

Flory theory for polymers

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TOPICAL REVIEW

Flory theory for polymers

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Online at stacks.iop.org/JPhysCM/25/503101**Abstract**

We review various simple analytical theories for homopolymers within a unified framework. The common guideline of our approach is the Flory theory, and its various avatars, with the attempt at being reasonably self-contained. We expect this review to be useful as an introduction to the topic at the graduate student level.

(Some figures may appear in colour only in the online journal)

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1. Introduction

Polymer physics, with an old and venerable history spanning more than 60 years, now occupies an important position in basic physics, providing conceptual support to a wide variety of problems [1–17].

A polymer, from a physicist’s point of view, is a set of units, called monomers, connected linearly as a chain. Such polymers are the natural or synthetic long chain molecules formed by bonding monomers chemically as in real polymers or bio-polymers like DNA and proteins, but they need not be restricted to those only. Polymers can also be the line defects in superconductors and other ordered media, the domain walls in two-dimensional systems and so on. Even if noninteracting, a polymer by virtue of its connectivity brings in correlations between monomers situated far away along the chain. This makes a polymer different from a collection of independent monomers. The basic problem of polymer physics is then to tackle the inherent correlations due to the long length of the string-like object.

A gas of N isolated monomers at any nonzero temperature T would like to occupy the whole available volume to maximize the entropy, but that would not be the case when they are connected linearly as a polymer. This brings in a quantity very special to polymers, namely the equilibrium size of a polymer, in addition to the usual thermodynamic quantities. Traditionally, thermodynamic quantities, at least for large N , are expected to show extensivity, i.e., proportionality to the number of constituent units, but the size of a polymer in thermal equilibrium need not respect that. In other words, if the length of a polymer is doubled, the size need not change by the same factor. Consequently, even the usual thermodynamic quantities would have an extra polymer length dependence which will not necessarily be extensive but would encode the special polymeric correlations mentioned above. How the equilibrium size of a polymer changes or scales, as its length is increased, whether this dependence shows any signature of phase transitions with any external parameter like temperature, and the consequent effects on other properties are some of the questions one confronts in the studies of polymers.

The success of exact methods, scaling arguments and the renormalization group has crafted the statistical physics approach to polymer physics into a well defined and recognized field. One of the first, and most successful, theoretical approaches to the thermophysical properties of

polymers is the celebrated Flory theory, which is the central topic of this review. This simple argument was a key step in the history of critical phenomena, in particular in marking the emergence of power laws and the role of dimensionality. To investigate the special effects of long-range correlations that develop near a critical point, one needs a fine tuning of parameters like temperature, pressure, fields etc, close to that special point. In contrast, the simple Flory theory showed that a polymer exhibits critical features, power laws in particular, and a dimensionality dependence beyond the purview of perturbation theories, all without any requirement for fine tuning. Here is an example of self-organized criticality—a phenomenon where a system shows critical-like features on its own without any external tuning parameter—though the name was coined decades after the Flory theory.

Various monographs [1–7, 9–19], have covered different aspects of methodologies and techniques. This notwithstanding, our aim is to bring out the nuances present in the Flory theory and to place it in the current context, to appreciate why this theory has stood the test of time as compared to other mean-field theories.

This review is organized as follows. After a recapitulation of the basic facts of a noninteracting polymer and the simple Flory theory in section 2, we introduce the Edwards continuum model [18, 19] (section 3) and the mean-field approximation to its free energy (section 5). This forms the basis for discussing the Flory approximation through a saddle point method (section 5.2). The results for the three regimes of a polymer (swollen, theta and compact) and the transition behaviour can also be found in the same section. How the Flory theory fares when compared with the current view of scale invariance, universality and scaling is discussed in section 4 and the role of a microscopic length scale is also discussed there. A few modifications [20, 21], and a simple extension to include external forces applied to one extreme of the polymer, are discussed in sections 6.2 and 7.3, respectively.

While the original Flory theory describes the size at a fixed temperature, as the number of monomers increases, it is possible to go beyond power laws in the current framework. The analysis allows one to discuss the temperature dependence of the size at a fixed number of monomers (assumed to be sufficiently large). This crossover effect is discussed in section 7. A particularly interesting case appears to be the two-dimensional case, discussed in section 6.4, where the scaling function can be computed exactly. Section 6.5 discusses the uniform expansion method [5] along with its relationship to a perturbative approach [22–24].

Besides the three states mentioned above, there is an obvious state of a polymer, namely a stretched or rod-like state. This state can be achieved by a force at one end, keeping the other end fixed, or by assigning a penalty for bending. In the absence of any interaction, there is no transition from this rod-like state to any of the other states. But still, for completeness, the universal features of the crossover behaviour need to be discussed. This is done in the last part of the paper, which is devoted to the semiflexible chain, in which bending rigidity competes with entropy. The response

of the polymer when a pulling force is applied to an extremum is discussed in section 8, with an eye on the interpolating formula between flexible and semiflexible regimes [25–28]. Ancillary results for the structure factor and the end-to-end distance are presented in section 8.6.

Several technical issues are relegated to the appendices. A few Gaussian transformations that are frequently employed are listed in appendix A. A discussion of the central limit theorem as applied to polymers and a possible deviation can be found in appendix B. In appendix C, the theoretical framework of perturbation theory [22, 23] is introduced at the simplest possible level, and the lowest order calculation is explicitly performed to show how the method works. Finally, for completeness, appendices E–H include the explicit derivation of some results that are used in the main text.

We end this introduction with a few definitions. If all the monomers, and therefore the bonds, can be taken as similar, then the polymer is called a homopolymer. If there is any heterogeneity either in monomers or in bonds, it will be a heteropolymer. In the case of two types of monomers arranged in a regular pattern, the polymer is called a copolymer. Two different types of polymers connected together is an example of a block-copolymer. This review focuses on the homopolymer case only.

We use the symbol \sim to denote the dependence on certain quantities, ignoring prefactors and dimensional analysis, while the symbol \approx is used for approximate equality.

2. Elementary version of the Flory theory

2.1. Gaussian behaviour

2.1.1. Freely jointed chain. Consider an isolated homopolymer formed by $N + 1$ monomers at positions $\{\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N\}$ in space, and let b be the monomer–monomer distance (sometimes referred to as the Kuhn length). This is depicted in figure 1.

We further introduce the bond variable $\boldsymbol{\tau}_j$ ($|\boldsymbol{\tau}_j| = b$) and the end-to-end distance \mathbf{R} ,

$$\begin{aligned} \boldsymbol{\tau}_j &= \mathbf{r}_j - \mathbf{r}_{j-1}, & \text{and} \\ \mathbf{R} &= \mathbf{r}_N - \mathbf{r}_0 = \sum_{j=1}^N \boldsymbol{\tau}_j. \end{aligned} \quad (2.1)$$

A flexible polymer is defined as one for which the bond vectors are completely independent so that each bond can orient in any direction in space irrespective of the orientations of the others. This freedom is expressed as an absence of any correlation between *any* two different bonds, that is

$$\langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \rangle = b^2 \delta_{ij}. \quad (2.2)$$

This is the basis of the freely jointed chain (FJC). As the monomer–monomer distance is fixed, the average in equation (2.2) is an average over all possible orientations. This ensemble averaging is denoted by the angular brackets $\langle \dots \rangle$. A more realistic model, where there is an orientational correlation between successive bonds, called the worm-like chain (WLC) model (or Kratky–Porod model), is the paradigm of the stiff polymer, and will be discussed later.

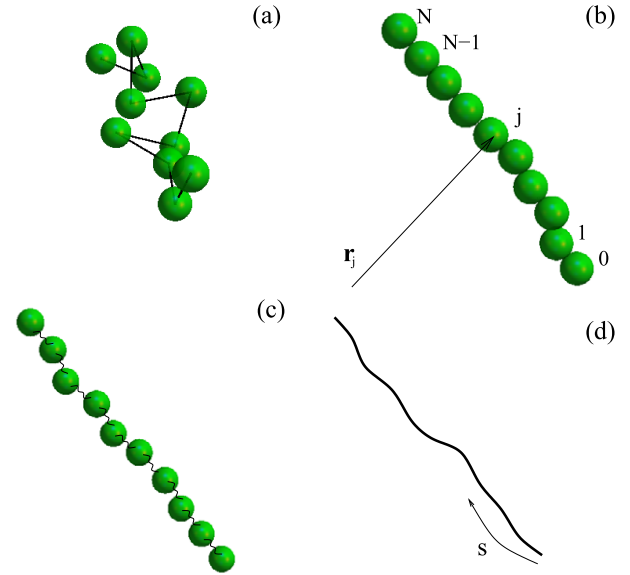


Figure 1. Various representations of a polymer. (a) Freely jointed chain: rigid bonds with full free rotations. The beads and bonds may cross without any penalty. (b) A collection of N tethered spheres (monomers) at positions \mathbf{r}_j , with $j = 0, 1, \dots, N$. The size of the monomers could be indicative of the excluded volume interaction of the monomers. (c) A bead spring model where the harmonic springs take care of the polymer connectivity. (d) Continuum model—no details of the polymeric structure are important. The location of a monomer is given by a length s .

2.1.2. Size of a polymer. Use of equations (2.1) and (2.2) leads to

$$\langle R^2 \rangle = \sum_{i,j=1}^N \langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \rangle = Nb^2, \quad (2.3)$$

so that the size R , measured by the root mean square (rms) end-to-end distance of a polymer, depends on its length N as

$$R \sim bN^\nu, \quad (2.4)$$

with $\nu = 1/2$ for the FJC. The exponent ν is called the size exponent. We are using the rms value as the size of the polymer because by symmetry (i.e. isotropy) $\langle \mathbf{R} \rangle = 0$. A judicious choice of origin can always remove a nonzero average of any probability distribution, whereas it would be impossible to make the variance zero. Hence the importance of the rms value as a measure of the size.

The behaviour described by equation (2.4) can also be read as follows. If a sphere of radius R is drawn with its centre in a random position along the chain, the total length of the polymer contained in the sphere is about R^{d_F} , with $d_F = 1/\nu$ being what is known as the fractal dimension. So, the fractal dimension of our noninteracting polymer is $d_F = 2$.

The probability distribution $P(\mathbf{R}, N)$ of the end-to-end distance is a Gaussian (see appendix B for details) and in $d = 3$ it is (see equation (B.7))

$$P(\mathbf{R}, N) \approx \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp \left[-\frac{3}{2} \frac{R^2}{Nb^2} \right]. \quad (2.5)$$

The standard deviation, which determines the width of this distribution, gives the rms size R of equation (2.4).

A chain characterized by Gaussian behaviour (2.5) is also called an *ideal or phantom* chain. It also goes by the names of Gaussian polymer and non-self-interacting polymer. These names are used interchangeably.

The size of a polymer discussed above is an example of a critical-like power law whose origin can be traced to correlations. Even though the bonds are uncorrelated, the monomers are not. This can be seen from equations (2.1) and (2.2) as the positions of monomers i and j satisfy

$$\langle |\mathbf{r}_j - \mathbf{r}_i|^2 \rangle = \sum_{l,m=i+1}^j \langle \boldsymbol{\tau}_l \cdot \boldsymbol{\tau}_m \rangle = (j-i)b^2. \quad (2.6)$$

Generalizing equation (2.5), the conditional probability density of monomer j to be at \mathbf{r}' if the i th monomer is at \mathbf{r} is given by

$$P(\mathbf{r}', j | \mathbf{r}, i) \propto \exp \left[-\frac{3}{2} \frac{(\mathbf{r}' - \mathbf{r})^2}{|j-i|b^2} \right]. \quad (2.7)$$

The distribution becomes wide as $j-i$ increases and it is not factorizable. This is to be contrasted with the case of noninteracting monomers without polymeric connections. There this joint probability distribution is the product of the individual probability densities and hence devoid of any correlations⁶. The behaviour of an ideal chain as formulated here is purely entropic in origin because all the configurations are taken to have the same energy.

If one generalizes equation (2.2) by substituting δ_{ij} by a general correlation g_{ij} which (a) depends only on $|i-j|$, and (b) is such that $\sum_j g_{ij} < \infty$, then the results, like $R^2 \sim N$, remain essentially the same, since equation (2.3) is modified by a multiplicative constant. In this case, the decay length of the correlation g_{ij} gives the Kuhn length.

2.2. Non-Gaussian behaviour

To go beyond the Gaussian behaviour, let us introduce the repulsive interaction of the monomers, e.g., the athermal excluded volume interaction. The question of interest is how this repulsion of the monomers affects the size of the polymer. Does it just change the amplitude in equation (2.4) or does it change the exponent? A change in the exponent needs to be taken more seriously than a change in the amplitude because the latter is equivalent to a change in the unit of measurement while the former changes the fractal dimension of the polymer.

2.2.1. Simple Flory theory. A simple way to account for the fact that non-consecutive spheres (i.e. monomers) cannot interpenetrate is provided by a hard-sphere repulsion, which is proportional to the excluded volume v_{exc} of each pair of

monomers multiplied by the number of monomer pairs (N^2) per unit of available volume (R^3), that is

$$\text{repulsive energy} \sim v_{\text{exc}} \frac{N^2}{R^3}. \quad (2.8)$$

The total free energy $F_N(R)$ of the system can then be quickly estimated as follows [4, 29].

From equation (2.5)

$$S_N(R) = k_B \log P(R, N) \sim -\frac{R^2}{Nb^2} \quad (2.9)$$

is the entropy of the chain⁷, where k_B is the Boltzmann constant, so that at temperature T one has

$$F_N(R) = F_0 + e_0 \frac{R^2}{Nb^2} + e_1 v_{\text{exc}} \frac{N^2}{R^3}, \quad (2.10)$$

where e_0 and e_1 are T -dependent constants and F_0 is the remaining part of the free energy. Equation (2.10) is to be interpreted as the free energy of a polymer chain of N monomers with excluded volume interaction if it had a size of radius R . The size of an unconstrained polymer would come from a minimization of $F_N(R)$ with respect to R , which amounts to equating the two R -dependent terms in equation (2.10). The size still has the form of equation (2.4), but with

$$\nu = 3/5. \quad (2.11)$$

This ν is called the Flory exponent. This is the most elementary version of the Flory theory which experienced remarkable success in explaining the experimental evidence in the swelling of real polymers. This success is thought to be accidental, but we shall see later on that more systematic arguments do lead to equations (2.10) and (2.11).

The above argument can be generalized to arbitrary dimensions d . The entropy term as given by equation (2.9) is independent of d , but the excluded volume term in equation (2.8) would be replaced by N^2/R^d , with R^d being the volume occupied by the polymer. A minimization of the free energy then gives the Flory exponent as $\nu = \frac{3}{d+2}$. However, for $d > 4$, it gives a size exponent less than $1/2$, which is not possible, because a repulsion cannot make a polymer more compact than a free chain. One therefore expects the free chain value $\nu = 1/2$, so that the general Flory exponent would be

$$\nu = \begin{cases} \frac{3}{d+2}, & \text{for } d \leq 4, \text{ (swollen phase)} \\ \frac{1}{2}, & \text{for } d > 4, \end{cases} \quad (2.12)$$

which agrees with the known exact results like $\nu = 1$ for $d = 1$, $\nu = 3/4$ for $d = 2$, $\nu = 1/2$ for $d > 4$ and is very close to the best estimate $\nu \approx 0.588$ known for $d = 3$ [30, 31].

⁷ The entropy should be $k_B \log[\text{number of chains of } N \text{ monomers and end-to-end distance} = R]$. However, the number in the argument of the logarithm is proportional to $P(R, N)$, and so—apart from an additive, N -dependent, constant—we get equation (2.9).

⁶ Two random variables x, y are correlated, i.e. $\langle xy \rangle \neq \langle x \rangle \langle y \rangle$, if and only if $P(x, y) \neq p(x)p(y)$.

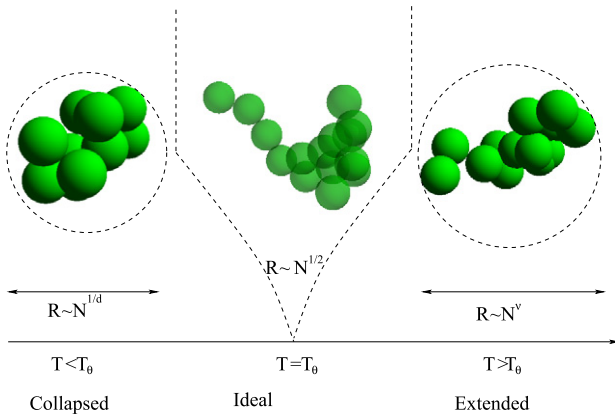


Figure 2. Schematic phase diagram of an isolated homopolymer. At high temperature $T > T_\theta$, the polymer is in a swollen phase (right), whereas one expects a compact globule at sufficiently low temperatures $T < T_\theta$ (left). These two regimes are separated by a transition regime at $T = T_\theta$ (centre) where the polymer behaves more or less as a Gaussian chain, at least in $d > 3$.

2.2.2. Collapse. The case of attractive interaction may also be mentioned here. With attraction and hard-core repulsion, the monomers would like to stay as close as possible. This gives a more or less compact packing of spheres so that the monomer density inside a sphere enclosing the polymer is $O(1)$ in N . Note that the density for the repulsive case $N/R^d \sim N^{1-d\nu} \rightarrow 0$, for large N . A compact phase, also called a globule, would then have

$$R \sim N^{1/d}, \quad \text{i.e., } \nu = \frac{1}{d} \text{ (compact)}. \quad (2.13)$$

The collapsed state is not a unique state and the polymeric nature is important in determining its overall property.

One expects a generic phase diagram, as schematically depicted in figure 2, with a theta point at $T = T_\theta$, a high temperature ($T > T_\theta$) swollen or coiled phase and a low temperature ($T < T_\theta$) compact phase. This will be discussed in detail in section 5.

3. The Edwards continuum model

3.1. Discrete Gaussian model

The central limit theorem, as explained in appendix A, allows us to describe a polymer by the distribution $W(\mathbf{r}_0, \dots, \mathbf{r}_N)$ of N bonds, $\boldsymbol{\tau}_1 = \mathbf{r}_1 - \mathbf{r}_0, \dots, \boldsymbol{\tau}_N = \mathbf{r}_N - \mathbf{r}_{N-1}$, each having a Gaussian distribution, as

$$W(\mathbf{r}_0, \dots, \mathbf{r}_N) = \prod_{j=1}^N p(\boldsymbol{\tau}_j) = \prod_{j=1}^N \left\{ \left(\frac{1}{2\pi b^2} \right)^{d/2} \exp \left[-\frac{1}{2} \frac{\boldsymbol{\tau}_j^2}{b^2} \right] \right\} \quad (3.1a)$$

$$= Z_G^{-1} \exp[-\beta H_G], \quad (3.1b)$$

where we have introduced the Gaussian Hamiltonian

$$\beta H_G = \frac{1}{2b^2} \sum_{j=1}^N \boldsymbol{\tau}_j^2 = \frac{1}{2b^2} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{r}_{j-1})^2, \quad (3.1c)$$

with the partition function $Z_G = (2\pi b^2)^{Nd/2}$.

The Gaussian Hamiltonian is another representation of a polymer where the monomers are connected by harmonic springs (figure 1(c)). At any nonzero temperature, the equipartition theorem gives $\langle \boldsymbol{\tau}_j^2 \rangle / b^2 = d$, which allows the bonds to have a nonzero rms length. The size of the polymer is given by $\langle R^2 \rangle = db^2 N$.

The Gaussian Hamiltonian, being quadratic, makes analytical calculations simpler compared to the FJC case with rigid bond constraints. In contrast, the extensibility of the springs allows the polymer to have a size $R > Nb$ with a nonzero probability as seen from equation (2.5). However, the probabilities, being in the tail of the Gaussian distribution, are too small to contribute to the average. Consequently, most of the physical behaviour will be controlled by the configurations around the peak of the distribution and not by rare extreme configurations. With this caveat in mind, the Gaussian Hamiltonian can be used in most cases, unless certain stretched states become important.

There is a subtle difference between this Gaussian Hamiltonian approach and the FJC of the previous section. Unlike the FJC, here we are associating energies with conformations and the behaviour is not strictly entropic in origin. However, the ‘springs’ help us in maintaining the polymeric connectivity and the total elasticity of the Gaussian polymer would be the same as the entropic elasticity of the ideal chain. In that respect, the elasticity of the Gaussian chain, equation (2.9), could be termed as entropic in origin.

3.2. Continuum model

A simple-minded way of taking the continuum limit $N \rightarrow \infty, b \rightarrow 0$ with the length Nb a constant, would lead to a vanishing $\langle R^2 \rangle$ as defined by equation (2.3). This is avoided by introducing a curvilinear coordinate $s = jb^2, 0 \leq s \leq L = Nb^2$ for the monomer and a vector position $\mathbf{r}(s)$ associated with it. The Gaussian Hamiltonian of equation (3.1c) takes the limiting form

$$\beta H_G = \frac{1}{2} \sum_{j=1}^N b^2 \frac{1}{b^4} (\mathbf{r}_j - \mathbf{r}_{j-1})^2 \rightarrow \beta H_L^{(0)},$$

$$\text{with } \beta H_L^{(0)} = \frac{1}{2} \int_0^L ds \left(\frac{\partial \mathbf{r}}{\partial s} \right)^2. \quad (3.2)$$

In the above form, one end point of the polymer can be anywhere in the whole volume available and it would contribute a volume factor to the partition function, of no concern to us. We may get rid of this perfect gas like redundant factor by fixing one monomer, preferably the end point at $s = 0$, at the origin. The continuum limit of the corresponding distribution (equation (3.1a)) is given

$$W(\mathbf{r}_0, \dots, \mathbf{r}_N) \rightarrow W[\mathbf{r}(s)] = \frac{1}{Z_0} \exp[-\beta H_L^{(0)}[\mathbf{r}(s)]], \quad (3.3)$$

with the ‘configurational partition function’ written formally as⁸

$$Z_0 = \int \mathcal{D}\mathbf{r} \exp[-\beta H_L^{(0)}[\mathbf{r}(s)]] \delta^d(\mathbf{r}(0)). \quad (3.4)$$

The notation $\int \mathcal{D}\mathbf{r}$ represents a formal sum over all possible paths or polymer configurations, but it is ill-defined if taken literally as a $b \rightarrow 0$ limit of the measure expected from equation (3.1a). This continuum language, patterned after the path integral representation in quantum mechanics [32], was introduced by Edwards [5, 18, 19]. The path integral, also known as the Wiener measure in the context of diffusion, is to be interpreted as a limit of the discrete sum. With appropriate care, the limit process may be traded with standard integrals, as will be done in this review.

