Chap 5. Dynamics in Condensed Phases

• <u>Generalized Langevin Equation</u>

Phenomenological introduction

$$m\dot{v} = -m\int_0^t \Gamma(t-\tau)v(\tau)d\tau + R(t)$$

$$\left[\begin{array}{l} \Gamma(t) : \text{friction kernel} \sim \text{friction depends on the past} \\ \qquad (= \text{memory effect : delayed response of the surrounding media}) \\ R(t) : \text{random force} \end{array}\right]$$

Later, GLE will be derived from a model Hamiltonian

(and thus, GLE may be <u>time reversible</u>)

• **Coarse graining**

If : $\Gamma(t) \simeq 2\bar{\gamma}\delta(t)$ (no delay)

$$\Rightarrow m\dot{v} = -\bar{\gamma} m v(t) + R(t) \qquad (\textbf{Langevin eq})$$

Similarly, if we look at the dynamics in (macroscopic) time scale Δt

much larger than the (microscopic) decay time of $\Gamma(t)$,

(i.e., **"coarse-graining"** in time)

$$m\dot{v}(t) = -\bar{\Gamma} m v(t) + R(t) \qquad \left(\bar{\Gamma} \equiv \int_0^{\Delta t} \Gamma(\tau) d\tau \simeq \int_0^{\infty} \Gamma(\tau) d\tau \right)$$

In this way, the time reversibility of the (classical mechanical) dynamics is lost by the coarse-graining of time scale.

(But, GLE may be time reversible)

- **Laplace transform** [*math preparation*]

Definition : $\mathcal{L}\{f(t)\} = \int_0^\infty e^{-st} f(t)dt = \tilde{f}(s)$ where $(s > 0\ )$

Derivatives : $\mathcal{L}\{\dot{f}(t)\} = s\tilde{f}(s) - f(0)\ ,\ \mathcal{L}\{\ddot{f}(t)\} = s^2\tilde{f}(s) - sf(0) - \dot{f}(0)$

Convolution : $\mathcal{L}\{f(t)\} \cdot \mathcal{L}\{g(t)\} = \mathcal{L}\{\int_0^t f(t-\tau)g(\tau)d\tau\}$

[proof : right hand side $= \int_0^\infty dt e^{-st} \int_0^t f(t-\tau)g(\tau)d\tau$
variable transformation $(t,\tau) \rightarrow (\tau, \tau' \equiv t-\tau)$ (Jacobian = 1)
$= \int_0^\infty d\tau \int_0^\infty d\tau' e^{-s(\tau+\tau')} f(\tau')g(\tau)$
$= \{\int_0^\infty e^{-s\tau'} f(\tau')d\tau'\}\{\int_0^\infty e^{-s\tau} g(\tau)d\tau\} = \mathcal{L}\{f\}\mathcal{L}\{g\}$]

Useful stuffs :

- $\mathcal{L}\{e^{i\omega t}\} = \displaystyle\int_0^\infty e^{-s(s-i\omega)t} dt = \frac{1}{s-i\omega}$
- $\mathcal{L}\{\cos\omega t\} = \mathcal{L}\{(e^{i\omega t} + e^{-i\omega t})/2\} = \dfrac{1}{2}[\dfrac{1}{s-i\omega} + \dfrac{1}{s+i\omega}] = \dfrac{s}{s^2+\omega^2}$
- $\mathcal{L}\{\cos\omega t\} = \dfrac{\omega}{s^2+\omega^2}$

Microscopic model for GLE

- **System + Harmonic bath**

$$H = \frac{p_s^2}{2} + V(s) + \sum_i (\frac{p_i^2}{2} + \frac{\omega_i^2}{2} x_i^2) + \sum_i c_i x_i s$$

System-bath coupling : $c_i = \left(\frac{\partial V(s,x)}{\partial s \partial x_i} \right)_{\text{pot min}}$

Classical eqs of motion :

$$\dot{s} = \frac{\partial H}{\partial p_s},\ \dot{p}_s = -\frac{\partial H}{\partial s}\ ,\ \dot{x}_i = \frac{\partial H}{\partial p_i}\ ,\ \dot{p}_i = -\frac{\partial H}{\partial x_i}$$

$$\Rightarrow \ddot{s} = -\frac{\partial V(s)}{\partial s} - \sum_i c_i x_i\ , \qquad \ddot{x}_i = -\omega_i^2 x_i - c_i s$$

