Equilibrium and Dynamics of Dilute Polymer Solutions

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Abstract Polymers show universal behavior at long length and time scales. In this chapter, the equilibrium and dynamics of dilute polymer solutions is presented in terms of theoretical models that form the basis of polymer physics. The size of an ideal polymer is calculated from the freely jointed chain model, the freely rotating chain model and the Gaussian equivalent chain model. The Edwards Hamiltonian for a continuous ideal chain is obtained from a continuous limit of the Gaussian equivalent chains. The size of a real chain in good and poor solvents is estimated from the free energy that includes entropic and enthalpic contributions. The temperature dependence of chain size is discussed using the concept of thermal blobs. The force-extension relations for ideal and real polymers are illustrated using the tension blobs. A brief introduction to stiff chains is presented in terms of the wormlike chain model. Starting from the Langevin equation for a Brownian particle, the salient features of the Rouse and Zimm models are presented. The behavior of polymers under extensional, rotational, simple shear and linear-mixed flows is discussed using the finitely extensible Rouse chain.

1 Introduction

Polymers are large molecules composed of many smaller repeating units (monomers) bonded together. Solvent induced thermal fluctuations bring about the internal rotation of bonds generating large numbers of conformational states [1-4]. On time scales much larger than the rotational rates, experimental measurements typically capture the average effects of the rapid fluctuations in the conformations. Even instantaneous measurements involve averages over large ensembles of identical molecules. Given that the system

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has a large number of degrees of freedom, there is no general methodology, either classical or quantum mechanical, that can treat the system exactly. Apart from the enormously large number of conformations, each polymeric system is characterized by its own unique chemistry at the microscopic level because of the different chemical structures of the monomers. Nevertheless, at one level, polymeric systems can be quite simple, as the following suggests: the macroscopic properties of a collection of small molecules strongly depend on the intrinsic chemical details of the molecules, but when the same set of chemical species are bonded to form a long molecule, they exhibit universal behavior. In other words, at length scales much larger than the monomer size, the properties are insensitive to the structure of the individual molecules of the chain, but depends on the universal chain-like nature of the polymer. Thus, long wavelength properties can be described using general statistical mechanical methods that depend on a few system dependent phenomenological parameters \[1-11\]. In what follows, we describe the theoretical methods that form the basis of polymer physics. Minimal models that depends on a few phenomenological parameters to describe long length-scale chain-like properties of the polymers is presented in the next section.

2 Ideal Polymers

An equilibrium property that governs the behavior of a polymer solution is the chain size and its dependence on temperature. The understanding of the chain structure is key to unraveling the thermodynamical, mechanical and dynamical properties of polymer solutions. The size of a polymer depends on the quality of solvent in which it is dissolved. In a real polymer, the relative strengths of the monomer-monomer and monomer-solvent interactions determine if the chain is swollen or collapsed. At high temperatures, the effective monomer-monomer interactions are repulsive and polymers are found in a swollen state. At low temperature, polymers form globules due to dominance of attractive interactions. At a special temperature, called the \(\theta\)-temperature, the attractive and repulsive parts of the effective monomer-monomer interactions cancel each other resulting in nearly ideal chain conformations. It is worth mentioning that concentrated polymer solutions and linear polymer melt show near ideal chain behavior since surrounding polymers screen the interactions between monomers. The conformational behavior of an ideal polymer forms the basis of most models in polymer physics \[1-11\]. In what follows, we describe several different models that estimate the size of an ideal polymer.

The end-to-end vector, \(\mathbf{R}\), of a flexible polymer consisting on \(n\) bond vectors is given by

\[
\mathbf{R} = \sum_{i=1}^{n} \mathbf{r}_i,
\]
where \( \mathbf{r}_i \) is the \( i^{th} \) bond vector of magnitude \( |\mathbf{r}_i| = l \). The mean square end-to-end distance of this chain is given by

\[
\langle R^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} (\mathbf{r}_i \cdot \mathbf{r}_j) = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} (\cos \theta_{ij}),
\]

where \( \theta_{ij} \) represents the angle between the bond vectors \( \mathbf{r}_i \) and \( \mathbf{r}_j \) and \( \langle \cdots \rangle \) corresponds to the ensemble average. Figure 1 represents a freely jointed chain. In a freely jointed chain model, all bond vectors are completely uncorrelated with each other, that is, \( \langle \cos \theta_{ij} \rangle = 0 \) for \( i \neq j \). This leads to a very simple expression for the mean square distance, \( \langle R^2 \rangle = nl^2 \). In general, restricted bond-angle rotations and steric hinderance lead to local correlations between bond vectors along the chain backbone. These local correlations are accounted for by defining Flory’s characteristic ratio,

\[
C_n = \frac{1}{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos \theta_{ij} \rangle.
\]

In terms of Flory’s characteristic ratio, the mean square distance is given by

\[
\langle R^2 \rangle = C_n nl^2.
\]

Flory’s characteristic ratio, \( C_n \), increases with the increase in the number of monomers. For \( n \gg 1 \), it saturates to a finite value \( C_\infty \) yielding \( \langle R^2 \rangle \approx C_\infty nl^2 \). For many flexible polymers, \( C_\infty \) is typically 7-9.

A simple estimate of \( C_\infty \) is provided by the freely rotating chain model. The free rotating model assumes all torsional angles to be equally probable. It accounts for the local correlation by estimating \( \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = l^2 (\cos \theta)^{|i-j|} \).

