LANGEVIN'S THEORY

We have already seen that equilibrium is characterised by fluctuations. What is the effect of these fluctuations? One of the effects is Brownian motion. We consider the simplest case of a free Brownian particle in a fluid — a pollen grain in water or a dust particle in air etc. This particle is acted upon only by the ~~x~~ force arising from random molecular bombardment. We write the equation of motion of the particle as:

$$M\frac{dv}{dt} = \mathcal{F}(t)$$

Langevin suggested that the force can be decomposed into two parts (a) an averaged-out part which is the viscous drag due to the fluid and is given by $-\frac{v}{B}$ (B is a mobility, for eg $B = \frac{1}{6\pi\eta a}$ if the particle is a sphere in a liquid), and (b) a rapidly fluctuating part $F(t)$, which over long intervals of time compared to τ^* (later) averages out to zero.

$$M\frac{dv}{dt} = -\frac{v}{B} + F(t) \; ; \quad \overline{F(t)} = 0$$

Now imagine that we are ~~xx~~ looking at a large number of such systems consisting of a particle in a fluid. At any instant of time we average over all theses systems (ensemble average)

$$M\frac{d}{dt}\langle v\rangle = -\frac{1}{B}\langle v\rangle$$

$$\langle v(t)\rangle = v(0)\exp(-t/\tau), \text{ where } \tau = MB$$

The drift velocity of the particle decays at a rate determined by the relaxation time τ. This is a result typical of dissipative systems. Now

$$\frac{dv}{dt} = -\frac{v}{\tau} + A(t) \,; \qquad \overline{A(t)} = 0$$

We construct the (scalar) product of the position $r(t)$ of the particle with the equation above:

$$\frac{d^2}{dt^2}\langle r^2 \rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2 \rangle = 2\langle v^2 \rangle$$

We have used: $r.v = \frac{1}{2}\frac{dr^2}{dt}$

$$r.\frac{dv}{dt} = \frac{1}{2}\frac{d^2 r^2}{dt^2} - v^2$$

$$\langle r \cdot A \rangle = 0$$

The last equation is a consequence of the fact that the position $r(t)$ of the particle and the force exerted on it $F(t)$ are not correlated. If the Brownian particle has already attained equilibrium then

$$\langle v^2 \rangle = \frac{3 k_B T}{M} \qquad \left(\frac{1}{2}M\left(v_x^2+v_y^2+v_z^2\right) = 3\left(\frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT\right)\right)$$

In that case we can write:

$$\frac{d^2}{dt^2}\langle r^2 \rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2 \rangle = \frac{6 k_B T}{M}$$

which can be integrated to obtain,

$$\langle r^2 \rangle = \frac{6 k_B T}{M}\tau^2 \left\{\frac{t}{\tau} - \left(1 - e^{-t/\tau}\right)\right\}$$

where we have chosen ~~to~~ two constants of integration such that $\langle r^2(0) \rangle = 0$ and $\frac{d}{dt}\langle r^2(0) \rangle = 0$.

Now for $t \ll \tau$ we observe that

$$\langle r^2 \rangle \approx \frac{3k_BT}{M} t^2 = \langle v^2 \rangle t^2$$

which is consistent with the reversible equations of motion (of Newton) from which we expect $\underline{r} = \underline{v}\,t$.

Again for $t \gg \tau$ we see that

$$\langle r^2 \rangle = \frac{6k_BT\tau}{M} t = (6Bk_BT)t$$

We see that $\langle r^2 \rangle = 6Dt$ where $D = Bk_BT$. The diffusion constant is related to the mobility of the particle and they both have their origin in the forces exerted by the fluid. The incessant motion of the molecules of the fluid (fluctuations) are responsible for the dissipative properties. The fluctuations around eqbm are small but they manifest themselves in macroscopically observable properties. $\underline{D = Bk_BT}$ is referred to as the Nernst-Einstein relation, after those that derived it.

We will now discuss an aside the Equipartition Theorem. Imagine a system of particles described by a Hamiltonian $H = H(q,p)$. We will think of the variables x_i and x_j as any of the generalised co-ordinates (q,p). Then there is a theorem which says something about the expected value of the quantity $x_i \frac{\partial H}{\partial x_j}$.

Theorem:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} k_BT$$

Proof: In the canonical ensemble the expected value

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} \exp(-\beta H)\, dp_1 dp_2 \ldots dq_1 dq_2 \ldots}{\int \exp(-\beta H)\, dp_1 dp_2 \ldots dq_1 dq_2 \ldots}$$

Consider the integral on the numerator and integrate by parts w.r.t x_j:

$$\int \left[-\frac{1}{\beta} x_i \exp(-\beta H) \Big|_{(x_j)_1}^{(x_j)_2} + \frac{1}{\beta} \int \left(\frac{\partial x_i}{\partial x_j} \right) \exp(-\beta H)\, dx_j \right] d\omega_{(j)}$$

where $(x_j)_1$ and $(x_j)_2$ are the "extreme" values of the co-ordinate x_j, while $d\omega_{(j)}$ denotes $d\omega = dp_1 dp_2 \ldots dq_1 dq_2 \ldots$ but devoid of dx_j. The first term vanishes identically since H will become infinite at the extreme values of x_j. If x_j is the space variable (for an ideal gas, say) then it will correspond to the "walls of the container" where the potential energy of the system is infinite. The momentum variable can itself go to infinity (classically). Hence we are left with

$$\text{(A)} \longleftarrow \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\frac{1}{\beta} \delta_{ij} \int \exp(-\beta H)\, d\omega}{\int \exp(-\beta H)\, d\omega} = \delta_{ij} k_B T.$$

(QED)

Now in many physical situations the Hamiltonian of a system is a quadratic function of the co-ordinates. Through a transformation we can write,

$$\text{(B)} \longleftarrow H = \sum_j A_j P_j^2 + \sum_j B_j Q_j^2$$

where P_j and Q_j are transformed co-ordinates and A_j and B_j are constants of the problem. We clearly have

$$\sum_j \left(P_j \frac{\partial H}{\partial P_j} + Q_j \frac{\partial H}{\partial Q_j} \right) = 2H$$

and by averaging and using result (A) we get

$$\langle H \rangle = \frac{1}{2} f k_B T$$

where 'f' is the number of non-vanishing co-efficients in the expansion (B). Hence, we conclude that each harmonic term in the transformed Hamiltonian makes a contribution of $\frac{1}{2}k_BT$ towards the internal energy. For the distribution of kinetic energy the theorem was stated by Boltzmann in 1871. This theorem (equipartition) is valid only when the relevant degrees of freedom can be freely excited, hence works well at high enough T.

Now, we go back to the discussion of Langevin's equation and its consequences. We assumed $\langle v^2\rangle = \frac{3k_BT}{M}$ which is valid at eqbm. We would like to understand the consequences when eqbm has not been reached yet. For this we start with

$$\frac{dv}{dt'} = -\frac{v}{\tau} + A(t') \, ; \quad \overline{A(t')} = 0$$

Multiply both sides by $\exp(t'/\tau)$, rearrange and integrate from $t'=0$ to $t'=t$, to get,

$$v(t) = v(0)\, e^{-t/\tau} + e^{-t/\tau}\int_0^t e^{t'/\tau} A(t')\,dt'$$

Clearly $v(t)$ is fluctuating function of time but $\langle v(t)\rangle$ is ~~clearly~~ given by $v(0)\,e^{-t/\tau}$, since the second term will evaporate when we take the average. Now let us determine the mean-square velocity.

$$\langle v^2(t)\rangle = v^2(0)\,e^{-2t/\tau} + 2e^{-2t/\tau}\left[v(0)\cdot\int_0^t e^{-t'/\tau}\langle A(t')\rangle dt'\right]$$
$$+ e^{-2t/\tau}\int_0^t\int_0^t e^{\frac{(t_1+t_2)}{\tau}}\langle A(t_1)\cdot A(t_2)\rangle\, dt_1\, dt_2$$

The second term in the RHS is identically zero since $\langle A(t')\rangle = 0$ at all t'. The third term contains the expression $\langle A(t_1)\cdot A(t_2)\rangle$ which is a measure of the "statistical correlation" between ~~the value of~~ the value of the fluctuating variable A at time t_1 and its value at time t_2. It is the <u>autocorrelation function</u> of the random variable A. We will denote the autocorrelation function by $K(t_1, t_2)$. It is in order to discuss some properties of this function $K(t_1, t_2)$.

1. In a <u>stationary ensemble</u> (macroscopic behavior not changing with time), the function $K(t_1, t_2)$ depends only on $t_1 - t_2 = s$. Hence,
$$K(t_1, t_1+s) \equiv \langle A(t_1)\cdot A(t_1+s)\rangle = K(s) \;\forall\, t_1$$
2. $K(0)$ is positive definite and if the ensemble is stationary then $K(0) = \text{const} > 0$
3. For any value of s, the magnitude of the function $K(s)$ cannot exceed $K(0)$.

