Coarse Graining & Free Energy Functionals

Ideal Gas, Canonical Ensemble, Helmholtz Free Energy

\[ A(N,V,T) = N k T \left[ \log \left( \frac{N}{V} \left( \frac{\hbar}{2 \pi m k T} \right)^{3/2} \right) - 1 \right] \]

Thermal Wavelength \( \lambda = \frac{\hbar}{\sqrt{2 \pi m k T}} = \frac{\hbar}{\left( \frac{2 \pi m k T}{\hbar^2} \right)^{1/2}} \)

\( N/V = \rho \)

\[ \mathcal{F}(\rho, T) = \frac{A(N,V,T)}{V} = \rho k T \left[ \log (\rho \lambda^3) - 1 \right] \]

Free Energy Density

Define local density \( \rho(x) = \int G(x-x') \delta(x' - x_n) \, dx' \)

- Smears out discrete nature of atoms
- Width \( W \gg \) mean-free-path
  \( \ll \) macroscopic density gradients

\[ \mathcal{F}(\rho(x), T) = \rho(x) k T \left[ \log (\rho(x) \lambda^3) - 1 \right] \]

\[ Z = e^{- \int \mathcal{F}(\rho(x), T) \, dx / k T} \]
Chemical Potential
\[ \mu = \frac{\partial A}{\partial N} = \frac{\partial (A/V)}{\partial (N/V)} = \frac{\partial F}{\partial \rho} \]

Chemical Potential Varies with Space
\[ \mu(X) = \frac{\delta F(X)}{\delta \rho} \]

\[ \frac{\delta F}{\delta \rho} = \frac{\delta}{\delta \rho} \left( \rho kT \left[ \log(\rho \lambda^3) - 1 \right] \right) = kT \frac{\partial}{\partial \rho} (\log(\rho \lambda^3)) + \frac{\rho kT}{\rho} \]
\[ \mu = \frac{\delta F}{\delta \rho} = kT \log(\rho \lambda^3) \]

\[ \mu = \text{"Pressure" on atoms} \]
\[ -\frac{\partial \mu}{\partial x} = \text{"Pressure" gradient = Force on atom} \]

\[ \eta \left( \frac{\partial \mu}{\partial x} \right) \rho = J \]
\[ J = \text{Current of atoms} \] (Assume linear response to external/ internal force)

\[ \frac{\partial \mu}{\partial x} = \frac{\partial}{\partial x} \left( kT \log(\rho \lambda^3) \right) = \frac{kT}{\rho} \frac{\partial \rho}{\partial x} \]
\[ J = -\eta \left( \frac{kT}{\rho} \frac{\partial \rho}{\partial x} \right) \rho = -\eta kT \frac{\partial \rho}{\partial x} \]
\[ \frac{\partial \rho}{\partial t} = -\nabla \cdot J = \eta kT \frac{\partial^2 \rho}{\partial x^2} \]

**Conservation Law (Gauss' Law)**
Notice:

(1) Derived diffusion equation
\[ \frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} \]
from free energy density, linear response

(2) Rediscovered Einstein relation
\[ D = \eta kT \]

(3) \(-\frac{\partial \mu}{\partial x}\) acts just like an external force,
Even though \(\mu\) comes from ideal gas
(no potential energy at all)

(4) Linear response \(J = -\eta p \frac{\partial \mu}{\partial x}\) only makes sense if collision length \(\ll\) variations of \(p\) \((\frac{\partial p}{\partial x})\),
-Non-ideal gas!

(5) Actual \(\eta\) is surely density dependent
\((\eta(p) \rightarrow 0\) as \(p \rightarrow 0\) : nothing to collide with\)
\[ J = -\eta(p) kT \frac{\partial p}{\partial x} = -D(p) \frac{\partial^2 p}{\partial x^2} \]
\[ \frac{\partial p}{\partial t} = \frac{1}{\delta x} \left[ D(p) \frac{\partial p}{\partial x} \right] = \nabla \cdot \left[ D(p) \nabla p \right] \]
Correct Density-Dependent Diffusion Equation