1. **Computing radial distribution functions from the Percus-Yevick approximation**

   The Ornstein-Zernicke equation,

$$h(r) = c(r) + \bar{\rho} \int d\mathbf{r}'\, h(|\mathbf{r} - \mathbf{r}'|)c(r'),$$

   can be viewed as a definition of the direct correlation function $c(r)$ in terms of $h(r) = g(r) - 1$. In practice it often forms the basis of approximate theories for $h(r)$, which make physically motivated assumptions about the form of $c(r)$.

   Percus and Yevick offered an approximation for $c(r)$ that is particularly simple in the case of hard sphere fluids:

$$c(r) = 0, \quad r > d$$

   where d is the hard sphere diameter. Together with the result of strict volume exclusion,

$$h(r) = -1, \quad r < d$$

   this assertion closes the Ornstein-Zernicke equation, forming a complete (though approximate) theory for density correlations. Unlike most such theories, it has an analytical solution:

$$c(r) = \left[\lambda_1 + \lambda_2 \left(\frac{r}{d}\right) + \lambda_3 \left(\frac{r}{d}\right)^3\right] \theta(d - r), \tag{1}$$

   where

$$\theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases}$$

   is the Heaviside step function. The coefficients λ_i depend on the macroscopic density $\bar{\rho}$. This dependence is more compactly expressed through the packing fraction $\eta = (\pi/6)\bar{\rho}d^3$:

$$\lambda_1 = -\frac{(1 + 2\eta)^2}{(1 - \eta)^4}$$
$$\lambda_2 = 6\eta \frac{(1 + \eta/2)^2}{(1 - \eta)^4}$$
$$\lambda_3 = \frac{\eta}{2}\lambda_1$$

   The solution for $h(r)$ cannot be written in such a simple analytical form. Here you will determine it numerically through the Ornstein-Zernicke equation.

(i) For hard spheres, the functions $h(r)$ and $c(r)$ are discontinuous at $r = d$. Their Fourier transforms are therefore highly oscillatory and troublesome to contend with numerically. Their difference,

$$I(r) = h(r) - c(r),$$

however, is a continuous function of r. (You are not required to explain this smoothness, but you might think about how it is guaranteed by the Ornstein-Zernicke equation.) Write the Fourier transform of this difference, $\hat{I}(k)$, solely in terms of $\hat{c}(k)$ and the density $\bar{\rho}$.

As usual, we define spatial Fourier transforms according to

$$\hat{f}(\mathbf{k}) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}), \qquad f(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^3}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{f}(\mathbf{k}).$$

As in the previous assignment, you should find it useful to exploit the convolution theorem. Specifically, for a convolution $z(\mathbf{r})$ of two functions $x(\mathbf{r})$ and $y(\mathbf{r})$,

$$z(\mathbf{r}) = \int d\mathbf{r}'\, x(\mathbf{r} - \mathbf{r}')y(\mathbf{r}'),$$

Fourier integration yields

$$\hat{z}(\mathbf{k}) = \hat{x}(\mathbf{k})\hat{y}(\mathbf{k}).$$

(ii) By writing $h(r)$, rather than $h(\mathbf{r})$, we have already acknowledged that correlations in an isotropic fluid do not depend upon direction, only on distance $r = |\mathbf{r}|$. For such rotationally symmetric functions, the angular part of Fourier transform integrals can be performed straightforwardly.

For a function $f(r)$ of distance r only, show that

$$\hat{f}(k) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} f(r) = \frac{4\pi}{k} \int dr\, r\, \sin(kr) f(r),$$

indicating that the Fourier transform of $f(r)$ depends only on the magnitude $k = |\mathbf{k}|$ of wavevector $\mathbf{k}$. Similarly, show that

$$f(r) = \left(2\pi^2 r\right)^{-1} \int dk\, k\, \sin(kr)\hat{f}(k)$$

[**Hint:** When integrating over the position $\mathbf{r}$, it is convenient to take the z-axis to point in the same direction as $\mathbf{k}$. This choice is innocuous, since $\mathbf{k}$ is constant within the integral, and because any Cartesian coordinate system must yield the same result regardless of orientation. You should find that it makes evaluation of the integral in spherical polar coordinates very simple.]

