

1.5: Appendix: Applications to Brownian Motion

Brownian motion is one of the simplest physical examples of a system whose description necessitates a nonequilibrium statistical description. As such, it is the token example that unifies all of the topics in this course, from Markov processes (Ch. 1) and response functions (Ch. 2) to diffusion constants (Ch. 3) and generalized Langevin equations (Ch. 4). In this appendix, the salient features of Brownian motion and the key results about Brownian motion that will be developed during the course are explicated together as a handy reference. Some basic properties of relevant integral transformations are also included in this Appendix.

The discovery of Brownian motion predates the development of statistical mechanics and provided important insight to physicists of the early twentieth century in their first formulations of an atomic description of matter. A fine example of the importance of keeping an eye open for the unexpected in experimental science, Brownian motion was discovered somewhat serendipitously in 1828 by botanist Robert Brown while he was studying pollen under a microscope. Though many others before him had observed the jittery, random motion of fine particles in a fluid, Brown was the first to catalogue his observations [4] and use them to test hypotheses about the nature of the motion.

Interest in the phenomenon was revived in 1905 by Albert Einstein, who successfully related observations about Brownian motion to underlying atomic properties. Einstein's work on Brownian motion [5] is perhaps the least well known of the four paradigm-shifting papers he published in his "Miracle Year" of 1905, which goes to show just how extraordinary his early accomplishments were (the other three papers described the photoelectric effect, special relativity, and mass-energy equivalence)! Einstein determined that the diffusion of a Brownian particle in a fluid is proportional to the system temperature and inversely related to a coefficient of friction ζ characteristic of the fluid,

$$D = \frac{1}{\beta\zeta} \quad (1.5.1)$$

Any physical description of Brownian motion will boil down to an equation of motion for the Brownian particle. The simplest way, conceptually, to model the system is to perform Newtonian dynamics on the Brownian particle and N particles comprising the fluid, with random initial conditions (positions and velocities) for the fluid particles. By performing such calculations for all possible initial configurations of the fluid and averaging the results, we can obtain the correct picture of the stochastic dynamics. This procedure, however, is impossibly time-consuming in practice, and so a number of statistical techniques, such as Monte Carlo simulation, have been developed to make such calculations more practical.

Alternatively, we can gain qualitative insight into Brownian dynamics by mean-field methods; that is, instead of treating each particle in the fluid explicitly, we can devise a means to describe their average influence on the Brownian particle, circumventing the tedium of tracking each particle's trajectory independently. This approach gives rise to the Langevin equation of section 1.4, under the assumption that the fluid exerts a random force $f(t)$ on the Brownian particle that obeys the conditions of Gaussian white noise.

For instantaneous (gas-phase) collisions of the fluid and Brownian particle, a Langevin equation with constant frictional coefficient ζ suffices,

$$m\dot{v}(t) + \zeta v(t) = f(t) \quad (1.5.2)$$

However, if fluid-particle collisions are correlated, which is the case for any condensed-phase system, this correlation must be taken into account by imbuing the Brownian particle with memory of its previous interactions, embodied by a memory kernel γ ,

$$m\dot{v}(t) + m \int_0^t \gamma(t-\tau)v(\tau)d\tau = f(t) \quad (1.5.3)$$

where $\gamma(t) \rightarrow \zeta\delta(t)$ in the limit of uncorrelated collisions.

We now present some of the key features of Brownian motion. Some of these results are derived in section 1.4; others are presented here for reference. Please consult the references at the end of this chapter for further details about the derivation of these properties.

- Fick's Law: The spreading of the Brownian particle's spatial probability distribution over time is governed by Fick's Law,

$$\frac{\partial}{\partial t} P(\mathbf{r}, t) = -D\nabla^2 P(\mathbf{r}, t) \quad (1.5.4)$$

- Green-Kubo relation: The diffusion constant D is tied to the particle's velocity-velocity correlation function $C(t)$ by the Green-Kubo relation,

$$D = \int_0^\infty C(t) dt \quad (1.5.5)$$

This essentially means that the diffusion constant is the area under the velocity-velocity correlation curve across all times $t > 0$.

