A. Langevin Equation for Diffusion in a Restoring Potential

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

B. 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:
  \[ r \cdot \frac{d^2r}{dt^2} + \frac{1}{\tau} r \cdot \frac{dr}{dt} + \omega^2 r \cdot r = r \cdot A(t) \]
- Using the same relationships that we used for the Langevin equation for free diffusion we obtain a differential equation for \( r^2 \):
  \[ \frac{1}{2} \frac{d^2r^2}{dt^2} - v^2 + \frac{1}{2\tau} \frac{dr^2}{dt} + \omega^2 r^2 = r \cdot A(t) \]
- Now we take the average of both sides of the equation and using the same assumptions as before:
  \[ \frac{d^2\langle r^2 \rangle}{dt^2} + \frac{1}{\tau} \frac{d\langle r^2 \rangle}{dt} + 2\omega^2 \langle r^2 \rangle = 2\langle v^2 \rangle \]
- Now we take the equipartition limit for \( \langle v^2 \rangle = \frac{3k_BT}{M} \) and obtain
This second order ordinary differential equation can be solved by the methods of parameter variation. The solution is:

\[
\langle r^2 (t) \rangle = \mu_+ (t) e^{\alpha_+ t} + \mu_- (t) e^{\alpha_- t}
\]

\[
= -\frac{6k_B T}{M} \left[ \frac{1 - e^{-\alpha_+ t}}{\alpha_+ (\alpha_+ - \alpha_-)} - \frac{1 - e^{-\alpha_- t}}{\alpha_- (\alpha_+ - \alpha_-)} \right]
\]

where \( \mu_{\pm} (t) = \mp \frac{6k_B T}{a_{\pm} M} \left( e^{-\alpha_{\pm} t} - 1 \right) \) and \( a_{\pm} = -\frac{1}{2\tau} \pm \frac{1}{2\tau} \sqrt{1 - 8\omega^2 \tau^2} \)

It is useful to check this answer in the limit that \( t \to \infty \):

\[
\langle r^2 (t) \rangle = -\frac{6k_B T}{M (\alpha_+ - \alpha_-)} \left[ \frac{1}{\alpha_+} - \frac{1}{\alpha_-} \right] = \frac{6k_B T}{M (\alpha_+ - \alpha_-)} \left[ \frac{\alpha_-}{\alpha_+ \alpha_-} \right] = \frac{6k_B T}{Ma_+ a_-}
\]

Using the fact that \( a_+ a_- = \frac{2\kappa}{M} \), we obtain \( \langle r^2 \rangle = \frac{3k_B T}{\kappa} \), which is the result expected from the equipartition theorem: \( \frac{\kappa}{2} \langle r^2 \rangle = \frac{3k_B T}{2} \)

C. Markov Processes and Conditional Probabilities

For a completely random process, the condition of a system at a time \( t \) is independent of its history so

\[
W_n \left( x_n, t_n; x_{n-1}, t_{n-1}; \ldots; x_0, t_0 \right) = W_1 \left( x_0, t_0 \right) W_1 \left( x_1, t_1 \right) \cdots W_1 \left( x_n, t_n \right)
\]

(1.12)

The next level of complexity is called a Markov Process. To define such a process we first define a conditional probability

\[
P_n \left( x_n, t_n | x_{n-1}, t_{n-1}; \ldots; x_1, t_1; x_0, t_0 \right) \text{ where } t_0 < t_1 < \cdots < t_n \text{ which is the probability that a system is at } x_n \text{ at } t_n \text{ granted that it was at } x_0 \text{ at } t_0, x_1 \text{ at } t_1, \text{ etc. Some useful properties of joint and conditional probabilities follow…}
\]

(1.13)

Examples

\[
W_2 \left( x_1, t_1; x_0, t_0 \right) = W_1 \left( x_0, t_0 \right) P_2 \left( x_1, t_1 | x_0, t_0 \right)
\]

\[
W_3 \left( x_2, t_2; x_1, t_1; x_0, t_0 \right) = W_2 \left( x_1, t_1; x_0, t_0 \right) P_3 \left( x_2, t_2 | x_1, t_1; x_0, t_0 \right)
\]

(1.14)
• For a Markov process the probability that a system is at \( x_n \) at time \( t_n \) is only dependent upon its immediate and most recent history.

\[
P_n (x_n, t_n | x_{n-1}, t_{n-1}, \ldots, x_t, t_0) = P_2 (x_n, t_n | x_{n-1}, t_{n-1}).
\]

(1.16)

• For a Markov Process

\[
W_n (x_n, t_n; x_{n-1}, t_{n-1}; \ldots, x_t, t_0) = P_2 (x_n, t_n | x_{n-1}, t_{n-1}) \times W_{n-1} (x_{n-1}, t_{n-1}; \ldots, x_t, t_0)
\]

\[
\therefore W_2 (x_1, t_1; x_0, t_0) = P_2 (x_1, t_1 | x_0, t_0) \times W_1 (x_0, t_0)
\]

