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05. Polymers II

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5. Polymers II

Single Polymer in Solution [pln49]

Polymer in the form of N monomers linked into a chain by covalent bonds.

Sources of entropy S:

- Relative angles (polar and azimuthal) between successive monomers may have several local energy minima. Depending on how energy barriers relate to k_BT, angular coordinates are treated as discrete or continuous variables. Multiplicity of available conformational microstates contributes to entropy.
- Interface between polymer and solvent depends on polymer conformation (coil, helix, globule, ...). Solvent molecules bound to polymer in any particular conformation contribute negatively to entropy.

Sources of enthalpy H:

- Elastic energy between successive monomers (bending and stretching).
- Interactions between monomers that are distant or nearby on contour.
- Interactions between polymer and solvent molecules.

Gibbs free energy: $G = H - TS$.

- Coil conformation is most disordered. Conformational entropy has a maximum.
- To an application of tension between its ends, the polymer responds by stretching out, causing enthalpic and entropic changes. The macrostate settles such that G assumes a minimum.
- An attractive interaction between distant monomers may favor the formation of a polymeric globule, a form of intramolecular condensation. This brings an enthalpic gain, $\Delta H < 0$, but at an entropic cost, $\Delta S > 0$. The cost $T\Delta S$ is bigger at high T than at low T.
- An attractive interaction between nearby monomers may favor the formation of a helix conformation (in polypetides), a form of intramolecular crystallization. Unlike globules, which are more or less amorphous in structure, the helix is highly ordered. Therefore, it is formed at a higher entropic price. The enthalpic gain is associated with the formation of internal H-bonds.
- Either conformational change also involves enthalpic and entropic contributions associated with the interaction interfacial structure between polymer and solvent.

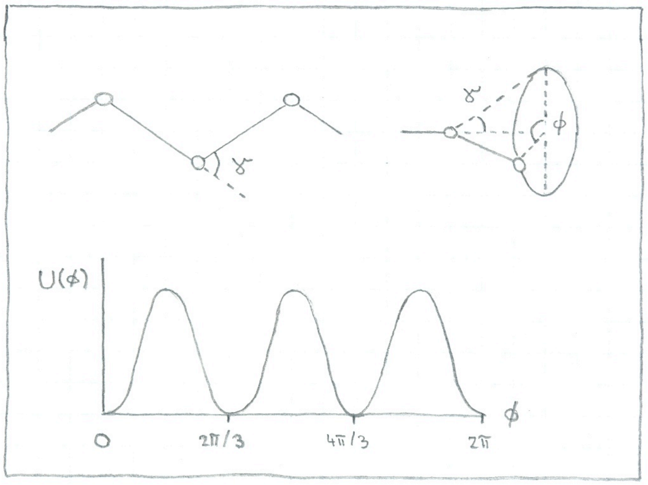
Ideal polymer chain (mathematical model):

- chain of immaterial links between successive monomers,
- no interactions between more distant monomers,
- interactions with solvent molecules accounted for by random force.

Models of ideal polymer chains differ in link structure (constraints) and type of bonding (energies). Such models help us understand the constraints on thermal motion and the restrictions on conformational entropy of polymers.

Flexibility is a characteristic attribute of polymers, which is modeled in various ways including geometric constraints or energetic discriminations on link configurations.

For example, a model may allow one particular valence angle γ and a continuum of internal rotation angles ϕ associated with a potential enrgy $U(\phi)$.



Measures of polymer size in common use:

Na: contour length, where N is the number of monomers of length a.

R_0: rms end-to-end distance,

R_g: radius of gyration defined as the rms distance of a monomer from the center of mass.

Freely Jointed Chain (FJC) [pln50]

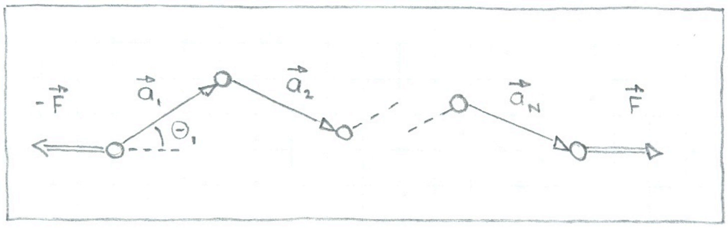
Random walk:

In the presence of only a random force exerted by the medium on each monomer the equilibrium conformation of an FJC polymer is a random walk. Self-avoidance and other volume interactions are negelcted as are constraints or elastic energies associated with the joints.

