More on Fluctuations

If we generalize this calculation to d dimensions of space and hence $d-1$ dimensions of the surface we find

$$\langle \overline{h^2} \rangle \sim \int \frac{d^{d-1}q}{(2\pi)^{d-1}} \frac{k_B T}{\gamma q^2} \sim \frac{k_B T}{\gamma} \int dq \frac{q^{d-2}}{q^2}$$

$$\sim \frac{k_B T}{\gamma} \frac{q^{d-3}}{d-3} \Big|_{\mathrm{q_{min}}}^{\mathrm{q_{max}}} \qquad (d > 3)$$

$$\sim \frac{k_B T}{\gamma} \ln\left(\frac{\mathrm{q_{max}}}{\mathrm{q_{min}}}\right) \sim \frac{k_B T}{\gamma} \ln\left(\frac{L}{a}\right) \qquad (d = 3)$$

More on Fluctuations

Now we consider a two-dimensional interface endowed with surface tension and in a gravitational field, with a density difference $\Delta\rho$ between the fluids on either side. Once again we expand the surface deformation

$$h(\mathbf{r}) = \sum_{q} \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}} \hat{h}(\mathbf{q})$$

The quadratic energy functional is

$$\begin{aligned} E &= \frac{1}{2} \int \int dx dy \left[\sigma (\nabla h)^2 + \Delta\rho g h^2 \right] \\ &= \frac{\sigma A}{2} \sum_{\mathbf{q}} (q^2 + l_c^{-2}) |\hat{h}(\mathbf{q})|^2 \end{aligned}$$

where l_c is once again the capillary length. Again by equipartition we find

$$\langle |\hat{h}(\mathbf{q})|^2 \rangle = \frac{k_B T}{\sigma A} \frac{1}{l_c^{-2} + q^2}.$$

This shows that the capillary length provides a cutoff on what would otherwise be divergent fluctuation amplitudes as $q \to 0$.

More on Fluctuations

Introducing both large-scale and small-scale cutoffs, the average variance of the displacement field is

$$\overline{\langle h^2 \rangle} = \frac{k_B T}{2\pi\sigma} \int \frac{q\,dq}{l_c^{-2} + q^2}$$

$$\frac{k_B T}{4\pi\sigma} \ln \left[\frac{1 + 2\left(\pi l_c / l\right)^2}{1 + 2\left(\pi l_c / L\right)^2} \right]$$

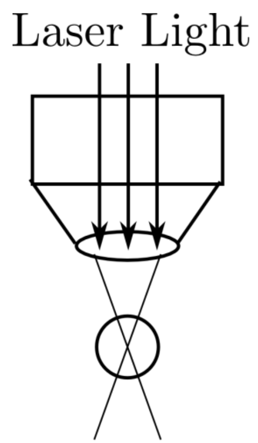
In the thermodynamic limit $(L \to \infty)$, which is now possible at finite g,

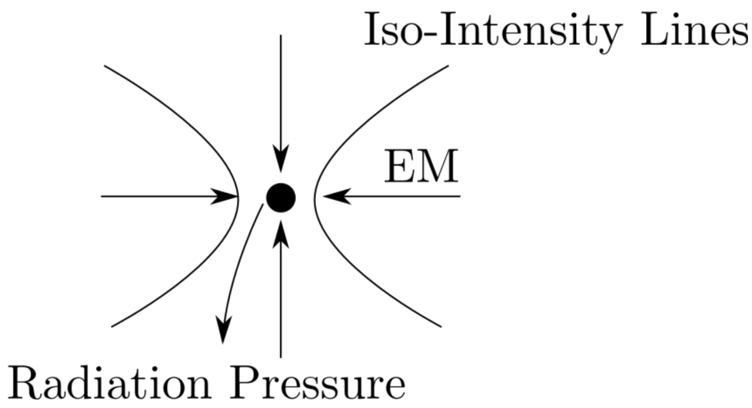
$$\langle \overline{h^2} \rangle \sim \frac{k_B T}{4\pi\sigma} \ln \left[1 + 2\left(\frac{\pi l_c}{l}\right)^2 \right]$$

