Different from the ideal chain description, the persistent chain model is not only able to deal with short chains, but also addresses the effect of temperature. Another model, which will introduced as the 'Ising chain' in the next section, accomplishes these tasks in an even more detailed, rather perfect manner.

2.5 The Ising Chain

A discussion of the properties of a polymer chain only on the basis of the global scaling laws or with the aid of Eqs. (2.125) and (2.138) would be incomplete. The description of specific properties of a given polymer molecule, as for example its internal energy or entropy, requires a different approach. For this purpose, one needs a treatment that takes the energetics of the chain into account. As was explained at the beginning of this chapter, chain conformations may be described microscopically in terms of the accessible rotational isomeric states. Now we shall see that this representation of a polymer corresponds exactly to the one-dimensional Ising model, also known as the **Ising chain**, which is an important concept in general statistical mechanics. As the tools for the treatment of Ising chains are well-known, Birshtein and Ptitsyn, and Flory adapted the Ising model to the polymer problem. This adaption addressed in the literature as the **rotational isomeric state (RIS) model**, opens a straightforward way to calculate the thermodynamic functions and the specific structural properties of a given polymer chain.

The general Ising chain is set up by an array of interacting particles, with each particle being able to change between a certain number of different states. In the simplest case, interactions are restricted to adjacent pairs. Then the total energy of the chain equals the sum of the interaction energies between neighbors and for n particles is given by

$$u = \sum_{i=2}^{n} u(\varphi_{i-1}, \varphi_i) \, . \tag{2.139}$$

Here φ_i denotes the state of particle i and $u(\varphi_{i-1}, \varphi_i)$ is the pair interaction energy.

The relation to a polymer chain becomes clear when one considers that the energy of one conformational state is a function of the rotational isomeric states of all N_b backbone bonds. The latter correspond to the 'particles' of the Ising chain. Conditions would be trivial if all bonds were energetically independent, since then the chain energy would be equal to N_b times the mean energy of a single bond. In reality, however, adjacent bonds may well affect each other. This is nicely exemplified by polyethylene, where the 'pentane effect', indicated in Fig. 2.22, becomes effective. The depicted conformation represents the sequence gauche$^+$-gauche$^-$, and pentane is the shortest n-alkane, for which this sequence may be built up. As we see, a sharp fold

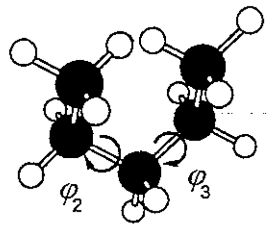

Fig. 2.22. The conformation of pentane associated with a sequence $\varphi_2 \mathrel{\widehat{=}}$ gauche$^+$, $\varphi_3 \mathrel{\widehat{=}}$ gauche$^-$. A sharp fold with elevated energy is formed

is formed, and it is clear that this requires more energy than is necessary to form two independent gauche-states. Since the Ising model deals with energies depending on the states of both partners in a pair, it can take this situation into account.

The main task in the computation of thermodynamic functions is the calculation of the partition function, denoted Z. In our case, its basic form can be formulated directly, as

$$Z = \sum_{\{\varphi_i\}} \exp - \frac{u\{\varphi_i\}}{kT} . \tag{2.140}$$

The summation includes all conformational states, here shortly designated by $\{\varphi_i\}$, each state being determined by specifying the conformations of all bonds

$$\{\varphi_i\} \mathrel{\widehat{=}} (\varphi_1, \varphi_2, \ldots, \varphi_{N_b}) .$$

The energy for each conformational state of the chain follows from Eq. (2.139).

Knowing the partition function, we can employ general laws of thermodynamics in order to deduce the free energy per polymer chain, using

$$f_p = -kT \ln Z , \tag{2.141}$$

the entropy per chain, by

$$s_p = -\frac{\partial f_p}{\partial T} , \tag{2.142}$$

and the internal energy per polymer, by

$$e_p = f_p + T s_p . \tag{2.143}$$

The partition function Z can be evaluated in straightforward manner. We write

$$\begin{aligned} Z &= \sum_{\varphi_2} \cdots \sum_{\varphi_{N_b - 1}} \exp\left(-\frac{1}{kT} \sum_{i=2}^{N_b} u(\varphi_{i-1}, \varphi_i) \right) \\ &= \sum_{\varphi_2} \cdots \sum_{\varphi_{N_b - 1}} \prod_{i=2}^{N_b} \exp\left(-\frac{1}{kT} u(\varphi_{i-1}, \varphi_i) \right) , \end{aligned} \tag{2.144}$$

or, introducing the **statistical weights**

$$t(\varphi_{i-1},\varphi_i) = \exp\left(-\frac{1}{kT}u(\varphi_{i-1},\varphi_i)\right) \tag{2.145}$$

briefly

$$Z = \sum_{\varphi_2}\cdots\sum_{\varphi_{N_b-1}}\prod_{i=2}^{N_b} t(\varphi_{i-1},\varphi_i)\ . \tag{2.146}$$

