University of Washington
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Lecture 3: Random Flight Polymers
Text Reading: Chandrasekhar, Ch. 1.1

A. Application: Random Flight Polymer

- Suppose we have a linear polymer composed of N monomeric segments each of length ℓ. We can imagine that a vector is drawn from one end of the polymer to the other. Designate the end-to-end vector $\vec{r}$. Now if the shape of the polymer obeys random flight statistics the mean value of this vector is $\langle \vec{r} \rangle = 0$.
- Let us assume h is the projection of a unit bond onto the z axis. Then in terms of the monomer length h is $h = \ell \cos\theta$. The z component of the distribution function has the form

$$f(z) = \frac{1}{\sqrt{2\pi N\sigma^2}} e^{-z^2/2\sigma^2 N} \tag{3.1}$$

  where θ is the angle between the bond and the z axis and $\sigma^2 = \langle h^2 \rangle$.
- Now the angle θ can vary in a random flight because different bonds can be at different angles to the z axis. Therefore

$$\begin{aligned}\sigma^2 &= \langle h^2 \rangle = \langle \ell^2 \cos^2\theta \rangle = \ell^2 \langle \cos^2\theta \rangle \\ &= \ell^2 \int_0^\pi d\theta \sin\theta \cos^2\theta = \ell^2/3\end{aligned} \tag{3.2}$$

- Put (3.2) into (13.1)…

$$f(z) = \frac{1}{\sqrt{2\pi N\sigma^2}} e^{-z^2/2\sigma^2 N} = \frac{\sqrt{3}}{\sqrt{2\pi N\ell^2}} e^{-3z^2/2\ell^2 N} \tag{3.3}$$

- F(z)dz is the probability that a polymer vector projects onto the z axis between z and z+dz. If random flight statistics are obeyed the x, y, and z excursions are independent such that

$$\begin{aligned}&f(x,y,z)\,dxdydz = f(x)\,f(y)\,f(z)\,dxdydz \\ &= \left(\frac{3}{2\pi N\ell^2}\right)^{3/2} e^{-3\left(x^2+y^2+z^2\right)/2\ell^2 N} dxdydz = \left(\frac{3}{2\pi N\ell^2}\right)^{3/2} e^{-3r^2/2\ell^2 N} d\varphi \sin\theta d\theta r^2 dr\end{aligned} \tag{3.4}$$

  where it is further assumed in (3.4) that the x, y, and z excursions of the polymer are equivalent on average.
- It is more general to use the radial distribution function which is obtained after integrating over θ and φ:

$$f(r)4\pi r^2 dr = \left(\frac{3}{2\pi N\ell^2}\right)^{3/2} e^{-3r^2/2\ell^2 N} 4\pi r^2 dr \tag{3.5}$$

- Equation 3.5 is valid for a three dimensional random flight polymer and requires that $\langle r^2\rangle = N\ell^2$ or $r_{rms} = \sqrt{\langle r^2\rangle} = N^{1/2}\ell$. Because N is proportional to the molecular weight M, this means the mean square end-to-end vector is proportional to the square root of molecular weight if the polymer obeys the RFM. The expression can be generalized as:

$$f(r)4\pi r^2 dr = 4\pi\left(\frac{3}{2\pi\langle r^2\rangle}\right)^{3/2} e^{-3r^2/2\langle r^2\rangle} r^2 dr \tag{3.6}$$

where $\langle r^2\rangle$ can deviate from the RFM result. Examples are found below…

C. Realistic Polymers

- Suppose the jth bond in the main chain of a polymer is designated by a vector $\vec{\ell}_j$. These vectors are at a fixed angle θ relative to each other but the polymer chain can reorient randomly about each bond. The mean-end-to-end vector is:

$$\begin{aligned}\langle r^2\rangle &= \left\langle \sum_{j,k} \vec{\ell}_j \bullet \vec{\ell}_k \right\rangle = \sum_{j,k}\left\langle \vec{\ell}_j \bullet \vec{\ell}_k \right\rangle = \sum_j \left\langle \vec{\ell}_j \bullet \vec{\ell}_j \right\rangle + 2\sum_j \left\langle \vec{\ell}_j \bullet \vec{\ell}_{j+1} \right\rangle + 2\sum_j \left\langle \vec{\ell}_j \bullet \vec{\ell}_{j+2} \right\rangle + \dots \\ &= N\ell^2 + 2(N-1)\left\langle \vec{\ell}_1 \bullet \vec{\ell}_2 \right\rangle + 2(N-2)\left\langle \vec{\ell}_1 \bullet \vec{\ell}_3 \right\rangle + \dots + 2\left\langle \vec{\ell}_1 \bullet \vec{\ell}_N \right\rangle\end{aligned} \tag{3.7}$$

