

# Day 3 Notes

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## 1 Intro

One fundamental formula for surfaces & adsorption is the differential 1-form

$$-d\gamma = \bar{S}dT - \tau dP + \sum_{n=1}^e \Gamma_n d\mu_n \quad (1)$$

Where  $\bar{S}, \tau, \{\Gamma_c\}$  are excess quantities.

A second formula is the Gibbs' phase rule

$$f = c - p + 2 \quad (2)$$

(2) requires that any two of the excess must be set to zero. That determines the "Convention". The lecture today will start from this point.

- The "Gibbs convention"  $\tau = 0, \Gamma_1 = 0$
- The "Hansen convention"  $\Gamma_1 = 0, \Gamma_2 = 0$

## 2 Surface excess entropy

$$\bar{S} \times \mathbf{A} \equiv S^s$$

- $\bar{S}$  is intensive,  $S^s$  is extensive.
- Surface excess entropy is defined using  $\lambda_1$  and  $\lambda_2$  determined with (1).
- Be sure to tell the reader the convention you're using!

Also

$$\tau \times \mathbf{A} \equiv V^s \text{Volume Excess}$$

$$\Gamma_c \times \mathbf{A} \equiv N_c^s \text{Mole Number Excess}$$

$$U = ST - PV + \sum_{c=1}^N \mu_c N + \gamma A$$

$$\check{U}^+ = \check{S}^+ T - P + \sum_{c=1}^N \mu_c \check{N}^+$$

$$\check{U}^- = \check{S}^- T - P + \sum_{c=1}^N \mu_c \check{N}^-$$

$$U^s = U - \lambda^+ \check{U}^+ - \lambda^- \check{U}^- \text{similar for } S^s, \text{ etc.}$$

$$\therefore U^s = S^s T - PV^s + \sum_{c=1}^N \mu_c N_c^s + \gamma A$$

**Note:**  $F$  is the Helmholtz Free Energy, typically defined in texts as  $A$

Now to compute  $dU^s$ . Recall that we know a 1-form for  $-d\gamma$  so that

$$dU^s = T dS^s - P dV^s + \sum_{c=1}^N \mu_c dN_c^s + \gamma dA$$

Now recall the Euler Integral theorem to find

$$U^s = TS^s - P dV^s + \sum_{c=1}^N \mu_c N_c^s + \gamma A H^s \equiv U^s + PV^s$$

$$F^s \equiv U^s - TS^s$$

$$dF^s = -S^s dT - P dV^s + \sum_{c=2}^{\text{\#components}} \mu_c dN_c^s + \gamma dA$$

If  $T$  is constant,  $dT = 0$ , and in the Gibbs convention,  $V^s = 0$ , and  $N_1^s = 0$ .

Also if the composition is constant,  $dN_2^s = 0, dN_3^s = 0, \dots$  Then

$$dF^s = \gamma dA$$

(Here  $\gamma$  is the Helmholtz free Energy per Area  $\gamma = \frac{\partial F}{\partial \text{Area}}$ )

## 2.1 Some Details

$$F^s = U^s - TS^s$$

$$dF^s = dU^s - T dS^s - S^s dT$$

You have a differential 1-form for  $dU^s$ , upon substitution  $+TdS^s$  adds out the  $-TdS^s$  term.

$$\begin{aligned}dU^s &= TdS^s - PdV^s + \sum_{i=1}^N \mu_c dN_c^s + \gamma dA \\H^s &= U^s + PV^s \\F^s &= U^s - TS^s \\dF^s &= -S^s dT - p dV^s\end{aligned}$$

If  $T$  is constant and the mole numbers are constant,  $dT = 0$ ,  $dN_c^s = 0$ , assume Gibbs convention  $V^s = 0$ . Then  $dF^s = \gamma dA$  Here  $\gamma$  is Helmholtz free energy per unit area

