1. **Microscopic density fields as dynamical normal modes**

In previous assignments you have shown that the response of a liquid's microscopic density to time-*independent* perturbations is linear to a remarkable degree. Here you will examine how such variables respond to forces that vary in time. This computational exercise requires you to extend and apply the molecular dynamics (MD) simulation program you have developed for a liquid of Lennard-Jones particles.

We will add to the Lennard-Jones Hamiltonian $\mathcal{H}_{\rm LJ}$ an explicitly time-dependent term,

$$\mathcal{H} = \mathcal{H}_{\rm LJ} - f(t)X(r^N). \tag{1}$$

The external force $f(t)$ acts on a collective variable

$$X = \frac{\mathrm{Re}[\hat{\rho}(\mathbf{k})]}{\sqrt{N}},$$

where $\hat{\rho}(\mathbf{k}) = \sum_{j=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_j}$ is a Fourier component of the liquid's microscopic density field.

We will consider only wavevectors $\mathbf{k} = k\,\hat{x}$ that point in the $x$-direction. (The scalar quantity $k$ refers to this wavevector's magnitude, $k = |\mathbf{k}|$.) The external force we have added thus encourages variations in density that are periodic in $x$ with a wavelength $2\pi/k$.

(i) Adding the external perturbation to your simulation requires computing the corresponding forces experienced by each particle. Show first that these forces are nonzero only in the $x$-direction. Then show that the force on particle $j$ has magnitude

$$F_j = f(t)\frac{k\sin(kx_j)}{\sqrt{N}}$$

(ii) We will consider a specific (and familiar) form for the external force:

$$f(t) = \begin{cases} f_0, & -\infty < t < 0 \\ 0, & 0 < t < \infty, \end{cases}$$

corresponding to relaxation from one equilibrium state (with Hamiltonian $\mathcal{H}_{\rm LJ} - f_0 X$) to another (with Hamiltonian $\mathcal{H}_{\rm LJ}$). In order to calculate the average time-dependent response $\overline{X}(t)$ for $t > 0$, you can therefore (i) sample configurations from the initial equilibrium state (by performing standard MD in the presence of a static force $f_0$), and then (ii) propagate these configurations in time according to undisturbed Lennard-Jones dynamics.

Perform this calculation for a system with $N = 125$ particles at density $\rho^* = 0.5$ and temperature $T^* = 1.5$. Consider three different perturbation strengths: $f_0 = 3, 5$, and 10 and three different wavevectors $k = 12\pi/L$, $24\pi/L$, and $36\pi/L$. (For this choice of $\rho^*$ and $N$, the box length is $L = 250^{1/3}\sigma$.) Plot $\overline{X}(t)/(\beta f_0)$ as a function of time over the range $0 < t < 1$ (where $t$ is a dimensionless time implicitly in units of $\tau = \sqrt{m\sigma^2/\epsilon}$). Specifically, make a separate plot for each value of $f_0$, showing results for all three wavevectors (i.e., 3 graphs, each with 3 curves). You will need to average over many different initial configurations; report how many you find necessary to achieve a respectably converged result.

(iii) The linear response theory we developed in lecture suggests that the results of these relaxation "experiments" should, for small enough $f_0$, be well predicted by an appropriate equilibrium time

correlation function. Show this to be true. Specifically, write an equation relating $\overline{X}(t)/(\beta f_0)$ to the "intermediate scattering function"

$$S(k,t) \equiv \frac{\langle \hat{\rho}(k)\hat{\rho}(-k,t)\rangle_0}{N},$$

where the subscript "0" indicates an average in the absence of external forces ($f = 0$). Your result should be accurate to linear order in $f_0$. You may quote any pertinent results from lecture.

(iv) Using MD simulations, compute $S(k,t)$ for the same wavevectors ($k = 12\pi/L$, $24\pi/L$, and $36\pi/L$) and parameters ($N = 125$, $\rho^* = 0.5$, and $T^* = 1.5$) as in part (ii). You should need only one long equilibrium trajectory to to do so (and you may want to exploit appropriate symmetries).

Make a plot showing $S(k,t)/2$ as a function of time for each of the three wavevectors.

(v) Comparing your results from parts (ii) and (iv), comment on the accuracy of linear response theory for predicting $\overline{X}(t)/(\beta f_0)$. In particular, is it reasonably valid for all values of $f_0$? For only a particular range of $f_0$? For all times?

2. Consider the dynamics of a classical oscillator in a fluctuating environment, e.g., a low-frequency intramolecular vibration of a solute molecule in a dense liquid. In class we developed a simple equation of motion for such a coordinate $x$, caricaturing its surroundings as a collection of harmonic oscillators. If the tagged vibrational mode is also harmonic, and the environment relaxes very rapidly, then $x(t)$ satisfies a Langevin equation:

$$m\ddot{x} = -\gamma\dot{x} - m\omega_0^2 x + f(t) + \eta(t). \tag{2}$$

Here, $m$ is the oscillator's mass, $\omega_0$ is its intrinsic vibrational frequency, and $f(t)$ is a time-dependent external force. The forces $-\gamma\dot{x}$ and $\eta(t)$ represent the bath's influence on $x(t)$, contributing frictional damping and random buffeting (with $\langle\eta(t)\rangle = 0$), respectively. The strengths of these contributions are related by a fluctuation-dissipation theorem.

(i) Using Laplace transforms,

$$\tilde{g}(s) = \int_0^\infty dt\, g(t)\, e^{-st},$$

solve for the average response $\langle\tilde{x}(s)\rangle_f$ to the external force $f(t)$. More specifically, calculate the response function $\tilde{\chi}(s)$ that governs linear response, $\langle\tilde{x}(s)\rangle_f = \langle\tilde{x}(s)\rangle_0 + \tilde{\chi}(s)\tilde{f}(s)$.

