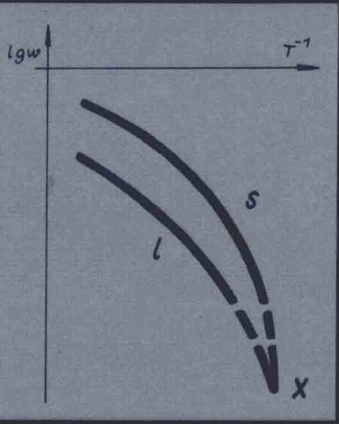
Ernst-Joachim Donth



Relaxation and Thermodynamics in Polymers

Glass Transition

Akademie Verlag

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E. Donth
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Preface

This book is intended to be a modern, but simple review for newcomers who wish to cooperate with polymer experts in the field of dynamics, relaxation, and thermodynamics: students, physicists, chemists, and material engineers. As this field is rapidly growing the author tries to maintain a certain distance from the matter. I thought about a cartographer making a coarsening in the scale 1 : 200 000 from a topographic map 1 : 25 000 with large white and grey spots. I had to decide: which are the main points (phenomena in a spatial scale 2 . . . 20 nm), which are the main connections (relations in space and time), and which are the details that may be dropped (many experimental details and configurational details along the polymer chains). However many basic results from related small-molecule systems are included to sharpen the view to the particularities of polymers.

The necessary repetitions – I chose the inductive method – are used to offer different views to the basic facts. Coarsening inquires a strong code. The author stakes on the intuitive power of the reader to understand a coarse situation best in space and time. It is a new paradigm to discuss relaxation in terms of both time and space; till now this was reserved for scattering. I often tried to make a rough, but consistent sketch even if the elements are not always cleared up. Although some important results from proud theoretical physics are included, the main part is at a descriptive level – there are still too many white spots in polymer science.

To keep a map readable only a small number of important aspects can be included. The subject is therefore restricted to widespread, common materials such as polyethylene (PE), polystyrene (PS) and similar polymers with flexible chains. Their study is necessary for the business with functional and special polymers, liquid crystalline polymers and the many other topics in modern polymer science.

Some general aspects of relaxation and thermodynamics are also the subject of the book. There are still basic problems e.g. with broad spectral distributions, and with the subsystem concept in thermodynamics, especially when the latter will be applied to small scales of order the correlation and structure lengths. The central subject of the book is the glass transition. One can turn the tables: Polymers represent not only a complication compared to the situation in simple liquids, but they mark, by their structure, some new length scales in the 2 . . . 20 nm range that can be used to study spatial aspects of thermodynamics and relaxation. The spatial scales are "spread" and differentiated in polymers so that they can separately be felt by different kinds of experiments. Additionally, the time scale can conveniently be controlled by relatively small changes in temperature.

For all the molecular and experimental details the reader is referred to standard books (e.g. Refs. 1–9). A descriptive introduction to the whole field of polymer science is for instance Ref. 10. There are excellent encyclopedic books or series, e.g. Refs. 11–14, and many journals that document the progress, e.g. "Macromolecules", "Polymer", or "Journal of Polymer Science". In this book about 400 references to original papers and books are included that can help the reader to find more information, also from the references therein, and so on.

I wish to express my thanks to colleagues that supported this book by reading the preliminary drafts of some chapters: Dr. M. Schulz and Dr. J.-U. Sommer in Merseburg, by edition and typing the manuscript: Dr. K. Schröter and Mrs. K. Herfurt, and by drawing the figures: Mrs. R. Dohnert; and to Mrs. H. Höpcke, reader in the Akademie Verlag, for the good collaboration.

Merseburg, March 29, 1992 E. Donth

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Introduction

In small-molecule liquids and ordinary glass-forming substances the characteristic lengths of interest to structure and dynamics are of order one nanometer: next neighbors, network elements, and so on. Only in critical states and in crystals are the interesting length scales much larger than 1 nm: critical correlations, grain size, decay of disclination fields etc. Flexible polymers with stable, covalently bonded chains, e.g. vinyl polymers, have, besides the monomer scale (bond length $l_0 \approx 0.15\,\mathrm{m}$, van der Waals chain diameter $\sigma \approx 0.5\,\mathrm{nm}$ with a number density of order 10 monomeric units per nm^3), further length scales: coil radius $R_0 \approx 20\,\mathrm{nm}$ monitored by chain length, Kuhn step length $l_K \approx 1.5\,\mathrm{nm}$, entanglement spacing $d_E \approx 7\,\mathrm{nm}$, fold length in crystal lamellas $l \approx 10\,\mathrm{nm}$ controlled by undercooling, and, in networks, a length describing the mean distance between the crosslinks.