In terms of the exponential function, \( (\cos \theta)^{|i-j|} = \exp(-|i-j|l/l_p) \), where \( l_p = -l/\ln(\cos \theta) \) defines the length scale at which the correlations between the bond vectors decay. Thus, the mean-square end-to-end distance of a freely rotating chain is given by

\[
\langle R^2 \rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \exp(-|i-j|l/l_p),
\]
which simplifies to yield

$$\langle R^2 \rangle = nt^2 \frac{1 + \cos \theta}{1 - \cos \theta},$$  \hspace{1cm} (5)

where $C_{\infty} = (1 + \cos \theta)/(1 - \cos \theta)$. For flexible polymers, the value of $C_{\infty}$ calculated from the freely rotating chain model is less than expected. However, the freely jointed chain model provides a rough estimate of the local correlations between the bond vectors. In the next section, a unified description of ideal flexible polymers is provided in terms of the Gaussian equivalent chains.

### 3 Gaussian Equivalent Chains

As a rough approximation, the conformation of a flexible chain can be viewed as the trajectory of a random walker that makes $n$ independent steps of fixed step length $l$ to cover a certain distance $R$ [12, 13]. What is the probability for $R$? Since the steps are completely uncorrelated with respect to each other, the overall probability of a given conformation is the product of the probabilities of the individual steps, that is,

$$P = \prod_{i=0}^{n} p(r_i),$$  \hspace{1cm} (6)

where $r_i$ is the bond vector of the $i$th step. Since the magnitude of the bond (step) length is fixed, the simplest way to define the bond probability is

$$p(r_i) = \frac{1}{4\pi l^2} \delta(|r_i| - l).$$  \hspace{1cm} (7)

The bond probability defined above accounts for the constraint of a constant bond length, but it leads to a rather complicated distribution function for $R$, the vectorial distance from one end of the chain to the other. At the same time, since $R$ is the sum of a large number of random variables (bond vectors), the probability function can be described by a Gaussian function according to the central limit theorem. For large enough $n$ and distance much less than $nl$, the distribution is given by

$$P(R, n) = \left( \frac{3}{2\pi nl^2} \right)^{3/2} \exp \left( -\frac{3R^2}{2nl^2} \right).$$  \hspace{1cm} (8)

The above distribution can be exactly produced by a bond probability that is given, not by Eq. (1), but by
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\[ p(r_i) = \left( \frac{3}{2\pi l^2} \right)^{3/2} \exp \left( -\frac{3r_i^2}{2l^2} \right). \]  

A chain described by the above bond distribution function is referred to as a Gaussian chain. Since the Gaussian chain is made up of several Gaussian links, each effective step of the random walk is itself a random walk. The Gaussian chain is, therefore, a self-similar object, or fractal [14]. Its structure looks the same on any length scale. If we group \( n_0 \) monomers together to form a single unit, the polymer chain is again a random walk of larger step length. To be specific, there are \( N = n/n_0 \) effective steps of step length \( b = n_0^{1/2}l \), with \( \langle R^2 \rangle = Nb^2 = nl^2 \). In other words, averaging over certain degrees of freedom (coarse-graining) does not change the general scaling behavior of the long wavelength properties of the chain. In particular, the distribution function depends on the ratio \( R^2 / \langle R^2 \rangle \), which is scale invariant. The step length defined above is a coarse-grained length, which is the average over a large number of successive bond vectors. The chain thus obtained is a coarse-grained description of a real chain, and is equivalent to it at this level of description. The chain can, therefore, be called an equivalent Gaussian chain. The notion of equivalent chains was first introduced by Werner Kuhn [8, 9]. The coarse-grained length \( b \) is hence commonly referred to as the Kuhn length. In terms of the bond length \( l \) and the the number of monomers \( n \), the Kuhn length and the effective number of monomers are given by \( b = C_\infty l / \cos \theta / 2 \) and \( N = n \cos^2 \theta / 2 / C_\infty \). As long as the Kuhn length is much smaller than the contour length, an equivalent chain describes a flexible polymer. An equivalent chain is a good approximation to a real chain for long wavelength properties. Indeed, most theoretical approaches model flexible chains in terms of the equivalent chain description.

The equivalent Gaussian chain has the unphysical feature that it can extend more than its contour length. In fact, the chain has an infinite stored length. This feature is the reflection of the underlying Gaussian nature of the distribution function, which has a long length tail, and hence a finite probability for extension beyond its contour length. The infinite extensibility is often a serious limitation when describing chain extension under various kinds of force fields. Some of these issues are discussed in Sect. 9, where a finitely extensible Gaussian model is presented for chain extension under shear flow.

4 Continuous Chains

The equivalent Gaussian chain can be subjected to a further level of coarse-graining by letting \( b \to 0 \), \( N \to \infty \) and \( R_{max} = Nb \) constant. This leads to a representation of the polymer as a continuous path with fixed ends. The probability that such a path begins at \( R_0 \) and ends at \( R \) is given by a path
integral representation:

\[ G(\mathbf{R}, \mathbf{R}_0; N) = \int_{\mathbf{r}_0 = \mathbf{R}_0}^{\mathbf{r}_N = \mathbf{R}} D[\mathbf{r}_n] \exp \left\{ -\frac{3}{2b^2} \int_0^N dn |\dot{\mathbf{r}}_n|^2 \right\}, \quad (10) \]

where \( \mathbf{r}_n \) is the position vector of the \( n \)th monomer. \( N \) is the effective number of monomers in the polymer. The integral over \( D[\mathbf{r}_n] \) is a continuous representation of the discrete sum over all possible chain conformations, and it contains factors that ensure that \( G(\mathbf{R}, \mathbf{R}_0; N) \) is normalized. The advantages of going over to a continuum chain description lie in the fact that path integrals can be evaluated using established techniques in quantum and statistical mechanics [15, 16]. Moreover, the end-vector distribution function defined above satisfies a diffusion equation that is formally equivalent to the Schrödinger equation in quantum mechanics. The formal analogy is useful in treating many of the problems concerning a polymer in an external field.

