1. Fluids

What is a fluid? Almost everything that we will discuss is soft matter under physiological temperature conditions: liquids and solutions, cytoplasm and cytosol, DNA and proteins in solution, membranes, micelles, colloids, gels… All of these materials can in some respect be considered a fluid. So, what is a fluid?

- A substance that flows, deforms, and changes shape when subject to a force, or stress.
- It has no fixed shape, but adapts its surface to the shape of its container. Gasses are also fluids, but we will focus on fluids that are mostly incompressible.

For physicists, fluids are commonly associated with flow—a non-equilibrium property—and how matter responds to forces (i.e., “Newtonian fluids”). This topic—“rheology”—will be discussed in more detail later. From this perspective, all soft condensed matter can be considered a fluid.

For chemists, fluids most commonly appear as liquids and solutions. Chemists typically use a molecular description for the solute, but less so for the solvent. However, chemists have a clear appreciation of how liquids influence chemical behavior and reactivity, a topic commonly called “solvation”.

The most common perspective of fluids is as continuous dielectric media, however fluids can be multicomponent heterogeneous mixtures.

For our biophysical purposes, we use the perspectives above, with a particular interest in the uniquely biological fluid: water. Since we are particularly interested in molecular-scale phenomena, we will add some additional criteria:

- **Composition**: Fluids are dense media composed of particulate matter (atoms, molecules, proteins…) that can interact with one another. Since no two particles can occupy the same volume, each particle in a fluid has “excluded volume” that is not available to the remaining particles in the system.

- **“Structure”**: Fluids are structured locally on the distance scale of the particle size by their packing and cohesive interactions, but are macroscopically disordered.

- **The midrange or mesoscale distances** involve interactions between multiple particles, leading to correlated motions of the constituents.

- **“Flow”** is a manifestation of these correlated structural motions in the mesoscale structure.

- **Most important**: The cohesive forces (intermolecular interactions) between the constituents of a fluid, and the energy barriers to changing structure, are on the order of
$k_B T$ ("thermal energy"). Thermal forces are enough to cause spontaneous flow on a microscopic level even at equilibrium.

Fluids may appear time-invariant at equilibrium, but they are microscopically dynamic. In many cases, "structure" (the positioning of constituents in space) and the "dynamics" (time-dependent changes to position) are intimately coupled.
Radial Distribution Function

“Structure” implies that the positioning of particles is regular and predictable. This is possible in a fluid to some degree when considering the short-range position and packing of particles. The local particle density variation should show some structure in a statistically averaged sense. Structure requires a reference point, and in the case of a fluid we choose a single particle as the reference and describe the positioning of other particles relative to that. Since each particle of a fluid experiences a different local environment, this information must be statistically averaged, which is our first example of a correlation function. For distances longer than a “correlation length”, we should lose the ability to predict the relative position of a specific pair of particles. On this longer length scale, the fluid is homogeneous.

The radial distribution function, \( g(r) \), is the most useful measure of the “structure” of a fluid at molecular length scales. Although it invokes a continuum description, by “fluid” we mean any dense, disordered system which has local variation in the position of its constituent particles but is macroscopically isotropic. \( g(r) \) provides a statistical description of the local packing and particle density of the system, by describing the average distribution of particles around a central reference particle. We define the radial distribution function as the ratio of \( \langle \rho(r) \rangle \), the average local number density of particles at a distance \( r \), to the bulk density of particles, \( \rho \):

\[
g(r) = \frac{\langle \rho(r) \rangle}{\rho}
\]

In a dense system, \( g(r) \) starts at zero (since it does not count the reference particle), rises to a peak at the distance characterizing the first shell of particles surrounding the reference particle (i.e., the 1st solvation shell), and approaches 1 for long distances in isotropic media. The probability of finding a particle at a distance \( r \) in a shell of thickness \( dr \) is \( P(r) = 4 \pi r^2 g(r) \, dr \), so integrating \( \rho \cdot g(r) \) over the first peak in gives the average number of particles in the first shell.

The radial distribution function is most commonly used in gasses, liquids, and solutions, since it can be used to calculate thermodynamic properties such as the internal energy and pressure of the system. But is relevant at any size scale, such as packing of colloids, and is useful in complex heterogeneous media, such as the distribution of ions around DNA. For correlating the position of different types of particles, the radial distribution function is defined as the ratio of the local density of “b” particles at a distance \( r \) from “a” particles, \( g_{ab}(r) = \frac{\langle \rho_{ab}(r) \rangle}{\rho} \). In practice, \( \rho_{ab}(r) \) is
calculated by looking radially from an “a” particle at a shell at distance \( r \) and of thickness \( dr \), counting the number of “b” particles within that shell, and normalizing the count by the volume of that shell.

