A. Steady State Motion in a Periodic Potential

- Molecular conformations may be modeled as periodic Brownian motions. In the high damping limit the potential term in the Smoluchowski equation is

\[ U(x) = \sum_{n=-\infty}^{+\infty} U_n e^{-inx} \]  

where

\[ U_n = \frac{1}{2\pi} \int_0^{2\pi} U(x) e^{inx} dx \]  

- We assume the conditional probability is similarly periodic

\[ P(x|x_0, t) = \frac{1}{2} \sum_{m,n=-\infty}^{\infty} f_{nm}(t) e^{inx} e^{-imx_0} \]  

- Substituting the relationships

\[ \frac{\partial^2 P}{\partial x^2} = -\frac{1}{2} \sum_{n,m} n^2 f_{nm}(t) e^{inx} e^{-imx_0} \]  

into the Smoluchowski equation:

\[ \frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + \frac{D}{kT} \frac{\partial}{\partial x} \left( P \frac{\partial U}{\partial x} \right) \]  

we obtain

\[ \frac{df_{nm}}{dt} = \sum_s B_{ns} f_{sm} \]  

where \( B_{ns} = \delta_{ns} s^2 - \frac{1}{kT} n(n-s) U_{s-n} \).

- Example: Suppose

\[ U(x) = \frac{\alpha}{2} (1 - \cos 3x) \]  

Then
\[ U_{s-n} = \frac{\alpha}{4\pi} \int_0^{2\pi} (1 - \cos 3x) e^{i(s-n)x} \, dx \]
\[ = \frac{\alpha}{4\pi} \int_0^{2\pi} (1 - \cos 3x) \left( \cos(s-n)x + i \sin(s-n)x \right) \, dx \]
\[ = \frac{\alpha}{4\pi} \int_0^{2\pi} \left[ e^{i(s-n)x} - \cos 3x \left( \cos(s-n)x + i \sin(s-n)x \right) \right] \, dx \]
\[ = \frac{\alpha}{4\pi} \int_0^{2\pi} \left[ e^{i(s-n)x} - \frac{1}{2} \left[ \cos(3+n-s)x + \cos(3-n+s)x + i \sin(3+n-s)x + i \sin(3-n+s)x \right] \right] \, dx \]
\[ = \frac{\alpha}{4\pi} \int_0^{2\pi} \left[ e^{i(s-n)x} - \frac{1}{2} \left[ e^{i(3+n-s)x} + e^{i(3-n+s)x} \right] \right] \, dx = -\frac{\alpha}{4\pi} \left[ \pi \delta_{s,n+3} + \pi \delta_{s,n-3} \right] \]

(16.8)

- Using the expression for \( U_{s-n} \) in \( B_{sn} \):
\[ B_{ns} = \delta_{sn}s^2 - \frac{1}{kT} n(n-s)U_{s-n} = \delta_{sn}s^2 - \frac{1}{kT} n(n-s) \left[ -\frac{\alpha}{4\pi} \left[ \pi \delta_{s,n+3} + \pi \delta_{s,n-3} \right] \right] \]
\[ = \delta_{sn}s^2 + \frac{3\alpha}{4kT} n \left[ -\delta_{s,n+3} + \delta_{s,n-3} \right] \]

(16.9)

- According to the theory of systems of first order differential equations discussed in class we expect a solution of the form
\[ f_{mn}(t) = \sum_s C_{ms} Y_{sn} e^{-\lambda_s t} \]

(16.10)

where \( \lambda_s \) is the \( s \)th eigenvalue, \( C_{ms} \) is a constant and \( Y_{sn} \) is the \( n \)th component of the eigenvector corresponding to \( \lambda_s \).

- The delta function initial condition \( P\left(x | x_0, 0\right) = \delta(x - x_0) \) converts to
\[ f_{mn}(0) = \delta_{nm} \] and can be used to solve for \( C_{ms} \):
\[ f_{mn}(0) = \delta_{nm} = \sum_s C_{ms} Y_{sn} \Rightarrow C_{ms} = Y_{sn}^{-1} \]

(16.11)

- From (15.10) it follows that
\[ f_{mn}(t) = \sum_s Y_{ms}^{-1} Y_{sn} e^{-\lambda_s t} \]

(16.12)

- Substituting (15.12) into (15.3) we obtain:
\[ P\left(x | x_0, t\right) = \frac{1}{2\pi} \sum_{m,n,s} Y_{ms}^{-1} Y_{sn} e^{-\lambda_s t} e^{inx} e^{i\delta_{nm}} \]

(16.13)

- The a priori probability is obtained by integrating over the initial condition \( x_0 \) and taking the limit \( t \to \infty \). In the summation (15.13) non-zero terms will only result for \( s=m=0 \). Then using the fact that \( Y_{0,0}^{-1} = 1 \) (15.13) becomes:
\[ P\left(x, t \to \infty \right) = \frac{1}{2\pi} \sum_n Y_{0,n} e^{inx} \]

(16.14)
• The lowest non-zero eigenvalue, i.e. $\lambda_1$, corresponds to the time scale associated with barrier crossing. The eigenvalue $\lambda_1$ generally decreases with barrier height. Larger eigenvalues correspond to motions within the wells with correspondingly smaller amplitudes.

• Equations (15.13) and (15.14) can be used to calculate correlation functions for molecular reorientations. For example, suppose a bond undergoes periodic motions modeled as diffusion in a periodic potential. If the molecule undergoes isotropic reorientation the correlation function for the bonds internal motion is

$$
C(t) = \langle e^{ix} e^{-i\lambda_1 t} \rangle = \int_0^{2\pi} dx \int_0^{2\pi} dx_0 e^{ix} e^{-i\lambda_1 x_0} P(x|x_0, t) W(x_0) \quad (16.15)
$$