

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 λ_1 and λ_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 γ 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 γ 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

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

γ, ν constant.???

4 How to find a derivative given noisy function

At some point you will be taking experimental γ 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 γ 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 ϵ 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

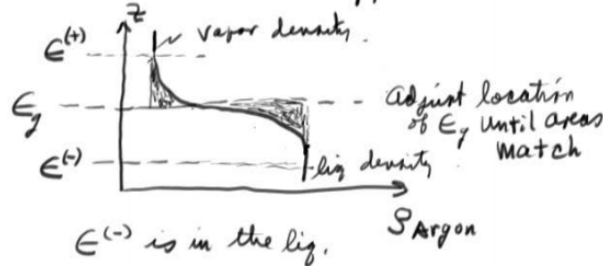


Figure 1: A system of liquid and vapor Argon. The vertical axis is distance normal to the surface, and the horizontal axis is density of Argon, ρ_{Argon} . The density is constant at some distance from the interface, then changes (following a hyperbolic tangent curve) as the interface is approached.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

Consider the gibbs approach. Define ϵ^+ as the vapor, ϵ^- 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 ε_g such that in/out $\Gamma_1 = 0$. By correlation, this fixes the location of the gibbs surface at ε_g .

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

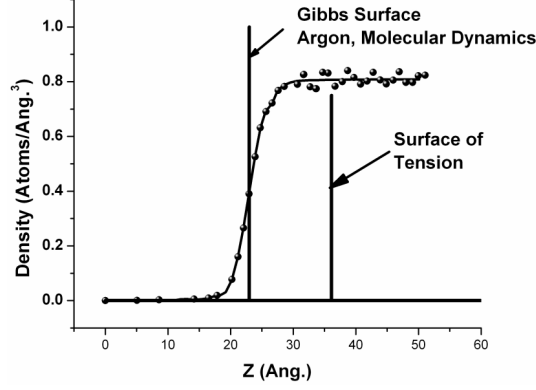


Figure 2: Work done by Mann with MD simulation showing the agreement with a tanh curve, and showing the Gibbs Surface of Argon.

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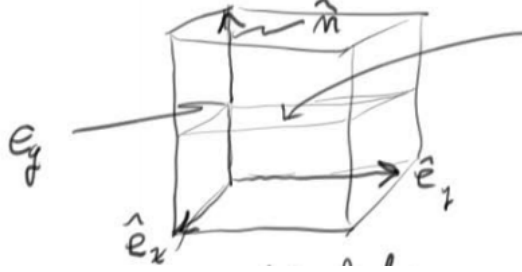


Figure 3: Gibbs Surface Corresponding to ε_g

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

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

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

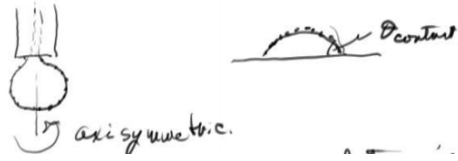


Figure 4: The pendant drop method. This method is axisymmetric, and takes advantage of the fact that the contact angle of a drop on a surface, θ , is a constant.

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,

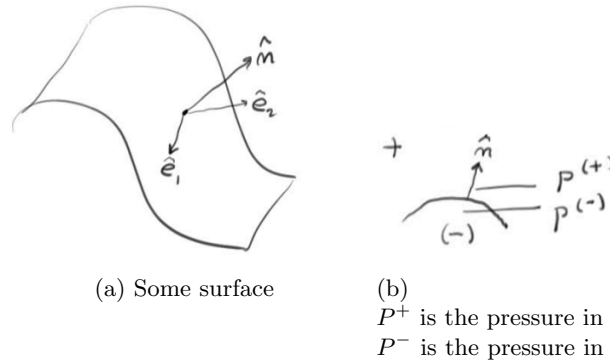


Figure 5: A generic curved surface. \hat{e}_1, \hat{e}_2 are tangent to the surface, making $\hat{n} = \hat{e}_1 \times \hat{e}_2$ normal to the surface, provided $\hat{e}_1 \neq \hat{e}_2$

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

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