G25.2651: Statistical Mechanics

Notes for Lecture 9

I. DISTRIBUTION FUNCTIONS IN CLASSICAL LIQUIDS AND GASES (CONT'D)

A. General correlation functions

A general correlation function can be defined in terms of the probability distribution function $\rho^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n)$ according to

$$
\begin{aligned}
g^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n) &= \frac{1}{\rho^n} \rho^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n) \\
&= \frac{V^n N!}{Z_N N^n (N-n)!} \int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, ..., \mathbf{r}_N)}
\end{aligned}
$$

Another useful way to write the correlation function is

$$
\begin{aligned}
g^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n) &= \frac{V^n N!}{Z_N N^n (N-n)!} \int d\mathbf{r}_1' \cdots d\mathbf{r}_N' e^{-\beta U(\mathbf{r}_1', ..., \mathbf{r}_N')} \delta(\mathbf{r}_1 - \mathbf{r}_1') \cdots \delta(\mathbf{r}_n - \mathbf{r}_n') \\
&= \frac{V^n N!}{Z_N N^n (N-n)!} \left\langle \prod_{i=1}^n \delta(\mathbf{r}_i - \mathbf{r}_i') \right\rangle_{\mathbf{r}_1', ..., \mathbf{r}_N'}
\end{aligned}
$$

i.e., the general n-particle correlation function can be expressed as an ensemble average of the product of δ-functions, with the integration being taken over the variables $\mathbf{r}_1', ..., \mathbf{r}_N'$.

B. The pair correlation function

Of particular importance is the case $n = 2$, or the correlation function $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ known as the *pair correlation function*. The explicit expression for $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is

$$
\begin{aligned}
g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{V^2 N!}{N^2 (N-2)!} \left\langle \delta(\mathbf{r}_1 - \mathbf{r}_1') \delta(\mathbf{r}_2 - \mathbf{r}_2') \right\rangle \\
&= \frac{V^2 (N-1)}{N Z_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, ..., \mathbf{r}_N)} \\
&= \frac{N(N-1)}{\rho^2} \left\langle \delta(\mathbf{r}_1 - \mathbf{r}_1') \delta(\mathbf{r}_2 - \mathbf{r}_2') \right\rangle_{\mathbf{r}_1', ..., \mathbf{r}_N'}
\end{aligned}
$$

In general, for homogeneous systems in equilibrium, there are no special points in space, so that $g^{(2)}$ should depend only on the relative position of the particles or the difference $\mathbf{r}_1 - \mathbf{r}_2$. In this case, it proves useful to introduce the change of variables

$$
\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \qquad \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)
$$

$$
\mathbf{r}_1 = \mathbf{R} + \frac{1}{2}\mathbf{r}, \qquad \mathbf{r}_2 = \mathbf{R} - \frac{1}{2}\mathbf{r}
$$

Then, we obtain a new function $\tilde{g}^{(2)}$, a function of $\mathbf{r}$ and $\mathbf{R}$:

$$
\begin{aligned}
\tilde{g}^{(2)}(\mathbf{r}, \mathbf{R}) &= \frac{V^2 (N-1)}{N Z_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{R} + \frac{1}{2}\mathbf{r}, \mathbf{R} - \frac{1}{2}\mathbf{r}, \mathbf{r}_3, ..., \mathbf{r}_N)} \\
&= \frac{N(N-1)}{\rho^2} \left\langle \delta\left(\mathbf{R} + \frac{1}{2}\mathbf{r} - \mathbf{r}_1'\right) \delta\left(\mathbf{R} - \frac{1}{2}\mathbf{r} - \mathbf{r}_2'\right) \right\rangle_{\mathbf{r}_1', ..., \mathbf{r}_N'}
\end{aligned}
$$

In general, we are only interested in the dependence on $\mathbf{r}$. Thus, we integrate this expression over $\mathbf{R}$ and obtain a new correlation function $\tilde{g}(\mathbf{r})$ defined by

$$\tilde{g}(\mathbf{r}) = \frac{1}{V} \int d\mathbf{R} \tilde{g}^{(2)}(\mathbf{r}, \mathbf{R})$$
$$= \frac{V(N-1)}{NZ_N} \int d\mathbf{R} d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{R}+\frac{1}{2}\mathbf{r}, \mathbf{R}-\frac{1}{2}\mathbf{r}, \mathbf{r}_3, \ldots, \mathbf{r}_N)}$$
$$= \frac{(N-1)}{\rho Z_N} \int d\mathbf{R} d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{R}+\frac{1}{2}\mathbf{r}, \mathbf{R}-\frac{1}{2}\mathbf{r}, \mathbf{r}_3, \ldots, \mathbf{r}_N)}$$

