Brief Introduction to the Physical Chemistry of Polymers

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Last updated 12/9/2024

Contents

1 Preface

This is meant to be a brief introduction to polymers. Emphasis was given to

- simple arguments and explanations (hopefully never crossing the line between simple and too simple)
- the comparison to other materials
- function

With regard to simplicity, the text sometimes borrows from Rubinstein/Colby.[1] These authors often say that some energy is about k_BT, whenever entropy is involved. That is good enough for a start. Another example: The segment volume is assumed to be the same as the volume of a solvent molecule in section 6. That is good enough for the concepts, but not good enough for the comparison with experiment. When applying the concepts to practical problems, be prepared for cumbersome details.

The terminology mostly follows Rubinstein/Colby. Other sources are given footnotes 2, 3, and 4.

This short introduction does not touch on (or hardly touches on)

- Polyelectrolytes
- Block copolymers
- Gels
- Hyperbranched polymers and dendrimers
- Proteins (often well-defined folding pattern)
- Polymer synthesis
- Polymer characterization

These are lecture notes, this is not a textbook. Suggestions for improvement are welcome (johannsmann@pc.tu-clausthal.de).

2 Historical remarks

In terms of technology (no understanding yet)

- 1820s: Goodyear vulcanized the resin from Hevea brasiliensis, obtaining a rubber.
- 1840s: Schönbein produced what to today is a variant of "regenerated cellulose". He obtained nitrocellulose (a soluble thermoplastic).
  Nitrocellulose readily explodes, which is a side aspect unrelated to it being a polymer.[5]
  Later, celluloid was obtained in similar ways. Celluloid was more successful, commercially, than nitrocellulose.
- ~ 1900: Bakeland prepared phenolic resins.
  The trade name was "Bakelite". These were thermosets They were entirely synthetic (not derived from a biopolymer).
  1940s: Carothers and others: Many polymers, derived from mineral oil

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[1] Rubinstein, Colby: *Polymer Physics*
mostly on theory, carefully written, sometimes with an emphasis on simple arguments

[2] Young, Lovell: *Introduction to Polymers*
not new, but still a well-balanced, short introduction

[3] H.G. Elias: An Introduction to Polymer Science, Wiley. A few volumes, comprehensive

[4] G. Strobl: The Physics if Polymer
Shorter than Rubinstein/Colby and a bit more accessible, occasionally. Strobl does not shy away from opinions, which makes it an interesting read.

[5] Today, explosives are often formulated as thermoplastic materials for ease of handling.

Scientific insight

- Early 19th century: Rubber heats when stretched (similar to the gas in a bicycle pump).
- 19th century:
  Polymers were considered to be colloids because of the low osmotic pressure.
  But: Π/c depended on concentration (modern explanation: second virial coefficient).
- Actually, the word "colloid" derives from Greek "gluey". Polymers are more tacky than other colloids
- Π/c stayed low, regardless of the solvent (unlike Π/c of the association colloids, the reason being that polymers are covalently bound chains).
- 1920's Staudinger: Polymers are linear "macromolecules" (evidence: x-ray diffraction)
- Soon later: Rubber elasticity

Comments on the current situation:

- Polymers are of immense technical importance.
- Polymers often are part of composites and research responds to that.
- There are new polymers for medical applications.
- Analytical theory is demanding but can still count as a success.
- Simulations have been a success and continue to complement analytical theory. Simulations are mostly based on coarse-grained models.
- Living polymerization allows to control molecular weight, branching, tacticity and sequentiality[6] of copolymers rather well. The same is true for the metallocene catalysts in the case of polyolefins.[7]
- An opinion: Polymer recycling is difficult and will stay difficult for a while. Burning them will be common practice for a while.
- An opinion: Biobased polymers have their right, but petrochemicals will stay the main resource for a while.

3 Polymers as materials

On the positive side:

- Easily modified (additives, chemical transformation, copolymers)
- Light-weight materials (but fiber-reinforced plastics were a disappointment for the car industry)
- Never fully crystalline
  → stress relaxation, no brittle fracture
  → stress relaxation, film formation, printing
- Amorphous component undergoes glass transition
  → gradual dependence of viscosity on temperature, thermoplastic processing
- Long chains → transient network or entanglements
  → high viscosity
  → polymer welding
- Light crosslinking leads to elastomers, rubbers, and gels
- Biocompatible and bioactive polymers exist

On the side of problems:

- Maximum temperature: 400°C (typical: 200°C)

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[6] Sequentiality denotes to order (or the lack thereof) of the different types of segments in copolymers.

[7] Polyolefins only contain the elements C and H. Polyethylene and polypropylene are examples. As of 2024, polyolefins accounted for about 50% of the polymer market in Europe. Polyolefins mostly are semi-crystalline. They are mostly produced by Ziegler-Natta catalysts. There are few good solvents.

- Resistance to chemicals often poor (exception: PEEK)
- Polymers rarely are “high barrier materials’. Oxygen and water may permeate, which is a problem in food packaging.
- Polymeric electronics not easy
- Purification not easy
- Recycling not easy
- Characterization not easy

4 Molecular weight distributions, branching

The peculiar properties of polymers are to a large extent linked to polymers containing flexible linear chains.[8] Graphite (which is an organic material) does not count as polymer, because it contains sheets rather than linear chains. Flexible chains imply the possibility of transitions between different conformations, even at temperatures below the glass transition. Those dissipate energy under deformation. Polymers rarely are brittle.

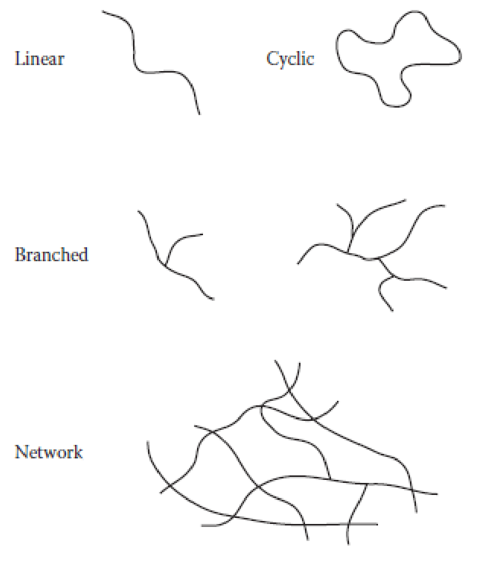

Fig. 4.1
There are different forms of chain topology. Polymers just about always contain linear chains. The strands can be short in the case of thermosets. Remarkably, the properties of cyclic polymers do not much differ from those of linear polymers.
Source: Rubinstein-Colby

Consider strictly linear flexible chains above the glass transition first. The longer the chains, the more viscous is the material. However, that is not the entire story. When plotting viscosity versus chain length in log-log form (Fig. 8.2), there is kink. The chain length at the kink is the entanglement molecular weight. Whether or not (and to what extent) chains are “entangled”. makes a large difference to the flow behavior. The picture is complicated by the fact that the chains in a given sample do not usually all have the same length. There is a chain length distribution, which easily stretches across a few decades. In 1990’s, methods were found to avoid such broad molecular weight distributions. The key development were the “living polymerizations”. Some of the important experiments in the history of polymer science were then repeated with those more well-defined samples (cf. Fig. 5.4). Mostly, the conclusions, which had been drawn from the earlier experiments, were confirmed. Conversely: Poor control over chain length and branching were a constant source of frustration in the early phases of polymer science.

Talking of polymerization: For some large-volume products, industry has developed processes and will stick to these unless the success of new methods justifies the rather extensive efforts of testing. An important property of a polymer is its availability and its price. Parts of polymer research are concerned with moderately well-defined polymers obtained from large-scale processes, simply because these processes exist and are what they are.

Many polymers are branched, at least slightly. The branches may be short (a few segments) or long (to the extent that the distinction between a main chain and a side chain is no longer possible). All types of branching affect crystallization (in case there is crystallization). Important examples are

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[8] Thermosets contain few flexible chains, but these few flexible strands still lead to a dissipation of energy under mechanical shock.

the different types of polyethylene. Long chain-branches strongly effect the flow behavior (section 8.7).

Fig. 4.1 shows different “chain topologies”.[9]

5 Conformation of the single chain

5.1 The ideal random walk

In the following we consider flexible linear chains. These follow random-walk statistics (known from diffusion). In consequence, the root-mean-square end-to-end distance is:

Eq. 5.1

$$R_E = \left\langle \left(\vec{r}_n - \vec{r}_0\right)^2 \right\rangle^{1/2} = \tilde{N}^{1/2} l$$

$\tilde{N}$ is the number of segments, and l is the length of each segment. 0 and n denote the first and last segment.

Eq. 5.1 assumes perfect flexibility. Most bonds are not perfectly flexible, but the random-walk model can be recovered by grouping neighboring segments, such that the orientation correlation is lost between these “statistical segments” with length b (b the “statistical segment length”, also "Kuhn length"):

Eq. 5.2

$$R_E = N^{1/2} b$$

A statistical segment contains multiple chemical segments. The contour length, L_c, is given as

Eq. 5.3

$$L_c = \tilde{N} l = Nb$$

It follows that $N = \tilde{N}l/b$. b and l are related by the characteristic ratio, C_∞, defined as

Eq. 5.4

$$C_\infty = \frac{b^2}{l^2}$$

The subscript ∞ indicates that this relation only applies for sufficiently long chains. Fig. 5.3 shows stiffness parameters for some technical polymers. There are different models predicting C_∞ from the properties of the bond (not discussed here).

A side remark: Polymer coils rarely are spherical (Fig. 5.6). One can approximate them as ellipses. On average, the lengths of principal axes are related to each other as 1:2.69:11.8 (following computer simulations).

When b is much larger than l, the chain is called semiflexible.[10] DNA and collagen are examples. Some biopolymers are semiflexible in that sense, the reason being that the large local stiffness leads to

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[9] The term “topology” in polymer science slightly differs from topology in mathematics. Two objects are topologically equivalent in mathematics, if they can be made to agree in shape by deformation only, never cutting anything. A linear chain and a cyclic chain are topologically inequivalent in polymer science and in mathematics. A branched chains is topologically different from a linear chain in polymer science but not in mathematics.

[10] When b exceeds L_c, the chain is a “rigid rod”.

an extended conformation and a correspondingly lowered polymer volume fraction – with rubber elasticity maintained (section 5.4).

Semiflexible chains are often modeled as “worm-like chains”. These are continuous paths in space (no discrete steps). There are some subtle differences between the flexible chain with large b and the worm-like chain. In simple terms, the Kuhn length from the freely jointed chain is equal to $2l_p$ with l_p the persistence length. The persistence length is the distance on the chain’s path, over which the orientation correlation function drops to 1/e. The differences between the freely jointed chain and the worm-like chain become apparent at strong elongation (section 5.5).

Scattering does not reveal the end-to-end distance.[11] It rather reveals the pair correlation function $g(r)$. The matter is discussed in some depth in the course on soft condensed matter. The pair correlation function essentially is the Fourier transform[12] of the structure factor $S(q)$ with $\mathbf{q} = \mathbf{k}_{out} - \mathbf{k}_{in}$ the scattering vector and $q = |\mathbf{q}|$. Letters in bold denote vectors. $\mathbf{k}$ is the wave vector. The structure factor is proportional to the scattering intensity.

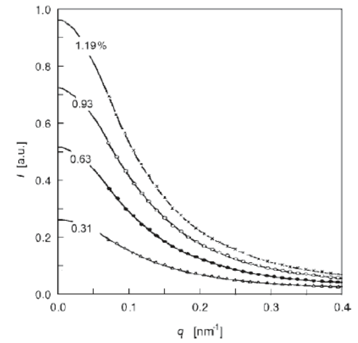

Fig. 2.15. Scattering curves obtained in a neutron scattering experiment on sol tions of PMMA (mol fractions as indicated) in d-PMMA. Data from Kirste et al. [

Fig. 5.1
G. Strobl: The Physics of Polymers

When studying the pair correlation function of liquids, one usually is interested in distances similar to the distance between molecules. $g(r)$ has a peak at the next-neighbor distance. In the limit of large r, it levels off to a plateau with a height proportional to the density, ρ. When studying single polymer chains, $g(r)$ levels off to zero at large distance because of the finite size of the coil. Typically, one is not interested in molecular details (such as the next neighbor distance). The interest is in intermediate range of r.

The literature usually quotes the structure factor rather than the pair correlation function. For the random coil, $S(q)$ is

Eq. 5.5

$$S(q) = \frac{2}{\left(qR_g\right)^4}\left(\left(qR_g\right)^2 - 1 + \exp\left(-\left(qR_g\right)^2\right)\right)$$

The right-hand side is the “Debye function”. Fig. 5.1 shows the Debye function as determined in experiment. R_g is the “radius of gyration”, defined as

Eq. 5.6

$$R_g = \left\langle \left(r - r_{CM}\right)^2 \right\rangle^{1/2}$$

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[11] R_E has been determined experimentally for DNA, which was fluorescently labeled at the ends. DNA is rather stiff. In consequence, R_E is large enough to be determined with optical microscopy.

[12] There are slight complications in the algebra.

CM stands for "center of mass". For the Gaussian chain, R_g and R_E are related as

Eq. 5.7

$$R_G = \frac{1}{\sqrt{6}} R_E$$

This result is not entirely correct for the self-avoiding chain (section 5.2).

In the low-q limit, $S(q)$ can be approximated as

Eq. 5.8

$$S(q) \approx 1 - \frac{1}{3} q^2 R_g^2$$

The way from Eq. 5.5 to Eq. 5.8 involves complications. Importantly, scattering experiments give access to R_g, as opposed to R_E. Static light scattering accesses the low-q range because the wavelength of light is larger than the coil diameter. It is customary in the context of static light scattering to not discuss the scattering intensity, but rather a function which is proportional to the inverse scattering intensity (Fig. 5.2). (More details are discussed in the course on polymer analysis.) Following Eq. 5.8, one expects $S^{-1}(q)$ to be proportional to $1/(1 - 1/3\, q^2R_g^2)$. If the second term is small, a Taylor expansion to first order in $q^2R_g^2$ can be applied, which leads to $S^{-1}(q) \propto 1+1/3\, q^2R_g^2$.[13]

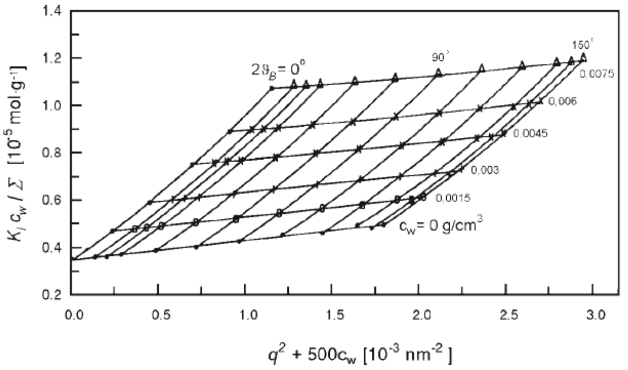

Fig. 3.5. Light scattering experiments on solutions of PS ($M = 2.8 \times 10^5$ g mol^{-1}) in toluene at 25 °C. Results are presented in a Zimm plot, enabling an extrapolation to $c_w = 0$ and $q = 0$. Data from Lechner et al. [11]

Fig. 5.2
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<u>Remember</u>

- Linear chains follow random-walk statistics.
- For the Gaussian chain, $R_E \propto N^{1/2}$.
- Due to local chain stiffness, the chemical segment length, *l*, is usually replaced by the statistical segment length, *b* (larger than *l* by a factor between 2 and 10)
- Scattering determines the radius of gyration, R_g.