In so-called inorganic polymers (glasses), as a rule, the networks are in dynamic equilibrium with bond breaking, and lengths 2 nm can only survive under special conditions.

Dynamics in polymers is influenced by the new length scales. The different scales of molecular movement are put in order by a general scaling principle: the larger the typical length, the larger the typical relaxation time.

Dynamic scattering (X-ray, neutron, light) can resolve both length and time scales, at least in principle.

Ordinary elastic scattering only resolves length scales, and relaxation only resolves time or frequency scales. It is difficult to complete the information without detailed models.

Equilibrium thermodynamic variables are integrals over these length scales or time (frequency) scales, e.g.

$$kT(\partial\tilde{n}/\partial p)_T = 1 - 4\pi \int c(r) r^2 dr, \tag{i}$$

or

$$C_p = k\overline{\Delta S^2} = k \int S^2(\omega)\, d\omega \tag{ii}$$

where the symbols will be defined later, see Eqs. 1.30, 2.54, and 7.1. As the general scaling principle is hidden by the integrations, it is difficult to see which length scale is responsible for thermodynamic variables.

The problem of what are the "particles" for polymer thermodynamics is also rather complex. In statistical considerations the "species", e.g. the units of placement on lattice sites, are often monomeric units or chain segments. But the presumed carrier of identity that defines the Gibbs factorial $\nu!$ in the configuration integral is the whole chain. Moreover, the element for thermodynamic analysis is the subsystem being, for the present, an intellectual construction that can have different, but not too small size. The analysis becomes rather difficult when this size is of order of the length scales listed above.

In the First Part of this book, tools for a dynamic and a thermodynamic treatment are described rather independently. Starting at Chap. 6, situations are described where both branches are more and more interweaved, such as in thermal glass transition, spinodal phase decomposition, and folded chain crystallization.

I Fundamentals

To familiarize the reader with macromolecular chains we shall consider four exercises about temporal and spatial aspects of Brownian motion.

(1) Fig. 1a shows a sketch of Perrin's original observation for a Brownian particle. The positions after constant time steps (Δt) are connected by straight lines. A simplified analysis (Ref. 15) is based on Fig. 1b. The integers 0, 1, 2, . . . , N are the time counts of a homogeneous time. [Of course, all symmetry properties of time and space refer to the average statistical situation in the materials described e.g. by distribution functions.]

Because of the space isotropy (i.e. no gradients) it is sufficient to consider one dimension with coordinate x. Then $x(t_i)$ is the position of the particle at time $t = t_i$, $i = 0, 1, 2, \ldots, N$. Put $t_0 = 0$ and $x(0) = 0$. Isotropy implies $\overline{x(t)} = 0$, or $\Sigma\, \overline{\Delta x_i} = 0$, with $\Delta x_i = x(t_i) - x(t_{i-1})$. More interesting is the mean square of $x(t)$,

$$\overline{x^2}(t) \;=\; \sum \overline{(\Delta x_i)^2} \;=\; \sum_{ij} \overline{\Delta x_i \Delta x_j}. \tag{1.1}$$

If Δt is large enough, then all succeeding x intervals are statistically independent, in other words, there is no correlation between them,

$$\overline{\Delta x_i \Delta x_j} \;=\; 0,\; i \neq j, \tag{1.2}$$

and we have

$$\overline{x^2}(t) \;=\; \sum \overline{(\Delta x_i)^2} \;=\; N\overline{\Delta x^2} \tag{1.3}$$

if all $\overline{(\Delta x_i)^2}$ are equivalent, e.g. equal in homogeneous space and time. There is no stochastic length larger than the the particle diameter.