Some more caution is needed here in interpreting the continuum Hamiltonian. Although s is introduced as a curvilinear coordinate measuring the arc length or contour length along the polymer, the string in the continuum (figure 1(d)) is not to be taken as a space curve. For a space curve $|\partial\mathbf{r}/\partial s| = 1$, which is not enforced in equation (3.2). In this interpretation, s remains a measure of the contour length obtained from the bead numbers, but the string remains Gaussian at the smallest scale. One may bypass this problem by assigning a new axis for s so that the polymer is viewed as a $d + 1$ dimensional string. To avoid the pitfalls of the Gaussian behaviour at all length scales, it may be necessary to use a lower cut-off in equation (3.2). Unless necessary this is not to be specified explicitly.

3.3. Interactions: the Edwards model

Next we consider a more general description, where the polymer can also interact. Since a polymer is generally in a solvent, the interactions need not be the actual microscopic interactions of the monomers. If a polymer is dissolved in a solvent, a monomer is surrounded mostly by solvent molecules. If we remove the solvent part from the problem, it would appear as if the monomers were staying away from each other. This situation of a polymer in a good solvent can be described by an effective repulsion among the monomers. On the other hand, if a polymer precipitates out from a solution, then there is a preference for the monomers to avoid the solvent molecules. This is the case of a polymer in a bad solvent whose effective description requires an attraction between the monomers. In this spirit of effective interactions, it suffices to consider the polymer as the sole object with interactions among the monomers, which depend on temperature, solvent quality and other parameters of the original problem. As pseudo-interactions, these need not be restricted to pairwise interactions only. A schematic representation of two-body $\Phi_2(\mathbf{r}, \mathbf{r}')$ and three-body interactions $\Phi_3(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ is shown in figure 3.

A polymer in a good solvent can be described by a simple choice of a pairwise contact repulsive interaction, represented

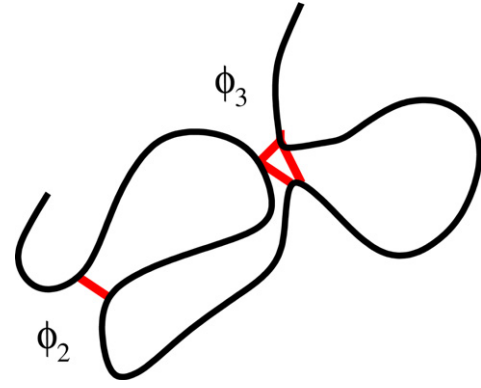


Figure 3. Schematic representation of the two-body Φ_2 and the three-body Φ_3 interactions. For contact interactions $\Phi_2(\mathbf{r}, \mathbf{r}') = u\delta(\mathbf{r}, \mathbf{r}')$, $\Phi_3(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = v\delta^d(\mathbf{r} - \mathbf{r}')\delta^d(\mathbf{r}' - \mathbf{r}'')$.

by a delta function, $\Phi_2 = u\delta^d(\mathbf{r})$, with a coupling parameter $u > 0$ so that ignoring all higher order terms,

$$\beta H_L[\mathbf{r}(s)] = \frac{1}{2} \int_0^L ds \left(\frac{\partial \mathbf{r}}{\partial s} \right)^2 + \frac{1}{2} u \int_0^L ds_1 \int_0^L ds_2 \delta^d(\mathbf{r}(s_2) - \mathbf{r}(s_1)). \quad (3.5)$$

The first term on the right-hand side of equation (3.5) is the usual Gaussian term, representing polymer connectivity, whereas the term penalizes any two-monomer contact. This particular form is known as the Edwards Hamiltonian [19] and is a representation of a self-avoiding walk or a polymer with excluded volume interaction. This is also called the minimal model for a polymer.

To describe the collapse, i.e., the poor solvent case, we need $u < 0$ for attraction and for stability of a repulsive three-body interaction. With the choice of the usual three-body contact pseudo-potential $\Phi_3 = v\delta^d(\mathbf{r} - \mathbf{r}')\delta^d(\mathbf{r}' - \mathbf{r}'')$, penalizing any three-monomer contact, the Edwards Hamiltonian becomes

$$\beta H_L[\mathbf{r}(s)] = \frac{1}{2} \int_0^L ds \left(\frac{\partial \mathbf{r}}{\partial s} \right)^2 + \frac{1}{2} u \int_0^L ds_1 \int_0^L ds_2 \delta^d(\mathbf{r}(s_2) - \mathbf{r}(s_1)) + \frac{1}{3!} v \int_0^L ds_1 \int_0^L ds_2 \int_0^L ds_3 \times \delta^d(\mathbf{r}(s_1) - \mathbf{r}(s_2))\delta^d(\mathbf{r}(s_2) - \mathbf{r}(s_3)). \quad (3.6)$$

$$\equiv \beta H_L^{(0)} + \beta V_L, \quad (3.7)$$

where $\beta H_L^{(0)}$ is given by equation (3.2) and βV_L represents the interaction part of the dimensionless Hamiltonian. These minimal models involve only three parameters: L , u and v .

Since a polymer can be precipitated out of a solution by cooling (section 2), it is assumed that a temperature T_θ exists such that

$$u \propto (T - T_\theta)/T_\theta,$$

so that $T > T_\theta$ ($u > 0$) corresponds to the repulsive case (a polymer in a good solvent) while $T < T_\theta$ ($u < 0$) for the

⁸ Note that, within the de Gennes mapping between spin models and polymers with the number of components going to zero, this quantity is in fact a compressibility (or a susceptibility). See [33].

attractive case (the bad solvent case). The transition point $T = T_\theta$ is the theta point, as in figure 2.

3.4. Green functions

The problem associated with $b \rightarrow 0, N \rightarrow \infty$ for partition functions (b^{Nd} in equation (3.1b)) is avoided by normalization by Z_0 . The probability that the free polymer has an end-to-end distance vector \mathbf{R} is written as

$$\begin{aligned} G_L^{(0)}(\mathbf{R}) &= Z_0^{-1} \int_{\mathbf{R}} \mathcal{D}\mathbf{r} \exp[-\beta H_L^{(0)}[\mathbf{r}(s)]] \\ &= (2\pi L)^{-d/2} e^{-R^2/(2L)}, \end{aligned} \quad (3.8)$$

where the notation

$$\int_{\mathbf{R}} \mathcal{D}\mathbf{r} \equiv \int \mathcal{D}\mathbf{r} \delta^d(\mathbf{R} - [\mathbf{r}(L) - \mathbf{r}(0)]) \delta^d(\mathbf{r}(0)) \quad (3.9)$$

is used to indicate the sum over all paths with fixed end-to-end distance \mathbf{R} with the $s = 0$ end fixed at the origin. The result, equation (3.8), is the d -dimensional analogue of the probability distribution in equation (2.5). For the interacting case, the normalized partition (Green) function is

$$G_L(\mathbf{R}) = Z_0^{-1} \int_{\mathbf{R}} \mathcal{D}\mathbf{r} \exp[-\beta H_L[\mathbf{r}(s)]], \quad (3.10)$$

which is related to the probability of the end-to-end vector being \mathbf{R} , but for the normalization. G is called the *Green function* or a *propagator* while $G_L^{(0)}(\mathbf{R})$ is the ‘free’ propagator.

The partition function of equation (3.4) corresponds to the case where the polymer end at length L is free, while the sum expressed by equation (3.9) corresponds to a constrained ensemble, the ensemble of all configurations with the same end-to-end distance \mathbf{R} . This is a fixed- \mathbf{R} ensemble. Its conjugate ensemble is the fixed-force ensemble where a force is applied at the free end. In a fixed- \mathbf{R} ensemble, the force required at the open end point is a fluctuating quantity whose average gives the force required to maintain that distance. In the fixed-force ensemble, the end-to-end distance fluctuates and the variance of this fluctuation is related to the elastic constant or response function of the polymer. This case will be taken up in section 7.3. As per standard arguments of statistical mechanics, the results are supposed to be independent of the ensemble used. However, polymers provide many examples of non-equivalence of these two ensembles [34, 35].

4. Flory theory in a modern perspective

The significance of the Flory theory can be brought out by looking at it from a modern point of view. The failure of the mean-field theory in phase transitions and critical phenomena led to the ideas of universality and scaling and the idea of studying problems at different length scales, as with renormalization group [6, 31]. The Flory theory, even though believed to be a mean-field type theory, showed all the aspects of the modern theory, in fact much more than a mean-field

theory is expected to do. In this section, we discuss the link between the Flory theory and the idea of scale invariance and universality, and the crossover behaviour.

4.1. Scaling analysis

The appearance of power laws as in the N dependence of the size of a polymer is associated with scale invariance or the absence of any typical scale. To see this, compare the two functions, $f_1(x) = Ax^{-\alpha}$ and $f_s(x) = Be^{-x/\xi}/x^\alpha$ for $x \rightarrow \infty$. For small α , it is not possible to define any scale for $f_1(x)$, apart from the size of its domain over which it is normalized, while $f_s(x)$ is characterized by a scale ξ of x . If x is measured on a different scale, i.e. $x' = \lambda x$, then we see that by changing the prefactor $A' = A\lambda^{-\alpha}$, the functional form of f_1 remains invariant. On this new scale one would still see the same power law behaviour, no matter what the scale factor λ is. Compare this with f_s . If $\lambda x \gg \xi$, then f_s becomes too small to be rejuvenated by increasing the coefficient B . This is generally true for any non-power law function. On the other hand, if under a scale change $x \rightarrow \lambda x$, a function $f(x)$ behaves as $f(\lambda x) = \lambda^{-p}f(x)$, then by choosing $\lambda = 1/x$, we get a power law form $f(x) \sim x^{-p}$. Therefore, a continuous scale invariance (i.e. any value of λ) implies power laws and vice versa.

As an example, consider the probability distribution of the end-to-end distance \mathbf{R} of a polymer of length L . This probability $P(\mathbf{R}, L)$ depends, in principle, on all the parameters of the problem, especially the starting microscopic length scales, in a way consistent with dimensional analysis. However, for the large distance behaviour, if the ratio of the bond length and the total length goes to zero, one expects dependence on L only.

If we change the scale of measuring length by a factor λ , then as per dimensional analysis all distances, small and large, need to be scaled. However, if we choose to scale only the large lengths keeping the microscopic scales unchanged, what we get is dependence of λ solely coming from the L part. Such a transformation is called a scale transformation. A scale transformation for polymers shows that if $L \rightarrow \lambda L$, then R is scaled by λ^ν , even though in real life both $\langle R^2 \rangle^{1/2}$ and $L^{1/2}$ are to be measured as lengths. There is no violation of dimensional analysis because a dimensionally correct form is $\langle R^2 \rangle^{1/2} = b^{1-2\nu}L^\nu$. If both b and L are scaled as $b \rightarrow \lambda^{1/2}b$ and $L \rightarrow \lambda L$, then $\langle R^2 \rangle^{1/2}$ will also be scaled by $\lambda^{1/2}$ like b . This distinction, between a scale transformation to get the scaling keeping microscopic scales fixed and a transformation that scales all the lengths as in dimensional analysis, is exploited in the renormalization group approach. In contrast, the Flory theory type approaches take advantage of this difference by assuming that only the large scales matter. We may amplify this by considering a particular example.

Let us take the example of $P(\mathbf{R}, L)$ obtained from a microscopic Hamiltonian defined earlier. We change only R and L , as $L \rightarrow \lambda L$ and $R \rightarrow \lambda^\nu R$. While doing this, we keep all other scales untouched, and therefore these will not be displayed. Then P can be claimed to show *scaling* if

$$P(\mathbf{R}, L) = \lambda^X P(\lambda^\nu \mathbf{R}, \lambda L), \quad (4.1)$$

for any λ . We are then free to choose $\lambda = 1/L$ to write

$$P(\mathbf{R}, L) = \frac{1}{L^X} \mathcal{P}\left(\frac{\mathbf{R}}{L^\nu}\right) \equiv \frac{1}{L^X} P\left(\frac{\mathbf{R}}{L^\nu}, 1\right), \quad (4.2)$$

where $\mathcal{P}(x)$ is called a scaling function. As advertised, this form emphasizes the large scales only, by suppressing the dependence on the small scales of the problem. As a probability, the normalization $\int d^d r P = 1$ can be used to deduce that $X = d\nu$. The scaling analysis therefore predicts the form of the probability distribution as

$$P(\mathbf{R}, L) = \frac{1}{L^{d\nu}} \mathcal{P}\left(\frac{\mathbf{R}}{L^\nu}\right), \quad (4.3)$$

which agrees with the Gaussian distribution for $\nu = 1/2$ (see equation (2.5)). We now use the result that the equilibrium size is given by $R_0 \sim N^\nu$, to argue in a different way. If only the large scale like R_0 matters, then dimensional analysis suggests that, being a density, $P(\mathbf{R}, N) \propto R_0^{-d}$, and the R dependence has to be in a dimensionless form. With R_0 as the only scale, the argument has to be \mathbf{R}/R_0 . This single scale assumption then tells us $P(\mathbf{R}, L) = R_0^{-d} \mathcal{P}(\mathbf{R}/R_0)$, in agreement with equation (4.3).

A different way to analyse the scale-invariant behaviour is to do a scale transformation of the underlying variables. Let us start with the Edwards Hamiltonian equation (3.5) and scale the length of the polymer by a factor λ , i.e., $s = \lambda s'$ so that $\mathbf{r} = \lambda^\nu \mathbf{r}'$, where ν is the polymer size exponent to be determined. The Hamiltonian now takes the form

$$H[\mathbf{r}(s)] = \frac{1}{2} \lambda^{2\nu-1} \int_0^{L/\lambda} ds \left(\frac{\partial \mathbf{r}}{\partial s}\right)^2 + \lambda^{2-d\nu} u \int_0^{L/\lambda} ds_1 \times \int_0^{L/\lambda} ds_2 \delta^d(\mathbf{r}(s_2) - \mathbf{r}(s_1)), \quad (4.4)$$

suppressing the primes on the variables. We tacitly assumed that u does not scale. For $L \rightarrow \infty$, the first term is scale invariant for the Gaussian value $\nu = 1/2$. This is ensured by the construction of the Hamiltonian in terms of \mathbf{r} and s . However, for this ν we find that the scaled interaction $u' = \lambda^{2-d/2} u$ increases with increasing λ for $d < 4$. This suggests that a Gaussian chain is unstable in the presence of the interaction in the continuum limit $\lambda \rightarrow \infty$ with $L \rightarrow \infty$. Such a term that grows on rescaling is called a *relevant term*. The question is, if the Gaussian behaviour is unstable, whether there is different scale-invariant stable behaviour. For the interaction to be important, we then demand that ν be such that both the terms scale in the same way so that H gets an overall scale factor. This requires $2\nu - 1 = 2 - d\nu$ or $\nu = \nu_F = 3/(d+2)$, as given in equation (2.12). In short, the scale invariance of the Hamiltonian of a noninteracting polymer gives the Gaussian value $\nu = 1/2$ while the scale invariance for a repulsive polymer gives the Flory exponent. By taking $L \rightarrow \infty$, the polymer is made scale invariant at all large scales. In this situation, the exponent is visible in the scaling of space and length. On the other hand, if L is finite but large, we expect the two terms to contribute equally even at the largest possible scale, namely, $\lambda = L$. One then recovers the Flory exponent because the two integrals, assumed convergent, are $O(1)$ in L as the integral limits are from 0 to 1.

What is actually required is the scale invariance of the free energy, to include the effects of entropy, not the Hamiltonian *per se*. This introduces corrections that require an additional scale factor for u . As it so happens, this correction (vertex correction) is small for polymers and the scale invariance of the Hamiltonian gives a close estimate.

4.2. Scaling functions and interpolation

Based on the Flory theory presented in section 4.1, we see the importance of the interactions u and ν in determining the size of a polymer, but most importantly, the dependence on N seems to be universal in the sense that the exponent does not depend on u, ν , but any nonzero u or ν change the Gaussian behaviour.

The dependence of the size on the interactions can be written in a form consistent with dimensional analysis. Taking the dimension of \mathbf{r} , the position vector, as length L , and the Hamiltonian as dimensionless, we have $[L] = L^2$ (see section 3.2). Although L is a measure of the polymer length it is dimensionally like a surface, because of the fractal dimension ($d_F = 2$) mentioned in section 2. Since $[\delta^d(\mathbf{r})] = L^{-d}$, the dimensions of u and ν in equations (3.5) and (3.6) are respectively L^{d-4} and $L^{2(d-3)}$. With the help of L , one may construct the dimensionless interaction parameters

$$z = c_1 u L^{(4-d)/2}, \quad \text{and} \quad w = c_2 \nu L^{3-d}, \quad (4.5)$$

with dimensionless constants c_1, c_2 chosen as per convenience. The size can be written as

$$R^2 = d L \psi^2(z, w), \quad (4.6)$$

where the function ψ gives the interpolation behaviour from the Gaussian to the swollen chain ($u > 0$). We suppress the w dependence in this discussion. Equation (4.6) of course assumes that the short-distance scale b , or the range of interaction of Φ_2, Φ_3 do not appear in the expression for the large N limit. This is a highly nontrivial assertion which we shall assume to hold good for the time being. The renormalization group approach tackles this issue but we do not get into that here. ψ is often called a scaling function or a crossover function.

One question may arise here. Just as equation (4.6) is meant for a crossover from the Gaussian to the swollen chain, could we have done it the other way round? We have seen that a polymer shows three different sizes: a theta chain separating the swollen phase ($u > 0$) and the collapsed phase ($u < 0$). There are situations (e.g., $d < 3$) for which none of these is Gaussian. For a temperature or solvent induced phase transition of a polymer, what should be the reference point to define the scaling function? In such cases, it is the unstable state that is to be taken as the primary size from which the interpolation formula or $\psi(z)$ has to be constructed. The Gaussian behaviour is unstable in the presence of any u , but the swollen state is the stable one for $u > 0$, justifying the form written in equation (4.6). It then has to be modified by substituting $L^{1/2}$ by L^{ν_0} for the collapse transition. This will be taken up later in section 7.

One way to express the interpolation behaviour is to study the behaviour of the size exponent as the parameters are varied. Let us consider the repulsive regime with $w = 0$. In this regime the power law behaviour is observable in realistic systems only for large lengths. The approach to the asymptotic value can be determined by studying the slope of ψ with L in a log-log plot. The effective exponent can be defined by a log-derivative

$$\sigma(z) = L \frac{\partial}{\partial L} \ln \psi = \frac{\epsilon}{2} z \frac{\partial}{\partial z} \ln \psi, \quad (\epsilon = 4 - d), \quad (4.7)$$

with the L derivative taken at a fixed u . For large z or L , $\sigma(z)$ should approach a constant that from equation (4.6) would give $R \sim L^{(1/2)+\sigma}$, i.e., $\nu = (1/2) + \sigma$.

The function ψ is analytic in the range $0 < z < \infty$, because for a finite chain the partition function, being a finite sum, cannot show any singularity. Also $\psi(0, 0) = 1$, by definition. It is therefore fair to expect leading behaviour

$$\psi(z) = (1 + az)^p, \quad (4.8)$$

so that

$$\psi(z) \stackrel{z \rightarrow \infty}{\sim} z^p,$$

$$\text{while } \psi(z) \stackrel{z \ll 1}{\sim} 1 + paz + \frac{p(p-1)}{2} (az)^2 + \dots, \quad (4.9)$$

and

$$\sigma(z) = \frac{\epsilon}{2} p \frac{az}{1+az} \stackrel{z \rightarrow \infty}{\rightarrow} \frac{\epsilon}{2} p. \quad (4.10)$$

It seems that the large z behaviour, of our immediate interest, can be obtained from the small z expansion of $\psi(z, 0)$. There are various approaches to get ψ . The perturbative renormalization group approach, not discussed here, tries to get a well-behaved series for σ , at least for small ϵ , by starting with a power series expansion in z . A perturbative approach for ψ will be taken up in appendix C. In contrast to these, the Flory theory is a *nonperturbative approach* to get ψ or σ in the large z limit directly.

As an example, we may quote the series for the scaling function obtained in a double expansion in z and ϵ [31] as

$$\psi^2(z) = 1 + \frac{2}{\epsilon} z - \frac{6}{\epsilon^2} z^2 + \dots \approx (1 + 8z/\epsilon)^{1/4}, \quad (4.11)$$

keeping only highest order of $1/\epsilon$ in the coefficient of powers of z . This series then gives $\sigma = \epsilon/16$, and

$$\nu = \frac{1}{2} + \frac{\epsilon}{16} + O(\epsilon^2).$$

For comparison, the Flory value has the ϵ -expansion,

$$\nu_F = \frac{3}{d+2} = \frac{1}{2} + \frac{\epsilon}{12} + \dots \quad (4.12)$$

4.2.1. Why exponent? The reason for focusing on the exponent ν can now be explained. The occurrence of an exponent different from $\nu = 1/2$ is noteworthy because R and L^ν are dimensionally different. The difference owes its origin to the interactions, but, still, the exponent obtained above does not depend on the parameters of the interaction.

Table 1. Lexicon of the variables involving $\{L, u, v\}$ and $\{b, N, u, v\}$. Here c represents some appropriate constant, not necessarily the same everywhere.

