

9.B. Thermodynamics and the Radial Distribution Function

Read §9.A of Reichl's text.

A classical fluid of N particles and volume V is described by the Hamiltonian

$$H^N(\mathbf{q}^N, \mathbf{p}^N) = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{(i,j)}^{N(N-1)/2} \mathcal{V}(\mathbf{q}_{ij}) \quad (9.1)$$

where the 2nd sum is over the $\frac{1}{2} N(N-1)$ pairs of particles and

$$\mathbf{q}^N = (\mathbf{q}_1, \dots, \mathbf{q}_N) \quad \mathbf{p}^N = (\mathbf{p}_1, \dots, \mathbf{p}_N)$$

$\mathbf{q}_{ij} = \mathbf{q}_j - \mathbf{q}_i =$ vector pointing from particle i to j .

In general, a 1-body phase function takes the form

$$O_1^N(\mathbf{q}^N) = \sum_{i=1}^N O(\mathbf{q}_i) \quad (9.1a)$$

and a 2-body one

$$O_2^N(\mathbf{q}^N) = \sum_{(i,j)}^{N(N-1)/2} O(\mathbf{q}_i, \mathbf{q}_j) \quad (9.1b)$$

For example, we have

$$K_1^N(\mathbf{p}^N) = \sum_{i=1}^N \frac{p_i^2}{2m} \quad (9.1c)$$

$$\mathcal{V}_2^N(\mathbf{q}^N) = \sum_{(i,j)}^{N(N-1)/2} \mathcal{V}(\mathbf{q}_{ij}) \quad (9.1d)$$

The thermal averages of these functions are given by

$$\langle O_1^N \rangle = \frac{1}{Z_N} \int d\mathbf{q}^N \int d\mathbf{p}^N e^{-\beta H^N} O_1^N(\mathbf{q}^N) \quad (9.2a)$$

$$\langle O_2^N \rangle = \frac{1}{Z_N} \int d\mathbf{q}^N \int d\mathbf{p}^N e^{-\beta H^N} O_2^N(\mathbf{q}^N) \quad (9.3a)$$

where

$$Z_N = \int d\mathbf{q}^N \int d\mathbf{p}^N e^{-\beta H^N} \quad (9.2b)$$

is the N -particle partition function.

It is understood that every \mathbf{q}_i -integral is over V and every \mathbf{p}_i -integral is over all space.

Using (9.1) on (9.2b) gives

$$\begin{aligned} Z_N &= \left(\prod_{j=1}^N \int d\mathbf{p}_j e^{-\beta p_j^2/2m} \right) \int d\mathbf{q}^N e^{-\beta \mathcal{V}_2^N} \\ &= z^N Q_N(V, T) \end{aligned} \quad (9.2c)$$

where V is the volume of the system and

$$z = \int d\mathbf{p} e^{-\beta p^2/2m} \quad (9.2d)$$

is the partition function for one free particle and

$$Q_N(V, T) = \int d\mathbf{q}^N e^{-\beta \mathcal{V}_2^N} \quad \beta = \frac{1}{k_B T} \quad (9.5)$$

is the **configuration integral**.

Similarly,

$$\begin{aligned}
 & \int d\mathbf{q}^N \int d\mathbf{p}^N e^{-\beta H^N} O_1^N(\mathbf{q}^N) \\
 &= z^N \sum_{i=1}^N \int d\mathbf{q}^N e^{-\beta \mathcal{V}_i^N} O(\mathbf{q}_i) \\
 &= z^N N \int d\mathbf{q}^N e^{-\beta \mathcal{V}_1^N} O(\mathbf{q}_1) \quad [\text{Integral gives same numerical value } \forall i.] \\
 &= z^N C_1^N \int d\mathbf{q}_1 O_1(\mathbf{q}_1) \int d\mathbf{q}_2 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \quad (9.2e)
 \end{aligned}$$

where

$$C_k^n = \frac{n!}{k!(n-k)!} = k\text{-combinations of } n \text{ objects.}$$

(9.2a) thus becomes

$$\begin{aligned}
 \langle O_1^N \rangle &= \frac{C_1^N}{Q_N(V, T)} \int d\mathbf{q}_1 O(\mathbf{q}_1) \int d\mathbf{q}_2 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \\
 &= \int d\mathbf{q}_1 O_1(\mathbf{q}_1) n_1^N(\mathbf{q}_1; V, T) \quad (9.2)
 \end{aligned}$$

where

$$n_1^N(\mathbf{q}_1; V, T) = \frac{C_1^N}{Q_N(V, T)} \int d\mathbf{q}_2 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \quad (9.4a)$$

is the **1-body reduced distribution function**. As can be seen from (9.2),

$$n_1^N(\mathbf{q}_1; V, T) \Delta \mathbf{q}_1 = \text{probability of finding a particle inside } \Delta \mathbf{q}_1 \text{ at } \mathbf{q}_1.$$

