5.1 Linear theory for liquid structure

5.1.1 Radial distribution function

Previously we worked out a theory for the structure of a dilute solution of ions, using the so-called Debye–Hückel theory. While that theory worked well for weak interactions, it yields unphysical results at short distances. To move beyond that weak interaction picture, it’s useful to consider the radial distribution function, and how it changes for different phases. We previously defined the \( g(r) \) as,

\[
g(r) = \frac{N - 1}{\bar{\rho}} \langle \delta(r - r_{12}) \rangle = \frac{1}{\bar{\rho} N} \left( \sum_{i \neq j}^{N} \delta(r - r_{ij}) \right)
\]

which is an equation that implements a conditional probability. Specifically, the \( g(r) \) is the probability of two particles being a distance \( r \) apart, or alternatively, the density of particles away from the origin given a particle is fixed at the origin. Two limits of the \( g(r) \) are clear. First, if a particle excludes volume, for example if it has a hard core, then \( r \to 0 \), \( g(r) \to 0 \). Certainly all atoms and molecules exclude volume due to Pauli’s principle. Another limit which is applicable to disordered material (e.g. liquids and gases) is that \( r \to \infty \), \( g(r) \to 1 \), which is to say that at large distances the particles should become uncorrelated. If the system exhibits long ranged order, like a crystal, then as \( r \to \infty \), \( g(r) \) will still depend on \( r \). Examples of \( g(r) \)'s for a simple monotonic liquid solid and gas, are shown in Fig. 5.1. As anticipated, for both a gas and a liquid, the \( g(r) \) decays to 1, while it continues to oscillate for a solid. In all cases however, given a diameter of the particle \( \sigma \), each phase exhibits a region of exclusion between \( r = 0 \) and \( r \approx \sigma \) where the \( g(r) \) is 0. Indeed, exclude volume dominates the density correlations even away from \( r = 0 \) for a liquid and a solid, where the deviations from 1 occur at regular values of \( \sigma \).

Not only does the radial distribution function contain important structural information, but it also encodes thermodynamics. For example, imagine a system that interacts through pairwise forces, \(-du(|r_i - r_j|)/dr_i\). The partition function for such a system is

\[
Q[u(r_{ij})] = \int d\mathbf{r}^N \exp \left[ -\beta/2 \sum_{i \neq j} u(|r_i - r_j|) \right]
\]

and its free energy follows as,

\[
A[u(r_{ij})] = -k_B T \ln Q[u(r_{ij})]
\]
which can be identified as a functional of that pair potential. More explicitly, we can relate how the
free energy of this system (or its configurational part) changes with changes to its pair potential by
taking a functional derivative,

\[
\frac{\delta A}{\delta u(r)} = -k_B T \frac{N}{Q} \int dr \left[ -\beta/2 \sum_{i \neq j} \delta(r - |r_i - r_j|) \right] e^{-\beta/2 \sum_{i \neq j} u(r_i - r_j)}
\]

where we can identify the expectation value as constants times the \( g(r) \). So the \( g(r) \) encodes how
the interactions amongst particles change their free energy.

We can make this more concrete by defining a pair potential that changes from one form to another
smoothly as a function of a control parameter \( \lambda \), such as

\[
u_\lambda(r) = u_o(r) + \lambda \Delta u(r)
\]

where \( \Delta u(r) = [u(r) - u_o(r)] \). Formally integrating the differential from above with these boundary
conditions we find

\[
A[u(r_{ij})] - A[u_o(r_{ij})] = \int_0^1 d\lambda \int dr \left. \frac{\delta A}{\delta u(r)} \right|_\lambda \Delta u(r)
\]

where \( g_\lambda(r) \) is the radial distribution function averaged with a potential energy function \( u_\lambda(r) \). This
is a direct connection between structure and thermodynamics, and is an example of an adiabatic
connection equation. It states that the free energy changes as the interactions amongst particles
change, by changing the pair correlations. If we evaluate that function with end points that are
\[ \lambda = 0, u_0(r) = 0, \text{ and } \lambda = 1, u_1(r) = u(r) \]

\[ A[u(r)] = A_{id} + \bar{\rho} N \int dr g(r) u(r) / 2 \]

we find that the free energy has an ideal piece, \( A_{id} \) (one which is independent of particle interactions), and an additional configurational piece due to those interactions. This follows from the fact that the \( A \) must be a state function, so the integral on the right hand side can be evaluated at its end points. From the identification of the relationship between the free energy and the \( g(r) \), which is exact if particles interact with pairwise potentials, then we can also compute the pressure as \( p = -dA/dV \),

\[ p = -\frac{d}{dV} \left( A_{id} + N^2 \int dx g(xV^{1/3}) u(xV^{1/3}) / 2 \right) \]
\[ = -\frac{dA_{id}}{dV} + N^2 \int dx g(xV^{1/3}) \frac{d}{dV} u(xV^{1/3}) / 2 \]
\[ = \rho k_B T - \frac{\rho^2}{6} \int \frac{d \mathbf{r}}{dV} g(\mathbf{r}, \rho, T) \frac{d u(r)}{d r} \]

where we have changed coordinates to \( r_i = V^{1/3} x_i \) to get rid of the volume in the limits of the integral, and identify the ideal part of the pressure with the ideal gas law. This relationship is known as the virial theorem. Collectively these relationships codify that the radial distribution function relates structure to thermodynamics. Next, we will see that it is also related to measurable.

