Foundations of Chemical Kinetics
Lecture 20:
Kramers theory

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The Langevin equation

- Langevin equations are an alternative way to treat diffusion in which we focus on a single particle.
- This particle experiences a drag force (as seen previously in the theory of diffusion) as well as random forces from collisions with the solvent.
- The separation of the force into drag and a random force is somewhat artificial: Both arise from collisions with the solvent. This separation recognizes that, if the particle has velocity v, this creates an asymmetry in the interaction with the solvent which can be separated from the (on average) isotropic term due to random motion of the solvent.
- In addition to interaction with the solvent, imagine that there is a potential energy $V(x)$.
- The drag force is $-fv$, and for now we write the random force as $F_r(t)$.

The Langevin equation (continued)

- The equations of motion for this system are

$$F = ma = m\frac{dv}{dt} = -\frac{dV}{dx} - fv + F_r(t)$$
$$\frac{dx}{dt} = v$$

  This is a version of a Langevin equation.

- This equation is a stochastic differential equation, i.e. a differential equation with random terms.

- To work with this equation, we need to say something about the randomly fluctuating force $F_r(t)$.

The Langevin equation (continued)

- The standard assumptions on $F_r(t)$ are that
  - The time average of $F_r(t)$ is zero.
  - The force varies rapidly in time so that its values at two different times t and t' are uncorrelated. Mathematically, we write

  $$\langle F_r(t)F_r(t')\rangle = \Gamma\delta(t - t')$$

  where the angle brackets denote a time average, here used to compute a correlation, $\delta(\cdot)$ is a delta function, and Γ is a constant to be determined later.

The Langevin equation

Ordinary diffusion

- In general, the Langevin equation is difficult to solve.
- Note that the very idea of "solving" an equation with a randomly fluctuating term needs to be defined.
- For now, we focus on the case of ordinary diffusion $(V(x) = 0)$.
  Our focus will be on the statistical properties of v.
- The equation for v is

$$\frac{dv}{dt} = -\frac{f}{m}v + \frac{1}{m}F_r(t)$$

- The formal solution of this equation with initial condition $v = v_0$ is

$$v(t) = v_0 \exp\left(-ft/m\right) + \frac{1}{m}\exp\left(-ft/m\right)\int_0^t F_r(t')\exp(ft'/m)\,dt'$$

The Langevin equation
Ordinary diffusion (continued)

$$v(t) = v_0 \exp\left(-ft/m\right) + \frac{1}{m} \exp\left(-ft/m\right) \int_0^t F_r(t') \exp(ft'/m) \, dt'$$

- If we are given $F_r(t)$, then we can compute $v(t)$ from the above formula.
- We can average v over an ensemble of particles each starting from the same initial condition but subject to its own realization of the random force F_r:

$$\begin{aligned}
\langle v(t) \rangle &= v_0 \exp\left(-ft/m\right) \\
&\quad + \frac{1}{m} \exp\left(-ft/m\right) \int_0^t \langle F_r(t') \rangle \exp(ft'/m) \, dt' \\
&= v_0 \exp\left(-ft/m\right)
\end{aligned}$$

since $\langle F_r(t) \rangle = 0$.

The Langevin equation
Ordinary diffusion (continued)

$$v(t) = v_0 \exp\left(-ft/m\right) + \frac{1}{m} \exp\left(-ft/m\right) \int_0^t F_r(t') \exp(ft'/m) \, dt'$$

- Squaring this equation, we get

$$
\begin{aligned}
v^2 = {} & v_0^2 \exp\left(-2ft/m\right) \\
& + \frac{2v_0}{m} \exp\left(-2ft/m\right) \int_0^t F_r(t') \exp(ft'/m) \, dt' \\
& + \frac{1}{m^2} \exp\left(-2ft/m\right) \int_0^t F_r(t') \exp(ft'/m) \, dt' \\
& \times \int_0^t F_r(t'') \exp(ft''/m) \, dt''
\end{aligned}
$$

The Langevin equation

Ordinary diffusion (continued)

$$\begin{aligned}
\therefore v^2 = {}& v_0^2 \exp\left(-2ft/m\right) \\
& + \frac{2v_0}{m} \exp\left(-2ft/m\right) \int_0^t F_r(t') \exp(ft'/m) \, dt' \\
& + \frac{1}{m^2} \exp\left(-2ft/m\right) \int_0^t dt' \int_0^t dt'' \exp[f(t'+t'')/m] F_r(t') F_r(t'')
\end{aligned}$$