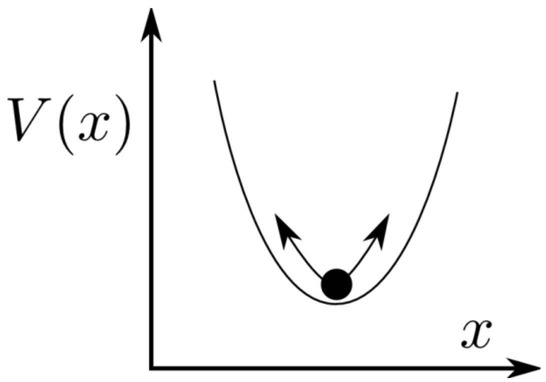
It is clear, with $k_B T \sim 10^{-14}$ erg and $\sigma \sim 50$ erg/cm^2 that even if $l_c / l \sim 10^7$ the fluctuations are still on the molecular scale.

On to Brownian Motion

Brownian motion can be investigated in modern laser trapping systems, first invented in the 1970's at Bell Labs The focus beam naturally converges on a small diffraction limited region:







Assuming that the trapping potential is quadratic in lateral displacements x, the overdamped equation of motion of a microsphere in the trap is

$$\zeta \dot{x} = -kx + \eta(t) \, .$$

where $\eta(t)$ is a random force. For μm sized spheres and moderate lasers, $k \sim 10$ fN/nm. For example, attaching spheres onto motor proteins allows the strength of interaction to be determined.

Analyzing the Langevin Equation

The stall force of motor proteins is a few pN. The relaxation time scale τ in the well comes from the spring constant and drag coefficient:$\tau = \zeta/k \sim 4$ ms.

There are two levels at which we can "solve" the Langevin equation. For any particular realization of the random noise $\xi(t)$ we can write down $x(t)$ directly. But we are also interested in *averages over realizations* of the noise, suitable to compare with experimental observations. In the first case, if we rescale the noise term the equation is

$$\dot{x} + \frac{1}{\tau}x = \xi(t)$$

We recognize an integrating factor:

$$e^{t/\tau}\left(\dot{x} + \frac{1}{\tau}x\right) = e^{t/\tau}\xi(t)$$

This allows a direct solution for any particular noise

$$x(t) - x_0 e^{-t/\tau} = \int_0^t dt' e^{-(t-t')/\tau}\xi(t')$$

Langevin Equation - continued

Now we find averages over realizations of the noise.

$$\langle x(t) - x_0 e^{-t/\tau} \rangle = \int_0^t dt' e^{-(t-t')/\tau} \langle \xi(t') \rangle = 0 \ .$$

Clearly, the average of the noise must vanish for an unbiased system, so we conclude

$$\boxed{\langle x(t) \rangle = x_0 e^{-t/\tau} \ .}$$

Now we consider the square of the deviation from simple relaxation:

$$\boxed{\langle (x(t) - x_0 e^{-t/\tau})^2 \rangle = \int_0^t dt' \int_0^t dt'' e^{-(t-t'')/\tau} e^{-(t-t')/\tau} \langle \xi(t') \xi(t'') \rangle}$$

The crucial assumption of the Langevin approach is that the correlation inside the integral is a sharply-peaked function of $|t - t''|$, decaying much faster than any relevant timescale of the particle. Calling this function $\phi(t' - t'')$, we make the change of variables $(J = 1/2)$

$$s = t' + t'' \qquad\qquad q = t' - t''$$

Langevin Equation – continued

The right hand side of the previous equation will then be (extending limits to $\pm\infty$)

$$\int_0^t dt' \int_0^t dt'' e^{-(t-t'')/\tau} e^{-(t-t')/\tau} \langle \xi(t')\xi(t'')\rangle = \frac{1}{2} e^{-2t/\tau} \int_0^{2t} ds e^{s/\tau} \int_{-\infty}^{\infty} dq \phi(q)$$

where the final integral is just a number (Γ). The average deviation squared is then

$$\langle (x(t) - x_0 e^{-t/\tau})^2 \rangle = \frac{\Gamma\tau}{2}(1 - e^{-2t/\tau})$$