(iii) Compute $I(r)$ by numerical Fourier inversion of your result from part (i). To do so, you will need to construct $\hat{c}(k)$ from Eq. 1. The following integrals should come in handy:

$$\int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, \theta(d-r) = 4\pi d^3 \left[-\frac{\cos kd}{(kd)^2} + \frac{\sin kd}{(kd)^3}\right]$$

$$\int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, \theta(d-r)\, \left(\frac{r}{d}\right) = 4\pi d^3 \left[-\frac{\cos kd}{(kd)^2} + 2\frac{\sin kd}{(kd)^3} + 2\frac{\cos kd - 1}{(kd)^4}\right]$$

$$\int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, \theta(d-r)\, \left(\frac{r}{d}\right)^3 = 4\pi d^3 \left[-\frac{\cos kd}{(kd)^2} + 4\frac{\sin kd}{(kd)^3} + 12\frac{\cos kd}{(kd)^4} - 24\frac{\sin kd}{(kd)^5} - 24\frac{\cos kd - 1}{(kd)^6}\right]$$

[**Caution:** These functions of k are mathematically well-behaved as $k \to 0$ but are numerically problematic to evaluate when k is very small. Before embarking on numerical integration, check that they are generating reasonable values for the range of k you are considering.]

Plot your results for $h(r)$ for densities $\bar{\rho}d^3 = 0.02$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9.

(v) Plot the Percus-Yevick predictions for $g(r)$ alongside results from Monte Carlo simulations for densities $\bar{\rho}d^3 = 0.1$, 0.4, 0.7, and 0.9. (You should have computed these quantities for Problem Set #3.) Comment on the quality of agreement.

2. **"Molecular" dynamics of a harmonic oscillator**

No introduction to dynamics would be complete without a study of harmonic oscillators. In this problem you will apply Verlet's algorithm to a one-dimensional, classical harmonic oscillator, approximately advancing its position r and velocity v in time.

Specifically, consider a particle of mass m moving in a one-dimensional potential

$$U = \frac{1}{2}kr^2.$$

Its equation of motion should be very familiar:

$$F = ma, \qquad \text{or} \qquad \begin{pmatrix} \dot{r} \\ \dot{v} \end{pmatrix} = \begin{pmatrix} v \\ F/m \end{pmatrix}$$

where $F = -dU/dr$ is the force. The reason for writing the pair of differential equations for r and v in vector form will become clear later.

(i) Adopt ℓ and $\tau = \sqrt{m/k}$ as units of length and time, respectively. Beginning with the Verlet equations for advancing r and v from time t to time $t + \Delta t$, write out corresponding equations for the dimensionless quantities

$$\bar{r} = r/\ell \qquad \text{and} \qquad \bar{v} = v\tau/\ell$$

Your answer should involve only $\bar{r}(\bar{t}+\bar{\Delta}t)$, $\bar{v}(\bar{t}+\bar{\Delta}t)$, $\bar{r}(\bar{t})$, $\bar{v}(\bar{t})$, and the dimensionless times $\bar{t} = t/\tau$ and $\bar{\Delta}t = \Delta t/\tau$.

(ii) From now on, we will work with these dimensionless quantities exclusively, i.e., the overbars on r, v, t, and Δt will be implied.

Implement your advancement equations from part (i) on a computer. As an initial condition, take

$$\begin{pmatrix} r(0) \\ v(0) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Use a time step of $\Delta t = 0.1$, and propagate the system for enough time steps to complete 10 periods of oscillation.

Make a plot of r and v as functions of time. Does the period of oscillation match your expectations? Explain.

Also make a plot of the kinetic, potential, and total energies as functions of time.

(iii) Make a parametric plot of $(r(t), v(t))$. That is to say, plot all of the ordered pairs (r, v) on a graph with r on the horizontal axis, v on the vertical axis. This type of plot, known as a phase portrait, can often reveal important structure about dynamical systems. If the energy of our harmonic oscillator were perfectly conserved, what shape would this plot trace out?

