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1 Statistical properties of polymer chains

This chapter reviews the elementary statistical properties of a single polymer chain in solvents of different nature. Starting with the ideal random coil conformation and its tension–elongation relation, the excluded-volume effect is introduced to study the swelling and collapse of a random coil. We then focus on the conformational transition of a polymer chain by hydrogen bonding. Coil–helix transition by the intramolecular hydrogen bonding between neighboring monomers, hydration of a polymer chain in aqueous media, and competition in hydrogen bonding in the mixed solvents are detailed.

1.1 Conformation of polymers

1.1.1 Internal coordinates of a polymer chain and its hindered rotation

The complete set of space coordinates which specifies the conformation of a polymer in three-dimensional space is called its **internal coordinates**. To study the positions of the carbon atoms along the linear chain of a polymer, let us consider three contiguous atoms -C-C-C- along the chain (gray circles in Figure 1.1). Because they are connected by covalent bonds, the length l of a bond is fixed at $l = 0.154$ nm, and the angle θ between the successive bonds is fixed at $\theta = 70.53°$ (tetrahedral angle with $\cos\theta = 1/3$). The bond to the fourth carbon atom, however, can rotate around the axis of the second bond although its length and angle are fixed. Such freedom of rotational motion is called the **internal rotation** of the polymer chain [1–5].

The rotation angle ϕ is conventionally measured in a clockwise direction relative to the reference position called the **trans position**. The trans position (t) is on the plane formed by the first three carbon atoms. Due to the molecular interaction, the potential energy of the fourth atom is a function of the rotation angle ϕ. For a simple symmetric polymer like polyethylene, the potential energy becomes minimum at the trans position, and there are two local minima at the angle $\phi = 120°, 240°$ (or equivalently $\pm 120°$). They are called the **gauche position**, and are indicated by the symbols g', g'' (or g^+, g^-). Transition between these minima is hindered by the potential barriers separating them. The conformations with different rotation angles which a polymer chain can take are called the **rotational isomeric states**. When all carbon atoms on the chain take the trans conformation, the chain is extended on a plane in zigzag form. This is called **planar zigzag conformation**.

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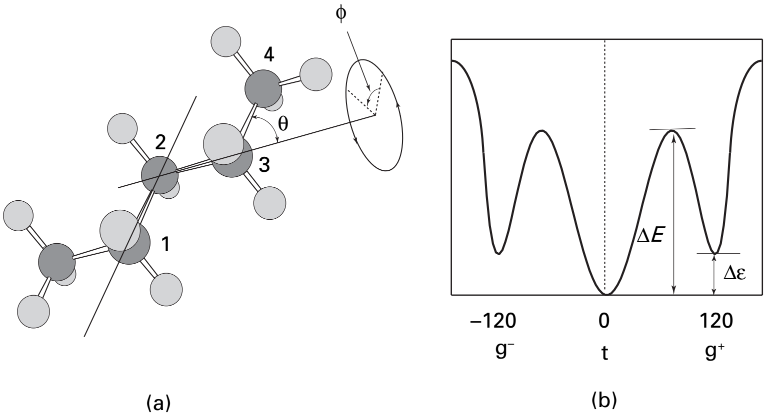


Fig. 1.1 Internal rotation of the carbon atom 4 in a contiguous sequence on a polymer chain. (a) The bond angle θ is fixed at $\cos\theta = 1/3$, while its rotational motion is described by the angle ϕ around the bond axis 2–3. (b) The potential energy is shown as a function of the rotation angle. For polyethylene, there are three minima at $\phi = 0$ (t) and $\phi = \pm 120°$ ($g^{\pm}$).

The energy difference $\Delta\epsilon$ between the t position and the g′, g″ positions decides the average population of the carbon atoms in thermal equilibrium state. It is related to the flexibility of the chain. For instance, the average length λ of the continuous trans sequence ttttt... is given by

$$\lambda = l \exp(\Delta\epsilon / k_B T), \tag{1.1}$$

where T is the absolute temperature, and k_B is the Boltzmann constant. This average length is called the **persistence length** of the polymer. It is, for example, approximately $\lambda = 5.1$ nm at room temperature if the energy difference is $\Delta\epsilon = 2.1$ kcal mol^{-1}.

