7.1: General Formulation of Distribution Functions

Recall the expression for the configurational partition function:

$$Z_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U(r_1,\ldots,r_N)}$$

Suppose that the potential U can be written as a sum of two contributions

$$U(\mathbf{r}_1,\ldots,\mathbf{r}_N) = U_0(\mathbf{r}_1,\ldots,\mathbf{r}_N) + U_1(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

where U_1 is, in some sense, small compared to U_0. An extra bonus can be had if the partition function for U_0 can be evaluated analytically.

Let

$$Z_N{}^{(0)} = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_0(r_1,\ldots,r_N)}$$

Then, we may express Z_N as

$$\begin{aligned} Z_N &= \frac{Z_N{}^{(0)}}{Z_N{}^{(0)}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_0(r_1,\ldots,r_N)} e^{-\beta U_1(r_1,\ldots,r_N)} \\ &= Z_N{}^{(0)} \langle e^{-\beta U_1(r_1,\ldots,r_N)} \rangle_0 \end{aligned}$$

where $\langle \cdots \rangle_0$ means average with respect to U_0 only. If U_1 is small, then the average can be expanded in powers of U_1:

$$\begin{aligned} \langle e^{-\beta U_1} \rangle_0 &= 1 - \beta \langle U_1 \rangle_0 + \frac{\beta^2}{2!} \langle U_1^2 \rangle_0 - \frac{\beta^3}{3!} \langle U_1^3 \rangle_0 + \cdots \\ &= \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0 \end{aligned}$$

The free energy is given by

$$A(N,V,T) = -\frac{1}{\beta} \ln\left(\frac{Z_N}{N!\lambda^{3N}}\right) = -\frac{1}{\beta} \ln\left(\frac{Z_N^{(0)}}{N!\lambda^{3N}}\right) - -\frac{1}{\beta} \ln\langle e^{-\beta U_1} \rangle_0$$

Separating A into two contributions, we have

$$A(N,V,T) = A^{(0)}(N,V,T) + A^{(1)}(N,V,T)$$

where $A^{(0)}$ is independent of U_1 and is given by

$$A^{(0)}(N,V,T) = -\frac{1}{\beta} \ln\left(\frac{Z_N{}^{(0)}}{N!\lambda^{3N}}\right)$$

and

$$\begin{aligned} A^{(1)}(N,V,T) &= -\frac{1}{\beta} \ln\langle e^{-\beta U_1} \rangle_0 \\ &= -\frac{1}{\beta} \ln\langle \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0 \end{aligned}$$

We wish to develop an expansion for $A^{(1)}$ of the general form

$$A^{(1)} = \sum_{k=1}^{\infty} \frac{(-\beta)^{k-1}}{k!} \omega_k$$

where ω_k are a set of expansion coefficients that are determined by the condition that such an expansion be consistent with $\ln\langle \sum_{k=0}^{\infty} (-\beta)^k \langle U_1^k \rangle_0 / k!$.

Using the fact that

$$\ln(1+x) = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{x^k}{k}$$

we have that

$$\begin{aligned} -\frac{1}{\beta}\ln\left(\sum_{k=0}^{\infty}\frac{(-\beta)^k}{k!}\langle U_1^k\rangle_0\right) &= -\frac{1}{\beta}\ln\left(1+\sum_{k=0}^{\infty}\frac{(-\beta)^k}{k!}\langle U_1^k\rangle_0\right) \\ &= -\frac{1}{\beta}\sum_{k=1}^{\infty}(-1)^{k-1}\frac{1}{k}\left(\sum_{l=1}^{\infty}\frac{(-\beta)^l}{l!}\langle U_1^l\rangle_0\right)^k \end{aligned}$$

Equating this expansion to the proposed expansion for $A^{(1)}$, we obtain

$$\sum_{k=1}^{\infty}(-1)^{k-1}\frac{1}{k}\left(\sum_{l=1}^{\infty}\frac{(-\beta)^l}{l!}\langle U_1^l\rangle_0\right)^k = \sum_{k=1}^{\infty}(-\beta)^k\frac{\omega_k}{k!}$$

