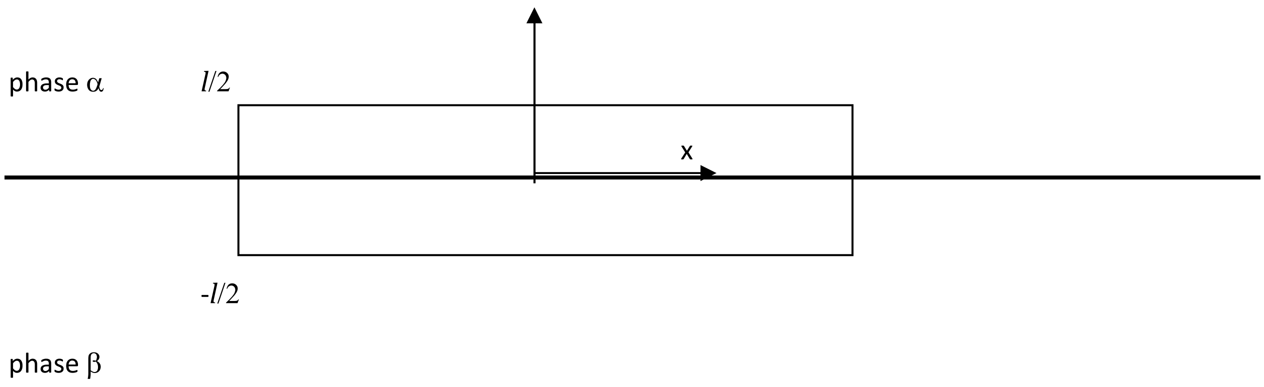
1. Thermodynamics of a planar fluid interface: derivation of Gibbs AdsorptionEquation

1.1 Definition of Surface Tension



Consider a planar interface between two fluid phases α and β. There is a transition region on the order or 10s of angstroms in which intensive properties of the system change continuously from their value in one phase to their value in the other. Locate a dividing surface of zero thickness between the two phases. Let theinterface be infinite in the x,y, plane. Let the fluids be at rest. Neglect gravity.

- Stresses in a single fluid at rest: pressure is isotropic- uniform in all directions.

$$\sigma = \begin{bmatrix} -P & 0 & 0 \\ 0 & -P & 0 \\ 0 & 0 & -P \end{bmatrix} \qquad (1.1.0)$$

- Stresses in a system containing an interface: INTERFACES TEND TO CONTRACT-there is anisotropy in the z-direction:

The stress tensor can be expressed:

$$\sigma = \begin{bmatrix} -P_T & 0 & 0 \\ 0 & -P_T & 0 \\ 0 & 0 & -P_N \end{bmatrix} \qquad (1.1.1)$$

e.g. if move the top of the box up work expended is

$$dW_{top} = -P_N dV \qquad (1.1.2)$$

e.g. if move the side of box work expended is

$$dW_{side} = -P_T dV \qquad (1.1.3)$$

$P_T < P_N$: interface tends to contract; far from interface $P_T \to P_N$

Construct a box traversing the interface

Define surface tension:

work=force o displacement

work to move wall to the right distance dx in the absence of interface:

$$dW_{no\,\mathrm{int}} = \int_{-l/2}^{l/2} -P_N L dz dx = \int_{-l/2}^{l/2} -P_N dz dA \tag{1.1.4}$$

work to move wall to the right distance dx in the presence of interface:

$$dW_{\mathrm{int}} = \int_{-l/2}^{l/2} -P_T L dz dx == \int_{-l/2}^{l/2} -P_T dz dA \tag{1.1.5}$$

Extra work required to extend area of interface by amount dA:

$$dW_{extra} = \lim_{l\to\infty} \int_{-l/2}^{l/2} \left(P_N - P_T\right) dz dA = \gamma dA \tag{1.1.6}$$

This is the additional work required to expand system because of the energy associated with the interface. Contractile interface: $\gamma>0$

This defines the surface tension in liquid-liquid or liquid-vapor systems. Note: definition is independent of location of dividing surface.

Pressure units: energy/volume or force per area

Surface tension units: energy/area=force/length

Surface tension is treated as a 2-D analogy to pressure. Like pressure, surface tension has thermodynamic and mechanical roles.

