

Polymer Physics
Quiz 4
February 5, 2021

Mitra D, Chatterji, *A Transient helix formation in charged semiflexible polymers without confinement effects*. J. Phys.: Condens. Matter **33** 044001 (2021) report on coarse grain Brownian dynamics simulations of a semi-flexible bead and spring model polymer chain. In the model, the beads on the chain are separated by a distance r . The bonds have a bending energy $u_b = \epsilon_b \cos(\theta)$ where θ is the angle between the bond vectors \mathbf{r}_i and \mathbf{r}_{i+1} . The beads have binary interactions with a harmonic spring potential energy $u_H = \kappa(r - a)^2$ where a is the separation distance between two beads. The spring constant is (A) $\kappa = 20kT/a^2$ or (B) $\kappa = 10kT/a^2$. In addition to bending energy and spring energy the beads have a repulsive Coulomb potential (charge repulsion) between beads, $u_c = \epsilon_c(a/r)$ with $\epsilon_c = 87.27kT$. The beads have a time dependent drag force $F = \zeta dx/dt$ where which in combination with the spring constant leads to a relaxation time constant for bead motion, $\tau = a^2 \zeta/kT$, which is the time for an isolated bead to diffuse a distance a . Case (B) includes excluded volume (long-range interactions) between beads at long index differences with two additional repulsive and hard-core potentials, notably $u_d = \epsilon_d (a/r)^3$ with $\epsilon_d = 107.70/kT$ and a hard-core cutoff at $r_c = 4a$ for long-range repulsive interactions. The simulation proceeds with: 1) random thermal motion of a monomer; 2) calculation of the total forces on each bead in the chain and; 3) motion of beads in response to these forces subject to the viscous drag term. This is repeated for all beads randomly for many iterations with each iteration representing one time-step of $\tau/10,000$. In most of the simulations the initial chain state is fully extended. The process is to relax the chain from the initial extended conformation. The point of the simulation is to observe the formation of transient helical structures associated with the Coulombic potential, u_c , which appear at about simulation time = τ . Mitra also studies the chains under stress and finds that the helical structures are stabilized when the chain is end-tethered.

- a) In the simulation the bending energy magnitude, ϵ_b , is used to tune the persistence length, l_p (eqns. 1 and 2). **Explain the origin of eqn. 2** by looking at the Strobl book p. 58 eqn. 2.138. Would you expect the persistence length to decrease with T ? Why?
- b) **Explain the origin of the harmonic spring potential** energy $u_H = \kappa(r - a)^2$. How does the force depend on the change in position $\Delta r = (r - a)$? How does this and the spring constant $\kappa = 20kT/a^2$ compare with our calculations for a Gaussian chain?
- c) **Explain why the equation $\tau = a^2 \zeta/kT$ reflects diffusive motion.** Obtain the mean square displacement for a Brownian particle and write it in terms of time = mean square distance. How does this compare with this expression? What is the diffusion coefficient from this equation? Does the functionality in temperature and with the drag coefficient make sense?

- d) Figure 1 shows a time sequence of a chain starting with (a) a rigid rod, then (b) showing “kinks” due to random thermal motion, then (c) relaxing the bending strain by forming a helix at a time $t = \tau$, then (d) relaxing the helix through thermal motion. **Explain how the three energy terms and the drag term for Case B control these stages of the transitory helix formation.**

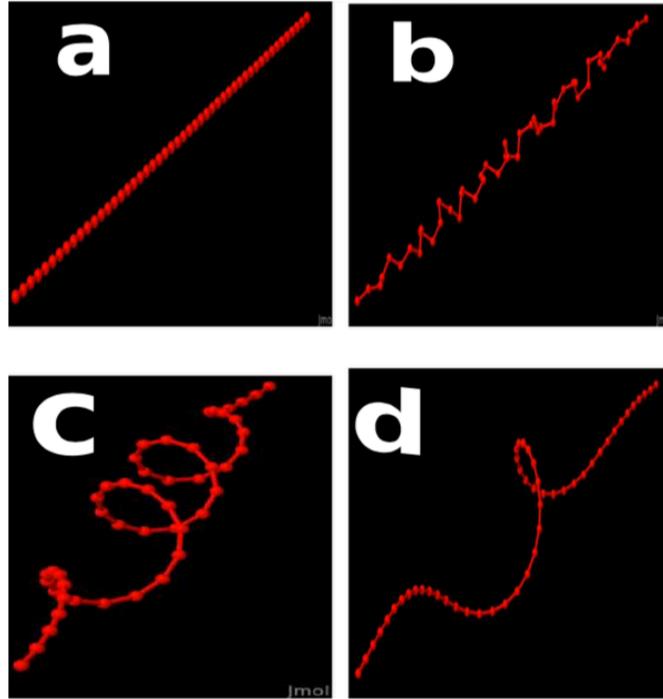


Figure 1. (a)–(d) shows various stages of the helical instability for a semi-flexible polymeric chain starting from the straight initial configuration with potential u_d : case B. The snapshots are (a) for the straight line initial configuration at time $t = 0$ with 49 monomers (b) the configuration at time $t = 3.3 \times 10^{-2}\tau$ ($H2 = 0.23, H4 = 0.006$) (c) the configuration at a subsequent time $t = \tau$, when the helix is formed ($H2 = 0.81, H4 = 0.43$) (d) configuration showing the unwinding of the helix at time $t = 5\tau$ ($H2 = 0.65, H4 = 0.29$). The corresponding snapshots with potential u_c (case A) are in the supplementary.

