Lecture 30 Chapter 18 & 19 Fluctuation-Dissipation and Kinetics

Announce:
- Seminar today!
- Special seminar on Monday! Good biochem/phys stuff

Outline:

Fluctuation-Dissipation
Brownian ratchets
Kinetics

Review

\[ D \propto \langle u \rangle \lambda \]  
(\( u \) is velocity, \( \lambda \) mean free path)

**Fick's second law** of diffusion (also called The Diffusion Equation):

\[
\left( \frac{\partial C}{\partial t} \right)_x = D \left( \frac{\partial^2 C}{\partial x^2} \right)_t
\]

\[ D = \frac{\langle d^2 \rangle}{2t} \]  
(one dimension Eq 18.53)

\[ D = \frac{\langle d^2 \rangle}{6t} \]  
(three dimensions)

Einstein-Smoluchowski Eq.  
\[ D = \frac{k_B T}{\eta} \]

Experimentally  
\[ f_{\text{EXP}} = \frac{k_B T}{D} \]

Theoretically  
\[ f_{\text{THEO}} = 6\pi \eta r \]

Fluctuation-dissipation theorem
Let’s briefly mention Langevin dynamics:
This comes from the fluctuation-dissipation theorem. This says that the fluctuations that occur at equilibrium are the very same motions that dissipate excess energy. Thus, the way the system returns to equilibrium is the same as the way the system behaves at equilibrium.

Langevin says that there are two forces acting on a diffusing particle – random (Brownian) forces and friction. Let’s put this together with Newton.

\[ m \frac{dv(t)}{dt} = F(t) -fv(t) \]

(frictional force is proportional to velocity)

Multiply through by \( v \) at time zero and average over our ensemble

\[ m \left< v(0) \frac{dv(t)}{dt} \right> = \left< v(0)F(t) \right> - f \left< v(0)v(t) \right> \]

velocity and force are unrelated so the average of the products is the same as the product of the averages

Also \( v(0) \) is constant so we can take it into the integral

\[ \frac{d}{dt} \left< v(0)v(t) \right> = \left< v(0) \right> \left< F(t) \right> - \frac{f}{m} \left< v(0)v(t) \right> \]

Because force is random \( \left< F(t) \right> = 0 \)

\[ \frac{d}{dt} \left< v(0)v(t) \right> = -\frac{f}{m} \left< v(0)v(t) \right> \]

You’ll see this kind of equation many times next semester: derivative of some function is a constant times the original function

**Solution is:**

\[ \left< v(0)v(t) \right> = \left< v^2(0) \right> e^{-\frac{ft}{m}} \]

The term on the left is the velocity autocorrelation function and what is on the right tells us that the average \( v \) at some time \( t \) is closely related to \( v \) at time 0 if \( t \) is small. The similarity decays away exponentially.

The above equation shows that the correlation time is \( m/f \). For a protein this is on the order of \( 10 \times 10^{-12} \). This means that in a few tens of ps the protein is moving in a new direction, unrelated to its previous motion.

These are very common things – autocorrelation functions, and decay of correlation. Very important in modern spectroscopies like NMR, lasers and so on.
Brownian Rachet

Sketch something like Fig 18.15
• asymmetric potential
• particle bound at minimum.
• particle released and then wanders randomly (diffuses)
• because potential is asymmetric, particle is more likely to diffuse over one boundary
  than the other. So, motion will generally go one direction.

(Try He balloon as particle. Three people are allowed to grab string on balloon – these
people represent the bottoms of the potentials (arranged asymmetrically). Rest of class
broken up into two groups, one group pushes balloon to left, one group to right.

Now onto the most fantastic topic of all – kinetics!

