Thermodynamic Relationships

\[
\left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z} \quad \text{FFF1}
\]

\[
\left( \frac{\partial y}{\partial x} \right)_z = \frac{\partial x}{\partial y} \quad \left( \frac{\partial z}{\partial x} \right)_y = -1 \quad \text{FFF3}
\]

\[
\left( \frac{\partial y}{\partial x} \right)_z = \frac{\partial x}{\partial y} \quad \frac{\partial z}{\partial x} \quad \frac{\partial z}{\partial y} \quad \text{FFF2}
\]

\[
\left( \frac{\partial x}{\partial y} \right)_w = \frac{\partial x}{\partial y} + \frac{\partial x}{\partial \frac{\partial}{\partial y}} \quad \frac{\partial z}{\partial y} \quad \text{FFF4}
\]

**Internal Energy**

\[ U = U(S,V,N) \]
\[ dU = TdS - pdV + \mu dN \]

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

**Maxwell Relations**

\[
\left( \frac{\partial T}{\partial V} \right)_{S,N} = -\left( \frac{\partial V}{\partial S} \right)_{V,N} \quad \frac{\partial T}{\partial N} = \left( \frac{\partial T}{\partial S} \right)_{S,V} = \beta \quad \frac{\partial T}{\partial V} = -\beta \mu
\]

**Equivalently: Entropy**

\[ S = S(U,V,N) \]
\[ dS = \beta dU + \beta pdV - \beta \mu dN \]

\[
\left( \frac{\partial S}{\partial U} \right)_{V,N} = \beta = \frac{1}{k_B T} \quad \left( \frac{\partial S}{\partial V} \right)_{U,N} = \beta p \quad \left( \frac{\partial S}{\partial N} \right)_{U,V} = -\beta \mu
\]

**Maxwell Relations**

\[
\left( \frac{\partial S}{\partial V} \right)_{U,N} = \left( \frac{\partial \beta p}{\partial U} \right)_{V,N} \quad \left( \frac{\partial S}{\partial U} \right)_{V,N} = -\left( \frac{\partial \mu}{\partial U} \right)_{V,N} \quad \left( \frac{\partial \beta p}{\partial N} \right)_{V,U} = -\left( \frac{\partial \mu}{\partial V} \right)_{N,U}
\]

**Helmholtz Free Energy**

\[ F = U - TS = F(T,V,N) \]
\[ dF = -SdT - pdV + \mu dN \]

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

**Maxwell Relations**

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

**Gibbs Free Energy**

\[ G = F + pV = U - TS + pV = G(T,p,N) = N \mu(T,p) \]
\[ dG = -SdT + Vdp + \mu dN \]

\[
\left( \frac{\partial G}{\partial T} \right)_{p,N} = -S \quad \left( \frac{\partial G}{\partial p} \right)_{T,N} = V \quad \left( \frac{\partial G}{\partial N} \right)_{T,p} = \mu
\]
Maxwell Relations
\[
\left( \frac{\partial S}{\partial p} \right)_{T,N} = -\left( \frac{\partial V}{\partial T} \right)_{P,N} \quad \left( \frac{\partial S}{\partial N} \right)_{T,P} = -\left( \frac{\partial \mu}{\partial T} \right)_{N,P} \quad \left( \frac{\partial V}{\partial N} \right)_{P,T} = \left( \frac{\partial \mu}{\partial p} \right)_{N,T}
\]
d\mu = -s dT + vdP
\[
\left( \frac{\partial \mu}{\partial T} \right)_{P,N} = -s = -\frac{S}{N} \quad \left( \frac{\partial \mu}{\partial P} \right)_{T,N} = v = \frac{V}{N}
\]
Maxwell relation for µ
\[
\left( \frac{\partial s}{\partial p} \right)_{T} = \left( \frac{\partial V}{\partial T} \right)_{P}
\]

Thermodynamic Potential
\[
\Pi = -F + \mu N = -U + TS + \mu N = \Pi(T,V,\mu) = Vp(T,\mu)
\]
d\Pi = SdT + pdV + Nd\mu
\[
\left( \frac{\partial \Pi}{\partial T} \right)_{V,\mu} = S \quad \left( \frac{\partial \Pi}{\partial V} \right)_{T,\mu} = p \quad \left( \frac{\partial \Pi}{\partial \mu} \right)_{T,V} = N
\]
Maxwell Relations
\[
\left( \frac{\partial S}{\partial V} \right)_{T,\mu} = \left( \frac{\partial p}{\partial T} \right)_{V,\mu} \quad \left( \frac{\partial S}{\partial \mu} \right)_{T,V} = \left( \frac{\partial N}{\partial T} \right)_{\mu,V} \quad \left( \frac{\partial p}{\partial \mu} \right)_{T,V} = \left( \frac{\partial N}{\partial V} \right)_{\mu,T}
\]
dP = s dT + n d\mu
\[
\left( \frac{\partial p}{\partial T} \right)_{V,\mu} = s = \frac{S}{V} \quad \left( \frac{\partial p}{\partial \mu} \right)_{T,V} = n = \frac{N}{V}
\]
Maxwell Relation for p
\[
\left( \frac{\partial s}{\partial \mu} \right)_{T,V} = \left( \frac{\partial n}{\partial T} \right)_{\mu,V}
\]