<u>Proof</u>: $\langle |A(t_1) \pm A(t_2)|^2\rangle = \langle A^2(t_1)\rangle + \langle A^2(t_2)\rangle \pm 2\langle A(t_1)\cdot A(t_2)\rangle$
$$= 2\{K(0) \pm K(s)\} \geq 0.$$
Hence, $-K(0) \leq K(s) \leq K(0) \Rightarrow |K(s)| \leq K(0) \;\forall s$

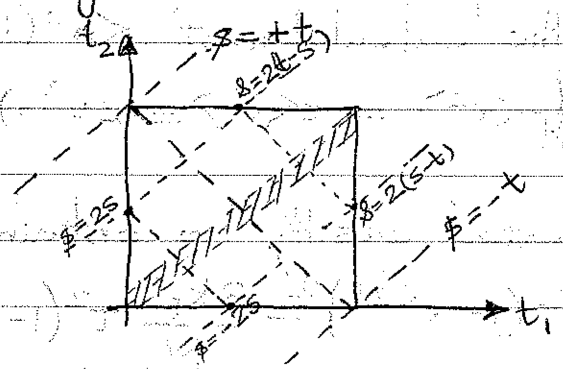
4. $K(s)$ is symmetric about $s=0 \Rightarrow K(s) = K(-s)$

<u>Proof</u>: $K(s) = \langle A(t_1)\cdot A(t_1+s)\rangle \equiv \langle A(t_1 - s)\cdot A(t_1)\rangle$
$$= \langle A(t_1)\cdot A(t_1 - s)\rangle \equiv K(-s)$$
5. As s becomes large in comparison with the characteristic time τ^*, the values $A(t_1)$ and $A(t_1+s)$ become uncorrelated, so that
$$K(s) \equiv \langle A(u_1)\cdot A(u_1+s)\rangle \xrightarrow[s \gg \tau^*]{} \langle A(u_1)\rangle \cdot \langle A(u_1+s)\rangle = 0$$
The magnitude of $K(s)$ is significant only when s is of the same

order as τ^*. Now consider the integral

$$I = \int_0^t \int_0^t e^{\frac{(t_1+t_2)}{\tau}} K(t_2 - t_1)\, dt_1\, dt_2$$

We will do a change of variables $S = \frac{1}{2}(t_1+t_2)$, $s = t_2 - t_1$ then the integrand becomes $e^{\frac{2S}{\tau}} K(s)\, dS\, ds$. The limits of integration will be modified for these variables.



$$I = \int_0^{t/2} e^{2S/\tau} dS \int_{-2S}^{2S} K(s)\, ds + \int_{t/2}^{t} e^{2S/\tau} dS \int_{-2(t-S)}^{2(t-S)} K(s)\, ds$$

When $0 \leq S \leq \frac{t}{2}$, s goes from $-2S$ to $+2S$ while when $\frac{t}{2} \leq S \leq t$, s goes from $-2(t-S)$ to $2(t-S)$.

The integrals over s draw major contributions from the shaded patch which is of the order τ^*. Therefore, if $t \gg \tau^*$ then the limits of integration for s can be changed to $-\infty$ to $+\infty$. Hence,

$$I \approx C \int_0^t e^{\frac{2S}{\tau}} dS = \frac{C\tau}{2}\left(e^{\frac{2t}{\tau}} - 1\right)$$

where $C = \int_{-\infty}^{\infty} K(s)\, ds$. (total area under the $K(s)$ curve)

Finally, we arrive at the result

$$\langle v^2(t) \rangle = v^2(0)\, e^{-\frac{2t}{\tau}} + \frac{C\tau}{2}\left(1 - e^{-\frac{2t}{\tau}}\right)$$

As $t \to \infty$ we must have $\langle v^2(t) \rangle = \frac{3k_BT}{M}$. Hence

$$C = \frac{6k_BT}{M\tau}$$

Moreover if $v^2(0) = \frac{3k_BT}{M}$ then $\langle v^2(t) \rangle$ would always remain the same, which shows that eqbm once attained, has a tendency to persist.

Going back to the calculation of $\langle r^2(t) \rangle$ we remember

$$\frac{d^2}{dt^2}\langle r^2 \rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2 \rangle = 2\langle v^2 \rangle = 2v^2(0)e^{-\frac{2t}{\tau}} + \frac{6k_BT}{M}\left(1 - e^{-\frac{2t}{\tau}}\right)$$

This can be integrated easily to obtain,

$$\langle r^2(t) \rangle = v^2(0)\tau^2\left(1 - e^{-t/\tau}\right)^2 - \frac{3k_BT}{M}\tau^2\left(1 - e^{-t/\tau}\right)\left(3 - e^{-t/\tau}\right) + \frac{6k_BT\tau}{M}t$$

Once again the initial conditions are that $\langle r^2(0) \rangle = 0$ and $\frac{d}{dt}\langle r^2 \rangle\Big|_{t=0} = 0$. We note yet again that

for $t \ll \tau$, $\langle r^2 \rangle \simeq v^2(0)t^2$ (reversible) and when $t \gg \tau$, $\langle r^2 \rangle \simeq (6Bk_BT)t$ (irreversible).

FLUCTUATION-DISSIPATION THEOREM

We found that $C = \frac{6k_BT}{M\tau}$. We use it as follows:

$$\frac{1}{B} = \frac{M}{\tau} = \frac{M^2}{6k_BT}C = \frac{M^2}{6k_BT}\int_{-\infty}^{\infty} K_A(s)\,ds = \frac{1}{6k_BT}\int_{-\infty}^{\infty} K_F(s)\,ds$$

$$K_A(s) = \langle A(0)\cdot A(s) \rangle = \frac{1}{M^2}\langle F(0)\cdot F(s) \rangle = \frac{1}{M^2}K_F(s)$$

The equation above establishes a deep relationship between the averaged out part of the forces exerted by the fluid on the Brownian particle and the statistical character of the fluctuating part of $F(t)$ of those forces. It connects the dissipative forces with the temporal character of the molecular fluctuations. It is called a <u>fluctuation-dissipation</u> theorem. It relates in a fundamental manner the fluctuations around eqbm to a non-equbm property such as viscosity. In this way the statistical mechanics of non-equilibrium processes is reduced to the statistical mechanics of eqbm states. Note also that

$$\frac{1}{D} = \frac{1}{6(k_B T)^2} \int_{-\infty}^{\infty} K_F(s)\, ds$$

In fact one can show after some algebra that

$$D = \frac{1}{6} \int_{-\infty}^{\infty} K_v(s)\, ds$$

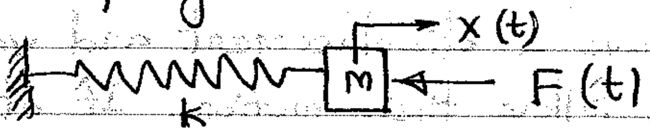
where $K_v(s) = \langle v(0) \cdot v(s) \rangle$ is the auto-correlation function of the velocity of the Brownian particle.

$$\frac{d^2x}{dt^2} + \beta\frac{dx}{dt} + \omega^2 x = \delta(t) \quad , \quad x\big|_{t=0} = \frac{dx}{dt}\Big|_{t=0} = 0$$

Solution $\rightarrow$ $x(t) = \frac{1}{\omega_1} e^{-\frac{\beta t}{2}} \sin\omega_1 t$

BROWNIAN MOTION OF ~~A~~ HARMONICALLY BOUDN MASS

This is one of the most important and useful models in Brownian motion. Imagine the following system with a mass and spring with a random external force.



The equation of motion of the particle is

$$\frac{d^2x}{dt^2} + \beta\frac{dx}{dt} + \omega^2 x = A(t) \qquad \omega^2 = \frac{k}{m}$$

When at $t=0$, $x = x_0$ and $u = \frac{dx}{dt} = u_0$ we know the solution to the differential equation above is:

$$u(t) = -\frac{2\omega^2 x_0 + \beta u_0}{2\omega_1} e^{-\frac{\beta t}{2}} \sin\omega_1 t + u_0 e^{-\frac{\beta t}{2}} \cos\omega_1 t$$
$$+ \frac{1}{\omega_1}\int_0^t A(\xi) e^{-\frac{\beta(t-\xi)}{2}} \left\{ -\frac{\beta}{2}\sin\omega_1(t-\xi) + \omega_1 \cos\omega_1(t-\xi)\right\} d\xi$$

$$x(t) = \frac{\beta x_0 + 2u_0}{2\omega_1} e^{-\frac{\beta t}{2}} \sin\omega_1 t + x_0 e^{-\frac{\beta t}{2}} \cos\omega_1 t$$
$$+ \frac{1}{\omega_1}\int_0^t A(\xi) e^{-\frac{\beta(t-\xi)}{2}} \sin\omega_1(t-\xi)\, d\xi$$

where, $\omega_1^2 = \omega^2 - \frac{\beta^2}{4}$. The solution is the sum of a solution to the homogeneous equation and a particular solution corresponding to the random forcing. The random force is such that

$$\langle A(\xi)\rangle_{x_0, u_0} = 0 \, ,$$

meaning, the average is zero no matter what values of x_0 and u_0 we choose. So immediately we get

$$(1) \longleftarrow \langle x(t)\rangle_{x_0, u_0} = \frac{\beta x_0 + 2u_0}{2\omega_1} e^{-\frac{\beta t}{2}} \sin(\omega_1 t) + x_0 e^{-\frac{\beta t}{2}} \cos(\omega_1 t)$$

