CHM1485: Molecular Dynamics and Chemical Dynamics in Liquids

Stochastic Models - Part II

October 25, 2005

7 Fokker-Planck Equation

- In many stochastic systems, only small jumps or changes in the state of the system occur on short time scales. In such situations, the *Fokker-Planck equation* offers an accurate description which is simpler than the full master equation.
- The derivation of the Fokker-Planck equation starts from the continuous master equation (5),

$$\frac{\partial P(\mathbf{x},t)}{\partial t} = \int d\mathbf{x}' \left[W(\mathbf{x}' \to \mathbf{x}) P(\mathbf{x}',t) - W(\mathbf{x} \to \mathbf{x}') P(\mathbf{x},t) \right], \tag{5}$$

  where $W(\mathbf{x} \to \mathbf{x}')d\mathbf{x}'$ is the transition probability per unit time to go from state $\mathbf{x}$ to another state between $\mathbf{x}'$ and $\mathbf{x}' + d\mathbf{x}'$.
- We make a transformation of integration variables from the states $\mathbf{x}'$ to the *jumps* $\Delta\mathbf{x} = \mathbf{x} - \mathbf{x}'$:

$$\frac{\partial P(\mathbf{x},t)}{\partial t} = \int d\Delta\mathbf{x} \left[W(\mathbf{x} - \Delta\mathbf{x} \to \mathbf{x}) P(\mathbf{x} - \Delta\mathbf{x},t) - W(\mathbf{x} \to \mathbf{x} - \Delta\mathbf{x}) P(\mathbf{x},t) \right]$$

- We reformulate the transition probability rate $W(\mathbf{x} \to \mathbf{x}')$ now as $\tilde{W}(\mathbf{x}, \mathbf{x}' - \mathbf{x})$, which is the transition probability rate to make a jump of size $\mathbf{x}' - \mathbf{x}$ starting from state $\mathbf{x}$:

$$\frac{\partial P(\mathbf{x},t)}{\partial t} = \int d\Delta\mathbf{x} \left[\tilde{W}(\mathbf{x} - \Delta\mathbf{x}, \Delta\mathbf{x}) P(\mathbf{x} - \Delta\mathbf{x},t) - \tilde{W}(\mathbf{x}, -\Delta\mathbf{x}) P(\mathbf{x},t) \right]$$

  We assume now that the jumps are small and of similar size, such that $W(\mathbf{x}, \Delta\mathbf{x})$ is sharply peaked in $\Delta\mathbf{x}$, but slowly varying in $\mathbf{x}$. We may then Taylor-expand the first term in the master equation and get

$$
\begin{aligned}
\frac{\partial P(\mathbf{x},t)}{\partial t} &= \int d\Delta\mathbf{x}\Big\{\tilde{W}(\mathbf{x},\Delta\mathbf{x})P(\mathbf{x},t) - \Delta\mathbf{x}\frac{\partial}{\partial\mathbf{x}}\cdot\Big[\tilde{W}(\mathbf{x},\Delta\mathbf{x})P(\mathbf{x},t)\Big] \\
&\quad + \frac{1}{2}[\Delta\mathbf{x}]^2 : \frac{\partial^2}{\partial\mathbf{x}^2}\Big[\tilde{W}(\mathbf{x},\Delta\mathbf{x})P(\mathbf{x},t)\Big] + \ldots - \tilde{W}(\mathbf{x},-\Delta\mathbf{x})P(\mathbf{x},t)\Big\} \\
&\approx \int d\Delta\mathbf{x}\Big\{-\Delta\mathbf{x}\frac{\partial}{\partial\mathbf{x}}\cdot\Big[\tilde{W}(\mathbf{x},\Delta\mathbf{x})P(\mathbf{x},t)\Big] + \frac{1}{2}[\Delta\mathbf{x}]^2 : \frac{\partial^2}{\partial\mathbf{x}^2}\Big[\tilde{W}(\mathbf{x},\Delta\mathbf{x})P(\mathbf{x},t)\Big]\Big\} \\
&= -\frac{\partial}{\partial\mathbf{x}}\cdot\Big[\int d\Delta\mathbf{x}\,\Delta\mathbf{x}\tilde{W}(\mathbf{x},\Delta\mathbf{x})P(\mathbf{x},t)\Big] + \frac{1}{2}\frac{\partial^2}{\partial\mathbf{x}^2} : \Big[\int d\Delta\mathbf{x}\,[\Delta\mathbf{x}]^2\tilde{W}(\mathbf{x},\Delta\mathbf{x})P(\mathbf{x},t)\Big].
\end{aligned}
$$

