CHM1485: Molecular Dynamics and Chemical Dynamics in Liquids

PROBLEM SET 4

Notes:

- This set contains 2 problems, with multiple parts to each problem.
- Please start each problem on a new page.
- Due date: December 6, 2005.

1 Microscopic Derivation of the Fokker-Planck Equation

Consider a system consisting of n large, *interacting* spherical Brownian particles of mass M with position $\mathbf{R}_i$ and momentum $\mathbf{P}_i$ immersed in a fluid of N spherical, light particles of mass m with positions $\mathbf{r}^{(N)}$ and momenta $\mathbf{p}^{(N)}$. Assume that the Hamiltonian of the system is of the form:

$$\begin{aligned} H &= \frac{\mathbf{P}\cdot\mathbf{P}}{2M} + V(\mathbf{R}) + \frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m} + U(\mathbf{r}^{(N)}) + \phi(\mathbf{r}^{(N)},\mathbf{R}) = H_B + H_S + \phi(\mathbf{r}^{(N)},\mathbf{R}) \\ V(\mathbf{R}) &= \sum_{i=1}^{n}\sum_{j<i} V(|\mathbf{R}_i-\mathbf{R}_j|) \qquad \phi(\mathbf{r}^{(N)},\mathbf{R}) = \sum_{i=1}^{n}\sum_{j=1}^{N}\phi(|\mathbf{R}_i-\mathbf{r}_j|) \qquad U(\mathbf{r}^{(N)}) = \sum_{i<j} U(|\mathbf{r}_{ij}|), \end{aligned}$$

where $\mathbf{R} = \{\mathbf{R}_1,\ldots\mathbf{R}_n\}$ and $\mathbf{P} = \{\mathbf{P}_1,\ldots,\mathbf{P}_n\}$. The goal of this exercise is to derive an equation of motion for the reduced distribution function

$$W(\mathbf{R},\mathbf{P},t) = \int d\mathbf{x}^{(N)}\rho(\mathbf{x}^{(N)},\mathbf{R},\mathbf{P},t).$$

It is convenient to introduce the equilibrium distribution functions

$$\begin{aligned} \rho_e &= \frac{e^{-\beta H}}{q} \\ W_e &= \frac{e^{-\beta H_B}\int d\mathbf{x}^{(N)}\, e^{-\beta H_S}e^{-\beta\phi}}{q} \end{aligned}$$

where $q = \int d\mathbf{R}d\mathbf{P}d\mathbf{x}^{(N)}\, e^{-\beta H_B}e^{-\beta H_S}e^{-\beta\phi}$. We also introduce the conditional distribution function for the bath degrees of freedom in the presence of fixed Brownian degrees of freedom:

$$\tilde{\rho} = \frac{\rho_e}{W_e}.$$

We also define the projection operator $\mathcal{P}$ by $\mathcal{P}B = \tilde{\rho}\int d\mathbf{x}^{(N)}\, B$.

a. Show that $\tilde{\rho} = \rho_s e^{-\beta\phi}e^{\beta\omega(\mathbf{R})}$, where $\rho_s(\mathbf{x}^{(N)})$ is the equilibrium probability density for the *isolated* bath. What is the physical interpretation of $\omega(\mathbf{R})$?

b. Verify that $\mathcal{P}$ is a projection operator.

c. Defining $y(t) = \mathcal{P}\rho(t)$ and $z(t) = (1-\mathcal{P})\rho(t)$, from the Liouville equation, show that the reduced non-equilibrium $W(\mathbf{R},\mathbf{P},t)$ obeys the exact equation;

$$\begin{aligned}\dot{W}(\mathbf{R},\mathbf{P},t) &= \mathcal{L}_B W(\mathbf{R},\mathbf{P},t) + \int d\mathbf{x}^{(N)}\,\tilde{\rho}\nabla_{\mathbf{R}}\phi\cdot\nabla_{\mathbf{P}}W(\mathbf{R},\mathbf{P},t)\\ &\quad+\nabla_{\mathbf{P}}\cdot\int d\mathbf{x}^{(N)}\,\nabla_{\mathbf{R}}\phi\,z(t),\end{aligned}$$

where $\mathcal{L}_B$ is the Liouville operator for the isolated Brownian particles.

d. Show that the formal solution of the time evolution of $z(t)$ can be written as:

$$z(t) = e^{\mathcal{Q}\mathcal{L}t}z(0) + \int_0^t d\tau\, e^{\mathcal{Q}\mathcal{L}\tau}\mathcal{Q}\mathcal{L}y(t-\tau),$$

where $\mathcal{Q} = 1-\mathcal{P}$.

