{2} \cdot 8.314 \text{ J (mole k)}} \underset{2 \text{ mole}}{=}$$

$$= 321.43 \text{ K}$$

$$T^{(1)} < T_{eq} < T^{(2)}$$

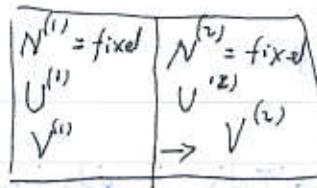
$$U^{(1)} = \frac{3}{2} N^{(1)} R T^{(1)}$$

$$U^{(2)} = \frac{5}{2} N^{(2)} R T^{(2)}$$

$$\left\{ \begin{array}{l} U^{(1)} + U^{(2)} = U \\ \frac{2}{3} U/N = \frac{2}{5} U/N^{(2)} \end{array} \right. \quad T = T_2$$

$$\begin{aligned} U^{(1)} + \frac{2}{5} U^{(2)} &= U \\ \frac{7}{5} U^{(1)} &= U \\ U^{(1)} &= \frac{5}{7} U^{(2)} \end{aligned}$$

Sec 2-7



Date _____

$$U^{(1)} + U^{(2)} = U = \text{const}$$

$$V^{(1)} + V^{(2)} = V = \text{const}$$

movable
diathermal
wall

$$S = S^{(1)} + S^{(2)}$$

when in equilibrium, there is no transfer of heat $T dS - SdT = 0$

$$0 = \partial S = \frac{\partial S}{\partial U^{(1)}} \Big|_{V^{(1)}, N^{(1)}} dU^{(1)} + \frac{\partial S}{\partial V^{(1)}} \Big|_{U^{(1)}, N^{(1)}} dV^{(1)} \quad dU^{(1)} + dU^{(2)} = 0$$

$$dV^{(1)} + dV^{(2)} = 0$$

$$+ \frac{\partial S}{\partial U^{(2)}} \Big|_{V^{(2)}, N^{(2)}} dU^{(2)} + \frac{\partial S}{\partial V^{(2)}} \Big|_{U^{(2)}, N^{(2)}} dV^{(2)}$$

$dU^{(2)}$ or same
 $dV^{(2)}$ each
- each

$$= \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}} \right) dV^{(1)} = 0$$

$\partial S = 0$ for arbitrary $dU^{(1)}$ and $dV^{(1)}$

$$\rightarrow \frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}, \quad \frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}} \rightarrow P^{(1)} = P^{(2)}$$

$$dU = T dS - P dV + \mu dN$$

$$= \left(\frac{\partial U}{\partial S} \right)_{V, N} dS + \left(\frac{\partial U}{\partial V} \right)_{S, N} dV + \left(\frac{\partial U}{\partial N} \right)_{S, V} dN$$

$$\rightarrow \partial S = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \rightarrow \left(\frac{\partial S}{\partial U} \right)_{V, N} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial N} \right)_{U, V} = -\frac{\mu}{T} \quad \left(\frac{\partial S}{\partial V} \right)_{U, N} = P/T$$

Ex 3-4 pse 66-68

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$$\frac{dU}{dV} = T dS - P dV + \mu dN$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

 $S(U, V, N)$ let $dN = 0$

$$= \frac{C_N K}{V} dU + \frac{N K T}{V^2} dV + 0$$

equations of state

$$\begin{cases} PV = NKT \\ U = C_N K T \end{cases}$$

$$\int dS = \int_{U_0}^U \frac{C_N K}{V} dU + \int_{V_0}^V \frac{N K T}{V} dV$$

$$S = S_0 +$$

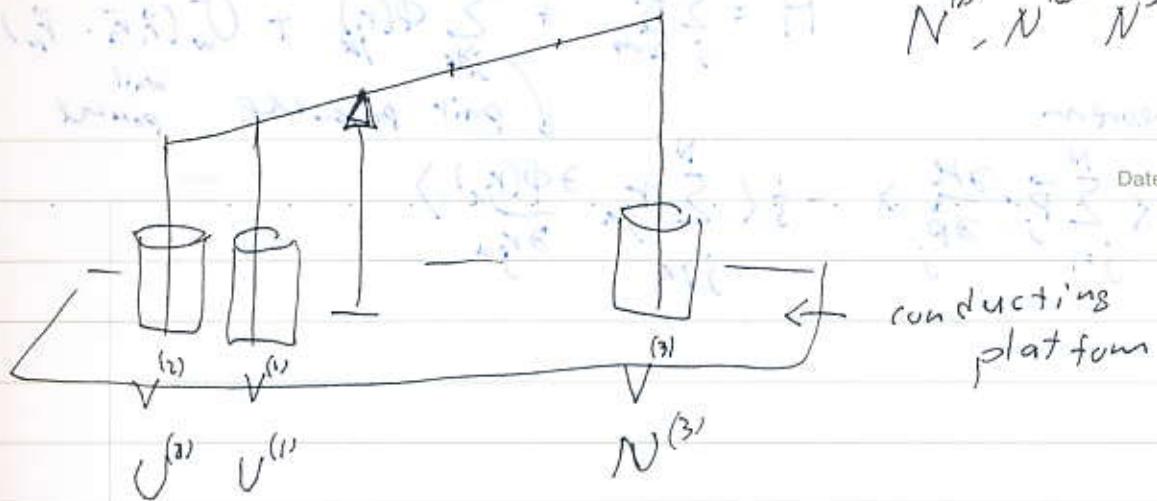
$$S(U, V, N) = \underbrace{S_0(U_0, V_0, N)}_{\text{unknown constant}} + C_N K \ln \frac{U}{U_0} + N K \ln \frac{V}{V_0}$$

