

Day 4 Notes

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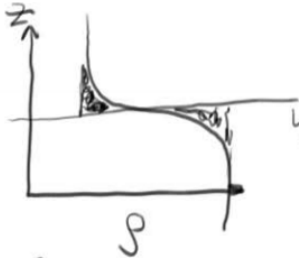
1 Main

Notice: The thermodynamics I have developed using the Hansen or Cahn approach is general: liquid/vapor; liquid/liquid; liquid/solid; solid/solid interfaces are included in defining the excess quantities.

The gibbs surface and surface of tension concepts require more work

- Recall the gibbs surface
- I will develop the surface of tension
- The Laplace equation when the surface is curved.

2 Gibbs surface



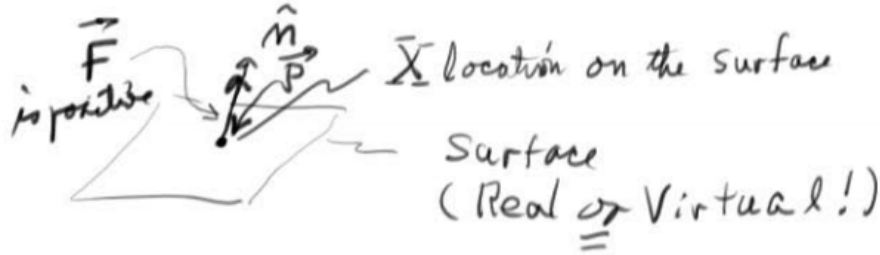
Equimolar surface Location.

- Comes from $\Gamma_1 = \int_{-\infty}^{+\infty} (\rho(z) - \rho^\pm) dz$
- Now Deal with pressure:
$$\gamma^{def} = - \int_{-\infty}^{+\infty} (P_{11} - P_n) dz$$
 - P_{11} is the pressure component parallel to the surface
 - P_n is the pressure component normal to the surface

This is the Gibbs surface definition of γ

- The pressure tensor is a rank 2 tensor which means that the pressure can be thought of in terms of a matrix $\mathbf{P} = \begin{pmatrix} P_{11} & P_{12} & P_{13} \\ P_{21} & P_{22} & P_{23} \\ P_{31} & P_{32} & P_{33} \end{pmatrix}$
- $\mathbf{P} = \mathbf{P}^T$ (The pressure tensor is symmetric)
- $\mathbf{P} \equiv -\boldsymbol{\sigma}$ (The pressure tensor is by definition the negative of the stress tensor)
- As soon as you say that the system could be anisotropic, a scalar Pressure is not valid. $\vec{F} = \hat{n} \cdot \boldsymbol{\sigma} F_j = n_i \sigma_{ij} \vec{P}_j = -n_i \sigma_{ij} P^{ij} = P^{ji}$? Most of the time.

3 Properties of P



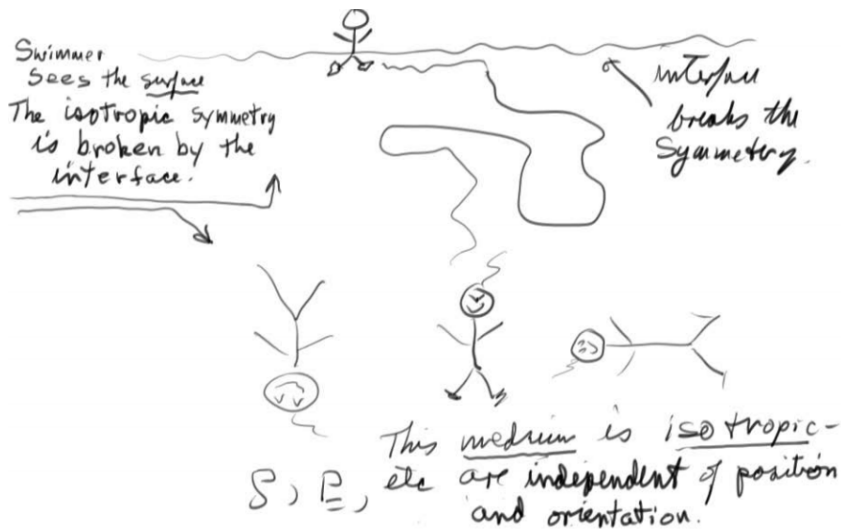
- $\vec{F} = \hat{n} \cdot \boldsymbol{\sigma}$ (Vector \cdot Rank-2 gives a vector!)
- $F_j = n_i \sigma_{ij}$ in component form.
- $\vec{P} = -n_i \sigma_{ij}$
- $n_i \sigma_{ij} = \sum_{i=1}^3 n_i \sigma_{ij}$
- $P_{ij} = P_{ji}$? Yes. This is symmetric.
- $P_{ij} \in \mathbb{R}$? Yes.
- $\hat{e}_j \vec{P}_i = -n_i \sigma_{ij} e_j = -e_j e_{ij} n_i$ (Where \hat{e}_j is a direction in 3-space. Note that $\hat{e} \cdot \mathbf{P} \cdot \hat{n}$ is a scalar Pressure.)