In the long time limit $(t/\tau \to \infty)$

$$\langle (x(t) - x_0 e^{-t/\tau})^2 \rangle = \langle x(t)^2 \rangle = \frac{\Gamma\tau}{2}$$

However, using the equipartition argument

$$\frac{1}{2} k \langle x^2 \rangle = \frac{1}{2} k_B T \qquad \Rightarrow \qquad \Gamma = \frac{2k_B T}{\zeta}$$

Langevin Equation - continued

Logically, we assume that there is a δ correlation for the noise:

$$\langle \xi(t)\xi(t') \rangle = \frac{2k_BT}{\zeta}\delta(t-t')$$

A further test of the result is to examine the short-time behaviour of the variance in the displacement. If we assume $x_0 = 0$ and $t/\tau \ll 1$, then

$$\langle x^2(t) \rangle \sim \frac{\Gamma\tau}{2}\left(\frac{2t}{\tau} + \ldots\right) \sim \frac{2k_BT}{\zeta}t + \cdots$$

which is just a random walk in 1D ($\langle x^2 \rangle = 2Dt$). Thus

$$D = \frac{k_BT}{\zeta}$$

and the Stokes-Einstein relation is recovered. The fun calculation is to do this in the presence of inertia (see examples sheet).

Brownian Diffusion

The diffusion coefficient is just the average of the movement rate per time at long times

$$D = \lim_{t\to\infty} \frac{1}{6t} \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle$$

