7.2: General Distribution Functions and Correlation Functions

We begin by considering a general N-particle system with Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(r_1, \cdots, r_N)$$

For simplicity, we consider the case that all the particles are of the same type. Having established the equivalence of the ensembles in the thermodynamic limit, we are free to choose the ensemble that is the most convenient on in which to work. Thus, we choose to work in the canonical ensemble, for which the partition function is

$$Q(N,V,T) = \frac{1}{N!h^{3N}} \int d^{3N}pd^{3N}re^{-\beta \sum_{i=1}^{3N} \frac{P_i^2}{2m}} e^{-\beta U(r_1,\cdots,r_N)}$$

The 3N integrations over momentum variables can be done straightforwardly, giving

$$\begin{aligned} Q(N,V,T) &= \frac{1}{N!\lambda^{3N}} \int dr_1 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \\ &= \frac{Z_N}{N!\lambda^{3N}} \end{aligned}$$

where $\lambda = \sqrt{\frac{\beta h^2}{2\pi m}}$ is the thermal wavelength and the quantity Z_N is known as the **configurational partition function**

$$Z_N = \int dr_1 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)}$$

The quantity

$$\frac{e^{-\beta U(r_1,\cdots,r_N)}}{Z_N} dr_1 \cdots dr_N \equiv P^{(N)}(r_1,\cdots,r_N) dr_1 \cdots dr_N$$

represents the probability that particle 1 will be found in a volume element dr_1 at the point r_1, particle 2 will be found in a volume element dr_2 at the point r_2,..., particle N will be found in a volume element dr_N at the point r_N. To obtain the probability associated with some number n;*SPMlt*;N of the particles, irrespective of the locations of the remaining n+1,...,N particles, we simply integrate this expression over the particles with indices n+1,...,N:

$$P^{(n)}(r_1,\cdots,r_n) dr_1 \cdots dr_n = \frac{1}{Z_N} \left[\int dr_{n+1} \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \right] dr_1 \cdots dr_n$$

The probability that *any* particle will be found in the volume element dr_1 at the point r_1 and *any* particle will be found in the volume element dr_2 at the point r_2,...,*any* particle will be found in the volume element dr_n at the point r_n is defined to be

$$P^{(n)}(r_1,\cdots,r_n) dr_1 \cdots dr_n = \frac{N!}{(N-n)!} P^{(n)}(r_1,\cdots,r_n) dr_1 \cdots dr_n$$

which comes about since the first particle can be chosen in N ways, the second chosen in N-1 ways, etc.

Consider the special case of $n = 1$. Then, by the above formula,

$$\begin{aligned} P^{(1)}(r_1) &= \frac{1}{Z_N} \frac{N!}{(N-1)!} \int dr_2 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \\ &= \frac{N}{Z_N} \int dr_2 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \end{aligned}$$

Thus, if we integrate over all r_1, we find that

$$\frac{1}{V} \int dr_1 p^{(1)}(r_1) = \frac{N}{V} = p$$

Thus, $P^{(1)}$ actually counts the number of particles likely to be found, on average, in the volume element dr_1 at the point r_1. Thus, integrating over the available volume, one finds, not surprisingly, all the particles in the system.