problem when $U \rightarrow 0$
or $V \rightarrow 0$

discuss eqn

how to determine

$$S \text{ from } dS = f(U, V) dU + g(U, V) dV ?$$

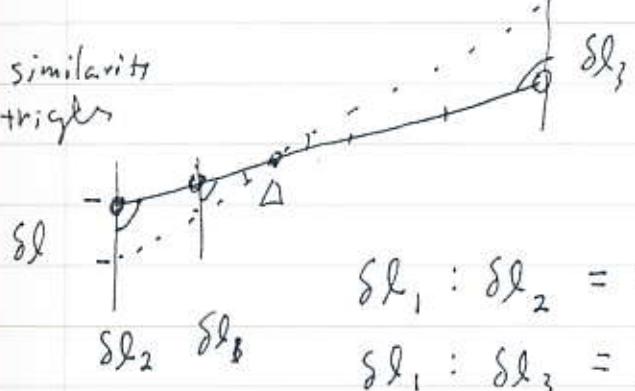


total system is isolated

$$U^{(1)} + U^{(2)} + U^{(3)} = U = \text{const}$$

$$S^{(1)} + S^{(2)} + S^{(3)} = S \uparrow \max$$

similarity
trigles



$$\rightarrow 2\delta V^{(1)} = \delta V^{(2)}$$

$$\delta V^{(3)} = -3\delta V^{(1)}$$

$$\frac{\delta l_1}{\delta l_2} = \frac{1}{2}$$

$$\delta l_2 = 2\delta l_1$$

$$\delta S = \frac{1}{T^{(1)}} \delta U^{(1)} + \frac{1}{T^{(2)}} \delta U^{(2)} + \frac{1}{T^{(3)}} \delta U^{(3)}$$

$$+ \frac{P^{(1)}}{T^{(1)}} \delta V^{(1)} + \frac{P^{(2)}}{T^{(2)}} \delta V^{(2)} + \frac{P^{(3)}}{T^{(3)}} \delta V^{(3)}$$

$$\delta U^{(1)} = -\delta U^{(2)} - \delta U^{(3)}$$

$$= \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(3)}} \right) \delta U^{(1)} + \left(\frac{1}{T^{(2)}} - \frac{1}{T^{(3)}} \right) \delta U^{(2)}$$

$$+ \left(\frac{P^{(1)}}{T^{(1)}} + 2 \frac{P^{(2)}}{T^{(2)}} - 3 \frac{P^{(3)}}{T^{(3)}} \right) \delta V^{(1)} = 0$$

$$\rightarrow T^{(1)} = T^{(3)}, \quad T^{(2)} = T^{(3)}$$

$$P^{(1)} + 2 P^{(2)} = 3 P^{(3)}$$

$$1 + 2 \frac{P^{(2)}}{P^{(1)}} = 3 \frac{P^{(3)}}{P^{(1)}}$$

\uparrow
no torque condition

$$P^{(1)} : P^{(2)} : P^{(3)} = ?$$

Hamilton's eq. of motion

$$\mathcal{H} = \sum_{j=1}^{3N} \frac{p_j^2}{2m} + V \quad \begin{matrix} \nearrow \\ \nwarrow \end{matrix} \text{important}$$

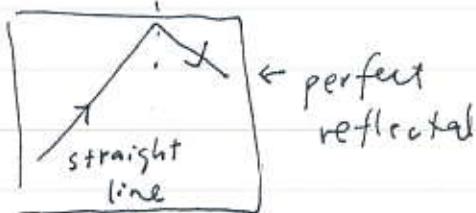
to state establish
equilibrium

$$\dot{p}_j = -\frac{\partial V}{\partial q_j} = 0$$

$$p_j = \text{const}$$

$$\dot{q}_j = \frac{\partial \mathcal{H}}{\partial p_j} = \frac{p_j}{m} \rightarrow p_j = m \dot{q}_j \quad \dot{q}_j = \text{const} + V_j$$

$$q_j = V_j t + \text{const}$$



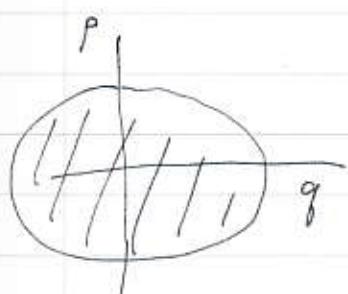
↓ how to count the # of states?

$$\text{Def } \Omega(U, V, N) = \frac{1}{N! h^{3N}} \int \dots \int dp_1 dp_2 \dots dp_{3N} dq_1 dq_2 \dots dq_{3N}$$

identical particles solve Gibbs paradox

$$U \leq \mathcal{H} \leq U + \Delta$$

$$\Delta \rightarrow 0$$



$$\oint p dq = nh$$

Boltz-Sommerfeld quantization condition

constraint is $0 \leq q_i \leq L$
coordinates

$$\Omega = \frac{1}{N! h^{3N}} \int \dots \int dp_1 dp_2 \dots dp_{3N} \cdot V^N$$

$$U \leq \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \dots + \frac{p_{3N}^2}{2m} \leq U + \Delta$$

← volume of a spherical shell

in $3N$ dimensions.

$$\delta P \equiv \int \dots \int dp_1 dp_2 \dots dp_{3N}$$

$$2mU \leq p_1^2 + p_2^2 + \dots + p_{3N}^2 \leq 2m(U + \Delta) \quad \begin{matrix} \leftarrow \text{the radius of the sphere} \\ \text{is from } \sqrt{2mU} \text{ to } \sqrt{2m(U + \Delta)} \end{matrix}$$

Euler:

47

$$\Gamma = \int \dots \int dP_1 dP_2 \dots dP_{3N} = R^{3N} \cdot C_{3N}$$

$$P_1^2 + P_2^2 + \dots + P_{3N}^2 \leq 2mU = R^2$$

$$R = \sqrt{2mU}$$

$$C_{3N} = \int_{x_1^2 + x_2^2 + \dots + x_{3N}^2 \leq 1} dx_1 dx_2 \dots dx_{3N} = \frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2} + 1)}$$

$$\frac{(3N)!}{(2)^{3N}}$$

$$\Gamma(x+1) = x! \Gamma(x)$$

$$\Gamma(x+1) = x!$$

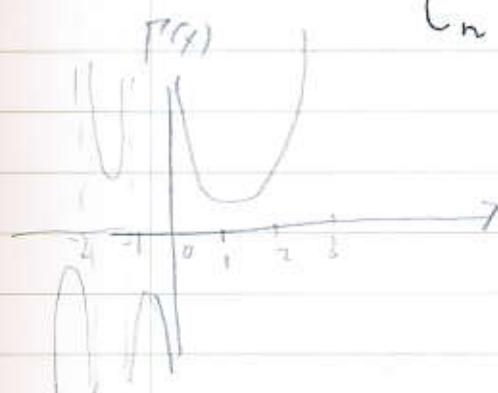
$$(\frac{1}{2})! = \Gamma(\frac{1}{2} + 1) = \sqrt{\pi}/2$$

$$\Gamma(\frac{1}{2}) = \sqrt{\pi}$$

$$(\frac{1}{2})^{-1} = \frac{\sqrt{\pi}}{2}$$

volume of n -dimensional sphere is

$$C_n = \frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2} + 1)}$$



n	C_n
1	2
2	π
3	$\frac{4}{3}\pi$

$$\Omega = \frac{1}{h^{3N} N!} V^N \left[[2m(U + \Delta)]^{\frac{3N}{2}} - 2mU^{\frac{3N}{2}} \right] \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!}$$