On the other hand, the frequencies of the transition between different isomeric states are determined by the potential barrier ΔE between t and g′, g″ positions (Figure 1.1). The average time τ for the transition from t to g′, g″ is given by

$$\tau = \tau_0 \exp(\Delta E / k_B T), \tag{1.2}$$

where τ_0 is the microscopic time scale of the torsional vibration of a C-C bond ($\tau_0 \approx 10^{-11}$s). When the temperature is lowered, there is a point where τ becomes sufficiently longer than the duration of observation so that the internal motion looks frozen. Such a transition from a random coil with thermal motion to a frozen rigid coil is called the **glass transition** of a single chain.

Polymers with simple chemical structure take values of order $\Delta\epsilon \simeq 1$ kcal mol^{-1}, $\Delta E \simeq 4$–5 kcal mol^{-1}, but the barrier height ΔE can be higher if the side groups are replaced with larger ones, and also if there is strong interaction, such as dipole interaction, hydrogen bonds, etc., between them.

1.1.2 Coarse-grained models of polymer chains

The **rotational isomeric state** model (RIS) is a model chain in which chain conformation is represented by the set of three states, t, $g^{\pm}$.

The RIS incorporates the potential of internal rotation, and is one of the most precise descriptions of a chain that preserves its chemical structure. To describe the assemblies of polymers such as polymer solutions, blends, melts, crystals, and glasses, however, RIS is still too complex and difficult to treat. To simplify the treatment of the many chain statistics, coarse-grained model chains are often used. Typical examples are described in Figure 1.2.

Random flight model

A model chain consisting of rigid rods linearly connected by freely rotating joints is called the **random flight model** (RF) (Figure 1.2(a)). Let a be the length of each rod and n the total number of the rods. Since the joint does not necessarily correspond to a single monomer but represents a group of monomers, a may be larger than the length of the C-C chemical bond. Also n may be smaller than the degree of polymerization of the chain. Let us call each unit (a set of joint and rod) a **statistical repeat unit**.

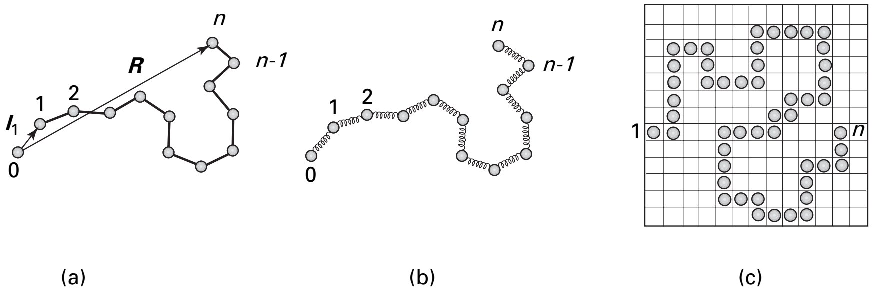
The probability $\rho(\mathbf{x}_i;\mathbf{x}_{i-1})$ to find the i-th joint at the position $\mathbf{x}_i$ when the $(i-1)$-th joint is fixed at the position $\mathbf{x}_{i-1}$ is given by

$$\rho(\mathbf{x}_i;\mathbf{x}_{i-1}) = \frac{1}{4\pi a^2}\delta(l_i - a), \tag{1.3}$$

where $\mathbf{l}_i \equiv \mathbf{x}_i - \mathbf{x}_{i-1}$ is the **bond vector**, $l_i \equiv |\mathbf{l}_i|$ is its absolute value, and $\delta(x)$ is Dirac delta function. The probability ρ characterizes a linear sequence of the statistical repeat units, and is often referred to as the **connectivity function**. The vector $\mathbf{R}$ which connects both ends of a chain is the **end-to-end vector**. Figure 1.3 shows an RF chain with $n = 200$ which is generated in three dimensions projected onto a plane.

Bead–spring model

A model chain with $n+1$ beads linearly connected by n springs is called the **bead–spring model** (BS) (Figure 1.2(b)). Each spring is assumed to have a spring constant



(a) (b) (c)

Fig. 1.2 Typical coarse-grained models of a polymer chain: (a) random flight model, (b) bead–spring model, (c) lattice model.

