Thermodynamic perturbation expansion [tln80]

Consider a classical dynamical system in the canonical ensemble.

$$\mathcal{H} = \mathcal{H}_0 + V.$$

The term $\mathcal{H}_0$ represents the dominant contribution to the energy of the system under the circumstances of interest. We assume that the Helmholtz free energy, $A_0(T, V, N)$, for that part alone can be calculated exactly:

$$e^{-\beta A_0} = \int d\Gamma\, e^{-\beta\mathcal{H}_0}, \qquad d\Gamma \doteq d^{6N}X, \qquad \beta \doteq \frac{1}{k_BT}.$$

We can then treat V perturbatively via the following expansion:

$$e^{-\beta A} = \int d\Gamma\, e^{-\beta(\mathcal{H}_0+V)} \simeq \int d\Gamma\, e^{-\beta\mathcal{H}_0}\left(1 - \beta V + \frac{1}{2}\beta^2V^2\right).$$

This expression is then further expanded by using $\ln(1-x) \simeq -x + x^2/2$:

$$\begin{aligned}
-\beta A &\simeq \ln\left(e^{-\beta A_0} - \beta\int d\Gamma\, V e^{-\beta A_0} + \frac{1}{2}\beta^2\int d\Gamma\, V^2 e^{-\beta\mathcal{H}_0}\right) \\
&\simeq -\beta A_0 + \ln\left(1 - \beta\int d\Gamma\, V e^{\beta(A_0-\mathcal{H}_0)} + \frac{1}{2}\beta^2\int d\Gamma\, V^2 e^{\beta(A_0-\mathcal{H}_0)}\right).
\end{aligned}$$

$$\Rightarrow\ A = A_0 + \int d\Gamma\left(V - \frac{1}{2}\beta V^2\right)e^{\beta(A_0-\mathcal{H}_0)} + \frac{1}{2}\beta\left[\int d\Gamma\, V e^{\beta(A_0-\mathcal{H}_0)}\right]^2.$$

With ensemble averages,

$$\langle V\rangle \doteq \frac{\int d\Gamma\, V e^{-\beta\mathcal{H}_0}}{\int d\Gamma\, e^{-\beta\mathcal{H}_0}} = \int d\Gamma\, V e^{\beta(A_0-\mathcal{H}_0)}, \qquad \langle V^2\rangle = \int d\Gamma\, V^2 e^{\beta(A_0-\mathcal{H}_0)},$$

and the relation

$$\langle V^2\rangle - \langle V\rangle^2 = \langle (V - \langle V\rangle)^2\rangle,$$

we can write

$$A = A_0 + \langle V\rangle - \frac{1}{2}\beta\langle (V - \langle V\rangle)^2\rangle.$$

The criterion of applicability for this expansion is $\langle V\rangle/N \ll k_BT$. Note that if $\langle V\rangle = 0$ then the leading-order perturbation always reduces the Helmholtz free energy.