Lecture 12

Recap: Krane’s Theory

\[ W_{AB} = \frac{V_{\text{attempt}}}{2\pi} e^{-\beta \Delta E} \]

\[ V_{\text{attempt}} = \begin{cases} V_A, & V_p < V_c \\ \frac{V_A V_c}{V_p^2}, & V_p \gg V_c \end{cases} \]

\[ V_p = \frac{V_e}{m}, \quad V_A = \frac{V_A}{m}, \quad V_c = \frac{V_c}{m} \]

Comments:
1. Asymptotic for \( \beta \Delta E \gg 1 \)
2. At smaller $\beta A E$, e.g. $\beta A E \ll 1$, a perturbative solution of the FP in powers of $\beta A E$ would be more appropriate.

3. Higher-dimensional versions are available. For $U(x)$, $x_i, i = 1, \ldots, n$, one finds saddle point extrema $x_c$, such that $\nabla U \big|_{x_c} = 0$.

The "Hessian" matrix $\nabla_i \nabla_j U \big|_{x_c} = \omega_c$ will have one negative eigenvalue and the corresponding eigenvector will be the reaction coordinate in the typical situation.

B. Master Equations

Having discussed how to derive microscopic expressions for transition rates, we now turn to examine equations of motion for jump processes. Here we are interested in the longer time transport behavior after
many "jumps" have occurred. The general tools in this field are kinetic equations for a phase space distribution function \( f_m(t) \), where \( m \) is a discrete RV and \( t \) is continuous time. More generally, \( m \) could be a vector of discrete RVs \( \rightarrow m \). Clearly there is an analogy with the PDF \( f(x, p, t) \) we have encountered in gas theory and Brownian motion:

\[
\begin{align*}
\text{continuous} & \quad \text{phase space} \\
\text{discrete} & \quad \text{phase space} \\
\text{fnc.} & \quad f(x, p, t) \\
\text{fnc.} & \quad f_m(t) \\
\text{normalization} & \quad \int dx\, dp \, f = 1 \\
\text{normalization} & \quad \sum_m f_m(t) = 1.
\end{align*}
\]

Eqs.: Fokker-Planck or Boltzmann/BBGKY or Liouville.

The Pauli Master equation, or commonly "Master Equation" can be written (for
one-component m):

\[ \frac{d}{dt} f_m(t) = \sum_n W_{mn} f_n(t) - \sum_n W_{nm} f_m(t) \]

"gain" "loss"

Here \( W_{mn} \) is the probability per unit time that the system transforms from state \( n \) to state \( m \) in some interval \( dt \).

We know how to compute these so-called "transition rate probabilities" using the Kramers approach!

It is common to define a related transition rate matrix by

\[ L_{mn} = W_{mn} - \delta_{mn} \frac{k}{T} W_{pm} \]

so the the ME becomes

\[ \frac{d}{dt} f_m(t) = \sum_n L_{mn} f_n(t) \]

or

\[ \frac{d}{dt} f(t) = \mathbf{L} \mathbf{f}(t) \]

A formal solution is:

\[ f(t) = (e^{\mathbf{L}t}) \mathbf{f}(0) \]
which is quite similar to our formal soln of the Liouville eqn

\[ f(\mathbf{r}, t) = e^{-\sqrt{t} f(\mathbf{r}, 0)} \]

It the state space is finite dimensional, then we can evaluate \( e^{\frac{1}{2} t} \) by finding the eigenvalues/eigenvectors of \( \mathbf{L} \). Otherwise, the ME is difficult in general to solve.