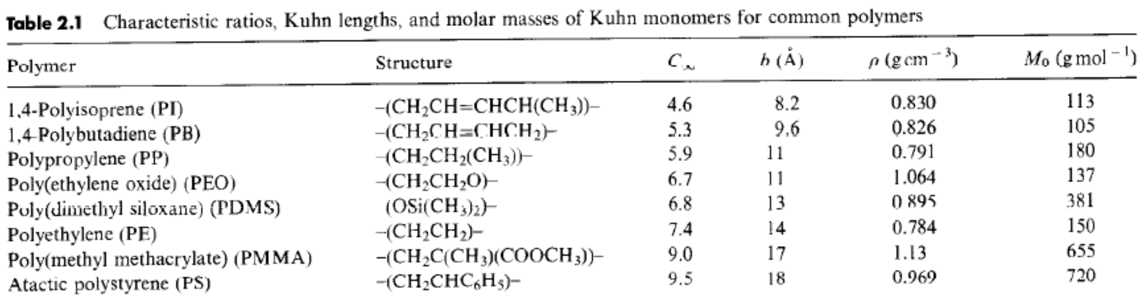

Table 2.1 Characteristic ratios, Kuhn lengths, and molar masses of Kuhn monomers for common polymers

Polymer	Structure	C_∞	b (Å)	ρ (g cm^{-3})	M_0 (g mol^{-1})
1,4-Polyisoprene (PI)	$-(CH_2CH{=}CHCH(CH_3))-$	4.6	8.2	0.830	113
1,4-Polybutadiene (PB)	$-(CH_2CH{=}CHCH_2)-$	5.3	9.6	0.826	105
Polypropylene (PP)	$-(CH_2CH_2(CH_3))-$	5.9	11	0.791	180
Poly(ethylene oxide) (PEO)	$-(CH_2CH_2O)-$	6.7	11	1.064	137
Poly(dimethyl siloxane) (PDMS)	$(OSi(CH_3)_2)-$	6.8	13	0.895	381
Polyethylene (PE)	$-(CH_2CH_2)-$	7.4	14	0.784	150
Poly(methyl methacrylate) (PMMA)	$-(CH_2C(CH_3)(COOCH_3))-$	9.0	17	1.13	655
Atactic polystyrene (PS)	$-(CH_2CHC_6H_5)-$	9.5	18	0.969	720

Fig. 5.3
Values pertaining to the local stain stiffness of some technical polymers.
Source: Rubinstein-Colby

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[13] The general form of this Taylor expansion is $(1 - \varepsilon)^{-1} \approx 1 + \varepsilon$..

5.2 *The self-avoiding random walk*

For chains in a good solvent, a modification to the model is required because two segments cannot occupy the same site. While diffusing particles may revisit all sites, the self-avoidance transforms the random walk into a "self-avoiding random walk" (SAW). Self-avoidance expands the chains, following[14]

Eq. 5.9

$$R_E = N^{\nu} l = N^{0.588} l$$

The self-avoiding random walk was among the first problems studied with computer simulations. Initially, the Rosenbluth algorithm was used.[15,16] According to Ref. 17 (which uses a different algorithm, namely the “pivot algorithm”), the current best value for the Flory exponent ν is 0.5875970 with an uncertainty of 4 in the last digit.[18]

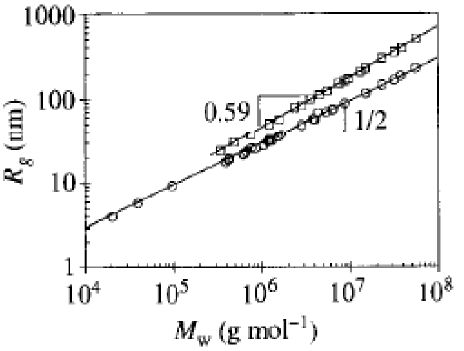

Fig. 3.6
Molar mass dependence of the radius of gyration from light scattering in dilute solutions for polystyrenes in a θ-solvent (cyclohexane at $\theta = 34.5\,°C$, circles) and in a good solvent (benzene at 25 °C, squares). Data are compiled in L. J. Fetters, *et al.*, *J. Phys. Chem. Ref. Data*, **23**, 619 (1994).

Fig. 5.4
from Rubinstein/Colby

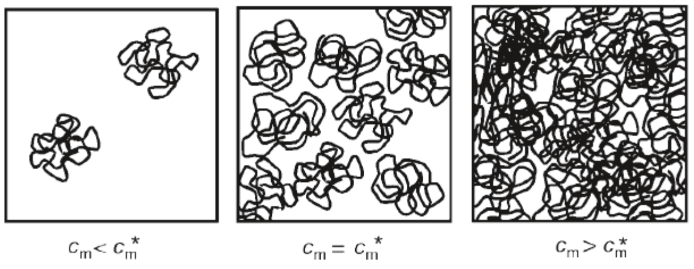

Fig. 3.1. Polymer solution: Dilute regime ($c_m < c_m^*$) and semidilute regime with overlapping chains ($c_m > c_m^*$). The cross-over occurs for $c_m = c_m^*$ when the volumes occupied by the individual chains just cover the sample volume

Fig. 5.5
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[14] The letter ν in this text denotes the Flory exponent. Elsewhere, it denotes the exponent in the relation $R_E \propto N^{\nu}$, whatever the value of this exponent might be. In these texts, one often encounters the term N^{ν}. Here, we prefer to write $N^{1/2}$ and keep in mind that the 1/2 may have to be replaced by 0.588 in good solvents.

[15] M. N. Rosenbluth, A. W. Rosenbluth, *J. Chem. Phys.* 1955, 23, 356.

[16] There is touching report of a researcher from the pre-computer time, who wrote down *all* possible paths of chains with up to 7 segments in 2D. That took a while. The deviation from square-root behavior were noticeable.
In modern simulations, one never covers all possible configurations of a sample. That is impossible because of the „combinatorial explosion“. One covers many configurations and hopes that these are representative of the entire ensemble.

[17] Clisby, N.; Dünweg, B., High-precision estimate of the hydrodynamic radius for self-avoiding walks. *Physical Review E* **2016,** 94, (5).

[18] Interestingly, the best value for a universal constant is obtained by simulation rather than analytical theory.

The value of ν does have practical implications. Consider a polymer chain with 10^6 segments. The difference between $(10^6)^{0.5}$ and $(10^6)^{0.588}$ amounts to about a factor of 3. Consider “dilute solutions”, which are solutions, in which the different coils hardly overlap. "Dilute polymer solutions" are Newtonian liquids. They have a concentration lower than the overlap concentration, where the "overlap concentration" is closely related to the coil diameter (Fig. 5.5). At concentrations larger than the overlap concentration, everything becomes more complicated.[19] For chains with $N = 10^6$, the difference between $\nu = 0.5$ and $\nu = 0.588$ changes the overlap concentration by a factor of 9.

Chains follow ideal random-walk statistics when the solvent is a ”θ-solvent”. In the θ-solvent, there is a slight attraction between segments, which compensates for the repulsion caused by self-avoidance. Fig. 5.4 shows experimental data. The chains studied had been prepared with living polymerization, meaning that the molecular weight distributions were narrow. Otherwise, it would have much more difficult to nail down self-avoidance, experimentally.

Chains follow ideal random-walk statistics in the melt. Th argument goes back to Flory and sounds simplistic. It was later confirmed with rigorous theory[20] and neutron scattering.[21] Flory argues that the swelling due to self-avoidance lets the neighboring chains to swell, as well. That affects the energy balance (section 5.8) to the extent that the chains do not actually swell.

Remember

- In good solvents, the exponent 1/2 in $R_E \propto N^{1/2}$ from random-walk statistic is replaced by $\nu = 0.588$.
- In θ-solvents and in the melt, the polymer conformation is „pseudo-ideal“, meaning $R_E \propto N^{1/2}$.
- Self-avoidance has in influence on the overlap concentration, below which chains do not overlap, thereby constituting a “dilute solution”.

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[19] „Semidilute solutions“ have overlap, but still display considerable fluctuations of the local segment concentration because the overlap is weak. „Concentrated solutions“ have small fluctuations in segment concentration. There is a transition to polymers plasticized by small molecules, dissolved in the polymer matrix.

[20] In 2007, detailed simulations revealed that this is almost correct, but not quite.* Revisiting the scattering data, the deviation was confirmed.

*Wittmer, JP, et al. doi.org/10.1209/0295-5075/77/56003.

[21] Neutron scattering was done on a small minority of protonated chains in a matrix of deuterated chains of the same type.[21] The proton and the deuteron have different neutron scattering lengths.
For the aficionados: At large molecular weight, protonated and deuterated polystyrene chains have a slight tendency to demix (have a non-zero χ-parameter larger, section 6). That is so because of the anharmonicity of the Morse potential and the zero-point energy. Because the deuteron is heavier than the neutron, the zero-point energy (proportional to $\hbar\omega = \hbar(\kappa/\mu)^{1/2}$) is lower for the deuteron. Because of the asymmetry of the Morse potential, the bond length is slightly decreased. Because the electronic polarizability is correlated to the volume of a molecule, the polarizability differs between the protonated and the deuterated molecules. The two slightly differ in van-der-Waals attraction and therefore have a slightly positive mixing enthalpy.

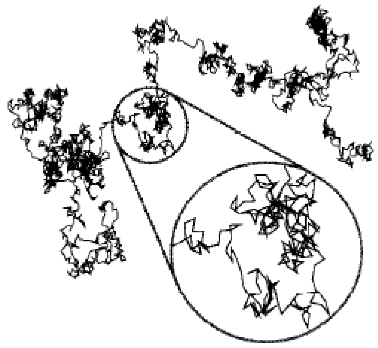

Fig. 1.14
Fractal structure of an ideal chain with fractal dimension $\mathcal{D} = 2$ obtained by computer simulation (courtesy of Q. Liao).

Fig. 5.6
Snap shot of a single chain.
If you zoom into the image, the statistical properties do not change. Of course, this only applies as long as neither the individual segment nor the chain as a whole can be seen. Note that the coil not at all spherical or nearly spherical.
from Rubinstein/Colby

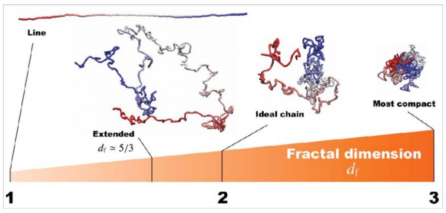

Fig. 5.7
The fractal dimensions of polymer coils depends on the extent to which they are collapsed or stretched.
www.researchgate.net/figure/Fractal-dimensions-for-polymers-to-characterize-the-effective-conformational-states-For_fig1_316112010

5.3 *Scale invariance, fractal geometry of polymer chains*

In the range of $q >> R_g^{-1}$, the structure factor from Eq. 5.5 can be approximated as

Eq. 5.10

$$S(q) = 2\left(qR_g\right)^{-2}$$

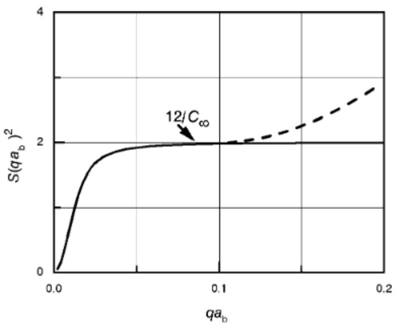

Fig. 2.10. Kratky plot of the scattering function of an ideal chain. The internal rigidity of the chain results in a change to a rod-like scattering at higher q's

Fig. 5.8
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$S(q)$ is a power law with a power-law index of –2. When plotted in log-log form, $S(q)$ is a straight line with slope –2. The “Kratky-plot” (Fig. 5.7) is adapted to that situation. In the range, where the power law holds, there is neither a peak nor a shoulder. More technically, there is no ”characteristic lengt”. The statistics of the chain is “scale-invariant” in the q-range between R_g^{-1} and b^{-1}, which is equivalent to a size range from slightly above b to slightly below R_g. The chain does not change its appearance (its statistics) upon zooming in on it (Fig. 5.6). Such objects are called “fractal”. Other examples are the dendritic structure resulting from diffusion limited aggregation[22] and the Mandelbrot set.[23] Fractal objects have a “fractal dimension”. Place a sphere with a certain radius around a segment on the chain and count the number of other segments inside the sphere. Repeat that for many segments and take the average. Repeat that for many radii

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[22] en.wikipedia.org/wiki/Diffusion-limited aggregation
[23] en.wikipedia.org/wiki/Mandelbrot_set

and plot the average number of segments, N_{sphere}, versus radius, R_{sphere}. For a dense medium, the number would scale as $R_{\mathrm{sphere}}{}^{3}$. For a flat sheet, the relation is $N_{\mathrm{sphere}} \propto R^{2}{}_{\mathrm{sphere}}$. For the stiff rod, one has $N_{\mathrm{sphere}} \propto R_{\mathrm{sphere}}$. In these cases, the fractal dimension is the same as the dimension of the space. For the random coil, one also has $N_{\mathrm{sphere}} \propto R^{2}{}_{\mathrm{sphere}}$ even though the coil is an object in three-dimensional space. The exponent of 2 follows from $R_{\mathrm{sphere}} \propto N^{1/2}{}_{\mathrm{sphere}}$, from which it follows that $N_{\mathrm{sphere}} \propto R^{2}{}_{\mathrm{sphere}}$. The fractal dimension of the ideal random walk is 2. For that reason, $S(q)$ scales as q^{-2}. For the self-avoiding walk, the fractal dimension is $0.588^{-2} \approx 2.892$. $S(q)$ scales as $q^{-2.892}$. (The self-avoiding walk also is scale-invariant, Fig. 5.7.)

Fractal structure is interesting because scale invariance is the prerequisite for a family of tools called "renormalization group theory". The fluctuations of density close to a critical point also are scale-invariant.[24] The power-law exponents (all of them, including the power-law exponent in $S(q)$) are universal. They do not depend on the material. The Flory exponent is closely linked to one the exponents from these theories.

The density fluctuations in polymer gels sometimes also display scale invariance (Fig. 5.9).

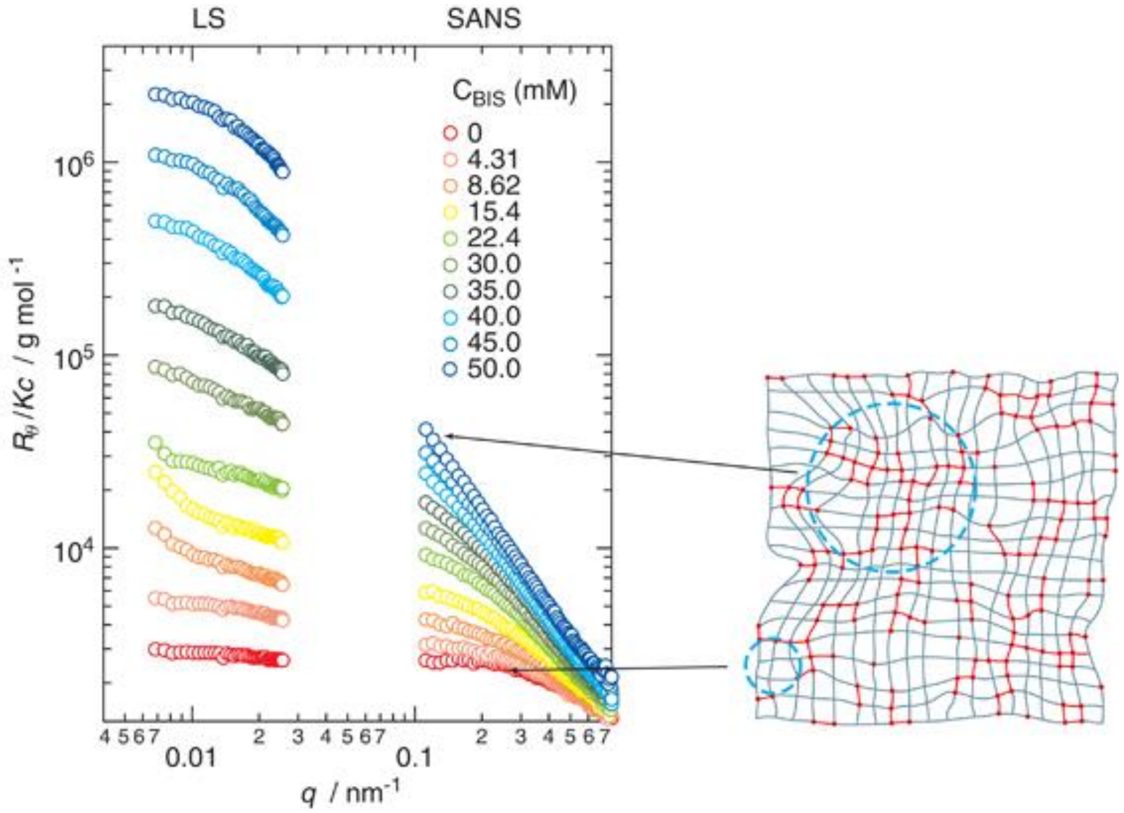

Fig. 5.9
Another example for scale invariance.
(a) Small-angle neutron scattering (SANS) and light scattering (LS) profiles of PNIPA gels and solution and (b) schematic representation of the gel network. Colors varying from red to blue denote increasing degree of crosslinking.
en.wikipedia.org/wiki/Polymer_scattering

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[24] The vacuum fluctuations in quantum mechanics are scale-invariant, as well. „Renormalization" avoids a few seemingly paradox phenomena, related to the vacuum fluctuations.

