

Chem 163, Lecture 4

Adam E. Cohen

9/15/22

1 Introduction

In the last class we wrote down the Diffusion Equation, and we discussed how it is analogous to a Schrödinger Equation, and in the time independent case it is analogous to Poisson's Equation in electrostatics. We considered two special cases: Steady state implies $\partial c/\partial t = 0$, and thermal equilibrium implies $\mathbf{j} = 0$.

When a particle is subject to external forces, the probability distribution evolves according to the Smoluchowski Equation:

$$\mathbf{j} = -D\nabla c - \frac{c}{\gamma}\nabla U. \quad (1)$$

The rate of change of concentration is still given by the negative divergence of the flux:

$$\frac{\partial c}{\partial t} = D\nabla^2 c + \nabla \cdot \left(\frac{c}{\gamma}\nabla U\right). \quad (2)$$

In the presence of external forces, we have a balance between the forces, which try to concentrate all the particles in the region of lowest energy, and entropy, which tries to distribute them broadly. This leads to inhomogeneous concentration profiles, with the thermal equilibrium profile given by the Boltzmann distribution:

$$c(\mathbf{r}) = c_0 \exp[-U(\mathbf{r})/k_B T]. \quad (3)$$

From this we derived the famous Stokes Einstein relation:

$$D = k_B T/\gamma. \quad (4)$$

1.1 Stochastic growth curves

Consider some random variable X . We often want to evaluate an expression of the form

$$\langle e^X \rangle. \quad (5)$$

For instance, you had to do this on the homework, where you knew that X was Gaussian distributed, and you wanted to find properties of the log-normal

distribution. There are some things we can say about this distribution without doing any math. For instance, we can state unequivocally that

$$\langle e^X \rangle > e^{\langle X \rangle}. \quad (6)$$

This fact is called Jensen's inequality. It applies for any concave function. [DRAW A PICTURE OF AN EXPONENTIAL AND A TANGENT LINE AT $\langle X \rangle$, i.e. the half-way point along the x-axis. The average value of the function defined by the straight line is $e^{\langle X \rangle}$. But the actual function e^x always lies above this tangent line, so its average must be higher. Another way of seeing this is to pair up points on the curve on the left and right sides of $\langle X \rangle$. The average of each pair of points lies above $e^{\langle X \rangle}$, so the whole average, $\langle e^X \rangle$ must exceed $e^{\langle X \rangle}$.]

The facts you derived about the log-normal distribution on the homework are very useful. You showed that if X is Gaussian distributed with mean μ and variance σ^2 , then

$$\langle e^X \rangle = e^{\mu + \sigma^2/2}. \quad (7)$$

This comes in handy for stochastic growth scenarios. Here's how. We all know that the solution to the equation

$$\frac{dP}{dt} = kP \quad (8)$$

is

$$P(t) = P(0)e^{kt}. \quad (9)$$

If k is a function of time, the equation is

$$\frac{dP}{dt} = k(t)P, \quad (10)$$

and the solution is

$$P(t) = P(0)e^{\int_0^t k(t')dt'}. \quad (11)$$

Now suppose $k(t)$ is a stochastically varying quantity with finite mean and variance. Let $B(t) = \int_0^t k(t')dt'$. Provided that t is much greater than the correlation time of k , B is Gaussian distributed with mean μt and variance $\sigma^2 t$ (thanks to the Central Limit Theorem). Then the mean of $P(t)$ is

$$\langle P(t) \rangle = P(0)e^{(\mu + \sigma^2/2)t}. \quad (12)$$

This was the surprising result from the homework, that variability in growth conditions leads to *faster* average growth than completely uniform growth conditions.

Incidentally, exactly the same formalism is useful in time-dependent quantum mechanics, where you have Schrödinger's equation

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \hat{H}(t)\psi. \quad (13)$$

If you have stochastic fluctuations in \hat{H} (e.g. from interactions with the environment), then you can use the same formalism to handle decoherence and dephasing.

1.2 Equipartition

We need three fundamental results for all of our studies of diffusion. We have two: Central Limit Theorem and Stokes-Einstein Relation. The third is the Equipartition Theorem. We'll start with that today, and then discuss another language for describing the motion of small particles. Along the way we'll take an interlude to discuss correlation functions.

The equipartition theorem states that for any degree of freedom where the energy depends quadratically on the coordinate, at thermal equilibrium the mean energy is $\frac{1}{2}k_B T$.