Note that contributions from the kinetic energy are cancelled out because we can write

$$e^{-\beta H^N} = e^{-\beta K_1^N} e^{-\beta \mathcal{V}_2^N}$$

Since this is not valid for a quantum system, what follows applies only to classical fluids.

The 2-body version of (9.2e) is easily found to be

$$\begin{aligned}
 & \int d\mathbf{q}^N \int d\mathbf{p}^N e^{-\beta H^N} O_2^N(\mathbf{q}^N) \\
 &= z^N C_2^N \int d\mathbf{q}_1 \int d\mathbf{q}_2 O(\mathbf{q}_{12}) \int d\mathbf{q}_3 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \quad (9.3b)
 \end{aligned}$$

(9.3a) thus becomes

$$\begin{aligned}
 \langle O_2^N \rangle &= \frac{C_2^N}{Q_N(V, T)} \int d\mathbf{q}_1 \int d\mathbf{q}_2 O(\mathbf{q}_{12}) \int d\mathbf{q}_3 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \\
 &= \frac{1}{2} \int d\mathbf{q}_1 \int d\mathbf{q}_2 O(\mathbf{q}_{12}) n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) \quad (9.3)
 \end{aligned}$$

where

$$n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) = \frac{2 C_2^N}{Q_N(V, T)} \int d\mathbf{q}_3 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \quad (9.4b)$$

is the **2-body reduced distribution function**. As can be seen from (9.3),

$$\begin{aligned}
 & n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) \Delta \mathbf{q}_1 \Delta \mathbf{q}_2 \\
 &= \text{probability of finding one particle inside } \Delta \mathbf{q}_1 \text{ at } \mathbf{q}_1 \\
 & \quad \text{\& another inside } \Delta \mathbf{q}_2 \text{ at } \mathbf{q}_2, \text{ simultaneously.}
 \end{aligned}$$

The prefactor $\frac{1}{2}$ in (9.3) is to cancel the double counting.

In general,

$$\langle O_k^N \rangle = \frac{1}{k!} \int d\mathbf{q}^k O(\mathbf{q}^k) n_k^N(\mathbf{q}^k; V, T) \quad (9.3c)$$

where

$$n_k^N(\mathbf{q}^k; V, T) = \frac{k! C_k^N}{Q_N(V, T)} \int d\mathbf{q}_{k+1} \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \quad (9.4)$$

is the k -body reduced distribution function. As before,

$$\begin{aligned} n_k^N(\mathbf{q}^k; V, T) \Delta \mathbf{q}_1 \dots \Delta \mathbf{q}_k & \quad (9.4a) \\ &= \text{probability of finding one particle inside } \Delta \mathbf{q}_1 \text{ at } \mathbf{q}_1, \\ & \quad \text{one inside } \Delta \mathbf{q}_2 \text{ at } \mathbf{q}_2, \dots, \text{ and one inside } \Delta \mathbf{q}_k \text{ at } \mathbf{q}_k, \text{ simultaneously.} \end{aligned}$$

The prefactor $\frac{1}{k!}$ in (9.3c) is necessary since permutations among $\mathbf{q}_1, \dots, \mathbf{q}_k$ correspond to rearrangements of the same set of particles, and hence describing the same physical configuration.

With the help of (9.5), we integrate (9.4) to get

$$\begin{aligned} \int d\mathbf{q}^k n_k^N(\mathbf{q}^k; V, T) &= \frac{k! C_k^N}{Q_N(V, T)} \int d\mathbf{q}_1 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^N} \\ &= k! C_k^N = \frac{N!}{(N-k)!} \end{aligned} \quad (9.6)$$

As an example, consider the **internal energy**, which is defined as the thermal average of the Hamiltonian [see (7.43-4) of §7.D.1]:

$$U(V, T, N) = \langle H^N \rangle = \langle K_1^N \rangle + \langle \mathcal{V}_2^N \rangle \quad (9.7a)$$