- A closed form for the averages would be: $\left\langle \vec{\ell}_1 \bullet \vec{\ell}_n \right\rangle = \ell^2 \cos^n\theta$ and (3.7) becomes:

$$\begin{aligned}\langle r^2\rangle &= N\ell^2 + 2(N-1)\left\langle \vec{\ell}_1 \bullet \vec{\ell}_2 \right\rangle + 2(N-2)\left\langle \vec{\ell}_1 \bullet \vec{\ell}_3 \right\rangle + \dots + 2\left\langle \vec{\ell}_1 \bullet \vec{\ell}_N \right\rangle \\ &= N\ell^2 + 2(N-1)\ell^2\cos\theta + 2(N-2)\ell^2\cos^2\theta + \dots + 2\ell^2\cos^{N-1}\theta\end{aligned} \tag{3.8}$$

- Because $cos^n\theta$<<1, this series converges quickly with n and we only have to retain terms for which N-n~N. Then (3.8) becomes:

$$\begin{aligned}\langle r^2\rangle &= N\ell^2 + 2(N-1)\ell^2\cos\theta + 2(N-2)\ell^2\cos^2\theta + \dots + 2(N-n)\cos^n\theta + \dots \\ &\approx N\ell^2\left(1 + 2\cos\theta + 2\cos^2\theta + \dots + 2\cos^n\theta + \dots\right) = N\ell^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right)\end{aligned} \tag{3.9}$$

where we have used the fact that $a\sum_{j=0}^{\infty} r^j = \frac{a}{1-r}$ for -1<r<1.

- For a polymer like polyethylene, $\theta = 70^\circ 32' \Rightarrow \cos\theta = \frac{1}{3}$ so that

$$\langle r^2\rangle = 2\ell^2 N \tag{3.10}$$

- If rotation around each bond is not free but associated with a potential u(φ), (3.9) becomes

$$\left\langle r^2\right\rangle = N\ell^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\left\langle\cos\varphi\right\rangle}{1-\left\langle\cos\varphi\right\rangle}\right) \tag{3.11}$$

where $\left\langle\cos\varphi\right\rangle = \dfrac{\int_0^{2\pi}\cos\varphi e^{-u(\varphi)/kT}d\varphi}{\int_0^{2\pi}e^{-u(\varphi)/kT}d\varphi}$

B. The Diffusion Coefficient

- Before proceeding to describe the Langevin theory of Brownian motion, we need to obtain a more physical view of the forces that produce this motion.
- Assume a particle moves in three dimensions under the influence of an external force. Note: Because we work here in three dimensions, we use the notation of vector calculus: grad and div.

$$F_{ext} = -grad\left(V\left(x,y,z\right)\right) = -\left(\frac{\partial V}{\partial x}+\frac{\partial V}{\partial y}+\frac{\partial V}{\partial z}\right) \tag{3.12}$$

where V(x,y,z) is the potential, the detailed nature of which will be discussed below. To save space, I would like to abbreviate V(x,y,z) as V(r).