- We now average over an ensemble of particles with a common initial velocity.
- Because $\langle F_r(t') F_r(t'') \rangle = \Gamma \delta(t'-t'')$, we get

$$\langle v^2 \rangle = v_0^2 \exp(-2ft/m) + \frac{\Gamma}{m^2} \exp(-2ft/m) \int_0^t dt' \exp(2ft'/m)$$

The Langevin equation

Ordinary diffusion (continued)

$$\therefore \langle v^2 \rangle = v_0^2 \exp(-2ft/m) + \frac{\Gamma}{2mf} \exp(-2ft/m) \exp(2ft'/m)\big|_0^t$$

$$= v_0^2 \exp(-2ft/m) + \frac{\Gamma}{2mf} [1 - \exp(-2ft/m)]$$

- Now note

$$\lim_{t\to\infty} \langle v^2 \rangle = \frac{\Gamma}{2mf}$$

- The kinetic theory of matter gives $\langle v^2 \rangle = k_B T/m$ so

$$\frac{\Gamma}{2f} = k_B T$$

This is a version of the fluctuation-dissipation theorem because it relates the size of the fluctuations (controlled by Γ) to the rate of dissipation (f).

The Langevin equation
Ordinary diffusion (continued)

- Finally note that, since $D = k_B T / f$ and $\Gamma = 2 f k_B T$,

$$\Gamma = 2 f^2 D$$

- Γ is therefore proportional to the diffusion coefficient.
  - The larger the random force, the faster diffusion will be at a given temperature. coefficient.

Simulation of the Langevin equation

- For an ordinary differential equation, we get a simple numerical method, Euler's method, by replacing the derivatives by ratios of small changes, e.g. $dv/dt \approx \Delta v/\Delta t$. We calculate Δv and Δx for a small Δt, then use these to update v and x.
- The random force term doesn't obey the normal rules of calculus. Instead, we need to use a special stochastic calculus, known as Itô calculus, to approximate this term when $\Delta t \not\to 0$.

Simulation of the Langevin equation

$$\frac{dv}{dt} = -\frac{f}{m}v + \frac{1}{m}F_r(t)$$
$$\frac{dx}{dt} = v$$

- For a force with the time autocorrelation
  $\langle F_r(t)F_r(t')\rangle = \Gamma\delta(t - t')$, the Euler-Maruyama scheme for the Langevin equation is

$$\Delta v = -\frac{fv}{m}\Delta t + \frac{\sqrt{\Gamma}}{m}\mathcal{N}(1)\sqrt{\Delta t}$$
$$\Delta x = v\Delta t$$

  These Δ's are added to the corresponding variables at each step.

Simulation of the Langevin equation (continued)

- Suppose we want to simulate the diffusion of sucrose in water for $1\,\mathrm{ns}$ at $20\,°\mathrm{C}$.

$$D = 5.7 \times 10^{-10}\,\mathrm{m^2 s^{-1}}$$
$$m = 5.68 \times 10^{-25}\,\mathrm{kg}$$

- Use

$$f = k_B T / D$$
$$\Gamma = 2 f k_B T$$

Simulation of the Langevin equation (continued)

Time step selection

- We want $|\Delta v/v|$ to be reasonably small.
- The rms speed $\sqrt{k_B T/m}$ gives a typical value for v.
- The first part of $\Delta v/v$ is $(f/m)\Delta t$.

$$(f/m)\Delta t \ll 1 \qquad \implies \Delta t \ll m/f$$

- The second part of $\Delta v/v$ is of amplitude $|\sqrt{\Gamma}\sqrt{\Delta t}/mv|$.

$$\left| \frac{\sqrt{\Gamma}\sqrt{\Delta t}}{mv} \right| \sim \frac{\sqrt{\Gamma}\sqrt{\Delta t}}{m}\sqrt{m}k_B T = \sqrt{\frac{\Gamma}{mk_B T}}\sqrt{\Delta t} \ll 1$$

$$\implies \Delta t \ll mk_B T/\Gamma$$

$$\Gamma = 2fk_B T \implies \Delta t \ll \frac{m}{2f}$$

- In this context "$\ll$" doesn't have to be tiny.
- Choose $\Delta t = m/10f$ (but smaller = more accurate)

Simulation of the Langevin equation (continued)
A check on the data

- We should have $\langle v^2 \rangle = k_B T / m$.
  It's pretty easy to check that this is approximately true after
  the program has run.