Δ small compare to U

$$\approx \frac{1}{h^{3N} N!} V^N \left[\frac{3N}{2} (2mU)^{\frac{3N}{2}-1} 2m\Delta \right] \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!}$$

$S(U, V, N)$

Take thermodynamic limit

$$\begin{aligned} & N \rightarrow \infty \\ & V \rightarrow \infty \\ & U \rightarrow \infty \end{aligned} \quad \text{but fixed ratio } \frac{V}{N} = \rho = \text{const}$$

$$\text{is } S(U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

No, recall

(Callen's entropy postulate)
entropy is const

valid for small N !

$$\text{regarding } \Omega = \frac{V^N}{h^{3N} N!} \left[(2\pi m V)^{\frac{3N}{2}} \left(\frac{3N}{2} \right) \frac{(2m\Delta)}{(2mV)} \right] \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2} - 1 \right)!}$$

$$= \left(\frac{V \cdot (2\pi m V)^{\frac{3}{2}}}{h^3} \right)^N \frac{\Delta}{V} \frac{1}{N! \left(\frac{3N}{2} - 1 \right)!} \xrightarrow{\text{ignore } 1 \text{ in } N!} X$$

Using Stirling's formula $\ln N! = N \ln N - N + O(\ln N)$

$$S = k_B \ln \Omega = N k_B \ln \frac{\sqrt{(2\pi m V)^{\frac{3}{2}}}}{h^3} + k_B \ln \frac{\Delta}{V} + O(\ln N)$$

$$\left. \begin{aligned} & k_B (-N \ln N + N - \left(\frac{3N}{2} - 1 \right) \ln \left(\frac{3N}{2} - 1 \right) + \frac{3N}{2} - 1 + O(\ln N)) \\ & -N \ln N + N - \underbrace{\frac{3}{2} N \ln \left(\frac{3N}{2} - 1 \right)}_{X} + \ln \left(\frac{3N}{2} - 1 \right) + \frac{3N}{2} - 1 \\ & -\frac{3}{2} N \left[\ln \left(N - \frac{3}{2} \right) + \ln \frac{3}{2} \right] \end{aligned} \right\} \begin{array}{l} N \gg 1 \Rightarrow N \\ N \gg 1 \end{array}$$

$$\downarrow -\frac{3}{2} \ln N \left(1 - \frac{3}{N} \right)$$

$$k_B \left(-\frac{5}{2} N \ln N + \frac{5}{2} N - \frac{3}{2} N \ln \frac{3}{2} \right)$$

$$= N k_B \ln \frac{\sqrt{(2\pi m V)^{\frac{3}{2}}}}{h^3} - \frac{5}{2} N k_B \ln N + \frac{5}{2} N k_B - \frac{3}{2} N k_B \ln \frac{3}{2}$$

$$= N k_B \ln \frac{\sqrt{(2\pi m V)^{\frac{3}{2}}}}{N^{\frac{5}{2}} h^3} + \frac{5}{2} N k_B + N k_B \ln \left(\frac{3}{2} \right)^{-\frac{3}{2}}$$

$$= N k_B \ln \left[\frac{V}{N^{\frac{5}{2}} h^3} \left(\frac{4\pi m V}{3} \right)^{\frac{3}{2}} \right] + \frac{5}{2} N k_B$$

Otto Sackur, Hugo Tetrode

Sackur-Tetrode formula (1912)

Equation of states

$$\partial U = T \partial S - P \partial V + \mu \partial N$$

homework 2
see pg 121

$$\rightarrow \partial S = \frac{1}{T} \partial U + \frac{P}{T} \partial V - \frac{\mu}{T} \partial N$$

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$$\begin{aligned} \frac{\partial S}{\partial V} &= \frac{1}{T} = \frac{\partial}{\partial V} \left[N k_B \ln V^{\frac{3}{2}} + \text{const} \right] \\ &\quad \text{with respect to } V \\ &= \frac{3}{2} N k_B \frac{1}{V} \quad \rightarrow \quad U = \frac{3}{2} N k_B T \end{aligned}$$

$$\frac{\partial S}{\partial V} = \frac{P}{T} = \frac{\partial}{\partial V} [N k_B \ln V + \text{const}] = \frac{N k_B}{V} \rightarrow PV = N k_B T$$

$$\frac{\partial S}{\partial N} = -\frac{\mu}{T} = \frac{\partial}{\partial N} \left[\frac{5}{2} N k_B \ln N + \text{const} \right] = \frac{5}{2} \frac{N k_B}{N} - \frac{5}{2} k_B \ln N$$

$$\frac{\partial}{\partial N} \left(N k_B \ln \frac{V}{N^{\frac{5}{2}} h^3} \left(\frac{4\pi m V}{3} \right)^{\frac{3}{2}} \right) + \frac{5}{2} N k_B$$

$$= k_B \ln \frac{V}{N^{\frac{5}{2}} h^3} \left(\frac{4\pi m V}{3} \right)^{\frac{3}{2}} + \frac{5}{2} k_B - \frac{5}{2} k_B$$

$$\mu = k_B T \ln \left[\frac{N \lambda^3}{V} \right] \quad \lambda = \frac{h N^{\frac{1}{2}}}{\left(\frac{4\pi m V}{3} \right)^{\frac{1}{2}}}$$

$$= \frac{h N^{\frac{1}{2}}}{\left(\frac{4\pi m}{3} \frac{N^{\frac{3}{2}} k_B T}{2} \right)^{\frac{1}{2}}}$$

$$\lambda = \frac{h}{2\pi m k_B T} \leftarrow \text{thermal wavelength}$$

Does S satisfy 3rd Law of thermodynamics? why?