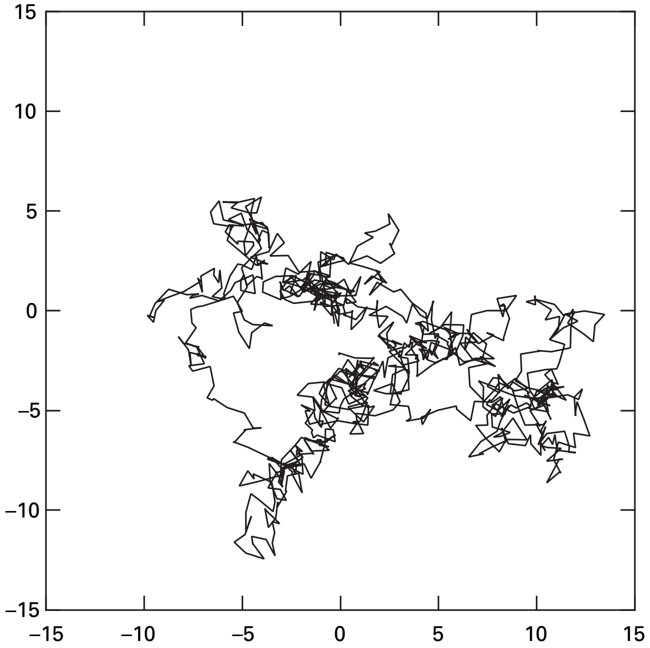


Fig. 1.3 Random coil formed with the random flight model with 200 bonds produced in three dimensions and projected onto a plane.

$k = 3k_BT/a^2$ with 0 equilibrium length. Because the energy of a spring stretched to length l is $kl^2/2$, its statistical weight is given by the Boltzmann factor

$$\rho(\mathbf{x}_i; \mathbf{x}_{i-1}) = \frac{1}{(2\pi a^2/3)^{3/2}} \exp(-3l_i^2/2a^2). \tag{1.4}$$

This is a Gaussian distribution with a mean square separation $\langle l_i^2 \rangle = a^2$ between adjacent beads. The bead in a BS chain also indicates a group of monomers as in RF.

The Gaussian bond (1.4) can easily be stretched to high extension, and allows unphysical mutual passing of bonds. To prevent this unrealistic mechanical property, the model potential, called the **finitely extensible nonlinear elastic potential** (FENE), and described by

$$\rho(\mathbf{x}_i; \mathbf{x}_{i-1}) = C \exp\left[\frac{k}{2}(l_{\max} - a)^2 \ln\left\{1 - \left(\frac{l_i - a}{l_{\max} - a}\right)^2\right\}\right], \tag{1.5}$$

is often used in the molecular simulation [6], where k is the spring constant and C is the normalization constant. The bond is nonlinear; its elongation is strictly limited in the finite region around the mean bond length a so that bonds can never cross each other.

Lattice model

A chain model described by the trajectory of a random walk on a lattice is called the **lattice model** (Figure 1.2(c)). The lattice constant a plays the role of the bond length. The simplest lattice model assumes that each step falls on the nearest neighboring lattice cell with equal probability [1], so that the connectivity function is given by

$$\rho(\mathbf{x}_i;\mathbf{x}_{i-1}) = \frac{1}{z}\sum_{\mathbf{e}} \delta(\mathbf{l}_i - a\mathbf{e}), \tag{1.6}$$

where z is the lattice coordination number, and the sum should be taken over all lattice vectors $\mathbf{e}$. For instance, $\mathbf{e}$ takes $\pm\mathbf{e}_x, \pm\mathbf{e}_y, \pm\mathbf{e}_z$ for the simple cubic lattice. In a more sophisticated lattice model, one of the nearest neighboring cells is selected as trans position and the rest are regarded as gauche position by introducing the energy difference $\Delta\epsilon$ described in Figure 1.1 [7, 8].

Because the statistical unit of a chain has finite volume, the condition implies that, in the random walk, a lattice cell should never be passed again once it is passed. A random walk with such a constraint is called a **self-avoiding random walk**.

