Generalized Force

why does $\frac{\partial \ln \Omega}{\partial V} = \beta P$?

More generally

$\ln \Omega (E, X)$

$$d \ln \Omega = \frac{\partial \ln \Omega}{\partial E}\bigg)_X dE + \frac{\partial \ln \Omega}{\partial X}\bigg)_E dX$$

$$\cancel{dE} = \cancel{\frac{\partial E}{\partial \ln \Omega}\bigg)_X d\ln\Omega} + \cancel{\frac{\partial E}{\partial X}\bigg)_{\ln\Omega} dX}$$

$\frac{\partial E}{\partial X}\bigg)_{\ln\Omega} = ?$ set $d\ln\Omega = 0$
since $\ln\Omega = $ Const

$$\frac{\partial E}{\partial X}\bigg)_{\ln\Omega} = \frac{\partial E}{\partial X}\bigg)_{\ln\Omega} = - \frac{\partial \ln\Omega}{\partial X}\bigg)_E \bigg/ \frac{\partial \ln\Omega}{\partial E}\bigg)_X$$

> using our partial derivative tricks

$$\frac{\partial \ln\Omega}{\partial X} = -\frac{\partial \ln\Omega}{\partial E} \frac{\partial E}{\partial X} = \beta \overline{X} \qquad \overline{X} = -\frac{\partial E}{\partial X}$$

"mean generalized force" conjugate to

if X is volume $\overline{X} = -\frac{\partial E}{\partial V} = P$

if X is displacement $\overline{X} = -\frac{\partial E}{\partial X} = $ force   like in a stretched rubber band

if X is $\vec{B}$ field $\overline{X} = -\frac{\partial E}{\partial B} = -\vec{M} = \sum_j \vec{m}_j$

magnetic dipole moments

Quasi Static process

Slow $\overline{E} \to \overline{E} + d\overline{E}$ & $\overline{X} \to \overline{X} + d\overline{X}$

$$d\ln\Omega(E,X) = \frac{\partial \ln\Omega}{\partial E} d\overline{E} + \frac{\partial \ln\Omega}{\partial X} d\overline{X}$$

$$= \beta\left[d\overline{E} + \overline{X} \, d\overline{X}\right]$$

$$d\ln\Omega = \beta\left[d\overline{E} + dW\right] = \beta \, dQ$$

$$\boxed{dS = \frac{dQ}{T}}$$

if Quasi Static process is also thermally isolated then $dQ = 0 \Rightarrow dS = 0$
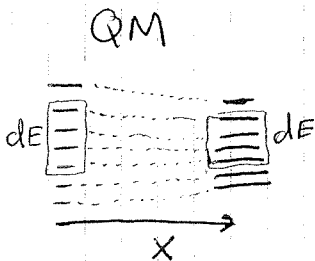
$$d\overline{E} = -dW$$

then process is said to be _Adiabatic_

Usually adiabatically means that Changes in Hamiltonian are slow or Quasi Static w/ respect to "microscopic timescales" & are fast with respect to time Scales associated w/ the failure to thermally isolate the system
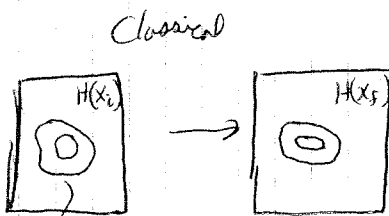
Adiabatic processes keep # of States available to system nearly the same $(dS=0)$ & are therefore reversible

Microscopic picture

Follow energy levels as a function of X & look at windows of width dE

QM

- Average energy changes as $\dfrac{\partial \bar{E}}{\partial X} = -\bar{X}$

- If we move window along w/ average energy, # of levels does not change

Classical

Surfaces of Constant energy don't cross under adiabatic evolution

$$\Omega(E_i, X_i) = \Omega(E_f, X_f)$$

areas enclosed by surfaces are constant due to Liouvilles Theorem

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Laws of Thermodynamics

Zeroth Law) Can define temperature. if $T_A = T_B$ & $T_B = T_C$ then $T_A = T_C$

First Law) Macrostate of a system can be defined by an internal energy $\bar{E}$ which can change by having system absorb heat or perform work

$$dE = dQ - dW \qquad \text{Conservation of energy}$$

Second Law) An equilibrium macrostate of a system can be characterized by a quantity S called the entropy which has the properties that:

$\Delta S \geq 0$ for a thermally isolated system
$\Delta S \geq \dfrac{dQ}{T}$ for non isolated systems $\left(\Delta S = \dfrac{dQ}{T} \text{ for quasi static processes} \right)$

3rd Law) if $T \to 0$ then $S \to S_0 = k \ln \Omega_0$

idea is that $\Omega_0 = 1$ so $S \to 0$ (Nerst theorem)

degenerate states

x

locally system tends towards 1 state

Kivelson's paper

This is not always true globally

$C \equiv N$ dimers ground state is highly degenerate

Spin systems Can have highly degenerate ground states @ $T=0$

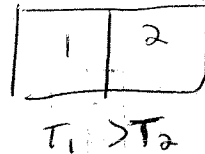Practically we are always extrapolating — impossible to measure $T=0$

Thermo. **Note:** Heat flow from high to Low T follows from 2nd law

Quasi Static

$$ dS = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} \geq 0 $$

$$ = dQ_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0 $$

$$ dQ_1 \leq 0 $$

1	2

$T_1 > T_2$

A taste of Stat mech

Note: If we knew $\Omega(E, x)$ we can calculate entropy & three equation of state. This gives us all we need to know in order to solve a thermodynamic problem

take the particle in a box example w/ no interactions between the particles

$$ \Omega \propto V^N \left(\frac{E}{3N} \right)^{3N/2} \qquad \frac{\partial \ln \Omega}{\partial V} = \beta P $$

$$ = \frac{\partial}{\partial V} (N \ln V) = \frac{N}{V} = \beta P $$

$$ \boxed{NkT = PV} \quad \text{ideal gas law!} $$

$$ \beta = \frac{\partial \ln \Omega}{\partial E} = \frac{3N}{2E} = \frac{1}{kT} \qquad E = \frac{3}{2} NkT = \frac{3}{2} \nu RT $$

moles

$E = E(T)$ no volume dependence

Conceptually we know this is true since gas molecules do not interact with one another. The potential between two particles is flat so the volume does not change the energy

 $E = \sum_i \frac{p_i^2}{2m} + U(V)^{0}$ for ideal gas.

With out Statistical Mechanics there is no way to make an abinitio Calculation ~~blablabla~~ to determine the entropy.

So How do we determine $\overset{\text{changes in}}{\wedge}$ entropy?   empirically - we do exp.!

Can we measure $\overset{\text{changes in}}{\wedge}$ entropy?   No

We must therefore relate it to quantities we can measure.

what are some of these?   Heat Capacity
                               Coefficient of expansion
| Compressability

If we can measure these quantities & figure out how entropy relates to them then we can calculate equation of state & solve any thermodynamic problem.

<u>Let us begin ~~bllbblablabla~~ with Heat Capacity</u>

$$\left.\frac{dQ}{dT}\right)_y \equiv C_y \qquad \text{if we add heat } dQ \text{ temperature changes by } dT$$
$$y \text{ fixed}$$

Obviously C_y depends on the amount of material we have

Specific heat $\quad c_y \equiv \dfrac{C_y}{V} = \dfrac{1}{V}\left.\dfrac{dQ}{dT}\right)_y \qquad \underset{\text{alternatively}}{\text{or}} \quad c_y' = \dfrac{1}{m}C_y$

two Cases of interest $\quad C_v, C_p \qquad$ which one is larger?

$dQ = dE + pdV \qquad$ if $V = $ Const system does no work & $\quad dQ = dE$

$\qquad\qquad\qquad\qquad$ if $P = $ Const heat goes to increase E & do work

Therefore relative to const V case, for a given amount of heat absorbed the energy E & hence the temp T will increase by a smaller amount

$$\left.\frac{dQ}{dT}\right)_p > \left.\frac{dQ}{dT}\right)_V$$

$$C_p \quad > C_v$$

how do we relate C_v & C_p to entropy? $\qquad dQ = TdS$

$$C_y = T\left.\frac{dS}{dT}\right)_y \qquad \text{Since } TdS = dE + pdV$$

$$C_y = \cancel{T}\left[\left(\frac{dE}{dT}\right)_y + \frac{\partial(PdV)}{\partial T}\right)_y\right] \quad \text{if } y = V \quad C_V = \cancel{T}\left.\frac{\partial E}{\partial T}\right)_V$$