### 3 Concentration and Surface Tension

$$-d\gamma = \bar{S}dT - \tau dP + \Gamma_{H_2O}d\mu_{H_2O} + \Gamma_s d\mu_s$$

Assume  $p$  is constant

$$\begin{aligned}\tau &= 0, \Gamma_{H_2O} = 0 \text{ (Gibbs Convention)} \\dT &= 0 \\ \text{then} \\ -d\gamma &= \Gamma_s d\mu_s \\ \Gamma_s &= -\frac{\partial \gamma}{\partial \mu_s} \\ \mu_s &= \mu_s^\circ + k_B T \ln(a_s) \\ a_s &= \alpha C_s\end{aligned}$$

$\gamma, \nu$  constant.???

### 4 How to find a derivative given noisy function

At some point you will be taking experimental  $\gamma$  vs  $C$  data and estimating  $\frac{\partial \gamma}{\partial \ln(C)}$  - how to do this keeping in mind that there is always some error associated with measuring  $\gamma$  is a point of interest. Suppose you know that a smooth formula works well in representing your data.

$y = f(x)$  so that  $\frac{dy}{dx} = f'(x)$  is smooth in the sense that

$$f'(x) = \lim_{h \rightarrow 0} \frac{(f(x-h) - f(x))}{h}$$

exists at each point  $x$ .

Now do a measurement and find that there is experimental error at each point so that  $y = f(x) + \epsilon(x)$  where  $\epsilon$  is a random number from the uncertainty of the measurement.

$$\frac{dy}{dx} = f(x) + \epsilon(x)$$

$$\epsilon'(x) = \lim_{h \rightarrow 0} \frac{\epsilon(x-h) - \epsilon(x)}{h} \quad (\text{In general, does not exist!})$$

## 5 Gibbs Approach

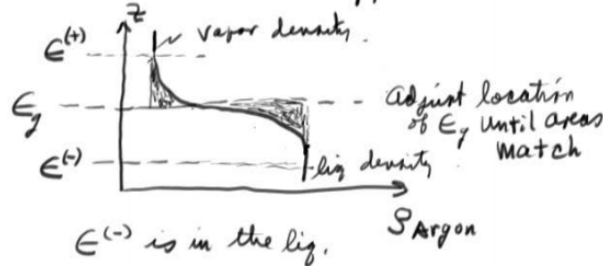


Figure 1: A system of liquid and vapor Argon. The vertical axis is distance normal to the surface, and the horizontal axis is density of Argon,  $\rho_{\text{Argon}}$ . The density is constant at some distance from the interface, then changes (following a hyperbolic tangent curve) as the interface is approached.  $\epsilon_g$  is defined as the line where the areas (above and below the curve) match.

Consider the gibbs approach. Define  $\epsilon^+$  as the vapor,  $\epsilon^-$  as the liquid (as in Figure 1). These are the two asymptotes of a hyperbolic tangent curve. Then we will have  $\rho^z - \rho^+ \geq 0$  for  $z$  in the range of tanh curve. Similarly  $\rho^z - \rho^- \leq 0$  for  $z$  in the same range.

$$\Gamma \equiv \int_{\epsilon_g}^{\epsilon^+} (\rho^z - \rho^+) dz + \int_{\epsilon^-}^{\epsilon_g} (\rho^z - \rho^-) dz$$

Now then:  $\Gamma_1 = 0$  therefore, excess of the major component is 0.  
More generally,

$$\Gamma_c = \int_{\epsilon^-}^{\epsilon_g} (\rho_c(z) - \rho_c^-) dz + \int_{\epsilon_g}^{\epsilon^+} (\rho_c(z) - \rho_c^+) dz$$

if  $\Gamma_1 = 0$  then there is some  $\varepsilon_g$  such that in/out  $\Gamma_1 = 0$ . By correlation, this fixes the location of the gibbs surface at  $\varepsilon_g$ .

However,  $\Gamma_c, c \neq 0$  may be either  $\Gamma_c > 0$  or  $\Gamma_c < 0$ , although for the usual surfactants,  $\Gamma_c > 0$ .