1.2 The ideal chain

1.2.1 Single-chain partition function

A polymer chain changes its conformation by thermal motion. The probability of finding a particular conformation of the chain in the heat reservoir of the absolute temperature T is given by the canonical distribution function. If one end $\mathbf{x}_0$ of a chain is fixed at the origin of the coordinates (Figure 1.4), and the other end $\mathbf{x}_n$ is fixed at the position vector $\mathbf{R}$, the end-to-end vector $\mathbf{R}$ is given by the sum of all bond vectors

$$\mathbf{R} = \sum_{i=1}^{n} \mathbf{l}_i . \tag{1.7}$$

The canonical partition function for the statistical distribution of the specified end-to-end vector is defined by

$$Z(\mathbf{R},T) = \int \ldots \int d\mathbf{x}_1 d\mathbf{x}_2 \ldots d\mathbf{x}_{n-1} \exp[-\beta(U+V)] \prod_{j=1}^{n} \rho(\mathbf{x}_j;\mathbf{x}_{j-1}), \tag{1.8}$$

where $\beta \equiv 1/k_{\mathrm{B}}T$ is the reciprocal temperature, and ρ is the connectivity function described in Section 1.1.2.

The interaction energy between the repeat units is separated into two fundamentally different types U and V. The part U is the potential energy of the internal rotation of

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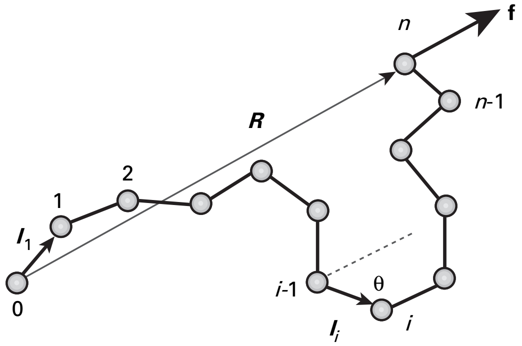

Fig. 1.4 The bond vectors $\mathbf{l}_i$, the first bond vector $\mathbf{l}_1$, and the end-to-end vector $\mathbf{R}$. Tension is applied at one end bead ($i = n$) with the other end bead ($i = 0$) fixed.

each repeat unit, and described in the sum

$$U = \sum_i u_1(\phi_i) + \sum_i u_2(\phi_{i-1}, \phi_i) + \cdots \tag{1.9}$$

by using the rotational angle ϕ of the bonds. The first term depends only upon the angle of the repeat unit under study (one-body term), the second term depends on the nearest neighboring pairs (two-body term), etc. Because the potential energies of the internal rotation involve only local neighbors along the chain, their interaction is called **local**, or **short-range interaction**. When interactions other than the one-body interaction are negligible, the rotation is called **independent internal rotation**. When all U is small enough to be neglected, the rotation is called **free rotation** [1, 2].

However, the potential energy V describes the interaction between the repeat units when they come close to each other in the space, even if the distance along the chain is far apart. It is usually given by the sum

$$V = \sum_{i<j} u(r_{ij}) \tag{1.10}$$

over all pairwise interactions, where $r_{ij} \equiv |\mathbf{x}_i - \mathbf{x}_j|$ is the distance between the i-th and j-th units. Such interaction between distant statistical units along the chain is called **long-range interaction**. For instance, van der Waals force, Coulomb force, etc., belong to this category [1].

A chain for which the interaction energy is negligibly small is called an **ideal chain**. For an ideal chain, we may treat $U = V = 0$, so that we have only to study the connectivity function ρ.

The Helmholtz free energy of a chain can be found by the logarithm of the partition function

$$F(\mathbf{R}, T) = -k_B T \ln Z(\mathbf{R}, T). \tag{1.11}$$

From the Helmholtz free energy, we can find the entropy S and the average tension $\mathbf{f}$ of the chain using the law of thermodynamics:

$$dF = -SdT + \mathbf{f} \cdot d\mathbf{R}. \tag{1.12}$$

To find the free energy of the ideal chain, we consider the integral

$$Z_0(\mathbf{R}, T) = \int \cdots \int \prod_{i=1}^{n} \rho(\mathbf{l}_i) d\mathbf{l}_1 d\mathbf{l}_2 \cdots d\mathbf{l}_n, \tag{1.13}$$

for the partition function. We have changed the integration variables from the position vectors of the joints (beads) to the bond vectors. The subscript 0 indicates that the chain is ideal. Because of the constraint (1.7), we cannot complete the integration in this form.