	Minimal model	With small scale
Microscopic length	None	b
Polymer length	L	Nb^2
Size (Gaussian polymer)	$R = d\sqrt{L}$	$R = db\sqrt{N}$
2-body parameter	$z = c u L^{(4-d)/2}$	$\alpha = c u b^{4-d}$
3-body parameter	$w = c v L^{(3-d)}$	$\gamma = c v b^{6-2d}$
Size (interacting)	$R \sim L^{1/2} z^p$	$R \sim b^{1-2\nu} L^\nu \sim bN^\nu$

Even for a general short-range interaction, instead of a contact potential in equation (3.7), the Flory argument in section 2 would produce the same ν as for the minimal model. This is universality.

There are two ways to motivate this universality. One way is to use z as in equation (4.5), where the interaction parameter is made dimensionless by L . For any other short-range interaction Φ_2 , one may define a z -like appropriate dimensionless parameter, e.g., by taking $u = \int d^d r \Phi_2(\mathbf{r})$. In this case, for $L \rightarrow \infty$, $z \rightarrow \infty$ for any value of $u > 0$ if $d < 4$, and the same asymptotic limit is reached for all interactions. The second way would be to use a microscopic parameter like the bond length, the range of interaction or the size of a monomer, let us call it b , to define a dimensionless interaction parameter $\alpha = ub^{4-d}$. If on successive rescaling of b ('coarse-graining') α approaches a fixed value α^* , then all short-range repulsions are ultimately described by α^* . The emergence of b , as an extra length scale, then allows a form $\langle R^2 \rangle \sim L(L/b^2)^{2\nu-1}$, with ν determined by α^* . Here, b appears as the saviour of an apparent violation of dimensional analysis.

Although the Flory theory does not require the microscopic length scales like b , we shall use both versions, often by using z to write $R \sim L^{1/2} z^p$, for some appropriate p , and often by introducing b to make the power of L explicit, as $R \sim b^{1-2\nu} L^\nu$. A lexicon of the two sets with and without b is given in table 1.

5. Flory mean-field theory

For an interacting polymer, the partition function, from equation (3.10), can be written as

$$\frac{Z}{Z_0} = \int d^d \mathbf{R} G_L(\mathbf{R}) = e^{-\beta \Delta F}, \quad (5.1)$$

with $\Delta F = -k_B T (\ln Z - \ln Z_0)$ as the excess free energy due to interaction. For the excluded volume case of equation (3.5), this excess free energy is called the free energy of swelling.

For the fixed- \mathbf{R} ensemble, the Helmholtz free energy is

$$F_L(\mathbf{R}) = E_L(\mathbf{R}) - TS_L(\mathbf{R}) \quad (5.2)$$

where the energy $E_L(\mathbf{R})$ is defined from a ratio similar to equation (5.1) but in terms of G_L and $G_L^{(0)}$, as

$$\exp[-\beta E_L(\mathbf{R})] \equiv \frac{G_L(\mathbf{R})}{G_L^{(0)}(\mathbf{R})} = \langle \exp[-\beta V_L[\mathbf{r}]] \rangle_{\mathbf{R}}^{(0)} \quad (5.3)$$

(the superscript (0) indicating an averaging with respect to $H_L^{(0)}$), and the corresponding Boltzmann entropy $S_L(\mathbf{R}) = k_B \ln[G_L^{(0)}(\mathbf{R}) Z_0]$.

The partition function Z of equation (5.1) is then given by

$$\begin{aligned} Z &= Z_0 \int d^d \mathbf{R} G_L^{(0)}(\mathbf{R}) \langle e^{-\beta V_L[\mathbf{r}]} \rangle_{\mathbf{R}}^{(0)} \\ &= \int d^d \mathbf{R} \exp[-\beta F_L(\mathbf{R})]. \end{aligned} \quad (5.4)$$

The Flory approximation discussed below attempts to get an approximation form for $F_L(\mathbf{R})$.

5.1. Mean-field approximation

Let us introduce the monomer density

$$\begin{aligned} \rho(\mathbf{r}) &= \int_0^L ds \delta^d(\mathbf{r} - \mathbf{r}(s)), \\ \text{with } \int d^d \mathbf{r} \rho(\mathbf{r}) &= L, \end{aligned} \quad (5.5)$$

so that ρ is related to the number concentration. The polymer Hamiltonian in equation (3.7) can be recast in terms of the concentration in the form

$$\beta V_L[\mathbf{r}] = \frac{u}{2!} \int d^d \mathbf{r} \rho^2(\mathbf{r}) + \frac{v}{3!} \int d^d \mathbf{r} \rho^3(\mathbf{r}), \quad (5.6)$$

which can be verified by direct substitution of equation (5.5).

The mean-field assumption is based on the (Gibbs–Bogoliubov) inequality

$$\langle e^{-\beta V_L(\mathbf{r})} \rangle_{\mathbf{R}} \geq e^{-\beta \langle V_L(\mathbf{r}) \rangle_{\mathbf{R}}}, \quad (5.7)$$

and to a maximization of the right-hand side with respect to a parameter, as elaborated below, with the additional approximation

$$\langle \rho \rho \cdots \rho \rangle_{\mathbf{R}} = \langle \rho \rangle_{\mathbf{R}} \langle \rho \rangle_{\mathbf{R}} \cdots \langle \rho \rangle_{\mathbf{R}} \cdots, \quad (5.8)$$

so that the two- and three-body potential terms are reduced to a product of the $\langle \rho(\mathbf{r}) \rangle_{\mathbf{R}}$. This factorization ignores all effects of density–density correlations. Since $\langle \rho(\mathbf{r}) \rangle_{\mathbf{R}}$ gives the spatial variation of the density of monomers of a single polymer, with the average density L/R^d , the r -dependence can be taken in a scaling form

$$\langle \rho(\mathbf{r}) \rangle_{\mathbf{R}} = \frac{L}{R^d} \Theta\left(\frac{r}{R}\right), \quad (5.9)$$

where $\Theta(x)$ is a well-behaved function. The assumption that has gone into writing this form is that the behaviour of the density for large L is determined solely by the large distance scale R and not the polymer-specific microscopic scales. The prefactor takes care of the dimensionality of the density so that the r -dependence has to be in a dimensionless form. Under the assumption that only the large scale R , the size of the polymer, matters, the dimensionless argument of the function has to be r/R . A uniform density sphere of radius R would have $\Theta(x) = \text{constant}$ for $0 < x \leq 1$ and zero otherwise but there is no need to assume a uniform distribution of monomers.

The mean-field expression for the Helmholtz free energy, from equation (5.2) using equations (5.7)–(5.9), gives the standard form of the Flory free energy

$$\begin{aligned} \beta F_L(R) &= \frac{1}{2} \frac{R^2}{L} - \frac{d}{2} \log\left(\frac{1}{2\pi L}\right) \\ &\quad + R^d \left[\tilde{u} \left(\frac{L}{R^d}\right)^2 + \tilde{v} \left(\frac{L}{R^d}\right)^3 + \cdots \right] \end{aligned} \quad (5.10a)$$

$$\approx \frac{1}{2} \frac{R^2}{L} + \tilde{u} \frac{L^2}{R^d} + \tilde{v} \frac{L^3}{R^{2d}}, \quad (5.10b)$$

where

$$\tilde{u} = \frac{1}{2!} u S_d \theta_{d-1}^2, \quad \text{and} \quad \tilde{v} = \frac{1}{3!} v S_d \theta_{d-1}^3 \quad (5.11)$$

are dependent on the density via the moments,

$$\theta_k^l = \int_0^\infty dx x^k \Theta^l(x), \quad (5.12)$$

with $S_d = 2\pi^{d/2}/\Gamma(d/2)$ coming from the $(d - 1)$ -dimensional angular integrals. Some explicit values in $d = 3$ (corresponding to $k = 2$) will be derived later. The resemblance of this free energy equation (5.10b) to the simple Flory argument of equation (2.10) should not go unnoticed.

The logarithmic term appearing in equation (5.10a) yields subdominant contributions under all circumstances, and will be neglected in most of the paper. However, this subdominant log-term is an extremely important property of a polymer as it signifies the probability of a polymer forming a loop with $\mathbf{R} = 0$. The coefficient ($d/2$ in this case) is called the reunion exponent. This exponent has certain universality [36] and is one of the characteristic exponents for polymers. Such a subleading term actually controls many polymeric thermodynamic phase transitions and the order of the transition in the $L \rightarrow \infty$ limit. The most well-known example in this class is the DNA melting [37].

5.2. Solution through steepest descent method

Our goal is to extract the dominant contribution to the integral (5.4) using a steepest descent (saddle point) method. This method has the advantage of being systematically improvable. In addition we are also interested in the result for the end-to-end distance

$$\langle R^2 \rangle = \frac{1}{Z} \int d^d \mathbf{R} R^2 \exp[-\beta F_L(R)]. \quad (5.13)$$

This clearly amounts to considering the expansion around the minimum \mathbf{R}^*

$$\begin{aligned} \beta F_L(R) &= \beta F_L(R^*) + \frac{1}{2!} \frac{\partial^2}{\partial R^2} [\beta F_L(R)] \Big|_{R=R^*} (R - R^*)^2 \\ &\quad + \cdots, \end{aligned} \quad (5.14)$$

where the steepest descent condition $\partial[\beta F_L(R)]/\partial R|_{R=R^*} = 0$ yields to lowest order

$$\frac{R^2}{dL} - 2\tilde{v} \frac{L^3}{R^{2d}} + \cdots = \tilde{u} \frac{L}{R^d}. \quad (5.15)$$

Table 2. Summary of the exponents predicted by Flory theory in various regimes as reported in section 5.2.

Flory regime	$T > T_\theta$	$\alpha > 0$	$2 \leq d \leq 4$	$\nu_F = \frac{3}{d+2}$
Flory regime	$T > T_\theta$	$\alpha > 0$	$d > 4$	$\nu_G = \frac{1}{2}$
Theta regime	$T = T_\theta$	$\alpha = 0$	$2 \leq d \leq 3$	$\nu_\theta = \frac{2}{d+1}$
Theta regime	$T = T_\theta$	$\alpha = 0$	$d > 3$	$\nu_G = \frac{1}{2}$
Compact regime	$T < T_\theta$	$\alpha < 0$	$\forall d$	$\nu_c = \frac{1}{d}$

Anticipating the emergence of non-Gaussian value of ν , a short-distance scale b (e.g. the bond length used earlier) can be introduced to define a dimensionless variable \mathbf{x} :

$$\mathbf{R} = bN^\nu \mathbf{x}, \quad \text{where } N = L/b^2. \quad (5.16)$$

With this x , the partition function and the size from equations (5.4) and (5.13) can be expressed as

$$Z = b^d N^{vd} \int d^d \mathbf{x} e^{-f(x,N)} \equiv b^d N^{vd} \widehat{Z},$$

and

$$\langle R^2 \rangle = b^2 N^{2\nu} \frac{1}{\widehat{Z}} \int d^d \mathbf{x} x^2 e^{-f(x,N)}, \quad (5.17)$$

where

$$f(x, N) = \frac{1}{2} x^2 N^{2\nu-1} + \alpha \frac{N^{2-\nu d}}{x^d} + \gamma \frac{N^{3-2\nu d}}{x^{2d}} \quad (5.18)$$

and

$$\alpha = \tilde{u} b^{4-d}, \quad \gamma = \tilde{v} b^{6-2d} \quad (5.19)$$

are dimensionless. The similarity of the powers of N in $f(x, N)$ equation (5.18) with the powers of λ in equation (4.4) should be noted.

One may compare α, γ of equation (5.19) with the dimensionless form z, w introduced earlier in equation (4.5). The latter are made dimensionless with L , the length, while here the small scale b is used for that purpose (see also table 2). Although Z and $\langle R^2 \rangle$ have been written above with an explicit b , it is possible to avoid this arbitrary scale b altogether. By defining $\mathbf{R} = L^{1/2} z^{(2\nu-1)/\epsilon} \mathbf{x}$, both Z and $\langle R^2 \rangle$ can be written in terms of L, z, w without any b .

The integrals involved in the above expressions behave differently in different temperature regimes. These are discussed below.

5.2.1. Flory regime ($\alpha > 0, T > T_\theta$). Let us first consider the good solvent case with $u > 0$. We still have to worry about the dimensionality dependence. There are two possibilities.

(a) Case $2 < d < 4$. Matching the first and second terms in the exponential of (5.17) we find the Flory exponent seen earlier, $\nu = \nu_F = 3/(d+2)$. In this case, the third term becomes subdominant in the $N \gg 1$ limit as $N^{3-2\nu_F d} = N^{-3(d-2)/(d+2)} \ll 1$. The size is then given by equations (5.17) and (5.18), with $\nu = \nu_F$ and

$$f(x, N) = N^{\frac{4-d}{d+2}} \left(\frac{1}{2} x^2 + \frac{\alpha}{x^d} \right). \quad (5.20)$$

The function $f(x, N)$ can then be expanded around the minimum $x^* = (\alpha d)^{1/(d+2)}$ resulting to lowest order

$$\langle R^2 \rangle \approx b^2 N^{2\nu_F} \alpha^{2/(d+2)} \quad (5.21)$$

absorbing some unimportant constants in the definition of b . This is the Flory regime.

(b) Case $d > 4$. In this case the above analysis is no longer valid as $N^{\frac{4-d}{d+2}} \ll 1$ in the large N limit and the steepest descent method cannot be applied. We then go back to equation (5.17) and assume that there is no N dependence in the entropic term. This amounts to setting $N^{2\nu-1} = 1$, or $\nu \equiv \nu_G = \frac{1}{2}$. Then all the other terms in (5.17) vanish in the $N \gg 1$ limit and equations (5.17) and (5.18) give

$$\langle R^2 \rangle \approx b^2 N. \quad (5.22)$$

Equations (5.21) and (5.22) can then be written as

$$\langle R^2 \rangle \approx C b^2 N^{2 \max(\nu_F, 1/2)}, \quad (5.23)$$

or $R \approx C^{1/2} b^{1-\nu} L^\nu,$

where $C = \alpha^{2/(d+2)}$ when $d < 4$ and $C = 1$ when $d \geq 4$, and $\nu = \max(\nu_F, 1/2)$.

That $d = 4$ is special is seen from the power of N in equation (5.20) and from the fact that u is dimensionless in $d = 4$ so that z becomes large as $L \rightarrow \infty$ for $d < 4$.

5.2.2. Theta regime ($\alpha = 0, T = T_\theta$). In this case, the term proportional to α is absent in both equations (5.17) and (5.18), and again there exist two different regimes, depending on the dimensionality of the system.

(a) Case $1 < d < 3$. Matching the first and third terms we find

$$\nu_\theta = \frac{2}{d+1} \quad (5.24)$$

which coincides with the Gaussian value $\nu_G = 1/2$ in $d = 3$ but is different from it in $d = 2$. However, the value $\nu = 2/3$ for $d = 2$ differs from the known exact value $\nu = 4/7$ [38, 39]. The Flory theory has also been extended to theta points on fractals [40] and dilute lattices [41].

Substituting in equation (5.17) we find

$$f(x, N) = N^{\frac{3-d}{d+1}} \left(\frac{1}{2} x^2 + \frac{\gamma}{x^{2d}} \right). \quad (5.25)$$

It is worth noticing that the matching choice (1st and 2nd terms for Flory regime $\alpha > 0$, 1st and 3rd terms for the θ -regime $\alpha = 0$) is *unique*, as any alternative choice would lead to inconsistent results.

Because $N^{\frac{3-d}{d+1}} \gg 1$ in this regime, we can apply the steepest descent method along the lines previously shown thus yielding the θ -regime.

Following the same reasoning as in the previous case, to leading order in the steepest descent expansion, we find

$$\begin{aligned} \langle R^2 \rangle &\approx b^2 N^{2\nu_\theta} (2\gamma)^{1/(d+1)}, \\ \text{or} \quad \langle R^2 \rangle &\approx Lw^{1/(d+1)}. \end{aligned} \quad (5.26)$$

- (b) Case $d > 3$. Again, the only possibility is to choose ν such that the entropic part has no N dependence, and this again leads to the Gaussian result, (5.22).

The final result for this case is then

$$\langle R^2 \rangle \approx C_\theta b^2 N^{2 \max(\nu_\theta, 1/2)}, \quad (5.27)$$

where $C_\theta = (2\gamma)^{1/(d+1)}$ when $d < 3$ and $C_\theta = 1$ when $d \geq 3$.

Here, $d = 3$ turns out to be special, unlike the good solvent case which has $d = 4$ as the special dimensionality. This is apparent from the power of N in equation (5.25) and the fact that ν is dimensionless for $d = 3$. For $d < 3$, w becomes large with length of the polymer.

5.2.3. Compact regime ($\alpha < 0, T < T_\theta$). We now go back to equations (5.17) and (5.18) where we set $\alpha = -|\alpha|$. In this case, the term proportional to γ becomes very important to guarantee the convergence of the integral. As the term proportional to α cannot be dropped, the only remaining possibility is to match these two terms. This leads to the result $\nu_c = \frac{1}{d}$, as noted in equation (2.13).

In this case $N^{2\nu_c-1} = N^{(2-d)/d} \ll 1$ and the Gaussian term is subdominant in the $N \gg 1$ limit. Note, however, that unlike previous cases, it *cannot* be dropped as it ensures the convergence of the integral at large x .⁹ This should also be taken into account on the integration domain of R since it should not extend beyond N . It is nevertheless irrelevant for the computation of average quantities such as $\langle R^2 \rangle$ given by equation (5.18).

To leading order, one finds

$$\langle R^2 \rangle \approx b^2 N^{2\nu_d} \left(\frac{2\gamma}{|\alpha|} \right)^{2/d}, \quad (5.28)$$

for any d . This value $\nu_d = 1/d$ is consistent with the idea of a compact sphere with density $\sim O(1)$. To prevent a complete collapse, one needs a repulsive interaction and the three-body term $\nu > 0$ helps in stabilization of the phase.

6. Additional remarks on Flory theory

6.1. Summary of Flory predictions

For each of the swollen and the theta cases, there is a critical dimensionality d_c above which the interactions are not significant enough to cause a change in the Gaussian behaviour. This critical dimensionality is $d_c = 4$ for the excluded volume interaction and $d_c = 3$ for the theta point. These are the dimensions at which the interaction constants u and v are dimensionless. For $d < d_c$, the interactions cannot be

ignored, no matter how small, but the magnitude does not play any role. The size exponents are not dependent on the strength of the interaction, so long it is nonzero and positive. The values of the exponents predicted by Flory theory in the above three regimes and different dimensionalities are recalled in table 2.

6.2. Modification of the entropic term and Flory interpolation formula

As remarked earlier, the equilibrium size of a polymer coil is determined by the balance between polymer interactions and polymer elasticity, which is entropic in nature. To derive an interpolation formula that would be applicable away from the asymptotic large N regime, an intuitively appealing argument can be made. The free energy in the fixed R ensemble, based on the Gaussian distribution and the interactions, is given by equation (5.10a). To this we may add an extra entropy coming from the possibility of placing one end point of the polymer anywhere in the volume R^d . This entropy is of the form $\sim \ln R^d$. Therefore the modified Flory free energy, obtained by adding this extra entropic contribution to the form given in equation (5.10a), is $\beta F_L(R)|_{\text{modified}} = \beta F_L(R) - d \ln R$, where $\beta F_L(R)$ is given by equation (5.10a).

In terms of the swelling factor ψ^2 that compares the size of a polymer with the corresponding Gaussian size as defined in equation (4.6), the modified free energy can be expressed as

$$\beta \bar{F}_L(\psi) \approx \frac{d}{2} \psi^2 - d \log(\psi) + \frac{d+1}{d} \frac{z}{\psi^d} + \frac{w}{\psi^{2d}}. \quad (6.1)$$

Here z, w defined in equation (4.5), with c_1, c_2 involving the θ of equation (5.11), are

$$\begin{aligned} z &= \frac{d^{(2-d)/2}}{2(d+1)} S_d \theta_{d-1}^2 u L^{\epsilon/2}, \\ w &= \frac{1}{3!} d^{-d} S_d \theta_{d-1}^3 v L^{3-d}. \end{aligned} \quad (6.2)$$

The corresponding steepest descent equation yields

$$\psi^{d+2} - \psi^d - 2w \frac{1}{\psi^d} = \frac{d+1}{d} z. \quad (6.3)$$

Note that this is basically equation (5.15) with an extra term (the second term on the left-hand side of equation (6.3)) that stems from the modification. In particular, for $d = 3$, the form [20, 21], is

$$\psi^5(z) - \psi^3(z) - \frac{2\tilde{v}}{\psi^3(z)} = \frac{4}{3} z, \quad (6.4)$$

with z as in equation (6.2) for $d = 3$. A comparison with the value of z used in equation (5.11) (see also equation (5.19)) yields a well defined value for θ_2^2 whose general expression appeared in equation (5.12), that is

$$\theta_2^2 = \frac{9}{\pi^2} \sqrt{\frac{1}{2\pi}} \quad (6.5)$$

⁹ Note that this resembles the role of the *irrelevant dangerous* variables in renormalization group theory.

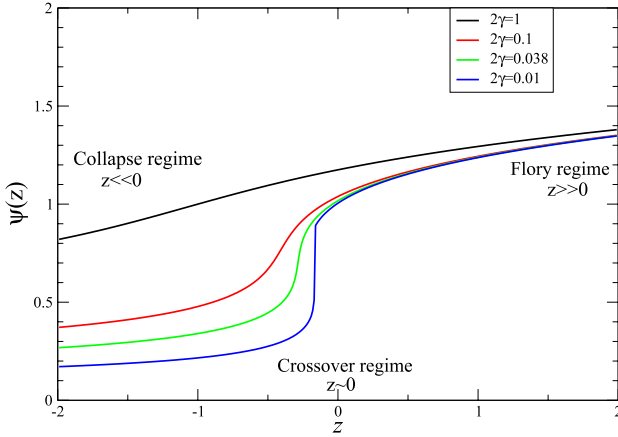


Figure 4. Numerical solution of equation (6.4) as in figure 1 of [21] with the same values of the parameters $2\gamma = 0.01, 0.038, 0.1, 1$.

so that inserting equation (5.11) into equation (6.2) we get

$$z = \left(\frac{3}{2\pi}\right)^{3/2} uL^{1/2}. \quad (6.6)$$

The behaviour of $\psi(z)$ is given in figure 4 which displays the ‘loop’ for sufficiently low values of parameter 2γ (see also equation (5.19)).

