Some supplemental notes on the random walk

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Directed diffusion: the role of potential energy and Einstein's relation

It was asked what role a potential plays in the diffusive process. I should have mentioned this in the lecture notes originally issued. When there is a potential energy, $V(\vec{x})$ that influences diffusers, or random walkers, then Fick's law is modified as follows.

$$\begin{aligned}\vec{j}(\vec{x}) &= -D_0\vec{\nabla}c(\vec{x}) + \Gamma\vec{F}(x)c(\vec{x}) \\ &= -D_0\vec{\nabla}c(\vec{x}) + \Gamma\left(-\vec{\nabla}V(x)\right)c(\vec{x}) \qquad \text{(A-1)}\end{aligned}$$

Here, I have suppressed the dependence on time and I have changed notation somewhat. The coefficient D_0, which was β in the notes has a name. It is called the **diffusion constant**. The coefficient Γ has a general name. It is known generically as a **transport coefficient**. Given the current density in (A-1), we can infer an equation for the time evolution of the diffuser concentration function $c(\vec{x}, t)$ (again, I am changing things somewhat, replacing the number of steps, N, by time)

$$\begin{aligned}\frac{\partial c(\vec{x}, t)}{\partial t} &= -\vec{\nabla}\cdot\vec{j} \\ &= D_0\nabla^2 c(\vec{x}, t) + \Gamma\vec{\nabla}\cdot\left(c(\vec{x}, t)\vec{\nabla}V(\vec{r})\right) \qquad \text{(A-2)}\end{aligned}$$

Because the right hand side of (A-2) contains perfect derivatives, its integral over all space will vanish, assuming as we do that the function $c(\vec{x}, t)$ goes to zero a sufficiently large $|\vec{x}|$. Thus the total number of diffusers is conserved, in the absence of course of absorbing barriers.

Now, we can ask what the condition is for equilibrium. Equilibrium is different from steady state, in that there is no net current of walkers. This requirement and Eq. (A-1) leads to the requirement

$$D_0 \vec{\nabla} c(\vec{x},t) - \Gamma c(\vec{x},t) \vec{\nabla} V(\vec{x}) = 0 \tag{A-3}$$

which leads to the equation

$$\begin{aligned} \frac{\vec{\nabla} c(\vec{x},t)}{c(\vec{x},t)} &= \vec{\nabla} \ln c(\vec{x},t) \\ &= -\frac{\Gamma}{D_0} \vec{\nabla} V(\vec{x}) \end{aligned} \tag{A-4}$$

The equation relating the derivative of $\ln c(\vec{x},t)$ to the derivative of $V(\vec{x})$ integrates up to the relationship

$$c(\vec{x},t) \propto \exp\left[-\frac{\Gamma}{D_0} V(x)\right] \tag{A-5}$$

Equation (A-5) makes sense as a condition for equilibrium if $\Gamma/D_0 = 1/k_B T$. Thus we arrive at the relationship between the diffusion constant, D_0, the transport coefficient, Γ, and $k_B T$. The relationship is

$$D_0 = \Gamma k_B T \tag{A-6}$$

which is known as **Einstein's equation**, or generically as a **fluctuation dissipation relation**.

Extensions of the generating function

In the notes, I talked about the structure and analytic properties of the generating function in the case of the ordinary random walk. When the walk is self-avoiding, as it is when used to model the configurational statistics of a randomly-coiled linear chain polymer, those analytical properties change. Here I am going to summarize the changes and what they mean without going into any of the details involved in justifying the alterations in form, as those details would fill a book.

First, we have seen that the spatial Fourier transform of the generating function has the general form

$$\begin{aligned}\frac{1}{(z_c - z) + q^2} &= (z_c - z)^{-1} \frac{1}{1 + (q(z_c - z)^{-1/2})^2} \\ &\equiv (z_c - z)^{-1} F(q(z_c - z)^{-1/2}) \qquad \text{(A-7)}\end{aligned}$$

Here, on the left hand side of (A-7), I have simplified the expression as much as possible, omitting any constants multiplying the q^2 term. In the case of the self-avoiding walk, this expression for the spatial Fourier transform of the generating function generalizes to

$$(z_c - z)^{-\gamma} \mathcal{F}(q(z_c - z)^{-\nu}) \qquad \text{(A-8)}$$

The quantities γ and ν are known generically as **critical exponents**. For a self-avoiding walk in three dimensions, $\gamma = 1.19$ and $\nu = 0.602$. As it turns out, both γ and ν depend on the number of dimensions in which the walkers execute their random motion.

The total number of walks follows from the Fourier transformed generating function at $\vec{q} = 0$. It goes as $(z_c - z)^{-\gamma}$, which, by the connection between singularities in the generating function and the coefficient of z^N in its power series expansion, implies that the total number of self-avoiding walks is proportional to $z_c^{-N} N^{\gamma-1}$. This is in contrast to the result that the number of ordinary walks grows strictly exponentially in the number of steps. The number of walks that return to the point of origin is obtained from the over $\vec{q}$ of the Fourier transformed generating function. A few details in the performance of that integral must be left out, as there are assumptions concerning the precise structure of the Fourier transformed generating function that go into extracting the proper result. Suffice it to say that the end result of that integration in d dimensions is something going as

$$(z_c - z)^{d\nu - 1} \qquad \text{(A-9)}$$

where d is the number of spatial dimensions in which the walker propagates. For the ordinary walker, the result goes as $(z_c - z)^{(d/2)-1}$, as shown in the main body of the notes. In three dimensions, the number of walkers returning to the point of origin then goes as $z_c^{-N} N^{-d\nu}$.

Finally a somewhat involved calculation tells us that the exponential dependence on the distance, r, between end-points governing the number of walks that start at x and end at y is altered as follows. Where originally it was as $\exp[-Ar^2/N]$, in the case of the self-avoiding walker, it goes as

$$\exp\left[-A\left(rN^{-\nu}\right)^{1/(1-\nu)}\right] \tag{A-10}$$

This non-gaussian behavior was originally predicted by Professor Fyl Pincus [Pincus, 1976].

References

[Pincus, 1976] Pincus, P. (1976). Excluded volume effects and stretched polymer-chains. *Macromolecules*, 9(3):386–388.