Using (9.2c), we have

$$\begin{aligned} \langle K_1^N \rangle &= \frac{1}{Z^N} \int d\mathbf{p}^N K_1^N e^{-\beta K_1^N} \\ &= \frac{1}{Z^N} \sum_{j=1}^N \left(\int d\mathbf{p}_j \frac{p_j^2}{2m} e^{-\beta p_j^2/2m} \prod_{i \neq j} \int d\mathbf{p}_i e^{-\beta p_i^2/2m} \right) \\ &= \frac{N}{Z} \int d\mathbf{p} \frac{p^2}{2m} e^{-\beta p^2/2m} \quad [(9.2d) \text{ used. }] \\ &= \frac{N}{Z} 4\pi \int_0^\infty dp \frac{p^4}{2m} e^{-\beta p^2/2m} \\ &= N \frac{3}{2\beta} \quad [\text{ See §Code }] \\ &= \frac{3}{2} N k_B T \end{aligned} \quad (9.7b)$$

where

$$Z = 4\pi \int_0^\infty dp p^2 e^{-\beta p^2/2m} = \left(\frac{2\pi m}{\beta} \right)^{3/2} \quad (9.7c)$$

With (9.3), we can write (9.7a) as

$$U(V, T, N) = \frac{3}{2} N k_B T + \frac{1}{2} \int d\mathbf{q}_1 \int d\mathbf{q}_2 \mathcal{V}(\mathbf{q}_{12}) n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) \quad (9.7)$$

Consider now the case where $\mathcal{V}(\mathbf{q}_{ij})$ is a central (or spherically symmetric) potential, i.e.,

$$\mathcal{V}(\mathbf{q}_{ij}) = \mathcal{V}(q_{ij}) \quad q_{ij} = |\mathbf{q}_{ij}| \quad (9.8a)$$

Introducing the center-of-mass coordinates

$$\mathbf{Q}_{ij} = \frac{1}{2} (\mathbf{q}_j + \mathbf{q}_i) \quad (9.8b)$$

we have

$$\mathbf{q}_i = \mathbf{Q}_{ij} - \frac{1}{2} \mathbf{q}_{ij} \quad \mathbf{q}_j = \mathbf{Q}_{ij} + \frac{1}{2} \mathbf{q}_{ij} \quad (9.8c)$$

The Jacobian of the transformation is

$$J = \frac{\partial(\mathbf{q}_i, \mathbf{q}_j)}{\partial(\mathbf{Q}_{ij}, \mathbf{q}_{ij})} = \begin{vmatrix} \frac{\partial \mathbf{q}_i}{\partial \mathbf{Q}_{ij}} & \frac{\partial \mathbf{q}_i}{\partial \mathbf{q}_{ij}} \\ \frac{\partial \mathbf{q}_j}{\partial \mathbf{Q}_{ij}} & \frac{\partial \mathbf{q}_j}{\partial \mathbf{q}_{ij}} \end{vmatrix} = \begin{vmatrix} I & -\frac{1}{2}I \\ I & \frac{1}{2}I \end{vmatrix} = \begin{vmatrix} 2I & \mathbf{0} \\ I & \frac{1}{2}I \end{vmatrix} = 1$$

where Gaussian elimination was used to obtain the 2nd to last expression.

Hence, (9.3) can be written as

$$\begin{aligned} \langle \mathcal{V}_2^N \rangle &= \frac{1}{2} \int d\mathbf{q}_{12} \int d\mathbf{Q}_{12} \mathcal{V}(\mathbf{q}_{12}) n_2^N(\mathbf{q}_{12}; V, T) \\ &= \frac{1}{2} V \int d\mathbf{q}_{12} \mathcal{V}(\mathbf{q}_{12}) n_2^N(\mathbf{q}_{12}; V, T) \end{aligned} \quad (9.8d)$$

For central potentials, (9.4b) becomes

$$n_2^N(\mathbf{q}_{12}; V, T) = \frac{2 C_2^N}{Q_N(V, T)} e^{-\beta \mathcal{V}(\mathbf{q}_{12})} \int d\mathbf{q}_3 \dots \int d\mathbf{q}_N e^{-\beta \mathcal{V}_2^{N-2}}$$

where \mathcal{V}_2^{N-2} is a sum of

1. interactions between particles 3, 4, ..., N .
2. interactions between particle 1 and particles 3, 4, ..., N .
3. interactions between particle 2 and particles 3, 4, ..., N .

For short-range potentials, boundary effects can be neglected. Contributions from items 2 & 3 can then only depend on q_{12} since taken individually, they are equivalent.