- e) Mitra interprets his results using global and local order parameters H4 and H2. They are based on the average cross product of the vectors $\mathbf{r}_i \times \mathbf{r}_{i+1}$. The cross product has direction orthogonal to the two vectors (normal to the plane made by the vectors) following the right-hand rule and having the magnitude of the sin of the angle between the vectors. For parallel vectors it is 0 and for orthogonal vectors it is maximum. The sum of \mathbf{u}_i (H4) would be 0 for a rod and maximum for a kinked chain with right angles between all bead vectors. The dot product of $\mathbf{u}_i \cdot \mathbf{u}_{i+1}$ (H2) is maximum if the cross products are parallel for neighboring beads and zero if they are orthogonal. **Explain how H4 reflects global ordering and H2 reflects local ordering of the chain in the context of transitory helix formation.**

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- a) *In the simulation the bending energy magnitude, ϵ_b , is used to tune the persistence length, l_p (eqns. 1 and 2). **Explain the origin of eqn. 2** by looking at the Strobl book p. 58 eqn. 2.138. Would you expect the persistence length to decrease with T ? Why?*

$$l_p \approx a\epsilon_b/k_B T \quad (2)$$

The Strobl discussion is good but seems to be a little confusing. Anyway, my read of it is, we know that $F_b = k_b r$ and that $du_b/dr = F_b$, so $u_b = \int k_b r dr = \frac{k_b r^2}{2}$. If you make a vector \mathbf{r}_i in the direction of the chain and \mathbf{r}_{i+1} in the curve at an angle θ , then $\Delta\mathbf{r} = \sin\theta$ if r is the unit vector. At small angles $\sin\theta \sim \theta$ in radians. So $u_b = \frac{k_b \theta^2}{2}$. If this energy equals kT then $kT = \frac{k_b \theta^2}{2}$. From the definition of the persistence length, $\langle t(r) \cdot t(r') \rangle = \exp\left(-\frac{\Delta r}{l_p}\right)$ for small arguments to the exponential this yields $\langle t(r) \cdot t(r') \rangle = \exp\left(-\frac{\Delta r}{l_p}\right) \sim 1 - \frac{\Delta r}{l_p}$ and from the definition of the dot product $\langle t(r) \cdot t(r') \rangle = \langle \cos\theta \rangle \sim 1 - \frac{\langle \theta^2 \rangle}{2} = 1 - \frac{\Delta r}{l_p}$ so $2\Delta r/l_p \sim \langle \theta^2 \rangle$. Then $kT = 2k_b \Delta r/l_p$ or $l_p \sim 2k_b \Delta r/kT$ so $a = \Delta r$, and $2k_b = \epsilon_b$.

- b) ***Explain the origin of the harmonic spring potential energy $u_H = \kappa(r - a)^2$. How does the force depend on the change in position $\Delta r = (r - a)$? How does this and the spring constant $\kappa = 20kT/a^2$ compare with our calculations for a Gaussian chain?***

For a spring $F = k_s \Delta r$ and $F = du/dr$, so $u_H = k_s \Delta r^2/2 = \kappa(r - a)^2$. For a Gaussian chain we found that $F = k_{spr} R$, and $k_{spr} = 3kT/\langle R^2 \rangle = 3kT/(nl^2)$. The spring constant is similar with $\langle R^2 \rangle$ replaced by a^2 , indicating that the beads are composed of Gaussian chains of average size $\langle R^2 \rangle^{1/2} = a$.

- c) ***Explain why the equation $\tau = a^2 \zeta/kT$ reflects diffusive motion. Obtain the mean square displacement for a Brownian particle and write it in terms of time = mean square distance. How does this compare with this expression? What is the diffusion coefficient from this equation? Does the functionality in temperature and with the drag coefficient make sense?***

For a Brownian particle starting at a position $x = 1$ for time $t = 0$, the density or concentration at a time t and position x can be expanded in a Taylor series either in time or in space (using a normalized, symmetric probability distribution, $P_G(\Delta x)$, (where Δx is the change in x from 0)). These two expansions must be equal:

$$\begin{aligned} \rho(x, t) + \tau \frac{\partial \rho(x)}{\partial t} + \dots \\ = \rho(x, t) \int_{-\infty}^{+\infty} P_G(\Delta x) d(\Delta x) + \frac{\partial \rho}{\partial x} \int_{-\infty}^{+\infty} \Delta x P_G(\Delta x) d(\Delta x) \\ + \frac{\partial^2 \rho}{\partial x^2} \int_{-\infty}^{+\infty} \frac{(\Delta x)^2}{2} P_G(\Delta x) d(\Delta x) + \dots \end{aligned}$$