(iv) How would you expect a histogram of the oscillator's position r, accumulated at regular time intervals over a long trajectory, to appear? (It is OK if your expectation is incorrect. I am just curious what it is.) Compute this probability distribution $p(r)$, appropriately normalized, from your simulated trajectory. Plot your result.

(v) The correct form of $p(r)$, in the limit $\Delta t \to 0$, can be obtained from a simple argument: Consider a small interval in the oscillator's position, between r and $r + dr$. The amount of time the oscillator spends in this interval, $p(r) \propto 1/|v(r)|$, is inversely proportional to its speed as it passes through. (Explain why this is so.) Using this fact, together with the conservation of energy, write $p(r)$ as a function of r.

3. **Molecular dynamics on a piece of paper**

Because the Verlet equations for the harmonic oscillator are so simple, we can work out their consequences analytically.

(i) Begin by rewriting the Verlet equations in the following form:

$$\begin{pmatrix} r(t+\Delta t) \\ v(t+\Delta t) \end{pmatrix} = \mathbf{W} \cdot \begin{pmatrix} r(t) \\ v(t) \end{pmatrix} \tag{2}$$

Identify the matrix $\mathbf{W}$, i.e., determine the elements W_{ij} of

$$\mathbf{W} = \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}$$

(ii) Calculate the eigenvalues λ_1 and λ_2 of $\mathbf{W}$. Consider the case $\Delta t < 2$, for which λ_1 and λ_2 are complex numbers. You are welcome to use a program like Mathematica for this and later parts of the problem.

(iii) The matrix $\mathbf{W}$ can be diagonalized by a similarity transformation

$$\mathbf{W} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}^{-1}$$

where

$$\mathbf{D} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

is a diagonal matrix whose nonzero entries are the eigenvalues of $\mathbf{W}$.

Given their importance, let's look more closely at these eigenvalues. As complex numbers they can be written in the form $\lambda = Ae^{i\phi}$, where A and ϕ are real numbers. Show that $A = 1$ for both eigenvalues. More specifically, show that the eigenvalues can be written as $\lambda_1 = e^{i\phi}$ and $\lambda_2 = e^{-i\phi}$. Identify ϕ in terms of Δt.

(iv) Time propagation of the simulated oscillator can be achieved by iterating Eq. 2:

$$\begin{pmatrix} r(t+2\Delta t) \\ v(t+2\Delta t) \end{pmatrix} = \mathbf{W}^2 \cdot \begin{pmatrix} r(t) \\ v(t) \end{pmatrix}, \quad \text{and more generally} \quad \begin{pmatrix} r(t+n\Delta t) \\ v(t+n\Delta t) \end{pmatrix} = \mathbf{W}^n \cdot \begin{pmatrix} r(t) \\ v(t) \end{pmatrix}.$$

Show that the n-step propagator can be written

$$\mathbf{W}^n = \mathbf{S} \cdot \begin{pmatrix} \lambda_1^n & 0 \\ 0 & \lambda_2^n \end{pmatrix} \cdot \mathbf{S}^{-1}$$

(iv) Here are the transformation matrices $\mathbf{S}$ and $\mathbf{S}^{-1}$:

$$\mathbf{S} = \begin{pmatrix} -1 & 1 \\ * & * \end{pmatrix}, \qquad \mathbf{S}^{-1} = \begin{pmatrix} -1/2 & * \\ 1/2 & * \end{pmatrix}.$$

(The matrix elements indicated by a * are ugly, and you should not need them.) With this information, show that the Verlet algorithm for this oscillator evolves from an initial state $r(0) = 1, v(0) = 0$ in a particularly simple way, $r(n\Delta t) = \cos(n\phi)$. Plot this result alongside the trajectory you simulated using a computer.

(vi) In light of the above analysis, what do you think happens when $\Delta t > 2$? Describe in words what aspects of the calculation change and how you expect $r(n\Delta t)$ to behave. Check this expectation numerically, and plot a few trajectories to illustrate the consequence of using too large a time step.