Here's the proof. The energy is:

$$U(q) = \frac{1}{2}kq^2, \quad (14)$$

where k is some constant, and q is the coordinate of the particle. We all know that the probability of a particle occupying a state with energy $U(q)$ is:

$$P(q) \propto \exp[-U(q)/k_B T], \quad (15)$$

where the constant of proportionality is whatever it takes to make

$$\int_{-\infty}^{\infty} P(q) dq = 1. \quad (16)$$

So for our quadratic degree of freedom we have:

$$P(q) \propto \exp\left[-\frac{kq^2}{2k_B T}\right]. \quad (17)$$

We can get the constant of proportionality by noting that this probability distribution is a Gaussian. So:

$$P(q) = \sqrt{\frac{k}{2\pi k_B T}} \exp\left[-\frac{kq^2}{2k_B T}\right]. \quad (18)$$

Now let's evaluate the expectation value of the energy. This is given by:

$$\langle U \rangle = \int_{-\infty}^{\infty} \frac{1}{2}kq^2 P(q) dq. \quad (19)$$

Well, we know that the expectation value $\langle q^2 \rangle$ for a Gaussian probability distribution is just the variance:

$$\langle q^2 \rangle = \frac{k_B T}{k}, \quad (20)$$

from which we see that

$$\langle U \rangle = \frac{1}{2}k_B T. \quad (21)$$

There you have it: the Equipartition Theorem.

1.3 Applications of equipartition

Let's talk about some places where this shows up. If you have a Brownian particle on a spring, its mean *potential* energy is $\frac{1}{2}k_B T$ in one dimension. In two dimensions, it has $\frac{1}{2}k_B T$ along each dimension, so the energy is just $k_B T$, and in three dimension it's $\frac{3}{2}k_B T$. Note that the spring constant dropped out of the calculation. It doesn't matter how tightly the particle is bound: it *always* has $\frac{1}{2}k_B T$ of potential energy.

The kinetic energy of a particle is $KE = \frac{1}{2}mv^2$. So in one dimension the mean kinetic energy is $\frac{1}{2}k_B T$, and in 2-D it's $k_B T$, and in 3-D $\frac{3}{2}k_B T$.

The equipartition theorem has multitudinous important consequences. The molar specific heat at constant volume of a monatomic ideal gas is:

$$\begin{aligned}c_v &= \frac{\partial E}{\partial T} \\ &= \frac{3}{2}R.\end{aligned}\tag{22}$$

(recall that $R \equiv N_A k_B$). If you have diatomic molecules that can rotate about two axes perpendicular to the axis of symmetry, then $c_v = \frac{5}{2}R$. If, furthermore, the temperature is high enough to excite the internal vibrations along the bond between the atoms, then you get two more degrees of freedom (a kinetic energy and a potential energy) and $c_v = \frac{7}{2}R$. In a free gas the atoms or molecules only have kinetic energy, no potential energy.

In a solid crystal, each atom has three translational degrees of freedom, each of which has a kinetic and a potential energy. Total number of quadratic coordinates: 6. So the molar specific heat should be $3R$. In fact, at high temperatures this is very nearly the case. This is called the law of Dulong and Petit. At lower temperatures (which for many materials includes room temperature), the fact that the vibrations are quantized becomes important, and this analysis breaks down. As a side note, Einstein tried to develop a quantum theory of the specific heat, but basically got it wrong, and later Debye got it right.

The Equipartition Theorem is the reason why $k_B T$ is used as the universal energy scale: everything has approximately $k_B T$ of energy (ok, actually $\frac{1}{2}k_B T$ per quadratic degree of freedom).

Of course energy doesn't always depend quadratically on a coordinate. But for any system at equilibrium, we can say that the energy is at a local minimum (if it weren't, the system would move until it were). This means that $\partial U / \partial q = 0$. So the first non-zero term in the Taylor series is the quadratic term, to which we can apply the equipartition theorem.

1.4 Mathematical interlude: correlation functions

Let's take another little mathematical interlude and discuss correlation functions. How would you describe the time-dependence of a randomly varying signal? You could have a signal that varies quickly, like this:

SQUIGGLY DRAWING

or you could have a function that varies slowly, like this:

SLOWLY VARYING DRAWING

The best way to describe the wiggleness of something is with the autocorrelation function, defined as:

$$\begin{aligned} c_{xx}(\tau) &= \langle \Delta x(t + \tau) \Delta x(t) \rangle \\ &= \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T \Delta x(t + \tau) \Delta x(t) dt. \end{aligned} \quad (23)$$

(You'll see different definitions floating around with respect to the normalization and whether you use x or $\Delta x \equiv x - \langle x \rangle$.) The way to visualize the correlation function is that you take the function, then you take a copy of it shifted by τ and multiply these two together, and take the mean.