On the righthand side the first integral is one by the definition of a normalized probability integral, the second integral term is zero by the definition of a symmetric probability function. If the diffusion coefficient is defined by,

$$D = \int_{-\infty}^{+\infty} \frac{(\Delta x)^2}{2\tau} P_G(\Delta x) d(\Delta x)$$

The Taylor series equality (ignoring higher order terms) becomes,

$$\frac{\partial \rho(x)}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$

Which is known as Fick's second law. For N particles starting at $x = 0$ and time = 0, the solution to this differential equation is a Gaussian distribution function,

$$\rho(x, t) = \frac{N}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

The first moment in space of this density distribution function is zero because it is symmetric (an initial assumption) but the second moment has a value,

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

From this equation it can be seen that the signature of diffusion is that the distance traveled $\langle x^2 \rangle^{1/2}$ is proportional to the square root of time, $t^{1/2}$. Which differs from ballistic motion where $x \sim t$. The equation $\tau = a^2 \zeta / kT$ reflects this behavior so it is a Brownian, diffusive expression.

From comparison of the two expressions, the diffusion coefficient is $D = kT/\zeta$. This is the Einstein/Stokes equation which reflects the fluctuation dissipation theorem if $\zeta = 6\pi\eta R_h$ where η is the solvent viscosity, the particles are spheres of radius R_h , the hydrodynamic radius.

Einstein obtained this expression in 1905 by considering a particle in a field which sets up a gradient mitigated by thermal diffusion such as sedimentation of particles in the gravitational field. The velocity of the particles due to gravity is $v_g = mg/(6\pi\eta R_h)$ following Stokes Law. For particles at $x = 0$ and $x=h$ height, the density difference is governed by a Boltzmann probability function,

$$\rho(h) = \rho_0 e^{-\frac{mgh}{kT}}$$

Fick's law gives the flux of particles, $J = -D dp/dh$, and $J = \rho v$, so $v = -(D/\rho) dp/dh$, and $dp/dh = -\rho_0 mg/(kT) e^{-mgh/kT} = -\rho mgh/(kT)$. Then, $v = Dmg/(kT)$. At equilibrium this speed equals the gravitational speed, $v_g = mg/(6\pi\eta R_h)$. Equating the two removes the details of the field, making a universal expression for any particle in any field, the Stokes-Einstein equation based on the Fluctuation Dissipation Theorem. (This was done in 1-d, the same applies in 3d.)

$$\frac{\langle x^2 \rangle}{2t} = D = \frac{kT}{6\pi\eta R_h} = \frac{RT}{6\pi\eta R_h N_A}$$

The latter expression was used to determine Avagadro's number from colloidal particles that could be counted, and then applied to molecular species to determine for the first time the molecular weight.

The idea that diffusion increases with temperature, given that it is based on thermal motion, makes sense. Also, the idea that diffusion slows down with drag also makes sense. So the functionality was predictable as a first guess.

- d) *Figure 1 shows a time sequence of a chain starting with (a) a rigid rod, then (b) showing “kinks” due to random thermal motion, then (c) relaxing the bending strain by forming a helix at a time $t = \tau$, then (d) relaxing the helix through thermal motion. **Explain how the three energy terms and the drag term for Case B control these stages of the transitory helix formation.***

This is explained in the text of the paper on page 3.

- e) *Mitra interprets his results using global and local order parameters H4 and H2. They are based on the average cross product of the vectors $\mathbf{r}_i \times \mathbf{r}_{i+1}$. The cross product has direction orthogonal to the two vectors (normal to the plane made by the vectors) following the right-hand rule and having the magnitude of the sin of the angle between the vectors. For parallel vectors it is 0 and for orthogonal vectors it is maximum. The sum of \mathbf{u}_i (H4) would be 0 for a rod and maximum for a kinked chain with right angles between all bead vectors. The dot product of $\mathbf{u}_i \cdot \mathbf{u}_{i+1}$ (H2) is maximum if the cross products are parallel for neighboring beads and zero if they are orthogonal. **Explain how H4 reflects global ordering and H2 reflects local ordering of the chain in the context of transitory helix formation.***

The two functions are rather complicated and their behavior is probably subject to different interpretations depending on the specific details of the structure. The authors are faced with the problem of quantitatively identifying the formation of helices in complex structures. They might be better off using an image recognition scheme and artificial intelligence computer code to identify helices in a learning procedure since the order parameter approach they have taken is rather complex and difficult to interpret. In any case, H4 is based on the cross products, so the sum of the cross products would reflect how non-linear the chain is with a maximum of $N-2$ since the two end groups do not contribute to H4. It isn't clear how this really relates to ordering or helical conformations. The sum of dot products of these cross products of neighboring vectors reflects on how neighboring beads are oriented with each other. So this is, in some sense, a local measure of how non-linear the chain is. Again, the connection with helicity is weak. Mitra was able to find signatures in these parameters at various transition points in the chain conformation with time which agree with changes in helicity. So he shows that they more or less work for his purpose.