Virial Theorem
Equipartition Theorem

The degree of freedom is S .

$$k_B T = \langle \vec{u} \cdot \vec{\nabla} H \rangle$$

\uparrow

microcanonical ans

$$\vec{u} = (u_1, u_2, \dots, u_{2S})$$

such that $\vec{\nabla} \cdot \vec{u} = 1$

$$\vec{\nabla} = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial q_S}, \frac{\partial}{\partial p_1}, \dots, \frac{\partial}{\partial p_S} \right)$$

E.g. Let $H = \sum_{j=1}^S \frac{p_j^2}{2m_j} + V(q_1, \dots, q_S)$

$$\vec{u} = (0, 0, \dots, 0, 0, \frac{p_1}{m_1}, \frac{p_2}{m_2}, \dots, \frac{p_S}{m_S})$$

$$\vec{\nabla} \cdot \vec{u} = 1$$

$$\vec{\nabla} H = \left(\frac{\partial H}{\partial q_1}, \frac{\partial H}{\partial q_2}, \dots, \frac{\partial H}{\partial q_S}, \frac{p_1}{m_1}, \frac{p_2}{m_2}, \dots, \frac{p_S}{m_S} \right)$$

$$k_B T = \left\langle \frac{p_i^2}{m_i} \right\rangle$$

p ifse
 q und

$$\left\langle \frac{1}{2} m_i v_i^2 \right\rangle = \frac{1}{2} k_B T$$

average kinetic energy of
each degree of freedom is

$$\frac{1}{2} k_B T$$

$$P = \begin{pmatrix} p \\ q \end{pmatrix} \quad \vec{\nabla} = \begin{pmatrix} \frac{\partial}{\partial p} \\ \frac{\partial}{\partial q} \end{pmatrix}$$

configurational temperature

$$\vec{u} = (0, \dots, q_i, 0, 0, \dots, 0)$$

$$k_B T = \left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = -\left\langle q_i F_i \right\rangle \quad F_i = -\frac{\partial V}{\partial q_i}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N} \quad \leftarrow \text{definition of temperature}$$

↙ Boltzmann's principle

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$$S(U, V, N) \equiv k_B \ln \Omega(U, V, N)$$

$$\Omega(U, V, N) = \frac{1}{N! h^{3N}} \int d\mathbf{q}_1 \dots d\mathbf{q}_{3N} \int d\mathbf{p}_1 \dots d\mathbf{p}_{3N}$$

$U \ll \hbar \ll U + \delta$

Let $\Gamma(E) = \int d\mathbf{p} \dots d\mathbf{q}$
 $H \ll E$

$$\frac{1}{T} = \frac{\partial}{\partial U} k_B \ln \Omega = k_B \frac{1}{\Omega} \frac{\partial \Omega}{\partial U}$$

$$\frac{\partial \Omega}{\partial U} = \frac{\Omega(U + \Delta U) - \Omega(U)}{\Delta U} \quad \Delta U \rightarrow 0$$

$$= \frac{\Gamma(U + \Delta U + \delta) - \Gamma(U + \Delta U) - \Gamma(U + \delta) + \Gamma(U)}{\Delta U}$$

~~(This)~~
 ~~$\Gamma(U + \Delta U + \delta) - \Gamma(U + \Delta U)$~~

$$\frac{\Gamma(U + \delta + \Delta U) - \Gamma(U + \delta)}{\Delta U} - \frac{\Gamma(U + \Delta U) - \Gamma(U)}{\Delta U}$$

$$S(U, V, N) = k_B \ln \left(\frac{\Gamma(U + \delta + \Delta U, V, N)}{\Gamma(U, V, N)} \right)$$

Alternative expression

(same as we use Ω in the thermodynamics part)

$$S(U, V, N) = k_B \ln \Gamma(U, V, N) \quad \text{differs from } \ln \Omega \text{ by at most } \log N !$$

$$\frac{1}{T} = \frac{k_B}{\Gamma} \frac{\partial \Gamma}{\partial U} = \frac{k_B}{\Gamma} \left(\frac{\Gamma(U + \Delta U, V, N) - \Gamma(U, V, N)}{\Delta U} \right)$$

$$\Delta U \rightarrow 0$$

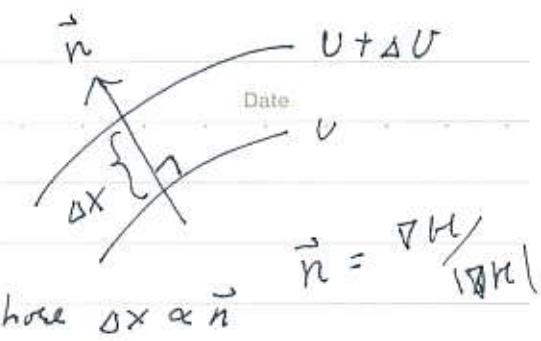
$$w = \frac{\partial U}{\partial V} = \frac{\Delta U}{\Delta V} = \frac{1}{\Delta V} \int dU \xleftarrow{\text{volume}} U < H < U + \Delta U$$

take $\Delta V \rightarrow 0$

limit

$$= \int d\sigma \cdot \frac{1}{|VH|} \xleftarrow{\text{surface}}$$

$$H = U \\ \text{surface}$$



$$\Delta U = \nabla H \cdot \Delta X = |\nabla H| \cdot \Delta X$$

$$dU = d\sigma \cdot \Delta X$$

$$k_B T = \frac{1}{\Gamma} \int \frac{d\sigma}{|VH|} \quad H = U$$

$$\xrightarrow{\text{proper measure on the surface of } H = U} = \frac{d\sigma \cdot \Delta U}{|\nabla H|}$$

$$= \frac{1}{\int d\Gamma} \int \frac{d\sigma}{|VH|} = \frac{\int \frac{d\sigma}{|VH|}}{\int \vec{V} \cdot \vec{n} d\Gamma} = \frac{\int \frac{d\sigma}{|VH|}}{\int \vec{u} \cdot \vec{n} d\sigma}$$

Gaussian plane in 3D *Divergence theorem*

$$k_B T = \frac{1}{\int \frac{d\sigma}{|VH|}} \int \vec{u} \cdot \nabla H \frac{d\sigma}{|VH|} = \langle \vec{u} \cdot \nabla H \rangle$$

microcanonical average

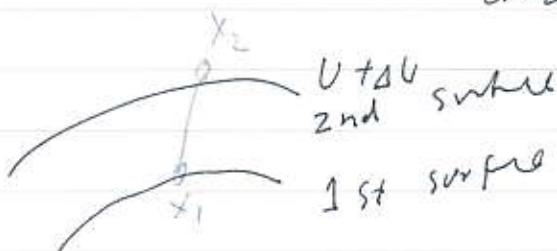
$$U_2 = U + \Delta U = H(\vec{r}_2)$$

$$U_1 = U = H(\vec{r}_1)$$

$$\Delta U = H(\vec{r}_2) - H(\vec{r}_1)$$

$$= \sum_j \frac{\partial H}{\partial q_j} dq_j + \sum_j \frac{\partial H}{\partial p_j} dp_j = \left. \nabla H \right|_{\vec{r}_1} \cdot d\vec{r} \Delta X$$