For an isotropic system such as a liquid or gas, where there is no preferred direction in space, only the maginitude or $\mathbf{r}$, $|\mathbf{r}| \equiv r$ is of relevance. Thus, we seek a choice of coordinates that involves r explicitly. The spherical-polar coordinates of the vector $\mathbf{r}$ is the most natural choice. If $\mathbf{r} = (x, y, z)$ then the spherical polar coordinates are

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$x = r \cos\theta$$
$$d\mathbf{r} = r^2 \sin\theta dr d\theta d\phi$$

where θ and ϕ are the polar and azimuthal angles, respectively. Also, note that

$$\mathbf{r} = r\mathbf{n}$$

where

$$\mathbf{n} = (\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta)$$

Thus, the function $g(r)$ that depends only on the distance r between two particles is defined to be

$$g(r) = \frac{1}{4\pi} \int sin\theta d\theta d\phi \tilde{g}(\mathbf{r})$$
$$= \frac{(N-1)}{4\pi\rho Z_N} \int sin\theta d\theta d\phi d\mathbf{R} d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{R}+\frac{1}{2}r\mathbf{n}, \mathbf{R}-\frac{1}{2}r\mathbf{n}, \mathbf{r}_3, \ldots, \mathbf{r}_N)}$$
$$= \frac{(N-1)}{4\pi\rho} \left\langle \frac{\delta(r-r')}{rr'} \right\rangle_{r', \theta', \phi', \mathbf{R}', \mathbf{r}'_3, \ldots, \mathbf{r}'_N}$$

Integrating $g(r)$ over the radial dependence, one finds that

$$4\pi\rho \int_0^\infty dr r^2 g(r) = N - 1 \approx N$$

The function $g(r)$ is important for many reasons. It tells us about the structure of complex, isotropic systems, as we will see below, it determines the thermodynamic quantities at the level of the pair potential approximation, and it can be measured in neutron and X-ray diffraction experiments. In such experiments, one observes the scattering of neutrons or X-rays from a particular sample. If a detector is placed at an angle θ from the wave-vector direction of an incident beam of particles, then the intensity $I(\theta)$ that one observes is proportional to the structure factor

$$I(\theta) \sim \frac{1}{N} \left\langle \left| \sum_m e^{i\mathbf{k}\cdot\mathbf{r}_m} \right|^2 \right\rangle$$
$$= \frac{1}{N} \left\langle \sum_{m,n} e^{i\mathbf{k}\cdot(\mathbf{r}_m - \mathbf{r}_n)} \right\rangle$$
$$\equiv S(\mathbf{k})$$

where $\mathbf{k}$ is the vector difference in the wave vector between the incident and scattered neutrons or X-rays (since neutrons and X-rays are quantum mechanical particles, they must be represented by plane waves of the form $\exp(i\mathbf{k}\cdot\mathbf{r})$).

By computing the ensemble average (see problem 4 of problem set #5), one finds that $S(\mathbf{k}) = S(k)$ and $S(k)$ is given by

$$S(k) = 1 + \frac{4\pi\rho}{k} \int_0^\infty dr\, r \sin(kr) g(r)$$

Thus, if one can measure $S(k)$, $g(r)$ can be determined by Fourier transformation.

C. Thermodynamic quantities in terms of $g(r)$

In the canonical ensemble, the average energy is given by

$$E = -\frac{\partial}{\partial\beta} \ln Q(N, V, \beta)$$

$$\ln Q(N, V, \beta) = \ln Z_N - 3N \ln \lambda(\beta) - \ln N!$$

Therefore,

$$E = \frac{3N}{\lambda} \frac{\partial\lambda}{\partial\beta} - \frac{1}{Z_N} \frac{\partial Z_N}{\partial\beta}$$