- Defining the *jump moments*

$$
\mathbf{a}_\nu(\mathbf{x}) = \int d\Delta\mathbf{x}\,[\Delta\mathbf{x}]^\nu\tilde{W}(\mathbf{x},\Delta\mathbf{x}),
$$

  we obtain the *Fokker-Planck equation*

$$
\frac{\partial P(\mathbf{x},t)}{\partial t} = -\frac{\partial}{\partial\mathbf{x}}\cdot[\mathbf{a}_1(\mathbf{x})P(\mathbf{x},t)] + \frac{1}{2}\frac{\partial^2}{\partial\mathbf{x}^2} : [\mathbf{a}_2(\mathbf{x})P(\mathbf{x},t)]. \tag{13}
$$

- Remembering that $\tilde{W}(\mathbf{x},\Delta\mathbf{x})$ is the transition probability per unit time given that the system starts at $\mathbf{x}$, we have

$$
\mathbf{a}_\nu(\mathbf{x}) = \lim_{\Delta t\to 0}\frac{\langle[\Delta\mathbf{x}(\Delta t)]^\nu\rangle_{\text{starting at }\mathbf{x}}}{\Delta t}. \tag{14}
$$

- Note that for a deterministic system, $\Delta\mathbf{x} = (d\mathbf{x}/dt)\Delta t$, so $\mathbf{a}_1 = d\mathbf{x}/dt$ and $\mathbf{a}_{n>1} = 0$. Equation (13) then reduces to the Liouville equation for deterministic systems.

- Equation (13) is in general an *approximate* equation because we neglected terms higher than second order in the Taylor expansion.

- The exact expression resulting from keeping all terms in the Taylor expansion of the master equation is called the Kramers-Moyal expansion.

- For systems described by the *Langevin equation* (to be discussed next), the jump moments $\mathbf{a}_\nu$ turn out to be zero for $\nu > 2$ (home work) so that the Fokker-Planck equation is then *exact*.

8 Brownian Motion

- The random walk is not unlike what happens to the Brownian particle but there are a couple of important differences:

- The random walk is on a discrete one-dimensional lattice, whereas the Brownian particle lives in a *continuous three dimensional space.*
- The random walker gets random displacements, but the Brownian particle gets *random kicks* (from collisions with the solvent molecules), which would change its *momentum* $m\mathbf{v}$, rather than its position.
- Even in the absence of randomness, we know that moving a heavy object through a fluid, there is a drag or *friction force* which, to first approximation is *linear* in and opposite to the velocity of the object.

- Thus the effect of the collisions of the solvent molecules with the Brownian particle is to exert a force that has a systematic part, namely a friction force, and a random part:

$$\mathbf{F}(t) = -\alpha\mathbf{v}(t) + \boldsymbol{\xi}(t)$$

where α is the friction coefficient and $\boldsymbol{\xi}(t)$ is a random fluctuating force.

- For a real (but spherical) Brownian particle, Stokes' formula gives $\alpha = 6\pi\eta R$, where R is the radius of the spherical Brownian particle and η is the shear viscosity coefficient of the solvent.
- Using $m\,d\mathbf{v}/dt = \mathbf{F}$, we find the *Langevin equation*:

$$m\frac{d\mathbf{v}}{dt} = -\alpha\mathbf{v}(t) + \boldsymbol{\xi}(t). \tag{15}$$

- This is an example of a *stochastic differential equation.*
- The formal solution of equation (15) is

$$\mathbf{v}(t) = e^{-\gamma t}\mathbf{v}(0) + \int_0^t d\tau\, e^{-\gamma(t-\tau)}\frac{\boldsymbol{\xi}(\tau)}{m}. \tag{16}$$

where

$$\gamma = \frac{\alpha}{m}$$

is the relaxation rate of the particle's velocity and is proportional to the friction.