We therefore have

$$n_2^N(\mathbf{q}_{12}; V, T) = n_2^N(q_{12}; V, T)$$

and (9.8d) becomes

$$\langle \mathcal{V}_2^N \rangle = \frac{1}{2} V 4 \pi \int d q q^2 \mathcal{V}(q) n_2^N(q; V, T) \quad (9.8e)$$

If we have only 1 particle, the probability of finding it inside $\Delta \mathbf{q}$ any where is $\frac{\Delta \mathbf{q}}{V}$.

If we have N non-interacting particles, then this probability becomes $N \frac{\Delta \mathbf{q}}{V} = n \Delta \mathbf{q}$, where $n = \frac{N}{V}$ is the average particle density.

Now,

$$n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) \Delta \mathbf{q}_1 \Delta \mathbf{q}_2 = P_1 P_{1|2} \quad (9.8f)$$

where

P_1 = probability of particle 1 in $\Delta \mathbf{q}_1$ at \mathbf{q}_1 .

$P_{1|2}$ = conditional probability of, given particle 1, finding particle 2 in $\Delta \mathbf{q}_2$ at \mathbf{q}_2 .

For non-interacting particles,

$$P_1 = \frac{N}{V} \Delta \mathbf{q}_1$$

$$P_{1|2} = \frac{N-1}{V} \Delta \mathbf{q}_2$$

$$\rightarrow n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) = \frac{N(N-1)}{V^2} \approx n^2 \quad \text{for } N \gg 1 \quad (9.8g)$$

This suggests writing

$$\begin{aligned} n_2^N(q; V, T) &\equiv \frac{N(N-1)}{V^2} g_2^N(q, V, T) \\ &\approx n^2 g_2^N(q, V, T) \end{aligned} \quad (9.8h)$$

where $g_2^N(q, V, T)$ is a correlation function known as the **radial distribution function**.

(9.7) thus becomes

$$U(V, T, N) = \frac{3}{2} N k_B T + \frac{1}{2} \frac{N^2}{V} 4 \pi \int d q q^2 \mathcal{V}(q) g_2^N(q, V, T) \quad (9.8)$$

Comparing (9.8h) with (9.8g), we have

$$g_2^N(q, V, T) = 1 \text{ for non-interacting particles (with no correlation)}$$

Thus, we expect

$$g_2^N(q, V, T) \xrightarrow{q \gg R} 1 \quad (9.8i)$$

where R is the range of \mathcal{V} .

The definition (9.8h) also means that [see (9.8f)]

$$n g_2^N(q, V, T) 4 \pi q^2 \Delta q \quad (9.8j)$$

= probability of finding a particle in the spherical shell of thickness Δq
and radius q centered at a given particle at the origin.

Exercise 9.1

The **static density correlation function** for the equilibrium fluid discussed above can be written as

$$C_{nn}(\mathbf{r}) = \frac{1}{N} \int d \mathbf{r}' \langle n(\mathbf{r}' + \mathbf{r}) n(\mathbf{r}') \rangle \quad (1a)$$

where the density phase function is given by

$$n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{q}_i) \quad (1b)$$

The Fourier transform of $C_{nn}(\mathbf{r})$ is called the structural factor:

$$S_{nn}(\mathbf{k}) = \int d \mathbf{r} e^{-i \mathbf{k} \cdot \mathbf{r}} C_{nn}(\mathbf{r}) \quad (1c)$$

Show that in the thermodynamic limit

$$N, V \rightarrow \infty \quad \text{with} \quad \frac{N}{V} = n$$

we can write

$$S_{nn}(\mathbf{k}) = 1 + (2 \pi)^3 n \delta(\mathbf{k}) + \frac{4 \pi}{k} n \int_0^\infty d q [g_2^N(q) - 1] q^2 \sin k q \quad (1d)$$

Answer

Putting (1a) into (1c) gives

$$\begin{aligned} S_{nn}(\mathbf{k}) &= \frac{1}{N} \int d \mathbf{r} e^{-i \mathbf{k} \cdot \mathbf{r}} \int d \mathbf{r}' \langle n(\mathbf{r}' + \mathbf{r}) n(\mathbf{r}') \rangle \\ &= \frac{1}{N} \sum_{i,j=1}^N \int d \mathbf{r} e^{-i \mathbf{k} \cdot \mathbf{r}} \int d \mathbf{r}' \langle \delta(\mathbf{r}' + \mathbf{r} - \mathbf{q}_i) \delta(\mathbf{r}' - \mathbf{q}_j) \rangle \quad \text{[(1b) used.]} \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{N} \sum_{i,j=1}^N \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle \delta(\mathbf{q}_j + \mathbf{r} - \mathbf{q}_i) \rangle \\
&= \frac{1}{N} \sum_{i,j=1}^N \langle e^{i\mathbf{k}\cdot(\mathbf{q}_j - \mathbf{q}_i)} \rangle \tag{1}
\end{aligned}$$

