University of Washington
Department of Chemistry
Chemistry 553
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Lecture 14: The Smoluchowski Equation (SE) for Diffusion in a Restoring Potential
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A. Steady State Motion of a Brownian Particle in a Harmonic Potential

- The Smoluchowski equation can be solved analytically for certain forms of U(x). Assume $U(x)=\frac{\kappa x^2}{2}$ so that the Brownian particle moves in a harmonic well and is subject to a viscous drag force and the usual random force. Then

$$U=\frac{\kappa x^2}{2} \; and \; U'(x)=\kappa x \tag{14.1}$$

- Substitute (14.1) into the Smoluchowski equation, and we obtain

$$\frac{\partial W}{\partial t}=\kappa B\frac{\partial}{\partial x}(xW)+BkT\frac{\partial^2 W}{\partial x^2} \tag{14.2}$$

- Assume the initial condition

$$P(x|x_0,0)=\delta(x-x_0) \tag{14.3}$$

- When the FPE has the property that the drift coefficient is linear: i.e. $D^{(1)}\propto x$ (or v) and the diffusion coefficient is a constant: $D^{(2)}=cons\tan t$, the physical process is called an Ornstein-Uhlenbeck process. Equation (14.2) is an Ornstein-Uhlenbeck process.
- Here we outline the process you can use to solve this equation. Details will be worked out in the homework.
  - Make the substitution $W(x,t)=W_{st}^{1/2}(x)g(x,t)$,

    $W_{st}(x)=\sqrt{\frac{\kappa}{2\pi k_B T}}e^{-\kappa x^2/2k_BT}$. The result is:

$$-\frac{\partial g}{\partial t}=D\left[-\frac{\partial^2 g}{\partial x^2}+\beta\left(\beta x^2-1\right)g\right] \tag{14.4}$$

    where $\beta=\kappa/2k_BT$. Equation (14.4) has the form of Schrodinger's equation. Technicaklly this means the Fokker-planck operator has been transfoprmed to Hermitian form (i.e. the new Fokk-=er-Planck operator is self-adjoint).
  - Separate variables with the substitution $g(x,t)=f(t)h(x)$. The result is two equations:

$$\frac{df}{dt}=-\frac{f}{\tau} \tag{14.5}$$

    and

$$\frac{d^2h}{dx^2}-\beta^2x^2h+\left(\beta+\frac{1}{\tau D}\right)h=0 \tag{14.6}$$

- (14.5) is easy to solve: $f(t)=e^{-t/\tau}$
- To solve equation (14.6) for h, which has the form of Schrodinger's equation for a harmonic oscillator, make the variable transformation $y=\beta^{1/2}x$ and make the substitution $h(y)=u(y)e^{-y^2/2}$. (14.6) becomes Hermite's equation

$$\frac{d^2u}{dy^2}-2y\frac{du}{dy}+2nu=0 \tag{14.7}$$

Where the eigenvalues $\frac{1}{\tau_n}=2n\beta D,\ n=0,1,2\ldots$ are of course real.

- The solution to Hermite's equation is $u_n(y)=H_n(y)=(-)^n e^{y^2}\frac{\partial^n}{\partial y^n}e^{-y^2}$
- Recalling $W(x,t)=ce^{-\beta x^2/2}f(t)h(x)$ and that $y=\beta^{1/2}x$ we find that

$$W(y,t)=e^{-y^2}\sum_n c_nH_n(y)e^{-t/\tau_n} \tag{14.8}$$

- To determine the constants c_n, use the initial condition $W(x,0)=\delta(x-x_0)$ and the orthogonality condition for Hermite polynomials:

$$\int_{-\infty}^{+\infty}dye^{-y^2}H_n(y)H_m(y)=\delta_{mn}2^m m!\sqrt{\pi} \tag{14.9}$$

- We get:

$$c_n=\frac{H_n(y_0)}{2^n n!\sqrt{\pi}} \tag{14.10}$$

- From (14..8)-(14.10) we get, after normalization the conditional probability:

$$P(y|y_0,t)=\sqrt{\frac{\kappa}{2\pi k_BT}}e^{-y^2}\sum_n\frac{H_n(y)H_n(y_0)}{n!}\left(\frac{e^{-t\kappa B}}{2}\right)^n \tag{14.11}$$

  - Using Mehler's expansion:

$$\sum_n H_n(y)H_n(y_0)\frac{z^n}{n!}=\frac{1}{\sqrt{1-4z^2}}\exp\left[-\frac{4z}{1-4z^2}\left(y_0y-zy^2-zy_0^2\right)\right] \tag{14.12}$$

we get the probability

$$P(x|x_0,t)=\left(\frac{\kappa}{2\pi kT\left(1-e^{-2\kappa Bt}\right)}\right)^{1/2}\exp\left\{-\frac{\kappa\left(x-x_0e^{-t\kappa B}\right)^2}{2kT\left(1-e^{-2\kappa Bt}\right)}\right\} \tag{14.13}$$

- It is interesting to check the validity of (14.13) from its limiting behavior. In the long time limit for which $t\to\infty$

$$W(x,t\to\infty)=\left(\frac{\kappa}{2\pi kT}\right)^{1/2}\exp\left\{-\frac{\kappa x^2}{2kT}\right\} \tag{14.14}$$

which is a solution to $\kappa B \frac{\partial}{\partial x}(xW) + D\frac{\partial^2 W}{\partial x^2} = 0$ and for which

$$\langle x \rangle = 0 \ldots \langle x^2 \rangle = \frac{kT}{\kappa} \qquad (14.15)$$

- Notice the expression for the mean-squared displacement is consistent with the results of the equipartition theorem i.e.

$$\frac{1}{2}\kappa \langle x^2 \rangle = \frac{kT}{2} \qquad (14.16)$$

  - Note the results in (14.15) differ from the free diffusion results. Free diffusion in the steady state is obtained by setting $U(x) = 0$ and the FPE in equation (14.2) then becomes

$$\frac{\partial W}{\partial t} = BkT\frac{\partial^2 W}{\partial x^2} = D\frac{\partial^2 W}{\partial x^2} \qquad (14.17)$$

  - In the case of free diffusion the average displacement is similarly zero, but the mean squared displacement increases linearly with time i.e.

$$\langle x \rangle = 0 \ldots \langle x^2 \rangle = 2Dt \qquad (14.18)$$

- This difference is due to the fact that the harmonic potential imposes a restoring force on the Brownian particle that ultimately limits the magnitude of the mean-squared displacement.
- Using the conditional probability in (14.13) we obtain even more general expressions for the mean displacement and the mean squared displacement…valid for all tiomes as long as the steady state approximation is valid...

$$\langle x \rangle = x_0 e^{-\kappa B t} \ldots \langle x^2 \rangle = x_0^2 e^{-2\kappa B t} + \frac{kT}{\kappa}\left(1 - e^{-2\kappa B t}\right) \qquad (14.19)$$