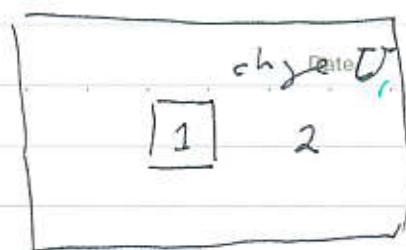
if \vec{r}_1 & \vec{r}_2 on the same surface $\Delta U = 0$ so $\vec{n} \cdot d\vec{r} = 0$



$$d\vec{r} = dr = (dq_1, dq_2, \dots, dp_1, \dots, dp_n)$$

fix $N \checkmark$

Canonical ensemble

phase space pt Γ 

$$\mathcal{H}_1(q_1, q_2, \dots, p_1, p_2, \dots) \quad P_1 = (q_1, q_2, \dots)$$

$$\mathcal{H}_2(q'_1, q'_2, \dots) \quad P_2 = (q'_1, q'_2, \dots)$$

$$\mathcal{H}(q_1, q_2, \dots, q'_1, q'_2, \dots)$$

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + V$$

$$\begin{matrix} & & & \leftarrow \text{small} \\ | & & & \\ O(N) & O(n) & O(N)^{2/3} \\ \text{finite} & \downarrow \text{too} \end{matrix}$$

start from microscopic microcanonical ensemble

$$\rho(P_1, P_2) = \begin{cases} \text{const} & U \leq \mathcal{H} \leq U + \Delta \\ 0 & \text{else} \end{cases}$$

$\rho(P_1, P_2) dP_1 dP_2$ gives the probability that state is in side values dP_1, dP_2 and joint distribution $P = (P_1, P_2)$

Take $N_2 \rightarrow \infty$ (also $N_1 \rightarrow \infty$)

what is probability that system 1 is at P_1 in value P_1 regardless system 2?

$$\rho_1(P_1) dP_1 = dP_1 \int \rho(P_1, P_2) dP_2 \underset{\substack{\text{constant} \\ \text{intg over } P_2}}{\propto} \Omega_2(E - E_1)$$

$$\rho(P_1, P_2) \underset{\substack{\uparrow \\ \text{max well} \\ E \text{ fixed}}}{\approx} \rho_1(E_1) \rho_2(P_2, E_2) \quad U \leq E_1 + E_2 = U + \Delta$$

$$E_1 - E_1 < E_2 < U - E_1 + \Delta$$

$$\rho_i(\Gamma_i) \propto \Omega_2(E - E_i)$$

the probability of the system

that can exchange energy

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with a heat bath is proportional

to the number of microstates of the
bath system at a energy of $E_2 = E - E_i$

$$k_B \ln \Omega_2(E - E_i) = S_2(E - E_i)$$

$$\begin{aligned} E_i &= \text{HGP} \\ &= S_2(E) - E_i \frac{\partial S_2(E)}{\partial E} - E_i^2 \frac{\partial^2 S_2(E)}{\partial E^2} + \dots \\ &= S_2(E) - E_i/T + \text{small.} \end{aligned}$$

$$\ln \Omega_2 = \frac{S_2}{k_B} - \frac{E_i}{k_B T} \quad \frac{1}{k_B T} = \beta \quad N \rightarrow \infty$$

$$\Omega_2 = e^{\frac{S_2}{k_B} - \frac{E_i}{k_B T}} \propto e^{-\beta E_i} \quad + k_B \ln \Omega = S/T$$

$$\rightarrow \rho_i(\Gamma_i) \propto e^{-\beta E_i(\Gamma_i)}$$

relation between canonical ensemble & thermodynamics

$$\text{def. } Z = \sum d\Gamma e^{-\beta H(\Gamma)} = \sum_{E_i} e^{-\beta E_i} S d\Gamma = \sum_i e^{-\beta E_i} \Omega_i$$

$$Q = Z = \sum_i e^{-\beta E_i} + S(E)/k_B$$

$$\Delta E = k_B T^2$$

$$U \sim O(N)$$

step 10
decrease

$$N \rightarrow \infty \quad \ln Z = -\min(\beta U + S(U)/k_B)$$

$$\ln Z = -\min_E (\beta E + S(E)/k_B)$$

let the min be $U = \langle E \rangle$

$$F = -k_B T \ln Z = U - S \cdot T$$

$$\boxed{F = U - TS}$$

Helmholtz free energy

Quantum statistical mechanics

(see Chap 8, K. Huang, 2nd ed)

Date

microcanonical

$$\rho \propto \sum |\Phi_n\rangle \langle \Phi_n|$$

where

$$U < E_n < U + \Delta$$

$$\hat{H}|\Phi_n\rangle = E_n|\Phi_n\rangle$$

canonical

$$\rho \propto e^{-\beta \hat{H}}$$

eigen states of
energy

grand canonical

$$\rho \propto e^{-\beta (\hat{H}_N - \mu \hat{N})}$$

\hat{N} operator
denote # of
particles

genl properties of
density operator ρ

eigenvalues of \hat{N} ::
 $0, 1, 2, 3, \dots$

(1) ρ is positive definite ($\hat{\rho}|\psi\rangle = w|\psi\rangle$)

(2) $\text{Tr}(\rho) = 1$ (proportionality const is fixed
by normalization)

(3) $\langle A \rangle = \text{Tr}(\rho A) = \sum_j \langle \psi_j | \rho A | \psi_j \rangle$

↑ some complete set
in Hilbert space / Fock space

classical

$$\int \frac{d\Gamma}{N! h^{3N}}$$

$$Z = \int \frac{d\Gamma}{N! h^{3N}} e^{-\beta H(p)}$$

quantum

$$\text{Tr}(\dots)$$

$$Z = \text{Tr}(e^{-\beta \hat{H}})$$

Three most common/useful ensembles

microcanonical

$$P(r) \approx \begin{cases} \text{const}, & r < H(r) < r_0 \\ 0 & \end{cases}$$

entropy

$$S(U, V, N) = k_B \ln \Omega$$

* of states/
phase space volume.