The meaning of the last equation is that suppose we have a canonical ensemble of harmonic oscillators, from which at $t=0$ we pick a sub-ensemble (A) of oscillators which have a displacement and velocity x_0, u_0 resp. and we follow their motion. If at time t we take an average of $x(t)$ then this average will be given by the previous equation. If we would follow a sub-ensembe (B) of which the members at $t=0$ had displacement x_0 but arbitrary velocity, we would get at time t a displacement, which will follow from eqn ① by taking the average over u_0. Since in a canonical ensemble of oscillators the displacement is not correlated with the velocity, we may put

$$\langle u_0 \rangle_{x_0} = 0 \qquad \langle u^2 \rangle_{x_0} = \frac{k_B T}{m}$$

Using this we get,

$$\langle x(t) \rangle_{x_0} = x_0 e^{-\frac{\beta t}{2}} \left(\frac{\beta}{2\omega_1} \sin \omega_1 t + \cos \omega_1 t \right)$$

We will now consider u^2 and x^2. Using the assumption

$$\langle A(t_1) A(t_2) \rangle_{x_0, u_0} = \phi(t_1 - t_2)$$

where $\phi(x)$ is an even function peaked at $x=0$, we can calculate the double integrals as we did for the unbound particle.

$$\langle x^2 \rangle_{x_0 u_0} = \left(\frac{\beta x_0 + 2u_0}{2\omega_1} e^{-\frac{\beta t}{2}} \sin \omega_1 t + x_0 e^{-\frac{\beta t}{2}} \cos \omega_1 t \right)^2$$

$$+ \frac{\tau_1}{2\omega_1^2 \beta} \left(1 - e^{-\beta t} \right) - \frac{\tau_2}{8\omega^2 \omega_1^2} \left(\beta - \beta e^{-\beta t} \cos 2\omega_1 t + 2\omega_1 e^{-\beta t} \sin 2\omega_1 t \right)$$

where $\tau_1 = \int_{-\infty}^{\infty} \phi(w) \cos \omega_1 w \, dw$; $\tau_2 = \int_{-\infty}^{\infty} \phi(w) \, dw$

This works only if the particle is harmonically bound, not when it is free. Think, $\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = \langle xu\rangle$.

The condition that for $t \to \infty$ we must get the equipartition value of $\langle x^2\rangle$ will give us one relation between τ_1 and τ_2. We expect to obtain a second relation using:

$$\lim_{t\to\infty} \langle u^2\rangle_{x_0,u_0} = \frac{k_B T}{m}$$

but we get exactly the same answer as the first condition. A third condition is imposed by asking $\langle x(t)u(t)\rangle_{x_0,u_0}$ tend to zero as $t \to \infty$, because for $t\to\infty$ ensemble (A) must again become a canonical ensemble. If we do this we get the answer that

$$\tau_1 = \tau_2 = \frac{2\beta k_B T}{m}$$

If we use this and average over u_0 we get,

$$\langle x^2\rangle_{x_0} = \frac{k_B T}{m\omega^2} + \left(x_0^2 - \frac{k_B T}{m\omega^2}\right)e^{-\beta t}\left(\cos\omega_1 t + \frac{\beta}{2\omega_1}\sin\omega_1 t\right)^2$$

which sows how the equipartition value is reached. The next result is perhaps interesting:

$$\langle xu\rangle_{x_0} = \frac{1}{\omega_1\omega^2}\left(\frac{k_B T}{m\omega^2} - x_0^2\right)e^{-\beta t}\sin\omega_1 t\left(\cos\omega_1 t + \frac{\beta}{2\omega_1}\sin\omega_1 t\right)$$

The correlation between x and u starts at zero, oscillates and goes to zero as $t\to\infty$.

This was the case when we have exponentially decaying oscillations, underdamped system. For an overdamped oscillator we get,

$$\langle x(t)\rangle_{x_0} = x_0 e^{-\frac{\beta t}{2}}\left(\cosh\omega' t + \frac{\beta}{2\omega'}\sinh\omega' t\right)$$

$$\langle x^2(t)\rangle_{x_0} = \frac{k_B T}{m\omega^2} + \left(x_0^2 - \frac{k_B T}{m\omega^2}\right)e^{-\beta t}\left(\cosh\omega' t + \frac{\beta}{2\omega'}\sinh\omega' t\right)^2$$

where $\omega'^2 = \frac{\beta^2}{4} - \omega^2 = -\omega_1^2$. When the damping is just at the critical value,

$$\langle x^2 \rangle_{x_0} = \frac{k_B T}{m\omega^2} + \left(x_0^2 - \frac{k_B T}{m\omega^2}\right)\left(1 + \frac{\beta t}{2}\right)^2 e^{-\beta t}$$

$$\langle x \rangle_{x_0} = x_0 \left(1 + \frac{\beta t}{2}\right) e^{-\frac{\beta t}{2}}.$$

In each of these cases $\langle x(t) u(t) \rangle_{x_0, u_0}$ goes to zero as $t \rightarrow \infty$.

We have until now used the methods of Ornstein and Uhlenbeck to obtain the mean values and variance of the velocity and displacement of a Brownian particle. It works very well when we have linear equations but becomes difficult to use when the equations of motion are non-linear. There is a ~~analogous~~ different approach which leads to similar results but which gives the entire probability distribution $G(x, u_0, t)$ for the Brownian particle. It is based on Fokker-Planck equation, which is a partial differential equation. To do this consider a probability distribution function $F(\phi_0, \phi, t)$ which gives the probability that a particle has velocity (position) ϕ after time t given that its velocity (position) is ϕ_0 at time $t = 0$. When t increases by Δt, ϕ will increase by a $\Delta\phi$ which is different for each particle. Let the probability for an increase between the limits $\Delta\phi$ and $\Delta\phi + d(\Delta\phi)$ be $\psi(\Delta\phi, \phi, t)\, d(\Delta\phi)$. Writing $\phi' = \phi + \Delta\phi$ we have

$$F(\phi_0, \phi', t + \Delta t) = \int F(\phi_0, \phi' - \Delta\phi, t)\, \psi(\Delta\phi, \phi' - \Delta\phi, t)\, d(\Delta\phi)$$

where we have supposed that the probability of an increase $\Delta\phi$ is independent of the fact that at $t=0$, $\phi = \phi_0$. We will now expand the integrand in powers of $\Delta\phi$.

$$F(\phi_0, \phi' - \Delta\phi, t)\,\psi(\Delta\phi, \phi' - \Delta\phi, t) = F(\phi_0, \phi', t)\,\psi(\Delta\phi, \phi', t)$$
$$- \Delta\phi\,(F'\psi + F\psi') + \frac{\Delta\phi^2}{2}(F''\psi + 2F'\psi' + F\psi'') + \cdots$$

The integrals that appear on the RHS have simple meanings. For instance,

$$\int \psi(\Delta\phi, \phi', t)\, d(\Delta\phi) = 1 \, ; \quad \int \Delta\phi\, \psi\, d(\Delta\phi) = \overline{\Delta\phi}$$

$$\int \Delta\phi^2\, \psi''\, d(\Delta\phi) = \frac{\partial^2}{\partial\phi'^2}\overline{\Delta\phi^2} \quad \text{etc.}$$

Now, we expand the LHS in powers of Δt using

$$\lim_{\Delta t \to 0} \frac{\overline{\Delta\phi}}{\Delta t} = f_1(\phi', t) \, ; \quad \lim_{\Delta t \to 0} \frac{\overline{\Delta\phi^2}}{\Delta t} = f_2(\phi', t)$$

and assuming that $\lim_{\Delta t \to 0} \frac{\overline{\Delta\phi^k}}{\Delta t} = 0$ for $k > 2$. We then get the following partial differential equation,

$$\frac{\partial F}{\partial t} = \frac{1}{2} f_2 \frac{\partial^2 F}{\partial \phi^2} + \left(\frac{\partial f_2}{\partial \phi} - f_1\right)\frac{\partial F}{\partial \phi} + \left(\frac{1}{2}\frac{\partial^2 f_2}{\partial \phi^2} - \frac{\partial f_1}{\partial \phi}\right) F$$

We must, in each special case, obtain f_1 and f_2 and verify that $\lim_{\Delta t \to 0} \frac{\overline{\Delta\phi^k}}{\Delta t} = 0$. This can always be done if we know the equation of motion. For instance for a free Brownian particle we know that

$$u' - u = \Delta u = -\beta u \Delta t + \int_t^{t+\Delta t} A(\xi)\, d\xi$$

$$\Rightarrow \quad \overline{\Delta u} = -\beta u \Delta t \;\Rightarrow\; \lim_{\Delta t \to 0} \frac{\overline{\Delta u}}{\Delta t} = -\beta u$$

