

Recap from L5TD state functions

$$dS = \frac{1}{T} dE - \frac{1}{T} \sum_i J_i dX_i - \frac{1}{T} \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

$$dE = \sum_i J_i dX_i + T dS + \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

$$dH = \sum_i X_i dJ_i - T dS + \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

$$dF = \sum_i J_i dX_i - SdT + \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

$$dG = - \sum_i X_i dJ_i - SdT + \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

$$dY = \sum_i J_i dX_i - SdT - \sum_{\alpha} N_{\alpha} dM_{\alpha}$$

Point the path to equilibrium

	$dQ=0$	const T
$dW=0$	$SS \geq 0$	$SF \leq 0$
const \vec{J}	$SH \leq 0$	$SG \leq 0$

* Extensivity Relations (for sufficiently short-range forces)

$$E(\lambda S, \lambda \vec{X}, \lambda \vec{N}) = \lambda E(S, \vec{X}, \vec{N})$$

$$\downarrow$$

$$E = TS + \vec{J} \cdot \vec{X} + \vec{M} \cdot \vec{N} \quad \text{"Fundamental relation"}$$

$$\downarrow$$

$$SdT + \vec{X} \cdot d\vec{J} + \vec{N} \cdot d\vec{M} = 0 \quad \text{"Gibbs-Duhem"}$$

(the intensive parameters T, \vec{J}, \vec{M} not indep.)

Maxwell Relations : wide range of relations between partial derivatives of TD variables

$$df(x,y) = \left. \frac{\partial f}{\partial x} \right|_y dx + \left. \frac{\partial f}{\partial y} \right|_x dy = A(x,y)dx + B(x,y)dy$$

* Maxwell relations follow from

$$\left. \frac{\partial}{\partial y} \left[\left. \frac{\partial f}{\partial x} \right|_y \right]_x = \left. \frac{\partial}{\partial x} \left[\left. \frac{\partial f}{\partial y} \right|_x \right]_y \right.$$

$$\left. \frac{\partial}{\partial y} A \right|_x \stackrel{\text{or}}{=} \left. \frac{\partial}{\partial x} B \right|_y$$

ex1: $dE = \sum_i J_i dx_i + T ds$

$$\therefore \left. \frac{\partial E}{\partial S} \right|_x = T \quad \left. \right\} \quad \text{Now use } \left. \frac{\partial}{\partial S} \left(\frac{\partial E}{\partial x_i} \right) \right|_S = \left. \frac{\partial}{\partial x_i} \left(\frac{\partial E}{\partial S} \right) \right|_S$$

$$\left. \frac{\partial E}{\partial x_i} \right|_{S, X_j \neq i} = J_i$$

$$\Rightarrow \boxed{\left. \frac{\partial T}{\partial x_i} \right|_{S, X_j \neq i} = \left. \frac{\partial J_i}{\partial S} \right|_x} \quad (*)$$

Ex 2: Say you want $\left. \frac{\partial S}{\partial J_i} \right|_{T,N} = ?$

* The usual procedure is to find the TD potential where S appears as a 1st derivative

∴ Candidates are

$$dF = \sum_i J_i dX_i - SdT + \sum_\alpha M_\alpha dN_\alpha$$

$$dG = -\sum_i X_i dJ_i - SdT + \sum_\alpha M_\alpha dN_\alpha$$

$$dH = \sum_i J_i dX_i - SdT - \sum_\alpha N_\alpha dM_\alpha$$

* But we want $\left. \frac{\partial S}{\partial J_i} \right|_{T,N} \Rightarrow \{J_i, T, N\}$ should be the indep. variables \Rightarrow use G

$$\therefore \left. \frac{\partial S}{\partial J_i} \right|_{T,N} = \left. \frac{\partial}{\partial J_i} \left[\left(-\frac{\partial G}{\partial T} \right)_{\vec{J}, \vec{N}} \right] \right|_{T, \vec{N}} = -\frac{\partial}{\partial T} \left[\left. \left(\frac{\partial G}{\partial J_i} \right) \right|_{T, \vec{N}} \right]_{\vec{J}, \vec{N}}$$

$$= -\frac{\partial}{\partial T} \left[-X_i \right]_{\vec{J}, \vec{N}}$$

$$\therefore \left. \frac{\partial S}{\partial J_i} \right|_{T, \vec{N}} = \left. \frac{\partial X_i}{\partial T} \right|_{\vec{J}, \vec{N}}$$

