

\* Recap from L4

## Approaches to equilibrium and TD Potentials

- \* Even though TD is a theory of equilibrium properties, it still gives valuable information on the "path" a system will take to establish a new equilibrium if you disturb the original state by removing some internal constraint
- \* Depending on the situation, there are different functions of State ( $S, F, G, \dots$ ) whose extrema point the way to the new equilibrium state.
- \* Some of the more useful ones:

① Entropy (Thermally + mechanically isolated  $\partial Q = \partial W = 0$ )

$$dS \geq 0$$

$S$  is maximized @ equilibrium

$$dS = \frac{1}{T} dE - \frac{1}{T} \sum_i J_i dx_i ; \quad S = S(E, \{x_i\})$$

② Enthalpy (Adiabatic with external work by const. force)

$$H = E - \vec{J} \cdot \vec{x}$$

$dH \leq 0$ ;  $H$  is minimized @ eq.

$$dH = TdS - \sum_i x_i dJ_i ; \quad H = H(S, \{J_i\})$$

③ Helmholtz Free Energy (isothermal with no ext. work)

$$F = E - TS$$

$dF \leq 0$ ; F minimized @ eq.

$$dF = \sum_i J_i dX_i - SdT; F = F(\{X_i\}, T)$$

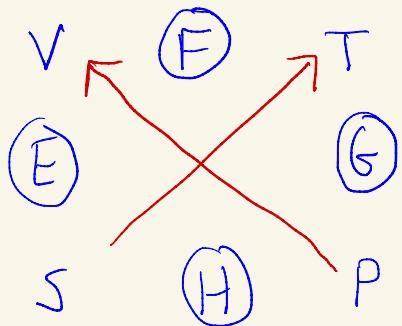
④ Gibbs Free Energy (isothermal with ext work by constant force)

$$G = E - TS - \vec{J} \cdot \vec{x}$$

$dG \leq 0$ ; G minimized @ eq.

$$dG = - \sum_i X_i dJ_i - SdT; G = G(\{J_i\}, T)$$

\* a useful mnemonic device (specializing to the case where  $\{J_i\} \rightarrow -P$ ,  $\{X_i\} \rightarrow V$ )



$$\text{e.g. } \left. \frac{\partial E}{\partial S} \right|_V = T$$

$$\left. \frac{\partial F}{\partial T} \right|_V = -S \quad \text{etc.}$$

\* each function F, G, H, E flanked by its natural arguments

\* derivative wrt to one of its arguments (other held fixed) found by going along diagonal line

\* pick up (-) sign if go against arrow

## 5) Chemical Potential addendum

\* problem:  $G = G(\{J_i\}, T)$  only depends on intensive quantities.  
there is no information on how big our system is since we traded  $\{x_i\}$  for  $\{J_i\}$ .

more generally:

\* Need to modify the above if have a system where  
# of particles of each species not constant (e.g.,  
chemical reactions or diffusion thru a membrane, etc.)

$$\text{chemical work } dW_{\text{chem}} \equiv \sum_{\alpha=1}^{\text{\# Species}} M_\alpha dN_\alpha$$



chem. potential  
= amt. of work to  
add an additional  
particle of species  $\alpha$

Net effect is extra  $dW_{\text{chem}}$  in the above eqs.

$$\text{eg: } dE = \sum_i J_i \cdot dx_i + TdS + \sum_\alpha M_\alpha dN_\alpha$$

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

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

etc..

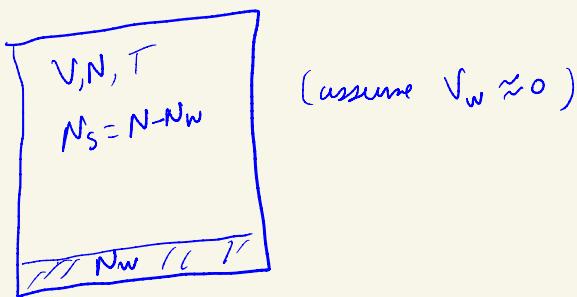
example:  $N$  supersaturated steam molecules