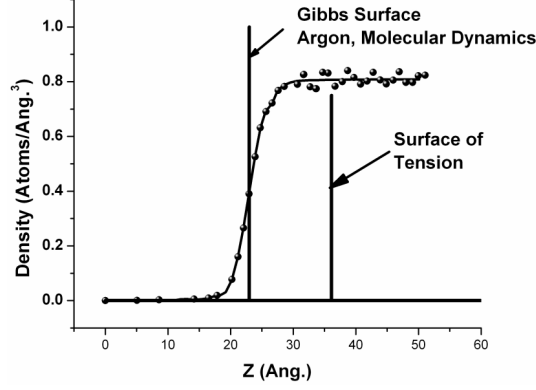


Figure 2: Work done by Mann with MD simulation showing the agreement with a tanh curve, and showing the Gibbs Surface of Argon.

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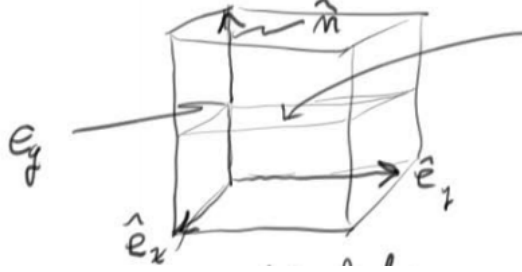


Figure 3: Gibbs Surface Corresponding to  $\varepsilon_g$

With this definition,  $\Gamma_{c(c \neq 1)} = \int_{-\infty}^{+\infty} \rho_c(z) - \rho_c^{(\pm)} dz$

$+, -$  are the two phases with density  $\rho_c^+, \rho_c^-$ . Only for  $c = 1$  does  $\Gamma_1 = 0$  which determines the rest of the excess. Also in the Gibbs convention,

$$V_{\text{total}} = V^+ + V^-$$

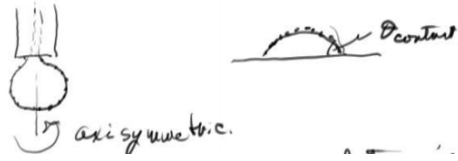


Figure 4: The pendant drop method. This method is axisymmetric, and takes advantage of the fact that the contact angle of a drop on a surface,  $\theta$ , is a constant.

## 7 The Case of Curved Surfaces

To determine the surface tension - you determine the boundary function, then fit it to a model. You need the relationship between the surface tension, the local radii of curvature, and the pressure drop across the interface - the jump of the pressure. Consider Figure 5. Anywhere on the curved surface of the phase,

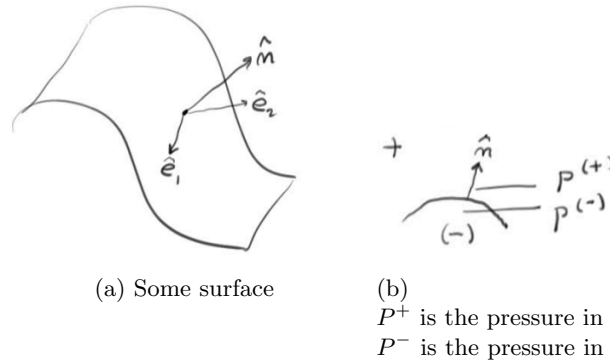


Figure 5: A generic curved surface.  $\hat{e}_1, \hat{e}_2$  are tangent to the surface, making  $\hat{n} = \hat{e}_1 \times \hat{e}_2$  normal to the surface, provided  $\hat{e}_1 \neq \hat{e}_2$

you can construct a normal. What you have to think about is the pressure drop across this interface. That is the jump in the pressure as you approach the interface

$$[P] \equiv \lim_{z \downarrow \text{surface}} (P^+) - \lim_{z \uparrow \text{surface}} (P^-)$$