For $\gamma = 0$ ($w = 0$), a power series solution for $\psi(z)$ can be constructed as

$$\psi(z) = 1 + \frac{2}{3}z - \frac{14}{9}z^2 + \frac{160}{27}z^3 + \dots, \quad (6.7)$$

which could be verified, order by order, by direct substitution in equation (6.4). Furthermore, this gives

$$\psi^2(z) = 1 + \frac{4}{3}z - 2.66667z^2 + 9.77778z^3 + \dots \quad (6.8)$$

This solution may be compared with a brute-force computation of the perturbative series in [23] (see appendix C),

$$\psi^2(z) = 1 + \frac{4}{3}z - 2.0754\dots z^2 + 6.2968\dots z^3 - 25.057\dots z^4 + \dots, \quad (6.9)$$

where z is as given in equation (6.6).

The interpolation formula given by equation (6.4) was verified for polystyrene in cyclohexane [42]. A slightly different form with a constant term on the right-hand side was however found for polymethyl methacrylate [43].

6.3. Modification of the Flory estimate

The idea of the fractal dimension introduced in section 2.1.2 suggests that the number of monomers in a sphere of radius R is R^{d_F} and therefore the energy term should be R^{2d_F-d} , d_F to be determined. This is not consistent with the estimate of the repulsive energy N^2/R^d which is crucial for the Flory exponent. A more refined argument would however favour the Flory estimate [44].

The polymer chain can be thought of as consisting of smaller blobs of n monomers within which the effect of repulsion is not significant and the spatial size can be taken as $\xi^2 \sim n$. The chain then consists of N/n such blobs. This

coarse-grained polymer will have $(N/n)^2(R/\xi)^{-d}$ contacts of blobs. There is a need to know the number of overlap of monomers of the two fractal blobs. The dimensionality of the intersections of two fractals follows a rule of addition of co-dimensions. For a D -dimensional fractal embedded in a d -dimensional space, the co-dimension is the dimensionality of complementary space and is $d-D$. The additivity rule says that the co-dimension of the intersections of two fractals is the sum of the co-dimensions of the two. In other words the fractal dimension D of the points of contact of two fractals of dimensions D_1 and D_2 would obey $d-D = (d-D_1) + (d-D_2)$, i.e., $D = D_1 + D_2 - d$. As per this rule the number of contacts of the two blobs will be ξ^{4-d} . Therefore, the repulsive energy will be

$$\frac{N^2}{n^2} \frac{\xi^d}{R^d} \xi^{4-d} = \frac{N^2}{R^d},$$

recovering the Flory estimate.

6.4. Explicit computation of the scaling function in $d = 2$

A rather interesting case occurs in $d = 2$ where the scaling function $\psi(z)$ can be computed explicitly. We go back to equations (5.17) for $d = 2$ and $\gamma = 0$. With a change of variable $\mathbf{R} = bN^{v_F}\mathbf{x}$ similar to equation (5.16) we get from equation (5.17) (in polar coordinates)

$$\langle R^n \rangle = b^n N^{nv_F} \frac{\int_0^\infty dx x^{n+1} \exp[-f_2(x, N)]}{\int_0^\infty dx x \exp[-f_2(x, N)]}, \quad (6.10)$$

where

$$f_2(x, N) = \frac{1}{2}N^{1/2}x^2 + \alpha N^{1/2} \frac{1}{x^2} \quad (6.11)$$

in the Flory regime $v_F = 3/4$ (for which γ and higher terms are irrelevant in the $N \gg 1$ limit). Here, f_2 is equation (5.20) in $d = 2$.

Let us introduce the ratio

$$\chi_2(N, \alpha) = \frac{\langle R^3 \rangle}{\langle R \rangle}, \quad (6.12)$$

which is also a definition of ‘polymer extension’ analogous to $\langle R^2 \rangle$. The scaling function is then $\psi^2 = \chi_2/(b^2N)$, which can be written as

$$\psi^2(N, \alpha) = N^{1/2} \frac{\int_0^\infty dx x^4 \exp[-N^{1/2}(\frac{x^2}{2} + \frac{\alpha}{x^2})]}{\int_0^\infty dx x^2 \exp[-N^{1/2}(\frac{x^2}{2} + \frac{\alpha}{x^2})]}. \quad (6.13)$$

Both integrals are easily evaluated within a steepest descent procedure with saddle point $x_0^2 = (2\alpha)^{1/2}$. The asymptotic form in the large N limit is

$$\psi^2(N, \alpha) = N^{1/2}\alpha^{1/2} \sim \sqrt{z}, \quad (6.14)$$

consistent with the large z behaviour of equation (6.3) for $d = 2$.

On the other hand, an exact calculation can also be carried out by using the following identities:

$$\int_0^\infty dx \exp\left[-bx^2 - \frac{a}{x^2}\right] = \frac{1}{2} \sqrt{\frac{\pi}{b}} \exp[-2\sqrt{ab}] \quad (6.15)$$

$$\begin{aligned} \int_0^\infty dx x^2 \exp\left[-bx^2 - \frac{a}{x^2}\right] \\ = \left(\frac{1}{2b} + \sqrt{\frac{a}{b}}\right) \frac{1}{2} \sqrt{\frac{\pi}{b}} \exp[-2\sqrt{ab}] \end{aligned} \quad (6.16)$$

$$\begin{aligned} \int_0^\infty dx x^4 \exp\left[-bx^2 - \frac{a}{x^2}\right] \\ = \left(\frac{3}{4b^2} + \frac{a}{b} + \frac{3}{2b} \sqrt{\frac{a}{b}}\right) \frac{1}{2} \sqrt{\frac{\pi}{b}} \exp[-2\sqrt{ab}]. \end{aligned} \quad (6.17)$$

The integral (6.15) is proven in [45], and the remaining two can be evaluated immediately by taking derivatives with respect to b . Then we find the exact result

$$\begin{aligned} \psi^2(N, \alpha) = \sqrt{N\alpha} \frac{1 + 3X + 3X^2}{1 + X}, \\ \text{with } X = \frac{1}{\sqrt{2\alpha N}}, \end{aligned} \quad (6.18)$$

so that for $N \gg 1$

$$\psi^2(N, \alpha) = \sqrt{N\alpha} \left[1 + \frac{1}{\sqrt{\alpha N}} + \mathcal{O}\left(\frac{1}{\alpha N}\right) \right] \quad (6.19)$$

in agreement with equation (6.14), while for $\alpha \rightarrow 0$, $\psi^2 \rightarrow 3/\sqrt{2}$.

In view of the exactness of the Flory exponent in $d = 2$, it would be extremely useful to see how this exact result on the crossover function fares with real experiments. This could be accessible in studies on polymers adsorbed on a surface or planar interface.

6.5. The uniform expansion method

We now attempt to get the interpolation formula, equation (6.4), in a more systematic but nonperturbative way. The basic idea is to introduce an effective Gaussian distribution with a new elastic constant ψ^{-2} in such a way that

$$\langle R^2 \rangle = \langle R^2 \rangle'_0, \quad (6.20)$$

where $\langle (\cdot \cdot \cdot) \rangle'_0$ is the Gaussian average with respect to the new distribution [5].

Let us write the Edwards Hamiltonian as (absorbing β in the Hamiltonian)

$$H = H'_0 + (H - H'_0) = H'_0 + \delta H, \quad (6.21a)$$

where

$$H'_0 = \frac{1}{2\psi^2} \int_0^L ds \left(\frac{\partial \mathbf{r}}{\partial s} \right)^2, \quad (6.21b)$$

$$\begin{aligned} \delta H = \frac{1}{2} (1 - \psi^{-2}) \int_0^L ds \left(\frac{\partial \mathbf{r}}{\partial s} \right)^2 \\ + \frac{1}{2!} u \int_0^L ds_1 \int_0^L ds_2 \delta(\mathbf{r}(s_2) - \mathbf{r}(s_1)) \end{aligned} \quad (6.21c)$$

$$\equiv \delta H_1 + \delta H_2. \quad (6.21d)$$

Here ψ^2 is a dimensionless ‘elastic constant’ such that for H'_0 , which is a Gaussian Hamiltonian, $\langle R^2 \rangle'_0 = d\psi^2 L$. Admittedly, ψ is reminiscent of the swelling factor of section 6.4, $\psi^2 = \langle R^2 \rangle'_0 / R_0^2$, and in fact it is the actual one if the condition expressed by equation (6.20) is satisfied.

Expanding $\langle R^2 \rangle$, to first order in δH , we have

$$\begin{aligned} \langle R^2 \rangle &= \frac{\int d^d \mathbf{R} R^2 G_L(\mathbf{R})}{\int d^d \mathbf{R} G_L(\mathbf{R})} \\ &= \langle R^2 \rangle'_0 - (\langle R^2 \delta H \rangle'_0 - \langle R^2 \rangle'_0 \langle \delta H \rangle'_0), \end{aligned} \quad (6.22)$$

where the prime denotes an averaging with H'_0 . The resulting Gaussian integrations can be performed to obtain

$$\langle R^2 \rangle = \langle R^2 \rangle'_0 - \langle R^2 \rangle'_0 \left[1 - \psi^2 + \frac{1}{\psi^3} \frac{4}{3} z + \dots \right]. \quad (6.23)$$

The details of the calculations are similar to those reported in appendix B, with the relevant result given by equation (C.11), but the occurrence of the ψ -terms can be understood from a transformation. Since H'_0 represents a Gaussian with the extra ψ factor, we have $G'_0(\mathbf{r}) = \psi^{-d/2} G_0(\mathbf{r}/\psi)$. Therefore, by scaling $R, \mathbf{r} \rightarrow R/\psi, \mathbf{r}/\psi$, one gets the factor ψ^4 coming from the correlation of R^2 and δH_1 . As H is dimensionless the correlation is dimensionally $\sim L$ because of R^2 . When these are combined with the factor $(1 - \psi^{-2})$ of δH_1 , we find the contribution $\sim L\psi^2(1 - \psi^{-2})$. A change in variable gives $\delta(\mathbf{r}) \rightarrow \psi^{-d} \delta(\mathbf{r}/\psi)$, so that the δH_2 correlation would be $\sim (L\psi^2)(\psi^{-3})(uL^{1/2})$, in three dimensions, as in equation (6.23).

The swelling factor analogue of equation (4.6) now reads

$$\psi^2 = \frac{\langle R^2 \rangle}{\langle R^2 \rangle'_0} = \frac{\langle R^2 \rangle'_0}{\langle R^2 \rangle'_0}. \quad (6.24)$$

The last step stems from the condition

$$\langle R^2 \rangle = \langle R^2 \rangle'_0, \quad (6.25)$$

which is the requirement of the uniform expansion method, equating the correction term in the square bracket to zero. This yields

$$\psi^5(z) - \psi^3(z) = \frac{4}{3} z \quad (6.26)$$

which coincides with equation (6.4) with $\gamma = 0$ (no 3-body term), as it should.

Although the scheme is based on the first-order perturbative result, the method via the choice of ψ makes it nonperturbative and applicable to a wide variety of situations.

6.6. Extension of Flory theory to more complex systems

As anticipated in the introduction, Flory theory is still a widely used tool in many different soft matter systems with increasing complexity. This is because, in spite of its simplicity and known limitations, it is able to capture the main essential competition between entropic and energetic contributions. There are clearly too many cases of extensions of Flory theory to these more complex systems to be

reproduced here. As representative examples, we confine ourselves to two important cases.

The first one is related to the possibility of having anisotropy with a preferred direction as, for instance, for directed linear or branched polymers [46, 47]. The same idea will also be taken up in section 7.3 where the case of the inclusion of an external force will be discussed.

For directed systems, with a preferred direction, we introduce a transverse typical radius R_{\perp} and a longitudinal radius R_{\parallel} , along with the corresponding exponents ν_{\perp} and ν_{\parallel} , so that $R_{\perp} \sim N^{\nu_{\perp}}$ and $R_{\parallel} \sim N^{\nu_{\parallel}}$. The extension of the free energy (2.10) to the present case then reads in general dimensionality d [46, 47] as

$$F_N(R_{\perp}, R_{\parallel}) = F_0 + e_0 \left(\frac{R_{\perp}^2}{N^2 b^2} + \frac{R_{\parallel}^2}{N b^2} \right) + e_1 v_{\text{exc}} \frac{N^2}{R_{\parallel} R_{\perp}^{d-1}}. \quad (6.27)$$

Note that the different N -dependence on the longitudinal and transverse Gaussian case stems from the fact that the system is directed along the longitudinal direction ($\nu_{\parallel}^0 = 1$) and diffusive along the transversal one ($\nu_{\perp}^0 = 1/2$). As in the isotropic case, the upper critical dimension d_c is found by assuming the repulsive part to be of the order of unity, thus obtaining $d_c = 3$. Upon minimizing with respect to R_{\perp} and R_{\parallel} one obtains a system of two coupled equations involving ν_{\perp} and ν_{\parallel} , whose result is

$$\nu_{\perp} = \frac{5}{2(d+2)} \quad \nu_{\parallel} = \frac{d+7}{2(d+2)}. \quad (6.28)$$

A second case of great interest and actuality concerns the case of branched polymers formed by several reacting multifunctional monomer units, which are often referred to as star-burst dendrimers [48]. In this case, the N monomers are distributed into g generations of successive growth, so that the size of a typical strand of g monomers is $R_0 \sim b g^{1/2}$.

In this case, specialized to the three-dimensional system to be specific, the repulsive term for a system of g monomers embedded into a system of density N/R^3 , will be proportional to gN/R^3 , thus leading to a further generalization of equation (2.10):

$$F_N(R) = F_0 + e_0 \frac{R^2}{N} + e_1 v_{\text{exc}} \frac{gN}{R^3}. \quad (6.29)$$

A minimization with respect to R then leads to an equation for the linear expansion factor R/R_0 akin to equation (6.4) for this case. A recent application of this methodology to several examples of branched polymers can be found in [49].

7. Temperature induced transition and external force

The scaling theory discussed in section 6 is an attempt to go beyond the Gaussian limit in each phase of a polymer. However, for arbitrary d , the interacting polymer may never be in the Gaussian limit. We have seen that as the quality of the

solvent is changed, the size exponent takes only three possible values, one for the repulsive, one for the attractive and one for the transition point. The universality of the exponents on the repulsive and the attractive sides (i.e. independent of the strength) suggests that the special situation is the transition point, not the Gaussian noninteracting one. The scaling behaviour should then be in terms of the deviations from the transition point. This we do now in this section. The law we obtain is analogous to the scaling observed in magnetic and fluid phase transitions near tricritical points. This is not surprising. To get the transition point we need to tune the two-body interaction and $N \rightarrow \infty$. In fact one more parameter is needed, the concentration of the polymer in solution, which also needs to be zero (dilute limit). A transition point with three relevant parameters (parameters that can destroy or change the nature of the transition) is called a tricritical point.

As in any phase transitions, in polymer theory too, the criticality is obtained only in the $N \rightarrow \infty$ limit. Near a phase transition point, a finite system then shows typical, often universal, size dependence which is characteristic of the infinite system. This is called finite size scaling. The phase transition that occurs at $T = T_{\theta}$ requires $N \rightarrow \infty$, but its character can be seen in finite N behaviour. One interesting, and largely overlooked, consequence of the polymer theory developed so far lies in the possibility of getting this finite $N \gg 1$ behaviour as one drives the transition upon changing the temperature. This is discussed in the present section where the Flory approach will be cast into a more general framework of a crossover between the three different regimes as driven by the temperature at large but fixed N . As before, we will study the dimensionality dependence of the system separately.

The polymer at the theta point is in a very special state because finiteness of the length or any change in temperature would take it away from the theta point. In such situations, the transition behaviour is expressed in terms of the theta point behaviour as

$$R = b N^{\nu_{\theta}} \Psi(\alpha N^{\phi}), \quad (7.1)$$

where $\Psi(0) = 1$ is the theta temperature behaviour ($\alpha = 0$). For higher temperatures, $\alpha > 0$, as $N \rightarrow \infty$, $\Psi(x) \sim x^q$ in such a way that the N dependence becomes the Flory value, the characteristic of the swollen phase. This requires $\nu_{\theta} + q\phi = \nu_F$. This is nicely corroborated by the Flory theory, as shown below.

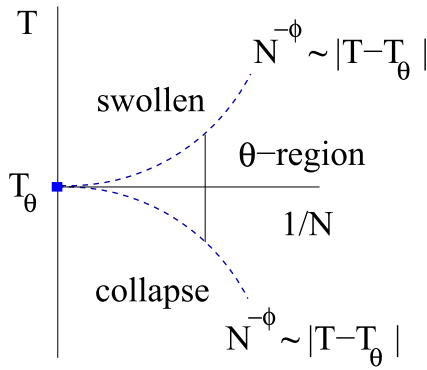
7.1. Case $2 \leq d \leq 3$

We now go back to the free energy as given by equation (5.10b), and consider the saddle point equation, equation (5.15), rearranged as

$$\left(\frac{R}{L^{\nu_{\theta}}} \right)^{2d+2} - \tilde{\alpha} L^{\frac{d-1}{d+1}} \left(\frac{R}{L^{\nu_{\theta}}} \right)^d - 2\tilde{\gamma} = 0$$

$$(\nu_{\theta} = 2/(d+1)). \quad (7.2)$$

We consider the θ -regime $T \rightarrow T_{\theta}$ and restrict to the case $2 \leq d \leq 3$. To allow for non-Gaussian behaviour, let us introduce



Dilute: zero concentration

Figure 5. Theta point region in a T versus $1/N$ plot (single chain). The theta point is at $T = T_\theta$, $1/N = 0$. There is a crossover region determined by the crossover exponent ϕ , emanating from the theta point (marked theta region) within which the theta point behaviour could be seen for shorter chains. Beyond the dashed line for $T > T_\theta$ one sees the swollen behaviour for long chains while below a similar line for $T < T_\theta$ one sees a collapse phase. The vertical solid line gives the width of the theta region for a finite chain. This is used in figure 8.

an arbitrary scale b with $N = L/b^2$ dimensionless as before. For the solution R of the steepest descent (equation (7.2)) we assume a scaling form of the type

$$R = bN^{v_\theta} \Psi(z), \quad (7.3)$$

where we have generalized the scaling variable

$$z = |\alpha|N^\phi,$$

involving the crossover exponent

$$\phi = \frac{d-1}{d+1}.$$

The scaling function $\Psi(z)$ (> 0) is a clear generalization of equation (4.6). Equation (7.2) can then be cast into the following form:

$$\Psi^{2d+2}(z) - \chi(T)z\Psi^d(z) - 2\gamma = 0, \quad (7.4)$$

where the function $\chi(T)$ is equal to 1 for $T > T_\theta$ and -1 for $T < T_\theta$. Because of this, we must distinguish two cases depending on T , and we will denote as Ψ_+ (Ψ_-) the solution of (7.4) when $T > T_\theta$ ($T < T_\theta$).

7.1.1. Case $T > T_\theta$. Equation (7.4) has only one solution for $\Psi_+ > 0$ which, at large z , behaves as

$$\Psi_+(z) = z^{\frac{1}{d+2}} \left(1 + \frac{2\gamma}{d+2} \frac{1}{z^{\frac{2d+2}{d+2}}} + \dots \right). \quad (7.5)$$

On the other hand, for $z \rightarrow 0$ ($T \rightarrow T_\theta^+$) we find $\Psi_+(z) \sim (2\gamma)^{1/(2d+2)}$. The scaling function then has the following behaviour:

$$\Psi_+(z) = \begin{cases} z^{\frac{1}{d+2}} & z \gg (2\gamma)^{\frac{d+2}{2d+2}} \\ (2\gamma)^{\frac{1}{2d+2}} & z \ll (2\gamma)^{\frac{d+2}{2d+2}} \end{cases} \quad (7.6)$$

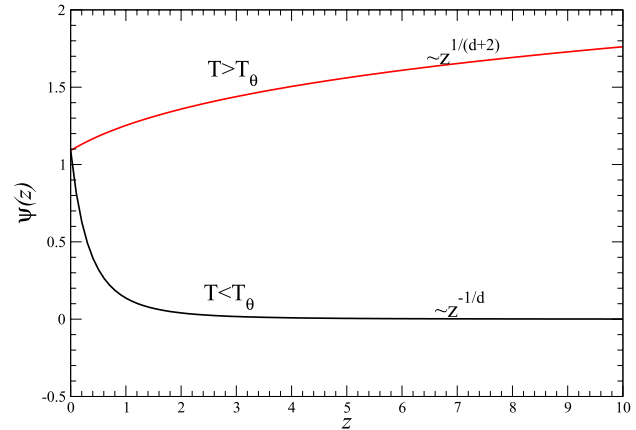


Figure 6. Plot of $R/(bN^{v_\theta}) = \Psi_\pm(z)$ as a function of z as given by equation (7.9) in $d = 3$ when $T > T_\theta$ and $T < T_\theta$.