In the same way we know that $\lim_{\Delta t \to 0} \frac{\overline{\Delta u^2}}{\Delta t} = \tau_1 = \frac{2\beta k_B T}{m}$

Hence, we get

$$f_1(u) = -\beta u \quad \text{and} \quad f_2(u) = \frac{2k_BT\beta}{m} = \text{const}$$

So plugging back into the Fokker-Planck equation we get,

$$\frac{\partial F}{\partial t} = \frac{1}{\cancel{2}}\frac{\cancel{2}\beta k_BT}{m}\frac{\partial^2 F}{\partial u^2} + (\beta u)\frac{\partial F}{\partial u} + \beta F$$

or,
$$\frac{\partial F}{\partial t} = \beta\frac{\partial}{\partial u}(uF) + \frac{\beta k_BT}{m}\frac{\partial^2 F}{\partial u^2}$$

This tell us how the probability distribution F would evolve. We would now like to solve this pde with some initial conditions. This can be done if one is so clever as to assume $F = \phi^{1/2}\exp\{-(u-u\chi)\phi\}$ where $\chi(t)$ and $\phi(t)$ are functions of t only. Substituting this solution back into the Fokker-Planck pde we see that $\chi(t)$ and $\phi(t)$ are solutions of the ordinary differential equations:

$$\frac{d\chi}{dt} = -\beta\chi$$

$$\frac{1}{\beta}\frac{d\phi}{dt} = 2\phi - 4\phi^2$$

These can be immediately integrated and the constants of integration are determined by imposing the conditions that at $t=0$ we must get $\delta(u-u_0)$ and for $t\to\infty$ the probability distribution should be Maxwells distribution.

$$G(u_0,u,t) = \left[\frac{m}{2\pi k_BT(1-e^{-2\beta t})}\right]^{1/2}\exp\left\{\frac{-m}{2k_BT}\frac{(u-u_0e^{-\beta t})^2}{1-e^{-2\beta t}}\right\}$$

This shows how the Maxwell distribution is reached.

The next application of the Fokker-Planck equation that we want to consider is the case of the Harmonically bound particle. In this case we have,

$$\frac{du}{dt} + \beta u = A(t) \overset{-}{\oplus} \frac{1}{m} K(x)$$

$$\text{Or,} \quad \Delta u = -\beta \Delta x + \int_t^{t+\Delta t} A(\xi)\, d\xi \overset{-}{\oplus} \frac{1}{m} K x(\Delta t)$$

If we neglect the effect of the velocity then we get,

I $\longleftarrow$ $$\beta \overline{\Delta x} = \overset{-}{\oplus}\frac{1}{m} K(x)\, \Delta t$$

$$\Rightarrow f_1(x) = \frac{\overset{-}{\oplus}1}{\beta m} K(x)$$

When Δt is not to small then we may put

II $\longleftarrow$ $$\langle \Delta x^2 \rangle = \frac{2k_B T}{m\beta} \Delta t = 2 D \Delta t \Rightarrow f_2(x) = 2D$$

Going back to the general F-P equation we get

$$\frac{\partial F}{\partial t} = \frac{\overset{+}{\ominus}1}{m\beta} \frac{\partial}{\partial x}\left(K(x) F\right) + D \frac{\partial^2 F}{\partial x^2}$$

Now for the case of a harmonically bound particle we know that $\frac{1}{m} K(x) = \overset{+}{\ominus}\omega^2 x$. Hence we get,

$$\frac{\partial F}{\partial t} = \frac{\omega^2}{\beta} \frac{\partial}{\partial x}(xF) + D \frac{\partial^2 F}{\partial x^2}$$

The fundamental solution to this equation is

$$F(x_0, x, t) = \left(\frac{\omega^2}{2\pi \beta D\left(1 - e^{-\frac{2\omega^2}{\beta}t}\right)}\right)^{1/2} \exp\left(-\frac{\omega^2}{2\beta D} \cdot \frac{\left(x - x_0 e^{-(\omega^2/\beta)t}\right)^2}{1 - e^{-\frac{2\omega^2}{\beta}t}}\right)$$

From this we can calculate $\langle x \rangle_{x_0}$ and $\langle x^2 \rangle_{x_0}$. The results are as follows:

$$\langle x \rangle_{x_0} = x_0 e^{-\frac{\omega^2}{\beta} t}$$

$$\langle x^2 \rangle_{x_0} = \frac{k_B T}{m\omega^2} + \left(x_0^2 - \frac{k_B T}{m\omega^2} \right) e^{-\frac{2\omega^2}{\beta} t}$$

This result rests on two assumptions (I) and (II). These are valid only when $t \gg \beta^{-1}$ and when β is very large so that the motion is strongly overdamped. The particle does not feel the effect of the spring. The correct way to derive the result is to integrate a two dimensional F-P equation where both position and velocity are involved.

SMOLUCHOWSKI'S EQUATION

If we are interested in finding a probability distribution that is time-independent, we must require that the probability not pile up anywhere, meaning that the equation should be independent of t. In other words we get,

$$0 = \frac{1}{2} f_2 \frac{\partial^2 F}{\partial \phi^2} + \left(\frac{\partial f_2}{\partial \phi} - f_1 \right) \frac{\partial F}{\partial \phi} + \left(\frac{1}{2} \frac{\partial^2 f_2}{\partial \phi^2} - \frac{\partial f_1}{\partial \phi} \right) F$$

This equation is called Smoluchowski's equation.
For the case of a particle bound to spring we will have

$$\frac{\partial^2 F}{\partial x^2} + \frac{1}{m\beta D} \frac{\partial}{\partial x} \left(-K(x) F \right) = 0$$

If we write $-K(x) = \frac{dU}{dx}$ where U is some potential energy, then,

$$\frac{\partial^2 F}{\partial x^2} + \underbrace{\frac{1}{m\beta D}}_{\text{const}} \frac{\partial}{\partial x} \left(F \frac{\partial U}{\partial x} \right) = 0$$

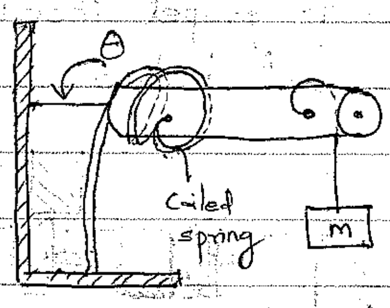
Clearly, the Boltzmann distribution which says that $P(x) = C \exp\left(-\frac{U(x)}{k_B T}\right)$ is a solution to this equation.

SMOLUCHOWSKI'S EQN APPLIED TO RATCHETS.

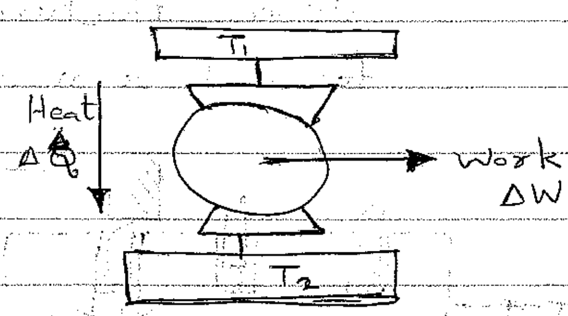
Before we go into the details of the mathematics let us do a short survey of molecular machines. Machines actively reverse the natural flow of some chemical or mechanical process by coupling it to another one. Machines can be of many types:

(a) One shot machine — They exhaust some internal source of free-energy.

(b) Cyclic machines — They process some external source of free energy such as food molecules, absorbed light, a difference in concentration of some molecule across a membrane, or an electrostatic potential difference.



One-shot machine

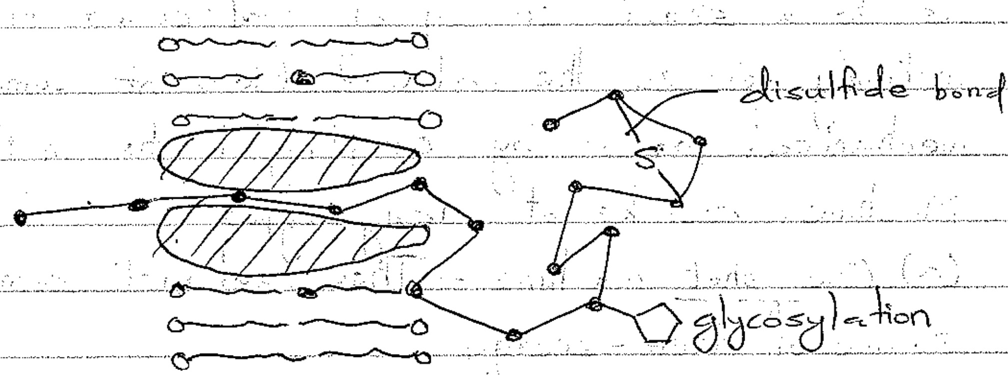


Cyclic Heat engine.