1. (formally) solve the 2nd EOM for x_i
2. enter back to the 1st EOM for s

Laplace transform : $\lambda^2 \tilde{x}_i(\lambda) - \lambda x_i(0) - \dot{x}_i(0) = -\omega_i^2 \tilde{x}_i(\lambda) - c_i \tilde{s}(\lambda)$

$$\tilde{x}_i(\lambda) = \frac{\lambda}{\lambda^2 + \omega_i^2} x_i(0) + \frac{1}{\lambda^2 + \omega_i^2} \dot{x}_i(0) - c_i \frac{1}{\lambda^2 + \omega_i^2} \tilde{s}(\lambda)$$

Back transformation

$$x_i(t) = x_i(0) \cos \omega_i t + \frac{\dot{x}_i(0)}{\omega_i} \sin \omega_i t - \frac{c_i}{\omega_i} \int_0^t \sin \omega_i (t - \tau) s(\tau) d\tau$$

Partial integration of the last integral

$$\int_0^t \sin \omega_i (t - \tau) s(\tau) d\tau = [\tfrac{1}{\omega_i} \cos \omega_i (t - \tau) s(\tau)]_0^t - \tfrac{1}{\omega_i} \int_0^t \cos \omega_i (t - \tau) \dot{s}(\tau) d\tau$$

Enter into EOM for s

$$\ddot{s} = -\frac{\partial V(s)}{\partial s} - \sum_i (\tfrac{c_i}{\omega_i})^2 \left\{ \int_0^t \cos \omega_i (t - \tau) \dot{s}(\tau) d\tau - s(t) + s(0) \cos \omega_i t \right\} + R(t)$$

$$R(t) \equiv -\sum_i c_i x_i(0) \cos \omega_i t - \sum_i \frac{c_i}{\omega_i} \dot{x}_i(0) \sin \omega_i t$$

Define friction kernel : $\Gamma(t) \equiv \sum_i (\frac{c_i}{\omega_i})^2 \cos \omega_i t$

GLE form :

$$\Rightarrow \quad \ddot{s} = -\frac{\partial V(s)}{\partial s} + \Gamma(0) s(t) - \int_0^t \Gamma(t - \tau) \dot{s}(\tau) d\tau - s(0) \Gamma(t) + R(t)$$

For harmonic $V(s) = \frac{\Omega^2}{2} s^2$: $-\frac{\partial V(s)}{\partial s} + \Gamma(0) s(t) \Rightarrow -\underbrace{(\Omega^2 - \Gamma(0))}_{\equiv -\Omega_{\text{eff}}^2} s(t)$

ie, frequency shift (potential softening) due to friction

Fluctuation-dissipation theorem

$$\langle R(0)R(t)\rangle = k_B T\ \Gamma(t)$$

TCF of random force = friction kernel × temperature

(Both stems from the medium motion)

For the harmonic bath system,

- $\langle x_i(0)x_j(0)\rangle = 0$ for $(i \neq j)$: bath modes are independent
- $\langle x_i(0)\dot{x}_i(0)\rangle = 0$ position and velocity are (locally) independent
- $\langle \frac{\omega_i^2}{2} x_i(0)^2\rangle = \frac{k_B T}{2}$: equipartition theorem

Thus,

$$\langle R(0)R(t)\rangle = \sum_i c_i^2 \langle x_i(0)\rangle^2 \cos\omega_i t$$

$$= k_B T \sum_i (\frac{c_i}{\omega_i})^2 \cos\omega_i t = k_B T\ \Gamma(t)$$

Matrix partitioning method

Multidimensional potential : $V(\mathbf{x})$

Expand around the minimum $\mathbf{x}_0$: (ie, $\left(\frac{\partial V}{\partial \mathbf{x}}\right)_{\mathbf{x}=\mathbf{x}_0} = \mathbf{0}$)

$$V(\mathbf{x}) = V(\mathbf{x}_0) + \frac{1}{2}\mathbf{\Omega}^2(\mathbf{x}-\mathbf{x}_0)^2 + \cdots \qquad \left[\ \mathbf{\Omega}^2 \equiv \left(\frac{\partial^2 V}{\partial \mathbf{x}^2}\right)_{\mathbf{x}_0}\ \right]$$

Off-diagonal $(\mathbf{\Omega}^2)_{ij}$ = coupling between $\mathbf{x}_i$ and $\mathbf{x}_j$

(Note : diagonalization of $\mathbf{\Omega}^2 \Rightarrow$ normal mode analysis)

Suppose :

- we are only interested in small number of $\mathbf{x}_i$ ($i = 1, 2, \cdots, n$) out of total N degrees of freedom. ($n < N$)
- Now we denote the rest of $\mathbf{x}_i$ ($i = n+1, \cdots, N$) by $\mathbf{y}_i$