- Note that the effect of the friction is to *dissipate* whatever velocity (and associated kinetic energy) is present initially, while the random force will cause the velocity to *fluctuate*.
- The *statistical properties of the random force* $\boldsymbol{\xi}(t)$ still need to be given. Because the systematic part (the friction force) has been extracted already, we should have

$$\langle\boldsymbol{\xi}(t)\rangle = 0$$

Because the fluctuations in the random force should occur on a much faster, microscopic time scale than the mesoscopic fluctuations of the position and the velocity of the Brownian particle (separation of time scales), one takes the random force to be uncorrelated at different (mesosopic) times

$$\langle \boldsymbol{\xi}(t_1)\boldsymbol{\xi}(t_2)\rangle = \Gamma \mathbb{1}\, \delta(t_1 - t_2).$$

where Γ is the strength of the fluctuations and $\mathbb{1}$ is the three-dimensional identity matrix that arises because of isotropy of the solvent fluid.

- The strength of the fluctuations can be determined by using that for long times, the system with the Brownian particle will reach equilibrium at the temperature T of the solvent fluid. Then, there will be equipartition of the kinetic energies, so

$$\lim_{t\to\infty} \langle \mathbf{v}(t) \cdot \mathbf{v}(t)\rangle = \frac{3kT}{m}.$$

Substituting the solution from equation (16) in this relation, one gets

$$\frac{3\Gamma}{2m^2\gamma} = \frac{3kT}{m}.$$

- Thus the strengths of the fluctuation and the dissipation are related by

$$\Gamma = 2kTm\gamma = 2kT\alpha.$$

This is (the simplest form of) the *fluctuation-dissipation theorem*.

- It can be shown that the mean square displacement of the Brownian particle grows linearly in time, by integrating equation (16)

$$\mathbf{r}(t) - \mathbf{r}(0) = \int_0^t dt'\, \mathbf{v}(t')$$

and then computing the $t \to \infty$ limit of $\langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle$. This leads to

$$\langle|\mathbf{r}(t) - \mathbf{r}(0)|^2\rangle = \frac{6kT}{\alpha} t,$$

from which we read off the Einstein relation for the diffusion constant of a Brownian particle (cf. equation (2) that states that $\langle|\mathbf{r}(t) - \mathbf{r}(0)|^2\rangle = 2dDt$):

$$D = \frac{kT}{\alpha} = \frac{kT}{6\pi\eta R}.$$

- In general, one can also make the Brownian particle subject to an external potential $U(\mathbf{r})$. This gives the *Langevin equation with an external field*:

$$\frac{d\mathbf{r}(t)}{dt} = \mathbf{v}(t) \tag{17a}$$

$$m\frac{d\mathbf{v}(t)}{dt} = -\frac{\partial U}{\partial \mathbf{r}} - \alpha\mathbf{v}(t) + \boldsymbol{\xi}(t). \tag{17b}$$

- For a general potential this Langevin equation is difficult to solve, and it is often more convenient to use the equivalent *Fokker-Planck equation*.

9 Kramers' Equation

- Application of the Fokker-Planck equation to the Brownian particle.
- State of the particle described by its position $\mathbf{r}$ and its velocity $\mathbf{v}$.
- In a short time interval Δt, we can integrate equations (17a) and (17b) to obtain

$$\begin{aligned} \Delta\mathbf{r}(\Delta t) &= \mathbf{v}\Delta t \\ m\Delta\mathbf{v}(\Delta t) &= -\frac{\partial U}{\partial \mathbf{r}}\Delta t - \alpha\mathbf{v}\Delta t + \int_t^{t+\Delta t} dt'\, \boldsymbol{\xi}(t'). \end{aligned}$$

  Note that $\boldsymbol{\xi}$ is fluctuating rapidly (separation of time scales), so we are not allowed to write the last term as $\boldsymbol{\xi}(0)\delta t$!