In biology molecular motors like kinesin, dyenin or myosin are examples of cyclic machines that utilise the energy by burning ATP and produce linear motion. Similarly flagella of a bacterium utilizes ATP and a Na^+ gradient to rotate, F_oF_1-ATPase utilizes H^+ gradient across the mitochondria to generate ATP. But there are other types of motion; they do not rely on cyclic machines rather on one-shot machines. For example, some proteins migrate across membrane pores in mitochondria and plasma membrane by utilising the free-energy change resulting

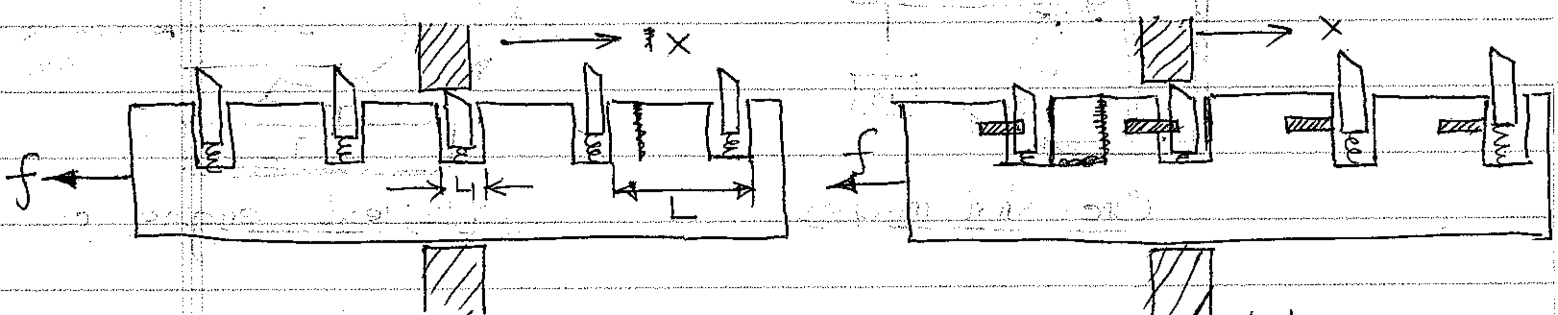
Translocation paper of Mandar might be a good example.

from chemical modification, such as glycosylation or



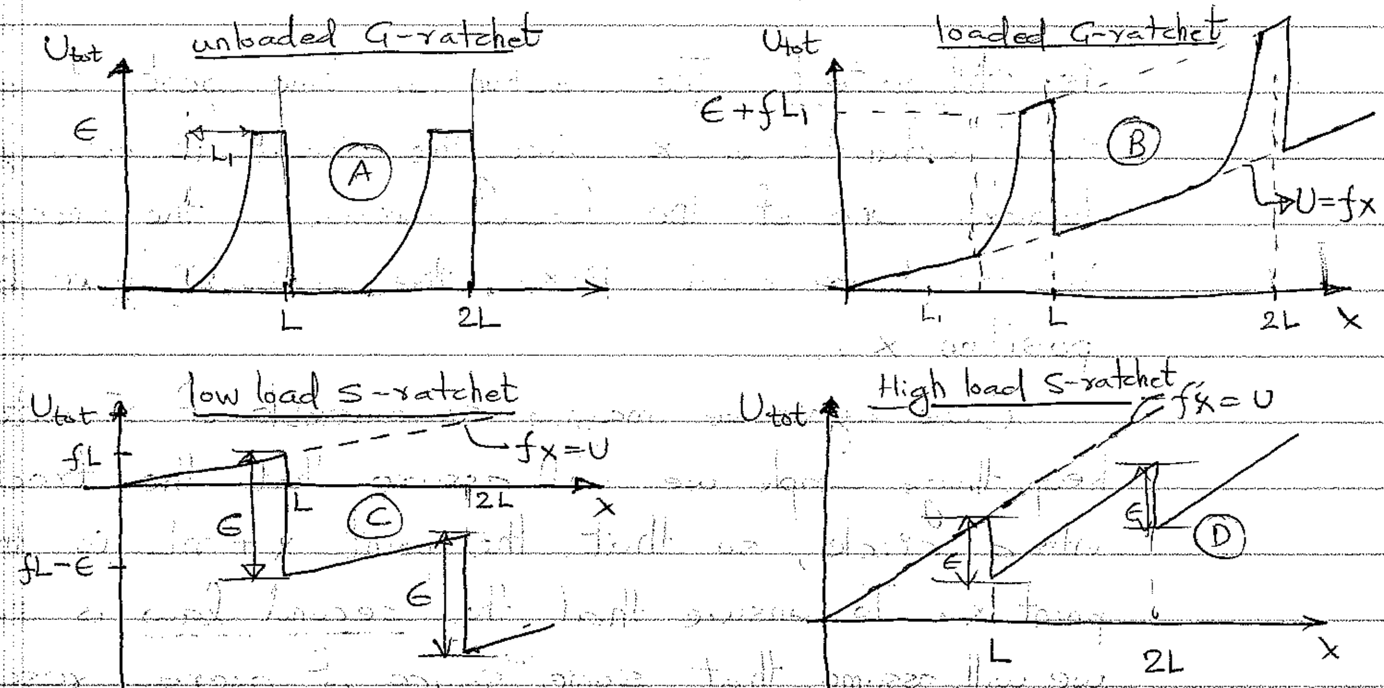
disulfide bond formation or chain coiling caused by differences in pH.

Our discussion today will be focussed on one-shot machines, such as the translocating molecule above. It utilises thermal fluctuations in order to propel itself. A model for such a machine is depicted below.



G-ratchet S-ratchet.

In the S-ratchet there is an agent that resets the bolt immediately after the membrane is crossed. This will be the "parallel" for glycosylation or coiling up etc. f is a force that tries to hinder the motion. The agent that resets the bolts clearly uses up some energy, but if this energy is overwhelmed by the energy released by the uncoiling spring then there is a decrease in potential energy. Working against a force obviously increases the potential energy of the system.



We note here that (B) and (D) are similar while (A) can be produced by setting $f = \frac{\epsilon}{L}$. Hence we will focus our analysis on S-ratchets alone. Note that the rate at which an S-ratchet steps to the right will reflect the probability of getting a kick of energy at least fL and the rate of stepping to the ~~right~~ left will tell us the probability of getting a kick ϵ. Assume now that $\epsilon \gg k_BT$, so that once a bolt pops up it rarely goes back spontaneously $\Rightarrow$ perfect ratchet.

Now if there is no restraining force then we have a descending staircase type energy landscape. Between steps the rod wanders freely with a diffusion constant D. A rod at $x=0$ will (on average) arrive at $x=L$ in time $t_{step} = \frac{L^2}{2D}$. Once it arrives at $x=L$ the bolt pops up preventing return and the average speed is:

$$v = \frac{L}{t_{step}} = \frac{2D}{L} \quad \text{(unloaded, perfect S-ratchet)}$$

Now imagine that a force f is applied but the ratchet

- Assume an infinitely long ratchet
- Big ensemble
- Wait for steady state.
- Motion is diffusive between falls
- Analysis valid only when $f \ll \frac{\epsilon}{L}$.

is still perfect. The fraction of time spent at any x is now a function of x since the load is always pushing toward one of the local minima of the energy landscape. We need to find $P(x)$, the probability of being at position x.

Once again we imagine an ensemble of S-ratchets. To keep things simple we will assume that the track is bent into a circle, so that the point $x + nL$ is the same as point x. To ensure that the second law is satisfied we will assume that some source of energy resets the bolt everytime it goes around full circle. We release all the ratchets at $t = 0$ at the same point $x = x_0$ and wait till steady state is established, when the probability $P(x)$ of finding a ratchet at x stops changing in time. However the net number of ratchets crossing $x = 0$ from left to right need not be zero in this state. We need the flux at any location 'a'. If there are a total of M ratchets then the flux at 'a' will be given by diffusive flux and drift flux. For the diffusive flux let us see what we can say:

$$\Delta t\, j_{diff} = \frac{1}{2} M \left[P(a) - P(a+\Delta x) \right] \Delta x \approx -\frac{1}{2} (\Delta x)^2 M \left.\frac{dP(x)}{dx}\right|_{x=a}$$

But remember $(\Delta x)^2 = 2 D \Delta t$ where D is a diffusion constant so that

$$\Delta t\, j_{diff} = -MD \frac{dP}{dx} \Delta t$$

The drift flux is due to the force $-\frac{dU_{tot}}{dx}$. This is simply $-\frac{MD}{k_B T} \frac{dU_{tot}}{dx} P(x)\, \Delta t = j_{drift}$

~~Hence~~ Hence the total number of crossings from left to right is

$$j^{(1d)} \equiv -MD\left(\frac{dP}{dx} + \frac{1}{k_BT} P \frac{dU_{tot}}{dx}\right)$$

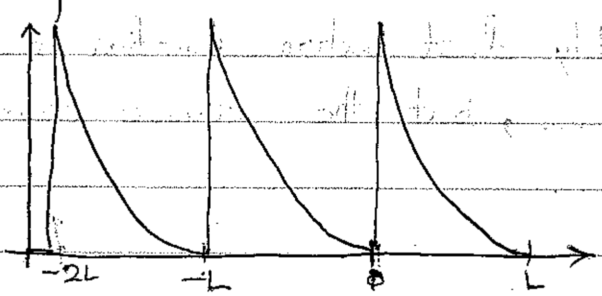
We want that this flux should be time independent and hence the probability should not pile up anywhere. This means that $j^{(1d)}$ should be independent of x. Hence we want,

$$\frac{d}{dx}\left(\frac{dP}{dx} + \frac{1}{k_BT} P \frac{dU_{tot}}{dx}\right) = 0$$

This is exactly Smoluchowski's equation.