7.1.2. Case $T < T_\theta$. Now $\chi(T) < 1$ and $\alpha = -|\alpha|$. Again equation (7.4) has only one solution:

$$\Psi_-(z) = \frac{2\gamma^{\frac{1}{d}}}{z} \left(1 - 2\gamma^{d+2} + dz^{\frac{2d+2}{d+2}} + \dots \right). \quad (7.7)$$

For $z \rightarrow 0$ we have the same behaviour as before, so that

$$\Psi_-(z) = \begin{cases} \frac{2\gamma^{\frac{1}{d}}}{z} & z \gg (2\gamma)^{\frac{d/2}{2d+2}} \\ (2\gamma)^{\frac{1}{2d+2}} & z \ll (2\gamma)^{\frac{d/2}{2d+2}} \end{cases} \quad (7.8)$$

7.1.3. Phase diagram. Inserting these findings for $\Psi(z)$ into the scaling ansatz (7.3) we obtain

$$\frac{R}{b} \approx \begin{cases} (T - T_\theta)^{\frac{1}{d+2}} N^{v_\theta}, & \text{when } N \gg |T - T_\theta|^{-1/\phi}, \quad T > T_\theta \\ (T_\theta - T)^{-\frac{1}{d}} N^{v_c}, & \text{when } N \gg |T - T_\theta|^{-1/\phi}, \quad T < T_\theta \\ N^{v_\theta}, & \text{when } N \ll |T - T_\theta|^{-1/\phi} \\ & \text{or } T = T_\theta. \end{cases} \quad (7.9)$$

A schematic diagram of the three regions is shown in figure 5. The crossover expressed by the exponent ϕ above is represented by the dashed (blue) lines. The region enclosing the x -axis is the theta region.

This behaviour is depicted in figure 6 in the particular case of $d = 3$.

7.2. Case $d > 3$

In this case the steepest descent solution of the modified free energy equation (6.1), accounting for Flory's correction, reads

$$\frac{R^2}{Nb^2} - 1 - \left[2\gamma b^{2d} \frac{N^3}{R^{2d}} + \dots \right] = \alpha N^2 \frac{b^d}{R^d} \quad (7.10)$$

where we have not included higher correction terms γ_{ij} that are necessary to ensure the convergence of the saddle point in equation (5.18) in the case $\alpha < 0$.

In analogy with what we have attempted in the previous case, we assume a scaling of the form

$$R = bN^{1/2}\Psi(z) \quad (7.11)$$

in view of the fact that $v_\theta = 1/2$ when $d > 3$. This yields

$$\Psi^{2d+2}(z) - \Psi^{2d}(z) - \left[\frac{2\gamma}{N^{d-3}} + \dots \right] = \frac{\alpha}{N^{d/2-2}}\Psi^d(z). \quad (7.12)$$

Note that, unlike the case $2 \leq d \leq 3$, it is *not* possible to cast equation (7.12) in terms of an equation for a single scaling variable z as both terms multiplying α, γ and higher terms depend upon N . We then assume $z = |\alpha|/N^{(d-4)/2}$ and $\chi(T) = 1$ when $T > T_\theta$ and -1 for $T < T_\theta$, so that the left-hand side of equation (7.12) reads $\chi(T)z\Psi^d(z)$.

Again we consider two cases.

7.2.1. Case $T > T_\theta$ ($\alpha > 0$). In this case, equation (7.12) becomes

$$\Psi_+^{2d+2}(z) - \Psi_+^{2d}(z) - 2\gamma N^{3-d} - z\Psi_+^d(z) = 0, \quad (7.13)$$

where $z > 0$ and $\Psi_+ > 0$. For small z and $d > 3$, the last two terms in the above equation (7.13) are negligible and $\Psi_+(z) \approx 1$. On the other hand, if $z \gg 1$ the first and last terms of equation (7.13) dominate leading to

$$\Psi_+(z) \approx (\alpha z)^{1/(d+2)}. \quad (7.14)$$

Depending on dimensionality d , we then get, using equation (7.11),

$$\frac{R}{b} \approx \begin{cases} N^{1/2} & 1 \ll N \ll (T - T_\theta)^{-2/(4-d)} \\ & 3 < d < 4 \\ (T - T_\theta)^{1/(d+2)} N^{v_F} & N \gg (T - T_\theta)^{-2/(4-d)} \quad 3 < d < 4 \\ N^{1/2} & N \gg 1 \quad d > 4. \end{cases} \quad (7.15)$$

Notice that, for this case, the Flory correction term (the second term in equation (7.13)) is important for the relatively small N regime but not for the large N regime where self-avoidance dominates. The γ term is, on the other hand, always irrelevant.

7.2.2. Case $T < T_\theta$ ($\alpha < 0$). Equation (7.12) becomes in this case

$$\Psi_-^{2d+2}(z) - \Psi_-^{2d}(z) - 2\gamma N^{3-d} + z\Psi_-^d(z) = 0. \quad (7.16)$$

Again, when $z \ll 1$ and $N \gg 1$ we have $\Psi_-(z) \approx 1$.

When $z \gg 1$ since $\Psi_-(z) > 0$ we have

$$\Psi_-(z) \approx \left(\frac{2\gamma}{zN^{d-3}} \right)^{1/d} = (2\gamma)^{1/d} (T_\theta - T)^{1/d} N^{-\frac{d-2}{2d}} \quad (7.17)$$

leading to

$$\frac{R}{b} \approx \begin{cases} N^{1/2} & 1 \ll N \ll (T_\theta - T)^{-2/(4-d)} \\ & 3 < d < 4 \\ (T_\theta - T)^{-1/d} N^{v_c} & N \gg (T_\theta - T)^{-2/(4-d)} \quad 3 < d < 4 \\ N^{1/2} & N \gg 1 \quad d > 4. \end{cases} \quad (7.18)$$

In this phase both terms, the Flory correction and the γ -term, are relevant depending on the N regime. Thus, the annoying N -dependence in equation (7.13) for $T > T_\theta$ can be neglected and Ψ_+ depends on z only in the large N regime, whereas when $T < T_\theta$, the N -dependence enters through the dangerous irrelevant γ -term which is necessary to ensure the convergence of the integral in equation (5.18).

7.3. Inclusion of an external force

The standard approach to probe any system is to perturb it by a small amount and look for the response. One would therefore like to obtain the response of a polymer in different phases to perturbations that try to change its size or shape. This would tell us about the stability of the size and also would give us information about the distribution function. One such perturbation would be an external force pulling at one end keeping the other fixed. This is equivalent to pulling the two ends with equal force in opposite directions. This is the fixed-force ensemble.

The Flory free energy given in equation (5.10b) can be extended to include the effect of an external force. A detailed analysis of this situation in the case of semiflexible polymer is given in section 8, but we here discuss the Flory result for the flexible case. Equation (5.10b) modifies as

$$\beta F_L(R) = \frac{d}{2} \frac{R^2}{Nb^2} + \alpha \frac{N^2}{R^d} + \gamma \frac{N^3}{R^{2d}} + \dots - \mathbf{f} \cdot \mathbf{R}, \quad (7.19)$$

where the last term accounts for the reduction in free energy for chain alignment along the (reduced) external force per unit of length \mathbf{f} . From a thermodynamic point of view, we are going from a fixed- R ensemble to a fixed-force ensemble.

The force introduces a cylindrical anisotropy so that

$$\mathbf{R} = \mathbf{R}_\parallel + \mathbf{R}_\perp, \quad (7.20)$$

where $\mathbf{R}_\parallel = (\mathbf{R} \cdot \hat{\mathbf{f}})\hat{\mathbf{f}}$ and $\hat{\mathbf{f}} = \mathbf{f}/f$ is the unit vector of \mathbf{f} .

In analogy with equation (5.16) we assume here a different scaling in the directions parallel and perpendicular to the applied force

$$R_\parallel = bN^{v_\parallel} x_\parallel \quad R_\perp = bN^{v_\perp} x_\perp, \quad (7.21)$$

where one expects $v_\parallel \approx 1 > v_\perp$ so that $x_\parallel > x_\perp/N^{v_\parallel - v_\perp}$.

In the $\alpha > 0$ case, i.e. for $T > T_\theta$, both the interaction terms in equation (7.19) (those proportional to α and γ) are subdominant with respect to the Gaussian and the force terms, so that one finds in the $N \gg 1$ limit

$$\beta F_L \approx N \left[\frac{d}{2} x_\parallel^2 - f b x_\parallel \right] + \frac{d}{2} \frac{R_\perp^2}{Nb^2} - \frac{\alpha d}{2 x_\parallel^{d+2}} \frac{R_\perp^2}{N^d b^2} + \text{less dominant terms}, \quad (7.22)$$

whose minimization with respect to R_{\perp} leads to $R_{\perp} \sim bN^{1/2}$ implying $\nu_{\perp} = 1/2$. Then

$$\beta F_L \approx N \left[\frac{d}{2} x_{\parallel}^2 - f b x_{\parallel} \right]. \quad (7.23)$$

This yields the saddle point

$$x_{\parallel}^* = \frac{fb}{d} \quad (7.24)$$

which can be inserted back into equation (7.23) to give the minimum of the swollen phase free energy

$$(\beta F_L)_S = -N \frac{(bf)^2}{2d}. \quad (7.25)$$

In the opposite case $\alpha = -|\alpha|$ (i.e. $T < T_{\theta}$) the phase is compact and hence both terms in equation (7.21) coincide with

$$R = bN^{1/d} x. \quad (7.26)$$

The external force term is then subdominant and one has to match the two interaction terms as in the absence of external force. Thus, equation (7.19) yields

$$\beta F_L = N \left[-\frac{|\alpha|}{x^d} + \frac{\gamma}{x^{2d}} \right]. \quad (7.27)$$

This yields the saddle point equation

$$x^* = \left(\frac{2\gamma}{|\alpha|} \right)^{1/d} \quad (7.28)$$

and a minimum of the compact phase free energy

$$(\beta F_L)_C = -N \frac{\alpha^2}{4\gamma}. \quad (7.29)$$

A first-order transition between the swollen and compact phase occurs when the two free energies (7.25) and (7.29) are equal, that is at the critical force f_c given by

$$bf_c = |\alpha| \sqrt{\frac{d}{2\gamma}}. \quad (7.30)$$

As α is proportional to $(T - T_{\theta})/T_{\theta}$, Flory theory then predicts linear dependence of the critical force f on the reduced temperature, as schematically illustrated in figure 7. This approach has been exploited to infer the unzipping transition in DNA [50–52].

7.4. Polymer solution

The single chain behaviour discussed so far is for a very dilute solution. The monomers on different chains also interact like monomers on the same chain. We discuss qualitatively the combined effect of additional chains and temperature. See figure 8.

For polymers in good solvent, one may start from a very dilute regime where each chain has its own size and they are too far apart to have any mutual interaction. Taking each chain to be a sphere of radius $R \sim N^{\nu}$, the dilute limit corresponds to

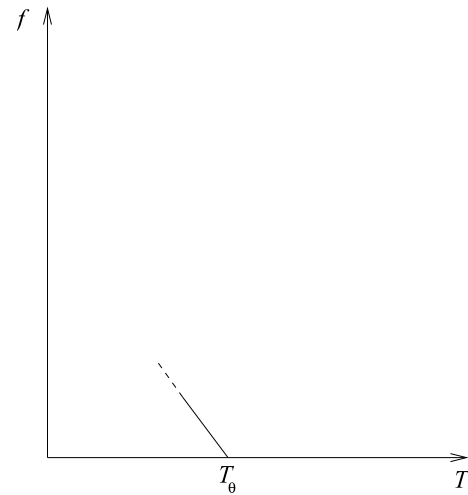


Figure 7. Schematic phase diagram, in the force–temperature plane, as predicted by the Flory theory.

the regime where the separation of the centre of the spheres Λ is much greater than R , $\Lambda \gg R$. Like any dilute solution, the polymers then exert an osmotic pressure well described by the perfect gas law,

$$\Pi = k_B T c_p, \quad (\Lambda \gg R), \quad (7.31)$$

where c_p is the polymer number concentration (number of polymers per unit volume). If we have n_p polymers in the solution of volume V , $c_p = n_p/V$.

Polymers are not hard spheres and so they start interacting when $\Lambda \sim R$. They start to interpenetrate. Under such a condition, monomer concentration

$$c = \frac{N n_p}{V} = N c_p, \quad (7.32)$$

is a more appropriate variable than c_p because the end points do not matter. In the dilute limit, the polymers are identifiable, the end points acting as labels for them. For the interpenetrating case, there is no noticeable distinction between the interior of the solution of n_p polymers each of N monomers and the interior of a single chain of length $n_p N$. The chain length ceases to be a suitable measure to characterize the solution. This regime is called the *semi-dilute* regime or a semi-dilute solution of polymers. The change from the dilute to the semi-dilute case is not a phase transition but a smooth crossover involving a concentration dependent length scale. From the transient network created by the interpenetration, one may identify a spatial length ξ within which a polymer segment is free and assumes the behaviour of a swollen chain ($\xi \sim n^{\nu}$). It looks like a solution of blobs of size ξ . Thanks to the interaction with other monomers, the long-range correlation of a single chain is lost. As a result, a long polymer, $N \gg n$, will be in a Gaussian state. This is a screening effect—the repulsive interactions with other monomers screening out the long-range effect of self-repulsion. In a T – c plane for a finite N , there will be a crossover line separating the dilute and the semi-dilute cases. See figure 8(a).

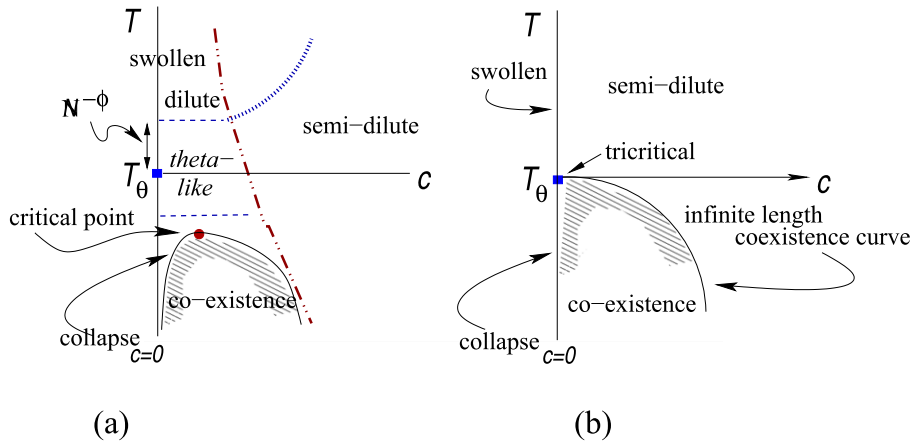


Figure 8. T versus c (concentration) diagram for (a) a finite chain and (b) infinite chain length. In (a) there is no true theta point but instead a critical point for phase separation of polymer solutions. With concentration, there is a crossover line for theta-like polymer solution to repulsive polymer solution (blue horizontal dashed lines). The dilute to semi-dilute crossover takes place at the overlap concentration where the polymer spheres in the dilute solution start to touch each other. This is indicated by a red dash-dotted line. The blue hashed line indicates the variation of the overlap concentration with N (the locus of a typical point on the red dashed line). Near the critical point the solution behaviour is controlled by the concentration fluctuations. In (b) there is a theta point (for $c = 0$) which is the end point of the line of critical points of phase separation. This is a tricritical point. There is a phase coexistence line from the theta point for infinitely long polymers. On this line the osmotic pressure is zero. The critical point is coincident with the $c = 0$ theta point. For any nonzero concentration it is a semi-dilute solution. The swollen and the collapsed states exist only on the $c = 0$ line.

The scale c^* for the crossover from dilute to semi-dilute case can be obtained from a physical picture. This is the concentration at which the individual spheres of size R just start to touch each other, $\Lambda \sim R$. In a sense, the overall monomer concentration matches the concentration inside a single polymer sphere, namely,

$$c_p \sim \frac{1}{\Lambda^d} \sim \frac{1}{R^d}, \quad \text{so that } c^* \sim \frac{L}{R^d} \sim N^{1-dv}. \quad (7.33)$$

With this scale, the osmotic pressure takes the form

$$\Pi = k_B T c_p f(c/c^*) = k_B T (c/N) f(c/c^*)$$

where the function $f(x)$ is such that for $c \gg c^*$, Π is independent of N . It then follows that $\Pi \sim c^{1/(dv-1)}$. The nonlinear dependence $\Pi \sim c^{5/4}$ in three dimensions (using the Flory value) has been observed experimentally in many polymer solutions [5].

The dilute–semi-dilute crossover is indicated by a dash-dotted line in figure 8(a). As N is decreased the crossover line shifts to higher values as indicated by a hashed blue line. For infinitely long chains any solution is in the semi-dilute regime ($c^* \rightarrow 0$) as in figure 8(b).

For attractive interaction, the theta temperature is strictly for an infinitely long chain. A solution of polymers of finite chains with attractive interaction would show a phase separation between very dilute and semi-dilute solutions similar to the phase separation of any binary mixture or alloy. Such a phase separation, in addition to a region of coexistence, would also have a critical point in the temperature concentration plane. The critical point is expected at a temperature $T_c < T_\theta$ with $T_c \rightarrow T_\theta$ at $c \rightarrow 0$ as $N \rightarrow \infty$. The behaviour close to the critical point (‘critical phenomenon’) is identical to other binary mixtures, controlled by concentration fluctuations. In a three-dimensional T – c – $1/N$ phase diagram

a line of these critical points ends at the theta point at $1/N = 0, c = 0$. See figure 8(b). We see the special status of the theta point: it is the confluence of two independent phenomena, the criticality of phase separation in solution and the collapse of a single long chain. Such a point is defined as a tricritical point. A tricritical point requires three critical lines meeting at a point. For $N \rightarrow \infty, c = 0$, the $T > T_\theta$ line is a critical line showing power law behaviour at every T . We therefore see two critical lines meeting at the theta point. Unfortunately, N, c are strictly positive and so a complete picture of the tricritical behaviour is not achievable. For $N \rightarrow \infty$, there is a phase separation between the collapsed phase and a semi-dilute solution. The phase separation line has zero osmotic pressure.

Figure 8(a) shows the various crossovers in the T – c plane for a fixed N , a slice of the three-dimensional phase diagram. There is a region close to the theta point with small c , marked by the horizontal lines $T_\theta \pm N^{-\phi}$ in the dilute regime where the signature of the theta point is visible.

There have been experimental attempts [53] to generate such a phase diagram for polymers in terms of theta point scaling but a Flory-like theory for these rich phenomena remains elusive.

8. Semiflexible chain under tension

So far we have discussed the properties of flexible chains, where the chain is Gaussian in the absence of any external interactions. The discussed Edwards model is then the continuum counterpart of a freely jointed chain. The two matched nicely because all the properties were controlled by the configurations near the peak of the distribution. We now discuss a case where one needs the extreme states for which the Gaussian approximation is not sufficient.

In addition to the three phases we have seen, there is the possibility of a stretched state or a rod-like state with $\nu = 1$ as, e.g., one expects for a repulsive polymer in $d = 1$. This state can be produced by stretching by a force or by bending rigidity. In both cases there is a competition with entropy. Since an extended state would correspond to configurations in the tail of a Gaussian distribution, the continuum model we used would not be of much use.

In this section, for completeness and for practical usefulness, we consider the situation of a polymer with bending rigidity, called a semiflexible polymer, in the presence of an external pulling force acting on one end of the chain [25, 26]. The small force and the large force regions are determined, from which an approximate interpolation formula is derived.

8.1. Discrete approach

Let us start with the FJC of section 2, with normalized bond vectors by $\hat{\mathbf{T}}_j = \boldsymbol{\tau}_j/b$. Instead of free joints, we admit a bending energy at every joint where there is an energy penalty if the two bonds are not parallel. This energy cost is taken as $\propto -\hat{\mathbf{T}}_{j-1} \cdot \hat{\mathbf{T}}_j$. If one end is fixed at the origin, then the force on the other end is equivalent to a orientational force on every bond because of the relation $\mathbf{R} = \sum_j \boldsymbol{\tau}_j$. The Hamiltonian can then be written as

$$\beta H = -K \sum_{j=1}^N \hat{\mathbf{T}}_{j+1} \cdot \hat{\mathbf{T}}_j - \sum_{j=1}^N b \mathbf{f} \cdot \hat{\mathbf{T}}_j, \quad (8.1)$$

with the partition function¹⁰

$$e^{-\beta F} = Z = \int \left[\prod_{j=1}^N \frac{d^3 \hat{\mathbf{T}}_j}{2\pi} \delta(\hat{\mathbf{T}}_j^2 - 1) \right] e^{-\beta H}. \quad (8.2)$$

The delta function in equation (8.1) maintains the fixed length constraint of each bond. It is this constraint that prevents the unwanted extensions (in the tail of the Gaussian distribution) of a continuous chain. We choose our axes such that the force is in the z -direction $\mathbf{f}_j = f \hat{\mathbf{z}}$ and the quantity of interest is the extension $\langle z \rangle = b \sum_i \langle T_i^{(\parallel)} \rangle$, where \parallel indicates the z -direction. Incidentally, the Hamiltonian equation (8.2) is identical to a classical ferromagnetic one-dimensional Heisenberg model in a field, if \mathbf{T} is treated as a fixed length spin vector.

Let us first consider the small force regime, where a linear response is expected, $\langle z \rangle = b^2 \chi_T f$, with the response function

$$\chi_T = \sum_{ij} \langle T_i^{(\parallel)} T_j^{(\parallel)} \rangle_0, \quad (8.3)$$

where the correlations are evaluated in the zero-force condition indicated by the subscript 0. For the classical one-dimensional model, these correlations decay exponentially for all temperatures,

$$\langle T_i^{(\parallel)} T_j^{(\parallel)} \rangle_0 \sim \exp(-|i-j|b/l_p). \quad (8.4)$$

¹⁰The factor 2π appearing in equation (8.2) in place of the usual normalization 4π is due to the presence of the $\hat{\mathbf{T}}^2 - 1$ in the argument of the δ -function, and to the fact that $\delta(x^2 - 1) = [\delta(x - 1) + \delta(x + 1)]/2$ with the second term not contributing to the result of the radial integral.

Here $\mathbf{T}^{\parallel} = \hat{\mathbf{z}}(\hat{\mathbf{T}} \cdot \hat{\mathbf{z}})$ and this also defines the perpendicular component \mathbf{T}^{\perp} as given in equation (8.6).