- Bond vector: $\mathbf{a}_i$,
- end-to-end distance vector: $\mathbf{r} = \sum_{i=1}^{N} \mathbf{a}_i$,
- free-joint condition: $\langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle = a^2 \delta_{ij}$,
- mean-square distance: $\langle \mathbf{r}^2 \rangle = \sum_{i,j=1}^{N} \langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle = Na^2$.
- rms end-to-end distance: $R_0 = \sqrt{N}a$.

Force-extension characteristics:

When the polymer experiences a stretching force F of growing strength, its conformation gets gradually more extended.



The FJC model approximates the stretching force as acting on each monomer in the same way, namely as a force seeking to align each monomer with the direction of the force in 3D space.

The solution of the FJC model is worked out in [pex53]. It shows some unphysical features associated with the entropy, which can be avoided by discretizing the orientations as shown in [pex54] and [pex55].

The continuous and discrete versions of the FJC model are equivalent to well-known models of ideal classical and quantum paramagnets, respectively.

[pex53] Freely jointed chain (FJC) model

Consider a chain of N freely jointed segments of length a subject to thermal fluctuations and to an external stretching force F. The FJC model approximates the stretching force as acting on each segment in the same way, namely as a force seeking to align each segment with the direction of the force in 3D space. The Hamiltonian splits into a sum of terms involving only individual segments,

$$\mathcal{H} = -\sum_{i=1}^{N} \vec{a}_i \cdot \vec{F} = -Fa \sum_{i=1}^{N} \cos\theta_i, \tag{1}$$

where θ_i is the polar angle of bond vector $\vec{a}_i$ relative to the direction $\vec{F}$. The canonical partition function factorizes and can be calculated as follows:

$$Z_N \doteq \mathrm{Tr}[e^{-\beta\mathcal{H}}] = Z_1^N, \quad Z_1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, e^{\beta Fa\cos\theta}, \quad \beta \doteq 1/k_BT. \tag{2}$$

(a) Evaluate Z_N and infer an expression from it for the Gibbs free energy $G(T,F,N) = -k_BT\ln Z_N$.
(b) Calculate the average end-to-end distance, $\langle L\rangle \doteq -(\partial G/\partial F)_{T,N} = \beta^{-1}\partial(\ln Z_N)/\partial F$. Plot a universal curve for the force-extension characteristic: scaled average length $\langle L\rangle/Na$ versus scaled force βFa. Find the leading term in an expansion of this function at weak forces.
(c) Calculate the fluctuations of the end-to-end distance, $\langle\langle L\rangle\rangle \doteq \langle L^2\rangle - \langle L\rangle^2 = \beta^{-2}\partial^2(\ln Z_N)/\partial F^2$. Plot the scaled mean-square distance $\langle\langle L^2\rangle\rangle/Na^2$ versus the scaled force βFa. Find the value of the mean-square distance in the absence of a force. Comment on all noteworthy features.
(d) Show that the entropy $S \doteq -(\partial G/\partial T)_{F,N}$ and the heat capacity $C_F \doteq T(\partial S/\partial T)_{F,N}$ are given by the following expressions:

$$\frac{S}{Nk_B} = \ln\left(4\pi\frac{\sinh(\beta Fa)}{\beta Fa}\right) + 1 - \beta Fa\coth(\beta Fa), \quad \frac{C_F}{Nk_B} = 1 - \frac{(\beta Fa)^2}{\sinh^2(\beta Fa)}. \tag{3}$$

Plot both functions over the range $0 < \beta Fa < 20$ and interpret the results. Note that βFa can be interpreted as scaled force at constant temperature or as inverse scaled temperature at constant force. Identify any features that are unphysical and, therefore, in need of being fixed by a better model.