3rd Law (Nernst 1906)

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- * Recall that the Clausius theorem only defines entropy differences via

$$S(B) - S(A) = \int_A^B \frac{dQ_{rev}}{T}$$

- * Nernst + others studied the T-dependence of the entropy differences for reversible isothermal processes

$$\Delta S(T; 1 \rightarrow 2) \equiv S(T; \vec{X}_2) - S(T; \vec{X}_1) = \int_{\vec{X}_1}^{\vec{X}_2} \left. \frac{dQ_{rev}}{T} \right|_{fixed}$$

\vec{X} = generic TD
coords other
than T

- * Noticed as $T \rightarrow 0$, $\Delta S(T; 1 \rightarrow 2) \rightarrow 0$ independent of substance and $\vec{X}_1 + \vec{X}_2$.

- * This led Nernst to make a stronger statement that became known as the 3rd Law:

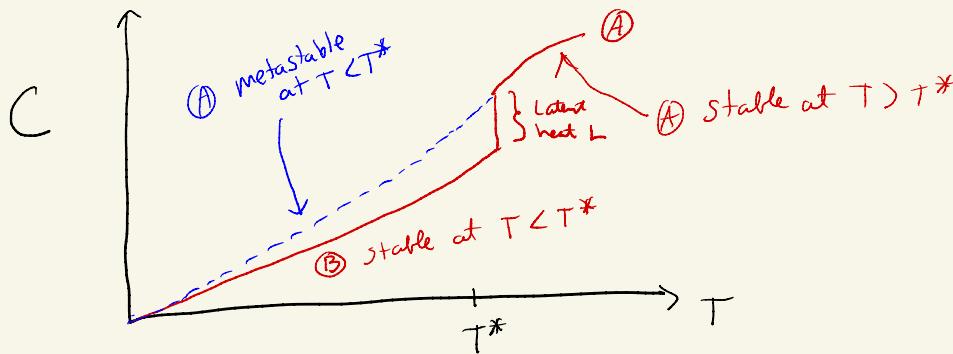
The entropy of all systems approaches a universal constant as $T \rightarrow 0^\circ K$ that we can take be zero

$$\text{i.e., } \lim_{T \rightarrow 0} S(T, \vec{X}) = 0$$

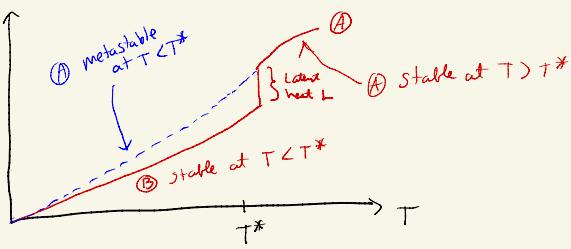
Experimental evidence for 3rd Law

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- * Certain materials can exist in a number of similar (but different) crystalline structures ("allotropes")
- * at a given T , only one of these allotropes is truly stable
- * e.g., consider a system w/ 2 allotropes (A) + (B)



- * If you cool the system slowly, there's a phase transition from (A) \rightarrow (B) releasing latent heat L .
- * If you cool the system sufficiently fast, then (A) \rightarrow (A) as T passes thru T^* .
- * Basic idea is to measure $C_A(T)$ + $C_B(T)$ + use it to compute entropy for $S_A(T^* + \epsilon)$ starting from $T=0$ using the 2 paths



$$S_A(T^* + \epsilon) - S_A(0) = \int_0^{T^* + \epsilon} \frac{dQ}{T'} = \int_0^{T^* + \epsilon} \frac{C_A(T')}{T'} dT' \quad \text{path ④} \rightarrow ①$$

$$S_A(T^* + \epsilon) - S_B(0) = \int_0^{T^* - \epsilon} \frac{C_B(T')}{T'} dT' + \frac{L}{T^*} \quad \text{path ⑤} \rightarrow ①$$

↓

Subtracting

$$S_B(0) - S_A(0) = \int_0^{T^*} \frac{C_A(T')}{T'} dT' - \int_0^{T^*} \frac{C_B(T')}{T'} dT' - \frac{L}{T^*}$$