To explain further, let us select polyethylene as an example. Here, for the three states per bond, nine different values t_{ij} exist. We collect them in a matrix $\mathbf{T}$

$$\mathbf{T} = \begin{pmatrix} 1 & w_0 & w_0 \\ 1 & w_0 & w_1 w_0 \\ 1 & w_1 w_0 & w_0 \end{pmatrix}\ . \tag{2.147}$$

Thereby we attribute to the different rotational isomeric states the following indices

$$\text{trans} \mathrel{\widehat{=}} 1, \qquad \text{gauche}^+ \mathrel{\widehat{=}} 2, \qquad \text{gauche}^- \mathrel{\widehat{=}} 3\ .$$

The matrix includes two parameters, denoted w_0 and w_1. To understand the matrix structure, imagine that a specific conformation is formed by subsequently arranging all bonds, emanating from the lowest energy state all-trans. We start at $i = 2$ and then proceed up to the end, $i = N_b - 1$ (the step to the last bond, $i = N_b$, can be omitted, since for this bond without a further neighbor no energy contribution arises). The coefficients of the matrix give the statistical weights associated with each step:

1. Since no energy is required if the trans-state is maintained, we have
$$u(i,1) = 0 \rightarrow t_{i1} = 1\ .$$
2. Formation of a gauche$^+$-state after a trans- or gauche$^+$-state requires an energy Δu_{tg} and thus carries a statistical weight
$$w_0 = \exp -\Delta u_{tg}/kT < 1\ . \tag{2.148}$$
3. Increased energies of formation are associated with the 'hairpin-bend'-conformations gauche$^+$-gauche$^-$ and gauche$^-$-gauche$^+$, resulting in lowered statistical weights, as expressed by the product $w_1 w_0$ with
$$w_1 < 1\ .$$

The evaluation of the partition function

$$Z = \sum_{\varphi_2} t(\varphi_t,\varphi_2)\cdot\sum_{\varphi_3} t(\varphi_2,\varphi_3)\cdots\sum_{\varphi_{N_b-2}} t(\varphi_{N_b-3},\varphi_{N_b-2})$$
$$\cdot\sum_{\varphi_{N_b-1}} t(\varphi_{N_b-2},\varphi_{N_b-1})t(\varphi_{N_b-1},\varphi_t) \tag{2.149}$$

can be rationalized using matrix multiplication rules. We can repeatedly apply the general summation rule

$$\sum_l t_{il} t_{lj} = (\mathbf{T}^2)_{ij} \tag{2.150}$$

for successive reductions:

$$\begin{aligned} Z &= \sum_{\varphi_2} t(\varphi_t, \varphi_2) \cdot \sum_{\varphi_3} t(\varphi_2, \varphi_3) \cdots \sum_{\varphi_{N_b-2}} t(\varphi_{N_b-3}, \varphi_{N_b-2}) \cdot (\mathbf{T}^2)_{\varphi_{N_b-2}, \varphi_t} \\ &= \sum_{\varphi_2} t(\varphi_t, \varphi_2) \cdot \sum_{\varphi_3} t(\varphi_2, \varphi_3) \cdots \sum_{\varphi_{N_b-3}} t(\varphi_{N_b-4}, \varphi_{N_b-3}) \cdot (\mathbf{T}^3)_{\varphi_{N_b-3}, \varphi_t} \\ &\;\;\vdots \\ &= (\mathbf{T}^{N_b-2})_{11} \, . \end{aligned} \tag{2.151}$$