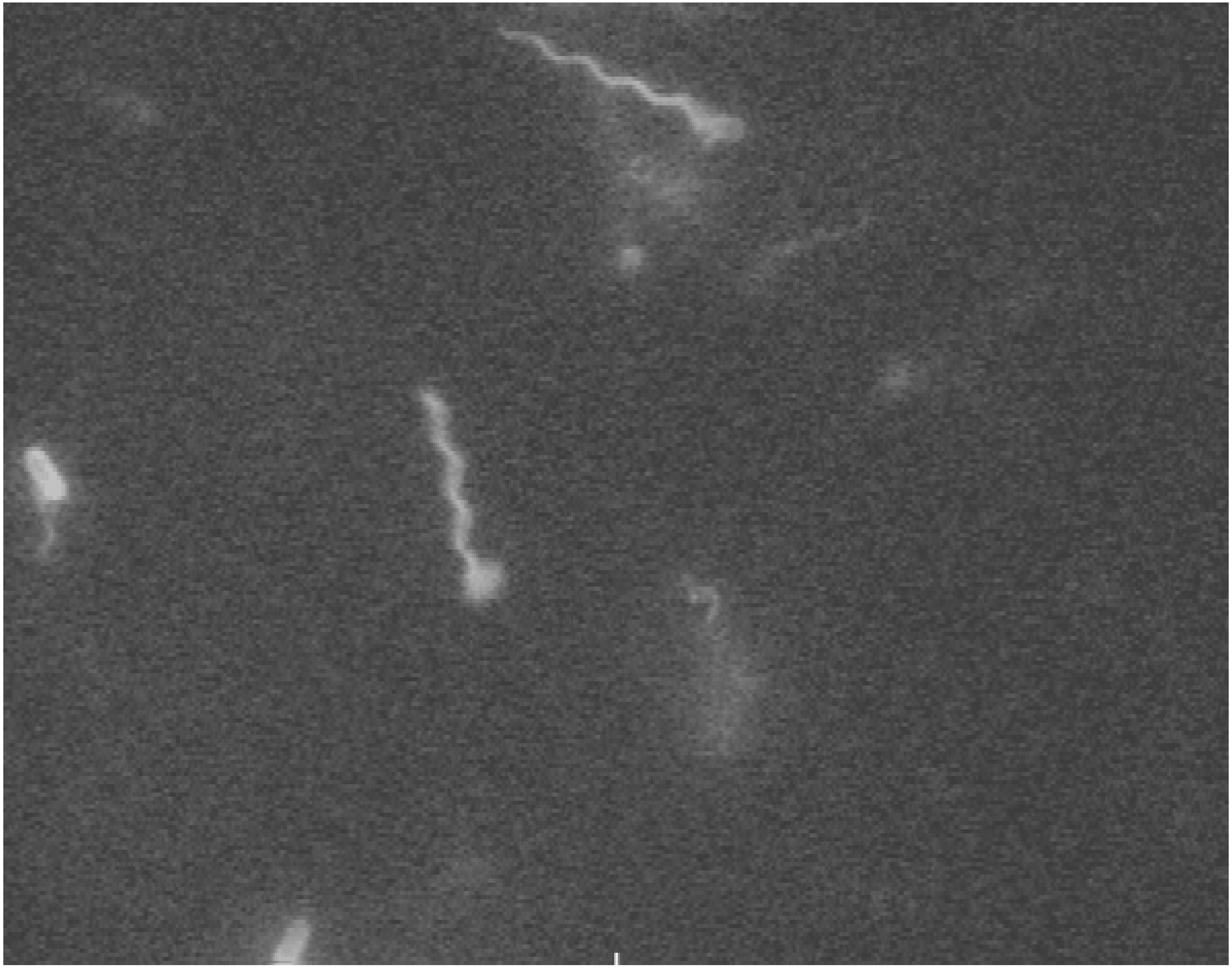
$$\text{where} \qquad \mathbf{r}(t) = \mathbf{r}(0) + \int \mathbf{u}(t')dt'$$

The diffusion coefficient term above holds provided that the correlation of velocities ($\langle \mathbf{u}(t') \cdot \mathbf{u}(t'') \rangle$) falls off fast enough. This yields

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \sim u^2 \tau$$

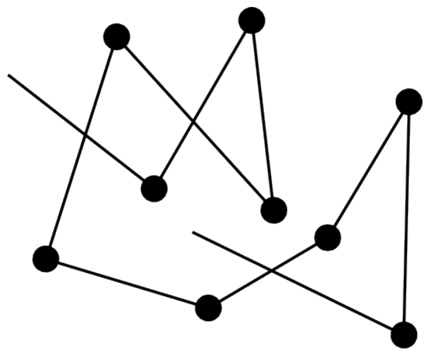
We can apply this to the run-and-tumble locomotion of bacteria. For *E. coli* the average velocity is about 20 μm/s, and the bacteria executes 1s of movement before randomly changing direction. This yields a diffusion coefficient of 4×10^{-6}cm^2/s, which is approximately the diffusion coefficient of a small molecule in water.

Run-and-Tumble Locomotion of *E. coli*



Brownian Motion and Polymer Statistics

Consider an arbitrary free polymer with each segment labeled as $\mathbf{r}_n$. Each segment is followed by another random segment of equal length ($|\zeta_n| = b$)



$$\mathbf{r}_{n+1} = \mathbf{r}_n + \zeta_n$$

The end-to-end displacement of the polymer is

$$\mathbf{r}_N - \mathbf{r}_0 = \sum_{n=1}^{N} \zeta_n \qquad \langle \mathbf{r}_N - \mathbf{r}_0 \rangle = \sum_{n=1}^{N} \langle \zeta_n \rangle = 0$$

by symmetry. The average of the displacement squared is

$$\langle (\mathbf{r}_N - \mathbf{r}_0)^2 \rangle = \sum_{m=1}^{N} \sum_{n=1}^{N} \langle \zeta_m \cdot \zeta_n \rangle = \sum_{m=1}^{N} \sum_{n=1}^{N} \delta_{mn} b^2 = Nb^2$$

The similarity with the Langevin formalism is apparent.