- In addition the particle moves through a continuous medium, which exerts on the particle a drag force $F_d=-\zeta v$, where v is the velocity of the particle. Now the number of particles within a volume V at time t is

$$f\left(V,t\right) = \int\int\int f\left(x,y,z,t\right)dxdydz = \int_V f\left(r,t\right)dV \tag{3.13}$$

- To conserve particles, if the number of particles within V changes, it must be accounted for exactly by the total flux of particles in or out. The particle current or flux is defined as $\vec{J} = \vec{v}f\left(x,y,z,t\right)$. The particles that enter or leave the volume as accounted for by integrating over the entire surface S of the volume, the component of flux parallel to the local vector normal n to the local surface dS:

$$\frac{\partial}{\partial t}f\left(V,t\right) = \frac{\partial}{\partial t}\int_V f\left(r,t\right)dV = -\int_S \vec{J}\bullet\vec{n}dS \tag{3.14}$$

- Equation (3.14) is called the equation of continuity, Gauss' theorem relates the flux integral on the rhs of (3.14) to a volume integration:

$$\int_S \vec{J}\bullet\vec{n}dS = \int_V div\vec{J}dV \tag{3.15}$$

where $div\vec{J} = \vec{\nabla}\bullet\vec{J} = \dfrac{\partial J_x}{\partial x}+\dfrac{\partial J_y}{\partial y}+\dfrac{\partial J_z}{\partial z}$

- Putting (3.15) into (3.14) we get:

$$\frac{\partial}{\partial t}\int_V f\left(r,t\right)dV = -\int_V div\vec{J}dV \tag{3.16}$$

- Equate the integrands within the volume integrals in (3.16) to get

$$\frac{\partial f\left(r,t\right)}{\partial t}=-div\vec{J}=-\left[\frac{\partial J_x}{\partial x}+\frac{\partial J_y}{\partial y}+\frac{\partial J_z}{\partial z}\right] \tag{3.17}$$

- Equation (3.17) does not seem to have much to do with the diffusion equation but they are in fact the same. We can learn something about the diffusion coefficient D by exploring the form of the flux J. At steady state, forces on the Brownian particle are in balance, i.e.

$$F_{ext}+F_d=F_{ext}-\zeta v=0 \tag{3.18}$$

- Assume F_{ext} arises from the gradient in the chemical potential of the Brownian particle…which in the dilute limit is:

$$F_{ext}=-grad\left[f^{\circ}+k_BT\ln f\left(r,t\right)\right]=-\frac{k_BT}{f\left(r,t\right)}grad\left(f\left(r,t\right)\right) \tag{3.19}$$

- Put (3.19) into the steady state equation (3.18);

$$\begin{gathered}F_{ext}-\zeta v=-\frac{k_BT}{f\left(r,t\right)}\left[\frac{\partial}{\partial x}+\frac{\partial}{\partial y}+\frac{\partial}{\partial z}\right]f\left(r,t\right)-\zeta v=0\\ \therefore J=vf\left(r,t\right)=-\frac{k_BT}{\zeta}gradf\left(r,t\right)\end{gathered} \tag{3.20}$$

- Put (3.20) into (3.17) to get:

$$\begin{aligned}&\frac{\partial f\left(r,t\right)}{\partial t}=-divJ=-div\left[-\frac{k_BT}{\zeta}gradf\left(r,t\right)\right]=\frac{k_BT}{\zeta}div\left[gradf\left(r,t\right)\right]\\ &=\frac{k_BT}{\zeta}\nabla^2f\left(r,t\right)=D\nabla^2f\left(r,t\right)\end{aligned} \tag{3.21}$$

where the coefficient of translational diffusion is now seen to be:

$$D=\frac{k_BT}{\zeta}=\frac{\left\langle\Delta^2\right\rangle}{2\tau} \tag{3.22}$$

- The coefficient of friction ζ is a function of the shape of the particle and the viscosity of the medium. For a spherical particle of radius R moving in a continuous fluid with viscosity η the coefficient of friction is given by Stokes' law

$$\zeta=6\pi\eta R \tag{3.23}$$

- A subtle point about equation 3.23 is that it assumes the fluid "sticks" to the particle in the sense that the relative fluid velocity at the particle surface is zero. This is called a stick boundary condition. If the fluid moves over the particle surface, i.e. a slip boundary condition, the coefficient of friction is

$$\zeta=4\pi\eta R \tag{3.24}$$

- The coefficient of friction can also be applied to non-spherical molecules. Macromolecular oligomers can be modeled as a straight chain of N beads each of diameter δ:

$$\zeta=\frac{3\pi\eta\delta N}{\ln N} \tag{3.25}$$