Eq. (10) can be recognized as the Weiner probability distribution. Although the chain conformation is considered to be a continuous curve, the continuous limit is mathematically subtle since the curve is not differentiable in the classical sense [17, 18]. In other words, the curve does not have a well-defined tangent at any point. This happens to be an inherent property of a self-similar object. However, Eq. (10) leads to a physically meaningful probability distribution that accounts for connectivity of the chain, which is completely entropic in origin. The “Hamiltonian” for the flexible polymer is of the form:

\[ \beta H = \frac{3}{2b^2} \int_0^N dn |\dot{\mathbf{r}}_n|^2, \quad (11) \]

where \( \beta = 1/k_B T \). Since the above Hamiltonian only accounts for the chain connectivity, it represents an ideal chain Hamiltonian. If the polymer interacts with the external field, the end-to-end vector distribution function of Eq. (10) is modified to

\[ G(\mathbf{R}, \mathbf{R}_0; N) = \int_{\mathbf{r}_0 = \mathbf{R}_0}^{\mathbf{r}_N = \mathbf{R}} D[\mathbf{r}_n] \exp \left\{ -\int_0^N dn \left( \frac{3}{2b^2} |\dot{\mathbf{r}}_n|^2 + V[\mathbf{r}_n] \right) \right\}, \quad (12) \]

where \( V[\mathbf{r}_n] \) may be a solvent field, a gravitational field, or a field due to intramolecular excluded volume interactions between different parts of the same chain. Non-local excluded volume and three-body interactions account for the quality of solvents in which polymers are dissolved. These interactions are often described by a two-body and three-body pseudo-potentials [8-11] given by

\[ \beta H = \frac{3}{2b^2} \int_0^N dn \left( \frac{\partial \mathbf{r}_n}{\partial n} \right)^2 - \frac{v}{2} \int_0^N dn \int_0^N dm \delta[\mathbf{r}_n - \mathbf{r}_m] \]
\[ + \frac{w}{6} \int_0^N dn \int_0^N dm \int_0^N dl \delta[r_n - r_m] \delta[r_m - r_i], \quad (13) \]

where the first term describes the entropic elasticity of the chain; the second and the third terms represent the two-body repulsive excluded volume and three-body repulsive interactions respectively; \( v \) and \( w \) represent the strengths of the two-body and three-body interactions respectively. The size of a flexible polymer is characterized by its mean square radius of gyration, \( \langle R^2 \rangle \). For a linear and flexible polymer, \( \langle R^2 \rangle = \langle R^2 \rangle / 6 \), where \( \langle R^2 \rangle \) is the mean square end-to-end distance. The mean square end-to-end distance can be evaluated from the following expression:

\[ \langle R^2 \rangle = \frac{\int_{-\infty}^{\infty} dR \ R^2 \ exp(-\beta H)}{\int_{-\infty}^{\infty} dR \ \ exp(-\beta H)}. \quad (14) \]

An ideal chain Hamiltonian is given by Eq.(11). The evaluation of the chain size involves a simple Gaussian integration, which yields \( \langle R^2 \rangle = N b^2 \). A real chain Hamiltonian, described by Eq. (13), involves both entropic and enthalpic contributions. The evaluation of the chain size is, therefore, a difficult task. In the next section, we provide a brief overview of the Flory theory which provides an estimate of the chain size in the presence of enthalpic interactions [1, 2].

5 Temperature Dependence of Polymer Size

The size of a polymer depends on the effective interactions between monomers, which are characterized by excluded volume (second virial coefficient) and three-body interaction parameters. The excluded volume parameter \( v \) estimates the effective interaction between the monomers, \( v = -\int f \ d^3r f \), where the Mayer \( f \)-function is \( f = \exp(-\beta H_c) - 1 \), and \( H_c \) represents the interaction between different monomers. A similar treatment for three-body potentials yields an expression for \( w \). Typical average values of these parameters are \( v \sim b^3 (1 - \theta/T) \) and \( w \sim b^6 \), where \( \theta \) is the temperature at which the chain is ideal [6-11]. Away from the \( \theta \) temperature, the sign of the excluded volume parameter \( v \) determines whether the effective two-body interactions are repulsive or attractive. For \( T > \theta \), the effective interactions between monomers are repulsive. At temperatures higher than the \( \theta \) temperature, therefore, monomers like the solvent in which they are dissolved and the solvent is termed as a good solvent. In the opposite limit of \( T < \theta \), the effective two-body interaction is attractive and the solvent is termed as a poor solvent.

The size of a real polymer was first estimated by Flory by identifying the entropic and energetic contributions to the total free energy \( F(R, N) \),
\[ F(R, N) = F_{\text{ent}}(R, N) + F_{\text{int}}(R, N), \] (15)

where \( N \) is the effective number of monomers and \( R \) is the end-to-end vector.