- Using equation (14), we get

$$a_1 = \lim_{\Delta t\to 0}\frac{1}{\Delta t}\begin{pmatrix} \mathbf{v}\Delta t \\ [-\frac{\partial U}{\partial \mathbf{r}}\Delta t - \alpha\mathbf{v}\Delta t + \int_t^{t+\Delta t} dt'\, \langle\boldsymbol{\xi}(t')\rangle]/m \end{pmatrix} = \begin{pmatrix} \mathbf{v} \\ -[\frac{\partial U}{\partial \mathbf{r}} + \alpha\mathbf{v}]/m \end{pmatrix}$$

  while similarly

$$a_2 = \begin{pmatrix} 0 & 0 \\ 0 & \displaystyle\lim_{\Delta t\to 0}\frac{1}{\Delta t}\int_t^{t+\Delta t} dt_1' \int_t^{t+\Delta t} dt_2' \langle\boldsymbol{\xi}(t_1')\boldsymbol{\xi}(t_2')\rangle/m^2 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & (2kT\alpha/m^2)\mathbb{1} \end{pmatrix}$$

- Substituting in equation (13) yields the Fokker-Planck equation for the Brownian particle in an external field:

$$\frac{\partial P(\mathbf{r},\mathbf{v},t)}{\partial t} = -\mathbf{v}\cdot\frac{\partial P(\mathbf{r},\mathbf{v},t)}{\partial \mathbf{r}} + \frac{\partial}{\partial \mathbf{v}}\left\{\frac{\alpha\mathbf{v} + \frac{\partial U}{\partial \mathbf{r}}}{m}P(\mathbf{r},\mathbf{v},t)\right\} + \frac{kT\alpha}{m^2}\Delta_{\mathbf{v}}P(\mathbf{r},\mathbf{v},t).$$

  where $\Delta_{\mathbf{v}} = \frac{\partial^2}{\partial v_x^2} + \frac{\partial^2}{\partial v_y^2} + \frac{\partial^2}{\partial v_z^2}$. Another way to write this is

$$\frac{\partial P(\mathbf{r},\mathbf{v},t)}{\partial t} + \mathbf{v}\cdot\frac{\partial P(\mathbf{r},\mathbf{v},t)}{\partial \mathbf{r}} - \frac{\frac{\partial U}{\partial \mathbf{r}}}{m}\cdot\frac{\partial P(\mathbf{r},\mathbf{v},t)}{\partial \mathbf{v}} = \gamma\left\{\frac{\partial}{\partial \mathbf{v}}\cdot\Big[\mathbf{v}P(\mathbf{r},\mathbf{v},t)\Big] + \frac{kT}{m}\Delta_{\mathbf{v}}P(\mathbf{r},\mathbf{v},t)\right\} \tag{18}$$

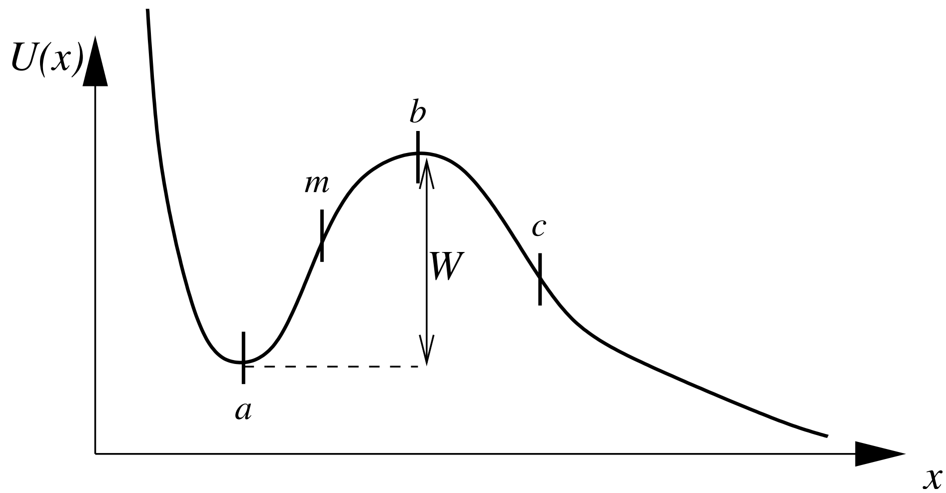
- This equation is known as the *Kramers' equation*.