RHS = exp. measured quantities,
found to add up to zero

$$\therefore S_B(T=0) = S_A(T=0) = 0$$

Consequences of 3rd Law

① Since $S(T=0; \vec{X})$ for all TD coords \vec{X}

$$\Rightarrow \boxed{\lim_{T \rightarrow 0} \left. \frac{\partial S}{\partial \vec{X}} \right|_T = 0}$$

② Vanishing Thermal Expansivities

$$\alpha_x \equiv \left. \frac{1}{x} \frac{\partial x}{\partial T} \right|_J \quad x = \text{some generalized displacement}$$

* Can show (try it!) that $\left. \frac{\partial x}{\partial T} \right|_J = \left. \frac{\partial S}{\partial J} \right|_T$ (Maxwell relation!)

$$\therefore \boxed{\left. \alpha_x \rightarrow 0 \right|_{as T \rightarrow 0}}$$

③ Vanishing Heat Capacities

$$S(T, \vec{X}) - S(0, \vec{X}) = \int_0^T \frac{dT'}{T'} C_x^{(T')}$$

Singular as $T \rightarrow 0$

Unless $C_x^{(T \rightarrow 0)} = 0$

④ Impossible to cool system to $T=0$ in finite # of steps

* See Huang §1.7 for details

* Using a combination of Maxwell relations and an empirical form of $C_p(T)$ deduced from experiment, you can show

$$\frac{V\alpha}{C_p} \xrightarrow{T \rightarrow 0} \text{finite constant} \\ (\alpha = \frac{1}{V} \frac{\partial V}{\partial T})_P$$

* Can also show for adiabatic cooling of a gas by changing the pressure by dP you get a cooling of dT :

$$dT = \left(\frac{V\alpha}{C_p} \right) T dP$$

* As $T \rightarrow 0$
 finite const

\therefore Would require $dP \rightarrow \infty$ to get a finite dT

Some final comments on the 0th, 1st, 2nd, + 3rd Laws of TD

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- * We've sketched the historical development of TD based on empirical observations of macroscopic systems without any knowledge of the underlying constituents + dynamics
- * A major focus of the rest of the class will be to understand the microscopic origin of these laws
- * For now, we make some qualitative remarks on the microscopic origins of these 4 laws

1st Law \Leftrightarrow conservation of energy embodied in the microscopic EOM (Classical or QM)
(no surprise here!)

0th + 2nd Laws \Rightarrow have to do with equilibrium and the fact that there's an "arrow of time" in the establishment of equilibrium (S increases, F decreases, etc.)

\Rightarrow Seems to run afoul of the underlying EOM which are time reversible

\Rightarrow Will ultimately be understood as the result of $N \gg 1$ degrees of freedom.

(*) 0th, 1st, + 2nd Laws are "good" irrespective of whether QM or CM is the underlying desc.

3rd law \Rightarrow will eventually see that microscopically

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$$S = k_B \ln \Lambda$$

$\Lambda = \#$ of microscopic states consistent
w/ observed macro TD properties

\therefore The 3rd law is a statement that $\Lambda \rightarrow 0(1)$ as $T \rightarrow 0$

I.e., it's a statement on the "uniqueness" of
the ground state as $T \rightarrow 0$.

* Classically, this is wildly violated (think of
an ideal gas $\Rightarrow \infty$ -# of configs w/ same energy)

* The 3rd Law is unique amongst the TD laws in
that it's really a macroscopic manifestation
of the fact that we live in a QM universe!

e.g. $\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P \stackrel{\text{ideal}}{=} \stackrel{\text{gas}}{\frac{1}{T}} \neq 0$ as $T \rightarrow 0$

Bottom line: 0th, 1st, & 2nd laws emerge from microscopic
theory independent of QM or CM treatment

3rd Law only emerges from QM.

* Now we turn to one of our main goals. How can we understand/derive TD from 1st principles (i.e., from knowledge of microscopic dof + dynamics)

* Let's first think classically. Say we have a gas of N particles ($N \sim 10^{23}$). If we work in the framework of Hamiltonian mechanics, our state is specified by

$$(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N, \vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) \quad \text{6N-dimensional phase space}$$

* as time evolves, the initial point in PS traces out a trajectory via Hamilton's eqns:

$$\text{EOM: } \frac{d\vec{q}_i}{dt} = \frac{\partial H(\vec{q}, \vec{p})}{\partial \vec{p}_i}$$

$$\frac{d\vec{p}_i}{dt} = -\frac{\partial H(\vec{q}, \vec{p})}{\partial \vec{q}_i}$$