Since

$$\lambda = \left[\frac{\beta h^2}{2\pi m} \right]^{1/2}$$

$$\frac{\partial\lambda}{\partial\beta} = \frac{1}{2\beta}\lambda$$

Thus,

$$E = \frac{3}{2} NkT + \frac{1}{Z_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N U(\mathbf{r}_1, ..., \mathbf{r}_N) e^{\beta U(\mathbf{r}_1, ..., \mathbf{r}_N)}$$

$$= \frac{3}{2} NkT + \langle U \rangle$$

In order to compute the average energy, therefore, one needs to be able to compute the average of the potential $\langle U \rangle$. In general, this is a nontrivial task, however, let us work out the average for the case of a *pairwise-additive* potential of the form

$$U(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{1}{2} \sum_{i,j,i\neq j} u(|\mathbf{r}_i - \mathbf{r}_j|) \equiv U_{\text{pair}}(\mathbf{r}_1, ..., \mathbf{r}_N)$$

i.e., U is a sum of terms that depend only the distance between two particles at a time. This form turns out to be an excellent approximation in many cases. U therefore contains $N(N-1)$ total terms, and $\langle U \rangle$ becomes

$$\langle U \rangle = \frac{1}{2Z_N} \sum_{i,j,i\neq j} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N u(|\mathbf{r}_i - \mathbf{r}_j|) e^{-\beta U_{\text{pair}}(\mathbf{r}_1, ..., \mathbf{r}_N)}$$

$$= \frac{N(N-1)}{2Z_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N u(|\mathbf{r}_1 - \mathbf{r}_2|) e^{-\beta U_{\text{pair}}(\mathbf{r}_1, ..., \mathbf{r}_N)}$$

The second line follows from the fact that all terms in the first line are the exact same integral, just with the labels changed. Thus,

$$\langle U \rangle = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) \left[\frac{N(N-1)}{Z_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U_{\mathrm{pair}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \right]$$

$$= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \frac{N^2}{2V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

Once again, we change variables to $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. Thus, we find that

$$\langle U \rangle = \frac{N^2}{2V^2} \int d\mathbf{r} d\mathbf{R} u(r) \tilde{g}^{(2)}(\mathbf{r}, \mathbf{R})$$

$$= \frac{N^2}{2V^2} \int d\mathbf{r} u(r) \int d\mathbf{R} \tilde{g}^{(2)}(\mathbf{r}, \mathbf{R})$$

$$= \frac{N^2}{2V} \int d\mathbf{r} u(r) \tilde{g}(\mathbf{r})$$

$$= \frac{N^2}{2V} \int_0^\infty dr 4\pi r^2 u(r) g(r)$$

Therefore, the average energy becomes

$$E = \frac{3}{2} NkT + \frac{N}{2} 4\pi\rho \int_0^\infty dr r^2 u(r) g(r)$$

Thus, we have an expression for E in terms of a simple integral over the pair potential form and the radial distribution function. It also makes explicit the deviation from "ideal gas" behavior, where $E = 3NkT/2$.

By a similar procedure, we can develop an equation for the pressure P in terms of $g(r)$. Recall that the pressure is given by

$$P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V}$$

$$= \frac{1}{\beta Z_N} \frac{\partial Z_N}{\partial \beta}$$

The volume dependence can be made explicit by changing variables of integration in Z_N to

$$\mathbf{s}_i = V^{-1/3} \mathbf{r}_i$$

Using these variables, Z_N becomes

$$Z_N = V^N \int d\mathbf{s}_1 \cdots d\mathbf{s}_N e^{-\beta U(V^{1/3}\mathbf{s}_1,\ldots,V^{1/3}\mathbf{s}_N)}$$

Carrying out the volume derivative gives

$$\frac{\partial Z_N}{\partial V} = \frac{N}{V} Z_N - \beta V^N \int d\mathbf{s}_1 \cdots d\mathbf{s}_N \frac{1}{3V} \sum_{i=1}^N \mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i} e^{-\beta U(V^{1/3}\mathbf{s}_1,\ldots,V^{1/3}\mathbf{s}_N)}$$

$$= \frac{N}{V} Z_N + \beta \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{1}{3V} \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

Thus,

$$\frac{1}{Z_N} \frac{\partial Z_N}{\partial V} = \frac{N}{V} + \frac{\beta}{3V} \left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle$$

Let us consider, once again, a pair potential. We showed in an earlier lecture that

4

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1} \sum_{j=1, j\neq i}^{N} \mathbf{r}_i \cdot \mathbf{F}_{ij}$$

where $\mathbf{F}_{ij}$ is the force on particle i due to particle j. By interchaning the i and j summations in the above expression, we obtain

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \frac{1}{2}\left[\sum_{i,j,i\neq j} \mathbf{r}_i \cdot \mathbf{F}_{ij} + \sum_{i,j,i\neq j} \mathbf{r}_j \cdot \mathbf{F}_{ji}\right]$$

