## 10. Friction and the Langevin Equation

Now let's relate the phenomena of Brownian motion and diffusion to the concept of friction, i.e., the resistance to movement that the particle in the fluid experiences. These concepts were developed by Einstein in the case of microscopic motion under thermal excitation, and macroscopically by George Stokes who was the father of hydrodynamic theory.

Langevin Equation

Consider the forces acting on a particle as we pull it through a fluid. We pull the particle with an external force f_{ext}, which is opposed by a drag force from the fluid, f_d. The drag or damping acts as resistance to motion of the particle, which results from trying to move the fluid out of the way.
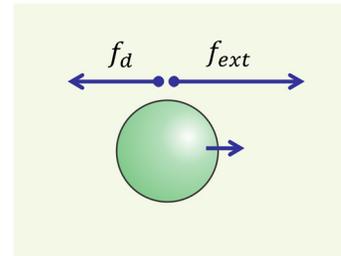
$$f_d = -\zeta v$$

A drag force requires movement, so it is proportional to the velocity of the particle $v = dx/dt = \dot{x}$ and the friction coefficient ζ is the proportionality constant that describes the magnitude of the damping. Newton's second law would say the acceleration of this particle is proportional to the sum of these forces: $ma = f_d + f_{ext}$.

Now microscopically, we also recognize that there are time-dependent random forces that the molecules of the fluid exert on a molecule (f_r). So that the specific molecular details of solute–solvent collisions can be averaged over, it is useful to think about a nanoscale solute in water (e.g., biological macromolecules) with dimensions large enough that its position is simultaneously influenced by many solvent molecules, but is also light enough that the constant interactions with the solvent leave an unbalanced force acting on the solute at any moment in time: $\bar{f}_r(t) = -\sum_i \bar{f}_i(t)$. Then Newton's second law is $ma = f_d + f_{ext} + f_r(t)$.
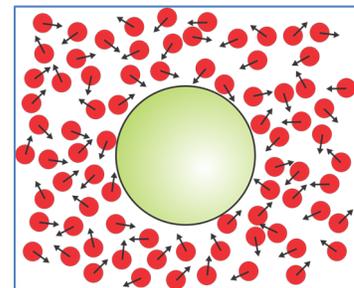
The drag force is present regardless of whether an external force is present, so in the absence of external forces (f_{ext}=0) the equation of motion governing the spontaneous fluctuations of this solute is determined from the forces due to drag and the random fluctuations:

$$ma = f_d + f_r(t) \tag{0}$$

$$m\ddot{x} + \zeta\dot{x} - f_r(t) = 0 \tag{0}$$

This equation of motion is the Langevin equation. An equation of motion such as this that includes a time-dependent random force is known as "stochastic".

Inserting a random process into a deterministic equation means that we need to use a statistical approach to solve this equation. We will be looking to describe the average and root-mean-squared position of the particle. First, what can we say about the random force? Although there may be momentary imbalances, on average the perturbations from the solvent on a larger particle will average to zero at equilibrium:

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

Equation (0) seems to imply that the drag force and the random force are independent, but in fact they originate in the same molecular forces. If the molecule of interest is a protein that experiences the fluctuations of many rapidly moving solvent molecules, then the averaged forces due to random fluctuations and the drag forces are related. The fluctuation–dissipation theorem is the general relationship that relates the friction to the correlation function for the random force. In the Markovian limit this is

$$\langle f_r(t) f_r(t') \rangle = 2\zeta k_B T \, \delta(t-t') \tag{0}$$

Markovian indicates that no correlation exists between the random force for $|t–t'| > 0$. More generally, we can recover the friction coefficient from the integral over the correlation function for the random force

$$\zeta = \frac{1}{2k_B T} \int_{-\infty}^{+\infty} dt \, \langle f_R(0) f_R(t) \rangle$$