WHY ARE INTERFACES CONTRACTILE? if molecules of α attract each other , and molecules of β attract each other more than α is attracted to β: the creation of the interface disrupts favorable self-interactions. The energy cost creates contractile tendency.

1.2 First Law for system; Gibbs-Duhem equation for system

The first law for the system comprising phase α,β and the interface

$$dU = dq + dW + \sum_i \mu_i dN_i \; ; \qquad (1.2.1)$$

$$dU = TdS - PdV + \gamma dA + \sum_i \mu_i dN_i \qquad (1.2.2)$$

where *T* is the temperature, *S* is the entropy, *V* is the volume, *A* is the area of the interface, μ_i is the chemical potential of species i and N_i is the number of moles of species i.

We will address:

- How do thermodynamics of system differ b/c of presence of interface?
- What are the implications of the surface tension term?

From dU: derive system's thermodynamic equations.

Define the Helmholtz free energy F:

$$F = U - TS \qquad (1.2.3)$$

Differentiating:

$$dF = dU - d(TS) \qquad (1.2.4)$$

Substituting 1.2.2:

$$dF = -SdT - PdV + \gamma dA + \sum_i \mu_i dN_i \qquad (1.2.5)$$

F is homogeneous in extensive variables V,A, N_i, i.e.

$$dF = -SdT - PdV + \gamma dA + \sum_i \mu_i dN_i \qquad (1.2.6)$$

Taking the exact derivative:

$$dF = \left(\frac{\partial F}{\partial V}\right)_{A,Ni} dV + \left(\frac{\partial F}{\partial A}\right)_{V,Ni} dA + \sum_i \left(\frac{\partial F}{\partial N_i}\right)_{V,A} N_i \qquad (1.2.7\text{ a})$$

So we see:

$$-P = \left(\frac{\partial F}{\partial V}\right)_{A,Ni}$$
$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{V,Ni} \qquad (1.2.7\text{b-d})$$
$$\mu_i = \sum_i \left(\frac{\partial F}{\partial N_i}\right)_{V,A} N_i$$

By Euler's theorem:

$$F = -PV + \gamma A + \sum_i \mu_i N_i \qquad (1.2.8)$$

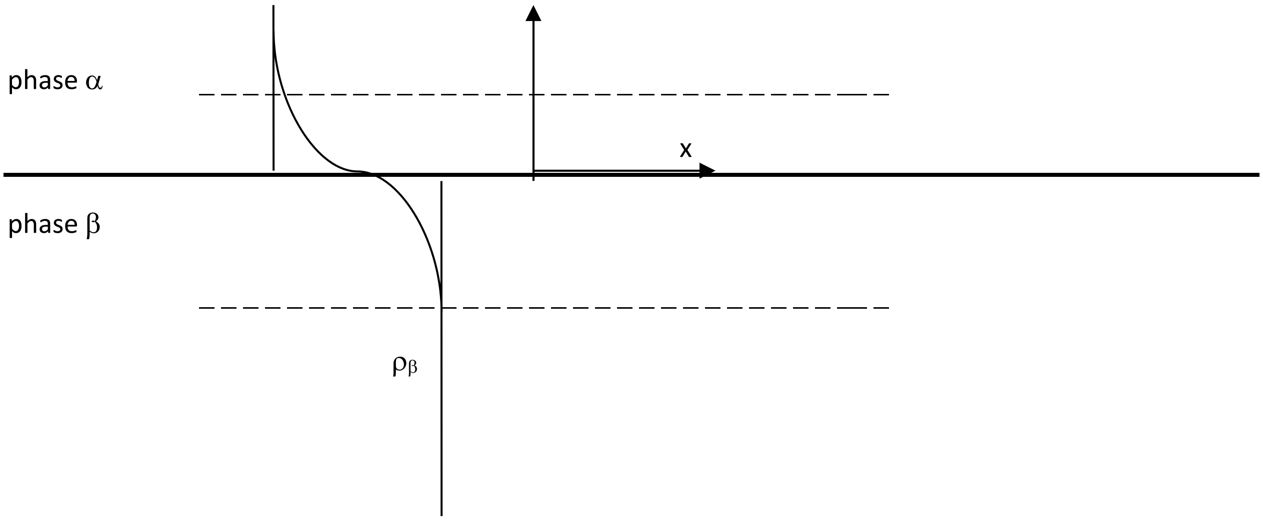
Taking the derivative of this expression and subtracting (1.2.6) yields the Gibbs Duhem relationship for the system, which relates the changes in intensive variables:

$$0 = -VdP + Ad\gamma + \sum_i N_i d\mu_i + SdT \qquad (1.2.9)$$

This is still to much information- we would like to be able to focus on the surface rather than on properties of the bulk systems and the surface.