- **Matrix partitioning**

$$\frac{d^2}{dt^2}\begin{bmatrix}\mathbf{x}\\ \mathbf{y}\end{bmatrix} = -\begin{bmatrix}\mathbf{\Omega}^2_{xx} & \mathbf{\Omega}^2_{xy}\\ \mathbf{\Omega}^2_{yx} & \mathbf{\Omega}^2_{yy}\end{bmatrix}\begin{bmatrix}\mathbf{x}\\ \mathbf{y}\end{bmatrix} \Rightarrow \begin{array}{l}\ddot{\mathbf{x}} = -\mathbf{\Omega}^2_{xx}\mathbf{x} - \mathbf{\Omega}^2_{xy}\mathbf{y}\\ \ddot{\mathbf{y}} = -\mathbf{\Omega}^2_{yx}\mathbf{x} - \mathbf{\Omega}^2_{yy}\mathbf{y}\end{array}$$

Similarly as before, (1) formally solve for $\mathbf{y}$, (2) enter back into eq for $\ddot{\mathbf{x}}$

$$\left[\begin{array}{l}
s^2\tilde{\mathbf{y}}(s) - s\mathbf{y}(0) + \dot{\mathbf{y}}(0) = -\mathbf{\Omega}^2_{yx}\tilde{\mathbf{x}}(s) - \mathbf{\Omega}^2_{yy}\tilde{\mathbf{y}}(s)\\
\tilde{\mathbf{y}}(s) = (s^2\mathbf{1} + \mathbf{\Omega}^2_{yy})^{-1}(s\mathbf{y}(0) - \dot{\mathbf{y}}(0) - \mathbf{\Omega}^2_{yx}\tilde{\mathbf{x}}(s))\\
\mathbf{y}(t) = \cos\mathbf{\Omega}_{yy}t\cdot\mathbf{y}(0) - \mathbf{\Omega}^{-1}_{yy}\sin\mathbf{\Omega}_{yy}t\cdot\dot{\mathbf{y}}(0) - \mathbf{\Omega}^{-1}_{yy}\int_0^t \sin\mathbf{\Omega}_{yy}(t-\tau)\cdot\mathbf{\Omega}^2_{yx}\mathbf{x}(\tau)d\tau\\
\text{Partial integration, and define random force and friction kernel}\\
\mathbf{R}(t) \equiv \mathbf{\Omega}^2_{xy}\cos\mathbf{\Omega}_{yy}t\cdot\mathbf{y}(0) - \mathbf{\Omega}^2_{xy}\mathbf{\Omega}^{-1}_{yy}\sin\mathbf{\Omega}_{yy}t\cdot\dot{\mathbf{y}}(0)\\
\mathbf{\Gamma}(t) \equiv \mathbf{\Omega}^2_{xy}\mathbf{\Omega}^{-2}_{yy}\cos\mathbf{\Omega}_{yy}t\cdot\mathbf{\Omega}^2_{yx}
\end{array}\right]$$

$\Rightarrow$ **GLE form :**

$$\ddot{\mathbf{x}} = -\mathbf{\Omega}^2_{eff}\mathbf{x}(t) - \int_0^t \mathbf{\Gamma}(t-\tau)\dot{\mathbf{x}}(\tau)d\tau - \mathbf{\Gamma}(t)\mathbf{x}(0) + \mathbf{R}(t)$$

(Verify Fluctuation-dissipation theorem : $\langle\mathbf{R}(0)\mathbf{R}(t)\rangle = k_BT\,\mathbf{\Gamma}(t)$)

- Set up models for $\mathbf{R}(t)$ $\Rightarrow$ Stochastic trajectory methods

Projection operator methods (1)

The division into $\mathbf{x}$ and $\mathbf{y}$ in the previous section is also obtained by applying projection operator matrices

$$\mathbf{P} \equiv \begin{bmatrix} \mathbf{1}_n & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \quad \text{and} \quad \mathbf{Q} \equiv \mathbf{1}_N - \mathbf{P} = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1}_{N-n} \end{bmatrix}$$

(Note : $\mathbf{P}^2 = \mathbf{P}$, $\mathbf{Q}^2 = \mathbf{Q}$ $\sim$ projection operator)