However, by Newton's third law, the force on particle i due to particle j is equal and opposite to the force on particle j due to particle i:

$$\mathbf{F}_{ij} = -\mathbf{F}_{ji}$$

Thus,

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \frac{1}{2}\left[\sum_{i,j,i\neq j} \mathbf{r}_i \cdot \mathbf{F}_{ij} - \sum_{i,j,i\neq j} \mathbf{r}_j \cdot \mathbf{F}_{ij}\right] = \frac{1}{2} \sum_{i,j,i\neq j} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} \equiv \frac{1}{2} \sum_{i,j,i\neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij}$$

The ensemble average of this quantity is

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = \frac{\beta}{6V}\left\langle \sum_{i,j,i\neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right\rangle = \frac{\beta}{6VZ_N}\int d\mathbf{r}_1\cdots d\mathbf{r}_N \sum_{i,j,i\neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij}e^{-\beta U_{pair}(\mathbf{r}_1,...,\mathbf{r}_N)}$$

As before, all integrals are exactly the same, so that

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = \frac{\beta N(N-1)}{6VZ_N}\int d\mathbf{r}_1\cdots\mathbf{r}_N\mathbf{r}_{12} \cdot \mathbf{F}_{12}e^{-\beta U_{pair}(\mathbf{r}_1,...,\mathbf{r}_N)}$$

$$= \frac{\beta}{6V}\int d\mathbf{r}_1 d\mathbf{r}_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12}\left[\frac{N(N-1)}{Z_N}\int d\mathbf{r}_3\cdots d\mathbf{r}_N e^{-\beta U_{pair}(\mathbf{r}_1,...,\mathbf{r}_N)}\right]$$

$$= \frac{\beta}{6V}\int d\mathbf{r}_1 d\mathbf{r}_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12}\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

$$= \frac{\beta N^2}{6V^3}\int d\mathbf{r}_1 d\mathbf{r}_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12}g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

Then, for a pair potential, we have

$$\mathbf{F}_{12} = -\frac{\partial U_{pair}}{\partial \mathbf{r}_{12}} = -u'(|\mathbf{r}_1 - \mathbf{r}_2|)\frac{(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} = -u'(r_{12})\frac{\mathbf{r}_{12}}{r_{12}}$$

where $u'(r) = du/dr$, and $r_{12} = |\mathbf{r}_{12}|$. Substituting this into the ensemble average gives

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = -\frac{\beta N^2}{6V^3}\int d\mathbf{r}_1 d\mathbf{r}_2 u'(r_{12})r_{12}g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

As in the case of the average energy, we change variables at this point to $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. This gives

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = -\frac{\beta N^2}{6V^3}\int d\mathbf{r}d\mathbf{R}u'(r)r\tilde{g}^{(2)}(\mathbf{r},\mathbf{R})$$

$$= -\frac{\beta N^2}{6V^2}\int d\mathbf{r}u'(r)r\tilde{g}(\mathbf{r})$$

$$= -\frac{\beta N^2}{6V^2}\int_0^{\infty} dr 4\pi r^3 u'(r)g(r)$$

5

Therefore, the pressure becomes

$$\frac{P}{kT} = \rho - \frac{\rho^2}{6kT} \int_0^\infty dr\, 4\pi r^3 u'(r) g(r)$$

which again gives a simple expression for the pressure in terms only of the derivative of the pair potential form and the radial distribution function. It also shows explicitly how the equation of state differs from the that of the ideal gas $P/kT = \rho$.

From the definition of $g(r)$ it can be seen that it depends on the density ρ and temperature T: $g(r) = g(r; \rho, T)$. Note, however, that the equation of state, derived above, has the general form

$$\frac{P}{kT} = \rho + B\rho^2$$

which looks like the first few terms in an expansion about ideal gas behavior. This suggests that it may be possible to develop a general expansion in all powers of the density ρ about ideal gas behavior. Consider representing $g(r; \rho, T)$ as such a power series:

$$g(r; \rho, T) = \sum_{j=0}^{\infty} \rho^j g_j(r; T)$$

Substituting this into the equation of state derived above, we obtain

$$\frac{P}{kT} = \rho + \sum_{j=0}^{\infty} B_{j+2}(T) \rho^{j+2}$$

This is known as the *virial equation of state*, and the coefficients $B_{j+2}(T)$ are given by

$$B_{j+2}(T) = -\frac{1}{6kT} \int_0^\infty dr\, 4\pi r^3 u'(r) g_j(r; T)$$

are known as the *virial coefficients*. The coefficient $B_2(T)$ is of particular interest, as it gives the leading order deviation from ideal gas behavior. It is known as the second virial coefficient. In the low density limit, $g(r; \rho, T) \approx g_0(r; T)$ and $B_2(T)$ is directly related to the radial distribution function.