You can also define a cross-correlation

$$c_{xy}(\tau) = \langle \Delta x(t + \tau) \Delta y(t) \rangle, \quad (24)$$

which is useful for comparing two different signals.

Let's mention some important properties of the autocorrelation function.

- $c(\tau) = c(-\tau)$ (prove this!)
- $c(0) = \text{var}(x)$ (prove this!)
- $c(\tau \neq 0) \leq c(0)$ (this is a consequence of the Cauchy-Schwarz inequality)
- For a periodic signal with period k , $c(\tau)$ is also periodic with period k .
- $c(\tau)$ for white noise is a δ -function.
- For a signal whose statistical properties do not change with time, we can equally well imagine following the properties of one particle and averaging over time, or of following many particles for a fixed time and averaging their final state, e.g.:

$$\langle \Delta x(t) \Delta x(t + \tau) \rangle_t = \langle \Delta x(0) \Delta x(\tau) \rangle_{\text{ensemble}}. \quad (25)$$

The correlation and convolution, which we talked about last time, are very closely related. You see:

$$\langle x(t) y(t + \tau) \rangle = x(t) \otimes y(-t). \quad (26)$$

Correlation functions and convolutions are the Yin and Yang of signal processing.

Here's one mathematical result which we'll use in the following. Suppose we have a stochastic function comprised of white noise, with mean 0 and variance ν , i.e. $\langle \xi(t) \xi(t + \tau) \rangle = \nu \delta(\tau)$. Let us define

$$B = \int_0^t \xi(t') dt'. \quad (27)$$

Then $\langle B \rangle = 0$, and

$$\begin{aligned}
 \langle B^2 \rangle &= \left\langle \int_0^t \int_0^t \xi(t_1)\xi(t_2)dt_1dt_2 \right\rangle \\
 &= \int_0^t \int_0^t \nu\delta(t_1 - t_2)dt_1dt_2 \\
 &= \nu t.
 \end{aligned} \tag{28}$$

This result is consistent with what you would expect from the central limit theorem, that the variance in B grows linearly with time (the number of random walk steps is proportional to time).

2 Alternative Derivation of Stokes Einstein Relation

The Stokes-Einstein formula is important enough that it's worth deriving the same formula in a completely different way.

2.1 Langevin Equation for motion of a particle in liquid

Now we're going to construct a microscopic picture of Brownian motion. This is roughly along the lines of Einstein's original theory. First we're going to consider the motion of the particle on short timescales: long compared to the fundamental timescale of collisions with the solvent, but still short enough that the particle's momentum matters; then we'll zoom out to slightly longer timescales, where the motion appears as a pure random walk. The macroscopic equation of motion is given by Newton's second law:

$$m \frac{dv}{dt} = -\gamma v + \xi(t). \tag{29}$$

Here we've explicitly separated the deterministic component and the stochastic component. This is called a Langevin equation. The term $\xi(t)$ is some rapidly varying function of time which leads to Brownian motion. We'll assume that $\xi(t)$ varies on time scales much shorter than any we are interested in. Thus we can write:

$$\langle \xi(t) \rangle = 0 \tag{30}$$

and

$$\langle \xi(t)\xi(t + \tau) \rangle = \nu\delta(\tau). \tag{31}$$

ν is some unknown constant. Our goal will be to relate ν to things we recognize.

The strategy will be to write down an explicit solution to this equation. Then from the solution we calculate $\langle v^2 \rangle$. Then we impose the constraint that $\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$ from Equipartition. Actually, we'll calculate the full autocorrelation of the motion, $\langle v(t)v(0) \rangle$, and then we'll look at the value at $t = 0$ since this will give us some additional information for free.

The Langevin equation is an inhomogeneous linear ordinary differential equation. Sometimes it's called a "stochastic differential equation" because of the random term $\xi(t)$. I'm going to simply quote the solution, which is the same for any inhomogeneous first order linear differential equation. The solution is:

$$v(t) = v(0) \exp[-t\gamma/m] + \frac{1}{m} \int_{-\infty}^t dt' \xi(t') \exp[-(t-t')\gamma/m]. \quad (32)$$