At eqbm we want to find some spatially periodic solutions to equation above. Suppose $U_{tot}(x)$ is periodic, meaning $U_{tot}(x) = U_{tot}(x+L)$, then we have an S-ratchet with force $f = \epsilon/L$. In this case $P(x) = Ce^{-\frac{U_{tot}(x)}{k_BT}}$ gives a periodic, time independent probability distribution. $j^{(1d)} = 0$ everywhere. This is the Boltzmann distribution.

Beyond eqbm: We assume perfect ratchet. As soon as the ratchet arrives at one of the steps it falls down and cannot return. $P(x)$ is nearly zero to the left of each step.



$P(x) = C\left(e^{-(x-L)f/k_BT} - 1\right)$ solves Smoluchowski's equation with $U_{tot}(x) = fx$. Moreover the flux is

$$j^{(1D)} = -MD\left(-\frac{Cf}{k_BT}e^{-\frac{(x-L)f}{k_BT}} + \frac{1}{k_BT}Cf\left(e^{-\frac{(x-L)f}{k_BT}} - 1\right)\right)$$

$$= +MD\frac{Cf}{k_BT} > 0 \quad \text{everywhere}$$

If we want to find the average velocity of a ratchet we need to determine how many ratchets are located between 0 and L and then determine the average time Δt it takes for all of them to cross $x=L$ from left to right using the flux $j^{(1D)}$ obtained above.

$$\Delta t = \frac{\int_0^L MP(x)\,dx}{j^{(1D)}}$$

And $v = \dfrac{L}{\Delta t} = \dfrac{Lj^{(1D)}}{\int_0^L MP(x)\,dx} = \dfrac{k_BT}{Df}\int_0^L\left(e^{-(x-L)f/k_BT} - 1\right)dx$

Or, $v = \left(\dfrac{fL}{k_BT}\right)^2\dfrac{D}{L}\left(e^{fL/k_BT} - 1 - \dfrac{fL}{k_BT}\right)^{-1}$

This model is valid only in the low force limit when $f \ll \frac{\epsilon}{L}$. To see why think about what the velocity should be when f is very large, the ratchet will be expected to move in reverse but it cannot. When $f=0$ then the probability distribution function is a constant between 0 and L, but the above expression gives $P(x)=0$.

DIFFUSION AS A RANDOM WALK.

One of the things we learnt fro a free Langevin particle was that after long times (at eqbm) $\langle r^2 \rangle = 6Dt$. Can we derive this result using simpler methods? We can do so by recognising that the motion of the Brownian particle is a random walk. A particle suffers displacements along a straight line in the form of a series of steps of equal length each being taken either in the forward or backward direction with equal probability 1/2.

After N steps particle could be at:

$-N, -N+1, ---, -1, 0, +1, ---, N-1, N$

<u>Question</u>: What is the probability $W(m, N)$ that the particle arrives at point m after suffering N displacement. We need to take $\frac{N+m}{2}$ steps forward and $\frac{N-m}{2}$ steps backward. Probability of any given sequence of N steps (in any direction is) $(\frac{1}{2})^N$. Hence,

$$W(m,N) = \frac{\lfloor N}{\lfloor \frac{1}{2}(N+m) \lfloor \frac{1}{2}(N-m)} \left(\frac{1}{2}\right)^N = {}^N C_{\frac{N+m}{2}} \left(\frac{1}{2}\right)^N.$$

note that both m and N need to be both odd or both even.

This is a Bernoulli distribution of the type $w(x) = {}^n C_x p^x (1-p)^{n-x}$.

$$\langle x \rangle_{av} = \sum_{x=1}^{N} x\, W(x)$$

$$= \sum_{x=1}^{n} x \times \{\text{coeff of } u^x \text{ in } (pu+q)^n\} \qquad q = 1-p$$

$$= \sum_{x=1}^{n} \text{coeff of } u^x \text{ in } \frac{d}{du}(pu+q)^n$$

$$= \left[\frac{d}{du}(pu+q)^n\right]_{u=1} = np(p+q) = np .$$

$$\langle x^2 \rangle_{av} = \sum_{x=1}^{n} x^2 \times \{\text{coeff of } u^x \text{ in } (pu+q)^n\}$$

$$= \sum_{x=1}^{n} \text{coeff of } u^x \text{ in } \frac{d}{du}\left(u\frac{d}{du}(pu+q)^n\right)$$

$$= \left[\frac{d}{du}\left(u\frac{d}{du}(pu+q)^n\right)\right]_{u=1}$$

$$\langle x^2\rangle_{av} = np + n(n-1)p^2$$

Moreover, $\delta^2 = \langle(x - \langle x\rangle_{av})^2\rangle = \sum_{x=1}^{n} x^2 W(x) - \langle x\rangle_{av}^2$

$$= np(1-p) = npq.$$

We get back to our random-walk problem and see

$$\frac{1}{2}\langle N+m\rangle_{av} = \frac{1}{2}N \Rightarrow \langle m\rangle_{av} = 0$$

$$\left\langle\left(\frac{1}{2}(N+m) - \frac{1}{2}N\right)^2\right\rangle = \frac{1}{4}N \Rightarrow \langle m^2\rangle_{av} = N$$

The root mean square displacement is $\sqrt{N}$. Let us make an approximation to the binomial distribution when N is large and $m \ll N$. Find $\log W(m,N)$.

$$\log W(m,N) = \log N! - \log\left(\tfrac{1}{2}(N+m)!\right) - \log\left(\tfrac{1}{2}(N-m)!\right) - N\log 2$$

Use two approximations:

(a) Stirling's formula $\rightarrow$ $\log \underline{n} = (n+\frac{1}{2})\log n - n + \frac{1}{2}\log 2\pi$

(b) $\log\left(1 \pm \frac{m}{N}\right) = \pm\frac{m}{N} - \frac{m^2}{2N^2} + \cdots$

$$\log W(m,N) \simeq (N+\tfrac{1}{2})\log N - \tfrac{1}{2}(N+m+1)\log\left[\frac{N}{2}\left(1+\frac{m}{N}\right)\right]$$

$$- \tfrac{1}{2}(N-m+1)\log\left[\frac{N}{2}\left(1-\frac{m}{N}\right)\right] - \tfrac{1}{2}\log 2\pi - N\log 2$$

Simplifying these expression gives,

$$W(m,N) = \left(\frac{2}{\pi N}\right)^{1/2} \exp\left(-\frac{m^2}{2N}\right)$$

If we now assume that $x = ml$ where l is the size of each step and ask for the probability density $W(x)$

of finding the particle between $x+\Delta x$ and x. This will be given by:

$$W(x,N) = \frac{W(m,N)}{2l}$$

Because the interval can only be $2l$ long depending on N even or odd.

Using $x = ml$ we can write,

$$W(x,N) = \left(\frac{1}{2\pi N l^2}\right)^{1/2} \exp\left(-\frac{x^2}{2Nl^2}\right)$$

Gaussian of the type $A\exp\left(-\frac{x^2}{2\sigma^2}\right)$

Here $\sigma^2 = \langle x^2 \rangle = 2Dt$

And if the particle takes 'n' displacements per unit time then we see that

$$W(x,t) = \frac{1}{2(\pi D t)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right) \quad \text{where } D = \frac{1}{2} N l^2.$$

We have assumed thus far that the length of each step is constant. What happens if this is not the case? Suppose we are given a set of numbers P_k which are the probability of taking a step of length kL. Let u be the mean value of k_j. (k_j is the value of k for step j).

$$u = \langle k_j \rangle = \sum_k k P_k .$$

'u' describes the drift motion superimposed on the random walk. Until now we assumed $P_{\pm 1} = \frac{1}{2}$ with all other $P_k = 0$. In this case $u = 0$. The mean position of the walker can now be written as,

$$\langle X_N \rangle = \langle X_{N-1} \rangle + L\langle k_N \rangle = \langle X_{N-1} \rangle + uL = NuL$$

We have used the fact that the mean displacement of each step is uL. Clearly for $P_{\pm 1} = \frac{1}{2}$ the mean displacement is 0. We are also interested in fluctuations around the mean.

$$\mathrm{var}(X_N) = \langle (X_N - \langle X_N \rangle)^2 \rangle = \langle (X_{N-1} + k_N L - NuL)^2 \rangle$$

$$= \langle ((X_{N-1} - u(N-1)L) + (k_N L - uL))^2 \rangle$$

$$= \langle (X_{N-1} - u(N-1)L)^2 \rangle + 2\langle (X_{N-1} - u(N-1)L)(k_N L - uL) \rangle + L^2 \langle (k_N - u)^2 \rangle$$

The N^{th} step length is a random variable that does not depend on the previous history. Hence for the middle term

$$2\langle (x_{N-1} - u(N-1)L)(k_N L - u)\rangle$$

$$= 2\langle x_{N-1} - u(N-1)L\rangle \langle k_N - u\rangle \quad = 0 \quad \text{(definition of } u\text{)}$$

We are left with,

$$\mathrm{var}(x_N) = \langle (x_{N-1} - \langle x_{N-1}\rangle)^2\rangle + L^2\langle (k_N - \langle k_N\rangle)^2\rangle$$

$$= \mathrm{var}(x_{N-1}) + L^2\,\mathrm{var}(k)$$

Hence after N steps the variance is $NL^2\,\mathrm{var}(k)$. If the steps come every Δt then,

$$\mathrm{var}(x_N) = 2Dt \quad \text{where} \quad D = \frac{L^2}{2\Delta t} \times \mathrm{var}(k)$$

We have found that diffusion is a powerful idea. As long as we have a random walk (with no history dependence) the idea that $\langle x^2\rangle \propto Dt$ is valid.