- Now let's write some code. . .

From Langevin to Kramers

- The Langevin equation tells us how to calculate realizations (individual particle trajectories) of the diffusion process.

- We could also ask how the probability density for position x and velocity v evolves. This is given by the Kramers equation. Specifically, let $\rho(x, v) \, dx \, dv$ be the probability that simultaneous measurements of the position and velocity are between x and $x + dx$, and v and $v + dv$, respectively.

- The derivation of the Kramers equation is time-consuming, so I just present it here without proof:

$$\frac{\partial \rho}{\partial t} + v \frac{\partial \rho}{\partial x} - \frac{1}{m} \frac{\partial V}{\partial x} \frac{\partial \rho}{\partial v} = \frac{f}{m} \left[\frac{\partial}{\partial v} \left(v \rho \right) + \frac{k_B T}{m} \frac{\partial^2 \rho}{\partial v^2} \right]$$

Kramers equation
Interpretation and application in kinetics

- The various terms in the Kramers equation have the same meanings as in the Langevin equation.
  In particular, f is a drag coefficient for a particle moving through a fluid and V is the potential energy of the particle.
- Now consider a chemical reaction in solution, possibly but not necessarily a simple isomerization $A \rightleftharpoons B$.
- The mass m is an effective mass for the reactive mode (e.g. a reduced mass μ from Gaussian).

Kramers equation

Interpretation and application in kinetics (continued)

- The reaction is associated with a potential energy surface. Along the reaction coordinate x, the PES reduces to a potential energy curve:
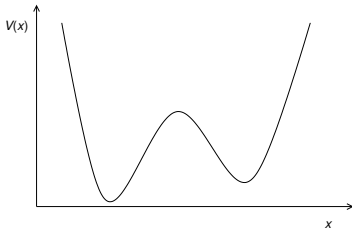
- Any rearrangements of the reactants to products (motion along x) requires the solvent molecules in the immediate neighborhood to move, causing drag. Accordingly, the motion of a particle through a solvent experiencing drag with the added force due to the potential energy is a good model for a chemical reaction in solution.

Kramers equation
Effects of the solvent

- The solution of the Kramers equation for a double-well
  potential introduces a correction (i.e. a transmission
  coefficient) to transition-state theory.
  The following is valid in the medium- to high-friction regime
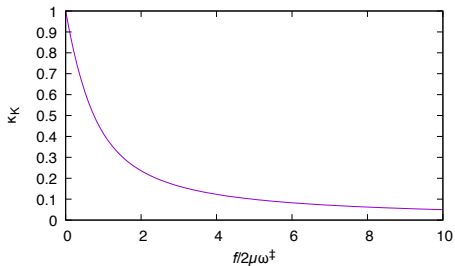 (generally appropriate for reactions in solution):

$$\kappa_K = \left[1 + \left(\frac{f}{2\mu^{\ddagger}\omega^{\ddagger}} \right)^2 \right]^{1/2} - \frac{f}{2\mu^{\ddagger}\omega^{\ddagger}}$$

- $\omega^{\ddagger}$ is the frequency associated with the reactive mode and $\mu^{\ddagger}$
  is the corresponding reduced mass.

Kramers equation

Effects of the solvent

$$\kappa_K = \left[1 + \left(\frac{f}{2\mu^{\ddagger}\omega^{\ddagger}} \right)^2 \right]^{1/2} - \frac{f}{2\mu^{\ddagger}\omega^{\ddagger}}$$

Kramers equation
The large friction limit

$$\kappa_K = \left[1 + \left(\frac{f}{2\mu^{\ddagger}\omega^{\ddagger}} \right)^2 \right]^{1/2} - \frac{f}{2\mu^{\ddagger}\omega^{\ddagger}}$$

- To study the high-friction limit, define $q = 2\mu^{\ddagger}\omega^{\ddagger}/f$, and take a Taylor expansion about $q = 0$:

$$\kappa_K = \left(1 + q^{-2} \right)^{1/2} - q^{-1}$$
$$= q^{-1} \left[(q^2 + 1)^{1/2} - 1 \right]$$
$$\therefore q\kappa_K = (q^2 + 1)^{1/2} - 1$$
$$\approx 0 + 0q + \frac{1}{2}(1)q^2$$
$$\therefore \kappa_K \approx q/2 = \mu^{\ddagger}\omega^{\ddagger}/f$$

Kramers equation
The large friction limit (continued)

$$\kappa_K \approx \mu^{\ddagger}\omega^{\ddagger}/f$$

- At low velocities, f is proportional to η.
  Example: Stokes-Einstein $f = 6\pi R\eta$
- Prediction: the transmission coefficient should decrease with increasing solvent viscosity.
- This has been confirmed experimentally.