We assume that the system has been running for a long time, so the initial transient has decayed. To describe the velocity fluctuations, let's calculate its autocorrelation function:

$$\begin{aligned} \langle v(t)v(t+\tau) \rangle &= \langle v(0)v(\tau) \rangle \\ &= \frac{1}{m^2} \int_{-\infty}^0 dt' \exp[t'\gamma/m] \int_{-\infty}^{\tau} dt'' \exp[-(\tau-t'')\gamma/m] \langle \xi(t')\xi(t'') \rangle \\ &= \frac{1}{m^2} \int_{-\infty}^0 dt' \exp[t'\gamma/m] \int_{-\infty}^{\tau} dt'' \exp[-(\tau-t'')\gamma/m] \nu \delta(t'-t'') \\ &= \frac{1}{m^2} \nu \exp[-\tau\gamma/m] \int_{-\infty}^0 dt' \exp[2t'\gamma/m] \\ &= \frac{\nu}{2\gamma m} \exp[-|\tau|\gamma/m]. \end{aligned} \quad (33)$$

In the last line I added the absolute value because we know the autocorrelation function has to be an even function of τ . Of particular relevance is the value of the autocorrelation at $\tau = 0$:

$$\langle v^2 \rangle = \frac{\nu}{2\gamma m}. \quad (34)$$

But we have another expression for $\langle v^2 \rangle$, this time based on our old friend, Equipartition. What's the average kinetic energy, $\frac{1}{2}mv^2$, along one axis of a particle in solution? It's $\frac{1}{2}k_B T$. This means that the mean-square velocity is:

$$\langle v^2 \rangle = k_B T/m. \quad (35)$$

From this we see that $\nu = 2k_B T\gamma$ (note that the mass dropped out). In summary, we found that the velocity autocorrelation function is:

$$\langle v(0)v(\tau) \rangle = \frac{k_B T}{m} \exp[-|\tau|\gamma/m]. \quad (36)$$

2.2 Langevin equation of an overdamped particle

How do these random forces relate to the diffusion coefficient? The velocity and displacement have a simple relation:

$$\Delta x(t) = \int_0^t v(t') dt'. \quad (37)$$

So the mean-square displacement in some time becomes:

$$\langle \Delta x(t)^2 \rangle = \int_0^t \int_0^t \langle v(t')v(t'') \rangle dt' dt''. \quad (38)$$

But we already calculated the quantity in on the r.h.s.! So we have:

$$\langle \Delta x(t)^2 \rangle = \frac{k_B T}{m} \int_0^t \int_0^t \exp[-|t' - t''|\gamma/m] dt' dt''. \quad (39)$$

Now let's assume we're looking at timescales long compared to the momentum relaxation time, m/γ . Then we can extend the limits of one of the integrals to $\pm\infty$. So we get:

$$\begin{aligned} \langle \Delta x(t)^2 \rangle &= \frac{2k_B T}{\gamma} \int_0^t dt' \\ &= \frac{2k_B T}{\gamma} t. \end{aligned} \quad (40)$$

From this we get our Stokes-Einstein result, $D = k_B T/\gamma$. Notice that the mass dropped out. The diffusion coefficient of an object is completely independent of its mass. That's not obvious.

Whenever you only care about timescales long compared to the momentum relaxation time (which is almost always the case), you can write the *overdamped* Langevin equation:

$$\gamma \frac{dx}{dt} = F(x, t) + \xi(t), \quad (41)$$

with $\langle \xi \rangle = 0$ and $\langle \xi(t)\xi(t + \tau) \rangle = 2k_B T \gamma \delta(\tau)$.

3 Brownian motion in a harmonic well

Finally, let's apply the correlation function technique to the problem of Brownian motion of a particle in a harmonic well. This is a paradigm for a great many problems, ranging from a particle held by laser tweezers to motion of subunits within a protein, to the motion of a bead tethered by a piece of DNA. In this case the easiest approach is to use the Langevin equation. Here we'll use a form of the equation in which we only consider motion on timescales long compared to the inertial relaxation time. Then the Langevin equation becomes:

$$\gamma \frac{dx}{dt} = -kx + \xi(t), \quad (42)$$

where $\langle \xi(t) \rangle = 0$ and $\langle \xi(t + \tau)\xi(t) \rangle = 2\gamma k_B T \delta(\tau)$. If you squint, this equation has exactly the same structure as the equation for the relaxation of velocity of a particle in fluid. Just substitute x for v and k/γ for γ/m . We can follow exactly the same procedure we followed before.