POLYMERS AS RANDOM WALKS

We had modeled a diffusing particle as a random walk with equal step lengths. We had determined that in one dimension the probability of finding the particle at a distance between x and $x+dx$ was given by

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

where $\sigma^2 = \langle x^2 \rangle = N b^2$ and 'b' was the step length. The steps could be links of a freely jointed chain (FJC) fluctuating because of thermal motions. If we think of 'x' as 'r_{ee}' the end-to-end distance and the polymer to be consisting of N links then the probability distribution function for r_{ee} is simply

$$P(r_{ee}) = \frac{1}{\sqrt{2\pi N b^2}} \exp\left(-\frac{r_{ee}^2}{2N b^2}\right)$$

We want to be more realistic and see what happens when the chain is not one-dimensional but three-dimensional. By projecting their configurations onto a set of Cartesian axes, three dimensional random chains can be treated as three separate one-dimensional chains. For example,

$$r_{ee,x} = \sum_i b_{i,x}$$

where $b_{i,x}$ is the x-projection of the monomer vector $\underline{b}_i$. The vectors $\underline{b}_i$ are all assumed to have the same length but $b_{i,x}$ will be of variable length. Even so we know that

$$P(r_{ee,x}) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{r_{ee,x}^2}{2\sigma^2}\right)$$

where $\sigma^2 = N\langle b_x^2 \rangle$. Because of symmetry we expect that $\langle b_x^2 \rangle = \langle b_y^2 \rangle = \langle b_z^2 \rangle = b^2/3$.

Hence $\sigma^2 = \dfrac{Nb^2}{3}$.

If we now want the probability that the end of the chain be between (x,y,z) and $(x+dx, y+dy, z+dz)$ then

$$P(x,y,z) = P(x)\,P(y)\,P(z) = \frac{1}{(2\pi\sigma^2)^{3/2}} \exp\left(-\frac{x^2+y^2+z^2}{2\sigma^2}\right)$$

and $\sigma^2 = Nb^2/3$ with $x \equiv r_{ee,x}$ etc. Now the probability for the chain having a radial end-to-end distance between r and $r+dr$ is $P_{rad}(r)\,dr$ where $P_{rad}(r)$ is a probability per unit length such that

$$P(x,y,z)\,dx\,dy\,dz = P_{rad}(r)\,dr$$

$$\Rightarrow \quad P(r) = 4\pi r^2 (2\pi\sigma^2)^{-3/2} \exp\left(-\frac{r^2}{2\sigma^2}\right)$$

$4\pi r^2$ comes from isotropic behavior. The most likely value of 'r' is obtained by doing $\frac{dP_{rad}(r)}{dr} = 0$.

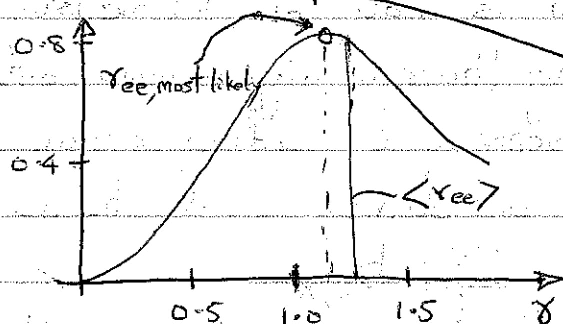
We find that,

0.8164

$$r_{ee,\text{most likely}} = \sqrt{\frac{2}{3}}\, N^{1/2} b$$

$$\langle r_{ee} \rangle = \sqrt{\frac{8}{3\pi}}\, N^{1/2} b \quad , \quad \langle r_{ee}^2 \rangle = Nb^2$$

0.9213

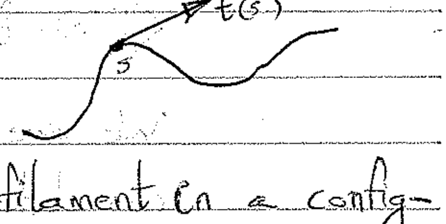


Clearly far more chains have end-to-end displacements close to the mean $\langle r_{ee} \rangle$, than to the contour length L_c. Hence $S = k_B \log \Omega$ (Ω is number of configurations) must decrease as the chain is stretched from its equilibrium length. The free energy of an ensemble of chains is $F = \cancel{E}^{\,0} - TS = -TS$ since all configuration have vanishing energy.

Thus S decreases and F increases as the chain is stretched at non-zero temperature. Work must be done to stretch the chain; this is <u>entropic elasticity</u>. For small displacements from equilibrium we can use Hookes Law to determine the stiffness of our entropic spring. If 'x' is the end-to-end distance of a Hookean spring then by the Boltzmann statstics $P(x) \sim \exp\left(-\frac{k_{sp}x^2}{2k_BT}\right)$ where k_{sp} is the spring constant. For our ideal chain $P(x) \sim \exp\left(-\frac{x^2}{2\sigma^2}\right)$. Comparing these two expressions we find that our entropic spring has a stiffness $k_{sp} = \frac{k_BT}{\sigma^2}$ where $\sigma^2 = \frac{Nb^2}{d}$ for ideal chains in 'd' dimensions. $k_{sp} = \frac{3k_BT}{Nb^2}$ in three-dimension. The spring constant increases with temperature, a signature of its entropic origins.

The parameter '<u>b</u>' appears in the expression above. It is the link length in the FJC model. We can think of the monomer size as a link length, but is there something deeper to consider here. Remember 'b' is such that the tangents at $\underline{x}$ and $\underline{x}+b$ are independent of each other or uncorrelated. At lengths much shorter than 'b' the tangents are strongly correlated. We will think of a polymer as a fluctuating rod which constantly exchanges energy with its environment by bending. The bending is governed by an energy

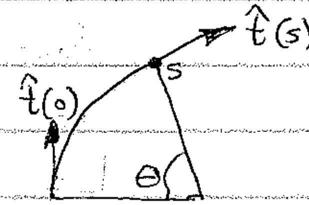
$$E_{bend} = \frac{K_b}{2}\int_0^{L_c}\left(\frac{\partial \hat{t}}{\partial s}\right)^2 ds$$



Now the probability P(E) of finding the filament in a configuration of energy E is proportional to $\exp\left(-\frac{E_{bend}}{k_BT}\right)$.

Let us assume that our filament can sustain only gentle curves, has constant curvature and is short.

This is shown as an arc of a circle.



For this arc, $E_{arc} = \dfrac{K_b \theta^2}{2s}$

The angle 'θ' changes as the filaments ~~xxxxx~~ fluctuates. At larger temperatures θ fluctuates a lot and vice-versa at lower temperatures. We can characterize these fluctuations by calculating $\langle \theta^2 \rangle$. Assuming the shapes in the ensemble are arcs of a circle we want

$$\langle \theta^2 \rangle = \frac{\int \theta^2 P(E_{arc})\, d\Omega}{\int P(E_{arc})\, d\Omega}$$

Here $d\Omega$ = solid angle = $\sin\theta \, d\theta \, d\phi$. This is the solid angle subtended by the end of the filament. E_{arc} is independent of ϕ hence,

$$\langle \theta^2 \rangle = \frac{\int \theta^2 \exp(-\beta E_{arc})\, d\theta \sin\theta}{\int \exp(-\beta E_{arc})\, d\theta \sin\theta}$$

Assume now that 'θ' is small then,

$$\langle \theta^2 \rangle = \frac{\int_{-\infty}^{+\infty} \theta^3 \exp(-\beta K_b \theta^2/2s)\, d\theta}{\int_{-\infty}^{+\infty} \theta \exp(-\beta K_b \theta^2/2s)\, d\theta} = \frac{2s}{\beta K_b}$$

We can change limits to $\pm\infty$ without much error. We find that $\langle \theta^2 \rangle = \dfrac{2s}{\beta K_b}$ for small oscillations.