The decay length l_p is the persistence length. The correlation here may be compared with the flexible case, equation (2.2). Ignoring end point effects (equivalent to assuming a circular polymer), and converting the sum to an integral, we get $\chi_T \sim Nl_p$. Therefore for small forces, we expect

$$\langle z \rangle = Nbl_p f + \mathcal{O}(f^2). \quad (8.5)$$

For large forces, the polymer is going to align with the force and be completely stretched except for thermal fluctuations. The fully stretched condition means $z = bN$ and therefore the delta function constraint in equation (8.2) is going to play an important role. The deviation from the fully stretched state comes because of transverse fluctuations and it would go to zero as $f \rightarrow \infty$. By writing

$$\hat{\mathbf{T}}_j = \mathbf{T}_j^{(\parallel)} + \mathbf{T}_j^{(\perp)} \quad (8.6)$$

with small transversal part, i.e. $|\mathbf{T}_j^{(\perp)}| \ll 1$ for $b f \gg 1$, we have

$$\begin{aligned} \langle z \rangle &= \sum_{l=1}^N b \langle \hat{\mathbf{T}}_l \cdot \hat{\mathbf{z}} \rangle = b \sum_{l=1}^N \left\langle \sqrt{1 - T_l^{(\perp)2}} \right\rangle \\ &\approx Nb - \frac{b}{2} \sum_{l=1}^N \langle T_l^{(\perp)2} \rangle. \end{aligned} \quad (8.7)$$

Under the same approximation for $f \gg 1$ as in equation (8.7), the Hamiltonian can be approximated, dropping redundant terms, as

$$\beta H = -K \sum_{j=1}^N \mathbf{T}_{j+1}^{(\perp)} \cdot \mathbf{T}_j^{(\perp)} + \frac{1}{2} \sum_{j=1}^N (bf + K_j) \mathbf{T}_j^{(\perp)2}, \quad (8.8)$$

where $K_j = 2K$, for all j except $K_1 = K_N = K$. In the following, we neglect this boundary effect and set $K_j = 2K$. For a very large force, the leading term of the Hamiltonian is $\beta H \approx \frac{1}{2} \sum_{j=1}^N b f \mathbf{T}_j^{(\perp)2}$. By the equipartition theorem, we then expect $b f \langle \mathbf{T}_j^{(\perp)2} \rangle = 2$. By using this result in equation (8.7), the behaviour is

$$\frac{\langle z \rangle}{Nb} \approx 1 - \frac{1}{bf}, \quad f \rightarrow \infty. \quad (8.9)$$

Both equations (8.5) and (8.9) agree with the small and large f limits obtained by the more elaborate calculation of sections 8.3 and 8.4. It is then possible to generate an interpolation formula that satisfies the two asymptotes, namely $f \rightarrow 0$ and $f \rightarrow \infty$. The interpolation formula is derived below *after* taking the continuum limit $b \rightarrow 0$ which requires a more detailed evaluation of the large force limit.

8.2. Continuum limit: a detour

The continuum limit of the discrete chain with bending energy does not follow from the procedure adopted for the FJC. The reason for this is that in the Edwards model the length L is

like an area or the chain is not a space curve. A semiflexible polymer configuration involves the tangent vectors \mathbf{T} for which it has to be taken as a space curve [54, 55]. Therefore two points on the polymer \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ separated by a contour length ds have to satisfy $(\partial\mathbf{r}/\partial s)^2 = 1$. This condition at every point on the curve can be enforced by a δ -function in the partition function and the Gaussian term of the Edwards model does not appear. By writing $-2\mathbf{T}_i \cdot \mathbf{T}_j = (\mathbf{T}_i - \mathbf{T}_j)^2 - 2$, a continuum limit for the bending energy for $b \rightarrow 0$ would give a derivative of

$$\hat{\mathbf{T}}(s) = \frac{\partial\mathbf{r}}{\partial s}, \quad (8.10)$$

i.e., $\partial^2\mathbf{r}/\partial s^2$.

With the above introduction, let us introduce the partition function and the free energy for a semiflexible chain under the action of an external force [25, 26],

$$e^{-\beta F} = Z = \int \mathcal{D}\mathbf{r} \left[\prod_s \delta(\hat{\mathbf{T}}^2(s) - 1) \right] e^{-\beta H}, \quad (8.11)$$

with a Hamiltonian

$$\beta H = \frac{l_p}{2} \int_0^L ds \left(\frac{\partial\hat{\mathbf{T}}}{\partial s} \right)^2 - \int_0^L ds \mathbf{f}(s) \cdot \hat{\mathbf{T}}(s). \quad (8.12)$$

In equation (8.12) l_p is the persistence length which is the tangent correlation length defined as

$$\langle \hat{\mathbf{T}}(s) \cdot \hat{\mathbf{T}}(s') \rangle \sim \exp \left[-\frac{|s - s'|}{l_p} \right], \quad (8.13)$$

the continuum analogue of equation (8.4). The fact that the l_p introduced in equation (8.12) coincides with the actual persistent length given in equation (8.13) will be shown below. If \mathbf{f} is a constant, then the last term in equation (8.12) becomes $\mathbf{f} \cdot [\mathbf{r}(L) - \mathbf{r}(0)]$ which is the standard force term.

If one softens the rigid constraint by a Gaussian weight factor, i.e., the $\delta(\hat{\mathbf{T}}^2(s) - 1)$ by $\exp(-\hat{\mathbf{T}}^2/2\sigma^2)$, and absorb this extra term in the Hamiltonian, we get

$$\beta H = \frac{l_p}{2} \int_0^L ds \left(\frac{\partial^2\mathbf{r}}{\partial s^2} \right)^2 + \frac{1}{2\sigma^2} \int_0^L ds \left(\frac{\partial\mathbf{r}}{\partial s} \right)^2 - \int_0^L ds \mathbf{f}(s) \cdot \hat{\mathbf{T}}(s), \quad (8.14)$$

which allows discussions of a crossover from the Gaussian to the semiflexible case [56].

We follow a discrete approach of [27, 28], that is simpler than a continuum formulation and yields the same results.

8.3. Large f limit: detailed calculations

Let us start with equation (8.2). We further assume the transversal part to be small, i.e. $|\mathbf{T}_j^{(\perp)}| \ll 1$, an assumption that holds in the large f limit. Then, to leading order,

$$\delta(\hat{\mathbf{T}}_j^2 - 1) = \frac{1}{2\sqrt{1 - T_j^{(\perp)2}}} \delta \left(T_j^{(\parallel)} - \sqrt{1 - T_j^{(\perp)2}} \right), \quad (8.15)$$

where the additional term containing $\delta(T_j^{(\parallel)} + \sqrt{1 - T_j^{(\perp)2}})$ has been neglected since it leads to subdominant contributions. To leading order, the square root term appearing in equation (8.15) can be exponentiated as

$$(1 - T_j^{(\perp)2})^{-1/2} \approx e^{T_j^{(\perp)2}/2}, \quad (8.16)$$

and in equation (8.2) we can further split $d^3\hat{\mathbf{T}}_j = dT_j^{(\parallel)} d^2\mathbf{T}_j^{(\perp)}$. The integral over the longitudinal part can be carried out immediately so that equation (8.2) can be written as

$$e^{-\beta F} = (\text{const}) \left[\int \left(\prod_{j=1}^N dT_j \right) \times \exp \left(-\frac{1}{2} \sum_{ij=1}^N T_i M_{ij} T_j \right) \right]^2, \quad (8.17)$$

where M_{ij} is a tri-diagonal matrix

$$M_{ij} = (bf + 2K + 1)\delta_{ij} - K(\delta_{ij+1} + \delta_{ij-1}), \quad (8.18)$$

and T_j is any of the two transversal components of $\hat{\mathbf{T}}_j$ whose range can be extended to the whole real line, $-\infty < T_j < \infty$. The multiplicative constant appearing in front of equation (8.17) is irrelevant and can be dropped. Being of Gaussian form, the computation of any correlation function of (8.18) can be easily done as it is related to the inverse matrix M_{ij}^{-1} (see appendix A). With the use of the result

$$\sum_l \langle T_l^{(\perp)2} \rangle = 2 \sum_l M_{ll}^{-1}, \quad (8.19)$$

one then finds from equation (8.7),

$$\frac{\langle z \rangle}{Nb} = 1 - \frac{1}{N} \text{Tr} \mathbf{M}^{-1}. \quad (8.20)$$

In order to compute the trace of the inverse matrix \mathbf{M}^{-1} one may switch to Fourier variables for diagonalization (since the boundary conditions are not relevant in the large N limit, we use periodic boundary conditions, as already done for K_j),

$$\sum_{l=1}^N M_{lm} e^{i\omega_n(l-m)} = \lambda(\omega_n), \quad \omega_n = \frac{2n\pi}{N} \quad (8.21)$$

where the eigenvalues are

$$\lambda(\omega) = u - 2K \cos \omega \quad (8.22)$$

with $u = bf + 2K + 1$. Then in the $N \rightarrow \infty$ limit

$$\begin{aligned} \frac{1}{N} \sum_{l=1}^N M_{ll}^{-1} &= \frac{1}{N} \sum_{n=0}^{N-1} \frac{1}{\lambda(\omega_n)} \xrightarrow{N \rightarrow \infty} \int_{-\pi}^{+\pi} \frac{d\omega}{2\pi} \frac{1}{\lambda(\omega)} \\ &= \frac{1}{\sqrt{(bf + 1)^2 + 4K(bf + 1)}}. \end{aligned} \quad (8.23)$$

The last equality in equation (8.23) has been obtained in the $N \rightarrow \infty$ limit by contour integration. Note that condition $u \geq 2K$ is required to ensure positive eigenvalues of the M_{lm} matrix and well defined integral in equation (8.17). This can

be inserted into equation (8.7) so that (assuming $bf \gg 1$)

$$\frac{\langle z \rangle}{Nb} = 1 - \frac{1}{\sqrt{b^2 f^2 + 4Kbf}}, \quad (8.24)$$

whose leading-order terms agree with equation (8.9).

8.4. Small force limit: detailed calculations

In the $f \rightarrow 0$ limit, we can expand the partition function Z given in equation (8.1). If Z_0 is the partition function associated with the $f = 0$ Hamiltonian in equation (8.1), we have

$$Z = Z_0 \left[1 + \frac{1}{2} b^2 \sum_{ij} \sum_{\mu, \nu=x, y, z} f_\mu f_\nu \langle \hat{T}_i^\mu \hat{T}_j^\nu \rangle_0 + \dots \right] \quad (8.25)$$

where the first-order term in the expansion vanishes because $\langle \hat{T}_j \rangle_0 = 0$ by symmetry. The averages denoted by the subscript 0 are with respect to Z_0 . Because of the rotational invariance of the zero-force Hamiltonian (8.1), we have that $\langle \hat{T}_i^\mu \rangle_0 = 0$ and $\langle \hat{T}_i^\mu \hat{T}_j^\nu \rangle_0 = (1/3) \delta^{\mu\nu} \langle \hat{\mathbf{T}}_i \cdot \hat{\mathbf{T}}_j \rangle_0$. Hence, one gets

$$Z = Z_0 \left[1 + \frac{1}{6} b^2 f^2 \sum_{ij} \langle \hat{\mathbf{T}}_i \hat{\mathbf{T}}_j \rangle_0 + \dots \right], \quad (8.26)$$

where

$$\langle \hat{\mathbf{T}}_i \hat{\mathbf{T}}_j \rangle_0 = \frac{1}{Z_0} \int \left[\prod_{n=1}^N \frac{d^3 \hat{\mathbf{T}}_n}{2\pi} \delta(\hat{\mathbf{T}}_n^2 - 1) \right] \times e^{K \sum_{l=1}^N \hat{\mathbf{T}}_{l+1} \cdot \hat{\mathbf{T}}_l} \langle \hat{\mathbf{T}}_i \hat{\mathbf{T}}_j \rangle. \quad (8.27)$$

In equation (8.27) we have assumed periodic boundary conditions so that $\hat{\mathbf{T}}_N = \hat{\mathbf{T}}_1$. Now, $\mathbf{R} = b \sum_j \hat{\mathbf{T}}_j$ so that the quantity

$$\sum_{i=0}^N \sum_{j=0}^N \langle \hat{\mathbf{T}}_i \cdot \hat{\mathbf{T}}_j \rangle_0 = \langle R^2 \rangle / b^2 \quad (8.28)$$

is the mean square end-to-end distance. We then have from equation (8.26)

$$Z = Z_0 [1 + \frac{1}{6} f^2 \langle R^2 \rangle + \dots], \quad (8.29)$$

and hence

$$\langle z \rangle = \frac{\partial}{\partial f} \ln Z = \frac{1}{3} f \langle R^2 \rangle + \dots, \quad (8.30)$$

which is consistent with the expected linear response mentioned earlier.

The connection between the response function and the polymer size raises an interesting question on the thermodynamic limit. This is discussed in appendix D.

8.4.1. Evaluation of $\langle R^2 \rangle$. We now evaluate $\langle R^2 \rangle$. Consider the quantity

$$I(K, \hat{\mathbf{T}}_{j-1}) = \int \frac{d^3 \hat{\mathbf{T}}_j}{2\pi} \delta(\hat{\mathbf{T}}_j^2 - 1) e^{K \hat{\mathbf{T}}_{j-1} \cdot \hat{\mathbf{T}}_j}. \quad (8.31)$$

This can be easily computed as an integral over the solid angle. With γ_j as the angle between $\hat{\mathbf{T}}_j$ and $\hat{\mathbf{T}}_{j-1}$, one gets

$$I(K, \hat{\mathbf{T}}_{j-1}) = \frac{1}{2\pi} \int d\Omega_j e^{K \cos \gamma_j} = \frac{\sinh K}{K} \equiv I_0(K), \quad (8.32)$$

independent of $\hat{\mathbf{T}}_{j-1}$. Then one can clearly integrate \mathbf{T} 's in equation (8.3) with $f = 0$, term by term, with the result

$$Z_0 = [I_0(K)]^{N+1}. \quad (8.33)$$

Likewise one can also compute the average involved in equation (8.27) as (assuming without loss of generality $j > i$)

$$\begin{aligned} \langle \hat{\mathbf{T}}_i \hat{\mathbf{T}}_j \rangle_0 &= \frac{1}{[I_0(K)]^{j-i}} \int \frac{d^3 \hat{\mathbf{T}}_i}{2\pi} \delta(\hat{\mathbf{T}}_i^2 - 1) \dots \\ &\times \int \frac{d^3 \hat{\mathbf{T}}_j}{2\pi} \delta(\hat{\mathbf{T}}_j^2 - 1) \\ &\times e^{K \sum_{l=i}^{j-1} \hat{\mathbf{T}}_{l+1} \cdot \hat{\mathbf{T}}_l} \langle \hat{\mathbf{T}}_i \hat{\mathbf{T}}_j \rangle. \end{aligned} \quad (8.34)$$

One then observes that

$$\frac{1}{I_0(K)} \int \frac{d^3 \hat{\mathbf{T}}_j}{2\pi} \delta(\hat{\mathbf{T}}_j^2 - 1) e^{K \hat{\mathbf{T}}_{j-1} \cdot \hat{\mathbf{T}}_j} = \mathcal{L}(K) \hat{\mathbf{T}}_{j-1}, \quad (8.35)$$

where

$$\mathcal{L}(K) = \frac{\partial}{\partial K} \log I_0(K) = \coth K - \frac{1}{K}. \quad (8.36)$$

Here $\mathcal{L}(K)$ is the Langevin function appearing in the exact solution of the FJC subject to an external force discussed in appendix F. In deriving equations (8.35) and (8.36) we have neglected subdominant terms in the limit $N \gg |i - j|$, and exploited the rotational invariance of the zero-force Hamiltonian (8.1).

Then, by iteration,

$$\langle \hat{\mathbf{T}}_i \hat{\mathbf{T}}_j \rangle_0 = \mathcal{L}(K) \langle \hat{\mathbf{T}}_i \hat{\mathbf{T}}_{j-1} \rangle_0 = [\mathcal{L}(K)]^{i-j}, \quad (8.37)$$

in the form of equation (8.4) with

$$l_p = b/|\ln \mathcal{L}(K)|. \quad (8.38)$$

For an explicit computation of $\langle R^2 \rangle$, note that

$$\begin{aligned} b^{-2} \langle R^2 \rangle &= \sum_{i=0}^N \sum_{j=0}^N [\mathcal{L}(K)]^{|i-j|} \\ &= \sum_{l=0}^N \sum_{m=0}^l \mathcal{L}^{l-m}(K) + \sum_{l=0}^N \sum_{m=l+1}^N \mathcal{L}^{m-l}(K). \end{aligned} \quad (8.39)$$

With the help of the summation formula

$$\sum_{l=0}^N \sum_{m=0}^l x^{l-m} = \frac{1}{1-x} \left[N+1 - \frac{x}{1-x} (1-x^{N+1}) \right], \quad (8.40)$$

and

$$\sum_{l=0}^N \sum_{m=l+1}^N x^{l-m} = \frac{x}{1-x} \left[N+1 - \frac{(1-x^{N+1})}{1-x} \right], \quad (8.41)$$

the final form is

$$\begin{aligned} \langle R^2 \rangle &= b^2(N+1) \frac{1 + \mathcal{L}(K)}{1 - \mathcal{L}(K)} \\ &\quad - 2b^2 \mathcal{L}(K) \frac{1 - \mathcal{L}^{N+1}(K)}{(1 - \mathcal{L}(K))^2}. \end{aligned} \quad (8.42)$$

Because $|\mathcal{L}| < 1$, we do see $\langle R^2 \rangle \sim N$ for $N \rightarrow \infty$, as claimed in section 2 (see below equation (2.7)). For $N \ll l_p/b$, a polymer would look like a rod in an extended state but for $N \gg l_p/b$ it would be Gaussian. The semiflexible regime corresponds to the intermediate case $N > l_p/b$. Since $|\mathcal{L}(K)| < 1$, l_p is always finite, except for $K \rightarrow \infty$. For large K , $\mathcal{L}(K) \approx 1 - \frac{1}{K}$ so that, from equation (8.38), $l_p \approx Kb$. In this limit, $(1 + \mathcal{L}(K))/(1 - \mathcal{L}(K)) \approx 2K$, so that the size can be written as

$$\langle R^2 \rangle = 2l_p L_c - 2l_p^2(1 - e^{-L_c/l_p}), \quad (8.43)$$

in terms of the length $L_c = Nb$. Note that in the limit $N \ll l_p/b$, equation (8.43) predicts a ballistic dependence $\langle R^2 \rangle \sim N^2$, as expected.

8.5. An interpolation formula

The result given in equation (8.24) can be reduced to its continuum counterpart [28], by considering the $b \rightarrow 0$ limit with $N, K \rightarrow \infty$, keeping the persistence length $l_p = Kb$ fixed and also the chain length $L_c = Nb$ [27]. From equation (8.1) we see that \mathbf{f} has dimensions of the inverse of a length. Upon introducing the ‘physical’ force $f_{\text{phys}} = f/\beta$, and the dimensionless ratio $\zeta = \langle z \rangle / (Nb)$, one obtains from equations (8.24) and (8.30)

$$\zeta = 1 - \frac{1}{2\sqrt{l_p \beta f_{\text{phys}}}} \quad (8.44)$$

in the large force limit. Notice that we are working in the limit $l_p \ll L_c$ so that the first term in the right-hand side of equation (8.43) is the dominant one.

The opposite limit $f \rightarrow 0$ can be obtained directly in the $\beta f_{\text{phys}} b \ll 1$ limit as given in section 8.4.1. Indeed, from equation (8.42) in the $b \rightarrow 0$ and $N \gg 1$ limit we get from equation (8.43)

$$\langle z \rangle = \frac{2}{3} l_p L_c \beta f_{\text{phys}} + \dots, \quad (8.45)$$

and hence

$$\zeta = \frac{2}{3} \beta f_{\text{phys}} l_p + \dots \quad (8.46)$$

Similar results can be obtained by considering a Gaussian chain subject to an external force. Within the discrete limit, we have the FJC model that can be solved exactly, as discussed in appendix F.

Notice that it can be shown that $b = 2l_p$ within the WLC model [9, 10], so that this relation agrees with equation (8.5).

The two above relations (8.44) and (8.46) can be inverted to yield

$$l_p \beta f_{\text{phys}} = \begin{cases} \frac{3}{2} \zeta & \text{if } \zeta \ll 1 \\ \frac{1}{4(1 - \zeta)^2} & \text{if } \zeta \lesssim 1. \end{cases} \quad (8.47)$$

Both regimes can be embodied into an interpolation formula [28]

$$l_p \beta f_{\text{phys}} = \zeta + \frac{1}{4(1 - \zeta)^2} - \frac{1}{4} \quad (8.48)$$

that reduces to the two limits given in equation (8.47) in the respective regimes. Additional discussions can be found in [57–61], while a recent discussion on the numerical supporting results can be found in [62].

8.6. Structure factor and end-to-end distance

A very useful quantity to connect with experiment is given by the structure factor. In the absence of external force, this was obtained by Shimada *et al* [63].

In the discrete representation, the structure factor is defined as

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{ij=1}^N \exp[i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle. \quad (8.49)$$

For a Gaussian FJC chain this can be easily evaluated by Gaussian integrals, as reported in appendix E with the result [5]

$$S_0(k) = NF_D(3R_g^2 k^2) \quad (8.50)$$

where $R_g = (Nb^2/6)^{1/2}$ is the radius of gyration and $F_D(x)$ is the Debye function

$$F_D(x) = \frac{2}{x^2} [e^{-x} - 1 + x]. \quad (8.51)$$

This structure factor was used in the study of a semi-dilute solution. Now consider the WLC model in the continuum formulation. Unlike the case of the Edwards model, we can consider the limit $b \rightarrow 0$ and $N \gg 1$ with $L_c = Nb$ fixed. Then $S(\mathbf{k})$ reads

$$\begin{aligned} S(\mathbf{k}) &= \frac{1}{L_c b} \int_0^{L_c} ds \int_0^{L_c} ds' \\ &\quad \times \langle \exp[i\mathbf{k} \cdot (\mathbf{R}(s) - \mathbf{R}(s'))] \rangle. \end{aligned} \quad (8.52)$$

Consider now the case $f = 0$. As discussed, the continuum limit of equation (8.37) is

$$\langle \hat{\mathbf{T}}(s) \cdot \hat{\mathbf{T}}(s') \rangle_0 = \exp \left[-\frac{1}{l_p} |s - s'| \right]. \quad (8.53)$$

This can be alternatively viewed by using a different scheme as detailed in appendix H (see equation (H.3)).

