Thermodynamic Relationships

\[
\left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z} \quad \text{FFF1} \quad \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right) = -1 \quad \text{FFF3}
\]

\[
\frac{\partial \left( \frac{\partial y}{\partial x} \right)_z}{\partial x} = \frac{\partial \left( \frac{\partial y}{\partial x} \right)_z}{\partial x} \quad \text{FFF2} \quad \frac{\partial x}{\partial y}_w = \frac{\partial x}{\partial y}_z + \left( \frac{\partial x}{\partial y}_z \right)_{y_w}
\]

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

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

Equivalently: Entropy

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

Maxwell Relations

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

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

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

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
\[
\left( \frac{\partial S}{\partial p} \right)_{T,N} = -\left( \frac{\partial V}{\partial T} \right)_{p,N} \quad \left( \frac{\partial S}{\partial N} \right)_{T,p} = -\left( \frac{\partial \mu}{\partial T} \right)_{N,p} \quad \left( \frac{\partial V}{\partial N} \right)_{p,T} = \left( \frac{\partial \mu}{\partial N} \right)_{N,T}
\]
\[d\mu = -sdT + vdp\]
\[\left( \frac{\partial \mu}{\partial T} \right)_{p,N} = -S = -\frac{S}{N} \quad \left( \frac{\partial \mu}{\partial p} \right)_{T,N} = v = \frac{V}{N}\]
Maxwell relation for \(\mu\)
\[\left( \frac{\partial s}{\partial \mu} \right)_{T} = -\left( \frac{\partial V}{\partial T} \right)_{p}\]

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
\[\left( \frac{\partial s}{\partial V} \right)_{T,\mu} = \left( \frac{\partial p}{\partial T} \right)_{V,\mu} \quad \left( \frac{\partial S}{\partial \mu} \right)_{T,V} = \left( \frac{\partial N}{\partial T} \right)_{\mu,V} \quad \left( \frac{\partial p}{\partial \mu} \right)_{T,V} = \left( \frac{\partial N}{\partial \mu} \right)_{\mu,T}\]
\[dp = sdT + nd\mu\]
\[\left( \frac{\partial p}{\partial T} \right)_{V,\mu} = s = \frac{S}{V} \quad \left( \frac{\partial p}{\partial \mu} \right)_{T,V} = n = \frac{N}{V}\]
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
\[
\frac{\partial S}{\partial H}_T = -\frac{\partial M}{\partial T}_H
\]

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
\[
C_p = T \left( \frac{\partial S}{\partial T} \right)_p \geq 0, ~ C_H = T \left( \frac{\partial S}{\partial T} \right)_H \geq 0 \quad \text{and} \quad C_M = T \left( \frac{\partial S}{\partial T} \right)_M \geq 0
\]
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
\[
\Omega(U,V,N) = \text{trace}(\Delta_{\mu}(H-U)) = \text{number of states in small energy range near } U
\]
\[
S(U,V,N) = \ln(\Omega(U,V,N))
\]
Canonical partition function
\[
Z(T,V,N) = \text{trace}(\exp(-\beta H)) = \sum_U e^{-\beta U} \Omega(U,V,N) = \frac{1}{N!h^N} \int d^N p d^N r e^{-\beta H}
\]
\[
F(T,V,N) = -k_B T \ln(Z(T,V,N))
\]

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

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
\[
\frac{dp_o}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{L}{T(v_2 - v_1)}
\]
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
\[
U = \left( \frac{\partial \beta F}{\partial \beta} \right)_{V,N} = \frac{\text{trace}(He^{-\beta H})}{\text{trace}(e^{-\beta H})} = \langle H \rangle = \langle E \rangle \quad \text{energy}
\]
\[
n = \left( \frac{\partial p}{\partial \mu} \right)_{T,V} = \frac{\text{trace}(Ne^{-\beta H + \beta \mu N})}{\text{trace}(e^{-\beta H + \beta \mu N})} = \frac{\langle N \rangle}{V} \quad \text{density}
\]
\[
M = -\left( \frac{\partial F}{\partial H} \right)_{T,N} = \frac{\text{trace}(Me^{-\beta H})}{\text{trace}(e^{-\beta H})} = \langle M \rangle \quad \text{magnetization}
\]

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