This must be solved for each of the undetermined parameters ω_k, which can be done by equating like powers of β on both sides of the equation. Thus, from the β^1 term, we find, from the right side:

$$\text{Right Side}: \quad -\frac{\beta\omega_1}{1!}$$

and from the left side, the $j=1$ and $k=1$ term contributes:

$$\text{Left Side}: \quad -\frac{\beta\langle U_1\rangle_0}{1!}$$

from which it can be easily seen that

$$\omega_1 = \langle U_1\rangle_0$$

Likewise, from the β^2 term,

$$\text{Right Side}: \quad \frac{\beta^2}{2!}\omega_2$$

and from the left side, we see that the $l=1, k=2$ and $l=2, k=1$ terms contribute:

$$\text{Left Side}: \quad \frac{\beta^2}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right)$$

Thus,

$$\omega_2 = \langle U_1^2\rangle_0 - \langle U_1\rangle_0^2$$

For β^3, the right sides gives:

$$\text{Right Side}: \quad -\frac{\beta^3}{3!}\omega_3$$

the left side contributes the $l=1, k=3, k=2, l=2$ and $l=3, k=1$ terms:

$$\text{Left Side}: -\frac{\beta^3}{6}\langle U_1^3\rangle + (-1)^2\frac{1}{3}(-\beta\langle U_1\rangle_0)^3 - \frac{1}{2}\left(-\beta\langle U_1\rangle_0 + \frac{1}{2}\beta^2\langle U_1^2\rangle\right)^2$$

Thus,

$$\omega_3 = \langle U_1^3\rangle_0 + 2\langle U_1\rangle_0^3 - 3\langle U_1\rangle_0\langle U_1^2\rangle_0$$

Now, the free energy, up to the third order term is given by

$$\begin{aligned} A &= A^{(0)} + \omega_1 - \frac{\beta}{2}\omega_2 + \frac{\beta^2}{6}\omega_3 \cdots \\ &= -\frac{1}{\beta}\ln\left(\frac{Z_N{}^{(0)}}{N!\lambda^{3N}}\right) + \langle U_1\rangle_0 - \frac{\beta}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right) + \frac{\beta^2}{6}\left(\langle U_1^3\rangle - 3\langle U_1\rangle_0\langle U_1^2\rangle_0 + 2\langle U_1\rangle_0^3\right) + \cdots \end{aligned}$$

In order to evaluate $\langle U_1\rangle_0$, suppose that U_1 is given by a pair potential

$$U_1(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{2}\sum_{i\neq j} u_1(|\mathbf{r}_i - \mathbf{r}_j|)$$

Then,

$$\begin{aligned} \langle U_1\rangle_0 &= \frac{1}{Z_N{}^{(0)}}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{1}{2}\sum_{i\neq j} u_1(|\mathbf{r}_i - \mathbf{r}_j|)e^{-\beta U_0(r_1,\ldots,r_N)} \\ &= \frac{N(N-1)}{2Z_N{}^{(0)}}\int d\mathbf{r}_1 d\mathbf{r}_2 u_1(|r_1 - r_2|)\int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ &= \frac{N^2}{2V^2}\int d\mathbf{r}_1 d\mathbf{r}_2 u_1(|\mathbf{r}_1 - \mathbf{r}_2|)g_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{\rho^2 V}{2}\int_0^\infty 4\pi r^2 u_1(r) g_0(r) dr \end{aligned}$$

The free energy is therefore given by

$$A(N,V,T) = -\frac{1}{\beta}\ln\left(\frac{Z_N^{(0)}}{N!\lambda^{3N}}\right) + \frac{1}{2}\rho^2 V\int_0^\infty 4\pi r^2 u_1(r) g_0(r) dr - \frac{\beta}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right)\cdots$$