$$\begin{aligned}
&= 1 + \frac{1}{N} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N \langle e^{i\mathbf{k}\cdot(\mathbf{q}_j - \mathbf{q}_i)} \rangle \\
&= 1 + \frac{2}{N} \sum_{(i,j)}^{N(N-1)/2} \langle e^{i\mathbf{k}\cdot(\mathbf{q}_j - \mathbf{q}_i)} \rangle \tag{2a}
\end{aligned}$$

Using (9.3), we have

$$\begin{aligned}
S_{nn}(\mathbf{k}) &= 1 + \frac{1}{N} \int d\mathbf{q}_1 \int d\mathbf{q}_2 e^{i\mathbf{k}\cdot(\mathbf{q}_2 - \mathbf{q}_1)} n_2^N(\mathbf{q}_1, \mathbf{q}_2; V, T) \\
&= 1 + \frac{V}{N} \int d\mathbf{q}_{12} e^{i\mathbf{k}\cdot\mathbf{q}_{12}} n_2^N(\mathbf{q}_{12}; V, T) \\
&= 1 + \frac{N}{V} \int d\mathbf{q}_{12} e^{i\mathbf{k}\cdot\mathbf{q}_{12}} g_2^N(\mathbf{q}_{12}; V, T) \quad [(9.8h) \text{ used.}] \tag{2}
\end{aligned}$$

Since $g_2^N \rightarrow 1$ for large q [see (9.8i)], the integral in (2) diverges for $\mathbf{k} = 0$ as $V \rightarrow \infty$.

Using

$$\frac{1}{V} \int d\mathbf{q} e^{i\mathbf{k}\cdot\mathbf{q}} = \delta_{\mathbf{k}0} = \frac{(2\pi)^3}{V} \delta(\mathbf{k})$$

we can extract this singularity outside the integral and write (2) as

$$\begin{aligned}
S_{nn}(\mathbf{k}) &= 1 + n (2\pi)^3 \delta(\mathbf{k}) + n \int d\mathbf{q}_{12} e^{i\mathbf{k}\cdot\mathbf{q}_{12}} [g_2^N(\mathbf{q}_{12}; V, T) - 1] \tag{3} \\
&= 1 + n (2\pi)^3 \delta(\mathbf{k}) + 2\pi n \int_{-1}^1 d\cos\theta \int d q q^2 e^{i k q \cos\theta} [g_2^N(q; V, T) - 1] \\
&= 1 + n (2\pi)^3 \delta(\mathbf{k}) + 2\pi n \int d q q^2 \frac{e^{i k q} - e^{-i k q}}{i k} [g_2^N(q; V, T) - 1] \\
&= 1 + n (2\pi)^3 \delta(\mathbf{k}) + \frac{4\pi n}{k} \int d q q^2 (\sin k q) [g_2^N(q; V, T) - 1] \tag{4}
\end{aligned}$$

$S_{nn}(\mathbf{k})$ is proportional to the scattering amplitude in the \mathbf{k} direction. The $\delta(\mathbf{k})$ term thus represents the forward scattering contribution. The result of a neutron scattering experiment is shown in Fig.9.1 in Reichl's text. Also shown is g_2^N obtained from the Fourier inverse of $S_{nn}(\mathbf{k})$.

Code

`z = Assuming[a > 0, Integrate[p^2 e^-a p^2 dp] /. a -> beta / (2 m);`

`z = 4 pi z // PowerExpand // Simplify`

$$\frac{2 \sqrt{2} m^{3/2} \pi^{3/2}}{\beta^{3/2}}$$

$$A = \text{Assuming}[a > 0, \int_0^{\infty} p^4 e^{-a p^2} dp] /. a \rightarrow \frac{\beta}{2 m};$$

$$4 \pi \frac{A}{2 m} // \text{PowerExpand} // \text{Simplify}$$

$$\frac{1}{z} 4 \pi \frac{A}{2 m} // \text{Simplify}$$

$$\frac{3 \sqrt{2} m^{3/2} \pi^{3/2}}{\beta^{5/2}}$$

$$\frac{3}{2 \beta}$$