To remove this constraint, we consider its Laplace transform

$$Q(\mathbf{f}, T) \equiv \int Z(\mathbf{R}, T) e^{\beta \mathbf{f} \cdot \mathbf{R}} d\mathbf{R}, \tag{1.14}$$

where $\beta \equiv 1/k_{\mathrm{B}}T$. The integration of the bond vectors is independent of each other in Q. We find

$$Q(t, T) = \tilde{g}(t)^n, \tag{1.15}$$

after integration, where the new function $\tilde{g}(t)$ is defined by the Laplace transform of the connectivity function

$$\tilde{g}(t) \equiv \int d\mathbf{l} \rho(\mathbf{l}) e^{\beta \mathbf{f} \cdot \mathbf{l}}. \tag{1.16}$$

It is a function of the dimensionless tension t defined by the work fa to elongate the chain by the fundamental length unit a divided by the thermal energy $k_{\mathrm{B}}T$:

$$t \equiv fa/k_{\mathrm{B}}T. \tag{1.17}$$

Let us define the new function $G(\mathbf{f}, T)$ by the log of the Laplace transformed partition function $Q(\mathbf{f}, T)$:

$$G(\mathbf{f}, T) \equiv -k_{\mathrm{B}}T \ln Q(\mathbf{f}, T). \tag{1.18}$$

Because the independent variable is changed from $\mathbf{R}$ to $\mathbf{f}$, the small change of G is given by

$$dG = -SdT - \mathbf{R} \cdot d\mathbf{f}. \tag{1.19}$$

Hence we find that G is identical to the Gibbs free energy. For the ideal chain, it takes the form

$$G_0(\mathbf{f}, T) = -nk_{\mathrm{B}}T \ln \tilde{g}(t), \tag{1.20}$$

from (1.15).

The function ρ of the RF chain (1.3) leads to

$$\tilde{g}(t) = \frac{\sinh t}{t}, \tag{1.21}$$

and hence the Gibbs free energy is

$$G_0(\mathbf{f}, T) = -nk_{\mathrm{B}}T \ln[(\sinh t)/t]. \tag{1.22}$$

The BS chain (1.4) gives the form

$$\tilde{g}(t) = \exp(t^2/6), \tag{1.23}$$

and hence

$$G_0(f, T) = -\frac{n}{6}k_{\mathrm{B}}Tt^2. \tag{1.24}$$

For small elongations of the chain, these two models give the same result.

1.2.2 Tension–elongation curve

Using the thermodynamic relation (1.19), we can find the average end vector **R** under a given tension **f** by the differentiation

$$\mathbf{R} = -\left(\frac{\partial G}{\partial \mathbf{f}}\right)_T. \tag{1.25}$$

Because the vector **R** lies in parallel to the tension, we can write the result for the RF model in terms of its absolute value as

$$\frac{R}{na} = L\left(\frac{fa}{k_{\mathrm{B}}T}\right), \tag{1.26}$$

where the function $L(t)$ is defined by

$$L(t) \equiv \frac{d}{dt}\left[\ln\left(\frac{\sinh t}{t}\right)\right] = \coth t - \frac{1}{t}, \tag{1.27}$$

and called the **Langevin function** [4]. The tension–elongation relation is shown in Figure 1.5.

In the linear region where the elongation is small, the graph is a straight line with slope 3, but there is an upturn in the high-extension region due to the nonlinear stretching of the chain. Such a nonlinear amplification in the tension in the high-elongation region is referred to as the **hardening effect**.

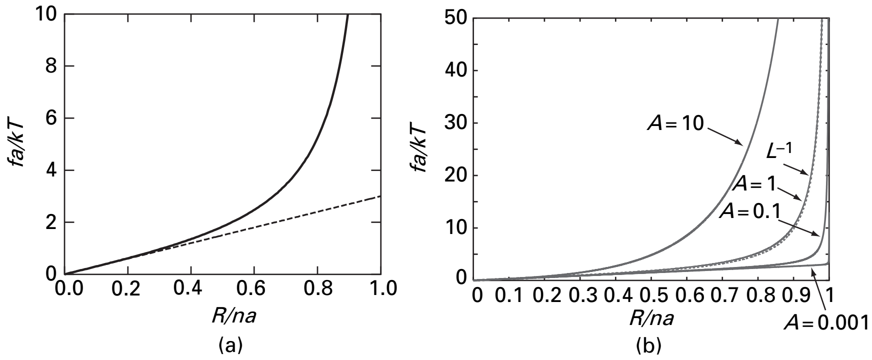

Fig. 1.5 (a) Tension–elongation curve of the Langevin chain (solid line) and its Gaussian approximation (broken line). (b) Simplified model (1.30) of a nonlinear chain for different nonlinear amplitude A. The curve with $A = 1$ (dotted line) is close to that of the Langevin chain.

