Distribution functions

1 Closed systems

In this section we consider a system where the independent variables are N, V, T (canonical ensemble). The probability distribution function for this system is given by the following expression,

$$P(\vec{q}_1 \cdots \vec{q}_N, \vec{p}_1 \cdots \vec{p}_N) = \frac{e^{-\beta\mathcal{H}}}{N! h^{3N} Q_N}, \tag{1}$$

where Q_N is the partition function. One can then integrate out the momentum degrees of freedom to obatin

$$P(\vec{q}_1 \cdots \vec{q}_N) = \frac{e^{-\beta U(\vec{q}_1 \cdots \vec{q}_N)}}{\mathcal{Z}_N}, \tag{2}$$

where $\mathcal{Z}_N$ is the configurational partition function. An important set of properties which is used to understand the structural aspects in the system are the $n(< N)$ body correlations. The n body correlation can be obtained from the above probability distribution in the following way,

$$P_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n) = \frac{1}{\mathcal{Z}_N} \int \cdots \int e^{-\beta U(\vec{q}_1 \cdots \vec{q}_N)} \mathrm{d}\vec{q}_{n+1} \cdots \mathrm{d}\vec{q}_N, \tag{3}$$

where $P_N^{(n)}$ is the probability of finding n particles at $\vec{q}_i = \{\vec{q}_1 \cdots \vec{q}_n\}$ irrespective of the configurations of the other $N - n$ particles. In the system consisting of identical particles, one can choose these n particles in $N!/(N-n)!$ ways. Following this, we define a modified n-body correlation function which has the following form,

$$\rho_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n) = \frac{N!}{(N-n)!} P_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n). \tag{4}$$

The difference between $\rho_N^{(n)}(q_1 \cdots q_n)$ and $P_N^{(n)}(q_1 \cdots q_n)$ is that after integration over all (N) particle positions , the former gives $N!/(N-n)!$ whereas the latter gives 1. In case of a mixture of A and B particles, the $n = n_A + n_B$ correlation takes the following form,

$$\rho_N^{(n_A,n_B)}(\vec{q}_1 \cdots \vec{q}_n) = \frac{N_A! N_B!}{(N - n_\mathrm{A}!)! \, (N - n_B)!} \frac{1}{\mathcal{Z}_N} \int \cdots \int e^{-\beta U(\vec{q}_1 \cdots \vec{q}_N)} \mathrm{d}\vec{q}_{n_A+1} \cdots \mathrm{d}\vec{q}_{N_A} \mathrm{d}\vec{q}_{n_B+1} \cdots \vec{q}_{N_B}. \tag{5}$$

Coming back to the system N identical particles, the one body correlation is then

$$\rho_N^{(1)}(\vec{q}_1) = N P_N^{(1)}(q_1 \cdots q_n). \tag{6}$$

In the case of ideal gas, the above correlation reduces to,

$$\rho_{N,\mathrm{ideal}}^{(1)}(\vec{q}_1) = \frac{N}{V} = \rho. \tag{7}$$

Following the above approach, the n body correlation for an ideal gas is,

$$\rho_{N,\mathrm{ideal}}^{(n)}(\vec{q}_1 \cdots \vec{q}_n) = \frac{N!}{(N-n)! V^n}. \tag{8}$$

One can then define a normalized distriubution function, $g_N^{(n)}$ which goes to unity when the system is in an ideal state,

$$g_N^{(n)} = \rho_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n) \frac{V^n}{N(N-1) \cdots (N-n)} = \frac{\rho_N^{(n)}}{\rho^n} \frac{1}{(1-1/N) \cdots (1-n/N)} \approx \frac{\rho_N^{(n)}}{\rho^n}, \tag{9}$$

where the last approximation is valid when $N >> n$. Let us consider the two body correlation $g_N^{(2)}$ which is known as the radial distribution function and is extensively used for characterizing the local structure or correlation in soft matter systems.

$$g_N^{(2)} = \frac{\rho_N^{(2)}}{\rho^2}. \tag{10}$$

Applying the above relation in Eq. (4), we obtain,

$$\rho^2 g_N^{(2)}(\vec{q}_1 \cdots \vec{q}_n) = \frac{N!}{(N-2)!} P_N^{(2)}(q_1, q_2), \tag{11}$$

integrating the above over the positions of all particles it can be seen that

$$\int\int \rho^2 g_N^{(2)}(\vec{q}_1, \vec{q}_2) \mathrm{d}\vec{q}_1 \mathrm{d}\vec{q}_2 = \int\int \frac{N!}{(N-2)!} P_N^{(2)}(\vec{q}_1, \vec{q}_n) \mathrm{d}\vec{q}_1 \mathrm{d}\vec{q}_2 = N(N-1), \tag{12}$$

if the interactions in the system are only dependent on the difference of the distance vectors then the above relation gets modified to

$$\begin{aligned} \int\int \rho^2 g_N^{(2)}(\vec{q}_2 - \vec{q}_1) \mathrm{d}\vec{q}_1 \mathrm{d}\vec{q}_2 &= N(N-1), \\ \int\int \rho^2 g_N^{(2)}(\vec{q}_{12}) \mathrm{d}\vec{q}_{12} \mathrm{d}\vec{Q}_{12} &= N(N-1), \\ V\rho^2 \int g_N^{(2)}(\vec{q}_{12}) \mathrm{d}\vec{q}_{12} &= N(N-1), \\ \rho \int g_N^{(2)}(\vec{q}_{12}) \mathrm{d}\vec{q}_{12} &= (N-1), \end{aligned} \tag{13}$$

if the interactions are rotationally invariant then the above expression gets simplifies to

$$\begin{aligned} 4\pi\rho \int g_N^{(2)}(|\vec{q}_{12}|)|\vec{q}_{12}|^2 \mathrm{d}|\vec{q}_{12}| &= (N-1), \\ &= N\left(1 - \frac{1}{N}\right), \\ &\approx N, \end{aligned} \tag{14}$$

where the last approximation is for the large N limit.