Hence, Z can be obtained by calculating the power $(N_b - 2)$ of $\mathbf{T}$ and extracting the 11-coefficient. The task of calculating the power $(N_b - 2)$ of $\mathbf{T}$ can be much simplified if $\mathbf{T}$ is first transformed into a diagonal form. This can be achieved as usual by solving the set of homogeneous linear equations

$$\sum_j T_{ij} A_j = \lambda A_i \, , \tag{2.152}$$

i.e., evaluating the determinant

$$|\mathbf{T} - \lambda \mathbf{1}| = 0 \, . \tag{2.153}$$

There are three eigenvalues, λ_1, λ_2 and λ_3, and they set up a diagonal matrix $\mathbf{\Lambda}$. The matrix $\mathbf{A}$ that transforms $\mathbf{T}$ into $\mathbf{\Lambda}$

$$\mathbf{\Lambda} = \mathbf{A}^{-1} \mathbf{T} \mathbf{A} \tag{2.154}$$

is composed of the three eigenvectors, $(A_{1,j}), (A_{2,j}), (A_{3,j})$. With the aid of $\mathbf{\Lambda}$, the matrix multiplication becomes very simple

$$\begin{aligned} \mathbf{T}^{N_b-2} &= (\mathbf{A} \mathbf{\Lambda} \mathbf{A}^{-1})^{N_b-2} \\ &= \mathbf{A} \mathbf{\Lambda} \mathbf{A}^{-1} \mathbf{A} \mathbf{\Lambda} \mathbf{A}^{-1} \cdots \mathbf{A} \mathbf{\Lambda} \mathbf{A}^{-1} \\ &= \mathbf{A} \mathbf{\Lambda}^{N_b-2} \mathbf{A}^{-1} \, . \end{aligned} \tag{2.155}$$

We employ this equation and obtain an explicit expression for the partition function Z

$$Z = A_{11} (A^{-1})_{11} \lambda_1^{N_b-2} + A_{12} (A^{-1})_{21} \lambda_2^{N_b-2} + A_{13} (A^{-1})_{31} \lambda_3^{N_b-2} \, . \tag{2.156}$$

Usually all three eigenvalues are different and one, say λ_1, is the largest

$$\lambda_1 > \lambda_2, \lambda_3 .$$

Since N_b is huge, the partition function is well approximated by

$$Z \approx A_{11}(A^{-1})_{11}\lambda_1^{N_b-2} . \tag{2.157}$$

The free energy then follows as

$$f_p = -kT\left((N_b - 2)\ln\lambda_1 + \ln\left(A_{11}A_{11}^{-1}\right)\right) . \tag{2.158}$$

For a polymer, where $N_b \gg 1$, we can ignore the constant second term. This leads us to a simple expression for the free energy per bond

$$\frac{f_p}{N_b} = -kT\ln\lambda_1 . \tag{2.159}$$

The entropy and the internal energy per bond follow as

$$\frac{s_p}{N_b} = k\ln\lambda_1 + \frac{kT}{\lambda_1}\frac{\partial\lambda_1}{\partial T} \tag{2.160}$$

and

$$\frac{e_p}{N_b} = \frac{f_p}{N_b} + T\frac{s_p}{N_b} . \tag{2.161}$$

As we can see, in the framework of the RIS model it is a simple matter of deriving the thermodynamic functions for a given polymer chain, the only requirement being a knowledge of the matrix $\mathbf{T}$ of the statistical weights.

Let us carry out the calculation for polyethylene. The determinant equation to be solved is

$$\begin{vmatrix} 1-\lambda & w_0 & w_0 \\ 1 & w_0-\lambda & w_0w_1 \\ 1 & w_0w_1 & w_0-\lambda \end{vmatrix} = 0 . \tag{2.162}$$

This is a third order equation, but an evaluation shows that it factorizes, having the form

$$(w_0 - \lambda - w_0w_1)[\lambda^2 - \lambda(w_0 + w_0w_1 + 1) + w_0(w_1 - 1)] = 0 . \tag{2.163}$$

Therefore, the solutions can be given analytically. The three eigenvalues are

$$\begin{aligned}\lambda_{1/2} &= \frac{1}{2}\left[(w_0 + w_0w_1 + 1) \pm \sqrt{(w_0 + w_0w_1 + 1)^2 + 4w_0(1 - w_1)}\right] \\ \lambda_3 &= w_0(1 - w_1) .\end{aligned} \tag{2.164}$$

As is obvious, the largest eigenvalue is λ_1.