* what we measure in a macroscopic system is really not an instantaneous value of some quantity, but a time average over some time $T \gg t_{\text{microscopic}}$

$$\text{e.g., } \overline{\mathcal{O}(\vec{q}, \vec{p})} = \frac{1}{T} \int_0^T dt \mathcal{O}(\vec{q}(t), \vec{p}(t)) \quad \mathcal{O} = \text{some observable}$$

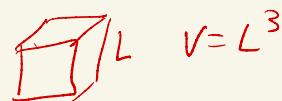
* This is a hopeless task trying to tackle it head-on
 (i.e., solving Hamilton's equations, which would be $\mathcal{O}(10^{23})$
 Coupled ODE's, & then performing the time-average)

* Moreover, even if you could integrate 10^{23} coupled ODE's,
 You would still have to plug in 10^{23} initial conditions
 to the general solutions (i.e., you would have to know
 the initial values of (\vec{p}, \vec{q}) for 10^{23} particles... absurd!)

* How to proceed? Use probability arguments!

① Whether we're using CM or QM, the fact is
 There is a many-to-1 mapping of microscopic
 States to an observed macroscopic State

e.g.: N non-interacting particles in a box



$$E = \sum_i n_i \varepsilon_i$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_i = \varepsilon_i \psi_i$$

$$N = \sum_i n_i$$

$$\psi_i(\text{walls}) = 0$$

Macro state: (E, N, V)

$$\varepsilon_i = \frac{\hbar^2 i^2}{2m L^2} \quad i=0, \pm 1, \dots$$

Micro state: $\{n_i, \varepsilon_i\}$ (Many possible configs
 that sum up to give
 E, N)

② Let $\mathcal{N}(N,V,E) = \# \text{ of micro configs}$
 that give the macro
 State N, V, E .

* $\mathcal{N}(N,V,E)$ is basically a measure of our ignorance or uncertainty about the system, since our macro measurements of E, N, V can't differentiate between the \mathcal{N} -microstates.



* Therefore, the most unbiased/reasonable thing we can do is to assume the system is in any of the $\mathcal{N}(E,N,V)$ microstates with equal probability

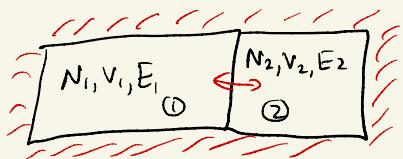


This "assumption of equal a-priori probabilities" is THE foundation of the entire field of Stat. Mech,

* Before calculating \mathcal{N} for a few simple models, let's see the implications + make our 1st connection to TD.

Boltzmann Entropy + TD entropy

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- * total system adiabatic
- * but ① + ② can exchange energy w/ each other

$$E^{(o)} = E_1 + E_2 = \text{const.}$$

total
of
micro
states

$$\begin{aligned} &= \mathcal{N}_1(E_1) \mathcal{N}_2(E_2) = \mathcal{N}_1(E_1) \mathcal{N}_2(E^{(o)} - E_1) \\ &\equiv \mathcal{N}^{(o)}(E^{(o)}, E_1) \end{aligned}$$

* What value will E_1 relax to over a long time?

* Applying our equal probability assumption for the macrostates, the equilibrium E_1 will maximize $\mathcal{N}^{(o)}$:

$$\Rightarrow \frac{d\mathcal{N}^{(o)}}{dE_1} = \mathcal{N}_2 \frac{d\mathcal{N}_1}{dE_1} + \mathcal{N}_1 \frac{d(E^{(o)} - E_1)}{dE_1} \cdot \frac{d\mathcal{N}_2}{d(E^{(o)} - E_1)}$$

$$= \mathcal{N}_2 \frac{d\mathcal{N}_1}{dE_1} - \mathcal{N}_1 \frac{d\mathcal{N}_2}{dE_2} = 0$$

$$\Rightarrow \boxed{\frac{d}{dE_1} \ln \mathcal{N}_1 = \frac{d}{dE_2} \ln \mathcal{N}_2}$$

$$*\text{let } \beta \equiv \left(\frac{\partial}{\partial E} \ln \mathcal{N}\right)_{N,V}$$

$\Rightarrow \beta_1 = \beta_2$ in equilibrium

*But we already learned (0th Law) about a quantity that is equal between 2 systems in equilibrium - the temperature!

∴ suspect β is closely related to T.