### 5.1.2 Structure from scattering

Most information about bulk structure, especially at the angstrom scale, is obtained via scattering of neutrons, electrons, or photons. The quantum mechanical transition rate between plane wave states of scattered particles can be calculated. Let \( \mathbf{k} \) and \( \mathbf{k}' \) be the incoming and outgoing plane wave of a scattered particle with respective momenta \( \hbar \mathbf{k} \) and \( \hbar \mathbf{k}' \). An example of this geometry is shown in Fig 5.2. If the scattered particle interacts with the scattering medium via a potential \( U \) (and the interaction is sufficiently weak that only lowest order scattering need be considered for the entire sample), then by Fermi’s golden rule, the transition rate between \( \mathbf{k} \) and \( \mathbf{k}' \) is proportional to the square of the matrix element,

\[ |M_{\mathbf{k}, \mathbf{k}'}|^2 = |\langle \mathbf{k} \vert U \vert \mathbf{k}' \rangle|^2 \]
\[ = \left| \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} U(\mathbf{r}) e^{i\mathbf{k}' \cdot \mathbf{r}} \right|^2 \]

where we have written out the plane wave states parameterized by these wave vectors.

If the incoming particle interacts with the sample on a particle by particle basis, then the total interaction potential can be written as a sum over \( N \) particles,

\[ U(\mathbf{r}) = \sum_\alpha u_\alpha(\mathbf{r} - \mathbf{r}_\alpha) \]
Figure 5.2: Geometry for a typical scattering experiment.

where $\alpha$ indexes the particles in the sample and $r$ the position of the incoming scattered particle. Under such circumstances, the matrix element becomes,

$$|M_{k,k'}|^2 = \left| \sum_{\alpha} \int dr e^{-ikr} u_\alpha(r - r_\alpha) e^{ik'r} \right|^2$$

If we make the following substitutions, $R_\alpha = r - r_\alpha$, and $q = k' - k$, we find,

$$M_{k,k'} = \sum_{\alpha} \int dR_\alpha e^{iqR_\alpha} u_\alpha(R_\alpha) e^{iqr_\alpha}$$

that the matrix element can be written as a Fourier transform of the potential, multiplied with a plane wave state that relates the change in momentum upon scattering. The assumption of single scattering events, and the use of Fermi’s golden rule, are known as the Born Approximation. If all the particles are the same, or if there are atoms that dominate the scattering, then we can pull $u_\alpha$ out of the sum, and

$$|M_{k,k'}|^2 = \sum_{\alpha,\alpha'} \hat{u}_\alpha(q) \hat{u}_{\alpha'}^*(q) e^{iq(r_\alpha - r_{\alpha'})}$$

the transition probability breaks up into two pieces. The first piece, $|\hat{u}_\alpha(q)|^2$ is known as the form factor, and includes the details of the interaction potential. The second piece contains information on the positions of the particles. In general, at finite temperature, these positions fluctuate. If the scattering experiment is performed on timescales long relative to a typical relaxation time, or the system is large enough that it self-averages, then the measured transition probability reflects a thermal average of this second quantity. We define the so-called structure function, $I(q)$, as

$$I(q) = \left\langle \sum_{\alpha,\alpha'} e^{iq(r_\alpha - r_{\alpha'})} \right\rangle$$
Lecture 5: February 2

which has $N^2$ terms. However, averaging over the complex numbers, with phases determined by the positions of the particles, if the positions are correlated over a finite range only the $O(N)$ terms with $r_\alpha \approx r_\alpha'$ will contribute. As such, the structure factor is an extensive quantity for liquids and other disordered states of matter. Normalizing the structure function by $N$, we define the structure factor, $S(q)$,

$$S(q) = \frac{1}{N} I(q)$$

using the standard convention for classical systems (for quantum systems, the structure factor is often normalized by the volume rather than the number of particles). For liquids, or systems with isotropic symmetry, the structure function is a function of solely the magnitude of $q$, i.e. $S(q) = S(q)$.

While it is clear that $I(q)$ contains information on the positions of the particles, we can show that it is in fact the Fourier transform of the density-density correlation function. To see this let us first consider the Fourier transform of the density, $\hat{\rho}(q)$,

$$\hat{\rho}(q) = \int d\mathbf{r} \rho(\mathbf{r}) e^{i\mathbf{qr}} = \sum_\alpha e^{i\mathbf{q} \cdot \mathbf{r}_\alpha}$$

where we have used our now standard delta function representation of the density. Squaring $\hat{\rho}(q)$ and taking its thermal average,

$$\langle |\hat{\rho}(q)|^2 \rangle = \langle \sum_{\alpha, \alpha'} e^{i\mathbf{q} \cdot (\mathbf{r}_\alpha - \mathbf{r}_{\alpha'})} \rangle = I(q) = N S(q)$$

we find that the Fourier transformed density is $N$ times the structure factor. Writing out the Fourier transforms explicitly

$$S(q) = \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} = \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \left( \hat{\rho}(\mathbf{r} - \mathbf{r}') + \hat{\rho}^2 g(\mathbf{r} - \mathbf{r}') \right) e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} = 1 + \bar{\rho} \int d\mathbf{R} g(\mathbf{R}) e^{i\mathbf{q} \cdot \mathbf{R}}$$

where the second line follows from our previous manipulations of the density-density correlation function, and the second results form a substitution $\mathbf{R} = \mathbf{r} - \mathbf{r}'$. Thus we find explicitly, that up to an additive constant, the structure factor is the Fourier transform of the radial distribution function.