$$P(r) = e^{-\beta H(r)}$$

partition function

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{d^N}{N! h^{3N}}$$

$$F(T, V, N) = -k_B T \ln \mathcal{Z}$$

\longleftrightarrow

$$F = U - TS$$

T without free
energy

\downarrow

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

$$dU = TdS - pdV + \mu dN$$

Gibbs free energy

$$G = G(T, P, N)$$

$$= U - TS + PV$$

\sim

$$\left(\frac{\partial \psi}{\partial T}\right)_{V, \mu} = -S,$$

$$\left(\frac{\partial \psi}{\partial V}\right)_{T, \mu} = -\gamma,$$

$$\left(\frac{\partial \psi}{\partial \mu}\right)_{T, V} = -\langle N \rangle = -\left(\frac{\partial \psi}{\partial \mu}\right)_{T, V}$$

grand-canonical

$$P(r, N) \propto e^{-\beta(H - \mu N)}$$

$$N = 0, 1, 2, \dots$$

grand partition function

$$\mathcal{G} = \sum_{N=0,1,2,\dots} \int \frac{d^N}{N! h^{3N}} e^{-\beta(H - \mu N)}$$

grand potential

$$U - TS - \mu N = -PV = \psi$$

$$= -k_B T \ln \mathcal{Z}(T, V, \mu)$$

$$\text{grand potential} \rightarrow$$

$$\text{grand potential} \rightarrow$$

$$\psi \text{ by Callen}$$

$$\text{grand potential} \rightarrow$$

$$\psi \text{ by Reich} \rightarrow$$

$$\psi \text{ by Plischke}$$

$$\psi \text{ by Gallen}$$

$$dU = TdS - pdV + \mu dN$$

$$= -SdT - pdV - Nd\mu$$

$$= U - TS + PV$$

\sim

$$\left(\frac{\partial \psi}{\partial T}\right)_{V, \mu} = -\gamma,$$

$$\left(\frac{\partial \psi}{\partial V}\right)_{T, \mu} = -\langle N \rangle = -\left(\frac{\partial \psi}{\partial \mu}\right)_{T, V}$$

$$\left(\frac{\partial \psi}{\partial \mu}\right)_{T, V} = -\langle N \rangle = -\left(\frac{\partial \psi}{\partial \mu}\right)_{T, V}$$

Applications harmonic
System A coupled oscillators (i.e. thermal vibrations of solids)

$$H = \sum_{j=1}^N \frac{p_j^2}{2m_j} + \frac{1}{2} \sum_{i,j=1}^N q_i K_{ij} q_j$$

lattice spring constant

e.g. $\text{constant} \cdot \frac{k}{\text{distance}}$

\vec{q}_i column vectors

$$\vec{q}_i = \begin{pmatrix} q_{i1} \\ q_{i2} \\ \vdots \\ q_{is} \end{pmatrix}$$

$$K = \begin{pmatrix} 2k & -k & 0 & \dots \\ -k & 2k & -k & \dots \\ 0 & -k & 2k & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$K^T = K$$

Transform into normal-mode representation

Jacobian from pq to u is

$$\left| \begin{array}{cc} \frac{\partial u_i}{\partial q_j} & \frac{\partial u_i}{\partial p_j} \end{array} \right|$$

$$\text{Lft } u_i = \sqrt{m_j} q_j *$$

$$\left| \begin{array}{cc} \frac{\partial u_i}{\partial q_j} & \frac{\partial u_i}{\partial p_j} \end{array} \right| = \begin{vmatrix} \sqrt{m_j} & 0 \\ 0 & \frac{1}{\sqrt{m_j}} \end{vmatrix} = 1$$

$$\sum \frac{1}{2} m_j \dot{q}_j^2 \rightarrow \sum \frac{1}{2} \dot{u}_j^2$$

$$\sum q_i K_{ij} q_j \rightarrow \sum u_i \frac{K_{ij}}{\sqrt{m_i m_j}} u_j = \sum u_i \bar{K}_{ij} u_j$$

$$\text{so } du_i du_j = \frac{\partial u_i}{\partial q_j} dq_j \frac{\partial u_j}{\partial p_i} dp_i$$

$$H = \frac{1}{2} \dot{u}^T \dot{u} + \frac{1}{2} u^T \bar{K} u$$

matrix (orthogonal)

$$\text{Let } AQ = u$$

Orthogonality $\Rightarrow \bar{K} A = A (\text{eigenvalue problem})$

$$A^T A = I$$

$$\det(A) = 1$$

$$H = \frac{1}{2} \dot{Q}^T A^T A \dot{Q} + \frac{1}{2} Q^T A^T \bar{K} A Q$$

$$= \frac{1}{2} \dot{Q}^T Q + \frac{1}{2} Q^T \begin{bmatrix} \omega_1^2 & 0 & \dots \\ 0 & \omega_2^2 & \dots \\ \vdots & \vdots & \ddots \end{bmatrix} Q$$

$$A^T \bar{K} A = \begin{pmatrix} \omega_1^2 & 0 & \dots \\ 0 & \omega_2^2 & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

A diagonal

$$= \sum_j \frac{1}{2} (\dot{Q}_j^2 + \omega_j^2 Q_j^2)$$

Chap 6 of Goldstein 3rd ed.

$$\bar{K}$$

compute in canonical ensemble classical ~~way~~)

$$Z = \frac{1}{h^N} \int d\dot{Q}_1 d\dot{Q}_2 \dots d\dot{Q}_N \int dQ_1 dQ_2 \dots dQ_N e^{-\beta \sum_{j=1}^N (Q_j^2 + \omega_j^2 Q_j^2)}$$

why not $N!$

$$= \frac{1}{h^N} \left[\int d\dot{Q}_1 e^{-\frac{\beta}{2} \dot{Q}_1^2} \right]^N \int dQ_1 e^{-\frac{\beta \omega_1^2}{2} Q_1^2} \int dQ_2 e^{-\frac{\beta \omega_2^2}{2} Q_2^2} \dots$$

$$= \frac{1}{(h^s)^N} \left[\int_{-\infty}^{\infty} dy e^{-\frac{y^2}{2}} \right]^N \prod_{j=1}^N \left(\frac{\sqrt{\beta \omega_j}}{\sqrt{2\pi}} \right) \prod_{j=1}^N \left(\frac{k_B T}{\hbar \omega_j} \right)$$