Brownian Motion and Polymers - continued

Let us try to formulate the problem more generally. defining the probability that a polymer will have segment positions at $\{\mathbf{r}_k\}$ as

$$p = \frac{1}{Z} G(\{\mathbf{r}_k\}) \qquad G = \mathrm{e}^{-\beta U(\{\mathbf{r}_k\})}$$

Let us suppose that the energy is a sum of near-neighbor interactions plus a contribution from some external potential,

$$U(\{\mathbf{r}_k\}) = \sum_{j=1}^{N} U_j(\mathbf{r}_{j-1}, \mathbf{r}_j) + W(\{\mathbf{r}_k\})$$

When $W = 0$, this is just a random flight model. Either way, this is a local model for the total energy, as it only relies on nearest neighbor interactions. We then introduce

$$\boxed{\tau_j(\mathbf{R}_j) = \exp[-\beta U_j(\mathbf{R}_j)]} \quad \text{where} \quad \mathbf{R}_j = \mathbf{r}_j - \mathbf{r}_{j-1}$$

and we can take it to be normalized ($\int d\mathbf{R}_j \tau(\mathbf{R}_j) = 1$).

Brownian Motion and Polymers - continued

We now define the fixed end-to-end-vector partition function as an integral over all degrees of freedom for which the end position is $\mathbf{R}$ (start at origin):

$$G(\mathbf{R};N) = \int d\{\mathbf{R}_k\}G(\{\mathbf{R}_k\})\delta(\mathbf{r}_N - \mathbf{R}) = \int d\{\mathbf{R}_k\}\prod_{j=1}^{N}\tau(\mathbf{R}_j)\delta\left(\sum_{j=1}^{N}\mathbf{R}_j - \mathbf{R}\right)$$

We shall see that molecular-level details will be coarse-grained away...

As an example, consider τ for a fixed-length segment:

$$\tau(\mathbf{R}_j) = \frac{1}{4\pi\ell^2}\delta\left(|\mathbf{R}_j| - \ell\right)$$

Now we use an integral representation of a delta function,

$$\delta\left(\sum_{j=1}^{N}\mathbf{R}_j - \mathbf{R}\right) = \int \frac{d^3k}{(2\pi)^3}\mathrm{e}^{i\mathbf{k}\cdot(\sum \mathbf{R}_j - \mathbf{R})}$$

Brownian Motion and Polymers - continued

The distribution function is then

$$G = \int \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{R}} \left[\int d\mathbf{R}_j \tau(\mathbf{R}_j) \exp(i\mathbf{k} \cdot \mathbf{R}_j) \right]^N$$

The bracketed term is a characteristic function $K(\mathbf{k}; N)$, and in this particular case is

$$K(\mathbf{k}; N) = \left(\frac{\sin(k\ell)}{k\ell} \right)^N$$

We expect N to be on the order of R^2 if dominated by diffusive behavior, and thus quite large. In the limit of large N (small k)

$$K(\mathbf{k}; N) \approx \left(1 - \frac{k^2\ell^2}{6} + \ldots \right)^N \sim \exp(-Nk^2\ell^2/6)$$

Inverse Fourier transforming,

$$G(\mathbf{R}; N) = \int \frac{d^3k}{(2\pi)^3} \exp(-i\mathbf{k} \cdot \mathbf{R}) \exp(-N\ell^2k^2/6) = \left(\frac{3}{2\pi\ell^2 N} \right)^{3/2} \exp\left(\frac{-3R^2}{2N\ell^2} \right)$$