To describe the time evolution of the position of our protein molecule, we would like to obtain an expression for mean-square displacement $\langle x^2(t) \rangle$. The position of the molecule can be described by integrating over its time-dependent velocity: $x(t) = \int_0^t dt' \dot{x}(t')$, so we can express the mean-square displacement in terms of the velocity autocorrelation function

$$\langle x^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle \dot{x}(t') \dot{x}(t'') \rangle \tag{0}$$

Our approach to obtaining $\langle x^2(t) \rangle$ starts by multiplying eq. (0) by x and then ensemble averaging.

$$m \left\langle x \frac{d}{dt} \dot{x} \right\rangle + \zeta \langle x \dot{x} \rangle - \langle x f_r(t) \rangle = 0 \tag{0}$$

From eq. (0), the last term is zero, and from the chain rule we know

$$\frac{d}{dt}(x\dot{x}) = x \frac{d}{dt}\dot{x} + \frac{dx}{dt}\dot{x} \tag{0}$$

Therefore we can write eq. (0) as

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$$m\left(\frac{d}{dt}\langle x\dot{x}\rangle - \langle\dot{x}\dot{x}\rangle\right) + \zeta\langle x\dot{x}\rangle = 0 \tag{0}$$

Further, the equipartition theorem states that for each translational degree of freedom the kinetic energy is partitioned as

$$\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{k_B T}{2} \tag{0}$$

So,
$$m\frac{d}{dt}\langle x\dot{x}\rangle + \zeta\langle x\dot{x}\rangle = k_B T \tag{0}$$

Here we are describing motion in 1D, but when fluctuations and displacement are included for 3D motion, then we switch $x \to r$ and $k_B T \to 3k_B T$. Integrating eq. (0) twice with respect to time, and using the initial condition $x(0) = 0$, we obtain

$$\langle x^2\rangle = \frac{2k_B T}{\zeta}\left\{t + \frac{m}{\zeta}\left[\exp\left(-\frac{\zeta}{m}t\right) - 1\right]\right\} \tag{0}$$

To investigate this equation, let's consider two limiting cases. From eq. (0) we see that m/ζ has units of time, and so we define the damping time

$$\tau_C = m/\zeta \tag{0}$$

and investigate time scale short and long compared to τ_C:

1) For $t \ll \tau_C$, we can expand the exponential in eq. (0) and retain the first three terms, which leads to

$$\langle x^2\rangle \approx \frac{k_B T}{m}t^2 = \langle v^2\rangle t^2 \qquad \text{(short time: inertial)} \tag{0}$$

2) For $t \gg \tau_C$, eq. (0) is dominated by the leading term:

$$\langle x^2\rangle = \frac{2k_B T}{\zeta}t \qquad \text{(long time: diffusive)} \tag{0}$$

In the diffusive limit the behavior of the molecule is governed entirely by the fluid, and its mass does not matter. The diffusive limit in a stochastic equation of motion is equivalent to setting $m \to 0$.

We see that τ_C is a time-scale separating motion in the inertial and diffusive limits. It is a correlation time for the randomization of the velocity of the
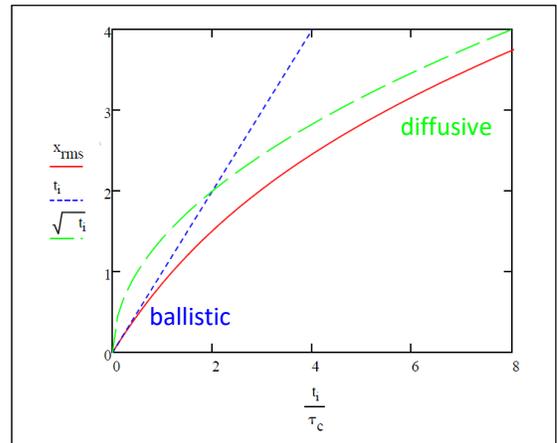
particle due to the random fluctuations of the environment.