$$x(t) = x(0) \exp\left[-\frac{kt}{\gamma}\right] + \frac{1}{\gamma} \int_{-\infty}^t dt' \exp\left[-\frac{(t-t')}{\tau}\right] \xi(t'), \quad (43)$$

where

$$\tau \equiv \gamma/k \quad (44)$$

is the relaxation time of the trap. Thus

$$\begin{aligned} \langle x(t)x(0) \rangle &= \frac{1}{\gamma^2} \int_{-\infty}^t dt' \int_{-\infty}^0 dt'' \exp[-(t-t'-t'')/\tau] \langle \xi(t')\xi(t'') \rangle \\ &= \frac{1}{\gamma^2} \int_{-\infty}^t dt' \int_{-\infty}^0 dt'' \exp[-(t-t'-t'')/\tau] 2\gamma k_B T \delta(t'-t'') \\ &= \frac{2k_B T}{\gamma} \int_{-\infty}^0 dt'' \exp[-(t-2t'')/\tau] \\ &= \frac{k_B T}{k} \exp(-t/\tau). \end{aligned} \quad (45)$$

In summary, there are two ways to describe the motion of a diffusing particle (or any stochastically fluctuating quantity, for that matter). There is the Smoluchowski approach in which one describes the time-evolution of the probability distribution, and there is the Langevin approach, in which one calculates the statistical properties of individual trajectories, and then averages over all trajectories. If handled correctly, these two approaches always give the same result. The Stokes Einstein relation is a special case of something called the fluctuation dissipation theorem which we will discuss next time.

A Appendix: Wiener Khinchin Formula

Here we prove a very important theorem called the Wiener-Khinchin theorem. First we need to establish an important relation between convolutions and Fourier transforms. For two functions f and g , recall the definition of the convolution:

$$f \otimes g = \int_{-\infty}^{\infty} ds_1 f(s_1) g(x - s_1). \quad (46)$$

We can expand that integral into a double integral by inserting a delta function (recall this is just the reverse of the process we followed when calculating the probability distribution for the displacement after two steps of a random walk).

$$f \otimes g = \int_{-\infty}^{\infty} ds_1 \int_{-\infty}^{\infty} ds_2 f(s_1) g(s_2) \delta(x - (s_1 + s_2)). \quad (47)$$

Now here's the sneaky bit. The δ -function can be expressed as:

$$\begin{aligned} \delta(x - s_1 - s_2) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ik(s_1+s_2-x)} \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{iks_1} e^{iks_2} e^{-ikx}. \end{aligned} \quad (48)$$

Substituting this into the expression for $f \otimes g$ gives:

$$f \otimes g = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-ikx} \int_{-\infty}^{\infty} ds_1 f(s_1) e^{iks_1} \int_{-\infty}^{\infty} ds_2 g(s_2) e^{iks_2}. \quad (49)$$

This equation is amazing. The two integrals over s_1 and s_2 are just the expressions for the Fourier transforms of the functions $f(s_1)$ and $g(s_2)$, respectively. And the first integral is just the formula for the inverse Fourier transform. This equation shows that to convolve two functions, all you have to do is take their Fourier transforms, multiply them together, and then take the inverse Fourier transforms. Convolutions are convoluted; but Fourier transforms and multiplication are our friends.

This result has an interesting consequence for calculations of correlation functions. We can write a correlation function in terms of a convolution:

$$c(\tau) = \Delta x(t) \otimes \Delta x(-t). \quad (50)$$

Let's take the Fourier Transform of both sides of this equation:

$$\begin{aligned} \tilde{c}(\omega) &= \tilde{\Delta x}(\omega) \times \tilde{\Delta x}(\omega)^* \\ &= |\tilde{\Delta x}(\omega)|^2. \end{aligned} \quad (51)$$

To get these results we used the fact that if the Fourier transform of $x(t)$ is $\tilde{x}(\omega)$, then the Fourier transform of $x(-t)$ is the complex conjugate, $\tilde{x}(\omega)^*$. The last equation is the Wiener-Khinchin formula. It tells us that the Fourier transform of the autocorrelation function is equal to the power spectrum. Sometimes it's useful to describe a signal in the time-domain by specifying its autocorrelation; sometimes it's useful to describe a signal in the frequency domain by specifying its power spectrum (that is how much energy it has at each frequency). The W-K theorem tells us that these two representations are equivalent; they both contain identical information and it is easy to switch from one to the other.

The W-K theorem appears all over the place. One example which we'll return to later in the course is that of spectral line shapes. The shape of the emission spectrum of a fluorescent molecule is just the Fourier transform of the autocorrelation of the dipole moment of the molecule (there's a little complication because we have to treat the dipole moment as a quantum mechanical operator, not as a classical quantity, but we'll deal with that later).