Defining a diffusion coefficient

$$D \;=\; \tfrac{1}{2}\overline{\Delta x^2}/\Delta t \tag{1.4}$$

we obtain $\overline{x^2}\,(t) = 2Dt$, $t = N\Delta t$; for 3 dimensions we have

$$\overline{r^2}(t) \;=\; 6Dt. \tag{1.5}$$

The square of mean Brownian shift is proportional to time. Consider a

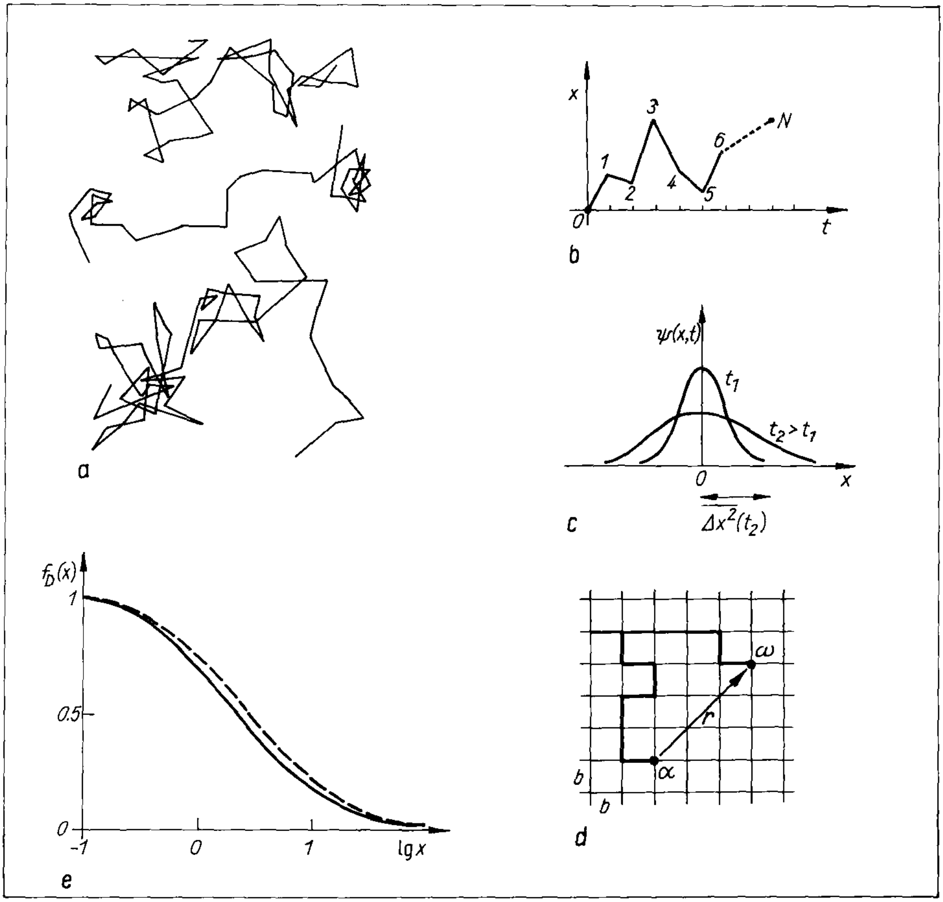

Fig. 1. Brownian motion.
a. Sketch of Perrin's observation. b. Brownian motion $x(t)$ in one dimension (for Eqs. 1.1 to 1.4). c. Diffusion of Brownian particles; $\psi(x, t)$ density. d. Random walk from α to ω on a square lattice with step length b. e. Debye structure factor, approximation Eq. 1.15b dotted; $x = q^2 R_{\mathrm{gyr}}^2$, q scattering vector.

larger number of independent Brownian particles starting from $x = 0$ at time $t = 0$. Then their concentration $\psi(\boldsymbol{r}, t)$ is controlled by the diffusion equation

$$D\Delta\psi - \partial\psi/\partial t = 0 \tag{1.6}$$

with the Laplacian $\Delta = \nabla^2$. This equation implies a constant particle number, and the situation of Fig. 1c defines a current proportional to the ψ gradient ($\nabla\psi$).

(2) Fig. 1a also stands for a snapshot of a flexible chain when the length b of segments is chosen to be so large that their orientations are statistically independent. To avoid mathematical difficulties connected with the time-space continuum (Wiener measure) the chain is considered to be a random walk (Ref. 16) on a primitive cubic lattice with step length b, see Fig. 1d. We follow the presentation of Ref. 4. Similar to the temporal case (1) we have

$$\boldsymbol{r} = \boldsymbol{b}_1 + \boldsymbol{b}_2 + \cdots + \boldsymbol{b}_N = \sum \boldsymbol{b}_i. \tag{1.7}$$

Hence the mean square *end-to-end distance* of the chain, R_0, is obtained analogously to Eq. 1.5,

$$R_0^2 = \overline{\boldsymbol{r}^2} = \sum_{ij} \overline{\boldsymbol{b}_i \boldsymbol{b}_j} = \sum \overline{\boldsymbol{b}_i^2} = N\boldsymbol{b}^2. \tag{1.8}$$