For very little friction or short time, the particle moves with traditional deterministic motion x_{rms} = $v_{rms} t$, where root-mean-square displacement $x_{rms} = \langle x^2 \rangle^{1/2}$ and v_{rms} comes from the average translational kinetic energy of the particle. For high-friction or long times, we see diffusive behavior with $x_{rms} \sim t^{1/2}$. Furthermore, by comparing eq. (0) to our earlier continuum result, $\langle x^2 \rangle = 2Dt$, we see that the diffusion constant can be related to the friction coefficient by

$$D = \frac{k_B T}{\zeta} \quad \text{(in 1D)} \tag{0}$$

This is the Einstein formula. For 3D problems, we replace $k_B T$ with $3k_B T$ in the expressions above and find $D_{3D} = 3k_B T/\zeta$.

How long does it take to approach the diffusive regime? Very fast. Consider a 100 kDa protein with $R = 3$ nm in water at T = 300 K, we find a characteristic correlation time for randomizing velocities of $\tau_C = 3 \times 10^{-12}$ s, which corresponds to a distance of about 10^{-2} nm before the onset of diffusive behavior.

We can find other relationships. Noting the relationship of $\langle x^2 \rangle$ to the velocity autocorrelation function in eq. (0), we find that the particle velocity is described by

$$\langle v_x(0)v_x(t) \rangle = \langle v_x^2 \rangle e^{-\zeta t/m} = \langle v_x^2 \rangle e^{-t/\tau_C} \qquad v_x = \dot{x}$$

which can be integrated over time to obtain the diffusion constant.

$$\int_0^\infty \langle v_x(0)v_x(t) \rangle dt = \frac{k_B T}{\zeta} = D \tag{0}$$

This expression is the Green–Kubo relationship. This is a practical way of analyzing molecular trajectories in simulations or using particle-tracking experiments to quantify diffusion constants or friction coefficients.

Friction and Viscosity

How is the microscopic friction originating in random forces related to macroscopic experimental observables that measure a fluid's resistance to moving an object? ζ is related to the dynamic viscosity of the fluid η and factors describing the size and shape of the object (but not its mass).

Viscosity measures the resistance to shear. A fluid is placed between two plates of area a separated along z, and one plate is moved relative to another by applying a force along x. Since the velocity of the fluid at the interface with a plate is taken to be the velocity of the plate (no-slip boundary conditions: $\vec{v}_x(z=0)=0$), this sets up a velocity gradient along z. The relationship between the shear velocity gradient and the force is

$$\vec{f}_x = a\eta \frac{d\vec{v}_x}{dz}$$

where η, the dynamic viscosity (kg m^{-1} s^{-1}), is the proportionality factor.
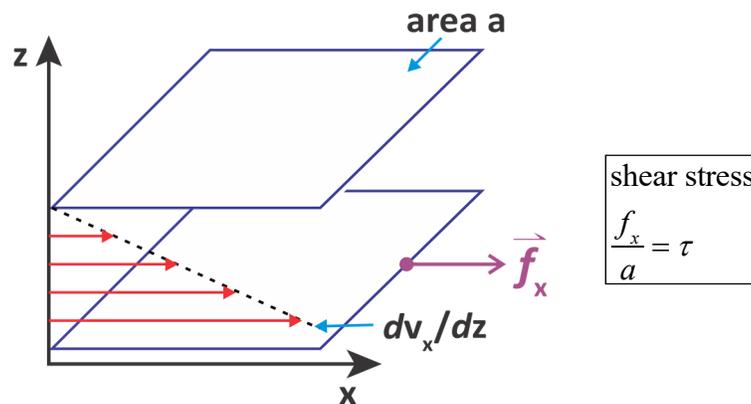