10 Reaction Rates and Kramers' Escape Problem

- Kramers applied equation (18) to chemical reactions, interpreting the coordinate as a *reaction coordinate*, which measures the progression of the reaction. This coordinate is a one-dimensional object, so that equation (18) becomes:

$$\frac{\partial P(x,v,t)}{\partial t} + v\frac{\partial P(x,v,t)}{\partial x} - \frac{U'}{m}\frac{\partial P(x,v,t)}{\partial v} = \gamma\frac{\partial}{\partial v}\left[vP(x,v,t) + \frac{kT}{m}\frac{\partial P(x,v,t)}{\partial v}\right] \tag{19}$$

- We call the reaction coordinate the position of the *Kramers' particle*.
- It is assumed that the Kramers' particle, i.e., the reaction coordinate x, is initially in a *metastable* *chemical state* a and decays to another, *stable product state*. In the simplest case only a single barrier W needs to be overcome to get out of the metastable state, where W is the energy difference between the metastable state a and an intermediate *transition state* b. In such a situation the potential U has roughly the following form:



- Kramers' problem is to find the rate of escape out of the metastable arrangement a and into the stable region, i.e. beyond the point c.
- Naive approach: Barrier W is high, so the system is almost in equilibrium in the potential well at a. The distribution inside the well is then quasi-stationary:

$$P(x, v) = C \exp\left[-\frac{\frac{1}{2}mv^2 + U(x)}{kT}\right].$$

where the prefactor C follows from the normalization condition $\int dv \int dx\, P(x, v) = 1$, and is (using a harmonic well approximation around $x = a$)

$$C \approx \frac{\sqrt{U''(a)m}}{2\pi kT} \exp\left[\frac{U(a)}{kT}\right]$$

The transition rate τ_{naive}^{-1} is now given by the flow to the right at barrier b:

$$\begin{aligned} \frac{1}{\tau_{\text{naive}}} &= \int_0^\infty dv\, v P(x = b, v) \\ &= \frac{1}{2\pi}\sqrt{\frac{U''(a)}{m}} \exp\left[-\frac{W}{kT}\right]. \end{aligned}$$

- Interpretation: The system oscillates in the metastable state with a frequency $\sqrt{U''(a)/m}$. In each oscillation, it tries to overcome the barrier, where its chance to succeed is given by the *Arrhenius factor* $\exp[-W/kT]$.

- Less naive approach: <u>*First-passage problem:*</u> What is the first time τ_{fp} that the system passes c starting from the stable state a?

  Note: This assumes that once the system is in the stable state it will not return to the metastable state. Although such a return is not really impossible, it requires the system to overcome a barrier $U(b)$, which takes a time $\propto \exp[U(b)/kT] \propto \exp[-U(a)] \times \tau_{\text{naive}}$, i.e., exponentially larger than τ_{naive}.

- We will now the case of large friction: $\gamma \gg 1$.

Large friction limit of the Kramers' equation

- Take equation (19) and rewrite it to

$$\mathcal{L}_0 P = \frac{1}{\gamma}\left[\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial x} - \frac{U'}{m}\frac{\partial P}{\partial v}\right].$$

  where

$$\mathcal{L}_0 f \equiv \frac{\partial}{\partial v}\left[vf + \frac{kT}{m}\frac{\partial f}{\partial v}\right] = \frac{kT}{m}\frac{\partial}{\partial v}\left[e^{-\frac{mv^2}{2kT}}\frac{\partial}{\partial v}\left\{e^{\frac{mv^2}{2kT}} f\right\}\right].$$

  and where for brevity, we omit the arguments x, v and t.

- Expand $P(x, v, t)$ in inverse powers of γ :

$$P = P^{(0)} + \gamma^{-1}P^{(1)} + \gamma^{-2}P^{(2)} + \dots$$

- Upon substitution and equating equal powers of γ, we get

$$\mathcal{L}_0 P^{(0)} = 0 \tag{20a}$$

$$\mathcal{L}_0 P^{(1)} = \frac{\partial P^{(0)}}{\partial t} + v\frac{\partial P^{(0)}}{\partial x} - \frac{U'}{m}\frac{\partial P^{(0)}}{\partial v} \tag{20b}$$

$$\mathcal{L}_0 P^{(2)} = \frac{\partial P^{(1)}}{\partial t} + v\frac{\partial P^{(1)}}{\partial x} - \frac{U'}{m}\frac{\partial P^{(1)}}{\partial v} \tag{20c}$$

