

3.1: Basic Thermodynamics

In the [microcanonical ensemble](#), the entropy S is a natural function of N, V and E , i.e., $S = S(N, V, E)$. This can be inverted to give the energy as a function of N, V , and S , i.e., $E = E(N, V, S)$. Consider using [Legendre transformation](#) to change from S to T using the fact that

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

The Legendre transform \tilde{E} of $E(N, V, S)$ is

$$\begin{aligned}\tilde{E}(N, V, T) &= E(N, V, S(T)) - S \frac{\partial E}{\partial S} \\ &= E(N, V, S(T)) - TS\end{aligned}$$

The quantity $\tilde{E}(N, V, T)$ is called the **Hemlholtz free energy** and is given the symbol $A(N, V, T)$ and is the fundamental energy in the canonical ensemble. The differential of A is

$$dA = \left(\frac{\partial A}{\partial T} \right)_{N,V} dT + \left(\frac{\partial A}{\partial V} \right)_{N,T} dV + \left(\frac{\partial A}{\partial N} \right)_{T,V} dN$$

However, from $A = E - TS$, we have

$$dA = dE - TdS - SdT$$

From the first law, dE is given by

$$dE = TdS - PdV + \mu dN$$

Thus,

$$dA = -PdV - SdT + \mu dN$$

Comparing the two expressions, we see that the thermodynamic relations are

$$S = - \left(\frac{\partial A}{\partial T} \right)_{N,V}$$

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N,T}$$

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T}$$

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