Magnetic Free Energy
\[
A = U(S,M) - TS = A(T,M,N)
\]
dA = -SdT + HdM
\[
\left( \frac{\partial A}{\partial T} \right)_{M} = -S \quad \left( \frac{\partial A}{\partial M} \right)_{T} = H
\]
Maxwell Relations
\[
\left( \frac{\partial S}{\partial M} \right)_{T} = -\left( \frac{\partial H}{\partial T} \right)_{M}
\]
Magnetic Free Energy
\[
F = A - HM = U - TS - HM = F(T,H)
\]
dF = -SdT - MdH
\[
\left( \frac{\partial F}{\partial T} \right)_{H} = -S \quad \left( \frac{\partial F}{\partial H} \right)_{T} = -M
\]
Maxwell Relations
\[ \left( \frac{\partial S}{\partial H} \right)_T = - \left( \frac{\partial M}{\partial T} \right)_H \]

Common thermodynamic second derivatives. These are all nonnegative because of the second law of thermodynamics.

Heat Capacity at constant volume
\[ C_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \geq 0 \]

All other heat capacities such that
\[ C_p = T \left( \frac{\partial S}{\partial T} \right)_p \geq 0, \quad C_H = T \left( \frac{\partial S}{\partial T} \right)_H \geq 0 \quad \text{and} \quad C_M = T \left( \frac{\partial S}{\partial T} \right)_M \geq 0 \]
are also non-negative.

Isothermal Compressibility
\[ K_T = \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_T = \frac{1}{n} \left( \frac{\partial n}{\partial p} \right)_T = \frac{1}{n^2} \left( \frac{\partial n}{\partial \mu} \right)_T = \frac{1}{n^2} \left( \frac{\partial^2 p}{\partial \mu^2} \right)_T \geq 0 \]

Isothermal Susceptibility
\[ \chi_T = \left( \frac{\partial M}{\partial H} \right)_T = \frac{1}{\left( \frac{\partial H}{\partial M} \right)_T} \geq 0 \]

Microcanonical partition function
\[ \Omega(U,V,N) = \text{trace}(\Delta_{\Delta U}(H - U)) = \text{number of states in small energy range near}\ U \]
\[ S(U,V,N) = \ln(\Omega(U,V,N)) \]

Canonical partition function
\[ Z(T,V,N) = \text{trace}(\exp(-\beta H)) = \sum U e^{-\beta U} \Omega(U,V,N) = \frac{1}{N!h^{3N}} \int d^N \vec{p} d^N \vec{r} e^{-\beta H} \]
\[ F(T,V,N) = -k_B T \ln(Z(T,V,N)) \]

Grand canonical partition function
\[ \Xi(T,V,\mu) = \text{trace}(\exp(-\beta H + \beta \mu N)) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T,V,N) \]
\[ \Pi(T,V,\mu) = k_B T \ln(\Xi(T,V,\mu)) = V p(T,\mu) \]
\[ p(T,\mu) = \frac{k_B T}{V} \ln(\Xi(T,V,\mu)) \]

Isobaric partition function
\[ Y(T,p,N) = \text{trace}(\exp(-\beta H - \beta p V)) = \int dV e^{-\beta p V} Z(T,V,N) \]
\[ G(T,p,N) = -k_B T \ln(Y(T,p,N)) = N\mu(T,p) \]
\[ \mu(T,p) = -\frac{k_B T}{N} \ln(Y(T,p,N)) \]
Clausius-Clapyron Equation
\[
dp_o = \frac{s_2 - s_1}{v_2 - v_1} = \frac{L}{T(v_2 - v_1)}
\]
where \( p_o (T) \) is the coexistence pressure curve between two phases, \( s \) is the entropy per particle of the phases, \( v \) is the volume per particle of the phases and \( l \) is the latent heat of transformation.

Statistical Relations for some common thermodynamic first derivatives
\[
U = \frac{\partial \beta F}{\partial \beta} = \text{trace}\left(He^{-\beta H}\right) = \frac{\langle H \rangle}{\langle E \rangle} \text{ energy}
\]
\[
n = \frac{\partial p}{\partial \mu} = \text{trace}\left(Ne^{-\beta H + \beta \mu N}\right) = \frac{\langle N \rangle}{V} \text{ density}
\]
\[
M = -\frac{\partial F}{\partial \mathcal{H}} = \text{trace}\left(Me^{-\beta E}\right) = \langle M \rangle \text{ magnetization}
\]

Statistical Relations that relate thermodynamic second derivatives to variances
\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_T = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2} \geq 0
\]
\[
K_T = \frac{1}{n^2} \left( \frac{\partial n}{\partial \mu} \right)_T = \frac{1}{n^2} \left( \frac{\partial^2 p}{\partial \mu^2} \right)_T = \frac{\langle N^2 \rangle - \langle N \rangle^2}{V k_B T} = \frac{1}{nk_B T} \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = K_T^{\text{ideal}} \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \geq 0
\]
\[
\chi_T = \left( \frac{\partial M}{\partial \mathcal{H}} \right)_T = -\frac{\langle M^2 \rangle - \langle M \rangle^2}{1/k_B T} \geq 0
\]