The entropic contribution to the free energy can be calculated from the probability distribution for end-to-end vector of an ideal polymer which follows Gaussian statistics,

\[ P(R, N) = \left( \frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right), \] (16)

resulting in the following entropic contributions to the free energy:

\[ S(R, N) = k_B \ln P(R, N) \]
\[ = S(0, N) - \frac{3k_B T R^2}{2Nb^2}. \] (17)

The free energy of a polymer is given by \( F(R, N) = U(R, N) - TS(R, N) \). For an ideal polymer there are no energetic contribution, and the entropic free energy is given by \( F_{\text{ent}}(R, N) = \frac{3k_B T R^2}{2Nb^2} \). For a real polymer, the energetic contribution to the free energy per unit volume can be calculated by carrying out a virial expansion in powers of the monomer number density \( c_n \). The coefficient of the \( c_n^2 \) term is proportional to the excluded volume \( v \) and the coefficient of the \( c_n^3 \) is related to the three body interaction coefficient \( w \approx b^6 \).

\[ \frac{F_{\text{int}}}{V} = \frac{k_B T}{2} (vc_n^2 + wc_n^3 + \cdots) \approx \frac{k_B T}{2} \left( v \frac{N^2}{R^6} + w \frac{N^3}{R^9} + \cdots \right) \] (19)

The total free energy, with contributions from entropic and enthalpic terms, is given by

\[ \frac{F(R, N)}{k_B T} \approx \frac{R^2}{Nb^2} + \frac{v N^2}{R^6} + \frac{w N^3}{R^9} \] (20)

From the above equation, the size of a real polymer in a good and poor can be evaluated.

In a good solvent, the repulsive nature of the effective monomer-monomer interactions swell the chain. Since under these conditions, the three body interaction term is not important, the size of the polymer can be evaluated by just retaining the entropic and the repulsive excluded volume interaction terms,

\[ \frac{F(R, N)}{k_B T} \approx \frac{R^2}{Nb^2} + \frac{v N^2}{R^6}. \] (21)

By minimizing the above free energy with respect to \( R \), i.e. \( \frac{\partial F(R, N)}{\partial R} = 0 \), the size of the polymer in a good solvent can be estimated. The equilibrium size is given by \( R \approx N^{3/5} v^{1/5} b^{3/5} \). The latter is a universal expression for the chain size in a good solvent. In contrast to the exponent of 0.6, the more sophisticated renormalization group theories estimate this exponent as 0.588.
In a poor solvent, the effective attractive monomer-monomer interactions lead to a collapsed globular structure. Since the resulting structure is highly compact, the entropic contributions are not important and the size of the polymer can be evaluated by just retaining the three-body repulsive and the two-body attractive excluded volume interaction terms,

$$\frac{F(R, N)}{k_B T} \approx -|v| \frac{N^2}{R^3} + \frac{N^3}{R^6}. \quad (22)$$

By minimizing the above free energy with respect to $R$, the equilibrium size in a poor solvent can be estimated as $R \approx (N/|v|)^{1/3} b$. Therefore, a globule-to-coil conformational transition can be brought about by changing the sign of the excluded volume interaction term, which amounts to changing the solvent quality or temperature.

To understand the temperature dependence of a real polymer, it is customary in polymer physics to introduce the concept of blobs [6]. Since polymers are large molecules, there exist a separation of length scales within the polymer structure. Irrespective of the nature of the interaction energy, the size of a blob corresponds to the length scale at which the interaction energy is of the order of the thermal energy, $k_B T$. On length scales smaller than the blob size, the chain follows the unperturbed statistics. On length scales larger than the blob size, the chain statistics is determined by the interaction energy.

The free energy of a real polymer has entropic and enthalpic contributions. The length scale at which the free energy is of the order of $k_B T$ determines the size of a thermal blob, $\xi_T$. The entropic contribution to the free energy is $\beta F_{\text{ent}} = R^2 / N b^2$. Since length scales below the blob size are dominated by entropy, we have $\xi_T \sim n_T^{1/2} b$ where $n_T$ is the number of monomers in a thermal blob. To determine $n_T$, we set $\beta F_{\text{int}} \sim 1$, which yields $n_T \sim b^6 / \nu^2$. On length scales larger than $\xi_T$, the thermal blobs are self-avoiding in a good solvent and space-filling in a poor solvent. In terms of the thermal blob, therefore, the size in a good and poor solvents are given by $R \sim (N/n_T)^{3/5} \xi_T \sim N^{3/5} v^{1/5} b^{3/5}$ and $R \sim (N/n_T)^{1/3} \xi_T \sim (N/|v|)^{1/3} b$. The latter expressions are the same as obtained from the Flory theory.

6 Polymers under tension

The free energy of an ideal polymer only has entropic contribution given by $F(R, N) = 3k_B T R^2 / 2N b^2$. In order to hold the chain at a fixed end-to-end vector $R$, one needs to apply equal and opposite force at the chain ends,

$$f = \frac{\partial F(R, N)}{\partial R} = \frac{3k_B T}{N b^2} R. \quad (23)$$
The force-extension relation is linear and follows Hooke’s law for small deformation. This is the result of the Gaussian approximation for the end-to-end vector distribution. The above relation suggests that the spring constant is \( k = 3k_B T/Nb^2 \). The dependence of the spring constant on temperature is a reflection of the entropic elasticity.