@ constant  $V + T$

↓

describe approach to equilibrium  
mix of  $N_w$  liquid molecules +  $N_s$  gas

⇒ appropriate potential to use  $F(V, T, N)$



$$F(V, T, N, N_w) = F_w(T, N_w) + F_s(V, T, N - N_w)$$

$$dF = \frac{\partial F_w}{\partial N_w} \Big|_{T, V} dN_w + \frac{\partial F_s}{\partial N_s} \Big|_{T, V} dN_s \quad \text{but } dN = dN_w + dN_s = 0 \\ \therefore dN_s = -dN_w$$

$$= dN_w \left( \frac{\partial F_w}{\partial N_w} \Big|_{T, V} - \frac{\partial F_s}{\partial N_s} \Big|_{T, V} \right)$$

$$= dN_w (M_w - M_s)$$

∴ equilibrium reached when  $M_w = M_s$ ,

## ⑥ Grand Potential (aka Landau Potential)

\* Just as we traded  $\{x_i\}$  for  $\{J_i\}$  in going from Helmholtz to Gibbs free energies, we can trade  $\{N_\alpha\}$  for  $\{m_\alpha\}$

$$\boxed{G = E - TS - \vec{\mu} \cdot \vec{N}}$$

$$dG = dE - SdT - Tds - \vec{N} \cdot d\vec{\mu} - \vec{\mu} \cdot d\vec{N}$$

$$= T \cancel{dS} + \vec{J} \cdot d\vec{x} - SdT - T \cancel{dS} + \vec{\mu} \cdot \cancel{dN} - \vec{N} \cdot \cancel{d\mu} - \vec{\mu} \cdot \cancel{dN}$$

$$\Rightarrow dG = \vec{J} \cdot d\vec{x} - SdT - \vec{N} \cdot d\vec{\mu}$$

$$\Rightarrow G = G(\{x_i\}, T, \{m_\alpha\})$$

\* Note: You might wonder if we can construct a useful TD potential subtracting both chem + mech work:

$$Y = E - TS - \vec{\mu} \cdot \vec{N} - \vec{J} \cdot \vec{x}$$

$$\Rightarrow dY = T \cancel{dS} + \vec{J} \cdot d\vec{x} + \vec{\mu} \cdot d\vec{N} - T \cancel{dS} - SdT - \vec{\mu} \cancel{dN} - \vec{N} \cdot d\vec{\mu} - \vec{J} \cancel{dx} - \vec{x} \cdot d\vec{J}$$

$$= -SdT - \vec{N} \cdot d\vec{\mu} - \vec{x} \cdot d\vec{J}$$

$$\Rightarrow Y = Y(T, \{m_\alpha\}, \{J_i\})$$

only intensive variables,

so again this would

not be a useful state function

Since it doesn't tell us how big our system is.

## Some useful Mathematical Relations

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\* One nice feature of TD is that it provides a set of mathematical relations between different measurable quantities.

Extensivity Relation:  $dE = TdS + \vec{J} \cdot d\vec{x} + \vec{\mu} \cdot d\vec{N} \Rightarrow E = E(S, \vec{x}, \vec{N})$

\* notice that  $dS$ ,  $d\vec{x}$ , +  $d\vec{N}$  all get proportionally bigger if our system is bigger. Therefore, so does  $dE$ .  
(just a restatement that  $E, S, \vec{x}, \vec{N}$  are extensive variables)

\* Suppose we increase our system size by a factor  $\lambda$

\* Expect\*\* that

$$E(\lambda S, \lambda \vec{x}, \lambda \vec{N}) \Rightarrow E(S, \vec{x}, \vec{N})$$

$\therefore$  taking  $\frac{d}{d\lambda} \Big|_{\lambda=1} \Rightarrow$

$$\begin{aligned} \text{LHS} &= \left. \frac{\partial(\lambda S)}{\partial \lambda} \frac{\partial E}{\partial (\lambda S)} \right|_{\lambda=1} + \left. \frac{\partial(\lambda \vec{x}_i)}{\partial \lambda} \frac{\partial E}{\partial (\lambda \vec{x}_i)} \right|_{\lambda=1} + \left. \frac{\partial(\lambda N_\alpha)}{\partial \lambda} \frac{\partial E}{\partial (\lambda N_\alpha)} \right|_{\lambda=1} \\ &= ST + \vec{x} \cdot \vec{J} + \vec{N} \cdot \vec{\mu} \end{aligned}$$

$$\text{RHS} = E$$

$$\therefore \boxed{E = TS + \vec{J} \cdot \vec{x} + \vec{\mu} \cdot \vec{N}} \quad (\times)$$