- For the γ^0 terms, the general solution can be found as follows:

$$\begin{aligned}
& \frac{\partial}{\partial v}\left[e^{-\frac{mv^2}{2kT}}\frac{\partial}{\partial v}\left\{e^{\frac{mv^2}{2kT}}P^{(0)}\right\}\right] &=&\ 0\\
\text{integrate over } v: \quad & e^{-\frac{mv^2}{2kT}}\frac{\partial}{\partial v}\left[e^{\frac{mv^2}{2kT}}P^{(0)}\right] &=&\ \sigma(x,t)\\
\text{rewrite:} \quad & \frac{\partial}{\partial v}\left[e^{\frac{mv^2}{2kT}}P^{(0)}\right] &=&\ \sigma(x,t)e^{\frac{mv^2}{2kT}}\\
\text{integrate over } v \text{ again:} \quad & e^{\frac{mv^2}{2kT}}P^{(0)} &=&\ \phi(x,t) + \sigma(x,t)\int_0^v dw\, e^{\frac{mw^2}{2kT}}\\
\text{so:} \quad & P^{(0)} &=&\ \phi e^{-\frac{mv^2}{2kT}} + \sigma\int_0^v dw\, e^{\frac{mw^2-mv^2}{2kT}}.
\end{aligned}$$

But the last term is negative for negative σv, while $P^{(0)}$ should satisfy $P^{(0)} \geq 0$ for all v, so σ must be zero. (Alternatively, one can argue that σ should be zero because the last term behaves as $1/v$ for large v, which cannot be normalized.) Thus we find

$$P^{(0)} = e^{-\frac{mv^2}{2kT}} \phi$$

with so far a general x and t dependent ϕ.

- Substituting this result in equation (20b) gives:

$$\mathcal{L}_0 P^{(1)} \quad = \quad \frac{\partial P^{(0)}}{\partial t} + v \frac{\partial P^{(0)}}{\partial x} - \frac{U'}{m} \frac{\partial P^{(0)}}{\partial v} \quad = \quad \left[\frac{\partial \phi}{\partial t} + v \left(\frac{\partial \phi}{\partial x} + \frac{U'}{kT} \phi \right) \right] e^{-\frac{mv^2}{2kT}}$$

- Because the operator $\mathcal{L}_0$ acting on $P^{(1)}$ on the left-hand side has a zero eigenvalue, this equation cannot be solved in general. We have to impose that the right hand side is orthogonal to the zero eigenvector. This is called the *solubility condition*.
- The left eigenvector with a zero eigenvalue is 1, as can be seen because the integral over v of $\mathcal{L}_0 f(x, v, t)$ is always zero for any $f(x, v, t)$.
- Thus, for the right hand-side to be orthogonal to this eigenvector, the integral over v of the right-hand side should also be zero, which gives:

$$\frac{\partial \phi}{\partial t} = 0.$$

  Hence we see that the previously general ϕ needs to be independent of t.
- The remaining equation for $P^{(1)}$ is thus:

$$\frac{\partial}{\partial v} \left[e^{-\frac{mv^2}{2kT}} \frac{\partial}{\partial v} \left(e^{\frac{mv^2}{2kT}} P^{(1)} \right) \right] \quad = \quad \frac{mv}{kT} \left[\frac{\partial \phi}{\partial x} + \frac{U'}{kT} \phi \right] e^{-\frac{mv^2}{2kT}}$$

- This can be solved using the same method as for $P^{(0)}$, i.e., integrating with respect to v twice and imposing normalizability. This gives:

$$P^{(1)} = \left[\psi - v \left(\frac{\partial \phi}{\partial x} + \frac{U'}{kT} \right) \right] e^{-\frac{mv^2}{2kT}},$$

  where ψ is a general x and t dependent function.
- Continuing with the equation for $P^{(2)}$, we find

$$\begin{aligned} \mathcal{L}_0 P^{(2)} \quad = \quad & \left[\frac{\partial \psi}{\partial t} + v \left(\frac{\partial \psi}{\partial x} + \frac{U'}{m} \psi \right) - v^2 \frac{\partial}{\partial x} \left(\frac{\partial \phi}{\partial x} + \frac{U'}{kT} \phi \right) \right. \\ & \left. + \frac{U'}{kT} \left(\frac{kT}{m} - v^2 \right) \left(\frac{\partial \phi}{\partial x} + \frac{U'}{kT} \phi \right) \right] e^{-\frac{mv^2}{2kT}} \end{aligned}$$