Specific heat of water at 1 atm & 15°c is 4.18 J/degree g

1 Calorie $\equiv$ 4.1840 Joules   1 food Calorie $\equiv$ 1000 Calories

If we put two equal sized systems of the same specific heat but different temperatures T_A, T_B in contact

$$T_f = \frac{T_A + T_B}{2}$$

What if two systems have different specific heats?

$$Q_A + Q_B = 0$$

$$Q_A = \int_{T_A}^{T_f} m_A C_A'(T') \, dT' \quad \text{if } C_A' \text{ is indep of } T' \text{ ie just a const}$$

$$= m_A C_A' \left(T_f - T_A \right)$$

$$Q_B = m_B C_B' \left(T_f - T_B \right)$$

$$m_A C_A' \left(T_f - T_A \right) + m_B C_B' \left(T_f - T_B \right) = 0$$

$$T_f = \frac{m_A C_A' T_A + m_B C_B' T_B}{m_A C_A' + m_B C_B'} \qquad \begin{array}{l}\text{if } m_A = m_B \ \& \ C_A' = C_B' \\ \text{this reduces to our} \\ \text{previous result}\end{array}$$

Note: if we do not have an empirical measurement of $C_y'(T)$ we cannot do the integral to determine Q
doesn't that annoy you?

Solution: Either you measure C_y' by experiment
  or   you calculate C_y' from stat mech!

Ex: for ideal gas $E = \frac{3}{2} N k T$

$$C_V = \frac{1}{v} \left. \frac{T \, dS}{\partial T} \right)_V = \frac{1}{v} \left. \frac{\partial E}{\partial T} \right)_V = \frac{3}{2} R$$

$$C_P = \frac{1}{v} \left. \frac{\partial Q}{\partial T} \right)_P = \overset{vC_V}{\frac{1}{v} \left. \frac{\partial E}{\partial T} \right)_P} + \left. \frac{\partial (P dV)}{\partial T} \right)_P$$

$$C_P = \frac{1}{v} \left[\frac{3}{2} v R + \left. \frac{\partial vRT}{\partial T} \right)_P + \left. \frac{\partial v dP}{\partial T} \right)_P \right] = \frac{3}{2} R + R$$

$$d(Pv) = vR dT$$
$$P dv + v dP = v R dT$$
$$P dv = v R dT + v dv$$

More generally For ideal gas $\qquad C_p = C_v + R = \frac{5}{2}R \qquad \gamma = \frac{C_p}{C_v} = 1 + \frac{R}{C_v}$ ⬤⬤⬤ $= \frac{5}{3}$

Reif table S.2.1 $\qquad 15°C \qquad 1$ Atm

	γ_{meas}	γ_{calc} (uses $\gamma = 1 + \frac{R}{C_v}$)
He, Ar	1.666	1.666
N_2	1.405	1.407
O_2	1.396	1.397

} need correction to ideal gas $\checkmark$ ⬤⬤ That account dimers But formula for γ still works!

energy (so that C_v change. would

note it so $"1 + \frac{R}{C_v}$

Isothermal vs. Adiabatic processes for ideal gas

Isothermal: $\qquad PV = Const \qquad$ since T is held fixed

Adiabatic: $\qquad dQ = 0 = \nu C_v dT + Pdv \qquad\qquad d(PV) = d(\nu RT)$

$\qquad\qquad = \nu C_v \left[\frac{P}{\nu R} dv + \frac{V}{\nu R} dP \right] + Pdv \qquad Pdv + Vdp = \nu RdT$

$\qquad\qquad = \left(\frac{C_v}{R} + 1 \right) Pdv + C_v \frac{V}{R} dP \qquad \frac{P}{\nu R} dv + \frac{V}{\nu R} dp = dT$

$\qquad\qquad = (C_v + R) Pdv + C_v VdP$

$\qquad\qquad\qquad$ divide by $C_v V P$

$\qquad\qquad \int 0 = \int_{V_i}^{V_f} \gamma \frac{dv}{V} + \int_{P_i}^{P_f} \frac{dP}{P}$

$\qquad\qquad Const = \gamma \ln V_f + \ln P_f$

$\qquad\qquad\qquad PV^\gamma = Const$

$\qquad\qquad or \qquad TV^{\gamma - 1} = Const$

Intensive vs. Extensive

Intensive: Quantity stays the same under doubling of system size
extensive: Quantity doubles under doubling of system size

intensive	extensive
C_γ	C_γ
P	E
T	V
γ density	S
$s = \frac{S}{V}$	

Should have read through Reif S.3 For Next class
need 5.11, 5.12 5.14