For large N the whole statistics is determined by many small independent steps, which means by a Gaussian distribution. Consider many random walks starting at $\boldsymbol{r} = 0$. Be $p(x, y, z)$ – compare it to $\psi(\boldsymbol{r})$ in (1) – the corresponding probability density to find the chain end (N) at $\boldsymbol{r} = (x, y, z)$. Gaussian means

$$p(x, y, z) = p(x) \cdot p(y) \cdot p(z) - N^{-3/2} \exp\left(-3r^2/2Nb^2\right) \tag{1.9}$$

or $p(x) \sim N^{-1/2} \exp\left(-x^2/2\overline{x^2}\right)$ with $\overline{x^2} = \overline{r^2}/3$, see Eq. 1.8, and with the measure dx.

A chain where Eq. 1.9 is also true for end-point distances of any (also small) parts is called a *Gauss chain*. In that case one can calculate the *radius of gyration* from Eq. 1.9, the result being $R_{\text{gyr}} = R_0/\sqrt{6}$.

Comparison of Eqs. 1.3 and 1.8 gives an equivalence between the temporal and spatial picture,

$$b^2 \Leftrightarrow 6D\Delta t \quad \text{or} \quad R_{\text{gyr}}^2 \Leftrightarrow Dt. \tag{1.10}$$

(3) Spatial correlations between the segments of a polymer chain in a solvent can be obtained by elastic scattering experiments. For Gauss chains one can calculate the correlations from Eq. 1.9. Expressed by a distribution $\phi(\boldsymbol{r}_i - \boldsymbol{r}_j)$, we have from Eq. 1.9

$$\phi(\boldsymbol{r}_i - \boldsymbol{r}_j) = \left(\frac{3}{2\pi b^2 |i - j|}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{(\boldsymbol{r}_i - \boldsymbol{r}_j)^2}{|i - j| b^2}\right) \tag{1.11}$$

with a mean value proportional to the half of the exponent denominator,

$$\langle (\boldsymbol{r}_i - \boldsymbol{r}_j)^2 \rangle = |i - j| b^2, \tag{1.12}$$

see also Eq. 1.8.

The scattering intensity of a volume with spatially isolated Gauss chain coils is proportional to the *structure factor* generally defined by

$$S(\boldsymbol{q}) = \langle \exp(i\boldsymbol{q}(\boldsymbol{r}_i - \boldsymbol{r}_j)) \rangle. \tag{1.13}$$

In this situation the spatial correlation is in a way measured by a "standing" wave with scattering vector $\boldsymbol{q}$ of magnitude

$$q = (4\pi/\lambda) \sin(\vartheta/2), \tag{1.14}$$

where λ is the wave length of the beam and ϑ is the scattering angle corresponding to a momentum exchange $\hbar q$. The ensemble average $\langle \ldots \rangle$ of Eq. 1.13 can be calculated for Gauss chains using the distribution ϕ of Eq. 1.11. We obtain the Debye structure factor

$$S_D(q) = \frac{1}{N} \int_0^N dn \int_0^N dm \exp(-(b^2 q^2/6)|n - m|) = N f_D(x) \tag{1.15a}$$

with

$$f_D(x) = \frac{2}{x^2}(e^{-x} - 1 + x) \approx \frac{1}{1 + x/3}, \quad x = q^2 R_{\text{gyr}}^2. \tag{1.15b}$$

The exact and the approximate Debye function are compared in Fig. 1e. The decrease is "logarithmically broad". This term will generally be used when the interesting part of a function $f(y)$ extends to one logarithmic decade in y (i.e. a factor 1 : 10) or more. A nearly linear diagram is obtained for S^{-1} vs. q^2. When parameterized by polymer concentration it is called Zimm plot and can be used to determine R_{gyr}, for instance by extrapolation.

(4) The entropy ΔS linked with the possibilities of Fig. 1d is a thermodynamic measure for the spatial correlation of a chain. One must count the number $\psi(N)$ of possible N-step ways from α and ω in Fig. 1d. Then

$$\Delta S = k \ln \psi(N). \tag{1.16}$$

It depends on the end-to-end distance $\boldsymbol{r}$. Counting Gauss chains we obtain

$$\Delta S(\boldsymbol{r}) = \Delta S(r) = \Delta S(0) - k\frac{3r^2}{2R_0^2}. \tag{1.17}$$