$$\beta \dot{Q}_1^2 = y^2$$

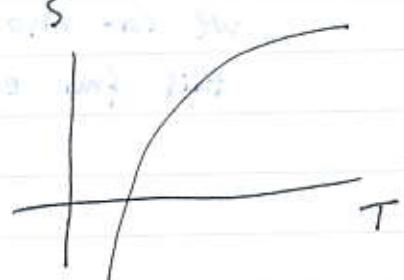
$$\bar{\dot{Q}}_1 = y$$

$$= (2\pi)^N \beta^N \prod_{j=1}^N \frac{1}{\hbar \omega_j} = \left(\frac{2\pi}{\beta} \right)^N \prod_{j=1}^N \frac{1}{\hbar \omega_j} \left(\frac{1}{2\pi} \right)$$

$$F = -\frac{1}{\beta} F(T, N) = -\frac{1}{\beta} \left[\ln \left(\left(\frac{2\pi}{\beta} \right)^N \prod_{j=1}^N \frac{1}{\hbar \omega_j} \right) + \sum_{j=1}^N \ln \omega_j \right]$$

$$\left\{ \begin{array}{l} S = -\frac{\partial F}{\partial T} = + \frac{1}{\beta} \left[-k_B T S + \ln k_B T + \right. \\ \left. = \frac{\partial}{\partial T} \left[-k_B T \left(\cancel{N} \cancel{\ln \left(\frac{2\pi}{\beta} \right)^N} + \ln \left(\frac{2\pi}{\beta} \right)^N \right) + \sum_{j=1}^N \ln \omega_j \right] \right] \\ = k_B \left[+N \ln \left(\frac{k_B T}{2\pi} \right)^{\frac{1}{2}} + \sum_{j=1}^N \ln \omega_j \right] + k_B N S \end{array} \right.$$

$$S = +Nk_B \ln T + \text{const.}$$



$$U = F + TS$$

$$= -k_B T \left[N \ln \left(2\pi k_B T \right) + \sum_{j=1}^N \ln \omega_j \right] + k_B T \left[N \ln \left(\frac{2\pi}{\beta} \right) + \sum_{j=1}^N \ln \omega_j \right]$$

$$= Nk_B T + Nk_B T$$

$$Z = \prod_{j=1}^N \frac{k_B T}{\hbar \omega_j}$$

$$F = -k_B T \ln Z$$

$$= -k_B T \sum_{j=1}^N \ln \left(\frac{k_B T}{\hbar \omega_j} \right)$$

$$S = -\frac{\partial F}{\partial T} = k_B \sum_{j=1}^N \ln \left(\frac{k_B T}{\hbar \omega_j} \right) + k_B N$$

$$= k_B \sum_{j=1}^N \ln \left(\frac{k_B T e}{\hbar \omega_j} \right)$$

$$U = F + TS$$

$$= -k_B T \ln Z + T \left(\frac{\partial}{\partial T} k_B T \ln Z \right)$$

$$= -k_B T \ln Z + k_B T \ln Z + k_B T^2 \frac{\partial \ln Z}{\partial T}$$

$$= k_B T^2 \frac{\partial \ln Z}{\partial T} = -\frac{\partial \ln Z}{\partial \beta}$$

$$= k_B T^2 \left[\frac{1}{T} \cdot N \right] = N k_B T = -\frac{\partial T}{\partial \beta} \frac{\partial \ln Z}{\partial T}$$

$$= -\frac{\partial T}{\partial k_B T}$$

we can also get

this from equipartition theorem

$$= k_B \frac{\partial T}{\frac{1}{T} \partial T} = k_B T^2 \frac{\partial}{\partial T} \ln Z$$

heat capacity

$$C_V = \frac{dU}{dT} = Nk_B = nR \leftarrow \text{indep of } T$$

Dulong - Petit law

for solids

Date

Quantum versions

$$Z = \text{Tr } e^{-\beta \hat{H}} = \sum_K \langle \phi_K | e^{-\beta \hat{H}} | \phi_K \rangle$$

$\phi_K(Q_1, Q_2, \dots, Q_N)$ \leftarrow some complete set of wave functions

use energy eigen states

$$\hat{H} \phi_K(Q_1, Q_2, \dots, Q_N) = E_K \phi_K(Q_1, Q_2, \dots, Q_N)$$

$$\hat{H} = \sum_j \frac{1}{2} (\dot{Q}_j^2 + \omega_j^2 Q_j^2)$$

$$= \sum_j \hat{h}_j(Q_j)$$

$$\dot{Q}_j \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial Q_j}$$

$$[Q_j, \dot{Q}_\ell] = i\hbar \delta_{j\ell}$$

$$\hat{h}_j(Q_j) = -\frac{1}{2}\hbar \frac{\partial^2}{\partial Q_j^2} + \frac{1}{2}\omega_j^2 Q_j^2$$

$$Q = \sqrt{m} \times$$

$$\hat{h}_j \phi_n = \hbar \omega_j (n + \frac{1}{2})$$

harmonic oscillator

$$\text{Let } \phi_K(Q_1, Q_2, \dots, Q_N) = \prod_j \phi_{n_j}(Q_j)$$

$$\text{quantum number } K = (n_1, n_2, n_3, \dots, n_N)$$

$$n_j = 0, 1, 2, 3, \dots$$

$$E_K = \sum_{j=1}^N \hbar \omega_j (n_j + \frac{1}{2})$$

$$Z = \sum_{(n_1, n_2, \dots, n_N)} e^{-\beta \sum_j \hbar \omega_j (n_j + \frac{1}{2})}$$

$$= \prod_j \sum_{n_j=0}^{\infty} e^{-\beta \hbar \omega_j (n_j + \frac{1}{2})} = \prod_j e^{-\beta \frac{\hbar \omega_j}{2}} \frac{1}{1 - e^{-\beta \hbar \omega_j}}$$

$$F = -k_B T \ln Z$$

$$= -k_B T \left\{ \sum_j \left[\left(-\beta \frac{\hbar \omega_j}{2} \right) - \ln \left(1 - e^{-\beta \hbar \omega_j} \right) \right] \right\}$$

$$\hbar \omega_{\text{ext}} = \frac{\hbar \omega_j}{2} = \frac{\omega_j}{2}$$

~~$$H = \sum_j \hbar \omega_j (\hat{a}_j^\dagger \hat{a}_j + \frac{1}{2})$$~~

Another approx

$$Z = \text{Tr } e^{-\beta \sum_j \hbar \omega_j (\hat{a}_j^\dagger \hat{a}_j + \frac{1}{2})}$$