(ii) Show that the dimensionless response function $\tilde{\chi}^*(s) = m\omega_0^2\tilde{\chi}(s)$ can be written solely in terms of the dimensionless Laplace frequency $s^* = s/\omega_0$ and the dimensionless parameter $\gamma^* = \gamma/(m\omega_0)$.

(iii) From now on, we will work exclusively with the dimensionless quantities of part (ii). The *'s will be implied. Additional time and frequency variables that appear later will also be implicitly scaled by $\omega_0$.

Rewrite your result for $\tilde{\chi}(s)$ in the form

$$\frac{1}{2ib}\left[\frac{1}{(s+a)-ib} - \frac{1}{(s+a)+ib}\right].$$

Identify $a$ and $b$ in terms of the parameters $\gamma$ and $\overline{\omega} = \sqrt{1-\gamma^2/4}$

(iv) Due to causality, there is a simple relationship between $\tilde{\chi}(s)$ and the Fourier transform

$$\hat{\chi}(\omega) = \int_{-\infty}^{\infty} dt\, \chi(t) e^{i\omega t}.$$

(Recall that $\hat{\chi}(\omega)$, $\omega$, and $t$ are implicitly dimensionless, i.e., they refer to $\hat{\chi}^*(\omega) = m\omega_0^2\hat{\chi}(\omega)$, $\omega^* = \omega/\omega_0$, and $t^* = t\omega_0$, respectively.) Determine this relationship, and use it together with your result from part (iii) to write $\hat{\chi}(\omega)$ in terms of $\omega$ and the parameters $\gamma$ and $\overline{\omega}$.

(v) By rationalizing the two terms in your expression for $\hat{\chi}(\omega)$ from part (iv), extract the real and imaginary parts of $\hat{\chi}(\omega) = \hat{\chi}'(\omega) + i\hat{\chi}''(\omega)$.

(vi) In lecture we showed that the imaginary part of $\hat{\chi}(\omega)$ relates directly to absorption. Write $\hat{\chi}''(\omega)$ in terms of a lineshape function $\hat{\phi}(\omega)$, so that

$$\hat{\chi}''(\omega) = \hat{\phi}(\omega - \omega_\mathrm{r}) - \hat{\phi}(\omega + \omega_\mathrm{r})$$

Your result should show that if $\gamma$ is not too large, then $\hat{\chi}''(\omega)$ features two well-separated spectral features, one centered at positive resonance frequency $\omega_\mathrm{r}$ and one at negative frequency $-\omega_\mathrm{r}$. Identify the center frequencies and widths of these peaks in terms of $\gamma$ and $\overline{\omega}$. (Note that the Lorentzian function $L(x) = \pi^{-1}\Gamma/(x^2 + \Gamma^2)$ has a characteristic width of $2\Gamma$.)

(vii) Plot $\hat{\chi}''(\omega)$ as a function of $\omega$ for the case $\gamma = 0.5$. Do the peak positions and widths correspond to your expectations from part (vi)? Make additional plots for $\gamma = 0.1$ and $\gamma = 1$.

3. In class we encountered the Fokker-Planck equation in its general form,

$$\frac{\partial f(\mathbf{a};t)}{\partial t} = -\frac{\partial}{\partial \mathbf{a}} \cdot (\mathbf{v}f) + \frac{1}{2}\frac{\partial}{\partial \mathbf{a}} \cdot \mathbf{B} \cdot \frac{\partial}{\partial \mathbf{a}} f,$$

where $f(\mathbf{a};t)$ is the probability distribution for a collection of variables $\mathbf{a} = \{a_1, a_2, \ldots\}$ that evolve in time according to stochastic equations of motion:

$$\frac{d\mathbf{a}}{dt} = \mathbf{v}(\mathbf{a}) + \boldsymbol{\eta}.$$

The random forces $\boldsymbol{\eta} = \{\eta_1, \eta_2, \ldots\}$ each have zero mean. Their Gaussian statistics are completely described by the set of (co)variances

$$\langle \eta_i(t)\eta_j(t')\rangle = B_{ij}\delta(t - t').$$

(i) Adapt this result to the specific case of single-particle Langevin dynamics:

$$m\ddot{r} = -\frac{dw(r)}{dr} - \gamma\dot{r} + \eta, \qquad \text{with} \qquad \langle \eta(t)\eta(t')\rangle = 2k_\mathrm{B}T\gamma\delta(t - t'),$$

where $m$ and $\gamma$ are positive constants, and $w(r)$ is the reversible work function governing the equilibrium distribution of $r$. Specifically, determine an equation for the phase space distribution $f(r, p; t)$, where $p$ is the particle's momentum. Write your result in the form

$$\frac{\partial f(r,p;t)}{\partial t} = (\ldots) + (\ldots)f + (\ldots)\frac{\partial f}{\partial r} + (\ldots)\frac{\partial f}{\partial p} + (\ldots)\frac{\partial^2 f}{\partial r^2} + (\ldots)\frac{\partial^2 f}{\partial p^2} + (\ldots)\frac{\partial^2 f}{\partial r \partial p}.$$

The unspecified quantities $(\ldots)$, some of which are zero, may depend on $r$, $p$, temperature, and model parameters.

(ii) Verify that the Boltzmann distribution, $f(r,p) \propto e^{-\beta\mathcal{H}}$, where $\mathcal{H} = p^2/(2m) + w(r)$, is a stationary solution to the Fokker-Planck equation you derived in part (i).