- The solubility condition $\int dv\, \mathcal{L}_0 P^{(2)} = 0$ gives in this case

$$\frac{\partial \psi}{\partial t} - \frac{\partial}{\partial x}\left(\frac{kT}{m}\frac{\partial \phi}{\partial x} + \frac{U'}{m}\phi\right) = 0 \tag{21}$$

- We will stop here and collect all the terms:

$$P(x,v,t) = e^{-\frac{mv^2}{2kT}}\left[\phi(x) + \gamma^{-1}\psi(x,t) - \gamma^{-1}v\left(\frac{\partial \phi(x)}{\partial x} + \frac{U'}{kT}\phi(x,t)\right) + \mathcal{O}(\gamma^{-2})\right]$$

- Note: The above perturbation scheme is called *singular perturbation*.
- We will mainly be interested in the distribution of x, which is

$$P(x,t) \;=\; \int dv\, P(x,v,t) = Z\left[\phi(x) + \gamma^{-1}\psi(x,t) + \mathcal{O}(\gamma^{-2})\right].$$

  where $Z = \sqrt{2\pi kT/m}$ and ϕ and ψ are connected through equation (21).
- Taking the time derivative of $P(x,t)$ gives

$$\begin{aligned}
\frac{\partial P(x,t)}{\partial t} &= Z\gamma^{-1}\frac{\partial \psi(x,t)}{\partial t} + \mathcal{O}(\gamma^{-2}) \\
&= Z\gamma^{-1}\frac{\partial}{\partial x}\left(\frac{kT}{m}\frac{\partial \phi(x)}{\partial x} + \frac{U'}{m}\phi(x)\right) + \mathcal{O}(\gamma^{-2}) \\
&= \gamma^{-1}\frac{\partial}{\partial x}\left(\frac{kT}{m}\frac{\partial P(x,t)}{\partial x} + \frac{U'}{m}P(x,t) + \mathcal{O}(\gamma^{-1})\right) + \mathcal{O}(\gamma^{-2}) \\
&= \frac{kT}{m\gamma}\frac{\partial^2 P(x,t)}{\partial x^2} + \frac{\partial}{\partial x}\left[\frac{U'}{m\gamma}P(x,t)\right] + \mathcal{O}(\gamma^{-2}).
\end{aligned}$$

- Using $\alpha = m\gamma$ and $D = kT/\alpha$, we see that this is to leading order the diffusion equation in an external potential (this is called a Smoluchovski equation):

$$\frac{\partial P(x,t)}{\partial t} \;=\; D\frac{\partial^2 P(x,t)}{\partial x^2} + \frac{\partial}{\partial x}\left[\frac{U'}{\alpha}P(x,t)\right]. \tag{22}$$

  I.e., to leading order in γ^{-1}, i.e., for large friction, the Kramers' particle performs a diffusive motion on top of the potential landscape sketched the above figure.
- A useful interpretation of this diffusion equation can be given by rewriting it as

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0.$$

  where

$$J(x,t) = -\frac{U'}{\alpha}P(x,t) - D\frac{\partial P(x,t)}{\partial x}$$

  is the *probability current*. The first term is due to the *drift* velocity $v_{\mathrm{drift}} = -U'/\alpha$, which is the velocity that balances the potential force $-U'$ and the friction force $-\alpha v$. The second term, on the other hand, is a diffusive current that arises because the probability is non-uniform.

First passage problem in the large friction limit

- Consider that case the Kramers' particle starts at a.
- To get the first passage time τ_{fp}, we modify the process such that we take out the particle as soon as it hits the point c.
- This turns the point c into an absorbing boundary:

$$P(c,t) = 0$$

- Since the particle is taken out as soon as they hit the point c yet, the probability not to have hit c at time t is $1 - \int_0^c dx\, P(x,t)$.
- Let $f(t)dt$ denote the probability for the Kramers' particle to hit the point c between a time t and $t + dt$. $f(t)$ can be written as

$$\begin{aligned}
f(t) &= \frac{Prob(\text{no hit before time } t) - Prob(\text{no hit before } t+dt)}{dt} \\
&\approx \frac{\partial}{\partial t}\left[1 - \int_0^c dx\, P(x,t)\right] \\
&= -\int_0^c dx\, \frac{\partial P(x,t)}{\partial t} \\
&= \int_0^c dx\, \frac{\partial J(x,t)}{\partial x} \\
&= J(c,t).
\end{aligned}$$

