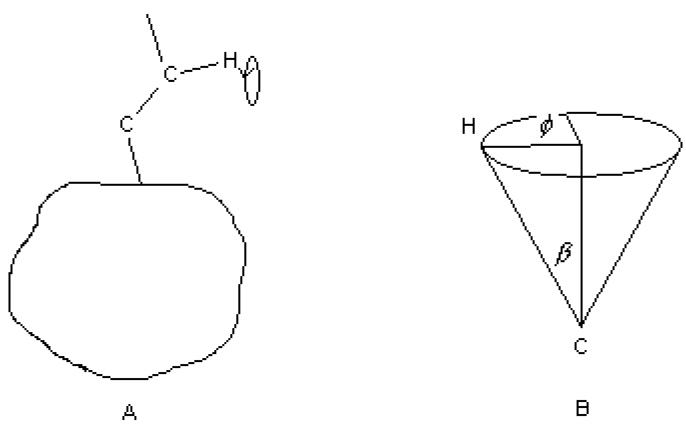
University of Washington
Department of Chemistry
Chemistry 553
Spring Quarter 2011

Lecture 13: Hindered Diffusion: Brownian particle in a Box
04/25/11

A. Restricted Diffusion: Boundary Conditions

- Diffusion of a C-H bond on the surface of a cone or diffusion of heat in a rod of finite length with insulated ends is modeled by boundary conditions of the second kind. This means we attach values to the derivative dW/dx at specific values of x.
- In many spectroscopies (i.e. fluorescence, NMR, EPR), signal intensities and line shapes are influenced by rotational motions of the molecule in solution. Dynamic effects in spectroscopy are commonly calculated using the correlation function formalism. How correlation functions are used to calculate spectral data will be considered later in the course. Here we explore how to calculate the correlation function for molecular motions using a particularly simple model for internal molecular motions.



- For the diffusion of a C-H bond of length a on the surface of a cone of half angle β and constrained to remain within a region of angular extent 2θ, the diffusion equation is

$$\frac{\partial W}{\partial t}=\frac{D}{a^2\sin^2\beta}\frac{\partial^2 W}{\partial\varphi^2}=D_i\frac{\partial^2 W}{\partial\varphi^2} \qquad (13.1)$$

The boundary and initial conditions are:

$$\left.\frac{\partial W}{\partial\varphi}\right|_{\varphi=0,2\theta}=0 \quad \text{and} \quad P\left(\varphi|\varphi_0,0\right)=\delta\left(\varphi-\varphi_0\right) \qquad (13.2)$$

- Equation (13.1) is solved by separation of variables:

$$W(\varphi,t)= f(t)\,g(\varphi) \tag{13.3}$$

- Substituting (13.3) into (13.1)

$$g\frac{\partial f}{\partial t}=D_i f\frac{\partial^2 g}{\partial\varphi^2}\Rightarrow\frac{1}{f}\frac{\partial f}{\partial t}=\frac{D_i}{g}\frac{\partial^2 g}{\partial\varphi^2}=-\frac{1}{\tau} \tag{13.4}$$

- The solution to the f equation is

$$f(t)=e^{-t/\tau} \tag{13.5}$$

- The general solution to the g equation is

$$g(\varphi)=A\cos\left(\frac{\varphi}{\sqrt{\tau D_i}}\right)+B\sin\left(\frac{\varphi}{\sqrt{\tau D_i}}\right) \tag{13.6}$$