It is instructive to consider the numerical results for polyethylene in a computation for its melting point, $T_f = 415\,\mathrm{K}$. For the energy required to form a gauche-state after a trans-state we choose the value $\Delta\tilde{u}_{tg} = 2\,\mathrm{kJ\,mol^{-1}}$ (see

Sect. 2.1) and obtain $w_0 = 0.56$. The second statistical weight that is needed, the product $w_0 w_1$, has so far not been experimentally determined. Estimates for the related energy of the hairpin-bend states have been obtained by potential energy calculations, using empirical expressions for the non-bonded interaction energies. Values in the range of $7\,\mathrm{kJ\,mol^{-1}}$ are thus indicated, corresponding to a statistical weight $w_0 w_1 = 0.13$. With these values the following results are obtained for the thermodynamic functions, expressed per mol of CH_2-units:

$$\tilde{f} = \mathrm{N_L} f_\mathrm{p}/N_\mathrm{b} = -2.28\,\mathrm{kJ\,mol^{-1}}\,,$$
$$\tilde{s} = \mathrm{N_L} s_\mathrm{p}/N_\mathrm{b} = 8.25\,\mathrm{J\,K^{-1}\,mol^{-1}}\,,$$
$$\tilde{e} = \mathrm{N_L} e_\mathrm{p}/N_\mathrm{b} = 1.14\,\mathrm{kJ\,mol^{-1}}\,.$$

It is interesting to compare these results with the measured heat of fusion and the entropy of fusion

$$\Delta\tilde{h}_\mathrm{f} = 4.10\,\mathrm{kJ\,mol^{-1}}\,,$$
$$\Delta\tilde{s}_\mathrm{f} = \Delta\tilde{h}^\mathrm{f}_\mathrm{m}/T_\mathrm{f} = 9.9\,\mathrm{J\,K^{-1}\,mol^{-1}}\,.$$

We notice that the experimental heat of fusion, $\Delta\tilde{h}_\mathrm{f}$, is much larger than can be accounted for by the change in the intramolecular conformational energy, as given by $\tilde{e}$. Hence, the major part of the heat of fusion seems to be related to a change in the intermolecular energy, i.e., to the increase in the specific volume (which amounts to 15%). With regard to the change in entropy, the conclusions are different. Here the major part is indeed contributed by the change of the conformation from the all-trans state into the coiled form, with only the smaller rest being due to the increase in free volume.

In Sect. 2.1 we carried out a first estimate of the fraction of trans-states and gauche-states in polyethylene. In this estimate, independence of the rotational isomeric states of different bonds was implicitly assumed. We now may check for the modification introduced by the pentane effect, because the Ising model also provides us with equations for the fractions of the different pairs of conformational states. We rewrite the partition function

$$Z = \sum_{\{\varphi_i\}} t(\varphi_1,\varphi_2)\ldots t(\varphi_{N_\mathrm{b}-2},\varphi_{N_\mathrm{b}})$$

and choose a special form that collects all conformations with l pairs of type (i,j). These pairs produce a factor t^l_{ij}. We extract this factor and denote the remainder $\Omega(i,j;l)$

$$Z = \sum_{l=0}^{N_\mathrm{b}-1} (t_{ij})^l \cdots \Omega(i,j;l)\,. \qquad (2.165)$$

The probability for one specific conformation, $p\{\varphi_i\}$, is given by

$$p\{\varphi_i\} = \frac{\exp(-u\{\varphi_i\}/kT)}{Z}\,. \qquad (2.166)$$

We first derive the probability $p(i,j;l)$ that l pairs of type (i,j) occur in the chain. The necessary summation over the corresponding states of the chain is already implied in our formulation, and we can write

$$p(i,j;l) = \frac{t_{ij}^l \Omega(i,j,l)}{Z} . \tag{2.167}$$

From this result it follows that the average number of pairs (i,j), denoted $\langle n_{ij} \rangle$, is given by

$$\langle n_{ij} \rangle = \sum_{l=0}^{N_\mathrm{b}-1} l \frac{t_{ij}^l \Omega(i,j,l)}{Z} . \tag{2.168}$$

or, using the above relations, by

$$\langle n_{ij} \rangle = \frac{t_{ij}}{Z} \frac{\partial Z}{\partial t_{ij}} = \frac{\partial \ln Z}{\partial \ln t_{ij}} = (N_\mathrm{b} - 1) \frac{\partial \ln \lambda_1}{\partial \ln t_{ij}} . \tag{2.169}$$

The probability for a sequence (i,j) in adjacent bonds, denoted ϕ_{ij}, is

$$\phi_{ij} = \frac{\langle n_{ij} \rangle}{N_\mathrm{b} - 1} = \frac{\partial \ln \lambda_1}{\partial \ln t_{ij}} . \tag{2.170}$$