Remember

- On spatial scales larger than b and smaller than R_g, the chain conformation is scale-invariant.
- The fractal dimensions are 2 for the ideal random walk and 2.892 for the self-avoiding random walk.
- In the scale-invariant regime $S(q)$ plotted in log-log form is a straight line, where the negative slope is equal to the fractal dimension. Straight lines in log-log plots are characteristic for scale invariance.
- Scale invariance has consequences for modeling. Renormalization group theory applies. The exponents are universal in a certain sense. (The Flory exponent is universal.)
  The numerous types of fluctuations close to critical points are scale-invariant as well.

5.4 Restoring force onto an extended chain

When a polymer network is stretched, each individual chain is stretched, as well. The number of accessible microconformations then decreases. In the limit of the fully stretched chain, there is only one such microconformation. Because of $S = k_B \ln\Omega$ (S the entropy, Ω the number of microconformations) the entropy decreases with stretching. Stretching increases the free energy A because of $A = U - TS$. The decrease in entropy creates a restoring force. (The force onto the piston of a bicycle pump also is of entropic origin, if the expansion occurs at constant temperature, Box 7.1.)

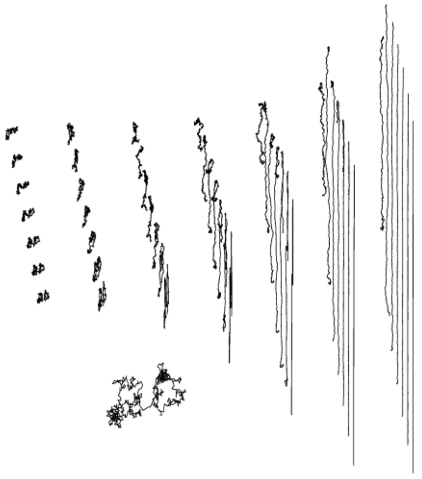


Fig. 5.10
Upon stretching, a polymer chain loses entropy. This loss of entropy drives rubber elasticity.
www.ahd.tudelft.nl/~frank/show-case.html

We make this argument quantitative below. The chain minimizes its free energy A, the latter given as

Eq. 5.11

$$A = U - TS = \text{const} - k_B T \ln\Omega(h)$$

h is the end-to-end distance (of the stretched or the unstretched chain). The number of microconformations is

Eq. 5.12

$$\Omega(h) \propto \Omega_0 \exp\left(-\frac{3h^2}{2\langle R_E^2\rangle}\right) = \Omega_0 \exp\left(-\frac{3h^2}{2Nb^2}\right)$$

Eq. 5.12 is more fundamental than Eq. 5.2. The distribution of end-to-end distances of a random walk with no correlations between steps[25] is a Gaussian. This is the content of the central limit theorem. It is relevant to all of statistics. The width of the Gaussian (often called σ) is $(Nb^2)^{1/2}$. Eq. 5.2 results from an integration of the form

---

[25] The absence of correlations is the central requirement for Gaussian statistics (even when errors in measurements are or are not distributed as Gaussians). Self-avoidance amounts to a correlation between segments, which are distant from each other on the chain. Such correlations between distant segments are not easily accounted for in modeling. The correlations between neighboring segments can be accounted for by grouping neighboring segments, such that they form „statistical segments“.

Eq. 5.13

$$\left\langle x^2 \right\rangle = \frac{\int\limits_{-\infty}^{\infty} x^2 \exp\left(-\frac{x^2}{2\sigma^2}\right)\mathrm{d}x}{\int\limits_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2\sigma^2}\right)\mathrm{d}x}$$

<x^2>It is the second moment of the underlying distribution of probabilities. If the distribution is a Gaussian, one has $\langle x^2\rangle = \sigma^2$. The integration leads to Eq. 5.2.

Ω_0 in Eq. 5.12 is a prefactor of no further interest. The factor of 3 in the numerator follows from the three dimensions. In increase in free energy caused by stretching is

Eq. 5.14

$$A_{stretch} = k_B T \frac{3h^2}{2Nb^2}$$

The elastic restoring force onto a stretched chain is[26]

Eq. 5.15

$$f_{el} = -\left(\frac{\mathrm{d}A}{\mathrm{d}h}\right)_{T,V} = -\left(\frac{\mathrm{d}\left(U - TS\right)}{\mathrm{d}h}\right)_{T,V} = k_B T\left(\frac{\mathrm{d}\ln\Omega\left(h\right)}{\mathrm{d}h}\right)_{T,V}$$

In the last step, we assumed that the internal energy, U, does not depend on chain stretching. (In steel, the internal energy, U, increases upon deformation. Steel shows enthalpy elasticity.[27]) Inserting Eq. 5.12 into Eq. 5.15 leads to:

Eq. 5.16

$$f_{el} = k_B T \frac{\mathrm{d}}{\mathrm{d}h}\left(\ln\left(\Omega_0\right) - \frac{3h^2}{2Nb^2}\right) = -\frac{3k_B T}{Nb^2} h = -\kappa_{rubber} h$$

In the last step, the spring constant, κ_{rubber}, was introduced. The spring constant in rubber elasticity is

Eq. 5.17

$$\kappa_{rubber} = -\left(\frac{\partial f_{el}}{\partial h}\right)_{T,V} = \frac{3k_B T}{Nb^2}$$

A reminder: We only considered the single chain. For networks see section 7.

<u>Remember</u>

- Rubber elasticity leads to an entropic force, which opposes the chain stretching.
- The spring constant of stretching is $3k_BT/(Nb^2)$.

---

[26] This reasoning behind this equation is sometimes called the "principle of virtual work". One also writes $\vec{F} = -\vec{\nabla}V$ with $\vec{F}$ the force and V the potential. In the case of rubber elasticity, the potential contains an entropic term.

[27] Enthalpy elasticity denotes an elasticity linked to potentials as opposed to an elasticity linked to kinetic energy. See Box 7.1.

5.5 Chains close to their maximum extension

At large extension, the force-displacement relation increases steeply because the length of the chain can never exceed the contour length. There are two separate equations for the freely jointed chain and the worm-like chain. DNA was shown to behave like a worm-like chain in experiments with optical tweezers (Fig. 5.12). The worm-like chain is flexible on all scales, while the freely jointed chain consists of rigid segments.

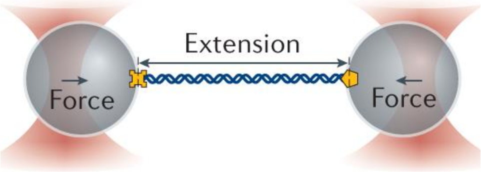


Fig. 5.11
Optical tweezers trap a glass sphere in the focus of a laser beam and closely monitor the sphere's position. The force onto the sphere is inferred from the slight displacement of the sphere away from the laser focus.
www.nature.com/articles/s43586-021-00021-6

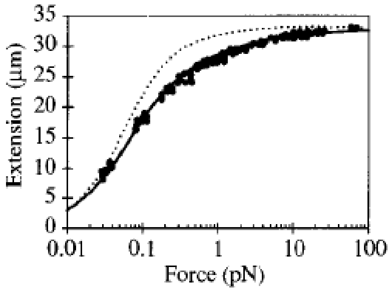


Fig. 2.16
Comparison of experimental force for 97 kilobase λ-DNA dimers with the worm-like chain model [solid curve is Eq. (2.119) with $R_{max} = 33\,\mu m$ and $b = 100\,nm$]. The dotted curve corresponds to the Langevin function of the freely jointed chain model [Eq. (2.112)]. Data are from R. H. Austin *et al.*, *Phys. Today*, Feb. 1997, p. 32.

Fig. 5.12
from Rubinstein/Colby
The measurement occurred with optical tweezers (Fig. 5.11)

Remember

- At large strain, rubber elasticity must be modified because the length of a chain can never exceed the contour length. Shortly before failure, the force-extension relation has a steep slope.

5.6 Deformed chains: thermal blobs

People, who appreciate simple arguments, derive the energy contained in strain stretching from the so-called "thermal blobs". On short scales, a stretched chain looks like random coil. A "short scale" here implies a sphere with the radius of a "blob". The entire chain is depicted as a sequence of blobs (Fig. 5.13). The line of reasoning is that every blob takes away one degree of freedom from the chain conformation. Following an argument similar to what is explained in section 5.8, every blob adds k_BT to free energy of the chain. S decreases and A increases in consequence. The energy contained in stretching is N_bk_BT with N_b the number of blobs. Let n_b be the number segments per blob. n_b is given an R_b^2/b^2 with R_b the radius of the blob.[28] We collect relations as follows:

---

[28] For the self-avoiding chain, the exponent of 2 is replaced by $0.588^{-2} = 2.892$.

Eq. 5.18

$$R_b = \sqrt{n_b}\, b = \sqrt{\frac{N}{N_b}}\, b = \sqrt{\frac{NR_b}{h}}\, b$$

$$R_b = \frac{N}{h} b^2$$

$$A_{stretch} = N_b k_B T = \frac{h}{R_b} k_B T = \frac{h^2}{Nb^2} k_B T$$

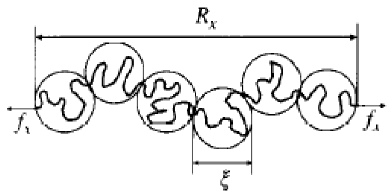


Fig. 2.13
An elongated chain is only stretched on its largest length scales. Inside the tension blob, the conformation of the chain is essentially unperturbed by the stretch.

Fig. 5.13
from Rubinstein/Colby

Ignoring the numerical factor of 3/2, this results agrees with Eq. 5.14.

<u>Remember</u>

– The energy contained in deformation is $N_b k_B T$ with N_b the number of blobs.

5.7 Chains confined to a slit

The blob picture is simple and good enough for quick estimates. We drive this insight home by estimating the energy needed to confine a chain to a slit of with *h*. The blob radius is *h*/2. The number of segments in a blob is $n_b = (h/(2b))^2$. The number of blobs is $N_b = N/n_b$ and the energy contained in the compression is

Eq. 5.19

$$A_{slit} = \frac{2Nb^2}{h^2} k_B T$$

Polymer chains resist compression. If a colloidal sphere is coated with a polymer brush, the brush resists compression. (The mathematics is slightly different from Eq. 5.19 in the case of the brush.[29]) This mechanism stabilizes colloids against aggregation (leads to “steric stabilization”).

<u>Remember</u>

– Polymer chains resist compression.
– This is exploited for the steric stabilization of colloids.

5.8 Derivation of the Flory exponent from an energy balance

Before the Flory exponent was determined by computer simulation, Flory had made a prediction of it, based on the energies contained in swelling and in the mutual exclusion of segments from the same site. He assumed the energy in swelling to be essentially the same as the energy in stretching, following rubber elasticity (where *R* states the role of *h*). Following Eq. 5.14, Flory assumed

Eq. 5.20

$$A_{swell} = \frac{3k_B T}{2Nb_2} R^2$$

---

[29] A polymer brush is an ensemble of terminally attached chains, where the high grafting density leads to a stretching of the chains away from the substrate.

For increase in free energy caused by the exclusions he assumed

Eq. 5.21

$$A_{exclusion,tot} = k_B T \quad \mathrm{v} b^3 c^2 \; R^3 = k_B T \quad \mathrm{v} b^3 \frac{N^2}{R^6} R^3$$

The terms make sense:

- Because the interaction is entropic in nature, the prefactor must be $k_\mathrm{B}T$.
- The probability of two segments hitting each other is proportional to the square of the concentration. Flory assumes the concentration to be everywhere the same inside the coil (a much simplifying approximation). Flory assumes $c \approx N/R^3$ in the second step.
- The probability of two segments hitting each other is proportional to the volume of the segments, $\mathrm{v}b^3$. More precisely, it is proportional to the “excluded volume” (section 6).
- The total energy in the overlap must be proportional to the volume of the coil, which is $4\pi/3\ R^3 \approx R^3$.

That the prefactor should be $k_\mathrm{B}T$ per exclusion (as opposed to, say, $10^{-6}\ k_\mathrm{B}T$) requires some hand-waiving. Consider the pressure-volume work in the ideal gas, which is $-p\mathrm{d}V = -nRT/V\ \mathrm{d}V = -Nk_BT/V\ \mathrm{d}V$. $N = N_\mathrm{A}n$ is the number of particles. In condensed matter (ignore the difference between a gas condensed matter), the volume is $V = N\mathrm{v}b^3$ with $\mathrm{v}b^3$ the volume per particle. If $\mathrm{d}V$ also is equal to $\mathrm{v}b^3$ (ignore the minus sign), the term $p\mathrm{d}V$ turns into $k_\mathrm{B}T$.

Flory equates the two energies:

Eq. 5.22

$$k_B T \quad \mathrm{v} b^3 \frac{N^2}{R^6} R^3 = \frac{3 k_B T}{N b^2} R^2$$

Some algebraic manipulation leads to

Eq. 5.23

$$R \propto N^{3/5} = N^{0.6}$$

Remember

- Self-avoidance leads to a loss of entropy and hence to an increase in free energy.
- The increase in free energy is $k_\mathrm{B}T$ per exclusion.
- Equating the energies contained in self-avoidance and in swelling, Flory arrived at a Flory exponent of 3/5.

6 Interactions between segments

6.1 *The 2nd virial coefficient*

Formally, the 2nd virial coefficient is related to the osmotic pressure. However, the 2nd virial coefficient is of much importance beyond osmosis. It quantifies the degree, to which segments repel or attract each other. If they repel each other, the chain swells and takes up solvent. This provides the link to osmosis. The interaction is more important than osmosis.

On a fundamental level, the osmotic pressure obeys

Eq. 6.1

$$\Pi = -\left(\frac{\mathrm{d}\left(\Delta_{mix}G\right)}{\mathrm{d}V}\right)_{nPol} = -\left(\frac{\mathrm{d}\left(\Delta_{mix}H - T\Delta_{mix}S\right)}{\mathrm{d}V}\right)_{nPol}$$

Note the analogy with ordinary pressure ($p = -(\mathrm{d}U/\mathrm{d}V)_S$ because $\mathrm{d}U = -p\mathrm{d}V + T\mathrm{d}S$). The mixing entropy is

Eq. 6.2

$$\Delta_{mix}S = -nR\left(x_1 \ln x_1 + x_2 \ln x_2\right)$$

1 and 2 denote the majority component (the solvent) and the minority component (the polymer). x is the mole fraction. Note: If the mass concentration of the polymer in units of g/L is known (it often is), the polymer mole fraction is only known if the molecular weight is known, as well.