Now, let’s define the general rxn: \[ v_A A + v_B B \rightarrow v_Y Y + v_Z Z \]

and its velocity \[ v(t) = \frac{d\left(\frac{\xi(t)}{V}\right)}{dt} = -\frac{1}{v_A} \frac{d[A]}{dt} = \frac{1}{v_Z} \frac{d[Z]}{dt} \]

For example, nitrogen dioxide formation \[ 2 \text{NO(g)} + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) \]

has the rate of reaction:\[ v(t) = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} \]

Define rate law
For most chemical reactions, \( v \) is a function of time, or really a
function of the species concentrations, which are themselves time
dependent. The relationship between the rate of reaction and the
species concentrations are given by the rate law. e.g.
\[ v(t) = k [\text{NO}]^2 [\text{O}_2] \]

This one happens to, but the rate law generally does NOT correspond
to the stoichiometry of the balanced reaction, because it depends on
the details of the reaction mechanism.
$k$ is constant and is called the **rate constant** for the reaction.

In general, rate laws look like:

$$v(t) = k [A]^{m_A} [B]^{m_B} \ldots$$

Each $m_j$ is called the order of the reaction for component $j$. The overall reaction order is simply the sum of all $m_j$.

$$\text{overall order} = m_A + m_B + \ldots$$

Reaction orders are usually integers, but fractions are possible if the mechanism is actually more complex than implied by the rate law. Often (many multistep rxns) a simple rate law cannot be written down and the order is undefined.

**How to determine a rate law**

Knowing the balanced chemical rxn does nothing to elucidate the rate law. The kinetics of the reaction must be measured. Understanding the rate law can then allow the rxn dynamics to be understood.

Back to our general reaction:

$$v_A A + v_B B \rightarrow v_Y Y + v_Z Z$$

Assume it has the rate law:

$$v = k [A]^{m_A} [B]^{m_B}$$

We can attempt to discover the reaction orders through a couple methods.

**Method of isolation**

If we put one of the components in huge excess (A for instance), then the concentration of that component is essentially constant throughout the reaction.

Therefore, $v = k [A]^{m_A} [B]^{m_B}$ becomes $v = k' [B]^{m_B}$

So, measuring rate as a function of [B] ([A] always $\gg$ [B])

This can easily be extended to reactions of many components.
Method of initial rates

If we can measure the rate over a very short time interval, i.e. $\xi$ is only slightly different at the beginning and end of the time interval, then [A] and [B] are both essentially constant. Doing this for two initial B concentrations gives:

$$v_1 = -\frac{1}{v_A} \left( \frac{\Delta A}{\Delta t} \right)_1 = k[A]^m[B]^n$$

$$v_2 = -\frac{1}{v_A} \left( \frac{\Delta A}{\Delta t} \right)_2 = k[A]^m[B]^n$$

Dividing these two equations gives:

$$\frac{v_1}{v_2} = \left( \frac{[B]}{[B]} \right)^m$$

or

$$mB = \ln \left( \frac{v_1}{v_2} \right)$$

Note that both methods are limited to reactions that are slower than the time it takes to mix things together – generally milliseconds. Methods exist for faster rxns.

Zero order reactions

$$v(t) = k$$

or

$$\frac{d[A]}{dt} = -v_Ak$$

Rearranging and integrating gives:

$$d[A] = -v_Akdt$$

$$\int_{[A]_0}^{[A]} d[A] = -v_Ak \int_0^t dt'$$

$$[A]_f - [A]_0 = -v_Akt$$

$$[A]_f = -v_Akt + [A]_0$$
So, plotting $[A]$ versus time gives a line.

Note that the half-life is given by

$$\frac{1}{2}[A]_0 = -\nu_A k t_{1/2} + [A]_0$$

$$t_{1/2} = [A]_0 / 2\nu_A k$$

**First order reactions (have them do?)**

$$v(t) = k [A] \quad \text{or} \quad \frac{d[A]}{dt} = -\nu_A k[A]$$

Similarly:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -\nu_A k \int_0^t dt'$$

$$\ln[A]_t - \ln[A]_0 = -\nu_A kt$$

$$\ln[A]_t = -\nu_A kt + \ln[A]_0$$

$$[A]_t = [A]_0 e^{-\nu_A kt}$$

So a plot of $\ln[A]$ versus time gives a line ($[A]$ vs. $t$ gives exp)

Note that for first order, the half life is:

$$t_{1/2} = \ln 2 / \nu_A k = 0.693 / \nu_A k$$

and is independent of the initial concentrations (radioactive decay and many simple photochemical reactions are first order)