Insertion of the statistical weights w_0 and $w_0 w_1$ yields

$$\begin{aligned} \phi_{\mathrm{tt}} &= 0.29 , \\ \phi_{\mathrm{g^+t}} = \phi_{\mathrm{tg^+}} = \phi_{\mathrm{g^-t}} &= \phi_{\mathrm{tg^-}} = 0.14 , \\ \phi_{\mathrm{g^+g^+}} &= \phi_{\mathrm{g^-g^-}} = 0.06 , \\ \phi_{\mathrm{g^+g^-}} &= \phi_{\mathrm{g^-g^+}} = 0.015 . \end{aligned}$$

The pentane effect shows up quite clearly, as the fraction of pairs with sequences gauche$^+$-gauche$^-$ and gauche$^-$-gauche$^+$ is rather low.

Finally, the fractions of trans- and gauche-conformational states in the polyethylene chains are obtained by

$$\phi_i = \sum_j \phi_{ij} , \tag{2.171}$$

resulting in

$$\begin{aligned} \phi_t &= 0.60 , \\ \phi_{\mathrm{g^+}} = \phi_{\mathrm{g^-}} &= 0.20 . \end{aligned}$$

As expected, compared to the estimate based on the assumption of independent rotational isomeric states, the fraction of trans-states is increased.

The RIS model also enables a computation of the characteristic ratio C_∞ to be made, if the stereochemical properties of the chain are included into the considerations. The calculations are more tedious but, using the algebraic properties of matrices, they can still be carried out in straightforward manner. As it turns out, the experimental value for polyethylene, $C_\infty = 6.7$, is reproduced for reasonable assumptions about the molecular parameters, namely a C–C–C valence angle of 112° and gauche-rotational angles $\varphi_{g+} = 127.5°$ and $\varphi_{g-} = 232.5°$.

One may even advance one step further and calculate structure factors of specific chains numerically, for a comparison with the results of scattering experiments. Figure 2.23 presents, as an example, neutron scattering data of polycarbonate obtained for mixtures of deuterated and protonated species. The experiment covers a large range of q's, and results are represented in the form of a Kratky plot.

We observe a plateau, characteristic for ideal chains, and then a rise at higher q's, for distances shorter than the persistence length where the microscopic chain structure takes over control. The peculiar shape of the curve in this range reflects specific properties of polycarbonate and indeed, these can be reproduced by calculations on the basis of the RIS model. The continuous curve represents the theoretical results, and even if the agreement is not perfect, it describes the main characteristics qualitatively correctly.

Calculations based on the RIS model now exist for the majority of common polymers, thus providing a quantitative representation of the energetic and structural properties of single macromolecules. The prerequisite is a knowledge about the energies $u(\varphi_{i-1}, \varphi_i)$ associated with the different pairs of conformational states. Information about these values has improved steadily with the number of carefully analyzed experiments. Clearly, the model does not account for the excluded volume interaction, but it provides a microscopic understanding for all situations with ideal chain behavior.

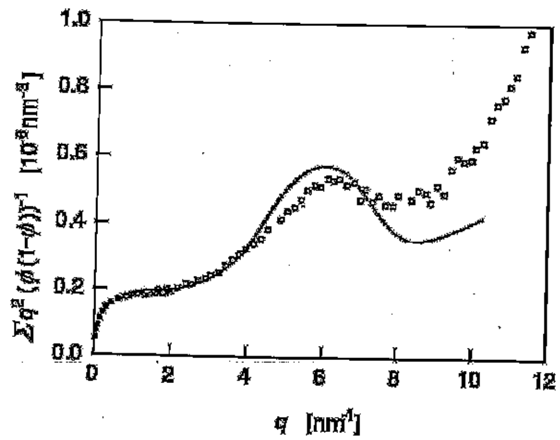

Fig. 2.23. Neutron scattering experiment on mixtures of PC and d-PC. The *continuous curve* has been calculated on the basis of the RIS model. Data from Gawrisch et al. [8]

Further Reading

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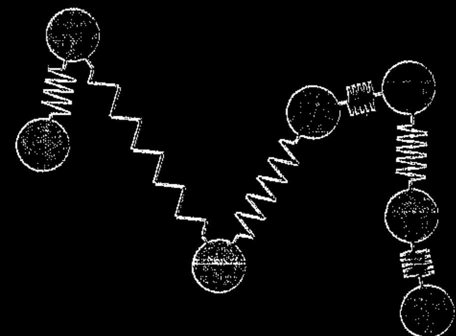

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