For small concentration, the van t'Hoff equation predicts:

Eq. 6.3

$$\Pi = RT\,\frac{n_{\mathrm{chain}}}{V}$$

In the dilute limit, the osmotic pressure depends only on the particle number (equivalent to amount of substance) of the minority component(s). Π is a "colligative property". Note again the analogy with the ideal gas ($p = RTn/V$).

We stay with the van t'Hoff equation for one more paragraph. For polymers, the number density of chains is given as

Eq. 6.4

$$\frac{n_{\mathrm{chain}}}{V} = \frac{1}{M_n}c$$

c is the concentration in units of g/L. It follows that the molecular weight M_n can be calculated from the osmotic pressure. $M_n = (\Sigma_i n_i M_i)/(\Sigma_i n_i)$ is the number-averaged molecular weight (to be distinguished from the weight-averaged molecular weight as determined in static light scattering).[30] Note: Short chains generate a large osmotic pressure because the short chains are the numerous chains (assuming a fixed mass concentration).

---

[30] Why, exactly, osmometry determines the number-averaged molecular weight, is not quickly explained.

If the chains are even moderately long, their number of chains is small even if the volume fraction is substantial. The 1st term of virial expansion then often is small and one must take the 2nd term into account. First to the general case: One writes:

E. 6.5

$$\Pi = RT\left(\frac{n}{V} + B_2\left(\frac{n}{V}\right)^2 + ...\right) = RT\frac{n}{V}\left(1 + B_2\frac{n}{V} + ...\right)$$

B_2 is the 2nd virial coefficient. It quantifies the influence of pair interactions on the osmotic pressure. That we deal with pair interactions, can be seen from the fact that B_2 is a coefficient to $(n/V)^2$. $(n/V)^2$ governs the probability that two particles meet.

B_2 has the dimensions of volume/mol. B_2 is also called "excluded volume", where "effective excluded volume" would be the more accurate term. In simple models (without attractive interactions), B_2 is the molar volume of the solute. In the context of polymers, one often writes $B_2 = N_A \mathrm{v} b^3$ with v the "excluded volume parameter". v is a dimensionless number of order 1. (v may be negative.)

Again, the molecular weight often is not known, a priori. However, osmometry determines both the molecular weight and the second virial coefficient. We leave that mathematics aside. For polymers, the virial expansion is written as:

Eq. 6.6

$$\frac{\Pi}{RTc} = \frac{1}{M_n} + A_{2,w}c$$

c is the concentration in units of g/L. $A_{2,w}$ is the "mass-based 2nd virial coefficient". For how $A_{2,w}$ is linked to v, see Eq. 6.14. The unit is $\mathrm{m^3\ kg^{-2}\ mol^{-1}}$. $A_{2,w}$ does not depend on molecular weight. Numerical values are tabulated in the polymer handbook for many polymer-solvent pairs. $A_{2,w}$ depends on temperature.

$A_{2,w}$ can be determined via osmometry. An alternative is static light scattering (more generally: are scattering methods). The more positive $A_{2,w}$, the lower the tendency of the solution to build up concentration fluctuations. Scattering methods make concentration fluctuations visible in one way or another. When the 2nd virial coefficient is negative, the system tends to segregate (depending on the molecular weight: long chains flocculate immediately, shorter chains somewhat later).

6.2 The χ-parameter and the excluded volume parameter, v

One might think that the 2nd virial coefficient was zero for "ideal" conditions. However, the 2nd virial coefficient is *not* zero, if the mixing enthalpy, $\Delta_{\mathrm{mix}}H$, vanishes. We take a step back and discuss some elements of the "regular solution theory". In regular solution theory $\Delta_{\mathrm{mix}}H$ is approximated as

Eq. 6.7

$$\frac{\Delta_{mix}H}{nRT} = \chi\, x_1 x_2$$

x_1 and x_2 are the mole fractions. This hypothesis was guided by the pair interaction. The probability of molecules "1" and "2" meeting each other is proportional to the product of the mole fractions. When the experiment disagrees with this assumption (if often does so, slightly) the χ-parameter becomes a function of concentration.

In order to let χ be dimensionless number of order unity, $\Delta_{\mathrm{mix}}H$ was divided by nRT. (The 2nd virial coefficient was divided by $N_A b^3$ with the same goal. This leads to the parameter v.) The χ-parameter is often (but not always) larger than zero. It is rarely much larger than 1. In regular-solution theory, the interactions have no influence on the mixing entropy. Also, the mixing volume is assumed to be zero.

Defining the χ-parameter this way is not meant to say that mixing enthalpy actually was proportional to temperature. On the contrary, it is not and χ therefore is a function of temperature. It often decreases with increasing temperature, meaning that the solubility increases with increasing temperature.

If χ becomes a function of composition, the predictive power of regular-solution theory is not all that great. It is still common to use the χ-parameter when discussing solutions and mixtures rather than $\Delta_{\mathrm{mix}}H(x_1,x_2,T)$. That is a matter of language, mostly. The Polymer Handbook contains numerous tables on how the χ-parameter of certain polymer-solvent pairs depends on temperature and polymer concentration.

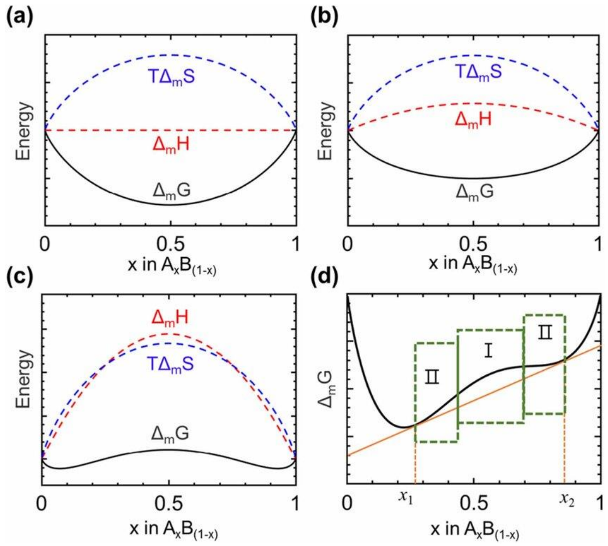


Fig. 6.1
The competition between a positive enthalpy of mixing and a negative entropy of mixing leads to the characteristic double-well structure in the plot of $\Delta_{\mathrm{mix}}G$ versus composition.
www.researchgate.net/figure/Mixing-free-enthalpy-D-mG-mixing-enthalpy-D-mH-and-mixing-entropy-term-TD-mS-for_fig1_357598481

For the free enthalpy of mixing, regular solution theory predicts

Eq. 6.8

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S = nRT\left(x_1 \ln x_1 + x_2 \ln x_2 + \chi x_1 x_2\right)$$

In the context of polymers, the mole fraction, x, is usually replaced by the volume fraction, ϕ

Eq. 6.9

$$\phi = \frac{b^3 n_{chain} N}{V}$$

The volume of a segment is assumed to be b^3. Moreover, the chain segments and the solvent molecules have the same volume. n_{chain} is the number of chains. N is the number of segments per chain and V is the total volume.

Using volume fractions instead of mole fractions, the free enthalpy of mixing is

Eq. 6.10

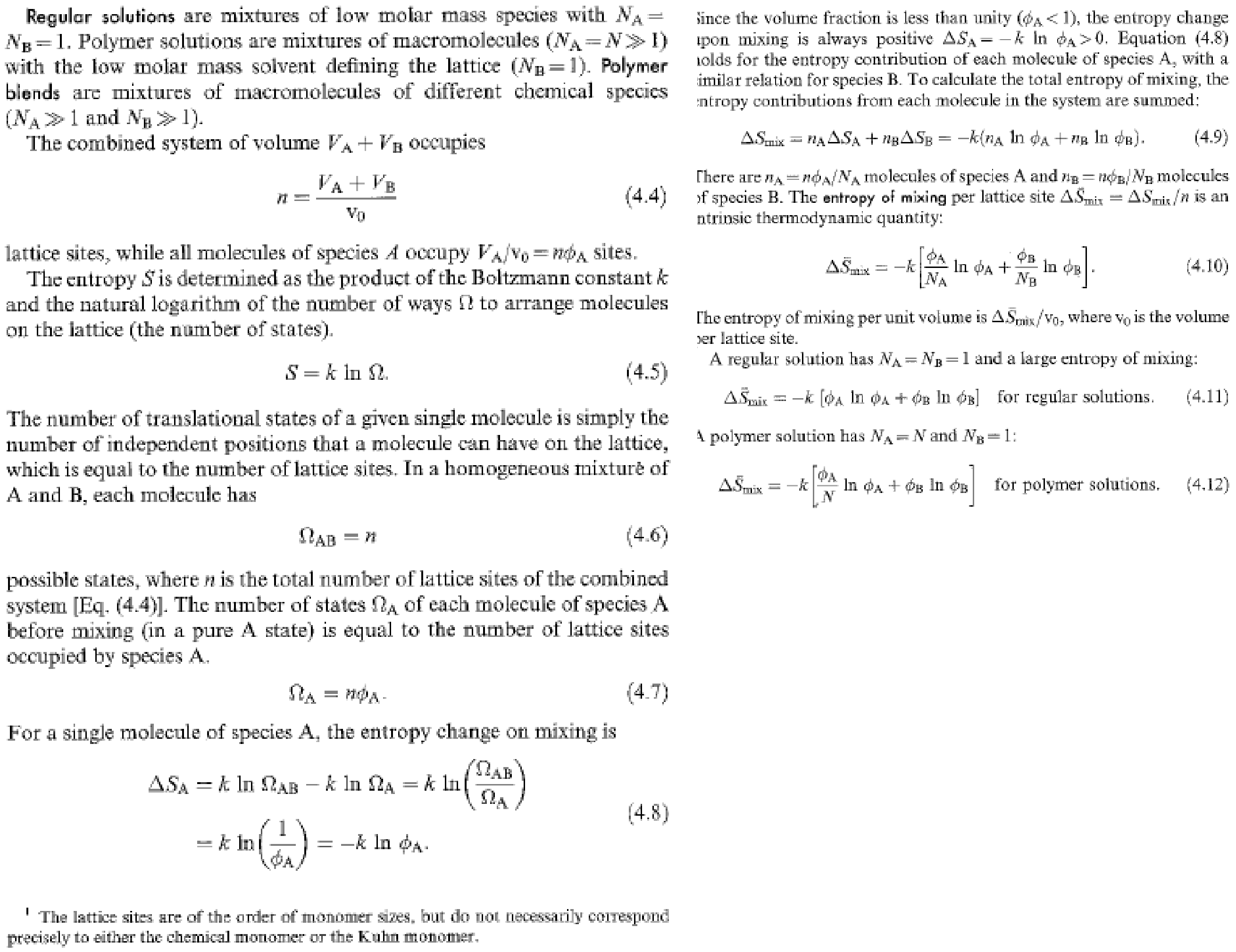
$$\Delta_{mix}G = nRT\left(\phi_1 \ln \phi_1 + \frac{1}{N}\phi_2 \ln \phi_2 + \chi\phi_1\phi_2\right)$$

The derivation is shown in Box 6.1. For the polymer in the solvent, ϕ^2 is renamed as $\phi_{pol} = \phi$. The relation $\phi_1 = 1 - \phi_2 = 1 - \phi$ leads to

Eq. 6.11

$$\Delta_{mix}G = nRT\left(\frac{1}{N}\phi\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right)$$

A side remark: When two polymers are mixed, there is a factor 1/*N* before both parts of the entropic term. The mixing entropy is small because the number of chains is small. Two polymers rarely mix well.[31] Copolymerization must be employed instead.[32]



Regular solutions are mixtures of low molar mass species with $N_A = N_B = 1$. Polymer solutions are mixtures of macromolecules ($N_A = N \gg 1$) with the low molar mass solvent defining the lattice ($N_B = 1$). **Polymer blends** are mixtures of macromolecules of different chemical species ($N_A \gg 1$ and $N_B \gg 1$).

The combined system of volume $V_A + V_B$ occupies

$$n = \frac{V_A + V_B}{v_0} \tag{4.4}$$

lattice sites, while all molecules of species *A* occupy $V_A/v_0 = n\phi_A$ sites.

The entropy *S* is determined as the product of the Boltzmann constant *k* and the natural logarithm of the number of ways Ω to arrange molecules on the lattice (the number of states).

$$S = k \ln \Omega. \tag{4.5}$$

The number of translational states of a given single molecule is simply the number of independent positions that a molecule can have on the lattice, which is equal to the number of lattice sites. In a homogeneous mixture of A and B, each molecule has

$$\Omega_{AB} = n \tag{4.6}$$

possible states, where *n* is the total number of lattice sites of the combined system [Eq. (4.4)]. The number of states Ω_A of each molecule of species A before mixing (in a pure A state) is equal to the number of lattice sites occupied by species A.

$$\Omega_A = n\phi_A. \tag{4.7}$$

For a single molecule of species A, the entropy change on mixing is

$$\begin{aligned}\Delta S_A &= k \ln \Omega_{AB} - k \ln \Omega_A = k \ln\left(\frac{\Omega_{AB}}{\Omega_A}\right)\\ &= k \ln\left(\frac{1}{\phi_A}\right) = -k \ln \phi_A.\end{aligned} \tag{4.8}$$

[1] The lattice sites are of the order of monomer sizes, but do not necessarily correspond precisely to either the chemical monomer or the Kuhn monomer.

ince the volume fraction is less than unity ($\phi_A < 1$), the entropy change pon mixing is always positive $\Delta S_A = -k \ln \phi_A > 0$. Equation (4.8) olds for the entropy contribution of each molecule of species A, with a imilar relation for species B. To calculate the total entropy of mixing, the ntropy contributions from each molecule in the system are summed:

$$\Delta S_{mix} = n_A \Delta S_A + n_B \Delta S_B = -k(n_A \ln \phi_A + n_B \ln \phi_B). \tag{4.9}$$

here are $n_A = n\phi_A/N_A$ molecules of species A and $n_B = n\phi_B/N_B$ molecules f species B. The **entropy of mixing** per lattice site $\Delta\bar{S}_{mix} = \Delta S_{mix}/n$ is an ntrinsic thermodynamic quantity:

$$\Delta\bar{S}_{mix} = -k\left[\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B\right]. \tag{4.10}$$

he entropy of mixing per unit volume is $\Delta\bar{S}_{mix}/v_0$, where v_0 is the volume er lattice site.