Starting from original (full N dim) : $\ddot{\mathbf{x}} = -\mathbf{\Omega}^2 \mathbf{x} = -\mathbf{\Omega}^2 (\mathbf{P} + \mathbf{Q}) \mathbf{x}$

$$(\mathbf{P}\times) \Rightarrow \quad \mathbf{P}\ddot{\mathbf{x}} = -(\mathbf{P}\mathbf{\Omega}^2\mathbf{P})(\mathbf{P}\mathbf{x}) - (\mathbf{P}\mathbf{\Omega}^2\mathbf{Q})(\mathbf{Q}\mathbf{x})$$

$$(\mathbf{Q}\times) \Rightarrow \quad \mathbf{Q}\ddot{\mathbf{x}} = -(\mathbf{Q}\mathbf{\Omega}^2\mathbf{P})(\mathbf{P}\mathbf{x}) - (\mathbf{Q}\mathbf{\Omega}^2\mathbf{Q})(\mathbf{Q}\mathbf{x})$$

$$\text{(Define } \mathbf{P}\mathbf{x} \equiv \mathbf{x}_P \text{ etc.)} \Rightarrow \begin{cases} \ddot{\mathbf{x}}_P = -\mathbf{\Omega}^2_{PP}\mathbf{x}_P - \mathbf{\Omega}^2_{PQ}\mathbf{x}_Q \\ \ddot{\mathbf{x}}_Q = -\mathbf{\Omega}^2_{QP}\mathbf{x}_P - \mathbf{\Omega}^2_{QQ}\mathbf{x}_Q \end{cases}$$

[We may try to define more general projection matrices to extract physical variables of specific interests.]

Projection operator methods (2)

Projector onto a (finite) target space $\{\phi_i\}$ $(i = 1, 2, \cdots, n)$

$$\hat{P} \equiv \sum_{i=1}^{n} |\phi_i\rangle\langle\phi_i|, \qquad \hat{Q} \equiv 1 - \hat{P} \;\; = \sum_{i=n+1}^{\infty} |\phi_i\rangle\langle\phi_i|$$

Time-dependent Schrodinger eq : $\dot{\psi} = -\frac{i}{\hbar}\hat{H}\psi = -\frac{i}{\hbar}\hat{H}(\hat{P}+\hat{Q})\psi$

$$\begin{array}{l} \hat{P}\dot{\psi} = -\frac{i}{\hbar}\{(\hat{P}\hat{H}\hat{P})\hat{P}\psi + (\hat{P}\hat{H}\hat{Q})\hat{Q}\psi\} \\ \hat{Q}\dot{\psi} = -\frac{i}{\hbar}\{(\hat{Q}\hat{H}\hat{P})\hat{P}\psi + (\hat{Q}\hat{H}\hat{Q})\hat{Q}\psi\} \end{array} \Rightarrow \begin{array}{l} \dot{\psi}_P = -\frac{i}{\hbar}(H_{PP}\psi_P + H_{PQ}\psi_Q) \\ \dot{\psi}_Q = -\frac{i}{\hbar}(H_{QP}\psi_P + H_{QQ}\psi_Q) \end{array}$$

[Formal solution of the 2nd line (Laplace Tr.)

$$s\tilde{\psi}_Q(s) - \psi_Q(0) = -\frac{i}{\hbar}H_{QP}\tilde{\psi}_P(s) - \frac{i}{\hbar}H_{QQ}\tilde{\psi}_Q(s)$$

$$\tilde{\psi}_Q(s) = \frac{1}{s+iH_{QQ}/\hbar}\{\psi_Q(0) - \frac{i}{\hbar}H_{QP}\tilde{\psi}_P(s)\}$$

$$\Rightarrow \psi_Q(t) = e^{-iH_{QQ}t/\hbar}\psi_Q(0) - \frac{i}{\hbar}\int_0^t e^{-iH_{QQ}(t-\tau)/\hbar}H_{QP}\psi_P(\tau)d\tau$$

]

Usually, we assume that the initial wavefunction $\psi(0)$ is in the target space, in other words, $\psi_Q(0) = \hat{Q}\psi(0) = 0$

Then the eq for ψ_P becomes

$$\frac{\partial}{\partial t}\psi_P(t) = -\frac{i}{\hbar}H_{PP}\psi_P(t) + (\frac{i}{\hbar})^2 \int_0^t H_{PQ} e^{-iH_{QQ}(t-\tau)/\hbar} H_{QP}\psi_P(\tau)d\tau$$

- 1st term = evolution due to H_{PP}
- 2nd term = transition from and to Q-space

(Note : Green's function representation ⇒ **damping theory**)

We can also carry out similar projection for the Liouville eq (cf Chap 7)

$$\frac{\partial}{\partial t}\rho = -i\hat{L}\rho \qquad \text{(Liouville operator } \hat{L}A \equiv \tfrac{1}{\hbar}[H, A] \text{)}$$

This leads to the **Master equation** formalism of the density matrix ρ