# Kramers equation
The large friction limit (continued)

Why is the transmission coefficient small for large friction?

- The large friction in this regime rapidly kills any momentum in the reactive mode, making the random force (i.e. momentum transfer due to collisions with solvent) more important.
- This causes the crossing of the transition state a random process, and one that is essentially undirected.
- In other words, there are many crossings and recrossings of the barrier for a typical reactive event, and many cases where reactants having reached the transition state return to the reactant valley.

Applying Kramers theory

$$\kappa_K = \left[1 + \left(\frac{f}{2\mu^{\ddagger}\omega^{\ddagger}}\right)^2\right]^{1/2} - \frac{f}{2\mu^{\ddagger}\omega^{\ddagger}}$$

- There is one significant problem applying this equation: we don't know how to compute f for motion along a reaction coordinate.
- We're going to have to improvise.
  What is moving during the reaction? How large a profile does it present to the solvent?

Example: $H_2 + {}^{\bullet}OH \longrightarrow {}^{\bullet}H + H_2O$
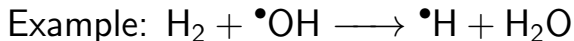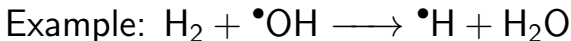
- Last lecture, we found that a straightforward TST calculation dramatically overestimated this rate constant.
- Transition state:

- The largest amplitude motion involves a hydrogen atom. Assume that $R \approx R_H = 1.10\,\text{Å}$ (vdW radius).
- $\eta_{H_2O} = 8.91 \times 10^{-4}\,\text{Pa s}$ at $25\,^{\circ}\text{C}$, so

$$f = 6\pi R \eta = 1.85 \times 10^{-12}\,\text{N s m}^{-1}$$

Example: $H_2 + {}^\bullet OH \longrightarrow {}^\bullet H + H_2O$

- From Gaussian, $\tilde{\nu}^{\ddagger} = 912\,\mathrm{cm}^{-1} \equiv$ and
  $\mu^{\ddagger} = 1.1155\,\mathrm{amu} \equiv 1.8523 \times 10^{-27}\,\mathrm{kg}$.
- $\omega^{\ddagger} = 2\pi c \nu^{\ddagger} = 1.72 \times 10^{14}\,\mathrm{s}^{-1}$
-
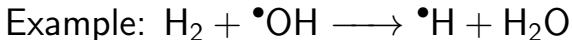
$$\frac{f}{2\mu^{\ddagger}\omega^{\ddagger}} = 2.90$$

$$\kappa_K = \left[1 + \left(\frac{f}{2\mu^{\ddagger}\omega^{\ddagger}}\right)^2\right]^{1/2} - \frac{f}{2\mu^{\ddagger}\omega^{\ddagger}}$$

$$= 0.17$$

- We had previously calculated $k_{\mathrm{TST}} = 2.9 \times 10^9\,\mathrm{L\,mol^{-1}s^{-1}}$, so the corrected value is

$$k_{\mathrm{Kramers}} = \kappa_K\, k_{\mathrm{TST}} = 4.9 \times 10^8\,\mathrm{L\,mol^{-1}s^{-1}}$$

- This is still 10 times larger than the experimental value.

Example: $H_2 + {}^{\bullet}OH \longrightarrow {}^{\bullet}H + H_2O$

- Lots of possible reasons for the mismatch:
  - TST tends to overestimate rate constants.
  - f underestimated
  - ${}^{\bullet}OH$ is not a normal solute; perhaps its interactions with the solvent play a role we have not taken into account.
    (Grotthuss mechanism delocalization of radical?)
- Directly applying TST in solution is difficult...
- but we can get lots of insight into factors that affect the rate from TST.