A regular solution has $N_A = N_B = 1$ and a large entropy of mixing:

$$\Delta\bar{S}_{mix} = -k\left[\phi_A \ln \phi_A + \phi_B \ln \phi_B\right] \quad \text{for regular solutions.} \tag{4.11}$$

polymer solution has $N_A = N$ and $N_B = 1$:

$$\Delta\bar{S}_{mix} = -k\left[\frac{\phi_A}{N}\ln\phi_A + \phi_B \ln\phi_B\right] \quad \text{for polymer solutions.} \tag{4.12}$$

Box 6.1: Derivation of Eq. 6.10.
Rubinstein/Colby: "Polymer Physics", Oxford University Press 2003

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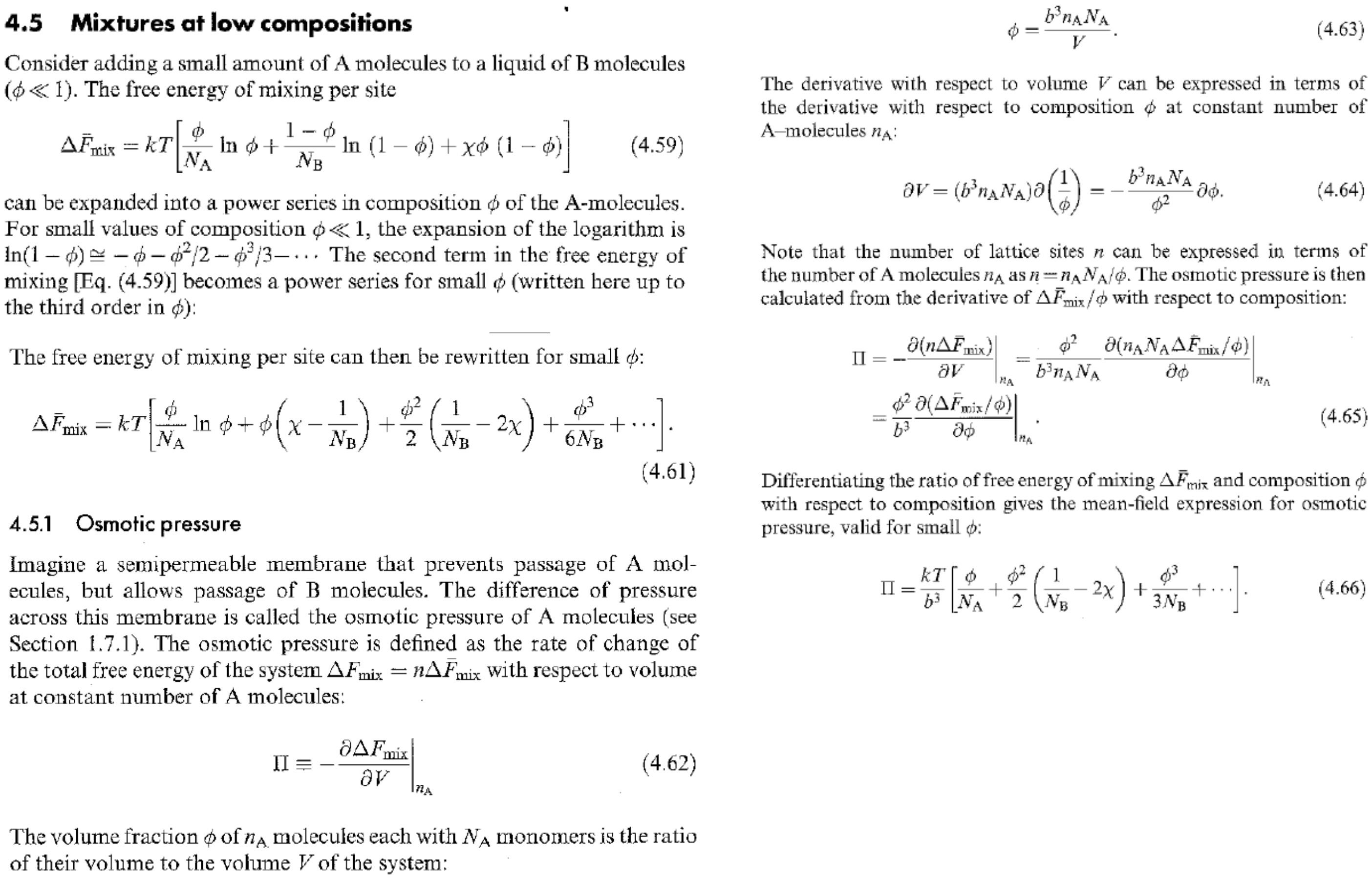
[31] When mixing two polymers by stirring and cooling this mixture to below the glass temperature, one obtains a „polymer blend“. A polymer blend consists of well interspersed phases of the two species. These are kinetically stable because the sample does not flow.

[32] Do not confuse copolymerization with „alloying“ as practiced with metals. Alloys often have properties much different from the constituents. (Think of the permanent magnets composed of $Nd_2Fe_{14}B$.) That does not happen with polymers. The properties of mixtures or copolymers usually are in-between the respective properties of the constituents.



4.5 Mixtures at low compositions

Consider adding a small amount of A molecules to a liquid of B molecules ($\phi \ll 1$). The free energy of mixing per site

$$\Delta\bar{F}_{\mathrm{mix}} = kT\left[\frac{\phi}{N_{\mathrm{A}}}\ln\phi + \frac{1-\phi}{N_{\mathrm{B}}}\ln(1-\phi) + \chi\phi(1-\phi)\right] \tag{4.59}$$

can be expanded into a power series in composition ϕ of the A-molecules. For small values of composition $\phi \ll 1$, the expansion of the logarithm is $\ln(1-\phi) \cong -\phi - \phi^2/2 - \phi^3/3 - \cdots$ The second term in the free energy of mixing [Eq. (4.59)] becomes a power series for small ϕ (written here up to the third order in ϕ):

The free energy of mixing per site can then be rewritten for small ϕ:

$$\Delta\bar{F}_{\mathrm{mix}} = kT\left[\frac{\phi}{N_{\mathrm{A}}}\ln\phi + \phi\left(\chi - \frac{1}{N_{\mathrm{B}}}\right) + \frac{\phi^2}{2}\left(\frac{1}{N_{\mathrm{B}}} - 2\chi\right) + \frac{\phi^3}{6N_{\mathrm{B}}} + \cdots\right]. \tag{4.61}$$

4.5.1 Osmotic pressure

Imagine a semipermeable membrane that prevents passage of A molecules, but allows passage of B molecules. The difference of pressure across this membrane is called the osmotic pressure of A molecules (see Section 1.7.1). The osmotic pressure is defined as the rate of change of the total free energy of the system $\Delta F_{\mathrm{mix}} = n\Delta\bar{F}_{\mathrm{mix}}$ with respect to volume at constant number of A molecules:

$$\Pi \equiv -\left.\frac{\partial \Delta F_{\mathrm{mix}}}{\partial V}\right|_{n_{\mathrm{A}}} \tag{4.62}$$

The volume fraction ϕ of n_{A} molecules each with N_{A} monomers is the ratio of their volume to the volume V of the system:

$$\phi = \frac{b^3 n_{\mathrm{A}} N_{\mathrm{A}}}{V}. \tag{4.63}$$

The derivative with respect to volume V can be expressed in terms of the derivative with respect to composition ϕ at constant number of A–molecules n_{A}:

$$\partial V = (b^3 n_{\mathrm{A}} N_{\mathrm{A}})\,\partial\left(\frac{1}{\phi}\right) = -\frac{b^3 n_{\mathrm{A}} N_{\mathrm{A}}}{\phi^2}\,\partial\phi. \tag{4.64}$$

Note that the number of lattice sites n can be expressed in terms of the number of A molecules n_{A} as $n = n_{\mathrm{A}} N_{\mathrm{A}}/\phi$. The osmotic pressure is then calculated from the derivative of $\Delta\bar{F}_{\mathrm{mix}}/\phi$ with respect to composition:

$$\begin{aligned}\Pi &= -\left.\frac{\partial(n\Delta\bar{F}_{\mathrm{mix}})}{\partial V}\right|_{n_{\mathrm{A}}} = \frac{\phi^2}{b^3 n_{\mathrm{A}} N_{\mathrm{A}}}\left.\frac{\partial(n_{\mathrm{A}} N_{\mathrm{A}}\Delta\bar{F}_{\mathrm{mix}}/\phi)}{\partial\phi}\right|_{n_{\mathrm{A}}} \\ &= \frac{\phi^2}{b^3}\left.\frac{\partial(\Delta\bar{F}_{\mathrm{mix}}/\phi)}{\partial\phi}\right|_{n_{\mathrm{A}}}.\end{aligned} \tag{4.65}$$

Differentiating the ratio of free energy of mixing $\Delta\bar{F}_{\mathrm{mix}}$ and composition ϕ with respect to composition gives the mean-field expression for osmotic pressure, valid for small ϕ:

$$\Pi = \frac{kT}{b^3}\left[\frac{\phi}{N_{\mathrm{A}}} + \frac{\phi^2}{2}\left(\frac{1}{N_{\mathrm{B}}} - 2\chi\right) + \frac{\phi^3}{3N_{\mathrm{B}}} + \cdots\right]. \tag{4.66}$$

Box 6.2: Derivation of Eq. 6.12.
Rubinstein/Colby: "Polymer Physics", Oxford University Press 2003

The calculation of the derivative $d\Delta_{mix}G/dV$ is tedious. It is reproduced in Box 6.2. It is found that

Eq. 6.12

$$\begin{aligned}\Pi &= \frac{RT}{N_A b^3}\left(\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2\right) \\ &\approx \frac{RT}{N_A b^3}\left(\left(\frac{1}{2} - \chi\right)\phi^2\right) = \frac{k_B T}{b^3}\frac{\mathrm{v}}{2}\phi^2\end{aligned}$$

In the 2nd step, the term proportional to $1/N$ was neglected. In the 3rd step the "excluded volume parameter", v, was introduced as

Eq. 6.13

$$\mathrm{v} = 1 - 2\chi$$

Sometimes “v” also is the excluded volume (“v” = $(1-2\chi)b^3$).

A few further remarks:

- v can be negative if there are attractive interactions.
- V and the "mass-based 2nd virial coefficient" (Eq. 6.6) are related as

$$\mathrm{v} = \frac{2M_0^2}{b^3 N_{Avo}} A_{2,w} = 1 - 2\chi$$ Eq. 6.14

M_0 is molecular weight of a segment.

- It is not true that the second virial coefficient would vanish at zero enthalpy of mixing. There are two separate meanings of in „ideal“. Ideal can either mean $d\Delta_{mix}H = 0$ or mean $\mathrm{v} = 0$.

If the $\mathrm{v} < 1$, there is an attractive interaction between the segments which lowers the excluded volume. Pseudo-ideal behavior results when χ = =1/2. This is the „θ-condition". At the θ-point, chains in a solvent obey the ideal random-walk statistics (synonymous to Gaussian statistics). Otherwise, they follow the self-avoiding random walk. At the θ-point, R_E scales as $N^{1/2}$. In a good solvent, it scales like N^{ν} with $\nu \approx 0.588$ the Flory exponent. For the collapsed single chain in the bad solvent, it scales like $N^{1/3}$, because the sphere radius scales as $V^{1/3}$ with V the sphere volume (but in this case the polymer usually precipitates). For an experimental example, see Fig. 6.2.

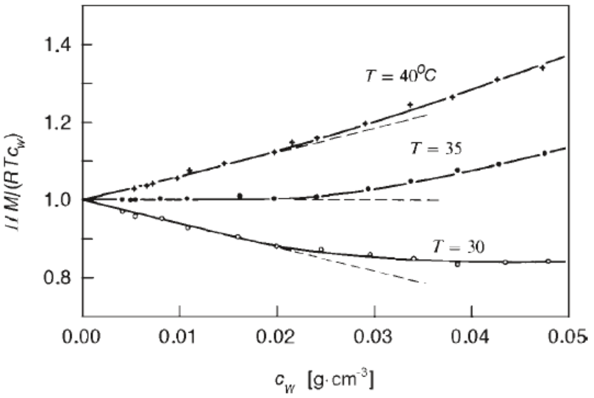


Fig. 2.12. Concentration and temperature dependence of the osmotic pressure measured for solutions of PS ($\overline{M}_n = 1.3 \times 10^5\,\mathrm{g\,mol^{-1}}$) in cyclohexane. Data from Strazielle in [2]

Fig. 6.2
G. Strobl: The Physics of Polymers

6.3 Phase separation, USCT and LCST behavior

At $\mathrm{v} < 0$, chains become compact, but that is not often observed in experiment, because the polymer-rich phase precipitates. There is demixing with a critical point. Because of the $1/N$-term in Eq. 6.11, the critical polymer volume fraction lies to the left in the diagram. ϕ_{crit} is less than 1/2. The higher the molecular weight, the lower is ϕ_{crit} (see Fig. 6.3).

If the χ-parameter would not depend on temperature, Eq. 6.11 would be athermal in the sense that the temperature was a prefactor and that the balance between the different terms therefore was not affected by temperature. However, the enthalpy of mixing is not usually proportional to T. (Why should that be so.) In consequence, χ is a function of T. In organic solvents, the mixing entropy favors mixing at high temperature and precipitation at low temperature. The USCT is the “upper critical solution temperature”. The temperature scale might converted into a χ-scale, where high temperature corresponds to low χ. The larger the molecular weight, the closer is χ_{crit} to 1/2.

In water the hydrophobic interaction increases in strength at high temperature because of its entropic origin. Water-soluble polymers often precipitate at high temperature, which leads to LCST behavior (LCST for “lower critical solution temperature”). Fig. 6.3 elaborates on UCST and LCST behavior.

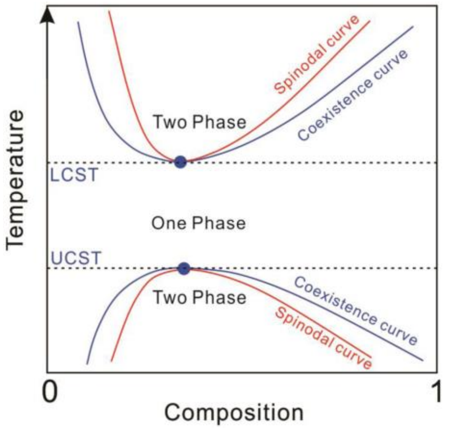


Fig. 6.3
UCST and LCST behavior
www.researchgate.net/figure/The-UCST-and-LCST-of-water_fig12_299584220

Remember

- For polymers, the mixing entropy tends to small because the small number of chains (compared to small molecules).
- Two polymers are rarely miscible for that reason.
- The 2nd virial coefficient is important for that reason. The 2nd virial coefficient quantifies the interactions between segments (repulsive, attractive, or neutral).
- The 2nd virial coefficient can be expressed in terms of the parameters $A_{2,w}$, χ, or v.
- At v = 0 (equivalent to $\chi = 1/2$) polymer solutions are pseudo-ideal (the θ-condition).
- χ usually depends on temperature. At large χ, there is phase separation. For large molecular weight, the critical point is at low polymer volume fraction and at χ slightly larger than 1/2.
- There is both UCST and LCST behavior.

7 Elastomers

7.1 Affine deformation

When modeling the mechanics of networks, one builds on the spring constant of the single chain. In the affine network, the crosslinks do not fluctuate. They are displaced in the same way as the entire sample is deformed, macroscopically. In a first step, we derive the shear modulus this network. The deformation is quantified in terms of relative extensions, λ_x ,λ_y, λ_z. The undeformed medium has $\lambda_x = \lambda_y = \lambda_z = 1$. The following text closely follows section 7.2.1 from Rubinstein/Colby with some omissions.

The entropy of a single deformed network strand[33] is

Eq. 7.1

$$
\begin{aligned}
S\left(N,\vec{R}\right)-S\left(N,\vec{R}_0\right) &= -\frac{3}{2}k_B\left(\frac{R_x^2+R_y^2+R_z^2}{Nb^2}-\frac{R_{x,0}^2+R_{y,0}^2+R_{z,0}^2}{Nb^2}\right)\\
&= -\frac{3}{2}k_B\left(\frac{\left(\lambda_x^2-1\right)R_{x,0}^2+\left(\lambda_y^2-1\right)R_{y,0}^2+\left(\lambda_z^2-1\right)R_{z,0}^2}{Nb^2}\right)
\end{aligned}
$$

For the entire network, we have

Eq. 7.2

$$
\begin{aligned}
\Delta S_{net} &= -\frac{3}{2}\frac{k_B}{Nb^2}\left(\left(\lambda_x^2-1\right)\sum_{strands}R_{x,0,i}^2+\left(\lambda_y^2-1\right)\sum_{strands}R_{y,0,i}^2+\left(\lambda_z^2-1\right)\sum_{strands}R_{z,0,i}^2\right)\\
&= -\frac{3}{2}\frac{k_B n}{Nb^2}\left(\left(\lambda_x^2-1\right)\left\langle R_{x,0,i}^2\right\rangle+\left(\lambda_y^2-1\right)\left\langle R_{y,0,i}^2\right\rangle+\left(\lambda_z^2-1\right)\left\langle R_{z,0,i}^2\right\rangle\right)
\end{aligned}
$$

n is the number of network strands. For the averages in Eq. 7.2 we have

Eq. 7.3

$$
\left\langle R_{x,0,i}^2\right\rangle=\left\langle R_{y,0,i}^2\right\rangle=\left\langle R_{y,0,i}^2\right\rangle=\frac{Nb^2}{3}
$$

The factor of 1/3 occurs because the sum of all three terms to the left equals Nb^2. Inserting Eq. 7.11 into Eq. 7.2 leads to

Eq. 7.4

$$
\begin{aligned}
\Delta S_{net} &= -\frac{3}{2}\frac{k_B}{Nb^2}\left(\left(\lambda_x^2-1\right)\frac{nNb^2}{3}+\left(\lambda_y^2-1\right)\frac{nNb^2}{3}+\left(\lambda_z^2-1\right)\frac{nNb^2}{3}\right)\\
&= -\frac{1}{2}k_B n\left(\lambda_x^2+\lambda_y^2+\lambda_z^2-3\right)
\end{aligned}
$$

The increase in free energy is

Eq. 7.5

$$
\Delta A_{net}=\Delta U_{net}-T\Delta S_{net}=\frac{1}{2}nk_BT\left(\lambda_x^2+\lambda_y^2+\lambda_z^2-3\right)
$$

---

[33] A network strand is a chain linking two crosslinks.