The linear relation for ideal chains can also be obtained from the concept of blobs [6, 7]. The length scale at which the free energy due to the applied force is of the order of \( k_B T \) defines the tension blob, \( \xi_f \sim k_B T/f \). For length scales shorter than the tension blob, the chain statistics is unperturbed and is governed by entropy, that is, \( \xi_f \sim n_f^{1/2} b \), where \( n_f \) is the number of monomers in the tension blob. For length scales larger than the tension blob, the chain statistics is determined by the applied force yielding a stretched state \( R \sim (N/n_f)\xi_f \sim Nb^2 f/k_B T \). The latter suggests that for an ideal chain \( f \sim (k_B T/Nb^2)R \). This recovers the linear relation between force and extension in agreement with Eq. (23).

For real chains at high temperatures, the unperturbed statistics is that of a self-avoiding walk. For length scales shorter than the tension blob, therefore, \( \xi_f \sim n_f^{3/5} b \). At large length scales, the chain is in a stretched state given by \( R \sim (N/n_f)\xi_f \sim Nb(fb/k_B T)^{2/3} \) implying \( f = k_B T/b(R/Nb)^{3/2} \). In contrast to ideal chains the force-extension relation for real chains is non-linear. The scaling arguments discussed in this section are only valid for small deformations. For large deformations, the force-extension relation can be derived from the wormlike chain model. In the next section the chain statistics of stiff polymers is presented in terms of the wormlike chain model.

7 Stiff Chains

The discussion so far has been limited to a class of polymers that are completely flexible. The flexibility in such molecules arises because of the unhindered rotation of bond vectors through a fixed bond angle. In stiff polymers, like double stranded DNA, the flexibility is due to the fluctuations of the contour length about a straight line. The wormlike chain (WLC) is a continuous chain description of stiff polymers. The WLC model is a special case of the freely rotating model for small bond angles. The concept of the wormlike chain was first introduced by Kratky and Porod. The wormlike chain is also referred to as the Kratky-Porod Chain. The mean-square distance of the wormlike chain can be calculated from Eq. (4). Since the WLC is a continuous description, the summations in Eq. (4) can be expressed as integrals,

\[
\langle R^2 \rangle = \int_0^L ds' \int_0^L ds \exp(-|s - s'|/\ell_p),
\]

(24)
where \( L = nl = Nb \), \( l_p = 2l/\theta^2 \) and \( b = 2l_p \) for \( \theta \ll 1 \). The resultant expression is given by
\[
\langle R^2 \rangle = 2Ll_p - 2l_p^2 (1 - \exp(-L/l_p)).
\] (25)

The persistence length, \( l_p \), is a measure of the distance over which the bond vectors are correlated, and hence determines the effective stiffness of the chain. That Eq. (25) is a valid description in both stiff and flexible limits can be seen as follows: when \( Ll_p \ll 1 \), \( \langle R^2 \rangle = L^2 \) (the rod limit); when \( Ll_p \gg 1 \), \( \langle R^2 \rangle = 2Ll_p = N\theta^2 \) (the flexible limit).

For a chain with a constant contour length, there exist a unit tangent vector given by \( u(s) = \partial r(s)/\partial s \), where \( r(s) \) is the position of a point at arc length \( s \) from one end of the chain. For a stiff chain, the orientation of the unit vector \( u(s) \) changes slowly with respect to the arc length variable \( s \). In general, for chains with variable stiffness, the bending energy is proportional to the change in the orientation of the unit vector with respect to the arc length variable \( s \), \( \partial u(s)/\partial s \). Thus the lowest order scalar function of \( \partial u(s)/\partial s \) that can contribute to the bending energy must be quadratic in this variable. Since \( u(s) \cdot \partial u(s)/\partial s = 0 \), the only quadratic form is
\[
H = \frac{\epsilon}{2} \int_0^L ds \left( \frac{\partial u(s)}{\partial s} \right)^2,
\] (26)

where \( \epsilon \) is the elastic energy for bending, which is equal to \( k_BTl_p \). The connectivity term in the above Hamiltonian is absent because of the constraint \(|u(s)| = 1\), which follows from simple differential geometry. Since the orientation of the unit tangent vector varies slowly along the stiff chain backbone, the unit tangent vectors are correlated over longer distances compared to a flexible chain. In general, the correlations between the unit tangent vectors at two different points along the chain backbone decay exponentially, and is of the form
\[
\langle u(s) \cdot u(s') \rangle = \exp(-L/l_p)
\] (27)

Saito, Takahashi and Yunoki (STY) have estimated the tangent vector distribution function in terms of an infinite series, with the above constraint on the unit tangent vector [19]. Their distribution provides a correct estimate for the second and fourth moments of the end-to-end distance, \( R \). However, the probability distribution for the end-to-end distance cannot be calculated within their formalism, even in terms of an infinite series. In order to simplify the analysis, Harris and Hearst relaxed the local constraint of constant unit tangent vectors to a global constraint of constant contour length by introducing a Lagrange multiplier, and treating it as a free parameter [20]. Although their approach reproduces the mean-square end-to-end distance by fixing the free parameter, it fails to yield other second moment quantities except in the rod and flexible limits. In a different approach, Freed relaxed the local constraint \(|u(s)| = 1\) to statistical constraint \( \langle u(s)^2 \rangle = 1 \), produc-
ing a rather simple model in which the chain Hamiltonian has a connectivity term along with a bending energy term [21]. The coefficient in front of the bending energy term is kept as a free parameter and is fixed by requiring that $\langle u(s)^2 \rangle = 1$. For this model, the probability distribution function that the chain ends are at $R$ with tangent vectors $U'$ and $U$ is of the form

$$G(R, 0; U, U'; N, 0) = \int_{u(0)=U'}^{u(L)=U} D[u(s)] \delta \left[ R - \int_0^L ds u(s) \right]$$

$$\exp \left[ - \left( \frac{3}{4l_p} \int_0^L ds |u(s)|^2 + \frac{l_p}{2} \int_0^L ds |\dot{u}(s)|^2 \right) \right] \tag{28}$$