Solution:

[pex54] Discretized FJC model I: force-extension characteristics

One unphysical feature of the FJC model discussed in [pex53] was that the heat capacity did not approach zero in the limit $T \to 0$. It stayed nonzero instead in violation of the third law of thermodynamics. This defect can be removed by discretizing the polar angle θ_i between the bond vector $\vec{a}_i$ and the direction of the applied force $\vec{F}$. We thus modify the Hamiltonian of [pex53] as follows:

$$\mathcal{H} = -Fa\sum_{i=1}^{N}\cos\theta_i = -Fa\sum_{i=1}^{N}\frac{m_i}{s}, \quad m_i = -s, -s+1, \ldots, s-1, s, \tag{1}$$

where s can assume any positive integer or half-integer value $\frac{1}{2}, 1, \frac{3}{2}, \ldots$. In the context of the Brillouin paramagnet [tex86], which is a different application of the same mathematical model, this discretization is very natural and represents spin quantization. The canonical partition function again factorizes and now involves the evaluation of a sum instead of an integral:

$$Z_N \doteq \mathrm{Tr}[e^{-\beta\mathcal{H}}] = Z_1^N, \quad Z_1 = \sum_{m=-s}^{+s} e^{\beta Fam/s}, \quad \beta \doteq 1/k_BT. \tag{2}$$

(a) Evaluate Z_N and infer the following expression for the Gibbs free energy from it:

$$G(T,F,N) = -k_BT\ln\left(\frac{\sinh\big(\beta Fa(1+1/2s)\big)}{\sinh(\beta Fa/2s)}\right). \tag{3}$$

(b) Calculate expressions for the average end-to-end distance via $\langle L\rangle \doteq \beta^{-1}\partial(\ln Z_N)/\partial F$ and the mean-square end-to-end distance $\langle\langle L^2\rangle\rangle \doteq \beta^{-2}\partial^2(\ln Z_N)/\partial F^2$. Show that in the limit $s \to \infty$ the expression derived in [pex53] for the same quantities naturally emerge.
(c) Plot a set of curves with $s = \frac{1}{2}, 1, \frac{3}{2}, 5, 10, 50$ for both quantities over the range $0 < \beta FA < 10$ as solid lines. Then add dashed curves for the results representing the original (continuum) FJC model. Interpret the results.

Solution:

[pex55] Discretized FJC model II: entropy and heat capacity

Here we examine how the unphysical features of the original (continuum) FJC detected in [pex53] are removed in the discretized version as solved in [pex54]. We begin with the expression for the Gibbs free energy:

$$G(T,F,N) = -k_BT\ln\left(\frac{\sinh\big(\beta Fa(1+1/2s)\big)}{\sinh(\beta Fa/2s)}\right) \tag{1}$$

(a) Calculate expressions for the entropy via $S \doteq -(\partial G/\partial T)_{F,N}$ and for the heat capacity via $C_F \doteq T(\partial S/\partial T)_{F,N}$. Show that in the limit $s \to \infty$ the expressions derived in [pex53] for the same quantities naturally emerge, except for an additive term in the entropy.
(b) Plot a set of curves with $s = \frac{1}{2}, 1, \frac{3}{2}, 5, 10, 50$ for $S/[Nk_B\ln(2s)]$ over the range $0 < (\beta FA)^{-1} < 2$ as solid lines. The extra scaling factor ensures convergence in the limit $s \to \infty$. Add a dashed line representing the same function for $s = 10000$ to represent a case much closer to the continuum limit. Describe what happens to entropy in the continuum limit. How does this result connect the result produced in [pex53]?
(c) Plot a set of curves with $s = \frac{1}{2}, 1, \frac{3}{2}, 5, 10, 50$ for $C_F/(Nk_B)$ over the range $0 < (\beta FA)^{-1} < 2$ as solid lines. Add a dashed line representing the result for $s \to \infty$ from [pex53]. Interpret what you observe.

