University of Washington
Department of Chemistry
Chemistry 553
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Lecture 6: Brownian Motion in a External Potential
4/08/11
Background Reading: Chandra.2.3. and McQ 22.2

A. Langevin Equation for Diffusion in a Restoring Potential

- We have thus far considered the Langevin equation for a freely diffusing particle:
$$M\frac{dv}{dt} = -\frac{v}{B} + F(t) \quad (6.1)$$
- We now consider the motion of a Brownian particle in a restoring potential: $M\frac{dv}{dt} = -\frac{v}{B} - \kappa r + F(t)$ (5.2)
- This Langevin equation can be rearranged to:
$$\frac{dv}{dt} = -\frac{v}{\tau} - \omega^2 r + A(t) \text{ where } \tau = MB, \omega^2 = \frac{\kappa}{M}, A(t) = \frac{F(t)}{M}. \quad (5.3)$$
- Now substitute $v = \frac{dr}{dt}$ and the Langevin equation becomes a second order differential equation: $\frac{d^2r}{dt^2} + \frac{1}{\tau}\frac{dr}{dr} + \omega^2 r = A(t)$ (5.4)

- Solution of the Langevin Equation in the limit of equilibrated velocity
  - A general solution of the Langevin equation will be done elsewhere. See homework set 3. Here we demonstrate solution of the Langevin equation in the limit of equilibrated velocity. In this limit it is easy to solve for $\langle r^2(t)\rangle$
  - Take the inner product of the Langevin equation with r:
$$r\cdot\frac{d^2r}{dt^2} + \frac{1}{\tau}r\cdot\frac{dr}{dt} + \omega^2 r\cdot r = r\cdot A(t) \quad (5.5)$$
  - Using the same relationships that we used for the Langevin equation for free diffusion we obtain a differential equation for r^2:
$$\frac{1}{2}\frac{d^2r^2}{dt^2} - v^2 + \frac{1}{2\tau}\frac{dr^2}{dt} + \omega^2 r^2 = r\cdot A(t) \quad (5.6)$$
  - Now we take the average of both sides of the equation and using the same assumptions as before:
$$\frac{d^2\langle r^2\rangle}{dt^2} + \frac{1}{\tau}\frac{d\langle r^2\rangle}{dt} + 2\omega^2\langle r^2\rangle = 2\langle v^2\rangle \quad (5.7)$$

- Now we take the equipartition limit for $\langle v^2 \rangle = \frac{3k_B T}{M}$ and obtain

$$\frac{d^2\langle r^2\rangle}{dt^2} + \frac{1}{\tau}\frac{d\langle r^2\rangle}{dt} + 2\omega^2\langle r^2\rangle = \frac{6k_B T}{M} \tag{5.8}$$

- This second order ordinary differential equation can be solved by the methods of parameter variation, which is outlined in Chandrasekahr's review. A somewhat different approach is used here. Define a coordinate change

$$u = \langle r^2\rangle - \frac{3k_B T}{\omega^2 M} \tag{5.9}$$

- Using (5.9), (5.8) becomes

$$\ddot{u} + \frac{\dot{u}}{\tau} + 2\omega^2 u = 0 \tag{5.10}$$

- . The solution for (5.10) is simple to obtain. We assume u has the form $u(t) = e^{-at}$ where a is a constant. Substitute this form into (5.100 and we obtain: $a^2 - \frac{a}{\tau} + 2\omega^2 = 0$ for which we obtain the solutions: $a_{\pm} = \frac{1}{2\tau}\left(1 \pm \sqrt{1-8\omega^2\tau^2}\right)$. The solution to (5.8) is thus

$$\langle r^2(t)\rangle = c_+ e^{-a_+ t} + c_- e^{-a_- t} + \frac{3k_B T}{\omega^2 M} \tag{5.11}$$

where $c_{\pm}$ are constants to be determined from initial conditions. Assuming $u(0) = \dot{u}(0) = 0$ we obtain:

$$\langle r^2(t)\rangle = \frac{3k_B T}{\omega^2 M}\left[1 + \frac{a_- e^{-a_+ t} - a_+ e^{-a_- t}}{a_+ - a_-}\right] \tag{5.10}$$

- It is useful to check this answer in the limits that $t \to 0$ and $t \to \infty$. In the latter case we clearly obtain: $\lim_{t\to\infty}\langle r^2\rangle = \frac{3k_B T}{\omega^2 M}$ or $\frac{\kappa}{2}\langle r^2\rangle = \frac{3k_B T}{2}$ which is the result expected from the equipartition theorem. For the short time limit we expand the exponentials and to second order obtain:

$$\langle r^2(t)\rangle \approx \frac{3k_B T}{\omega^2 M}\left(\frac{a_+^2 a_- - a_-^2 a_+}{a_+ - a_-}\right)t^2 = \frac{a}{\omega^2}\langle v^2\rangle t^2 \tag{5.11}$$

- Thus at short times the effect of solvent interactions is small and the mean squared displacement increases quadratically with time. At very long times the effect of the restoring force becomes important and the mean squared displacement approaches a constant. At intermediate times the solvent effects dominate and the mean squared displacement varies linearly with time.

C. Stationary Solution of the Langevin Equation:

- Thus far we have solved rigorously the Langevin equation and once a solution is obtained we evaluated the solution in various limits. A particular1uy useful limit is the steady state limit where the drag and fluctuating forces are balanced and acceleration ceases. Let's solve the Langevin equation in this limit. Start with:

$$\dot{v} + \frac{v}{\tau} + \omega^2 r = A(t) \tag{5.12}$$

- Neglect the acceleration term and obtain the first order equation

$$\frac{dr}{dt} + \tau\omega^2 r = \tau A(t) \tag{5.13}$$

- The solution is obtained as before:

$$r(t) = r_0 e^{-\tau\omega^2 t} + e^{-\tau\omega^2 t}\int_0^t ds e^{\tau\omega^2 s} A(s) \tag{5.14}$$

- As with the velocity calculation we can now calculate the mean-squared displacement

$$\left\langle r^2(t)\right\rangle = r_0^2 e^{-2\tau\omega^2 t} + e^{-2\tau\omega^2 t}\int_0^t ds_1 \int_0^t ds_2 e^{\tau\omega^2(s_1+s_2)} \left\langle A(s_1)A(s_2)\right\rangle \tag{5.15}$$

- Assuming a delta-function correlation force $\left\langle A(s_1)A(s_2)\right\rangle = \alpha\delta(s)$ we finally obtain:

$$\left\langle r^2(t)\right\rangle = r_0^2 e^{-2\kappa Bt} + \frac{3k_B T}{\kappa}\left(1-e^{-2\kappa Bt}\right) \tag{5.16}$$