However, the distribution function estimates $\langle R^2 \rangle = Ll_p$, which is just the flexible chain result. There is no dependence on the bending energy $\epsilon$. This spurious behavior is because of the inhomogeneous nature of the chain defined by Eq. (28). The inhomogeneity becomes more explicit when the mean square fluctuations, $\langle u(s)^2 \rangle$, of the tangent vectors are calculated at different points along the chain backbone. It turns out that there is as much as a factor of 2 increase in $\langle u(s)^2 \rangle$ for $s$ at the ends of the chain as compared to $s$ at the middle [22]. Therefore, the excess fluctuations at the chain ends need to be suppressed by incorporating an energy penalty for fluctuations at the ends. A Hamiltonian that does that is given by

$$\beta H = \frac{3}{4l_p} \int_0^L ds |u(s)|^2 + \frac{3l_p}{4} \int_0^L ds |\dot{u}(s)|^2 + \frac{3}{4} (|u_0|^2 + |u_N|^2). \tag{29}$$

The probability distribution for the end-to-end distance derived from this Hamiltonian provides correct predictions for various second moments. In particular, it reproduces the predictions of the Kratky-Porod model while remaining analytically tractable.

### 8 Rouse and Zimm Models

The diffusion of a large molecule in a solvent of small molecules generally follows Brownian motion. Since a Brownian particle is much heavier than the surrounding fluid particles, there exist a wide separation of time scales in their respective microscopic dynamics. The Brownian particle changes its velocity on a much slower time scale; the fluid particles, on the other hand, change their velocities on a much faster time scale. As a result, the Brownian particle suffers a large number of collisions with the fluid particles in its path through the fluid. It is, therefore, possible to identify the velocity of the Brownian particle as a slow mode of the system, and the velocities of the fluid particles as fast modes of the system. On time scales much longer
than the frequency and duration of individual collisions, the dynamics of the Brownian particle can be expressed in terms of an equation in which the details of the collision process are contained in the statistical properties of a stochastic variable (the fast modes). Such an equation was suggested by Langevin [23], and is given by

$$m\ddot{r}(t) = -\zeta \dot{r}(t) + f(t)$$  \hspace{1cm} (30)

The first term in this equation represents the inertial force. The second term is the systematic force with a mean $-\zeta v$, where $\zeta$ is the friction coefficient. The systematic force is the average frictional force, and is proportional to the velocity of the particle, but acts opposite to its direction of motion. The third term represents the random force $f(t)$ whose time average is zero. The random force contains details of the “fast” dynamics. It is the resultant of a large number of microscopic collisions, and so follows a Gaussian distribution by virtue of the central limit theorem [24-26]. These collisions can generally be assumed to be uncorrelated on time scales much longer than the collision time, and can be regarded as a sequence of independent impulses. Since the Brownian particle attains thermal equilibrium with the fluid particles over a sufficiently long time, these considerations dictate the second moment of the random force given by

$$\langle f_n(t)f_m(t') \rangle = 2k_B T \zeta \delta(t-t') \delta_{nm}. \hspace{1cm} (31)$$

The delta function indicates that the force at $t$ is uncorrelated with the force at $t'$. Since the process is also assumed to be Gaussian, all cumulants higher than the second are zero.

Eq. (31) is the simplest form of the fluctuation dissipation theorem [27]. It states the the dissipation due to frictional forces and the fluctuations due to random forces are related to one another since they have the same microscopic origin.
For long enough length and time scales, the Langevin equation describes the Brownian motion of the centre of mass of the polymer. In contrast, the chain-like dynamical properties are characterized by length and time-scales that are longer than the dynamics characteristic of the monomers, but that are shorter than the Brownian dynamics characteristic of the centre of mass. The dynamical behavior of the polymer in this intermediate regime is independent of the chemistry of the chain. The intermediate time regime, therefore, describes the dynamical aspects of the universal chain-like properties [28-31]. The simplest model that describes low frequency global features of the polymer dynamics through a few phenomenological parameters is referred to as the Rouse model [28]. This model considers the chain to be a Gaussian equivalent chain with $N$ beads and Kuhn length $b$. In the Rouse model, a polymer is represented as a bead and spring chain as shown in Figure 2. Apart from the inertial force, the frictional force and the random, the $i^{th}$ bead also experiences an elastic force from its immediate neighbors. The equation of motion for the $i^{th}$ bead is given by

\[ m\ddot{\mathbf{r}}_n(t) = -\zeta_b \dot{\mathbf{r}}_n(t) + \mathbf{f}_n(t) - \frac{3k_B T}{b^2} \sum_{n=1}^{N} A_{nm} \mathbf{r}_m(t), \quad (32) \]

where $\zeta_b$ is the bead friction coefficient, which is related to the random force $\mathbf{f}_n$, as in the case of the Brownian motion. The last term of the above equation accounts for the elastic force, with $A_{nm}$ being the Rouse matrix, defined as

\[ A_{nm} = 2\delta_{nm} - \delta_{n,m+1} - \delta_{n,m-1} \quad (33) \]