Solution:

Binomial, Poisson, and Gaussian Distributions [nln8]

Consider a set of N independent experiments, each having two possible outcomes occurring with given probabilities.

events	$A + B = S$
probabilities	$p + q = 1$
random variables	$n + m = N$

Binomial distribution:

$$P_N(n) = \frac{N!}{n!(N-n)!}\, p^n (1-p)^{N-n}.$$

Mean value: $\langle n\rangle = Np$.

Variance: $\langle\langle n^2\rangle\rangle = Npq$. [nex15]]

In the following we consider two different asymptotic distributions in the limit $N \to \infty$.

Poisson distribution:

Limit #1: $N \to \infty$, $p \to 0$ such that $Np = \langle n\rangle = a$ stays finite [nex15].

$$P(n) = \frac{a^n}{n!}\, e^{-a}.$$

Cumulants: $\langle\langle n^m\rangle\rangle = a$.

Factorial cumulants: $\langle\langle n^m\rangle\rangle_f = a\delta_{m,1}$. [nex16]

Single parameter: $\langle n\rangle = \langle\langle n^2\rangle\rangle = a$.

Gaussian distribution:

Limit #2: $N \gg 1$, $p > 0$ with $Np \gg \sqrt{Npq}$.

$$P_N(n) = \frac{1}{\sqrt{2\pi\langle\langle n^2\rangle\rangle}} \exp\left(-\frac{(n-\langle n\rangle)^2}{2\langle\langle n^2\rangle\rangle}\right).$$

Derivation: DeMoivre-Laplace limit theorem [nex21].

Two parameters: $\langle n\rangle = Np$, $\langle\langle n^2\rangle\rangle = Npq$.

Special case of central limit theorem [nln9].

Persistence Length and Kuhn Segment Length [pln51]

More realistic models than the FJC model [pln50] take into account (i) geometric constraints and (ii) elastic energies associated with joints.

Both features introduce spatial memory of chain direction. The FJC model has no such memory beyond the distance between successive joints.

The two most common measures for spatial memory of chain direction are the *persistence length* l_p and the the *Kuhn segment length* l_K. The former has a more direct physical interpretation while the latter is, in general, easier to calculate.

Persistence length:

If s is the distance along the contour of the polymer between two (microscopic or mesoscopic) segments oriented at an angle θ between them, then $\langle\cos\theta(s)\rangle$ is a convenient measure for the mean directional change of the polymer over that distance, expected to decay exponentially as argued in [pex28]:

$$\langle\cos\theta(s)\rangle = e^{-s/l_\mathrm{p}},$$

where the persistence length l_p can be shown to grow with increasing bending stiffness in the joints and to shrink with increasing temperature due to thermal fluctuations [pex28].

Kuhn segment length:

If the polymer of contour length $L = Na$ can be conceived as a chain of N_s effectively freely jointed segments of length l_K then we have $L = N_\mathrm{s} l_\mathrm{K}$ and the mean-square end-to-end distance becomes

$$R_0^2 \doteq \langle\mathbf{r}^2\rangle = N_\mathrm{s} l_\mathrm{K}^2 = L l_\mathrm{K}.$$

The Kuhn segment length is thus defined as the ratio between the mean-square end-to-end distance and the contour length:

$$l_\mathrm{K} \doteq \frac{R_0^2}{L}.$$

In the FJC case [pln50] we have $R_0^2 = Na^2$ and $L = Na$. The Kuhn segment length assumes its minimum value, the length of a monomer: $l_\mathrm{K} = a$.

[pex28] Persistence length of ideal polymer chain

Consider an ideal polymer divided into segments of microscopic or mesoscopic length. If s is the distance between two segments along the chain then $\langle\cos\theta(s)\rangle$ is a convenient measure for the mean directional change of the polymer over that distance. It is expected to be a monotonically decreasing function between $\langle\cos\theta(0)\rangle = 1$ and $\langle\cos\theta(\infty)\rangle = 0$.
(a) Show that if this measure satisfies the multiplicativity property,

$$\langle\cos\theta(s+s')\rangle = \langle\cos\theta(s)\rangle\langle\cos\theta(s')\rangle,$$

implying $\langle\sin\theta(s)\rangle = 0$, then it must be an exponential function,