e. Using the results from parts c. and d., show that W obeys the exact equation:

$$\begin{aligned}\dot{W}(\mathbf{R},\mathbf{P},t) &= \left(-\frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}}+\nabla_{\mathbf{R}}\left(V+\omega\right)\cdot\nabla_{\mathbf{P}}\right)W(t)\\ &\quad+\nabla_{\mathbf{P}}\cdot\int_0^t d\tau\int d\mathbf{x}^{(N)}\,\nabla_{\mathbf{R}}\phi e^{\mathcal{Q}\mathcal{L}\tau}\tilde{\rho}\nabla_{\mathbf{R}}(\phi-\omega)\cdot\left(\nabla_{\mathbf{P}}+\frac{\beta\mathbf{P}}{M}\right)W(t-\tau)\\ &\quad+\nabla_{\mathbf{P}}\cdot\int d\mathbf{x}^{(N)}\,\nabla_{\mathbf{R}}\phi e^{\mathcal{Q}\mathcal{L}t}z(0).\end{aligned}$$

f. Defining the mass ratio $\epsilon = \sqrt{(m/M)}$ and introducing the scaled momenta coordinates $\mathbf{P}^* = \epsilon\mathbf{P}$, show that for times longer than the bath relaxation time τ_s and to second order in powers of ϵ, we obtain the Fokker-Planck equation for the Brownian degrees of freedom:

$$\begin{aligned}\dot{W}(\mathbf{R},\mathbf{P},t) &= \left[\epsilon\left(-\frac{\mathbf{P}^*}{m}\cdot\nabla_{\mathbf{R}}+\nabla_{\mathbf{R}}\left(V+\omega\right)\cdot\nabla_{\mathbf{P}^*}\right)\right.\\ &\qquad\left.+\epsilon^2\nabla_{\mathbf{P}^*}\cdot\Gamma(\mathbf{R})\cdot\left(\nabla_{\mathbf{P}^*}+\frac{\beta\mathbf{P}^*}{m}\right)\right]W(t)+O\left(\epsilon^3\right),\end{aligned}$$

where

$$\Gamma(\mathbf{R}) = \int_0^\infty d\tau\,\left\langle\nabla_{\mathbf{R}}(\phi-\omega)\left(e^{(\mathcal{L}_s+\nabla_{\mathbf{r}^N}\phi\cdot\nabla_{\mathbf{p}^N})\tau}\right)\nabla_{\mathbf{R}}(\phi-\omega)\right\rangle.$$

How does this result differ from the Fokker-Planck equation for a single Brownian particle presented in class?

2 The Hydrodynamic Equations

Consider the general hydrodynamic matrix derived in class:

$$\mathbf{M}(\mathbf{k},z) = \begin{pmatrix} 0 & 0 & ik & 0 & 0 \\ 0 & -ak^2 & \frac{ikT}{n^2 c_v}\left(\frac{\partial P_h}{\partial T}\right)_n & 0 & 0 \\ \frac{ik}{m}\left(\frac{\partial P_h}{\partial n}\right)_T & \frac{ik}{m}\left(\frac{\partial P_h}{\partial T}\right)_n & -bk^2 & 0 & 0 \\ 0 & 0 & 0 & -\nu k^2 & 0 \\ 0 & 0 & 0 & 0 & -\nu k^2 \end{pmatrix}.$$

that gives the equations of motion for the linearized hydrodynamic densities

$$\tilde{A}(\mathbf{k},z) \quad = \quad [zI - M(\mathbf{k},z)]^{-1} \cdot A(\mathbf{k}),$$

where

$$\begin{aligned} \tilde{A}(\mathbf{k},z) &= \{\tilde{n}(\mathbf{k},z), \tilde{T}(\mathbf{k},z), \tilde{\mathbf{j}}^z(\mathbf{k},z), \tilde{\mathbf{j}}^x(\mathbf{k},z), \tilde{\mathbf{j}}^y(\mathbf{k},z)\} \\ A(\mathbf{k}) &= \{n(\mathbf{k}), T(\mathbf{k}), \mathbf{j}^z(\mathbf{k}), \mathbf{j}^x(\mathbf{k}), \mathbf{j}^y(\mathbf{k}).\}, \end{aligned}$$

a. By expanding $z_i = z_i^{(0)} + z_i^{(1)} k + z_i^{(2)} k^2 + \ldots$ in powers of k and solving for the coefficients $z_i^{(j)}$ order by order, show that the roots of the determinant $\det|z\mathbf{I} - \mathbf{M}(\mathbf{k},z)|$, to second order in k, are

$$z_0 = -\Gamma_T k^2 \qquad z_\pm = \pm c_0 k - \Gamma_s k^2$$

with

$$\Gamma_T = \frac{a}{\gamma} = \frac{\lambda}{nc_p} \qquad \Gamma_s = \frac{1}{2}\left[a(\gamma-1)/\gamma + b\right] \qquad \gamma = c_p/c_v.$$

b. Using the minor formula,

$$[z\mathbf{I} - \mathbf{M}(\mathbf{k},z)]^{-1}_{\alpha\beta} = \frac{(-1)^{\alpha+\beta}\mathcal{M}_{\beta\alpha}}{\det|z\mathbf{I} - \mathbf{M}(\mathbf{k},z)|},$$

derive an expression for the time dependence of $n(\mathbf{k},t)$, $T(\mathbf{k},t)$ and $\mathbf{v}(\mathbf{k},t)$.