- In principle, to obtain the mean first passage time τ_{fp} we have therefore to
  - solve the diffusion equation in a potential, equation (22), for $P(x,t)$ with initial condition that the Kramers' particle starts in a: $P(x,0) = \delta(x-a)$,
  - compute the probability current J at point c and at time t to get the probability $f(t) = J(c,t)$ to hit c at time t
  - and average t with $f(t)$ to get $\tau_{\text{fp}} = \int_0^\infty dt\, t\, f(t)$.
- However, for the mean first passage time there is a trick:
- The mean first passage time τ_{fp} is the average of t with $f(t) = -\int_0^c dx\, \frac{\partial P(x,t)}{\partial t}$, so

$$\begin{aligned}
\tau_{\text{fp}} &= -\int_0^\infty dt\, t \int_0^c dx\, \frac{\partial P(x,t)}{\partial t} \\
&= -\int_0^c dx \int_0^\infty dt\, t \frac{\partial P(x,t)}{\partial t} \\
&= \int_0^c dx \int_0^\infty dt\, P(x,t)
\end{aligned} \tag{23}$$

or

$$\tau_{\text{fp}} = \int_0^c dx\, \bar{P}(x) \tag{24}$$

where $\bar{P}(x)$ is the time integral of $P(x,t)$

$$\bar{P}(x) = \int_0^\infty dt\, P(x,t).$$

- The function $\bar{P}(x)$ only depends on x and satisfies an ordinary differential equation that can be found by integrating equation (22) over time:

$$\begin{aligned} \int_0^\infty dt\, \frac{\partial P(x,t)}{\partial t} &= D\frac{d^2\bar{P}(x)}{dx^2} + \frac{d}{dx}\left[\frac{U'}{\alpha}\bar{P}(x)\right] \\ -\delta(x-a) &= D\frac{d^2\bar{P}(x)}{dx^2} + \frac{d}{dx}\left[\frac{U'}{\alpha}\bar{P}(x)\right]. \end{aligned}$$

- This equation can be solved using similar techniques as before, leading to

$$\bar{P}(x) = D^{-1}e^{-\frac{U(x)}{kT}} \int_x^c dx'\, \Theta(x'-a)e^{\frac{U(x')}{kT}}$$

where Θ is the Heaviside step function, defined to be $\Theta(x) = 1$ if $x > 0$, $\Theta(x) = 0$ if $x < 0$ and we used the Einstein relation $D = kT/\alpha$.

- Using this in equation (24), we find

$$\tau_{\text{fp}} = D^{-1}\int_a^c dx\, e^{\frac{U(x)}{kT}} \int_0^x dx'\, e^{-\frac{U(x')}{kT}}.$$

- Noting that the factor $e^{\frac{U(x)}{kT}}$ is largest at the transition state point b and that therefore the region around it dominates the integral over x, we may use the *parabolic approximation*:

$$e^{\frac{U(x)}{kT}} \approx e^{\frac{U(b)}{kT} - \frac{|U''(b)|}{2kT}(x-b)^2}$$

- Likewise, with $x \approx b$, the dominant contribution of the x' integral comes from the point a, giving

$$\int_0^x dx'\, e^{-\frac{U(x')}{kT}} \approx \int_{-\infty}^\infty dx'\, e^{-\frac{U(a)}{kT} - \frac{U''(a)}{2kT}(x'-a)^2} = \sqrt{\frac{2\pi\alpha D}{U''(a)}}e^{-\frac{U(a)}{kT}}.$$

- Performing also the integral over x, we finally get

$$\tau_{\text{fp}} = \frac{2\pi\alpha}{\sqrt{U''(a)|U''(b)|}}e^{\frac{U(b)-U(a)}{kT}} \tag{25}$$

- Compared to the earlier time τ_{naive}, τ_{fp} takes into account things that happen at the transition point b. In fact, τ_{fp} has an addition *factor* $\gamma/\sqrt{|U''(b)|/m}$ compared to τ_{naive}. It reflects that if U is rather flat around b, crossing b does not necessarily lead to state c, but the Kramers' particle may jump back to the left. In this sense it takes care of *recrossings*.
- The case of **smaller friction** will be left for home work.