$$\langle\cos\theta(s)\rangle = e^{-s/l_\mathrm{p}}. \tag{1}$$

The persistent length l_p characterizes the contour distance over which memory of the chain direction is lost. In the synthetic polymer polystyrene the persistence length is estimated to be $l_\mathrm{p} \simeq 1.0-1.4$nm (about 4 to 5 links). In double-stranded DNA the estimate is $l_\mathrm{p} \simeq 50$nm (about 150 base pairs).
(b) Thermal fluctuations are expected to affect the persistence length. Here we explore that effect for the case of a stiff polymer with given bending stiffness in the face of thermally excited harmonic vibrations. Introducing classical bending modes of energy $\Delta E = (1/2)\Delta s\kappa(\Delta\theta/\Delta s)^2$, where $\Delta\theta/\Delta s$ is the curvature of a short segment and κ is the bending stiffness. Calculate the mean-square bending angle at thermal equilibrium from the relation

$$\langle(\Delta\theta)^2\rangle = 2\int_{-\infty}^{+\infty} d(\Delta\theta)(\Delta\theta)^2 e^{-\Delta E/k_BT} \Bigg/ \int_{-\infty}^{+\infty} d(\Delta\theta)e^{-\Delta E/k_BT}. \tag{2}$$

The integration boundaries are set to $\pm\infty$ for convenience. Contributions from unphysically large $|\theta|$ are strongly suppressed by the exponential weight factor. The factor 2 in the numerator accounts for the fact that bending takes place in two planes perpendicular to the local chain direction. Expand (1) for $\theta \ll 1$ and $s \ll \tilde{l}$ to arrive at the relation $\langle(\Delta\theta)^2\rangle = 2\Delta s/l_\mathrm{p}$. Substitute the result of (2) to show that the persistent length has the following T-dependence:

$$l_\mathrm{p} = \frac{\kappa}{k_BT}.$$

Conclusion: the persistent length is aided by bending stiffness and impeded by thermally excited bending modes.

[adapted from Grosberg and Khokhlov 1994]

Solution:

[pex29] Kuhn segment length of ideal polymer chain

Flexibility is an intrinsic property of polymers. Consider an ideal polymer chain with N links of length a. Its contour length is $L = Na$. If we divide that chain into segments of length $l \geq a$ then, with growing size of these segments, the joints become effectively less constrained and less stiff. At the Kuhn segment length l_K the joints become effectively free. The mean-square distance of a freely-jointed chain (FJC) is $\langle R^2 \rangle = Na^2 = La$ [pln50]. The natural definition of the Kuhn segment length, therefore, is [pln51]

$$l_\mathrm{K} \doteq \frac{\langle R^2 \rangle}{L}.$$

The Kuhn segment length l_K is a measure for the stiffness of the polymer chain just as the persistence length l_p investigated in [pex28] is. However, the two measures are not identical. The Kuhn segment length is easier to determine experimentally and theoretically but the persistence length has a more direct physical meaning. Here we explore the functional relation between l_K and l_p for an ideal polymer chain with persistent flexibility. On a mesoscopic scale we describe the conformation of the polymer by a vector function $\vec{r}(s)$ and replace the local bond vector $\vec{a}_i$ by the vector function $\vec{u}(s) = d\vec{r}/ds$ with s as defined in [pex28]. The end-to-end distance vector and its mean-square value can thus be expressed as follows:

$$\vec{R} = \int_0^L ds\, \vec{u}(s), \quad \langle R^2 \rangle = \int_0^L ds \int_0^L ds' \langle \vec{u}(s) \cdot \vec{u}(s') \rangle.$$

To calculate the latter we infer from [pex28] the relation

$$\langle \vec{u}(s) \cdot \vec{u}(s') \rangle = \langle \cos\theta(s - s') \rangle = e^{-|s-s'|/\tilde{l}}.$$

Perform the double integral to obtain an analytic expression of the scaled Kuhn segment length l_K/L as a function of the scaled persistence length l_p/L. Show in particular that for very long polymers ($L \gg \tilde{l}$), we have $l_\mathrm{K} \simeq 2l_\mathrm{p}$ and for very short polymers ($L \ll l_\mathrm{p}$) we have $l_\mathrm{K} \simeq L$. Plot l_K/L versus l_p/L over the range $0 < l_\mathrm{p}/L < 3$ to illustrate this behavior.