**Two-Particle Density Correlation Function**

Let’s look a little deeper, considering particles of the same type, as in an atomic liquid or granular material. If there are \( N \) particles in a volume \( V \), and the position of the \( i \)th particle is \( \vec{r}_i \), then the number density describes the position of particles,

\[
\rho(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)
\]

The average of a radially varying property given by \( X(r) \) is determined by

\[
\langle X(r) \rangle = \frac{1}{V} \int_{V} X(r) 4\pi r^2 dr
\]

Integrating \( \rho(\vec{r}) \) over a volume gives the particle number in that volume.

\[
\int_{V} \rho(r) 4\pi r^2 dr = N
\]

When the integral is over the entire volume, we can use this to obtain the average particle density:

\[
\frac{1}{V} \int_{0}^{\infty} \rho(r) 4\pi r^2 dr = \frac{N}{V} = \rho
\]

Next, we can consider the spatial correlations between two particles, \( i \) and \( j \). The two-particle density correlation function is

\[
\rho(\vec{r},\vec{r}') = \left\langle \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \sum_{j=1}^{N} \delta(\vec{r}' - \vec{r}_j) \right\rangle
\]

This describes the conditional probability of finding particle \( i \) at position \( r_i \) and particle \( j \) at position \( r_j \). We can expand and factor \( \rho(\vec{r},\vec{r}') \) into two terms depending on whether \( i = j \) or \( i \neq j \):

\[
\rho(\vec{r},\vec{r}') = N \left\langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \right\rangle + N (N-1) \left\langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \right\rangle
\]

\[
= \rho^{(1)} + \rho^{(2)}(\vec{r},\vec{r}')
\]

The first term describes the self-correlations, of which there are \( N \) terms: one for each atom.

\[
\rho^{(1)} = N \left\langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \right\rangle = \rho
\]

The second term describes the two-body correlations, of which there are \( N(N-1) \) terms.

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\[ \rho^{(2)}(\vec{r}, \vec{r}') = N(N-1)\langle \delta(\vec{r} - \vec{r}_i)\delta(\vec{r}' - \vec{r}_j) \rangle \]

\[ = \frac{N^2}{V^2} g(\vec{r}, \vec{r}') = \rho^2 g(\vec{r}, \vec{r}') \]

\( g(\vec{r}, \vec{r}') = \rho^{(2)}(\vec{r}, \vec{r}') / \rho^2 \) is the two-particle distribution function, which describes spatial correlation between two atoms or molecules. For isotropic media, it depends only on distance between particles, \( g(|\vec{r} - \vec{r}'|) = g(r) \), and is therefore also called the radial pair-distribution function.

We can generalize \( g(r) \) to a mixture of \( a \) and \( b \) particles by writing \( g_{ab}(r) \):

\[ g_{ab}(r) = \frac{\rho_{ab}(r)}{N_b / V} \]

\[ N_b = \int dr 4\pi r^2 \rho_{ab}(r) \]

**Potential of Mean Force**

One can use \( g(r) \) to describe the free energy for bringing two particles together as

\[ W(r) = -k_B T \ln g(r) \]

\( W(r) \) is known as the potential mean force. We are taking a free energy which is a function of many internal variables and projecting it onto a single coordinate. \( W(r) \) is a potential function that can be used to obtain the mean effective forces that a particle will experience at a given separation \( f = -\partial W / \partial r \).
**Excluded Volume**

One of the key concepts that arises from a particulate description of matter is excluded volume. Even in the absence of attractive interactions, at short range the particles of the fluid collide and experience repulsive forces. These repulsive forces are a manifestation of excluded volume, the volume occupied by one particle that is not available to another. This excluded volume gives rise to the structure of solvation shells that is reflected in the short-range form of $g(r)$ and $W(r)$. Excluded volume also has complex dynamic effects in dense fluids, because one particle cannot move far without many other particles also moving in some correlated manner.

The excluded volume can be related to $g(r)$ and $W(r)$, making note of the virial expansion. If we expand the equation of state in the density of the fluid ($\rho$):

$$\frac{p}{\rho k_B T} = 1 + B_2(T) \rho + \cdots$$

The second virial coefficient $B_2$ is half of the excluded volume of the system. This is the leading source of non-ideality in gasses reflected in the van der Waals equation of state.

$$2B_2(T) = \int_0^\infty r^2 (1 - g(r)) dr$$

$$= \int_0^\infty r^2 (1 - \exp[-W(r) / k_B T]) dr$$