$$\hat{a}_j^\dagger \hat{a}_j |n_j\rangle = n_j |n_j\rangle$$

~~$$\hat{a}_j = Q$$~~

$$\hat{a}_j = \sqrt{\frac{\hbar \omega_j}{2m}} (Q_j + i \frac{\hbar}{m} P_j)$$

$$[\hat{a}_j, \hat{a}_{j'}^\dagger] = \delta_{jj'}$$

$$\hbar \omega_{\text{ext}} = \hbar \omega_j + \hbar \omega_{j'} = \hbar \omega$$

$$\vec{q} = m \vec{A} = m \vec{\phi}$$

$$\vec{q} = \vec{B}$$

$$\vec{w} \vec{B} = (i) \vec{B} = \vec{S}$$

$$A(t) = e^{\frac{L}{m}t} A = A + tLA + \frac{1}{2}t^2 L^2 A + \dots$$

75

$$\dot{A}(t) = L e^{\frac{L}{m}t} A = L A(t) = [A(t), H]$$

Date _____

$$L f = [f, \frac{P^2}{2m} + \frac{1}{2}m\omega^2 q^2]$$

$$= [f, P^2] \frac{1}{2m} + [f, q^2] \frac{1}{2} m \omega^2$$

$$= P [f, P] \frac{1}{2m} + [f, P] P \frac{1}{2m}$$

$$+ q [f, q] \frac{1}{2} m \omega^2 + [f, q] q \frac{1}{2} m \omega^2$$

$$\text{Let } f = q$$

$$L q = \frac{1}{m} P$$

$$L^2 q = \frac{1}{m} L P = -m^2 q$$

$$L^3 q = L (-m^2) q = (-m^2) \frac{1}{m} P$$

$$L^4 q = (-m^2)^2 q$$

$$q(t) = q_f + \frac{t}{m} P + \frac{1}{2!} t^2 (-m^2) q_f + \frac{1}{3!} t^3 (-m^2) \frac{P}{m}$$

$$+ \frac{1}{4!} t^4 (-m^2)^2 q_f + \dots$$

$$= \left[1 - \frac{1}{2!} (+m^2 t)^2 + \frac{1}{4!} (-m^2 t)^4 + \dots \right] q_f$$

$$+ \left[t + \frac{1}{3!} (-m^2 t)^3 + \dots \right] \frac{P}{m}$$

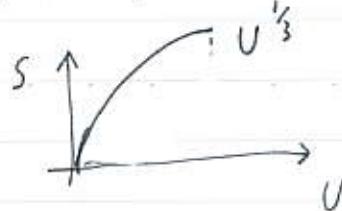
$$= q_f \cos mt + \frac{P}{m} \sin mt$$

+ ?

P III { ① homogen + order 1 ✓
 ② monotoniccrease w.r.t $U \checkmark$

Assignment 1

a)

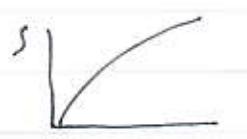


P IV { ③ $\frac{1}{T} = \frac{\partial S}{\partial U} = U^{-\frac{2}{3}}$ $T=0$ $S=0$ ✓
 Date _____

④ concave

$$\frac{\partial^2 S}{\partial U^2} < 0$$

b)

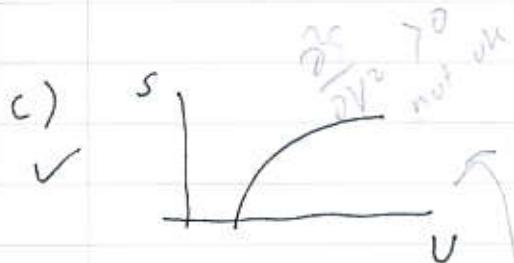


$$\left(\frac{NU}{V}\right)^{\frac{2}{3}} \rightarrow \left(\frac{\lambda^2}{\lambda}\right)^{\frac{2}{3}} = \lambda^{\frac{2}{3}}$$

X

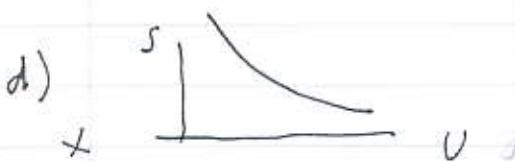
Not homogen

c)



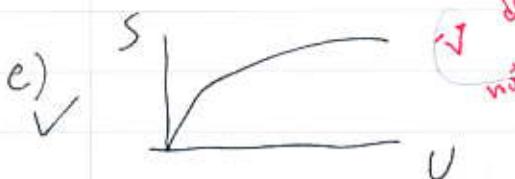
$$\frac{\partial S}{\partial U} = \frac{1}{(NU+bV^2)} = \infty \quad S=0$$

d)



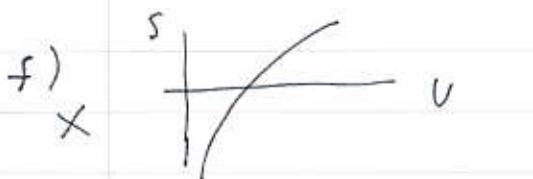
P III violated not increase w.r.t U

e)

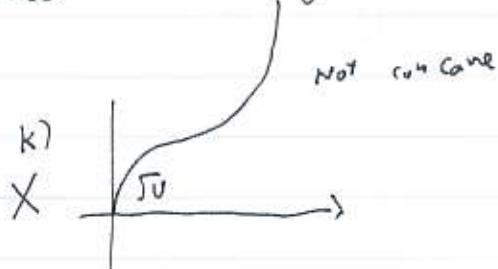


$$\frac{\partial S}{\partial U} = U^{-\frac{2}{5}}$$

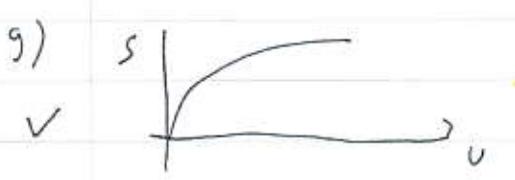
f)



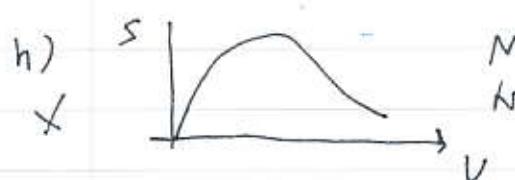
$S \rightarrow -\infty$



g)



h)



NOT monotonic
 NOT homogen

UV/N

i)