Next we consider the exact evaluation of the structure factor for the WLC model as an expansion in powers of k , that can be computed term by term.

The discretized version of equations (8.11) and (8.12) when $f = 0$ is equation (8.2), that is

$$\begin{aligned} Z &= \int \left[\prod_{j=0}^N \frac{d^3 \mathbf{T}_j}{2\pi} \delta(\mathbf{T}_j^2 - 1) \right] \\ &\quad \times \exp \left[-\frac{1}{2} \frac{l_p}{b} \sum_{j=1}^N (\mathbf{T}_j - \mathbf{T}_{j-1})^2 \right]. \end{aligned} \quad (8.54)$$

As before, \mathbf{T}_j is a vector tangent to the polymer axis at position \mathbf{r}_j and $d^3\mathbf{T}_j = d\hat{\mathbf{T}}_j dT_j T_j^2$ so that the integrals over all dT_j can be carried out immediately because of the delta function appearing in equation (8.54). Upon introducing the Green function

$$G_{0L_c}(\hat{\mathbf{T}}_0, \hat{\mathbf{T}}_N) = \int \left[\prod_{j=0}^N \frac{d\hat{\mathbf{T}}_j}{4\pi} \right] \times \exp \left[-\frac{1}{2} \frac{l_p}{b} \sum_{j=1}^N (\mathbf{T}_j - \mathbf{T}_{j-1})^2 \right] \quad (8.55)$$

we then have

$$Z = \int \frac{d\hat{\mathbf{T}}_0}{4\pi} \int \frac{d\hat{\mathbf{T}}_N}{4\pi} G_{0L_c}(\hat{\mathbf{T}}_0, \hat{\mathbf{T}}_N). \quad (8.56)$$

The Green function (8.55) has the following form in the $b \rightarrow 0$ limit with $L_c = Nb$ fixed as remarked (this is done in appendix G):

$$G_{0L_c}(\hat{\mathbf{T}}_0, \hat{\mathbf{T}}_N) = 4\pi \sum_{l=0}^{+\infty} \sum_{m=-l}^{+l} e^{-L_c l(l+1)/(2l_p)} Y_{lm}(\hat{\mathbf{T}}_0) Y_{lm}^*(\hat{\mathbf{T}}_N). \quad (8.57)$$

Next, we expand the exponential in the structure factor (8.52) in powers of k up to second order:

$$S(\mathbf{k}) = \frac{1}{L_c b} \int_0^{L_c} ds \int_0^{L_c} ds' \times \left[1 - \frac{1}{2} \langle [r_z(s) - r_z(s')]^2 \rangle + \dots \right] \quad (8.58)$$

where we have assumed $\mathbf{k} = k\hat{\mathbf{z}}$, and where (for $s > s'$) we have defined

$$\langle [r_z(s) - r_z(s')]^2 \rangle = \int_{s'}^s ds_1 \int_{s'}^s ds_2 \langle \hat{T}_z(s_1) \hat{T}_z(s_2) \rangle. \quad (8.59)$$

Note that all odd powers vanish by symmetry, so the power expansion is formed by even powers only. The integral (8.59) is computed in appendix H (see equation (H.4)), and can be inserted back into the expansion equation (8.58). Elementary integrations, along with the relation $b = 2l_p$ [10], then lead to

$$S(k) = \frac{L_c}{2l_p} \left\{ 1 - \frac{4}{3} \frac{l_p^5}{L_c} \left[\frac{1}{6} \left(\frac{L_c}{l_p} \right)^3 - \frac{1}{2} \left(\frac{L_c}{l_p} \right)^2 + \frac{L_c}{l_p} - 1 + e^{-L_c/l_p} \right] k^2 + \dots \right\}. \quad (8.60)$$

As a by-product of this calculation, we can obtain the end-to-end distance that can be compared with the mean-field calculation reported in [26]. Indeed, using equation (8.59), the end-to-end distance is given by

$$\langle R^2 \rangle \equiv \langle [\mathbf{r}(L_c) - \mathbf{r}(0)]^2 \rangle = 3 \langle [r_z(L_c) - r_z(0)]^2 \rangle = 2l_p^2 \left[\frac{L_c}{l_p} - 1 + e^{-L_c/l_p} \right], \quad (8.61)$$

where the last equality again stems from equation (H.4) (see appendix H). This agrees with the direct result obtained in

equation (8.43). Note that this result coincides also with that obtained in [26] with $f = 0$, provided that a mean-field translation $2l_p/3 \rightarrow l_p$ is carried out.

9. Outlook

The aim of this review was to introduce some well-known and less-well-known features of polymer physics, within a unified framework hinging upon the Flory theory as a pillar. In doing this, we have reviewed some formalisms, approximations and results briefly, but in a self-contained way, so that the review can be used as a first approach to these methods at the graduate student level.

Starting with the simplest and well-known version of the Flory approach given in section 2, we have proceeded by introducing the Edwards continuum approach in section 3 that is used as a toolbox for field-theoretical approaches to polymer physics.

One of the reasons that stimulated us to review this topic derives from the fact that the Flory theory is frequently exploited, in different forms, as a theoretical tool to tackle remarkably complex systems. Mean-field theories are the generic tools to handle interacting systems in a nonperturbative way, especially in problems without any small parameter. It ignores fluctuations and so provides results too coarse to distinguish the subtle effects of dimensionality and correlations. As a result the predictions of the nature of phase transitions or of the emergent phases become questionable. Although technically the Flory theory uses the saddle point, steepest descent method associated with mean-field theories, it remarkably provides us with signatures of dimensionality dependence. This is a point that often gets glossed over. Except for rare exact solutions and full fledged renormalization group calculations, no approaches other than the Flory theory give d -dependent results. Often the Flory results are very close to the correct ones.

The Flory theory can be used for systems with long-range correlations or with no relevant length scale other than the large one determined by the size. In this respect the approach is expected to be applicable to problems faced by different communities that hardly communicate with one another. Hence, our aim here was to focus on some specific aspects of the Flory theory that we regarded as the most useful for graduate students, rather than performing an exhaustive review. As a result, many important aspects and contributions to this topic have not been covered, nor cited, by the present work. One example of that is polymer solutions that have been synthesized in a short summary in section 7. The trade-off lies in the fact that we could stress some nuances and details—for instance the case of sections 5–7, where we have discussed in some detail the steepest descent approach to the Flory theory (section 5), the interpolation formula (section 6), and an interesting crossover effect related to finite size effects and tricritical point. We have also tried to cast the Flory theory within some modern perspectives (see section 4) that included the scaling theory and critical exponents.

The Flory mean-field approach can be simply modified by the addition of an external force, as described in section 8,

and this technique has become particularly useful in the last two decades due to the remarkable improvements in the experimental control of single-molecule stretching, with far reaching consequences in various biological systems, most notably DNA.

All in all, the Flory theory, and its variants, continues to be a very powerful tool in the study of polymer systems. We hope that this review will help to convey this message and to understand many different scale-invariant problems.

Appendix A. Gaussian integrals and the Hubbard–Stratonovich transformation

Consider the following Gaussian identity:

$$\int_{-\infty}^{+\infty} d\phi e^{-\frac{1}{2}a\phi^2 - i\phi x} = \sqrt{\frac{2\pi}{a}} e^{-\frac{1}{2}\frac{x^2}{a}} \quad (\text{A.1})$$

that can be easily proved by completing the square.

A generalization of this to n variables reads

$$e^{\frac{1}{2}\sum_{ij}\xi_i K_{ij}\xi_j} = [(2\pi)^n \det \mathbf{K}]^{-1/2} \int \left[\prod_l d\phi_l \right] \times e^{-\frac{1}{2}\sum_{ij}\phi_i K_{ij}^{-1}\phi_j + \sum_j \xi_j \phi_j}, \quad (\text{A.2})$$

where \mathbf{K} is any symmetric matrix with positive eigenvalues, and it is the basis of the so-called Hubbard–Stratonovich transformation.

For Gaussian variables, correlation functions of the type $\langle \phi_i \phi_j \rangle$ are related to the inverse matrix appearing in the interactions. This can be seen as follows. From equation (A.2) we have

$$\begin{aligned} \langle \phi_i \phi_j \rangle &= \frac{\int [\prod_l d\phi_l] \phi_i \phi_j e^{-\frac{1}{2}\sum_{lm}\phi_l K_{lm}^{-1}\phi_m}}{\int [\prod_l d\phi_l] e^{-\frac{1}{2}\sum_{lm}\phi_l K_{lm}^{-1}\phi_m}} \\ &= [(2\pi)^n \det \mathbf{K}]^{1/2} \int \left[\prod_l d\phi_l \right] \\ &\quad \times \phi_i \phi_j e^{-\frac{1}{2}\sum_{lm}\phi_l K_{lm}^{-1}\phi_m} \\ &= \frac{\partial^2}{\partial \xi_i \partial \xi_j} \left[e^{\frac{1}{2}\sum_{lm}\xi_l K_{lm}\xi_m} \right]_{\{\xi=0\}} = K_{ij}. \end{aligned} \quad (\text{A.3})$$

Appendix B. Distribution of the end-to-end distance in d dimensions

Introduce the bond $\boldsymbol{\tau}_j = \mathbf{r}_j - \mathbf{r}_{j-1}$, $j = 1, \dots, N$, as depicted in figure 1, and let $p(\boldsymbol{\tau}_j)$ be the probability distribution of the j th bond.

Then the probability distribution function for the end-to-end distance, $P(\mathbf{R}, N)$, as given in equation (2.1) reads

$$P(\mathbf{R}, N) = \int \prod_{i=1}^N d^d \boldsymbol{\tau}_i \delta^d \left(\mathbf{R} - \sum_{j=1}^N \boldsymbol{\tau}_j \right) \prod_{l=1}^N p(\boldsymbol{\tau}_l), \quad (\text{B.1})$$

where one can use the integral representation

$$\delta^d(\boldsymbol{\tau}_j) = \int \frac{d^d \mathbf{k}}{(2\pi)^d} e^{i\mathbf{k} \cdot \boldsymbol{\tau}_j}, \quad (\text{B.2})$$

to obtain

$$\begin{aligned} P(\mathbf{R}, N) &= \int \frac{d^d \mathbf{k}}{(2\pi)^d} e^{i\mathbf{k} \cdot \mathbf{R}} [\hat{p}(\mathbf{k})]^N \\ &= \int \frac{d^d \mathbf{k}}{(2\pi)^d} e^{i\mathbf{k} \cdot \mathbf{R}} e^{N \ln \hat{p}(\mathbf{k})}, \end{aligned} \quad (\text{B.3})$$

where

$$\hat{p}(\mathbf{k}) = \int d^d \boldsymbol{\tau}_j e^{-i\mathbf{k} \cdot \boldsymbol{\tau}_j} p(\boldsymbol{\tau}_j) \quad (\text{B.4})$$

is the Fourier transform of $p(\boldsymbol{\tau}_j)$.

The normalization condition guarantees that $\hat{p}(\mathbf{k} = 0) = 1$, while a spherically symmetric distribution implies $\hat{p}(\mathbf{k}) = \hat{p}(k)$. With these, a Taylor series expansion yields

$$\hat{p}(\mathbf{k}) = 1 - \frac{1}{2}(k\sigma)^2 + O(k^4), \quad (\text{B.5})$$

where σ^2 is the variance of the distribution $p(\boldsymbol{\tau})$.

For $N \gg 1$, our interest is in the overall description of the polymer set by the scale $1/k$ which is much larger than the microscopic scale set by σ , i.e., we can assume $k\sigma \ll 1$. Therefore,

$$\ln \hat{p}(\mathbf{k}) \approx -\frac{1}{2}(k\sigma)^2 \quad (k\sigma \ll 1). \quad (\text{B.6})$$

Substituting in equation (B.3) we then get

$$\begin{aligned} P(\mathbf{R}, N) &\approx \int \frac{d^d \mathbf{k}}{(2\pi)^d} e^{i\mathbf{k} \cdot \mathbf{R}} \exp \left[-\frac{N}{2}(k\sigma)^2 \right] \\ &\approx \left(\frac{1}{2\pi N\sigma^2} \right)^{d/2} \exp \left[-\frac{1}{2} \frac{R^2}{N\sigma^2} \right]. \end{aligned} \quad (\text{B.7})$$

In $d = 3$ this reduces to equation (2.5).

B.1. Examples

We consider two examples. One is the example of the distribution for the FJC

$$p(\boldsymbol{\tau}_j) = \frac{1}{S_d \tau_j^{d-1}} \delta(\tau_j - b), \quad (\text{B.8})$$

where $S_d = 2\pi^{d/2} / \Gamma(d/2)$ is the surface of a unit sphere in d -dimensions, and $\Gamma(z)$ is the Gamma function [65]. Note that this choice ensures $\int d^d \boldsymbol{\tau}_j p(\boldsymbol{\tau}_j) = 1$. Another possibility is a Gaussian distribution:

$$p(\boldsymbol{\tau}_j) = \left(\frac{1}{2\pi b^2} \right)^{d/2} \exp \left[-\frac{1}{2} \frac{\tau_j^2}{b^2} \right]. \quad (\text{B.9})$$

There is the obvious difference between the two—the first one has a fixed length but the second one has no fixed length. Many other choices are possible.

By using equation (B.8), one can easily compute that

$$\begin{aligned} \hat{p}(\mathbf{k}) &= \int_0^{+\infty} dr r^{d-1} \int d\Omega_d e^{-ikr\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}} \frac{1}{S_d r^{d-1}} \delta(r-b) \\ &= \frac{1}{S_d} \int_0^{2\pi} d\theta_1 \int_0^\pi d\theta_2 \sin\theta_2 \dots \int_0^\pi d\theta_{d-1} \\ &\quad \times \sin^{d-2}\theta_{d-1} e^{-ikb \cos\theta_{d-1}} \\ &= \frac{S_{d-1}}{S_d} \int_0^\pi d\theta_{d-1} \sin^{d-2}\theta_{d-1} e^{-ikb \cos\theta_{d-1}}. \end{aligned} \quad (\text{B.10})$$

In the limit of small kb , we expand the exponential $\exp(x) = 1 + x + x^2/2 \dots$. The first-order term will vanish by symmetry. The second-order term involves an integral $\int_0^\pi \sin^{d-2}\theta \cos^2\theta d\theta = \sqrt{\pi} \Gamma[(d-1)/2] / (2\Gamma[1+d/2])$. This matches equation (B.5) with $\sigma^2 = b^2/d$.

The integral in equation (B.10) can be handled exactly. We use the following result [64]:

$$\int_0^\pi d\theta \sin^{2\nu}\theta e^{i\beta \cos\theta} = \sqrt{\pi} \left(\frac{2}{\beta}\right)^\nu \Gamma\left(\nu + \frac{1}{2}\right) J_\nu(\beta) \quad (\text{B.11})$$

where $J_\nu(z)$ is a Bessel function with the property $J_\nu(-z) = (-1)^\nu J_\nu(z)$ [65], to obtain

$$\hat{p}(\mathbf{k}) = \left(\frac{2}{kb}\right)^{d/2-1} \Gamma\left(\frac{d}{2}\right) J_{d/2-1}(kb). \quad (\text{B.12})$$

By making use of the expansion [65]

$$J_\nu(z) = \left(\frac{1}{2z}\right)^\nu \sum_{n=0}^{+\infty} \frac{1}{n! \Gamma(\nu+n+1)} \left(-\frac{1}{4}z^2\right)^n \quad (\text{B.13})$$

and the property of the Gamma function $\Gamma(z+1) = z\Gamma(z)$, one obtains equation (B.5) with $\sigma^2 = b^2/d$.

For the Gaussian distribution, $\hat{p}(\mathbf{k}) = \exp(-k^2 b^2/2)$ and its Taylor series expansion around $k=0$ matches with equation (B.5). Here $\sigma = b$.

B.2. Non-Gaussian case

The above derivation, a version of the central limit theorem, is valid only if $\sigma < \infty$, otherwise the expansion in equation (B.5) is useless. There are important distributions which may not have finite variances. In those cases, a Gaussian distribution is not expected. An example is the Cauchy distribution

$$p(x) = \frac{1}{\pi} \frac{b}{x^2 + b^2}, \quad (\text{in one dimension}), \quad (\text{B.14})$$

with infinite mean and variance. $P(R, N)$, in equation (B.14), for large N , does not converge to a Gaussian but to another Cauchy distribution. The difference from the Gaussian distribution lies mainly in the tail (large $|x|$ behaviour) of this distribution—the large $|x|$ behaviour of equation (B.14) is responsible for the divergent mean and variance. It is precisely for this reason that we do not consider such distributions in this review. Our interest is in the behaviour of a polymer whose properties do not require special or exceptional contributions from very large sizes.

Appendix C. Perturbation theory

Instead of the Flory approach that explores the large z region directly, we here consider the small z case which in principle can be handled in a perturbative way. The ultimate difficulty is in tackling the series which in most cases turns out to be asymptotic in nature.

We go back to equation (5.3) and expand the right-hand side in powers of u (for $\nu = 0$):

$$G_L(\mathbf{R}) = G_L^{(0)}(\mathbf{R}) - uG_L^{(1)}(\mathbf{R}) + \dots \quad (\text{C.1})$$

where the first-order terms in the expansion of the two-body term shown in equation (C.1) is

$$\begin{aligned} G_L^{(1)}(\mathbf{R}) &= G_L^{(0)}(\mathbf{R}) \frac{1}{2!} b^{d-2} \int_0^L ds_1 \int_0^L ds_2 \\ &\quad \times \langle \delta^d(\mathbf{R}(s_2) - \mathbf{R}(s_1)) \rangle_{\mathbf{R}}. \end{aligned} \quad (\text{C.2})$$

The delta function ensures that there is one contact along the chain. The series has the interpretation that the first term is the partition function without any concern about the interactions while the second term $G_L^{(1)}$ is the sum over all configurations that have one interaction along the chain.

The calculation of the end-to-end distance

$$\langle R^2 \rangle = \frac{\int d^d \mathbf{R} R^2 G_L(\mathbf{R})}{\int d^d \mathbf{R} G_L(\mathbf{R})} \quad (\text{C.3})$$

also involves an expansion in u , coming from both the numerator and the denominator. It is more or less straightforward to calculate for the free case:

$$\langle R^2 \rangle_0 = \frac{\int d^d \mathbf{R} R^2 G_L^{(0)}(\mathbf{R})}{\int d^d \mathbf{R} G_L^{(0)}(\mathbf{R})} = Lb. \quad (\text{C.4})$$

For generality, especially for higher order corrections, two possible procedures to compute the first-order correction are discussed below.

C.1. Direct evaluation

The convolution property [5] of the Gaussian distribution

$$G_L^{(0)}(\mathbf{R}) = \int d^d \mathbf{R}' G_s^{(0)}(\mathbf{R}') G_{L-s}^{(0)}(\mathbf{R} - \mathbf{R}') \quad (\text{C.5})$$

states that the probability of a Gaussian polymer reaching \mathbf{R} at length L can be written as a product of its being at any point \mathbf{R}' at an intermediate length s and then from \mathbf{R}' to \mathbf{R} in the remaining $L-s$ length, with an integration over \mathbf{R}' .

With repeated use of the convolution property, equation (C.5), the relevant average required for the two-body correction term is

$$\begin{aligned} &\langle \delta^d(\mathbf{R}(s_1) - \mathbf{R}(s_2)) \rangle_{\mathbf{R}}^{(0)} \\ &= \frac{1}{G_L^{(0)}(\mathbf{R})} \int_{\mathbf{R}(0)=\mathbf{0}}^{\mathbf{R}(L)=\mathbf{R}} \mathcal{D}\mathbf{R}(s) \delta^d(\mathbf{R}(s_1) - \mathbf{R}(s_2)) \\ &\quad \times e^{-\frac{d}{2b} \int_0^L ds \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2} \end{aligned} \quad (\text{C.6a})$$

$$= \frac{1}{G_L^{(0)}(\mathbf{R})} \int d^d \mathbf{R}_1 \int d^d \mathbf{R}_2 \delta^d(\mathbf{R}_1 - \mathbf{R}_2) G_{L-s_2}^{(0)}(\mathbf{R} - \mathbf{R}_2) \times G_{s_2-s_1}^{(0)}(\mathbf{R}_2 - \mathbf{R}_1) G_{s_1}^{(0)}(\mathbf{R}_1) \quad (\text{C.6b})$$

$$= \frac{1}{G_L^{(0)}(\mathbf{R})} \int d^d \mathbf{R}' G_{L-s_2}^{(0)}(\mathbf{R} - \mathbf{R}') \times G_{s_2-s_1}^{(0)}(\mathbf{0}) G_{s_1}^{(0)}(\mathbf{R}'). \quad (\text{C.6c})$$

$$= \frac{G_{L-s_2+s_1}^{(0)}(\mathbf{R})}{G_L^{(0)}(\mathbf{R})} G_{s_2-s_1}^{(0)}(\mathbf{0}). \quad (\text{C.6d})$$

Equation (C.6b) has the interpretation of a polymer reaching \mathbf{R}' at length s_1 from the origin and then returning to \mathbf{R} at length s_2 from where it goes to the desired end point \mathbf{R} . Since s_1, s_2 could be any two points, there are integrals over each of them. The occurrence of $G_{s_2-s_1}^{(0)}(\mathbf{0})$ is the signature of a loop formation that contains the main aspect of the polymer correlations because it involves contact of two monomers which may be nearby ($s_2 - s_1$ small) or far apart ($s_2 - s_1$ large) along the chain. The eventual Gaussian integrals can be done. However the s_1, s_2 integrals are divergent. The integrals over s_1, s_2 involve a term of the type $\int_0^L ds s^{1-d/2}$ which is divergent for $d \leq 4$. Such divergent integrals can be handled by analytic continuation in d by performing the integration where it is convergent and then analytically continued to other dimensions. If d is such that the integral converges, then

$$\frac{1}{2!} \int_0^L ds_1 \int_0^L ds_2 |s_2 - s_1|^{1-d/2} = \frac{4}{(4-d)(6-d)} L^{3-d/2}, \quad (\text{C.7})$$

which can then be extended to all d . The poles at $d = 4$ and $d = 6$ are responsible for the divergence at other values of d .