1.3 Define surface excess quantities

In order to focus a on the interface, define surface excess properties:



There is a transition zone across the interface on the order of 10s of angstrom in which properties change from that of one fluid to the other (E.g. density). Place a mathematical dividing surface whose location is arbitrary. (zero thickness surface so it has no volume)

Let Λ be some extensive property; define surface excess:

$$\Lambda = \Lambda^{\alpha} + \Lambda^{\beta} + \Lambda^{s} \qquad (1.3.1)$$

For a system at equilibrium:

$$\begin{aligned} P &= P^{\alpha} = P^{\beta} \\ \mu_i^{\alpha} &= \mu_i^{\beta} = \mu_i^{s} = \mu_i \\ T &= T^{\alpha} = T^{\beta} \end{aligned} \qquad (1.3.2)$$

So, the Helmholz free energy for each phase and the surface excess Helmholz free energy become:

$$F^{\alpha} = -PV^{\alpha} + \sum_i \mu_i N_i^{\alpha} \qquad F^{\beta} = -PV^{\beta} + \sum_i \mu_i N_i^{\beta} \qquad (1.3.3)$$

$$F^{s} = \gamma A + \sum_i \mu_i N_i^{s} \qquad (1.3.4)$$

Note: $\frac{\partial F^{s}}{\partial A} = \gamma$ holds only if dividing surface selected so that surface excess moles are zero.

Differentiating (1.3.4) yields:

$$dF^{s} = Ad\gamma + \gamma dA + \sum_i \mu_i dN_i^{s} + N_i^{s} d\mu_i \qquad (1.3.5)$$

Working from

- definition of dF and using
- $dF^{s} = dF - dF^{\alpha} - dF^{\beta}$ yields:

$$dF^{s} = -S^{s}dT + \gamma dA + \sum_i \mu_i dN_i^{s} \qquad (1.3.6)$$

Taking 1.3.5-1.3.6 yields a Gibbs Duhem equation in terms of surface excess properties:

$$0 = -S^s dT + A d\gamma + \sum_i N_i^s d\mu_i \tag{1.3.7}$$

Dividing by the area and rearranging gives **the Gibb's Adsorption Equation**:

$$d\gamma = s^s dT - \sum_i \Gamma_i d\mu_i \tag{1.3.8}$$

This equation holds the key to thermocapillarity (surface tension dependence on temperature) and to surfactant adsorption effects (surface tension dependence on surface excess moles/area- i.e. to surfactant accumulation at the interface).

Equation 1.3.4 divided by area A yields:

$$f^s = \gamma + \sum_i \mu_i \Gamma_i$$

Differentiating we can show:

$$\left(\frac{\partial f^s}{\partial \Gamma_i} \right)_{T,\Gamma_j} = \mu_i$$

which implies that:

$\mu_i(T, \Gamma_j)$. Similarly, $\mu_i(T, C_j^{\alpha}); \mu_i(T, C_j^{\beta})$. Since chemical potentials are equal in all phases at equilibrium, and temperature is equal in all phases at equilibrium, this implies that there is a relationship at equilibrium that relates:

$$\Gamma_j(C_j^{\alpha}, C_j^{\beta});$$
$$C_j^{\alpha}(C_j^{\beta})$$

That is, that the species in the system partition between the interface and the solutions by obeying an adsorption isotherm and a distribution isotherm for a given temperature in a system at equilibrium.

We can use the Gibbs adsorption equation at constant temperature, assumptions about the solution (to relate chemical potential to concentration) and assumptions about the equilibrium isotherm to derive certain surface equations of state:

$$\left(\frac{\partial \gamma}{\partial \mu_i} \right)_T = -\Gamma_i$$