Shape Matters

A sphere, rod, or cube with the same mass and surface area will respond differently to flow. Stokes determined the relationships between drag coefficient and fluid viscosity. Specifically, considering the case where a sphere of radius R is resisted by laminar flow of the fluid, one finds that the drag force on the sphere is

$$f_d = 6\pi\eta R v$$

and the viscous force per unit area is entirely uniform across the surface of the sphere. This gives us Stokes' Law

$$\zeta = 6\pi\eta R \tag{0}$$
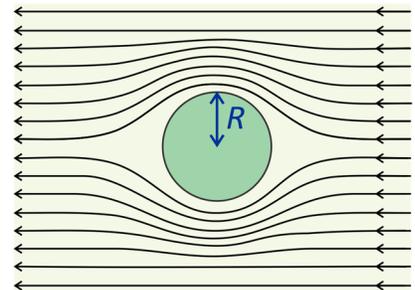
Here R is referred to as the hydrodynamic radius of the sphere, which refers to the radius at which one can apply the no-slip boundary condition, but which on a molecular scale may include water that is strongly bound to the molecule. Combining eq. (0) with eq. (0) gives the Stokes–Einstein relationship for the translation diffusion constant of the sphere[1]

$$D_{trans} = \frac{k_B T}{6\pi\eta R} \tag{0}$$

One can obtain a similar a Stokes–Einstein relationship for orientational diffusion of a sphere in a viscous fluid. Relating the orientational diffusion constant and the drag force that arises from resistance to shear, one obtains

$$D_{rot} = \frac{k_B T}{6V\eta}$$

$V=4\pi R^3/3$ is the volume of the sphere.

Reynolds Number

The Reynolds number is a dimensionless number that indicates whether the motion of a particle in a fluid is dominated by inertial or viscous forces.[2]

$$\mathcal{R} = \frac{inertial\ forces}{viscous\ forces}$$

When $\mathcal{R} > 1$, the particle moves freely, experiencing only weak resistance to its motion by the fluid. If $\mathcal{R} < 1$, it is dominated by the resistance and internal forces of the fluid. For the latter case, we can consider the limit $m \rightarrow 0$ in eq. (0), and find that the velocity of the particle is proportional to the random fluctuations: $v(t) = f_r(t)/\zeta$.

Hydrodynamically, for a sphere of radius r moving through a fluid with dynamic viscosity η and density ρ at velocity v,

$$\mathcal{R} = \frac{rv\rho}{\eta} \qquad \text{Using picture above:} \quad \mathcal{R} = \frac{v\rho(d\bar{v}/dz)}{\eta(d^2\bar{v}/dz^2)}$$

Consider for an object with radius 1 cm moving at 10 cm/s through water: $\mathcal{R}=10^3$. Now compare to a protein with radius 1 nm moving at 10 m/s: $\mathcal{R}=10^{-2}$.

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1. B. J. Berne and R. Pecora, *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics.* (Wiley, New York, 1976), pp. 78, 91.
2. E. M. Purcell, Life at low Reynolds number, Am. J. Phys. **45**, 3-11 (1977).

Drag Force in Hydrodynamics

The drag force on an object is determined by the force required to displace the fluid against the direction of flow,

$$f_d = \left[\frac{1}{2} \rho C_d v^2 \right] a$$

This expression takes the form of a pressure (term in brackets) exerted on the cross-sectional area of the object along the direction of flow, a. C_d is the drag coefficient, a dimensionless proportionality constant that depends on the shape of the object. In the case of a sphere of radius r: $a=\pi r^2$ in the turbulent flow regime ($\mathcal{R} > 1000$) C_d = 0.44–0.47. Determination of C_d is somewhat empirical since it depends on $\mathcal{R}$ and the type of flow around the sphere.

The drag coefficient for a sphere in the viscous/laminar/Stokes flow regimes ($\mathcal{R} < 1$) is $C_d = 24/\mathcal{R}$. This comes from using the Stokes Law for the drag force on a sphere $f_d = 6\pi\eta v r$ and the Reynolds number $\mathcal{R} = \rho v d / \eta$.

Readings

1. R. Zwanzig, *Nonequilibrium Statistical Mechanics*. (Oxford University Press, New York, 2001).

2. B. J. Berne and R. Pecora, *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics*. (Wiley, New York, 1976).