Maxwell’s relations, susceptibilities, and partial molar properties
New thermodynamic functions are needed!

Lipid bilayers can change their surface area per molecule, $A$. The value of $A$ at equilibrium could be found by minimizing $G(T, p, N, A)$. But so far we do not have a $G(T, p, N, A)$!

What is the area of a lipid bilayer at:

- $T=310$ K = const.
- $p=1$ atm = const.

Lipid bilayers can change their surface area per molecule, $A$. The value of $A$ at equilibrium could be found by minimizing $G(T, p, N, A)$. But so far we do not have a $G(T, p, N, A)$!
How to design general fundamental functions?

Introduce new extensive variable(s) $X$ into the fundamental energy equation:

$$ U = U(S,V,N,X) $$

Generalized force is defined as:

$$ \mathcal{F}_j = \left( \frac{\partial U}{\partial X_j} \right)_{S,V,N,X_{i \neq j}} $$

Each extensive degree of freedom has a conjugate force:

- $p$ is conjugate force for $V$
- $T$ is conjugate force for $S$
- $\mu$ is conjugate force for $N$
- $F$ is conjugate force for $L$
- $\gamma$ is conjugate force for $A$
- $\psi$ is conjugate force for $Q$
- $B$ is conjugate force for $I$

...and so on.

$$ dU = TdS - pdV + \sum_j \mu_j dN_j + f dL + \gamma dA + \psi dQ + B dI + \sum_j \mathcal{F}_j dX_j $$
Example: surface area and surface tension

Assume that surface area can change independently of the volume. Start with $U$ (always). The variables are: $(T, p, N, A)$. Then add a new term.

$$U = U(S, V, N, A)$$

$$dU = TdS - pdV + \sum_j \mu_j dN_j + \gamma dA$$

$$\gamma = \left( \frac{\partial U}{\partial A} \right)_{S, V, N} = \text{surface tension}$$

$(S, V, N, A)$ are difficult to control. $(T, p, N, A)$ would be desired. Switch to $G$.

$$G = U + pV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j + \gamma dA$$

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T, p, N} = \text{surface tension}$$

We will have to minimize $G$ to find the equilibrium.
Assume that we apply $N$ particles in $A$ lattice sites (= surface area) have.

$$A \gg N \quad \Rightarrow \quad W_A \approx A^N$$

(each molecule can be on any of the $A$ sites)

$$S(A) = k \ln(W) = Nk \ln(A)$$

$$dG = -SdT + Vdp - \gamma dA = 0 \quad \Rightarrow \quad \frac{V}{\gamma} = \frac{dA}{dP}$$

Bacteria are like balloons.
Susceptibilities: Thermal expansion coefficient

Susceptibilities define how a thermodynamic property (cause) affects another property (effect).

Example: The thermal expansion coefficient $\alpha$ defines how temperature affects volume:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p,N} = \left[ \frac{\partial \ln(V)}{\partial T} \right]_{p,N}$$

Rail anchor

Highway expansion joint
Insights from the thermal expansion coefficient

Susceptibilities can also give insights into fundamental quantities. For example:

\[
\alpha V = \left( \frac{\partial V}{\partial T} \right)_{p,N} = \left( \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial p} \right) \right)_{T,N} = \left( \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial T} \right) \right)_{p,N} = -\left( \frac{\partial S}{\partial p} \right)_{T,N}
\]

This is a **Maxwell relation**. It is a way to estimate something by measuring something else.

So, by measuring \( \alpha (V \text{ versus } T) \) we learn about how entropy depends on pressure.

\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p,N} > 0 \implies \left( \frac{\partial S}{\partial p} \right)_{T,N} < 0
\]

If a material expands when heated, then it also becomes ordered under pressure.
Thermal expansion coefficient: Examples

Most materials expand when heated: they become ordered under pressure.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p,N} > 0 \Rightarrow \left( \frac{\partial S}{\partial p} \right)_{T,N} < 0$$

However, cold water is anomalous:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p,N} < 0 \Rightarrow \left( \frac{\partial S}{\partial p} \right)_{T,N} > 0$$

![Graph showing thermal expansion of water, diethyl ether, and n-pentane compared to benzene. The graph indicates that water expands more than other typical materials as temperature increases.]
A recipe for finding Maxwell’s relations

Assume that we want to find how the entropy depends on volume:

\[ \left( \frac{\partial S}{\partial V} \right)_{T,N} \]

1). Identify the independent variables: \((V, T, N)\).

2). Find the natural thermodynamic function for these variables: \(F(T, V, N)\).

3). Express the total differential of the natural function:

\[ dF = -SdT - pdV + \sum_{j=1}^{M} \mu_j dN_j \]

4). Based on Euler’s relations, set equal the relevant cross-derivatives:

\[
\left( \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)_T \right)_V = \left( \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right)_V \right)_T \quad \rightarrow \quad \left( \frac{\partial S}{\partial V} \right)_{T,N} = \left( \frac{\partial p}{\partial T} \right)_{V,N}
\]

By measuring how pressure depends on temperature:
We learn how entropy depends on volume! 😊
A graphical method: Mnemonic diagrams

Fundamental equations from mnemonic diagrams:

\[
dU = TdS - pdV + \sum_{j=1}^{M} \mu_j dN_j
\]

Arrow towards U: negative sign
Variable near U: differential \(dS\)

\[
dF = -SdT - pdV + \sum_{j=1}^{M} \mu_j dN_j
\]

Arrow towards F: negative sign
Variable near F: differential \(dT\)

Maxwell’s relations can be inferred from mnemonic diagrams:

\[
\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial P}\right)_S
\]

\[
-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p
\]
Isothermal compressibility

Another susceptibility, \( \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,N} \), is the isothermal compressibility.

Typically, volume shrinks with pressure: \( \left( \frac{\partial V}{\partial p} \right)_{T,N} < 0 \Rightarrow \kappa > 0 \)

Gases are generally more compressible than liquids.
Isothermal compressibility

Typically, volume shrinks with pressure:

\[
\left( \frac{\partial V}{\partial p} \right)_{T,N} < 0 \Rightarrow \kappa > 0
\]

(water is again anomalous)

Slopes < 0 imply: \( \kappa \) for hexadecane (cetane) > 0
Dependence of energy on volume

How does energy change when you squeeze materials?
The dependence of $U$ on $V$ describes intermolecular forces in matter:

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT$$

$$dU = T dS - pdV$$

$$dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT$$

At constant $T$:

$$\left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT = T \left( \frac{\partial S}{\partial V} \right)_T dV + T \left( \frac{\partial S}{\partial T} \right)_V dT - pdV$$

For liquids:

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - p = T \left( \frac{\partial p}{\partial T} \right)_V - p$$

<0 at low densities
>0 at high densities

Thermal pressure coefficient
Retraction of rubber band: Is it driven by energy or entropy?

Start with the fundamental energy equation:

\[ dU = TdS - pdV + fdL \]

If \( T \) and \( p \) are constant, the natural function is:

\[ dG = -U + pV - TS = H - TS \]

\[ \Rightarrow dG = -SdT + Vdp + fdL \]

\[ f = \left( \frac{dG}{dL} \right)_{T,p} = \left( \frac{dH}{dL} \right)_{T,p} - T \left( \frac{dS}{dL} \right)_{T,p} \]

\[ \left( \frac{dS}{dL} \right)_{T,p} = -\left( \frac{df}{dT} \right)_{p,L} \quad \text{(Maxwell relation: a way to measure)} \]

\[ \left( \frac{dH}{dL} \right)_{T,p} = f - T \left( \frac{df}{dT} \right)_{p,L} \]
Surface forces in the Langmuir trough

The surface tension equals surface pressure.

\[ S(A) = k \ln(W) = Nk \ln(A) \]

\[ dG = -SdT + Vdp - \pi dA \]

\[ \left( \frac{dS}{dA} \right)_{T,p} = \left( \frac{d\pi}{dT} \right)_{p,A} = \frac{Nk}{A} \]

(Maxwell relation)

\[ \pi A = NkT \]

Two-dimensional ideal gas law
Partial molar volume

Consider a system with \( n \) moles of a substance, in volume \( V \).

The molar volume \( v \) is defined as \( v = \frac{V}{n} \).

If the system is composed of multiple chemical species, \( n = [n_1, n_2, n_3, \ldots n_M] \)

\[
v_j = \left( \frac{\partial V}{\partial n_j} \right)_{T,p,n_{i\neq j}} = \text{partial molar volume} = \text{volume change by adding 1 molecule}
\]

The change in total volume is

\[
dV = \sum_{j=1}^{M} \left( \frac{\partial V}{\partial n_j} \right)_{T,p,n_{i\neq j}} dn_j = \sum_{j=1}^{M} v_j dn_j
\]
Apparent partial molar volume: Alcohol

Mixing alcohol and water: total volume can be smaller than the sum of the two volumes.

\[ V \neq V_a + V_w \]  
Each volume changes: there are two unknowns at any concentration.

Plot the apparent volume of alcohol:  
\[ v_{\text{app}} = \frac{V - n_w v_w}{n_a} \]
Chemical potentials: Molar free energies

The chemical potential is part of the definition of 4 functions:

\[
dU = TdS - pdV + \sum_{j=1}^{M} \mu_j dN_j
\]

\[
dF = -SdT - pdV + \sum_{j=1}^{M} \mu_j dN_j
\]

\[
dH = TdS + Vdp + \sum_{j=1}^{M} \mu_j dN_j
\]

\[
dG = -SdT + Vdp + \sum_{j=1}^{M} \mu_j dN_j
\]

But molar quantities are measured at constant \(p\) and \(T\).
Thus, the chemical potential is the partial free energy per mole or molecule:

\[
\mu_j = \left( \frac{\partial G}{\partial N_j} \right)_{T,p,N_{i\neq j}} = \left( \frac{\partial H}{\partial N_j} \right)_{T,p,N_{i\neq j}} - T \left( \frac{\partial S}{\partial N_j} \right)_{T,p,N_{i\neq j}} = h_j - Ts_j
\]
Partial molar volume

Consider a system with $n$ moles of a substance, in volume $V$.

The molar volume $v$ is defined as $v = \frac{V}{n}$.

If the system is composed of multiple chemical species, $n = [n_1, n_2, n_3, \ldots n_M]$

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The change in total volume is

$$dV = \sum_{j=1}^{M} \left( \frac{\partial V}{\partial n_j} \right)_{T, p, n_{i \neq j}} dV_j = \sum_{j=1}^{M} v_j dn_j$$

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**Diagram:**

- A: Cylinder with many small spheres
- B: Cylinder with a few larger spheres
- C: Cylinder with a single large sphere
- D: Cylinder without spheres

**Graph:**

- $v_{\text{sand}}$ against moles of sand (A to D).
Chemical potentials: Molar free energies

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\[ dU = TdS - pdV + \sum_{j=1}^{M} \mu_j dN_j \]

\[ dF = -SdT - pdV + \sum_{j=1}^{M} \mu_j dN_j \]

\[ dH = TdS + Vdp + \sum_{j=1}^{M} \mu_j dN_j \]

\[ dG = -SdT + Vdp + \sum_{j=1}^{M} \mu_j dN_j \]

But molar quantities are measured at constant \( p \) and \( T \).

Thus, the chemical potential is the partial free energy per mole or molecule:

\[ \mu_j = \left( \frac{\partial G}{\partial N_j} \right)_{T,p,N_{i\neq j}} = \left( \frac{\partial H}{\partial N_j} \right)_{T,p,N_{i\neq j}} - T \left( \frac{\partial S}{\partial N_j} \right)_{T,p,N_{i\neq j}} = h_j - Ts_j \]
Boltzmann Distribution Law

\[ T_1 = 0 \text{ K} \quad T_2 > 0 \text{ K} \quad T_3 > T_2 \]
Deriving the Boltzmann Law

Controlling $T$ and $p$: minimize $F$ (Helmholtz free energy)

$$dF = \langle E \rangle - TdS = 0 \quad \text{where} \quad S / k = -\sum_i p_i \ln(p_i)$$

Constraints:

$$\begin{align*}
\sum_i p_i &= 1 \implies \sum_i dp_i = 0 \\
\sum_i \varepsilon_i p_i &= U = \langle E \rangle \implies \sum_i \varepsilon_i dp_i = 0
\end{align*}$$

Lagrange multipliers:

$$-\ln(p_i) - 1 - \alpha - \beta\varepsilon_i = 0 \implies p_i = e^{-(1-\alpha-\beta\varepsilon_i)}$$

$$\sum_i p_i = e^{-1-\alpha} \sum_i e^{-\beta\varepsilon_i} = 1 \implies p_i = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}} = \frac{e^{-\beta\varepsilon_i}}{Q}$$

$Q = \sum_i e^{-\beta\varepsilon_i}$ is called “partition function”.

where \( S / k \) is called “partition function”.
What is the air pressure versus altitude?

The energy of some air at altitude $z$ is: $\mathcal{E}(z) = mgz$

From the Boltzmann Law: $\frac{p_i}{p_j} = e^{-\beta[\mathcal{E}_i-\mathcal{E}_j]}$

The normalized density at altitude $z$:

$$\frac{n(z)}{n(0)} = e^{-\beta[\mathcal{E}_z-\mathcal{E}_0]} = e^{-\beta mgz}$$

$$\frac{p(z)}{p(0)} = e^{-\frac{mgz}{k_B T}}$$

Pressure drops exponentially with altitude.
Interpreting the partition function

\[ Q = \sum_i e^{-\beta \varepsilon_i} \quad \text{or} \quad Q = \sum_i e^{\frac{[\varepsilon_i - \varepsilon_0]}{k_B T}} \quad \text{if we set} \quad \varepsilon_0 = 0 \]

Q describes the accessible energy states:

- \( \varepsilon_i \to 0 \)  
  - or \( T \to \infty \)
  - \( p_i = \frac{1}{M} \)  
  - and \( Q \to T \)

- \( \varepsilon_i \to \infty \)  
  - or \( T \to 0 \)
  - \( p_0 = 1 \)  
  - and \( Q \to 1 \)
Density of states

Assume there are multiple ways for the system to have energy $\varepsilon_i$.

Then the density of state $\varepsilon_i$ is: $W(\varepsilon_i)$

The partition function becomes: $Q = \sum_i W(\varepsilon_i)e^{-\beta\varepsilon_i}$

For example, a 4-bead polymer chain can be:

open or compact