CHAPTER OVERVIEW

1: Stochastic Processes and Brownian Motion

Equilibrium thermodynamics and statistical mechanics are widely considered to be core subject matter for any practicing chemist [1]. There are plenty of reasons for this:

- A great many chemical phenomena encountered in the laboratory are well described by equilibrium thermodynamics.
- The physics of chemical systems at equilibrium is generally well understood and mathematically tractable.
- Equilibrium thermodynamics motivates our thinking and understanding about chemistry away from equilibrium.

This last point, however, raises a serious question: how well does equilibrium thermodynamics really motivate our understanding of nonequilibrium phenomena? Is it reasonable for an organometallic chemist to analyze a catalytic cycle in terms of rate-law kinetics, or for a biochemist to treat the concentration of a solute in an organelle as a bulk mixture of compounds? Under many circumstances, equilibrium thermodynamics suffices, but a growing number of outstanding problems in chemistry - from electron transfer in light-harvesting complexes to the chemical mechanisms behind immune system response- concern processes that are fundamentally out of equilibrium.

This course endeavors to introduce the key ideas that have been developed over the last century to describe nonequilibrium phenomena. These ideas are almost invariably founded upon a statistical description of matter, as in the equilibrium case. However, since nonequilibrium phenomena contain a more explicit time-dependence than their equilibrium counterparts (consider, for example, the decay of an NMR signal or the progress of a reaction), the probabilistic tools we develop will require some time-dependence as well.

In this chapter, we consider systems whose behavior is inherently nondeterministic, or stochastic, and we establish methods for describing the probability of finding the system in a particular state at a specified time.

Thumbnail: This is a simulation of the Brownian motion of a big particle (dust particle) that collides with a large set of smaller particles (molecules of a gas) which move with different velocities in different random directions. (CC BY-SA 3.0; Lookang via Wikipedia)