(\*\*) This is only true for sufficiently short-ranged interactions. So it is not true for e.g. gravitational systems on astronomical length scales

\* Now take a differential of eq.(\*):

$$dE = Tds + sdT + \vec{J} \cdot d\vec{x} + \vec{x} \cdot d\vec{J} + \vec{\mu} \cdot d\vec{N} + \vec{N} \cdot d\vec{\mu} \quad (1)$$

& but we also know from our 1st + 2nd Law studies that

$$dE = Tds + \vec{J} \cdot d\vec{x} + \vec{\mu} \cdot d\vec{N} \quad (2)$$

∴ Subtracting (1) + (2) + re-arranging

$$\Rightarrow \boxed{SdT + \vec{x} \cdot d\vec{J} + \vec{N} \cdot d\vec{\mu} = 0}$$

"Gibbs-Duhem Relation"

$\Rightarrow$  shows the intensive variables  
 $(T, \vec{J}, \vec{\mu})$  not all independent

$\Rightarrow$  This is the mathematical reason  
why the proposed TD potential

$$\Upsilon = E - TS - \vec{J} \cdot \vec{x} - \vec{N} \cdot \vec{\mu} = \Upsilon(T, \vec{J}, \vec{\mu})$$

from a couple pages back is  
not a useful function of state.

Example: Use Gibbs-Duhem to find an expression for  $\mu$  for ideal gas along an isotherm

$$SdT - VdP + N d\mu = 0$$

$$\text{or } \therefore d\mu = \frac{V}{N} dP \quad \text{but } PV = Nk_B T$$

$$\therefore \frac{V}{N} = \frac{k_B T}{P}$$

$$\Rightarrow d\mu = \frac{k_B T}{P} dP$$

$$\Rightarrow \mu - \mu_0 = k_B T \ln \left( \frac{P}{P_0} \right)$$

$$\Rightarrow \mu = \mu_0 + k_B T \ln \frac{P}{P_0}$$

Maxwell Relations (relations amongst various partial derivatives)

\* follow from basic calculus. Say we have some differential

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

$$= A(x,y)dx + B(x,y)dy$$

Then since  $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ ,  $\Rightarrow \left. \frac{\partial A}{\partial y} \right|_x = \left. \frac{\partial B}{\partial x} \right|_y$

ex1!:  $dE = \sum_i J_i dx_i + T dS$  (fixed N for simplicity)

$$\therefore \left. \frac{\partial E}{\partial S} \right|_{\vec{x}} = T \quad \left. \frac{\partial E}{\partial x_i} \right|_{S, x_{j \neq i}} = J_i$$

Now use  $\frac{\partial}{\partial S} \left( \frac{\partial E}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left( \frac{\partial E}{\partial S} \right)$

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

Note: Using the inverse derivative

$$\text{e.g., } \left. \frac{\partial x}{\partial f} \right|_y = - \frac{1}{\left. \frac{\partial f}{\partial x} \right|_y}$$

each Maxwell relation can be inverted

$$\text{e.g., } (*) \Rightarrow \boxed{\left. \frac{\partial x_i}{\partial T} \right|_{S, x_{j \neq i}} = \left. \frac{\partial S}{\partial J_i} \right|_{\vec{x}}}$$

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 1<sup>st</sup> derivative

i.e. Candidates are

$$dF = \sum_i J_i dx_i - SdT + \sum_\alpha \mu_\alpha dN_\alpha$$

$$dG = -\sum_i x_i dJ_i - SdT + \sum_\alpha \mu_\alpha dN_\alpha$$

$$dY = \sum_i J_i dx_i - SdT - \sum_\alpha N_\alpha d\mu_\alpha$$

\* 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  $G$

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

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

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