Since polymers are large molecules, the dynamics of polymers in solutions is dominated by viscous effects. In the over-damped limit, the inertial term in Eq. (32) can be ignored. Therefore, the equation of motion in the continuum limit is given by

\[ \zeta \dot{\mathbf{r}}_n(t) = \frac{3k_B T}{b^2} \frac{\partial^2 \mathbf{r}(n,t)}{\partial n^2} + \mathbf{f}_n(t) \quad (34) \]

In general, force acting on any point along the chain backbone can cause motion of the fluid around it, which in turn can affect the velocity of the other segments. This interaction, which is mediated by the motion of the solvent fluid, is called the hydrodynamic interaction. A more general expression for the dynamics of polymers is given by

\[ \zeta \dot{\mathbf{r}}_n(t) = -\int_0^N dn' D[\mathbf{r}_n - \mathbf{r}_{n'}] \frac{\delta H}{\delta \mathbf{r}_n} + \mathbf{f}_n(t), \quad (35) \]

where $H$ is the flexible chain Hamiltonian given by Eq. (11). The nonlocal hydrodynamic interaction is accounted for by kernel $D[\mathbf{r}_n - \mathbf{r}_{n'}]$. The Rouse model neglects the hydrodynamic interactions. It assumes that the velocity at any point along the chain backbone is determined only by the force acting
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on it. The kernel is, therefore, given by $\delta[r_n - r_{n'}]$. The model that accounts for nonlocal hydrodynamic interactions in pre-averaged fashion is referred to as the Zimm model [31].

A standard way of treating the Rouse model is to decompose the motion of the polymer into the normal coordinates such that each mode is capable of independent motion. The decomposition into independent modes is done by identifying the normal mode variable $q = 2\pi p/N$, where $p = 0, 1, 2, 3 \ldots$ are the Rouse mode variables. A small $q$ explores large length scales inside the chain; the $p = 0$ mode, therefore, represents the motion of the center of mass of the chain. Several dynamical quantities of interest can be expressed in terms of these normal modes [11]. However, a simple estimate of the diffusion coefficients and the relaxation times can be made from the following considerations: according to the Einstein’s relation, the diffusion coefficient of a Brownian particle is given by $D = k_BT/\zeta$; the relaxation time can be estimated by determining the time required for the particle to move a distance of its size, $\tau \sim R^2/D$. In the Rouse model, each bead has the friction coefficient of $\zeta$. So the total friction coefficient of the chain is $\zeta_R = N\zeta$. Therefore, the diffusion coefficient of the Rouse chain is $D_R = k_BT/N\zeta$ and the relaxation time is $\tau_R \sim N^2b^2\zeta/k_BT$. In the Zimm model, the hydrodynamic interactions couple the dynamics of different parts of the chain. As a result, the Zimm chain moves like a solid object with the friction coefficient governed by the Stoke’s law, $\zeta_Z \sim \eta R$, where $\eta$ is the solvent viscosity. The diffusion coefficient and the relaxation time of the Zimm chain are given by $D_Z = k_BT/\eta R$ and $\tau_Z \sim N^{3/2}b^3\eta/k_BT$ respectively.

In the next section, the estimation of a few dynamical quantities under flow fields is discussed by modifying the Rouse model to account for the effects of flow.

9 Polymers Under Flow

Polymers are known to deform under various kinds of flow, the extent of deformation depending strongly on the nature of flow [32-39]. A pure elongational flow produces large changes in the size of the polymer coil. A pure rotational flow, on the other hand, rotates the chain without inducing deformation. Most practical flows consist of a mixture of elongational and rotational components, so the dynamics of a chain in such flows depends on the relative magnitudes of these two components. In a simple shear flow, the magnitude of the rotational and elongational components are equal, the stretched state produced by the elongational component is destabilized by the rotational component. Therefore, the extended state of polymers in shear flow is inherently unstable and undergoes large fluctuations [32]. The variation of the mean polymer size as a function of the flow rate and decay of the time correlation function for various values of the flow rate are two
quantities that can be studied from statistical mechanical analysis [32-39]. If the hydrodynamic interactions are ignored, the dynamics can be described by the Rouse model, supplemented with a term that accounts for the force field due to flow

\[
\zeta \dot{r}_n(t) = k \frac{\partial^2 r(n, t)}{\partial n^2} + \dot{\gamma} A \cdot r_n(t) + f_n(t),
\]

(36)

where \( k = 3k_B T/b^2 \) is the spring constant, \( \dot{\gamma} \) is the flow rate, and \( A \) is the velocity gradient tensor, which contains the details of the applied flow. The velocity gradient tensor for linear-mixed flow is given by

\[
A = \begin{pmatrix}
0 & 1 & 0 \\
\alpha & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

where \( \alpha = 0 \) corresponds to simple shear, while \( \alpha = 1 \) and \( \alpha = -1 \) correspond to pure elongational and rotational flows respectively. Eq. (36) can be solved for the chain extension as a function of the flow rate. However, as discussed earlier, the Rouse chain is a bead and spring chain, consisting of Hookean springs that can be extended indefinitely. Real polymers show Hookean behavior only for very small extensions. The Hooke’s law is expected to break down at large values of the applied flow. Eq. (36) needs to account for the constraint of inextensibility. For a discrete polymer model, FENE (finitely extensible nonlinear elasticity) ansatz is often used by writing the spring constant as \( k' = k' / \left(1 - \frac{l_i^2}{l_m^2}\right) \), where \( k' = 3k_B T/b^2 \), \( l_i \) is the instantaneous bond extension, and \( l_m \) is the maximum extension of the bond. Thus, the chain pays a high penalty for extension beyond its maximum length. A more practical ansatz preaverages the instantaneous bond extension to yield \( k = k' / \left(1 - \frac{\langle R^2 \rangle}{\langle R^2 \rangle_m}\right) \). In the same vein, the following ansatz serves well for continuous chains [33-35]:

\[
k = k' \left(1 - \frac{\langle R^2 \rangle_0}{\langle R^2 \rangle_m}\right)
\]

(37)

where \( \langle R^2 \rangle \) and \( \langle R^2 \rangle_0 \) represent the mean square end-to-end distances in the presence and absence of flow. \( \langle R^2 \rangle_m \) is the maximum observed mean square end-to-end distance under flow.