Consider extension along x, let the medium be incompressible, and rename λ_x as λ.

Eq. 7.6

$$\begin{aligned}\lambda_x &= \lambda, \\ \lambda_y &= \lambda_z = \lambda^{-1/2}\end{aligned}$$

The restoring force created by the deformation is

Eq. 7.7

$$\begin{aligned}f_x &= \frac{\partial \Delta A}{\partial L_x} = \frac{\partial \Delta A}{\partial\left(\lambda L_{x,0}\right)} = \frac{\partial \Delta A}{\partial\left(\lambda L_{x,0}\right)} = \frac{1}{L_{x,0}}\frac{\partial}{\partial \lambda}\left(\frac{1}{2} n k_B T\left(\lambda^2 + \frac{2}{\lambda} - 3\right)\right) \\ &= \frac{1}{L_{x,0}} n k_B T\left(\lambda - \frac{1}{\lambda^2}\right)\end{aligned}$$

The "true" stress (to be distinguished from the engineering stress, see Eq. 7.15) is

Eq. 7.8

$$\sigma_{xx} = \frac{f_x}{L_y L_z} == \frac{1}{L_y L_z L_{x,0}} n k_B T\left(\lambda - \frac{1}{\lambda^2}\right) = \frac{\lambda}{V} n k_B T\left(\lambda - \frac{1}{\lambda^2}\right) = \frac{n}{V} k_B T\left(\lambda^2 - \frac{1}{\lambda}\right)$$

Box 7.1: Is the pressure of the ideal gas of entropic origin?

We have twice encountered expressions, which resembled the ideal gas law (Eq. 6.3 and Eq. 7.10). In both cases, entropy caused a pressure or a stress. Can the pressure of the ideal gas also be traced back to entropy? That depends on whether the expansion occurs adiabatically of isothermally. In the reversible adiabatic expansion, dS = 0 and one writes

$$p = -\left(\frac{\mathrm{d}U}{\mathrm{d}V}\right)_S$$

In this case, the pressure is caused by the kinetic energy. Deriving the ideal gas law from this relation is a bit tedious. The algebra is provided in box 8.2 in the notes of Physical Chemistry I.

For the isothermal expansion, one writes

$$p = -\left(\frac{\mathrm{d}A}{\mathrm{d}V}\right)_T = -\left(\frac{\mathrm{d}U}{\mathrm{d}V}\right)_T + T\left(\frac{\mathrm{d}S}{\mathrm{d}V}\right)_T$$

$(\mathrm{d}U/\mathrm{d}V)_T$ is zero for the ideal gas. The kinetic energy of the ideal gas does not depend on volume. The entropy of the ideal gas is given by the Sackur-Tetrode equation:

$$\frac{S}{k_B N} = \ln\frac{V}{\Lambda^3 N} + \frac{5}{2} = \ln V - \ln\left(\Lambda^3 N\right) + \frac{5}{2}$$

The thermal wavelength, Λ, does not depend on V. The differentiation leads to

$$p = T\left(\frac{\mathrm{d}S}{\mathrm{d}V}\right)_T = T\left(\frac{\mathrm{d}}{\mathrm{d}V}\left(k_B N \ln V\right)\right)_T = N\frac{k_B T}{V} = \frac{nRT}{V}$$

This is the ideal gas law.

To answer the question: The pressure of the ideal gas is of entropic origin, *when T is maintained constant.*

A similar argument can be made for the relation $G = \nu RT$. If stretching is done adiabatically, the temperature increases. When the rubber band is reversibly relaxed, the temperature decreases. The work, which it does while bringing the two ends holding it closer together, is extracted from the kinetic energy of the network strands wiggling around.

The small deformation limit, one writes $\lambda = 1 + \varepsilon$ with $\varepsilon \ll 1$. Start from Eq. 7.14, use $C_2 = 0$, and Taylor expand the result in ε:

Eq. 7.9

$$\sigma_{xx} = \frac{f_x}{L_y L_z} = \frac{1}{V} n k_B T \left((1+\varepsilon)^2 - \frac{1}{(1+\varepsilon)} \right) =$$
$$= \frac{1}{V} n k_B T \left((1+2\varepsilon) - (1-\varepsilon) \right) = \frac{n}{V} k_B T 3\varepsilon = E\varepsilon$$

The Youngs modulus $E = \sigma_{xx}/\varepsilon$ was introduced in the last step. Without proof we report that $E = 3G$ for incompressible media. This leads to

Eq. 7.10

$$G = \frac{E}{3} = \frac{1}{3}\frac{\sigma_{xx}}{\varepsilon} = \frac{n}{V} k_B T = \nu k_B T$$

The shear modulus is $k_B T$ times the density of network strands (called ν on the right-hand side). Note the similarity to the ideal gas law. Compare to Eq. 6.3 and also see Box 7.1.

Remember

- For the affine network, one has $G = n/V\, k_B T = \nu\, k_B T$ with the number density of network strands.

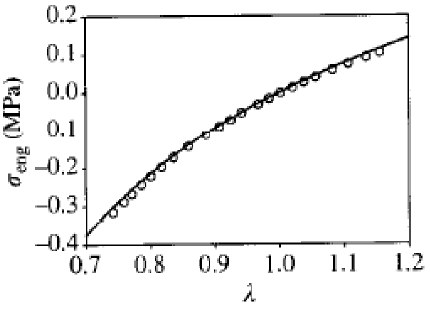


Fig. 7.3
Engineering stress in uniaxial compression ($\lambda < 1$ and $\sigma_{\text{eng}} < 0$) and tension ($\lambda > 1$ and $\sigma_{\text{eng}} > 0$) for a poly(dimethyl siloxane) network prepared by end-linking chains with $M_n = 18\,400\,\text{g mol}^{-1}$. The curve is the classical prediction of Eq. (7.33), with $G = 0.28$ MPa. Data are from W. Oppermann and N. Rennar, *Prog. Colloid Polym. Sci.* **75**, 49 (1987).

Fig. 7.1
From Rubinstein/Colby

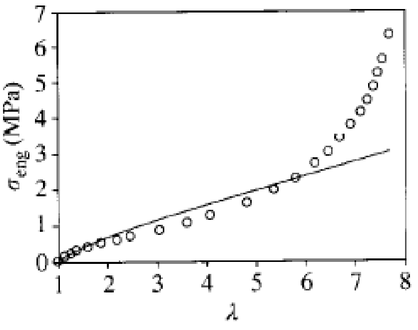


Fig. 7.8
Engineering stress in tension for a crosslinked rubber (data from L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd edition, Clarendon Press, Oxford, 1975). The solid curve is the classical form [Eq. (7.33)] fit to the small deformation data.

Fig. 7.2
From Rubinstein/Colby

7.2 The Mooney-Rivlin formalism

Money and Rivlin write the deformation energy as a function of "invariants" of λ_x ,λ_y and λ_z. Assuming isotropy, the strain energy cannot depend on any of these parameters alone. Rather, it must depend on invariants derived from these parameter, which do not depend on orientation. Because there are three parameters, there also are three invariants. Mooney and Rivlin choose them to be[34]

Eq. 7.11

$$\begin{aligned} I_1 &= \lambda_x^2 + \lambda_y^2 + \lambda_z^2 \\ I_2 &= \lambda_x^2\lambda_y^2 + \lambda_y^2\lambda_z^2 + \lambda_z^2\lambda_x^2 \\ I_3 &= \lambda_x\lambda_y\lambda_z \end{aligned}$$

For the incompressible medium, $I_3 \equiv 1$. The strain energy density, *A/V*, is written as

Eq. 7.12

$$\frac{A}{V} = C_1(I_1 - 3) + C_2(I_2 - 3)$$

The strain energy turns into

Eq. 7.13

$$\frac{A}{V} = C_1\left(\lambda^2 + \frac{2}{\lambda} - 3\right) + C_2\left(2\lambda + \frac{1}{\lambda^2} - 3\right)$$

The “true stress” is

Eq. 7.14

$$\begin{aligned} \sigma_{xx} &= \frac{1}{L_y L_z}\frac{\mathrm{d}A}{\mathrm{d}L_x} = \lambda\frac{\mathrm{d}(A/V)}{\mathrm{d}\lambda} \\ &= 2C_1\left(\lambda^2 - \frac{1}{\lambda}\right) + 2C_2\left(\lambda - \frac{1}{\lambda^2}\right) \end{aligned}$$

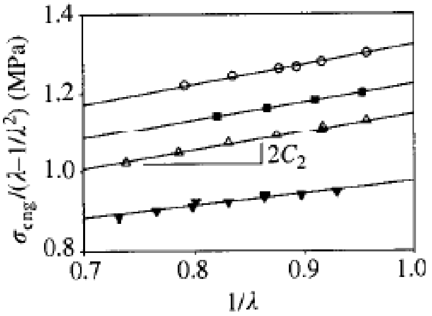


Fig. 7.13
Mooney–Rivlin plots for uniaxial tension data on three networks prepared from radiation-crosslinking a linear polybutadiene melt with $M_w = 344\,000\ \mathrm{g\,mol^{-1}}$, with four different doses, making four different crosslink densities. The lines are fits of Eq. (7.59) to each data set. Data of L. M. Dossin and W. W. Graessley, *Macromolecules* **12**, 123 (1979).

Fig. 7.3
Rubinstein/Colby

Comparison with Eq. 7.8 shows that the affine network model predicts $2C_1 = G$ and $C_2 = 0$

To be distinguished from the true stress is the “engineering stress”, which is a stress corrected for the shrinkage perpendicular to the pulling direction. It is ratio of the force to the area of the undeformed specimen. The engineering stress is easily derived from the force,[35] while the true stress is not.

Eq. 7.15

$$\begin{aligned} \sigma_{eng} &= \lambda_y\lambda_z\sigma_{xx} \\ &= \frac{1}{\lambda}\left[2C_1\left(\lambda^2 - \frac{1}{\lambda}\right) + 2C_2\left(\lambda - \frac{1}{\lambda^2}\right)\right] \end{aligned}$$

In the simplest model, C_2 is assumed to be zero, which leads to

Eq. 7.16

$$\sigma_{eng} = 2C_1\left(\lambda - \frac{1}{\lambda^2}\right)$$

---

[34] The parameter $\lambda_x + \lambda_y + \lambda_z$ would be invariant under rotation by 90°, but not under rotation by 45°.

[35] In such experiments, the sample usually is held by grippers at the end. These do not contract, laterally.

Fig. 7.1 shows experimental data together with a fit. The curve is slightly curved downwards (see also Fig. 7.2). The material is stiffer under compression than under extension.

Eq. 7.17

$$\frac{\sigma_{eng}}{\left(\lambda - \frac{1}{\lambda^2}\right)} = G + 2C_2 \frac{1}{\lambda}$$

Plotting the left hand side versus $1/\lambda$ should lead to horizontal lines if the affine network model was rigorously correct.. However, a positive slope is usually found (Fig. 7.3). The affine network model is not quite correct. Firstly, the crosslinks must be allowed to fluctuate. Also, those fluctuations are constrained in various ways. Entanglements (section 8.6) also play a role.

Fig. 7.2 shows a force-extension curve obtained on a piece of rubber. The nonlinearity has different sources:

- The strands between cross links cannot be stretched to beyond the contour length (section 5.5).
- The rubber band becomes thinner as it is stretched. The downward curvature at low extension is the consequence of “neo-Hookean” elasticity (Fig. 7.1).
- There is strain-induced crystallization.

Remember

- The affine-network model does not quite match experiment. Fluctuations of the crosslinks and constraints thereof play a role.
- One source of nonlinearity in the stress-strain relation is the fact that the specimen becomes thinner as it is stretched.
- The finite chain length and strain-induced crystallization are further sources of nonlinearity.

7.3 Aging and wear

In networks, the strands connecting the crosslinks are not all equally long. The shortest strands are under the largest tension. In consequence, the shortest chains break first. Rubbers age. The problem is known to car owners, who pay for the replacement of the timing belt (German: Zahnriemen) before it actually breaks.

Rubbers age, but there is no crack propagation as in ceramic materials. The strands carry the stress away from the crack tip, thereby avoiding a sharp maximum in stress at the crack tip. Strength and durability of elastomers and gels are topics of much current research. Careful control of the degree of crosslinking and the length of the chain between crosslinks (as well as the distribution thereof) helps.[36] Additives help. Additives include fillers (soot in the case of tires). If wear cannot be avoided in total, controlled and predictable wear is less problematic than catastrophic failure. This is achieved for tires (and also for the engines of cars).

Remember

- Because the shortest chains break first, rubbers age.
- Rubbers do not show brittle fracture (similar to most metals) because the chains carry the stress away from the crack tip.

---

[36] In the case of gels, the „double networks“ have been successful.

7.4 Thermoplastic elastomers

Covalent chemical crosslinks are permanent. In order to mold elastomers into a desired shape at elevated temperature, crosslinks are needed, which dissolve at elevated temperature. This cen be achieved with triblock-copolymers, where the terminal blocks phase-separate from the middle blocks, thereby forming physical crosslinks at a temperatures below the glass temperature of these islands. Styrene-butadiene-styrene rubber (SBS rubber, Fig. 7.4) is one of these materials.

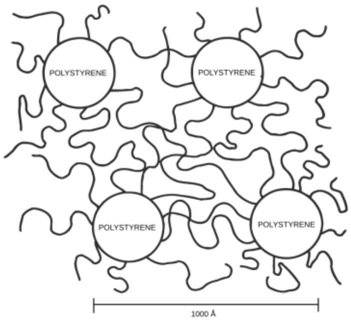


Fig. 7.4
The styrene end blocks of SBS rubber form physical crosslinks
en.wikipedia.org/wiki/Thermoplastic_elastomer

8 Chain dynamics

8.1 Dynamics of the single sphere

We prepare for the discussion of chain dynamics by collecting some relations for spheres. Following Einstein and Smoluchowski, the mean-square displacement (MSD) achieved by Fickian diffusion is

Eq. 8.1

$$\left\langle \left(\mathbf{r}(t)-\mathbf{r}(t=0)\right)^2 \right\rangle = 6Dt$$

D is the diffusivity. The sedimentation of the sphere under the influence of gravity obeys

Eq. 8.2

$$\mathbf{f} = \zeta\mathbf{v}$$

f is the force (of gravity or of some other origin). **v** is the velocity, ζ is the friction coefficient. When ζ pertains to a segment of a chain, it is called “monomer friction coefficient”. For spheres of radius R the friction coefficient is $6\pi\eta_S R$, following the Stokes law, but we stick to ζ. (η_S is the viscosity of the solvent, as opposed to the viscosity of the polymer solution.) According to the fluctuation-dissipation theorem, D and ζ are related as

Eq. 8.3

$$D = \frac{k_B T}{\xi}$$

If $\zeta = 6\pi\eta_S R$, Eq. 8.3 is equivalent to the Stokes-Einstein relation.