**Second and higher order reactions**

(is in the notes – definitely check it out)

$$v(t) = k [A]^2 \quad \text{or} \quad \frac{d[A]}{dt} = -\nu_A k[A]^2$$
\[
\left[ A \right] \frac{d[\text{A}]}{[\text{A}]^2} = -v_A k \int_{0}^{t} dt'
\]
\[
-\left( \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} \right) = -v_A k t
\]
\[
\frac{1}{[\text{A}]_t} = v_A k t + \frac{1}{[\text{A}]_0}
\]

So, a plot of $1/[\text{A}]$ versus time gives a line.

Higher order reactions are integrated exactly the same way and give
\[
\left[ \text{A} \right]^{-(n-1)} = (n - 1)v_A k t + \left[ \text{A} \right]^{-(n-1)}_0
\]

The half-life for a second order reaction is $t_{1/2} = 1 / v_A [\text{A}]_0$

You should be able to derive any of these integrated rate law expressions for arbitrary order along with their half-lives.

Reversible Reactions

Of course, reactions are always reversible to some extent. Many times, the back reaction is very slow and we can safely ignore it but not in general.

Usually, we write $\text{A} \leftrightarrow \text{Z}$ with forward rate $k_1$ and backward rate $k_{-1}$

At equilibrium we know 2 things?

The relative amounts of $\text{A}$ and $\text{Z}$: $K_{eq} = [\text{Z}]_{eq} / [\text{A}]_{eq}$

and the forward and backward rates must be equal: $k_1[\text{A}] = k_{-1}[\text{Z}]$

this is dynamic equilibrium and is described by the principle of detailed balance
How do we find $k_1$ and $k_{-1}$?

Let’s assume we have a rate law that is first order in both $A$ and $Z$. Then at any given time the rate of change in $A$ is:

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[Z]$$

If we started with $[A] = [A]_0$ and $[Z]_0 = 0$, then at any time $[Z] = [A]_0 - [A]$

so

$$-\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}[A]_0$$

Integrating similarly to before gives

$$\ln([A] - [A]_{eq}) = -(k_1 + k_{-1})t + \ln([A]_0 - [A]_{eq})$$

so plotting $\ln(A-A_{eq})$ vs. $t$ gives a line with the slope that is the sum of the rates.

But, we also know that at equilibrium $k_1[A]_{eq} = k_{-1}[Z]_{eq}$

so

$$\frac{k_1}{k_{-1}} = \frac{[Z]_{eq}}{[A]_{eq}} = K_{eq}$$

(Detailed Balance!)

Therefore, we can find both the sum and ratio of the rates and know both of them.

Relaxation methods

Many kinds of relaxation methods are used to measure these rates. We don’t have time to explore them, but they involve a fast perturbation of the equilibrium away from the current equilibrium (say a temperature jump with a capacitor or laser or something more subtle) and measuring how quickly the system adjusts itself. We can get into these in more detail during the last two days of the semester if you like.
Temperature dependence of rates

Empirically, we find that most reaction rates depend very strongly on temperature. Much more than you would expect just from the collision rates of molecules. From empirical studies,

\[
\frac{d \ln k}{dT} = \frac{\text{const}}{RT^2}
\]

This constant behaves like energy, and we call it activation energy.

\[
\frac{d \ln k}{dT} = \frac{E_a}{RT^2}
\]

or

\[
\frac{d \ln k}{d\left(\frac{1}{T}\right)} = -\frac{E_a}{R}
\]

This integrates to

\[
\int d(ln k) = \frac{E_a}{R} \int T^{-2} dT
\]

\[
\ln k = -\frac{E_a}{RT} + \text{Const}(\ln A)
\]

\[
k = Ae^{-E_a/RT}
\]

(Arrhenius 1889)

The constant \( A \) is called the pre-exponential factor. \( E_a \) is the (internal \( U \)) energy difference between reactants and the transition state along a coordinate called the reaction coordinate. For something like \( I_2 \) dissociating it is the I-I bond length. For other reactions it is a complex collection of coordinates.