4 Test for isotropy

Does there exist a coordinate transformation (i.e. a 3x3 matrix \mathbf{T} and its inverse

\mathbf{T}^{-1} such that $\mathbf{T}^{-1} \mathbf{P} \mathbf{T} = \begin{pmatrix} \vec{P}_{11} & 0 & 0 \\ 0 & \vec{P}_{22} & 0 \\ 0 & 0 & \vec{P}_{33} \end{pmatrix}$ If you can diagonalize the pressure tensor, so long as $P_{ij} = P_{ji}$ and P_{ij} are the real numbers, \mathbf{T} exists!

5 Isotropic Effects



- Things like ρ , P are independent of the observer orientation.
- Interfaces fundamentally break the symmetry of systems.
- Think of a swimmer at midnight when it's cloudy. Underwater, there is no sense of direction. When the swimmer breaks the surface, however, the symmetry is broken, and the swimmer knows which direction is up.
- There exists $T, TT^{-1} = I$ such that $T^{-1}PT = \mathcal{R} = \begin{pmatrix} \bar{P}_{11} & 0 & 0 \\ 0 & \bar{P}_{22} & 0 \\ 0 & 0 & \bar{P}_n \end{pmatrix}$
- $\mathcal{R} = \begin{pmatrix} \bar{P}_{11} & 0 & 0 \\ 0 & \bar{P}_{11} & 0 \\ 0 & 0 & \bar{P}_n \end{pmatrix}$ is a case of 2D isotropy. Use this to define γ Note that for a flat interface...
- $[P_n]_\Sigma = \lim_{z \downarrow \Sigma} P_n(z) - \lim_{z \uparrow \Sigma} P_n(z) = 0$ the jump in pressure is 0
- Surface must be flat, the pressure P_n is uniform along the normal.
- Therefore $\gamma = - \int_{-\infty}^{+\infty} (P_{11}(z) - P_n(z)) dz$ assuming 2D isotropy.

6 Anisotropy of Surface Tension

Suppose α_{11}, α_{22} in the surface differ.

- More Generally: define

$$\gamma = \begin{pmatrix} \gamma_{11} & \gamma_{12} \\ \gamma_{21} & \gamma_{22} \end{pmatrix} \text{ (which is also symmetric)}$$

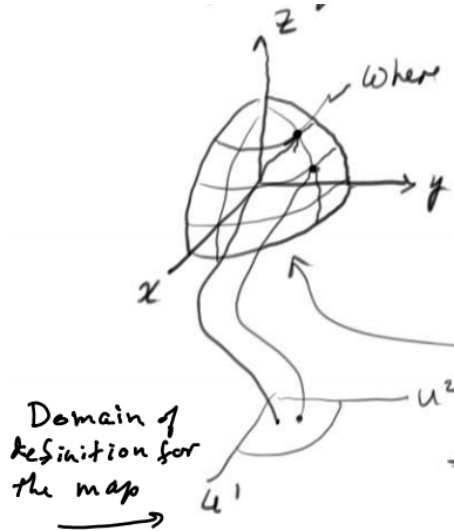
$$\gamma = \begin{pmatrix} \gamma_{11} & 0 \\ 0 & \gamma_{22} \end{pmatrix}$$

- Surface tension is a rank-2 tensor in the space of the interface - a 2-Dimensional space
- P is isotropic in 3D, γ is isotropic in 2D.

7 Curved interfaces

7.1 Soap Bubble

- $P_{\text{inside}} > P_{\text{outside}}$. This is related to the curvature of the sphere. Biophysical membranes are often quite strongly curved as well.
- We can represent curved surfaces by functions.
- Let's look at one octant of a soap bubble.



This could be expressed as

$$r^2 = x^2 + y^2 + z^2 \Rightarrow z = \sqrt{r^2 - x^2 - y^2}$$

$$\Sigma := \begin{cases} x &= u_1 \\ y &= u_2 \\ z &= \pm \sqrt{r^2 - (u_1)^2 - (u_2)^2} \end{cases}$$

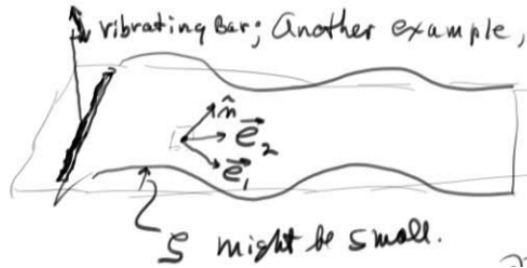
- In general:= Monge Representation

$$\Sigma := \begin{cases} x &= u_1 \\ y &= u_2 \\ z &= f(u_1, u_2, t) \end{cases}$$

- This representation has useful properties.

7.2 Vibrating Bar

- Imagine a wave running down a sheet. This could also be waves generated on a liquid/vapor interface.



- Assume

$$\Sigma := \begin{cases} x &= u_1 \\ y &= u_2 \\ z &= \zeta(u_1, u_2, t) \end{cases}$$

$$dxu_1 = 1$$

$$dyu_1 = 0$$

$$d\zeta u_1 = \zeta_1$$

$$d\Sigma := \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ \zeta_1 & \zeta_2 \end{pmatrix}$$

$$\vec{e}_1 = \begin{pmatrix} 1 \\ 0 \\ \zeta_1 \end{pmatrix}$$

$$\vec{e}_2 = \begin{pmatrix} 0 \\ 1 \\ \zeta_2 \end{pmatrix}$$

$$\vec{n} = \vec{e}_1 \times \vec{e}_2 = |\vec{e}_1||\vec{e}_2|\sin\theta_{12}\hat{e}_3$$

- This example will become a flat, plane-like interface when $\zeta(u_1, u_2, t) = 0$

- Compute

$$\begin{aligned}\vec{e}_1 \times \vec{e}_2 &= \begin{bmatrix} \hat{i} & \hat{j} & \hat{k} \\ 1 & 0 & \zeta_1 \\ 0 & 1 & \zeta_2 \end{bmatrix} \\ \vec{n} &= \hat{i}(-\zeta_1) - \hat{j}(\zeta_2) + \hat{k} \\ \vec{n} &= \begin{pmatrix} -\zeta_1 \\ -\zeta_2 \\ 1 \end{pmatrix}\end{aligned}$$

- Note if $\zeta_1 = \zeta_2 = 0$ the $\vec{n} = (0, 0, 1)$ along the \hat{k} axis.
- This construction provides a vector defining the local normal; viz.
 $\vec{n} \cdot \vec{e}_1 = \vec{n} \cdot \vec{e}_2 = 0$, however $\vec{n} \cdot \vec{n} \neq 1$ generally.
- Suppose you compute $\vec{n} \cdot \vec{n} = 1 + (\zeta_1)^2 + (\zeta_2)^2$ so that $\hat{n} = \frac{\vec{n}}{\sqrt{1 + (\zeta_1)^2 + (\zeta_2)^2}}$
 $\hat{n} \cdot \hat{n} = 1$, $\hat{n} \cdot \vec{e}_1 = 0$, $\hat{n} \cdot \vec{e}_2 = 0$ $\vec{e}_1 \times \vec{e}_2$ think of this as an area.
 $\therefore dA \equiv \text{differential area} \equiv \sqrt{1 + (\zeta_1)^2 + (\zeta_2)^2} du_1 du_2$
- Note: When $\zeta_1 = 0, \zeta_2 = 0$, then $dA = du_1 du_2$ as expected.

8 Metric Tensor

- $\vec{e}_1 \cdot \vec{e}_1 = 1 + (\zeta_1)^2$
- $\vec{e}_2 \cdot \vec{e}_2 = 1 + (\zeta_2)^2$
- $\vec{e}_1 \cdot \vec{e}_2 = \vec{e}_2 \cdot \vec{e}_1 = \zeta_1 \zeta_2$
- $\begin{pmatrix} 1 + (\zeta_1)^2 & \zeta_1 \zeta_2 \\ \zeta_1 \zeta_2 & 1 + (\zeta_2)^2 \end{pmatrix} \equiv \mathbf{a}$
- \mathbf{a} is the metric tensor for Σ
- Very important. This is the Metric
- $d\zeta^2 = a_{\alpha\beta} du_\alpha du_\beta$, $\alpha, \beta = 1, 2$ $d\zeta$ is a distance along the surface.
- $\det \mathbf{a} = 1 + (\zeta_1)^2 + (\zeta_2)^2$
- Note: $dA = \sqrt{1 + (\zeta_1)^2 + (\zeta_2)^2} du_1 du_2 = \sqrt{a} du_1 du_2$ [this is the area for integrating over the surface.]
- How much work to create this surface?

$$R = \int_{A_0} [P]_n \zeta(u_1, u_2, t) \sqrt{a} du_1 du_2 + \int_{A_0} \gamma \sqrt{a} du_1 du_2$$

- Minimization of the work with respect to ζ yields the Laplace equation, which looks like this.

$$[P]_n = 2\gamma R_{\text{mean}} \quad \text{Where } R_{\text{mean}} = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \text{ [the mean radius of curvature.]}$$