$\beta K_b = \dfrac{K_b}{k_B T} = \xi_p$ is the persistence length. Now,

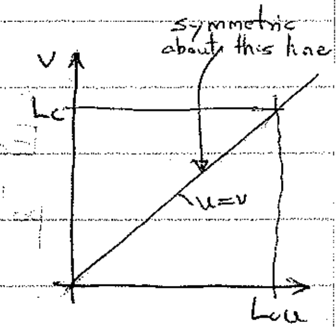
$$\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \langle \cos\theta \rangle \sim \left\langle 1 - \frac{\theta^2}{2} \right\rangle = 1 - \frac{s}{\xi_p}$$

We see clearly that when oscillations are small the correlation function of the tangent vector decreases with length. In fact, the correct expression is $\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \exp(-s/\xi_p)$.

We will now connect the tangent-tangent correlation function back to r_{ee} the end-to-end vector. Remember,

$$\underline{r}(s) = \underline{r}(0) + \int_0^s du\, \hat{t}(u)$$

Hence $\langle \underline{r}_{ee}^2 \rangle = \int_0^{L_c} du \int_0^{L_c} dv \langle \hat{t}(u) \cdot \hat{t}(v) \rangle$



$$= \int_0^{L_c} du \int_0^{L_c} dv \exp\left(-\frac{|u-v|}{\xi_p}\right)$$

$$= 2 \int_0^{L_c} du \int_0^{u} dv \exp\left(-\frac{(u-v)}{\xi_p}\right)$$

$$= 2 \int_0^{L_c} du \exp\left(-\frac{u}{\xi_p}\right) \xi_p \cdot \left[\exp\left(\frac{u}{\xi_p}\right) - 1\right]$$

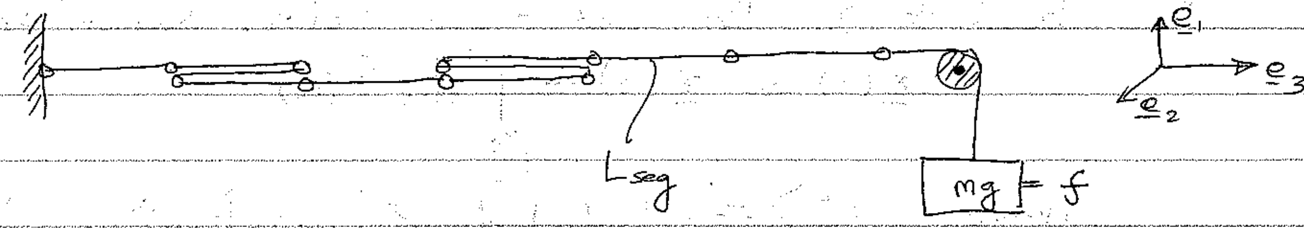
$$= 2\xi_p^2 \int_0^{L_c/\xi_p} dw \left[1 - \exp(-w)\right]$$

We finally get $\langle \underline{r}_{ee}^2 \rangle = 2\xi L_c - 2\xi_p^2 \left[1 - \exp\left(-\frac{L_c}{\xi_p}\right)\right]$

If $\xi_p \gg L_c$ then $\langle \underline{r}_{ee}^2 \rangle^{1/2} = L_c$ (rod like) while if $\xi_p \ll L_c$ $\langle \underline{r}_{ee}^2 \rangle \sim 2\xi_p L_c$. But we already saw that in the FJC model $\langle \underline{r}_{ee}^2 \rangle = Nb^2 = bL_c$. Hence, the fluctuating rod model is equivalent to the FJC model with $b = 2\xi_p$.

ENTROPIC ELASTICITY OF FJC.

Let us first consider a two state system in one-dimension.



Each link can either point backward or forward. The potential energy of a given realization of the chain is

$$-fz = -f L_{seg} \sum_{i=1}^{N} \sigma_i \qquad (\sigma_i = \pm 1)$$

$$P(\sigma_1, \sigma_2, \dots, \sigma_N) = Z^{-1} \exp\left(+ \frac{f L_{seg}}{k_B T} \sum_{i=1}^{N} \sigma_i\right)$$

Z is the partition function. Now the desired average extension for some force 'f' will be,

$$\langle z \rangle = \sum_{\sigma_1=\pm1} \sum_{\sigma_2=\pm1} \dots \sum_{\sigma_N=\pm1} P(\sigma_1, \sigma_2, \dots, \sigma_N)\, z$$

$$= Z^{-1} \sum_{\sigma_1=\pm1} \sum_{\sigma_2=\pm1} \dots \sum_{\sigma_N=\pm1} e^{\left(\frac{f L_{seg}}{k_B T} \sum_{i=1}^{N} \sigma_i\right)} L_{seg} \sum_{i=1}^{N} \sigma_i$$

$$= k_B T \frac{d}{df} \overbrace{\log\left[\sum_{\sigma_1=\pm1} \sum_{\sigma_2=\pm1} \dots \sum_{\sigma_N=\pm1} \exp\left(\frac{f L_{seg}}{k_B T} \sum_{i=1}^{N} \sigma_i\right)\right]}^{\log Z}$$

$$= k_B T \frac{d}{df} \log\left[\left(\sum_{\sigma_1=\pm1} \exp\left(\frac{f L_{seg} \sigma_1}{k_B T}\right) \sum_{\sigma_2=\pm1} \exp\left(\frac{f L_{seg} \sigma_2}{k_B T}\right) \dots \right.\right]$$

$$= k_B T \frac{d}{df} \log\left(e^{\frac{f L_{seg}}{k_B T}} + e^{-\frac{f L_{seg}}{k_B T}}\right)^N$$

$$\langle z \rangle = N L_{seg} \tanh\left(\frac{f L_{seg}}{k_B T}\right) \Rightarrow \frac{\langle z \rangle}{L_{tot}} = \tanh\left(\frac{f L_{seg}}{k_B T}\right)$$

This is the force versus extension of 1D FJC. Clearly for large forces the extension $\frac{\langle z \rangle}{L_{tot}}$ will come close to 1 and the same goes for low temperatures as well. We will now try to repeat this calculation in 3D.

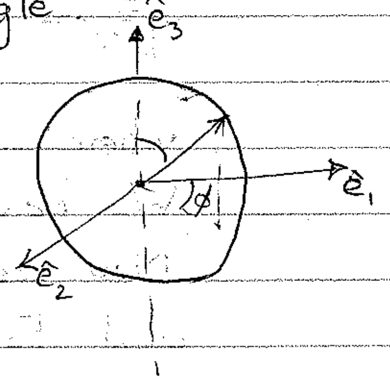
When we have a 3D chain of segments the segments need not point in the $\pm\hat{e}_3$ directions. They can point whicever way they like. This time the end-to-end extension is $\sum_i L_{seg}\hat{t}_i\cdot\hat{e}_3$. The probability of finding a configuration with given $\hat{t}_i$ is,

$$P(\hat{t}_1,\hat{t}_2,\ldots,\hat{t}_N) = Z^{-1}\exp\left(\frac{fL_{seg}}{k_BT}\sum_i \hat{t}_i\cdot\hat{e}_3\right)$$

We can repeat some of the steps from before and find

$$Z = \left[\exp\left(\frac{fL_{seg}}{k_BT}\int_{\substack{\text{sum over}\\ \text{all config}}} \hat{t}_i\cdot\hat{e}_3\right)\right]^N$$

We are integrating over all possible values of $\hat{t}_i$. But $\hat{t}$ is parametrized by two angles (θ,ϕ) where θ is the angle to $\hat{e}_3$ axis and ϕ is the other angle.



$$Z = \left[2\pi\int_0^{\pi}\exp\left(\frac{fL_{seg}}{k_BT}\cos\theta\right)\sin\theta\, d\theta\right]^N$$

$$Z = \left[\frac{2\pi k_BT}{fL_{seg}}\left(e^{\frac{fL_{seg}}{k_BT}} - e^{-\frac{fL_{seg}}{k_BT}}\right)\right]^N$$

Now the free energy is $-k_BT\log Z = F$. And $\frac{dF}{df}$ is the extension.

$$\langle z\rangle = \frac{d}{df}\left(N\log\left[\frac{2\pi k_BT}{fL_{seg}}\left(e^{\frac{fL_{seg}}{k_BT}} - e^{-\frac{fL_{seg}}{k_BT}}\right)\right]\right)$$

$$\frac{\langle z\rangle}{L_{tot}} = \frac{d}{dx}\log\left(\frac{1}{x}\sinh(x)\right) \qquad \text{where } x = \frac{fL_{seg}}{k_BT}$$

$$= \frac{\cosh(x)}{\sinh(x)} - \frac{1}{x} \Rightarrow \boxed{\frac{\langle z\rangle}{L_{tot}} = \coth\left(\frac{fL_{seg}}{k_BT}\right) - \frac{k_BT}{fL_{seg}}}$$

This will go to zero as $x\to 0$ and will go to 1 as $x\to\infty$.