Diffusion is linked to a characteristic time, τ, which is the time needed to let the MSD be equal to the square of the size of the object under study (this size being called “R” in the following)

Eq. 8.4

$$\tau = \frac{R^2}{D} = \frac{R^2\eta_S}{k_B T}$$

Eq. 8.4 follows from Eq. 8.3, where a factor 6π was ignored.

The friction coefficient is a function of the viscosity of the ambient medium, η_S, and the size of the object R. Looking at the dimensions, one finds that this relation must be

Eq. 8.5

$$\zeta = \eta_S R$$

Numerical factors (like the factor 6π in the Stokes law) have been neglected.[37]

Remember

- The fluctuation-dissipation theorem predicts $D = k_B T/\zeta$.
- There is a characteristic time of diffusion, which is $\tau = R^2/D$ with R the size of object in question.

---

[37] Kirkwood and Risemann have analyzed this situation and state that the hydrodynamic radius of polymer coils was about a factor 2/3 smaller than R_g, that is, they arrive at $D = k_B T/(4\pi\eta_S R_g)$.

– The friction coefficient is about $\eta_S R$.

8.2 The Rouse model

Rouse depicts the chain as an assembly of springs and beads (Fig. 8.1). For the motion of the entire chain, the friction coefficient simply is the sum the friction coefficients of the spheres

Eq. 8.6

$$\zeta_R = N\zeta$$

The subscript *R* stands for “Rouse”. The diffusivity follows as

Eq. 8.7

$$D_R = \frac{k_B T}{N\zeta}$$

The characteristic time (the “Rouse time”) is

Eq. 8.8

$$\tau_R = \frac{\zeta}{k_B T} N R^2$$

Assuming a Gaussian chain,[38] the radius, *R*, obeys

Eq. 8.9

$$R^2 = N b^2$$

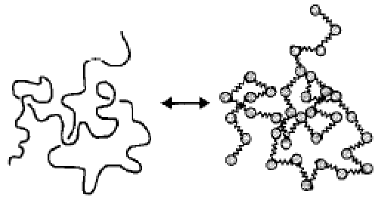


Fig. 8.2
In the Rouse model, a chain of N monomers is mapped onto a bead-spring chain of N beads connected by springs.

Fig. 8.1
from Rubinstein/Colby

We arrive at

Eq. 8.10

$$\tau_R = \frac{\zeta b^2}{k_B T} N^2$$

This discussion is limited to time scales larger than τ_R. For shorter time scales see the text around Fig. 8.3 and Fig. 9.5.

<u>Remember</u>

- The Rouse model is a bead-spring model.
- The Rouse model applies to short chains in a melt (German: “durchspültes Knäuel”).
- The friction coefficient of the entire chain is $N\zeta$ with ζ the monomer friction coefficient.
- The Rouse time scales as N^2.

8.3 The Zimm model

The Zimm model applies to chains in a solvent. It assumes that the solvent molecules are trapped inside the coil. More specifically, the segments of the chain mostly interact hydrodynamically. Why hydrodynamic interaction entails trapped solvent is not easily explained. Other chains in a melt are not trapped in the same away The Rouse model applies in the melt for reasons, which again are not easily explained. The explanation is one of the achievement of polymer science from the second half

---

[38] It will turn out that the Rouse model holds in the melt. In the melt, chains obey Gaussian statistics (ideal random-walk statistics).

of the last century. There is an analogy to the size of chains in the melt, which obeys ideal random-walk statistics.

When the solvent is trapped, the chains behaves like a sphere with radius R. The friction coefficient is

Eq. 8.11

$$\zeta_Z = \eta_S R$$

(A factor of 4π/3) was neglected. The subscript Z stands for Zimm. The radius, R, and the chain length, N, are related as

Eq. 8.12

$$R = bN^{\nu}$$

The exponent, ν, here may be either 0.5 or 0.588, depending on the solvent quality. It is 0.5 in the θ-solvent and 0.588 in the good solvent. The diffusivity follows as

Eq. 8.13

$$D_Z = \frac{k_B T}{\zeta_Z} = \frac{k_B T}{\eta_S b N^{\nu}}$$

The Zimm time is

Eq. 8.14

$$\tau_Z = \frac{R^2}{D_Z} = \frac{\eta_S R^3}{k_B T} = \frac{\eta_S b^3}{k_B T} N^{3\nu}$$

<u>Remember</u>

- The Zimm model also is a bead-spring model, but the solvent molecules are locked to the chain (German: “undurchspültes Knäuel”).
- The friction coefficient of the chain is $\eta_S R^3$.
- The Zimm time scales as $N^{3\nu}$.

8.4 Intrinsic viscosity, the Mark-Houwink relation

In the discussion of the viscosity of dilute solutions, one usually focusses on the “intrinsic viscosity”, which is

Eq. 8.15

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_S}{\eta_S c}$$

[η] has dimensions of an inverse concentration (L/g). Before coming to polymers, we briefly recall Einstein’s prediction for the viscosity of a solution containing dispersed spheres,[39] which is

Eq. 8.16

$$\eta = \eta_S \left(1 + \frac{5}{2}\phi + \ldots\right)$$

---

[39] We deviate from the discussion in Rubinstein/Colby here.

$\phi = V_{\mathrm{Sph}}/(M_{\mathrm{chain}}/N_{\mathrm{Avo}})\, c$ is the volume fraction. V_{Sph} is the volume of the sphere. M_{chain} is the molecular weight of the chain in units of g/mol. c is the concentration in units of g/L. Converting from ϕ to c in Eq. 8.16 leads to

Eq. 8.17

$$\eta = \eta_S \left(1 + \frac{5}{2} \frac{V_{Sph}^2 N_A}{M_{chain}} c + \ldots \right)$$

For the intrinsic viscosity, we find

Eq. 8.18

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_S}{\eta_S c} \propto \frac{V_{Sph}}{N} \propto N^{3\nu - 1}$$

In practical terms, the "Mark-Houwink relation" states that

Eq. 8.19

$$[\eta] = K M_\eta^\alpha$$

K is a constant (determined by calibration). M_η is the "viscosity-averaged molecular weight". The Mark-Houwink exponent, α, is equal to $3\nu-1$. For θ-solvents, α is 0.5. In good solvents, α increases because the chains swell. α then takes values in the range of 0.7 – 0.8.

Approximations have entered this derivation.[40] In particular, the softness of the coils was ignored. In experiment, the Mark-Houwink exponent varies. It is not strictly equal to $3\nu - 1$.

Remember

- The intrinsic viscosity is defined as the low-concentration limit of $(\eta-\eta_S)/(c\eta_S)$.
- The Einstein relation predicts $\eta = \eta_S(1 + 5/2\phi + \ldots)$.
- Converting between ϕ and c, one finds $[\eta] \propto N^{3\nu-1}$ for a dilute solution of polymer coils.

8.5 Viscosity of short-chain melts

We first report a relation for the steady-shear viscosity:

Eq. 8.20

$$\eta = \int_0^\infty G(t)\,\mathrm{d}t$$

$G(t)$ is the ratio of stress to strain after a step in strain. We assume a "viscoelastic liquid", meaning that the stress eventually decays to zero. For simplicity, we approximate the integral as

Eq. 8.21

$$\eta \approx G_{char} \tau_R$$

---

[40] Strobl in the reference from footnote 4 says the „hydrodynamic radius" to be used here was 7/8 R_g. That is interesting, because the hydrodynamic radius entering the Stokes-Einstein relation is 2/3 R_g. The two should be the same, following the fluctuation dissipation theorem. Strobl says that things evidently are a bit complicated. Rubinstein/Colby derive the Mark-Houwink relation in an entirely different way – which, however, is not very accessible. They appear to be aware of the problem and avoid it, rather than discussing it.

We are only interested in the dependence of the viscosity on N. Following rubber elasticity, the characteristic shear modulus will be proportional to $k_BT/(Nb^2)$, that is, will scale as $1/N$. From equation Eq. 8.10, $\tau_R \propto N^2$. It follows that

$$\eta_{Rouse} \propto N \qquad \text{Eq. 8.22}$$

The viscosity according to Eq. 8.22 applies on time scales larger than τ_R. For shorter time-scales (that is, at higher frequencies) see Fig. 9.5.

Remember

- The viscosity has dimensions of a shear modulus multiplied by a relaxation time.
- For the Rouse model, one finds $\eta \propto N$

8.6 Long chains in the melt: reptation

If the chain length exceeds a certain threshold, the entanglements influence the flow behavior.[41] The transition is, for instance, seen in plots of log(η) versus log(M) (Fig. 8.2). There is a kink at the "*entanglement molecular weight*". Below the kink, the slope is 1 (i.e. $\eta \propto M^1$, following the Rouse model, section 8.5). Above the kink, the slope is 3.4 ($\eta \propto M^{3.4}$). The dynamics of polymers with entanglement is described by *reptation theory*. All of the entanglements create a tube in which the polymer moves ("reptates") like a snake (Fig. 8.4).

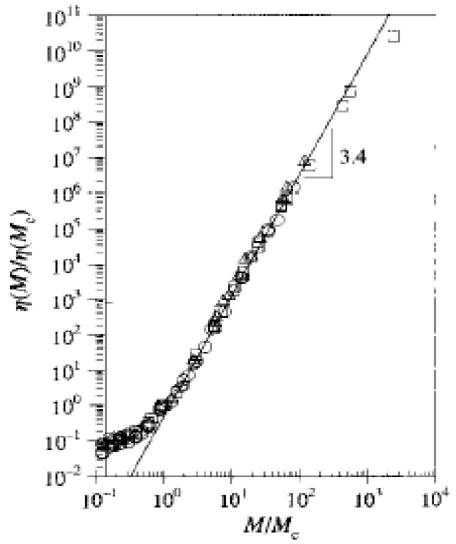


Fig. 9.5
Molar mass dependence of viscosity for polymer melts reduced by their critical molar mass. Open circles are polyisobutylene with $M_c = 14000\ \mathrm{g\,mol^{-1}}$, from T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.* **70**, 2384 (1948) and *J. Phys. Chem.* **55**, 221 (1951). Open squares are polybutadiene with $M_c = 6700\ \mathrm{g\,mol^{-1}}$, from R. H. Colby *et al.*, *Macromolecules* **20**, 2226 (1987). Open triangles are hydrogenated polybutadiene with $M_c = 8100\ \mathrm{g\,mol^{-1}}$, from D. S. Pearson *et al.*, *Macromolecules* **27**, 711 (1994).

Fig. 8.2
from Rubinstein/Colby

The consequences of reptation can be illustrated in a plot of log(MSD) versus log(t) (Fig. 8.3). MSD is the mean-square displacement (cf. Eq. 8.1). On time scales longer than all characteristic times (to the right in Fig. 8.5), chains move following Fickian diffusion. The MSD is proportional to t, as expressed in Eq. 8.1. The slope in the log-log plot is 1. On short time scales, the segments move following the Rouse model. We expand on the discussion of the Rouse model in section 8.2 here, in that we discuss times smaller than the Rouse time. We deviate from Rubinstein/Colby and provide a much

---

[41] The transient entanglement network is also visible in the rheological spectra (section 9).

simplified argument of why the MSD should scale as $t^{1/2}$ on short time scales. The random motion of the segments of chain is a collective motion of a few segments. The larger the MSD, the more segments must move cooperatively to achieve this displacement. Start from Eq. 8.1, but let the effective diffusivity be a function of the MSD:

Eq. 8.23

$$\left\langle \left(\mathbf{r}(t)-\mathbf{r}(t=0)\right)^2 \right\rangle = MSD \propto D_{eff}(t)\,t$$

Following Eq. 8.7, the effective diffusivity is $k_BT/(N\zeta)$ with N the number of segments contributing to the motion. Following random-walk statistics, N is proportional to the MSD, which leads to

Eq. 8.24

$$MSD \propto \frac{k_BT}{MSD\,\zeta}\,t$$

Solving the for MSD, one finds that the MSD is proportional to $t^{1/2}$.

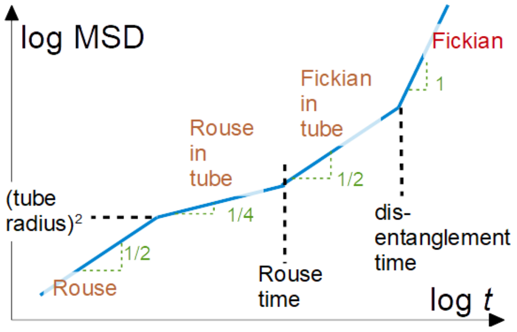


Fig. 8.3
Mean-square displacement versus time in the different regimes.

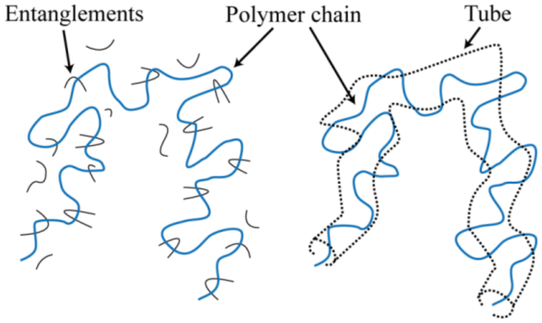


Fig. 8.4
Entanglements create a tube
www.researchgate.net/figure/a-Schematic-representation-of-a-polymer-chain-entangled-with-neighbouring-chains-b_fig5_341652080

Rouse-type motion proceeds until the segments hit the wall of the tube. The tube (the “primitive path”) itself obeys random-walk statistics. The segments now move according to the Rouse model, but they do so on the curvilinear primitive path. The shape of the primitive path adds another factor of 1/2 to the exponent in the relation linking the MSD to time. In this regime, the MSD scales as $t^{1/4}$. At the Rouse time, Rouse-type diffusion turns into Fickian diffusion and the factor of 1/2 in the exponent related to Rouse-type motion turns into 1. Motion still occurs inside the tube, meaning that the MSD scales as $t^{1/2}$. At the disentanglement time, τ_D, the chain leaves its tube (Fig. 8.5). From thereon, diffusion is Fickian.

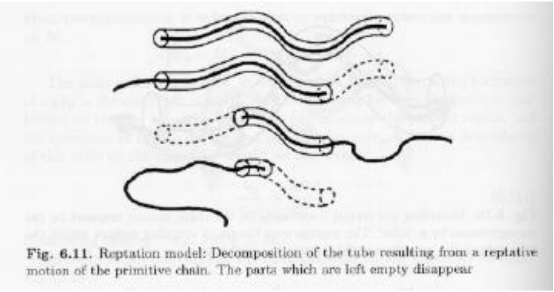


Fig. 6.11. Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

Fig. 8.5
A chain leaves its tube within the disentanglement time, τ_D.
G. Strobl: The Physics of Polymers

Fig. 8.5 is idealized in a few ways. It is difficult to nail down experimental evidence for this curve for one single sample. (Note the wide range of time scales.) Still, the concept of reptation as such is widely accepted and has gained experimental support.

We now come back to the exponent of 3.4 for the long chains in Fig. 8.3. Following the argument that the viscosity is product of a shear modulus (of the order k_BT/b^3) multiplied with a relaxation time, we need to estimate the disentanglement time, τ_D. τ_D is given as L_{pp}^2/D_{Rouse} with L_{pp} the contour length of the primitive path, which is proportional to N. Given that $D_{Rouse} \propto 1/N$ following Eq. 8.7, this leads to

Eq. 8.25

$$\tau_D \propto N^3$$

The exponent found in experiment is 3.4 rather than 3, which has to do with the fact that parts of the chain occasionally leave the tube. The technical term is “constraint release”.

Fig. 8.6 collects entanglement parameters for selected polymers.