In terms of the normal modes, \( r_p(t) = \frac{1}{N} \int_0^N d\eta r_{\eta}(t) \cos(2\pi\eta n/N) \), the above equations can be rewritten as

\[
\zeta_p \frac{\partial r_p(t)}{\partial t} = k_p r_p(t) + \dot{\gamma} r_p(t) + f_p(t),
\]

(38)

where \( k_p = p^2 \pi^2 k/N \), \( \zeta_0 = N\zeta \) and \( \zeta_{p \neq 0} = 2N\zeta \). The above expression can be solved for the chain extension under steady state to yield
Eq. 3 Mean fractional extension, \( x \) versus the Weissenberg number, \( Wi \) for different fixed values of \( \alpha \). The full lines are the theoretical curves calculated from Eqs. (40) and (41). The symbols represent data from simulations of Ref.[39] with the following meanings: open squares, 100\%E; plus signs, 51\%E; crosses, 50\%E, open circles, 49.5\%E; asterisks, 0\%E. This figure has been reproduced from Ref. [35]

\[
\langle R^2 \rangle = \frac{8}{N} \sum_{p=1,odd} \left[ \frac{1}{k_p} + \frac{\dot{\gamma}^2 \zeta^2 (1 + \alpha)^2}{2k_p(k_p^2 - \dot{\gamma}^2 \zeta^2 \alpha)} \right]. 
\]

If \( \tau = \zeta N^2 b^2 / 3 \pi^2 k_B T \) is defined as the longest relaxation time and \( Wi = \dot{\gamma} \tau \) as the Weissenberg number, the above equation can be rewritten as

\[
z = \beta \left[ \frac{1 - z}{1 - \beta} \right] + \frac{4}{3 \pi^2} \left( \frac{1 - z}{1 - \beta} \right)^3 Wi^2 (1 + \alpha)^2 S,
\]

where \( z = \langle R^2 \rangle / \langle R^2 \rangle_m \), \( \beta = \langle R^2 \rangle / \langle R^2 \rangle_m \), and \( S \) is given by

\[
S = - \frac{\pi^2}{8\alpha Wi^2} \left( \frac{1 - \beta}{1 - z} \right)^2 + \frac{\pi}{8\alpha Wi^2} \left( \frac{1 - \beta}{1 - z} \right)^{5/2} \left( \tan(a \pi/2) + \tanh(a \pi/2) \right),
\]

where \( a = (\alpha Wi^2)^{1/4}((1 - \beta)/(1 - z))^{1/2} \).

If the mean fractional extension of the chain is defined as \( x = \sqrt{z} \), the results can be presented in terms of Figs. 3 and 4, which show the variation of the mean fractional extension as a function of the Weissenberg number \( Wi \) [35].

Figure 3 compares the theoretical result for the mean fraction extension as a function of \( Wi \) with results from the Brownian dynamics simulations of Chu et al. [39] for six different values of \( \alpha \) represented in terms of \( \%E = 50(1 + \alpha) \).

In a pure extensional flow (100\%E), the chain undergoes a sudden increase in its size at very small value of \( Wi \). In a pure rotational flow (0\%E), the chain only rotates and does not extend. In the case of simple shear, the presence of a large number of fluctuations results in 50\% full extension. In the latter case, our theoretical curves reproduce the trend seen in single molecule experiments on DNA under shear [37, 38]. Figure (4) represents the variation of mean extension as a function of \( Wi^{eff} = \sqrt{\alpha Wi} \). A significant degree
Fig. 4 Mean fractional extension, $x$ versus the effective Weissenberg number, $W_{i}\text{eff} = \sqrt{\alpha}W_{i}$ for $\alpha > 0$. The full lines are the theoretical curves calculated from Eqs. (40) and (41). The symbols represent data from simulations of Ref.[39]. This figure has been reproduced from Ref. [35]

of data collapse suggest $W_{i}\text{eff}$ is a reasonable scaling variable for $\alpha > 0$. Our theoretical predictions compare well with simulation and experimental data on polymers under flow. The neglect of the hydrodynamic interactions leads to deviations at low Weissenberg numbers. The finitely extensible Zimm model can provide a better comparison at low Weissenberg numbers.

10 Conclusions

In this chapter, a unified description of ideal polymers is presented in terms of the Gaussian equivalent chains. The static properties of the Gaussian equivalent chains, like the size and its dependence on solvent quality and temperature, are discussed in terms of simple scaling arguments and theories based on statistical mechanics. The non-linearity in the force-extension relation for real polymers is obtained from the concept of tension blobs. The diffusion coefficient and the relaxation time of a polymer are calculated from the Rouse model. In the presence of the hydrodynamic interactions, the dynamic quantities of interest are estimated from the Zimm model. The behavior of polymers under flow is presented in terms of the finitely extensible Rouse model, which is shown to provide a reasonable accurate description of polymers in extensional, rotational, simple shear and linear-mixed flows for weak flows.

References

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