A similar expansion in z can be performed for the end-to-end distance given by equation (C.3), by collecting terms of similar order from both the numerator and the denominator. To first order the correction would look like

$$\langle R^2 \rangle = \langle R^2 \rangle_0 - u \int dR R^2 \mathcal{G}_L^{(1)}(\mathbf{R}) + u \int dR R^2 \times G_L^{(0)}(\mathbf{R}) \int dR \mathcal{G}_L^{(1)}(\mathbf{R}) + \dots \quad (\text{C.8})$$

With the use of equations (C.2) and (C.6d), and the standard results of Gaussian integrals, the two u -dependent terms can be written as

$$\int dR R^2 \mathcal{G}_L^{(1)}(\mathbf{R}) = \int_0^L ds_1 \int_0^L ds_2 (L - s_2 + s_1) G_{|s_2-s_1|}^{(0)}(\mathbf{0}) \quad (\text{C.9})$$

$$\int dR R^2 G_L^{(0)}(\mathbf{R}) \int dR \mathcal{G}_L^{(1)}(\mathbf{R}) = L \int_0^L ds_1 \int_0^L ds_2 G_{|s_2-s_1|}^{(0)}(\mathbf{0}), \quad (\text{C.10})$$

so that we are left with the integral of equation (C.7). With the analytic continuation, the end-to-end distance is given by

$$\langle R^2 \rangle = \langle R^2 \rangle_0 \left[1 + \frac{4}{(4-d)(6-d)} z + \dots \right], \quad (\text{C.11})$$

with z as in equation (4.5) with $c_1 = (1/2\pi)^{d/2}$. The divergence as $d \rightarrow 4$ is an important outcome of this perturbative analysis and its handling is part of the renormalization group machinery.

C.2. Laplace–Fourier approach

The same result can be obtained by using the Laplace–Fourier approach [23]. This method requires an integral over the length from zero to infinity and therefore may be called ‘grand canonical’ compared to the approach of the previous section, which may be termed ‘canonical’.

The Laplace–Fourier transform is defined by

$$\tilde{F}_E(\mathbf{k}) = \int_0^{+\infty} dL e^{-EL} \widehat{F}_L(\mathbf{R}) = \int_0^{+\infty} dL e^{-EL} \int d^d \mathbf{R} e^{-i\mathbf{k} \cdot \mathbf{R}} F_L(\mathbf{R}) \quad (\text{C.12})$$

along with its inverse

$$F_L(\mathbf{R}) = \int \frac{d^d \mathbf{k}}{(2\pi)^d} e^{+i\mathbf{k} \cdot \mathbf{R}} \widehat{F}(\mathbf{k}) = \int \frac{d^d \mathbf{k}}{(2\pi)^d} e^{+i\mathbf{k} \cdot \mathbf{R}} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dE}{2\pi i} e^{EL} \tilde{F}_E(\mathbf{k}). \quad (\text{C.13})$$

As usual, in equation (C.13) γ is a real constant that exceeds the real part of all the singularities of $\tilde{F}_E(\mathbf{k})$.

We now go back to the expansion (C.1) that can be Laplace–Fourier transformed to obtain

$$\tilde{\mathcal{G}}_E(\mathbf{k}) = \tilde{\mathcal{G}}_E^{(0)}(\mathbf{k}) - u \tilde{\mathcal{G}}_E^{(12)}(\mathbf{k}) + \dots \quad (\text{C.14})$$

For simplicity, we limit here the discussion to the two-body interactions, but additional terms can be also considered.

Given that, the end-to-end distance can be computed from

$$\langle R^2 \rangle = \left\{ \frac{\int_{\gamma-i\infty}^{\gamma+i\infty} dE e^{EL} [-\nabla_{\mathbf{k}^2} \tilde{\mathcal{G}}_E(\mathbf{k})]}{\int_{\gamma-i\infty}^{\gamma+i\infty} dE e^{EL} \tilde{\mathcal{G}}_E(\mathbf{k})} \right\}_{\mathbf{k}=\mathbf{0}}. \quad (\text{C.15})$$

The great advantage of the Laplace–Fourier transform is clearly that both the \mathbf{R} and s convolutions appearing in equation (C.6c) can be decoupled so that

$$\tilde{\mathcal{G}}_E^{(12)}(\mathbf{k}) = \frac{1}{2!} \int_0^{+\infty} dL e^{-EL} b^{d-2} \int \frac{d^d \mathbf{q}}{(2\pi)^d} \times e^{+i\mathbf{k} \cdot \mathbf{R}} \int_0^L ds_2 \int_0^L ds_1 \times \widehat{\mathcal{G}}_{L-s_2}^{(0)}(\mathbf{k}) \widehat{\mathcal{G}}_{s_2-s_1}^{(0)}(\mathbf{q}) \widehat{\mathcal{G}}_{s_1}^{(0)}(\mathbf{k}) = b^{d-2} \int \frac{d^d \mathbf{q}}{(2\pi)^d} \tilde{\mathcal{G}}_E^{(0)}(\mathbf{k}) \tilde{\mathcal{G}}_E^{(0)}(\mathbf{q}) \tilde{\mathcal{G}}_E^{(0)}(\mathbf{k}) \quad (\text{C.16})$$

that is

$$\tilde{G}_E^{(12)}(\mathbf{k}) = b^{d-2} [\tilde{G}_E^{(0)}(\mathbf{k})]^2 \int \frac{d^d \mathbf{q}}{(2\pi)^d} \tilde{G}_E^{(0)}(\mathbf{q}) \quad (\text{C.17})$$

where [23]

$$\tilde{G}_E^{(0)}(\mathbf{k}) = \lim_{\epsilon \rightarrow 0} \frac{1}{E + bk^2/(2d) + \epsilon k^4}. \quad (\text{C.18})$$

In equation (C.18) we have included an ϵk^4 term to keep all integrals convergent, with the understanding that the limit $\epsilon \rightarrow 0$ will be taken at the end of the calculation [23]. The integral appearing in equation (C.17) is given by

$$\begin{aligned} I_d(E, \epsilon) &\equiv \int \frac{d^d \mathbf{q}}{(2\pi)^d} \tilde{G}_E^{(0)}(\mathbf{q}) \\ &= \frac{S_d}{(2\pi)^d} \int_0^{+\infty} dq \frac{q^{d-1}}{E + bq^2/(2d) + \epsilon q^4}. \end{aligned} \quad (\text{C.19})$$

Let us now compute the first correction $\tilde{G}_E^{(12)}(\mathbf{k})$ explicitly. Equation (C.14) yields

$$\tilde{G}_E(\mathbf{k}) = \tilde{G}_E^{(0)}(\mathbf{k}) - b^{d-2} \tilde{\Sigma}_E^{(12)} [\tilde{G}_E^{(0)}(\mathbf{k})]^2 + \dots \quad (\text{C.20})$$

where we have introduced the ‘self-energy’

$$\tilde{\Sigma}_E^{(12)} = u I_d(E, \epsilon). \quad (\text{C.21})$$

Then we next note that because the Green function is always a function of k^2 rather than the wavevector \mathbf{k} itself, we can write

$$\nabla_{\mathbf{k}} \tilde{G}_E(\mathbf{k}) = 2\mathbf{k} \frac{\partial}{\partial k^2} \tilde{G}_E(\mathbf{k}) \quad (\text{C.22})$$

and

$$\nabla_{\mathbf{k}}^2 \tilde{G}_E(\mathbf{k}) \Big|_{\mathbf{k}=0} = 2d \frac{\partial}{\partial k^2} \tilde{G}_E(\mathbf{k}) \Big|_{\mathbf{k}=0}. \quad (\text{C.23})$$

Using equations (C.20), (C.21) and (C.23) in equation (C.15) one gets

$$\langle R^2 \rangle = b \frac{\int_{\gamma-i\infty}^{\gamma+i\infty} dE \frac{e^{EL}}{[E + u I_d(E, \epsilon)]^2}}{\int_{\gamma-i\infty}^{\gamma+i\infty} dE \frac{e^{EL}}{[E + u I_d(E, \epsilon)]}}. \quad (\text{C.24})$$

This completes the scheme for the solution.

C.2.1. First-order correction from perturbation theory. In $d = 3$, the relevant integral (C.19) reads

$$I_3(E, \epsilon) = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} dq \frac{q^2}{E + bq^2/6 + \epsilon q^4} \quad (\text{C.25})$$

where the integral has been extended to negative values by taking advantage of the parity of the integrand. The integral can be easily computed by contour method by extending the contour in the upper plane and noting that only two of the four poles are then included. These are to lowest order in ϵ , $q_1 = +i\sqrt{6Eb}$ and $q_2 = +i\sqrt{6b\epsilon}$. This produces the result

$$I_3(E, \epsilon) = -\frac{3}{2\pi b} \sqrt{\frac{6E}{b}} + \frac{1}{4\pi} \sqrt{\frac{6}{b\epsilon}}. \quad (\text{C.26})$$

Once again, only the lowest correction in ϵ has been included. Clearly the integral is divergent for $\epsilon \rightarrow 0$ but this divergence can be accounted for using a renormalizing procedure, as explained in [24] and they turn out to be irrelevant for the computation of the $\langle R^2 \rangle$ as they should.

On dropping the ϵ dependent term in equation (C.26), this can be inserted into equation (C.24), that can then be expanded in powers of βu to first order. The result is

$$\begin{aligned} \langle R^2 \rangle &= b \left(\left[\int_{\gamma-i\infty}^{\gamma+i\infty} dE \frac{e^{EL}}{E^2} + 2u \frac{3}{2\pi} \sqrt{\frac{6}{b}} \right. \right. \\ &\quad \left. \left. \times \int_{\gamma-i\infty}^{\gamma+i\infty} dE \frac{e^{EL}}{E^{5/2}} + \dots \right] \right) \left(\left[\int_{\gamma-i\infty}^{\gamma+i\infty} dE \frac{e^{EL}}{E} \right. \right. \\ &\quad \left. \left. + u \frac{3}{2\pi} \sqrt{\frac{6}{b}} \int_{\gamma-i\infty}^{\gamma+i\infty} dE \frac{e^{EL}}{E^{3/2}} + \dots \right] \right)^{-1}. \end{aligned} \quad (\text{C.27})$$

All integrals can then be performed by using the result

$$\int_{\gamma-i\infty}^{\gamma+i\infty} dE \frac{e^{EL}}{E^{\nu}} = \frac{L^{\nu-1}}{\Gamma(\nu)}. \quad (\text{C.28})$$

Higher orders and additional details can be found in [23]. The final result has been quoted in equation (6.9).

Appendix D. Issue of thermodynamic limit

The size of a polymer R is a geometric quantity which is generally not a conventional thermodynamic variable. However the discrete polymer model introduced here allows one to translate the polymer problem to a more familiar language for which one may associate standard thermodynamic quantities.

The bond variables introduced in equations (2.1), and (8.1) can be taken as spin-like variables whose allowed orientations depend on the dimensionality and the topology of the space (e.g., continuum or lattice). The interactions of the monomers can also be expressed as interactions among the spins, not necessarily restricted to simple two-spin interactions as in equation (8.1). The polymer problem is then exactly equivalent to a statistical mechanical problem of a collection of spins at a given temperature T . The response function of such a collection of spins is the susceptibility which measures the response of the total spin (i.e. total magnetization) to a uniform magnetic field. The end-to-end distance of the polymer \mathbf{R} turns out to be the total spin $\mathbf{M} = \sum_i \mathbf{r}_i$, as noted in section 8.1.

The fluctuation-response theorem connects the susceptibility χ_N to the fluctuation of the total spin, (see section 8.4) as

$$\chi_N \sim \langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2 \sim \langle R^2 \rangle - \langle \mathbf{R} \rangle^2, \quad (\text{D.1})$$

and by symmetry, $\langle \mathbf{R} \rangle = 0$. Therefore the susceptibility of the spin system, as a magnetic model, corresponds to the mean square end-to-end distance of the polymer. As a magnetic system, the primary requirement is to have an extensive susceptibility which means $\chi_N \propto N$ for N spins, at least for large N . The stringent requirement of a thermodynamic

limit as a magnetic model would enforce only the Gaussian behaviour of the polymer. In contrast, the susceptibility per spin would behave as

$$\chi \equiv \lim_{N \rightarrow \infty} \frac{\chi N}{N} \sim N^{2\nu-1} \rightarrow \begin{cases} \infty & \text{(good solvent),} \\ 0 & \text{(poor solvent),} \end{cases} \quad (\text{D.2})$$

for the spin models that correspond to an interacting discrete polymer. Interestingly, the polymer size exponent is linked to the finite size behaviour of the spin problem as $N \rightarrow \infty$.

This points towards the care needed in using thermodynamics and extensivity in polymer problems.

Appendix E. The structure factor of a Gaussian chain

Consider the structure factor

$$S_0(\mathbf{k}) = \frac{1}{N} \sum_{ij=1}^N \langle e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle_0. \quad (\text{E.1})$$

For a Gaussian chain, we know that

$$\begin{aligned} \langle (\mathbf{r}_i - \mathbf{r}_j)_\mu (\mathbf{r}_i - \mathbf{r}_j)_\nu \rangle_0 &= \frac{\delta_{\mu\nu}}{d} \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle_0 \\ &= \frac{\delta_{\mu\nu}}{d} |i - j| b^2, \end{aligned} \quad (\text{E.2})$$

and hence

$$\begin{aligned} \langle e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle_0 &= \exp \left[-\frac{1}{2} \sum_{\mu\nu} k_\mu k_\nu \langle (\mathbf{r}_i - \mathbf{r}_j)_\mu (\mathbf{r}_i - \mathbf{r}_j)_\nu \rangle_0 \right] \\ &= e^{-\frac{1}{2} k^2 \frac{|i-j|}{d}}. \end{aligned} \quad (\text{E.3})$$

Therefore we find

$$\begin{aligned} S_0(\mathbf{k}) &\sim \frac{1}{N} \int_0^N dn_1 \int_0^N dn_2 e^{-\frac{1}{2} k^2 \frac{|n_1 - n_2|}{d}} \\ &= N F_D \left(N \frac{k^2 b^2}{2d} \right), \end{aligned} \quad (\text{E.4})$$

where we have introduced the Debye function

$$F_D(x) = \frac{2}{x^2} (x - 1 + e^{-x}). \quad (\text{E.5})$$

Dimensionally, k is like an inverse of length and we see that the structure factor involves the dimensionless variable kR_0 . The scale for k is set by the overall size of the polymer, not its microscopic scales.

Appendix F. Exact solution of the freely jointed chain model with external force

The partition function equation (8.2) can be solved exactly in the absence of the interaction term ($K = 0$), when the model reduces to the freely jointed chain (FJC) [5]. In this case each term of equation (8.2) decouples and we can use the result

$$\int d^3 \hat{\mathbf{T}} \frac{1}{2\pi} \delta(\hat{\mathbf{T}}^2 - 1) e^{b\mathbf{f} \cdot \hat{\mathbf{T}}} = \frac{\sinh(fb)}{fb} \quad (\text{F.1})$$

so that the configurational partition function becomes

$$Z = \left[\frac{\sinh(fb)}{fb} \right]^N. \quad (\text{F.2})$$

Introducing the physical force $f_{\text{phys}} = f/\beta$, we then have that

$$\langle z \rangle = \frac{\partial}{\partial (\beta f_{\text{phys}})} \ln Z(f_{\text{phys}}). \quad (\text{F.3})$$

This gives the well-known result

$$\frac{\langle z \rangle}{Nb} = \mathcal{L}(\beta f_{\text{phys}} b), \quad (\text{F.4})$$

where the Langevin function \mathcal{L} is defined as

$$\mathcal{L}(x) = \coth(x) - \frac{1}{x}. \quad (\text{F.5})$$

In the $\beta f_{\text{phys}} b \ll 1$ limit, equation (F.3) can be expanded and gives to leading order [66]

$$\frac{\langle z \rangle}{Nb} = \frac{1}{3} \beta f_{\text{phys}} b + \dots \quad (\text{F.6})$$

Appendix G. Derivation of the Green function for semiflexible polymer

We start from the following addition theorem [32]:

$$e^{\mu \hat{\mathbf{T}} \cdot \hat{\mathbf{T}}'} = 4\pi \sqrt{\frac{\pi}{2\mu}} \sum_{l=0}^{+\infty} \sum_{m=-l}^{+l} I_{l+1/2}(\mu) Y_{lm}(\hat{\mathbf{T}}) Y_{lm}^*(\hat{\mathbf{T}}'), \quad (\text{G.1})$$

where $I_\nu(z)$ is the modified Bessel function [65] so that equation (8.55) becomes

$$\begin{aligned} G_{0L}(\hat{\mathbf{T}}_0, \hat{\mathbf{T}}_N) &= e^{-Nl_p/b} \frac{1}{(4\pi)^{N-1}} \left(\frac{\pi b}{2l_p} \right)^{N/2} (4\pi)^N \\ &\times \sum_{l_1, \dots, l_N} \sum_{m_1, \dots, m_N} I_{l_1+1/2} \left(\frac{l_p}{b} \right) \dots I_{l_N+1/2} \\ &\times \left(\frac{l_p}{b} \right) Y_{l_1 m_1}(\hat{\mathbf{T}}_0) Y_{l_N m_N}^*(\hat{\mathbf{T}}_N) \\ &\times \int d\hat{\mathbf{T}}_1 Y_{l_1 m_1}^*(\hat{\mathbf{T}}_1) Y_{l_1 m_1}(\hat{\mathbf{T}}_1) \dots \\ &\times \int d\hat{\mathbf{T}}_{N-1} Y_{l_{N-1} m_{N-1}}^*(\hat{\mathbf{T}}_{N-1}) \\ &\times Y_{l_N m_N}(\hat{\mathbf{T}}_{N-1}). \end{aligned} \quad (\text{G.2})$$

Using the orthogonality relation [65]

$$\int d\hat{\mathbf{T}} Y_{l_1 m_1}(\hat{\mathbf{T}}) Y_{l_2 m_2}^*(\hat{\mathbf{T}}) = \delta_{l_1 l_2} \delta_{m_1 m_2} \quad (\text{G.3})$$

equation (G.2) reduces to

$$\begin{aligned} G_{0L_c}(\hat{\mathbf{T}}_0, \hat{\mathbf{T}}_N) &= 4\pi \left(\frac{\pi b}{2l_p} \right)^{N/2} \sum_{l=0}^{+\infty} \sum_{m=-l}^{+l} I_{l+1/2}^N(\mu) \\ &\times Y_{lm}(\hat{\mathbf{T}}_0) Y_{lm}^*(\hat{\mathbf{T}}_N). \end{aligned} \quad (\text{G.4})$$

In the limit $b \rightarrow 0$ we can use the asymptotic expansion for the Bessel function for $|z| \gg 1$ [65]

$$I_\nu(z) = \frac{e^z}{\sqrt{2\pi z}} \left[1 - \frac{4\nu^2 - 1}{8z} + \dots \right] \quad (\text{G.5})$$

to obtain

$$G_{0L_c}(\hat{\mathbf{T}}_0, \hat{\mathbf{T}}_N) = 4\pi \sum_{l=0}^{+\infty} \sum_{m=-l}^{+l} e^{-L_c l(l+1)/(2l_p)} \times Y_{lm}(\hat{\mathbf{T}}_0) Y_{lm}^*(\hat{\mathbf{T}}_N) \quad (\text{G.6})$$

which is the result given in equation (8.57). Note that in obtaining (G.4) and (G.6), we have set $L_c = Nb$ and used the relation $b = 2l_p$ between the Kuhn and the persistence length for the WLC model [10].

Appendix H. Calculation of $\langle [r_z(s) - r_z(s')]^2 \rangle$

To compute $\langle [r_z(s) - r_z(s')] \rangle$ given in equation (8.59), we need to compute the average quantity

$$\langle \hat{T}_z(s_1) \hat{T}_z(s_2) \rangle = \frac{\int d\hat{\mathbf{T}}_1 \int d\hat{\mathbf{T}}_2 G_{s_1 s_2}(\hat{\mathbf{T}}_1, \hat{\mathbf{T}}_2) \hat{T}_{1z} \hat{T}_{2z}}{\int d\hat{\mathbf{T}}_1 \int d\hat{\mathbf{T}}_2 G_{s_1 s_2}(\hat{\mathbf{T}}_1, \hat{\mathbf{T}}_2)}. \quad (\text{H.1})$$

Using the first two spherical harmonics [65]

$$Y_{00}(\hat{\mathbf{T}}) = \frac{1}{\sqrt{4\pi}} \quad Y_{01}(\hat{\mathbf{T}}) = \sqrt{\frac{3}{4\pi}} \hat{T}_z \quad (\text{H.2})$$

and the orthogonality relations (G.3), equation (H.1) reduces after a few steps to

$$\langle \hat{T}_z(s_1) \hat{T}_z(s_2) \rangle = \frac{1}{3} \exp \left[\frac{|s_2 - s_1|}{l_p} \right] \quad (\text{H.3})$$

which coincides with the expected result (equation (8.53)), taking into account the other two components x and y .

Upon inserting this result into equation (8.59), one can use a s -ordering procedure so that ($s > s'$)

$$\begin{aligned} \langle [r_z(s) - r_z(s')]^2 \rangle &= 2 \int_{s'}^s ds_1 \int_{s'}^{s_1} ds_2 \frac{1}{3} e^{(s_1 - s_2)/l_p} \\ &= \frac{2}{3} l_p^2 \left[\frac{s - s'}{l_p} - 1 + e^{-(s - s')/l_p} \right]. \end{aligned} \quad (\text{H.4})$$

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