2 Open systems

In the last section, we saw the distribution functions for a canonical ensemble. Let us extend them to the case of a grand canonical ensemble where the independent variables are μ, V, T. As the number of particles in the system is not fixed, the distribution function in Eq. (4) takes the following form

$$\rho_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n) = \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} P_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n), \tag{15}$$

where

$$P_N^{(n)}(q_1 \cdots q_n) = e^{\beta\mu N} \frac{1}{\mathcal{Z}'} \int \cdots \int e^{-\beta U(\vec{q}_1 \cdots \vec{q}_N)} \mathrm{d}\vec{q}_{n+1} \cdots \mathrm{d}\vec{q}_N, \tag{16}$$

where $\mathcal{Z}'$ is the configurational part of the grand canonical partition function. Integrating the above expression over all the particle positions gives,

$$\begin{aligned} \int \cdots \int \rho_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n) \mathrm{d}\vec{q}_1 \cdots \mathrm{d}\vec{q}_n &= \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} \int \cdots \int P_N^{(n)}(q_1 \cdots q_n) \mathrm{d}\vec{q}_1 \cdots \mathrm{d}\vec{q}_n, \\ &= \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} e^{\beta\mu N} \frac{1}{\mathcal{Z}'} \int \cdots \int e^{-\beta U(\vec{q}_1 \cdots \vec{q}_N)} \mathrm{d}\vec{q}_1 \cdots \mathrm{d}\vec{q}_N, \\ &= \left\langle \frac{N!}{(N-n)!} \right\rangle, \end{aligned} \tag{17}$$

so, the relation for the one and two body correlation are,

$$\begin{aligned} \int \rho_N^{(1)}(\vec{q}_1) \mathrm{d}\vec{q}_1 &= \langle N \rangle, \\ \int\int \rho_N^{(2)}(\vec{q}_1, \vec{q}_2) \mathrm{d}\vec{q}_1 \mathrm{d}\vec{q}_2 &= \langle N(N-1) \rangle = \langle N^2 \rangle - \langle N \rangle. \end{aligned} \tag{18}$$

Following from the previous section, the one body correlation in the ideal gas case is

$$\rho_{N,\mathrm{ideal}}^{(1)}(\vec{q}_1) = \sum_{N=1}^{\infty} N P_{N,\mathrm{ideal}}^{(n)}(\vec{q}_1) = \frac{\langle N \rangle}{V}. \tag{19}$$

Further, the normalised two body correlation is,

$$
\begin{aligned}
g_N^{(2)} &= \frac{\rho_N^{(2)}}{\left(\rho_{N,\mathrm{ideal}}^{(1)}\right)^2}, \\
\int\int \left(\rho_{N,\mathrm{ideal}}^{(1)}\right)^2 g_N^{(2)}(\vec{q}_1,\vec{q}_2)\mathrm{d}\vec{q}_1\mathrm{d}\vec{q}_2 &= \langle N^2\rangle - \langle N\rangle .
\end{aligned}
\tag{20}
$$

The total correlation function $h(\vec{q}_1,\vec{q}_2)$ is the difference between the correlation in the system to that in the ideal state and is given by,

$$
\begin{aligned}
h(\vec{q}_1,\vec{q}_2) &= g_N^{(2)}(\vec{q}_1,\vec{q}_2) - 1, \\
\int\int \left(\rho_{N,\mathrm{ideal}}^{(1)}\right)^2 h(\vec{q}_1,\vec{q}_2)\mathrm{d}\vec{q}_1\mathrm{d}\vec{q}_2 &= \int\int \left(\rho_{N,\mathrm{ideal}}^{(1)}\right)^2 \left(g_N^{(2)}(\vec{q}_1,\vec{q}_2) - 1\right)\mathrm{d}\vec{q}_1\mathrm{d}\vec{q}_2, \\
&= \int\int \left(\rho_{N,\mathrm{ideal}}^{(1)}\right)^2 g_N^{(2)}(\vec{q}_1,\vec{q}_2)\mathrm{d}\vec{q}_1\mathrm{d}\vec{q}_2 - \int\int \left(\rho_{N,\mathrm{ideal}}^{(1)}\right)^2 \mathrm{d}\vec{q}_1\mathrm{d}\vec{q}_2, \\
&= \langle N^2\rangle - \langle N\rangle - \langle N\rangle^2 , \\
&= \langle N\rangle \left(\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle} - 1\right), \\
&= \langle N\rangle\, k_\mathrm{B} T \rho_{N,\mathrm{ideal}}^{(1)} \chi_T,
\end{aligned}
\tag{21}
$$

where the last equality in applicable in the thermodynamic limit. A point to note here is that the connection between the radial distribution function and the isothermal compressibility can only be made in the grand canonical ensemble.