[adapted from Grosberg and Khokhlov 1994]

Solution:

[pex30] Ideal polymer chain with fixed valence angle I

Consider an ideal polymer chain of N links of length a with fixed valence angle γ between successive links. The internal rotational angle is assumed to be unconstrained and not subject to a potential: $U(\varphi) = 0$. Calculate the mean-square end-to-end distance from the expression,

$$\langle R^2 \rangle = \left\langle \left(\sum_{i=1}^{N} \vec{u}_i \right)^2 \right\rangle = Na^2 + 2a^2 \sum_{i=1}^{N} \sum_{k=1}^{N-i} \langle \cos\theta_{i,i+k} \rangle,$$

where the $\vec{u}_i$ are bond vectors of length a. For given uniform valence angle γ use the multiplicativity property $\langle \cos\theta_{i,i+k} \rangle = (\cos\gamma)^k$ for the angle between further-neighbor bond vectors. Show that the result can be written in the form,

$$\langle R^2 \rangle = Na^2 \left[\frac{1+\cos\gamma}{1-\cos\gamma} - N^{-1} \frac{2\cos\gamma}{1-\cos\gamma} \frac{1-(\cos\gamma)^N}{1-\cos\gamma} \right].$$

In very long polymers only the first term survives. Explain this solution for $N = 1, 2, 3$ in geometric terms.

[adapted from Grosberg and Khokhlov 1994]

Solution:

[pex31] Ideal polymer chain with fixed valence angle II

The mean-square end-to-end distance of a very long, ideal polymer chain with fixed valence angle and free internal rotation angle is

$$\langle R^2\rangle = Na^2 + 2a^2\sum_{i=1}^{N}\sum_{k=1}^{N-i}\langle\cos\theta_{i,i+k}\rangle \overset{N\gg 1}{\rightsquigarrow} Na^2\frac{1+\cos\gamma}{1-\cos\gamma}$$

as calculated in [pex30].
(a) Use the last expression to calculate the Kuhn segment length l_K and use the multiplicativity property, $\langle\cos\theta_{i,i+k}\rangle = (\cos\gamma)^k$, to calculate the persistent length $\tilde{l}$. The former is defined in [pex29] and the latter in [pex28].
(b) Plot l_K/a, $\tilde{l}/a$, and $l_K/\tilde{l}$ versus valence angle for $0 < \gamma < \pi/2$. Interpret your results and analyze the singularities of all three curves.

[adapted from Grosberg and Khokhlov 1994]

Solution:

[pex32] Ideal polymer chain: flexibility from rigid constraints

Here we connect the results for the mean-square end-to-end distance,

$$\langle R^2\rangle = 2l_\mathrm{p}\left[L - l_\mathrm{p}\big(1 - e^{-L/l_\mathrm{p}}\big)\right], \tag{1}$$

for a flexible polymer chain with contour length L and persistence length l_p from [pex29] and,

$$\langle R^2\rangle = Na^2\left[\frac{1+\cos\gamma}{1-\cos\gamma} - N^{-1}\frac{2\cos\gamma}{1-\cos\gamma}\,\frac{1-(\cos\gamma)^N}{1-\cos\gamma}\right], \tag{2}$$

for a polymer chain with $N = L/a$ links of size a and fixed valence angle γ from [pex30]. The persistence length l_p for this model is calculated in [pex31]. Show that in the combined limit $\gamma \ll 1$ and $l_\mathrm{p} \gg a$ the result (2) for a chain with rigidly constrained valence angle turns into the result (1) for a chain whose flexibility can be described by a bending stiffness as in [pex28].