The Langevin function $\tilde{r} = L(t)$, described by the dimensionless elongation $\tilde{r} \equiv R/na$, is measured relative to the total chain length na, and its inverse function can be expanded in the power series

$$\tilde{r} = L(t) = \frac{1}{3}t - \frac{1}{45}t^3 + \frac{2}{945}t^5 - \frac{1}{4725}t^7 + \cdots, \tag{1.28a}$$

$$t = L^{-1}(\tilde{r}) = 3\tilde{r} + \frac{9}{5}\tilde{r}^3 + \frac{297}{175}\tilde{r}^5 + \frac{1539}{875}\tilde{r}^7 + \cdots. \tag{1.28b}$$

Hence, in the linear region, the tension is proportional to the elongation as

$$f = \frac{3k_\mathrm{B}T}{na^2}R, \tag{1.29}$$

so that it obeys **Hooke's law**. A chain that obeys Hooke's law is called a **Gaussian chain**. The proportionality constant depends on the temperature. The BS model with a linear spring obeys a similar law. Because the origin of the tension is not the intermolecular force but the entropy of the chain conformation, the spring constant of the chain increases in proportion to the temperature. This is the opposite tendency to the elastic constant of solids made up of low molecular weight molecules such as metals.

Because the Langevin function and its inverse function are mathematically difficult to treat, we introduce here a simple nonlinear model chain whose tension is described by

$$t = 3\tilde{r}\left[1 + \frac{2}{3}A\frac{\tilde{r}^2}{1-\tilde{r}^2}\right], \tag{1.30}$$

where A is a parameter to specify the degree of nonlinearity of the chain (Figure 1.5(b)), and referred to as the nonlinear amplitude [9, 10]. When $A = 0$, the chain is Gaussian. It deviates from Gaussian with an increase in A, and the nonlinear effect caused by chain

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stretching becomes stronger. For $A = 1$, the chain is close to a Langevin chain with very high accuracy (95%). This simplified model of the tension is used extensively for the study of shear thickening and strain hardening in transient networks in Chapter 9.

We can describe the **temperature coefficient of chain tension** $(\partial f/\partial T)_R$ in terms of the coefficient of the **thermal expansion** $\alpha \equiv (\partial R/\partial T)_f/R$ at constant tension and the extensivity $\kappa_T \equiv (\partial R/\partial f)_T/R$ as

$$\left(\frac{\partial f}{\partial T}\right)_R = \frac{\alpha}{\kappa_T}. \tag{1.31}$$

We thus recognize the similarity to the thermodynamic law

$$(\partial p/\partial T)_V = \alpha/\kappa_T, \tag{1.32}$$

for gases, and hence infer that the origin of the chain elasticity is the entropy as for the temperature coefficient of gases.

1.2.3 Distribution of the end-to-end vector

From the thermodynamic law (1.12), the Helmholtz free energy at a constant temperature is given by the work $\int_0^{\mathbf{r}} \mathbf{f} \cdot d\mathbf{R}$ done for stretching the end vector from $\mathbf{0}$ to $\mathbf{R}$. By the relation (1.11), the partition function is given by

$$\begin{aligned} Z(\mathbf{R}, T) &= \exp\left\{-n \int_0^{R/na} L^{-1}(y)dy\right\} \\ &= \exp\left\{-\frac{3R^2}{2na^2}\left[1 + C_1\left(\frac{R}{na}\right)^2 + C_2\left(\frac{R}{na}\right)^4 + \cdots\right]\right\}, \end{aligned} \tag{1.33}$$

where C_1 and C_2 are numerical constants. They are found to be $C_1 = 3/10, C_2 = 33/125$ from the expansion (1.28b) for a Langevin chain.

The partition function, when regarded as a function of the end vector, is proportional to the probability of finding the end vector at a position $\mathbf{R}$. It gives the **canonical distribution function** of the end vector after normalization. If the chain is sufficiently long, or the degree of elongation is small, terms higher than C_1 can be neglected, so that the probability is found to be

$$\Phi_0(\mathbf{R}) = \left(\frac{3}{2\pi na^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2na^2}\right). \tag{1.34}$$

Since this is a Gaussian distribution, a chain with this probability distribution function is called a **Gaussian chain**. The mean square end-to-end distance of a Gaussian chain is given by

$$\langle R^2 \rangle_0 = na^2. \tag{1.35}$$