As a simple example of the use of a ME, consider the problem of impurity (or vacancy) hopping in a crystalline solid. Imagine we have:

\[ \bullet \quad \bullet \quad \bullet \quad \bullet \]
\[ \times \quad \times \quad \times \quad \times \]
\[ \bullet \quad \bullet \quad \bullet \quad \bullet \]
\[ \times \quad \rightarrow \quad \times \quad \times \]
\[ \bullet \quad \bullet \quad \bullet \quad \bullet \]

The \( \bullet \) sites are occupied by atoms and the \( \times \) sites are vacant sites.
where impurity atoms can reside. Further suppose that the energy barrier $\Delta E_y$ to vertical hopping is much greater than the barrier $\Delta E_x$ to horizontal hopping, but both $\gg kT$.

Let's further assume that hops occur only between nearest-neighbor vacant sites on the lattice:

$$W_{mn} = W_0 \delta_{m,n+1} + W_0 \delta_{m,n-1}$$

$$W_0 = \nu e^{-\beta \Delta E_x}$$

Now, the ME reduces to a 1D NN hopping model:

$$\frac{\partial}{\partial t} f_m(t) = W_0 \left[ f_{m-1}(t) + f_{m+1}(t) \right] - 2W_0 f_m(t), \quad m = 0, 1, \ldots, t$$

We will solve this model by a Fourier transform method. Let

$$f(k,t) = \sum_{m=-\infty}^{\infty} e^{ikm} f_m(t)$$
Then, the "inverse transform" is:

\[ f_m(t) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dk \ e^{-ikm} f(k, t) \]

Applying \( \sum_m e^{ikm} \) to the ME:

\[ \frac{\partial}{\partial t} f(k, t) = -2\omega_0 f(k, t) \]

\[ + \omega_0 \sum_m e^{ikm} f_{m-1}(t) \]

\[ + \omega_0 \sum_m e^{ikm} f_{m+1}(t) \]

\[ = -2\omega_0 f(k, t) \]

\[ + \omega_0 e^{ik} f(k, t) \]

\[ + \omega_0 e^{-ik} f(k, t) \]

\[ = 2\omega_0 \left[ \frac{(e^{ik} + e^{-ik})}{2} - 1 \right] f(k, t) \]

Thus,

\[ f(k, t) = e^{2\omega_0 t (\cos k - 1)} f(k, 0) \]

Now, let's look for a fundamental solution.
corresponding to the IC \( f_m (0) = \delta_{m,0} \),
i.e. the particle is located at the origin at time 0.

\[
f_k(k, 0) = \sum_m e^{ikm} \delta_{m,0} = 1
\]

So,

\[
f_k(k, t) = e^{-2W_0 t (\cos k - 1)}
\]

\[
f_m(t) = \frac{1}{2\pi} e^{\frac{-2W_0 t}{\pi}} \int_{-\pi}^{\pi} e^{2W_0 t \cos k - ikm} dk
\]

Because the integrand of \( J \) is even in \( k \):

\[
J = 2 \int_{0}^{\pi} e^{2W_0 t \cos k} \cos (km) dk
\]

\[
= 2\pi \frac{1}{\pi} \int_{0}^{\pi} e^{2W_0 t \cos k} \cos (km) dk
\]

\[
= \text{modifed Bessel func. of 2nd order, m th order}
\]

Thus

\[
f_m(t) = e^{-2W_0 t} I_m(2W_0 t)
\]

\[
I_m(2W_0 t) \approx \delta_{m,0}, \quad 2W_0 t \ll 1
\]

\[
\approx \frac{e^{2W_0 t}}{\sqrt{4\pi W_0 t}} \left[ 1 + \frac{1 - 4m^2}{12(2W_0 t)} + \ldots \right]
\]
The probability that the impurity is still at the origin at some time \( t \gg W_0^{-1} \) is thus

\[
f_0(+) \propto \frac{1}{\sqrt{4\pi W_0 t}}
\]

Notice that this is very similar to the Green's func soln of the 1-D diffusion

\[
a_t = D \frac{\partial^2}{\partial x^2} f, \quad f(x,0) = \delta(x-x_0)
\]

\[
f(x_0,t; x_0) = \frac{1}{\sqrt{4\pi Dt}}
\]

Thus, the hopping process looks diffusive at long times, i.e. for \( t \gg W_0^{-1} \).