(1.17)

• For stationary Markov Processes

\[
P_2 (x_n, t_n | x_{n-1}, t_{n-1}) = P_2 (x_n | x_{n-1}, t_n - t_{n-1}) = P_2 (x_n | x_{n-1}, \tau)
\]

\[
\therefore W_2 (x_1, t_1; x_0, t_0) = W_2 (x_1; x_0, \tau) = W_1 (x_0) P_2 (x_1 | x_0, \tau)
\]

(1.18)

• The conditional probability plays an important role in non-equilibrium statistical mechanics. It is used in the expression for the correlation function for property A whose change in time is described as a stationary Markov process:

\[
K (\tau = \Delta t) = \int \cdots \int dp dq dp dq W_2 (p_1, q_i; p_0, q_0, \tau) A(p_0, q_0) A(p_1, q_i)
\]

\[
= \int \cdots \int dp dq dp dq W_1 (p_0, q_0) P_2 (p_1, q_i | p_0, q_0, \tau) A(p_0, q_0) A(p_1, q_i)
\]

(1.19)

D. How to Obtain Conditional Probabilities: Master Equations

• Conditional probabilities are calculated using differential equations called master equations. Master equations may be thought of as rate equations and they utilize transition rate probabilities. Example: \( w_{j \rightarrow l} d\tau dl = w_{jl} d\tau dl \) is the probability that in a short period of length \( dt \), a transition is made from \( j \) to \( l+dl \). As such \( w_{jl} \) is a transition rate probability. A pleasant feature of master equations is that their derivation and use is pretty clear to a chemist.

• To obtain the master equation we need a mathematical relationship called Markov’s Integral Equation, also called the Chapman-Kolmogorov (CK) Equation:

\[
P_2 (x_2, t_2 | x_0, t_0) = \int P_2 (x_1, t_1 | x_0, t_0) P_3 (x_2, t_2 | x_1, t_1; x_0, t_0) dx_1
\]

\[
= \int P_2 (x_1, t_1 | x_0, t_0) P_2 (x_2, t_2 | x_1, t_1) dx_1
\]

(1.20)

\[
= \int P_2 (x_1 | x_0, t_1 - t_0) P_2 (x_2 | x_1, t_2 - t_1) dx_1 = P_2 (x_2 | x_0, t_2 + t_0)
\]

where the second and third steps assume the process is Markovian and stationary.

o Equation 1.20 has the discrete form:

\[
P_2 (l | l_0 ; t + \tau) = \sum_j P_2 (j | l_0 ; t) P_2 (l | j; \tau)
\]

(1.21)

• We also need to take note of two important properties possessed by conditional probabilities:
The system or property A has to make a transition to some other state in a time \( t_1 - t_0 = \Delta t = \tau \):
\[
\int P(l|j, \tau)dl = 1.
\]
For discrete states this can be written as
\[
\sum_i P(l|i, \tau) = 1
\]

The system or property cannot change instantaneously:
\[
P(l|j, \tau = 0) = \delta_{jl}
\]
Note for convenience we dropped the subscript 2, because it is understood that from now on we deal with stationary Markov processes.

- Three steps to setting up a master equation...
  - Because a system cannot change instantaneously
    \[
P(l|j, \tau) \to 0 \text{ as } \tau \to 0. \quad \therefore P(l|j, \tau) \approx \tau w_{jl}
    \]
    and
    \[
P(l|l, \tau) \to 1 \text{ as } \tau \to 0. \quad \therefore P(l|l, \tau) \approx 1 - \tau \sum_k w_{lk}
    \]
  - Combine these two equations:
    \[
P(l|j; \tau) = \tau w_{jl} + \delta_{jl} \left(1 - \tau \sum_k w_{lk}\right)
    \]

- We take (1.20c) and put it into the discrete for of the C-K equation to obtain
    \[
    \frac{P(l|j; t + \tau) - P(l|j; t)}{\tau} = \sum_j \left[w_{jl}P(j|j; t) - w_{lj}P(l|j; t)\right]
    \]

  (1.21) can be written as a differential equation in the limit \( \tau \to 0 \)
    \[
    \lim_{\tau \to 0} \frac{P(l|j; t + \tau) - P(l|j; t)}{\tau} = \frac{\partial P(l|j; t)}{\partial t} = \sum_j \left[w_{lj}P(j|j; t) - w_{lj}P(l|j; t)\right]
    \]

  which in continuous form is:
    \[
    \frac{\partial P(l|j; t)}{\partial t} = \int_{-\infty}^{+\infty} \left[w_{lj}P(j|j; t) - w_{lj}P(l|j; t)\right]dj
    \]