[adapted from Grosberg and Khokhlov 1994]

Solution:

[pex33] Polymer with energetically favored internal rotation angles I

Consider an ideal polymer chain with fixed valence angle $\cos\theta_{i,i+1} = \gamma$ and an internal rotation angle $\phi_{i,i+1} \doteq \phi_i$ subject to a potential $U(\phi_i)$. As a first step in the calculation of the mean-square end-to end distance $\langle R^2\rangle$ as expressed in [pex30] we must express the angle $\theta_{i,i+k}$ between links as a function of γ and $\phi_i, \ldots \phi_{i+k-1}$. For that purpose we introduce local coordinate systems $\vec{n}_i$ with (i) n_i^x parallel to the bond vector, (ii) n_i^y in the plane of $\vec{n}_i$ and $\vec{n}_{i-1}$ and orientation such that the angle between the directions of n_{i-1}^x and n_i^y is acute, and (iii) n_i^z to complete a right-handed Cartesian system. The internal rotation angles are measured from the trans-planar zigzag conformation. Express the relative orientation of adjacent local coordinate systems in the form

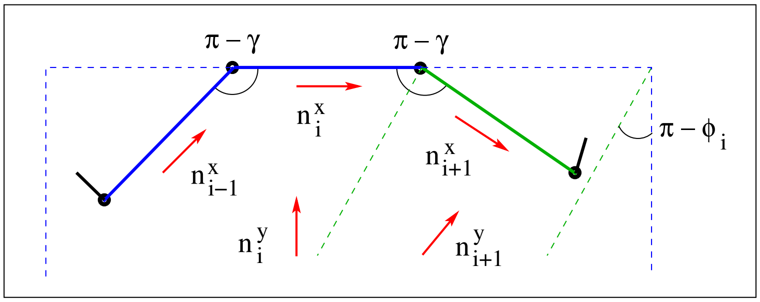
$$n_{i+1}^{\mu} = \sum_{\nu=x,y,z} T_i^{\mu\nu} n_i^{\nu}$$

(a) Find the matrix $\mathbf{T}_i(\gamma, \phi_i)$ and show that it is orthonormal.
(b) Given that the bond vector in the local coordinate system is $\vec{u}_i = (1, 0, 0)$ calculate

$$\cos\theta_{i,i+1} = \vec{u}_i \cdot \vec{u}_{i+1} = \vec{u}_i \cdot \mathbf{T}_i \cdot \vec{u}_i.$$

(c) Generalize this expression for the angle $\cos\theta_{i,i+k}$.

[adapted from Grosberg and Khokhlov 1994]



Solution:

[pex34] Polymer with energetically favored internal rotation angles II

Consider an ideal polymer chain with fixed valence angle $\cos_{i,i+1} = \gamma$ and an internal rotation angle $\phi_{i,i+1} \doteq \phi_i$ subject to a potential $U(\phi_i)$ with symmetry $U(-\phi_i) = U(\phi_i)$. Here we use the result from [pex33] for the angle $\theta_{i,i+k}$ between links i and k to calculate the thermal average $\langle\theta_{i,i+k}\rangle$ for use in the expression from [pex30] for the mean-square end-to-end distance $\langle R^2\rangle$.
(a) Provide a chain of reasoning that leads to the following result:

$$\langle\theta_{i,i+k}\rangle = \left[\langle\mathbf{T}\rangle^k\right]_{11}, \quad \langle\mathbf{T}\rangle = \left(\begin{array}{ccc} \cos\gamma & \sin\gamma\langle\cos\phi\rangle & 0 \\ \sin\gamma & -\cos\gamma\langle\cos\phi\rangle & 0 \\ 0 & 0 & -\langle\cos\phi\rangle \end{array}\right).$$

(b) Provide a chain of reasoning that leads to the following expression for the mean-square end-to-end distance:

$$\langle R^2\rangle \overset{N\gg1}{\leadsto} Na^2\left[\frac{\mathbf{E}+\langle\mathbf{T}\rangle}{\mathbf{E}-\langle\mathbf{T}\rangle}\right]_{11}, \quad \mathbf{E} = \left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right).$$

(c) Evaluate this expression via the solution of the matrix equation $\mathbf{X}\cdot(\mathbf{E}-\langle\mathbf{T}\rangle) = \mathbf{E}+\langle\mathbf{T}\rangle$.

[adapted from Grosberg and Khokhlov 1994]

Solution: