Maxwell Relations and Susceptibilities

\[
\begin{align*}
A &= BC \\
\alpha &= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \\
\kappa &= -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\end{align*}
\]

\[
\begin{align*}
\left( \frac{\partial T}{\partial V} \right)_S &= - \left( \frac{\partial T}{\partial S} \right)_V \\
\left( \frac{\partial S}{\partial V} \right)_T &= - \left( \frac{\partial S}{\partial T} \right)_P \\
\left( \frac{\partial P}{\partial V} \right)_S &= \frac{\alpha}{V} \\
\left( \frac{\partial P}{\partial T} \right)_V &= \frac{1}{\kappa V} \\
\left( \frac{\partial T}{\partial V} \right)_P &= -\frac{\kappa}{\alpha}
\end{align*}
\]
Practice the Maxwell Relations!

Find a way to estimate how the entropy $S$ depends on pressure $p$!

$$
\left( \frac{\partial S}{\partial p} \right)_{T,N} = ?
$$

Hint:

$$
dG = -SdT + Vdp + \sum_{j=1}^{M} \mu_j dN_j
$$
Practice the Maxwell Relations!

Solution:

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

By measuring “volume vs. temperature”, we learn about “entropy vs. pressure”.

The susceptibility of volume to temperature is the **thermal expansion coefficient**:

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

If a material expands when heated, then it also becomes ordered under pressure.
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
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 coefficients for water, diethyl ether, n-pentane, and benzene]
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: \( \left( \frac{\partial V}{\partial p} \right)_{T,N} < 0 \iff \kappa > 0 \)

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

\( \kappa \) (Pa\(^{-1}\))

- 2.4 \( \times \) 10\(^{-9}\) for diethyl ether
- 1.4 \( \times \) 10\(^{-9}\) for benzene
- 0.4 \( \times \) 10\(^{-9}\) for water
Dependence of energy on volume

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

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

$$dU = TdS - pdV$$

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

At constant $T$:

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

, for liquids:

$\left\{ \begin{array}{l}
<0 \text{ at low densities} \\
>0 \text{ at high densities}
\end{array} \right.$

Thermal pressure coefficient
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 general change in 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.

\[ V \neq V_a + V_w \quad \text{Each partial volume changes and is unknown at any concentration.} \]

Plot the apparent volume of alcohol:

\[ v_{app} = \frac{V - n_w v_w}{n_a} \]
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:

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

\[ p_i = \frac{e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}} = \frac{e^{-\beta \varepsilon_i}}{Q} \]
Deriving the Boltzmann Law

Controlling $T$: minimize $F$ (Helmholtz free energy).

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

Constraints:

$$\begin{cases} 
\sum_i p_i = 1 & \Rightarrow & \sum_i dp_i = 0 \\
\sum_i \varepsilon_i p_i = U = \langle E \rangle & \Rightarrow & d\langle E \rangle = \sum_i \varepsilon_i dp_i = 0 
\end{cases}$$

Lagrange multipliers:

$$\varepsilon_i + kT[\ln(p_i) + 1] - \alpha = 0 \quad \Rightarrow \quad p_i = e^{\frac{\varepsilon_i}{kT} - 1 + \frac{\alpha}{kT}}$$

$$\sum_i p_i = e^{-1-\alpha} \sum_i e^{\frac{\varepsilon_i}{kT}} = 1 \quad \Rightarrow \quad p_i = \frac{e^{\frac{\varepsilon_i}{kT}}}{\sum_i e^{\frac{\varepsilon_i}{kT}}} = \frac{e^{\frac{\varepsilon_i}{kT}}}{Q}$$

$$Q = \sum_i e^{\frac{\varepsilon_i}{kT}} \quad \text{is called "partition function".}$$
What is the air pressure versus altitude?

The energy of some air at altitude $z$ is: $\varepsilon(z) = mgz$

From the Boltzmann Law:

$$\frac{p_i}{p_j} = e^{-\beta[\varepsilon_i - \varepsilon_j]}$$

The normalized density at altitude $z$:

$$\frac{n(z)}{n(0)} = e^{-\beta[\varepsilon_z - \varepsilon_0]} = e^{-\beta mgz}$$

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

Pressure drops exponentially with altitude.
Interpreting the partition function

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

if we set \( \varepsilon_0 = 0 \)

\[ \beta = \frac{1}{k_B T} \]

Q describes the accessible energy states:

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

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

$p(E)$

Lower Temperature

Higher Temperature

\[ E \]

\[ j \]

**Low T**

- 9
- 8
- 7
- 6
- 5
- 4
- 3
- 2
- 1

**Medium T**

- 9
- 8
- 7
- 6
- 5
- 4
- 3
- 2
- 1

**High T**

- 9
- 8
- 7
- 6
- 5
- 4
- 3
- 2
- 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
4-bead polymer chain

The partition function is:

\[ Q = W(\varepsilon_o) e^{-\beta \varepsilon_o} + W(\varepsilon_c) e^{-\beta \varepsilon_c} = 1 + 4 e^{-\beta \varepsilon_c} \]

The probability of the compact state:

\[ p_c = \frac{1}{1 + 4 e^{-\beta \varepsilon_c}} \]

The probability of the open state:

\[ p_o = \frac{4 e^{-\beta \varepsilon_c}}{1 + 4 e^{-\beta \varepsilon_c}} \]
Multiplicities of states for a 6-bead chain