- Imposing boundary conditions we obtain B=0 and

$$W(\varphi,t)=\sum_{n=0}^{\infty}A_n\cos\left(\frac{\varphi}{\sqrt{\tau_n D_i}}\right)e^{-t/\tau_n}=\sum_{n=0}^{\infty}A_n\cos\left(\frac{n\pi\varphi}{2\theta}\right)e^{-t/\tau_n} \tag{13.7}$$

where

$$\frac{1}{\tau_n}=\left(\frac{n\pi}{2\theta}\right)^2 D_i \tag{13.8}$$

- Using the delta function initial condition the constants A_n can be determined:

$$P(\varphi|\varphi_0,0)=\delta(\varphi-\varphi_0)=\sum_{n=0}^{\infty}A_n\cos\left(\frac{n\pi\varphi}{2\theta}\right)$$

$$\int_0^{2\theta}P(\varphi|\varphi_0,0)\cos\left(\frac{m\pi\varphi}{2\theta}\right)d\varphi=\sum_{n=0}^{\infty}A_n\int_0^{2\theta}\cos\left(\frac{m\pi\varphi}{2\theta}\right)\cos\left(\frac{n\pi\varphi}{2\theta}\right)d\varphi$$

(13.9)

- Case 1: $n=0\Rightarrow A_0=\frac{1}{2\theta}$ (13.10)
- Case 2: $n\geq1\Rightarrow A_n=\frac{1}{\theta}\cos\left(\frac{n\pi\varphi_0}{2\theta}\right)$ (13.11)
- Combining equations (13.9)-(13.10) we get

$$P(\varphi|\varphi_0,t)=\sum_{n=0}^{\infty}A_n\cos\left(\frac{\varphi+\theta}{\sqrt{\tau_n D_i}}\right)e^{-t/\tau_n}=\frac{1}{2\theta}+\frac{1}{\theta}\sum_{n=1}^{\infty}\cos\left(\frac{n\pi\varphi_0}{2\theta}\right)\cos\left(\frac{n\pi\varphi}{2\theta}\right)e^{-t/\tau_n} \tag{13.12}$$

B. Calculation of the Correlation Function:

- We now want to calculate the average $\left\langle e^{i\ell\varphi_0}e^{-i\ell'\varphi}\right\rangle$. This can be done using the expression:

$$\left\langle e^{i\ell\varphi_0} e^{-i\ell'\varphi} \right\rangle = \int_{-\pi}^{+\pi} d\varphi \int_{-\pi}^{+\pi} d\varphi_0 e^{i\ell\varphi_0} e^{-i\ell'\varphi} W_2(\varphi;\varphi_0,t)$$
$$= \int_{-\pi}^{+\pi} d\varphi \int_{-\pi}^{+\pi} d\varphi_0 e^{i\ell\varphi_0} e^{-i\ell'\varphi} P_2(\varphi|\varphi_0,t) W_1(\varphi_0) \quad (13.13)$$

- Note $W_1(\varphi_0)$ is the a priori probability and can be obtained by evaluating $P_2(\varphi|\varphi_0,t)$ in the limit $t \to \infty$. Using equation (13.12) all terms but the n=0 term go to zero in the infinite time limit. The result is:

$$W_1(\varphi_0) = \underset{t\to\infty}{Lim} P(\varphi|\varphi_0,t) = \frac{1}{2\theta} \quad (13.14)$$

- Equation (13.14) reflects an important principle in statistical mechanics called the principle of equal a priori probabilities. According to this principle, absent any way to distinguish the states initially available to the system, all states will occur with equal probability. With equation (13.12) and (13.14), equation (13.13) becomes

$$\left\langle e^{i\ell\varphi_0} e^{-i\ell'\varphi} \right\rangle = \frac{1}{2\theta} \int_{-\pi}^{+\pi} d\varphi \int_{-\pi}^{+\pi} d\varphi_0 e^{i\ell\varphi_0} e^{-i\ell'\varphi} P(\varphi|\varphi_0,t)$$
$$= \frac{1}{2\theta} \int_{-\pi}^{+\pi} d\varphi \int_{-\pi}^{+\pi} d\varphi_0 e^{i\ell\varphi_0} e^{-i\ell'\varphi} \left[\frac{1}{2\theta} + \frac{1}{\theta} \sum_{n=1}^{\infty} \cos\left(\frac{n\pi\varphi_0}{2\theta}\right) \cos\left(\frac{n\pi\varphi}{2\theta}\right) e^{-t/\tau_n} \right]$$

(13.15)