To clarify this, look at the time for the mean squared displacement:

\[
\langle x^2(t) \rangle = \sum_m f_m(t) (ma)^2 \quad a = \text{lattice spacing}
\]

\[
= \frac{a^2}{(i)^2} \frac{\partial^2}{\partial k^2} \sum_m f_m(t) \bigg|_{k=0}
\]

\[
= \delta \left. \frac{\partial^2}{\partial k^2} f(k,t) \right|_{k=0}
\]
\[
\frac{d}{dk} e^{2W_0 t \cos k} = e^{2W_0 t \cos k} 2W_0 t (-\sin k)
\]
\[
\frac{d^2}{dk^2} \left[ e^{2W_0 t \cos k} \right] = 2W_0 t \cos k \left( e^{2W_0 t} \right) (-\sin k)^2 + e^{2W_0 t \cos k} 2W_0 t (-\sin k)
\]
\[
\langle x^2(t) \rangle = -a^2 e^{-2W_0 t} e^{2W_0 t} (-2W_0 t)\]
\[
= 2(W_0 a^2) t
\]
\[
= 2 D t
\]
\[
D = \frac{W_0 a^2}{6}
\]

Diffusion coefficient for 1-D hopping process.

Since \( W_0 \) is itself activated, we have a nice example of a predication of an activated macrotransport process:

\[
D = \nu, e a^2
\]
8. Polymer Dynamics

We now turn to consider how to build models of time-dependent phenomena in solutions and melts of polymeric liquids. We begin by discussing dilute solutions of a polymer in a good solvent.

A. Dilute Solutions

Consider a very dilute solution of a flexible polymer, e.g., polyethylene

\[
\left( \text{CH}_2\text{CH}_2 \right)_N, \quad N \approx 10^4 - 10^5
\]

dissolved in a simple hydrocarbon solvent, e.g., cyclohexane. Viewed on a large scale (without resolving 1-10 Å details):

The polymers are well separated in the solvent and adopt "random coil"
conformational states. You probably recall from CHE 210B that the equilibrium size of a coil, e.g., its RMS end-to-end vector, \( \langle R^2 \rangle \)
scales with the degree of polymerization \( N \) as:

\[
R = \langle R^2 \rangle^{1/2} = \langle R \cdot R \rangle^{1/2} \sim b N^\nu, \quad N \to \infty
\]

where \( \nu \) is a so-called scaling exponent that takes the values:

\[
\nu = 0.588..., \quad \text{good solvent}
\]

\[
\approx 3/5 \quad (\text{Flory approx.})
\]

\[
\nu = 1/2 \quad \text{theta solvent}
\]

\[
\nu = 1/3 \quad \text{poor solvent (collapsed chain)}
\]

In a good solvent, the so-called excluded volume effect leads to an expanded coil beyond a pure random walk prediction \( \nu = 1/2 \).

\( \nu = 0.588... \)

self-avoiding random walk
In a "theta solvent" the decreasing solvent quality exactly compensates the excluded volume effect, so \( v = \frac{1}{2} \) is the random walk value. Notice the analogy with the trajectory of a Brownian particle:

\[
\langle R^2(t) \rangle^{1/2} = (6D)^{1/2} t^{1/2}
\]
diffusion process

\[
\langle R^2(N) \rangle^{1/2} = bN^{1/2}
\]
"ideal" polymer random walk exponent

Next, let's discuss how to model the dynamics of a polymer in a good or theta solvent. Obviously, if we want to model the very fast dynamics of "local" motions of polymer segments, e.g., C-C rotations, \( 1 \text{ ps} < \tau < 1 \text{ ns} \), we obviously have to build an atomistic model that captures all the details of polymer and solvent. However, often we are primarily interested in the slower dynamics, associated with collective motions of many polymer segments or the whole polymer in the solvent.