- Solution of the Langevin Equation: All of the information we require from the Langevin equation is contained in the correlation function. Multiplication of the Langevin equation for $v(t_1)$ by the velocity $v(t_2)$ yields a differential equation for the correlation function,

$$\dot{C} + \int_0^t \gamma(t-\tau)C(\tau) d\tau = 0 \quad (1.5.6)$$

The Laplace transform of this equation,

$$s\hat{C}(s) - C(0) + \hat{\gamma}(s)\hat{C}(s) = 0 \quad (1.5.7)$$

has as its solution

$$\hat{C}(s) = \frac{C(0)}{s + \hat{\gamma}(s)} \quad (1.5.8)$$

where $C(0)$ is the non-transformed velocity-velocity correlation function at $t = 0$ and s is the Laplace variable. - Einstein relation: The solution to the Langevin equation tells us that

$$\hat{C}(0) = \frac{C(0)}{\hat{\gamma}(0)} \quad (1.5.9)$$

Additionally, a comparison of the Green-Kubo relation to the formula for the Laplace transform indicates that $C(0) = D$. Finally, we can conclude from the equipartition theorem that $C(0) = \frac{1}{m\beta}$. Combining this information together, we arrive at Einstein's relation,

$$D = \frac{1}{m\beta\hat{\gamma}(0)} \quad (1.5.10)$$

In Chapter 4, the behavior of the velocity-velocity correlation function is explored for the cases in which the fluid is a bath of harmonic oscillators, a simple liquid, and an elastic solid. Their general functional forms are summarized here; further details can be found in Chapter 4.

- Harmonic oscillators: $C(t)$ is periodic with amplitude $C(0)$ and frequency Ω_0 (the Einstein frequency), where $\Omega_0^2 = \gamma(0)$.
- Liquids: $C(t)$ exhibits a few oscillations while decaying, eventually leveling out to zero.
- Solids: Like a liquid, $C(t)$ will be damped, but like the harmonic oscillator model, the periodic structure of the solid will prevent $C(t)$ from decaying to zero; some oscillation at the Einstein frequency will continue indefinitely.

Finally, we summarize the response of a Brownian particle to an external force F . The modified Langevin equation for this situation is

$$\dot{v}(t) + \gamma v(t) = \frac{f(t)}{m} + \frac{F(t)}{m} \quad (1.5.11)$$

In general, this Langevin equation is difficult to work with, but many forces of interest (such as EM fields) are oscillatory, so we assume an oscillatory form for the external force,

$$F(t) = F_\omega e^{-i\omega t} \quad (1.5.12)$$

Then we can use the techniques developed in Chapter 2 to determine that the velocity in Fourier space is given by

$$\tilde{v}(\omega) = \chi(\omega)\tilde{F}(\omega) \quad (1.5.13)$$

Finally, from this information it can be determined that the response function $K(t)$ is (see Chapter 2)

$$K(t) = \frac{1}{2\pi} \int_0^\infty \frac{e^{-i\omega t}}{-i\omega + \gamma} d\omega = e^t \theta(t) \quad (1.5.14)$$

These formulas are the basis for the Debye theory of dipole reorganization in a solvent, in the case where F corresponds to the force due to the electric field $E(\omega)$ generated by the oscillating dipoles.

Integral Transformations: We conclude with a summary of the Laplace and Fourier transforms, which are used regularly in this course and in chemical physics generally to solve and analyze differential equations. 1. Laplace transform: The Laplace transform of an arbitrary function $f(t)$ is

$$\hat{f}(s) = \int_0^\infty e^{-st} f(t) dt \quad (1.5.15)$$

Both the Laplace and Fourier transforms convert certain types of differential equations into algebraic equations, hence their utility in solving differential equations. Consequently, it is often useful to have expressions for the first and second derivatives of $\hat{f}(s)$ on hand:

$$\begin{aligned} \hat{f}^{(1)}(s) &= s\hat{f}(s) - f(0) \\ \hat{f}^{(2)}(s) &= s^2\hat{f}(s) - sf(0) - \hat{f}^{(1)}(0) \end{aligned}$$

A convolution of two functions

$$F(t) = \int_0^t f(t)g(t-\tau)d\tau \quad (1.5.16)$$

is also simplified by Laplace transformation; in Laplace space, it is just a simple product,

$$\hat{F}(s) = \hat{f}(s)\hat{g}(s) \quad (1.5.17)$$

3. Fourier transform: The Fourier transform of an arbitrary function $f(t)$ is

$$\tilde{f}(\omega) = \int_{-\infty}^\infty e^{i\omega t} f(t) dt \quad (1.5.18)$$

Its derivatives are even simpler in structure than those of the Laplace transform:

$$\begin{aligned} \tilde{f}^{(1)}(\omega) &= -i\omega \tilde{f}(\omega) \\ \tilde{f}^{(2)}(\omega) &= -\omega^2 \tilde{f}(\omega) \end{aligned}$$

For an even function $f(t)$, the relationship between the Fourier and Laplace transforms can be determined by taking a Laplace transform of f at $s = i\omega$, from which we discover that

$$\tilde{f}(\omega) = 2 \operatorname{Re} \hat{f}(-i\omega) \quad (1.5.19)$$

References

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