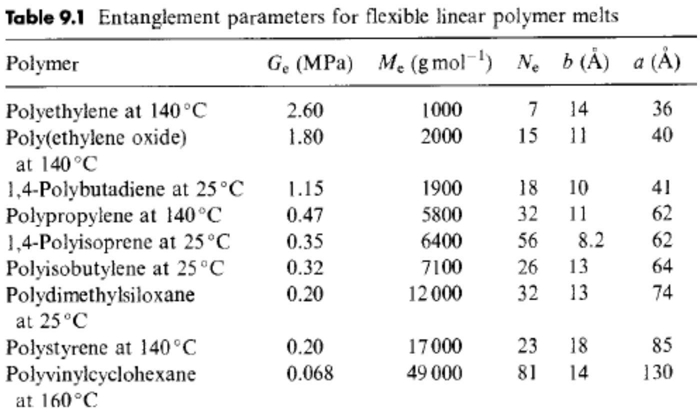


Table 9.1 Entanglement parameters for flexible linear polymer melts

Polymer	G_e (MPa)	M_e (g mol^{-1})	N_e	b (Å)	a (Å)
Polyethylene at 140 °C	2.60	1000	7	14	36
Poly(ethylene oxide) at 140 °C	1.80	2000	15	11	40
1,4-Polybutadiene at 25 °C	1.15	1900	18	10	41
Polypropylene at 140 °C	0.47	5800	32	11	62
1,4-Polyisoprene at 25 °C	0.35	6400	56	8.2	62
Polyisobutylene at 25 °C	0.32	7100	26	13	64
Polydimethylsiloxane at 25 °C	0.20	12 000	32	13	74
Polystyrene at 140 °C	0.20	17 000	23	18	85
Polyvinylcyclohexane at 160 °C	0.068	49 000	81	14	130

Fig. 8.6
Entanglement parameters for selected polymers. G_c is the height of the rubber plateau in Fig. 9.2. M_e is the entanglement molecular weight. N_e is the number von Kuhn segments (with length b) pertaining to a coil, which fits into the tube. a is the diameter of the tube.
from Rubinstein/Colby

Remember

- Long chains in the melt move slowly because of the entanglement.
- The viscosity is correspondingly high.
- Entanglements are among the characteristics of polymers.

8.7 The viscosity at large deformation rates

There are rather intricate analytical theories of polymer flow, which produce fair agreement with experiment. For branched polymers, people mostly rely on simulations. (Simulations require assumptions, similar to analytical theories.) In some cases, the simulations reveal insights which are general and which can a posteriori by justified with general arguments. In other cases, the simulations stay close to some problem. Once the answer is on the table, the practitioner accepts this one answer, not searching for more general insight.

This section concerns a side remark on nonlinear rheology. In linear rheology, there is not much of a difference between shear flow and elongational flow. The

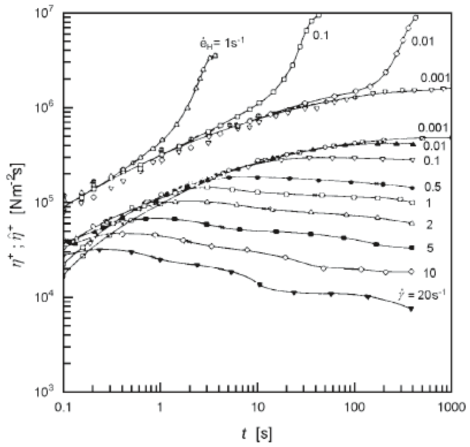


Fig. 9.18. Results of stress growth experiments in shear, $\eta^+(t)$, and extension, $\hat{\eta}^+(t)$, at different deformation rates $\dot{\gamma}$ and $\dot{e}_H$, respectively, carried out for PE at 150 °C. Measurements by Meissner [117]

Fig. 8.7
On shear thinning and strain hardening under elongation.
G. Strobl: The Physics of Polymers

two viscosities are related by a factor of 3. This is different at high deformation rates (Fig. 8.7). In shear, the viscosity decreases (“shear thinning”). That is important, because the strain rate for a flow in the tube is highest at the wall. The viscosity decreases, which – under a constant overall pressure gradient along the tube – further increases the strain rate. There is positive feedback, which eventually results in plug flow (as in tooth paste). Shear thinning is very important for polymer extrusion.

Under elongational flow (unidirectional or bidirectional, spinning fibers or blowing films), the viscosity increases at high deformation rate. That is important because it stabilizes the fibers and the lamellae. Long-chain branching enhances this effect.

Remember

- At large deformation rates, there is shear thinning (shear flow) and strain hardening (elongational flow). Both are of much practical importance in polymer processing.

8.8 In polyelectrolytes, viscosity may increase with decreasing polymer concentration

The viscosity of polyelectrolytes (of charged chains) is special in that the viscosity sometimes *decreases* as the polymer concentration increases. This is surprising at first glance. The phenomenon is known as the "polyelectrolyte effect". The solution to the puzzle lies in the numerous counter ions. At high concentrations, these lead to a small Debye length and, in consequence, to an electrostatic screening of the interaction between ions on the chain. The charged chain stretches at low concentrations (and in the absence of added salt, Fig. 8.9) because of the increased inter-charge repulsion. This is why the viscosity increases at low concentrations (Fig. 8.9). This effect is stronger than the effect of dilution (which also exists).

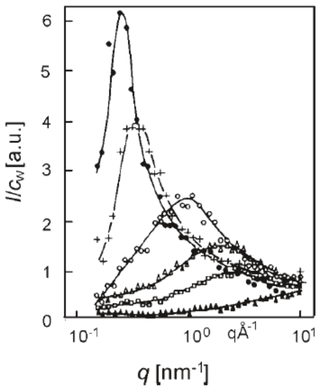


Fig. 3.14. Small angle neutron scattering curves obtained for salt-free aqueous solutions of NaPSS ($\overline{M}_w = 3.54 \times 10^5\,\mathrm{g\,mol^{-1}}$). The polymer concentration varies between $1.0 \times 10^{-5}\,\mathrm{g\,l^{-1}}$ (*filled circles*) and $2.3 \times 10^{-4}\,\mathrm{g\,l^{-1}}$ (*filled triangles*). From Nierlich et al. [16]

Fig. 8.8
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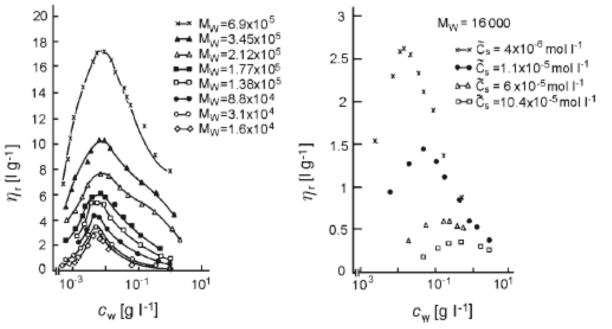

Fig. 8.20. Concentration dependence of the reduced excess viscosity measured for aqueous solutions of NaPSS for (*left*) various molar masses at a constant salt concentration $\tilde{c}_s = 4 \times 10^{-6}\,\mathrm{mol\,l^{-1}}$ and (*right*) for a sample with a molar mass $M_w = 1.6 \times 10^4\,\mathrm{g\,mol^{-1}}$ for different concentrations of NaCl. From Cohen et al. [108]

Fig. 8.9
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Strictly speaking, this is an effect of geometry. The dynamics follows geometry. The coil diameter increases with decreasing concentration (and decreasing concentration of the counter ions).

Remember

- In polyelectrolytes, the counter ions screen the electrostatic interactions. This affects the coil size and the viscosity.

- Because the concentration of the counter-ions decreases with decreasing polymer concentration, the electrostatic interaction between the charges on the chain increases. In consequence, the viscosity may increase with decreasing polymer concentration.

9 Linear polymer rheology

Rheology is the science of how materials flow. Rheology can be enormously complicated and, also, be enormously interesting. In particular, there is a link between structure and flow. A recommended book in this regard was written by R.G. Larson and is entitled “The Structure and Rheology of Complex Fluids”. R.G. Larson is a rheologist and certainly knows his craft. The book is about rheology, yes, but Larson’s heart is with the structure as much as with the flow.

We cannot to elaborate on rheology in all its beauty here. The rheology of polymers often is nonlinear, meaning that the ratios of stress to strain (or to strain rate) depend on the strain (or the strain rate). Nonlinear rheology is always discussed against the background of linear rheology. In linear rheology, the strain and the strain rate are maintained small enough to ensure linear stress-strain relations.

Linear rheology is discussed in some length in the notes on soft condensed matter. The discussion is not repeated here. We collect a few results.

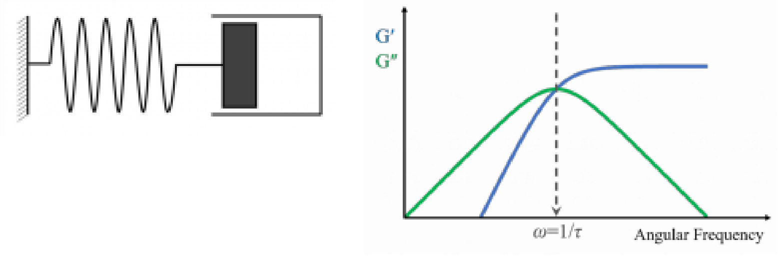

Fig. 9.1
The Maxwell model is the simplest model of a viscoelastic liquid. The mechanical equivalent circuit is shown to the left. The loss modulus has a broad maximum on the inverse relaxation time.
lsinstruments.ch/en/theory/rheology/maxwell-model

- We mostly discuss shear deformation and the shear modulus *G*. In linear rheology, there are simple relations between the *G* and *E*, where *E* is the Youngs modulus, describing elongation. (These simple relations break down in nonlinear rheology.)
- The modulus of compression mostly is much larger than *G*. Soft matter mostly is incompressible.
- For soft matter (synonymous to complex fluids), there is an evolution of stress after a step in shear strain (cf. Eq. 8.20). The ratio of the two is the time-dependent shear modulus, *G*(*t*).
- From an experimental point of view, the study of linear rheology is easier in the frequency domain than in the time domain. Excitation occurs with sine waves of variable frequency, ω, where the values of ω span a few decades. The shear modulus turns into a complex function of frequency $\tilde{G}(\omega) = G'(\omega) + iG''(\omega)$. G' is the storage modulus (related to elastic behavior). G'' is the loss modulus (related to viscous behavior).
- The fact that $\tilde{G}(\omega)$ depends on ω is called “viscoelastic dispersion”. Strong viscoelastic dispersion is indicative of relaxations with rates comparable to the inverse of the respective frequency.
- An idealized viscoelastic liquid (a Maxwell-type liquid) only has one relaxation time. The equivalent circuit (a spring in series with a dashpot) is shown to the left in Fig. 9.1. The rheological spectrum has a broad maximum in $G''(\omega)$ at the inverse of the relaxation time, which is $\tau = \zeta/\kappa$ with κ the spring constant of the spring and ζ the friction coefficient of the dashpot (cf. Eq. 8.21).

Box 9.1: Rheological spectrum of the Maxwell fluid
To understand the viscoelastic spectrum of the Maxwell-fluid, compute the effect spring constant of the Maxwell element. In mechanics, inverse spring constants are additive when elements are placed in series.
The effective complex spring constant is

$$\frac{1}{\kappa_{eff}} = \frac{1}{\kappa} + \frac{1}{i\omega\zeta}$$

It follows that

$$\kappa_{eff} = \frac{\kappa i\omega\zeta}{\kappa + i\omega\zeta} = \zeta\frac{i\omega}{1+i\omega\frac{\zeta}{\kappa}} = \zeta\frac{i\omega}{1+i\omega\tau}$$

$\tau = \zeta/\kappa$ is the relaxation time. Separate the real from imaginary part as

$$\kappa_{eff} = \zeta\frac{i\omega(1-i\omega\tau)}{(1+i\omega\tau)(1-i\omega\tau)}$$

$$= \zeta\frac{\omega^2\tau}{1+\omega^2\tau^2} + i\zeta\frac{\omega}{1+\omega^2\tau^2}$$

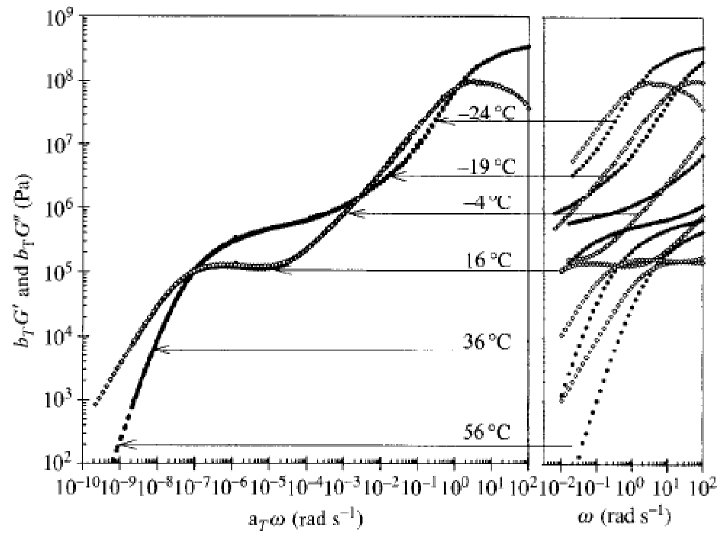

Fig. 8.15
Demonstration of the time–temperature superposition principle, using oscillatory shear data (G', filled circles and G'', open diamonds) on a PVME melt with $M_w = 124\,000$ g mol^{-1}. The right-hand plot shows the data that were acquired at the six temperatures indicated, with $T_g = -24$ °C chosen as the reference temperature. All data were shifted empirically on the modulus and frequency scales to superimpose, constructing master curves for G' and G'' in the left-hand plot. Data and plot courtesy of J. A. Pathak.

Fig. 9.2
A rheological spectrum obtained on a melt of long-chain linear polymer.
from Rubinstein/Colby

- Time-temperature-superposition (TTS) sometimes holds. If it holds, increasing the frequency of the measurement is equivalent to decreasing the temperature of the sample. Rather than speeding up the measurement, one slows down the dynamics in the sample. The way, in which "master curves" are created based on TTS, is illustrated on the right-hand side in Fig. 9.2. Fluids, for which that works, are called "thermorheologically simple". Leaving complication aside, TTS works if the temperature dependence of G is entirely the consequence of a temperature dependence of the monomer friction coefficient (cf. Eq. 8.2). The shape of $\tilde{G}(\omega)$ then mostly is the consequence of the chain topology. TTS breaks down when the material crystallizes.[42] Fig. 9.4 illustrates that TTS applies in time-domain experiments, as well.

Fig. 9.2 shows a rheological spectrum of a long-chain linear polymer. This plot is remarkable in the following regards:

- The two maxima in $G''(\omega)$ correspond to the segment relaxation (fast) and to disentanglement (slow). Fig. 9.3 shows how the slow relaxation moves to the left as the molecular weight decreases.
- The value of G' on the plateau is characteristic of the density of strands between entanglements. Based on Eq. 7.10 ($G = \nu k_B T$ with ν the density of network strands), the plateau modulus allows to infer the entanglement molecular weight (cf. Fig. 8.2).
- At high frequency (at low temperature), the material is in the glassy state.

Fig. 9.5 is not of much practical relevance, but we discuss it as a follow-up to the discussion of the Rouse model. The figure shows the rheological spectrum of a Rouse-type fluid. At low frequency, G' and G'' scale as ω^2 and ω, respectively, similar to the Maxwell fluid (Fig. 9.1). When the inverse frequency is larger than the longest relaxation time, the internal dynamics of the chain has no effect on the rheology.

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[42] There are other reasons why TTS might not work or not work well. TTS does not work well for blends. TTS does not work well when water is involved because the structure of water depends on temperature.

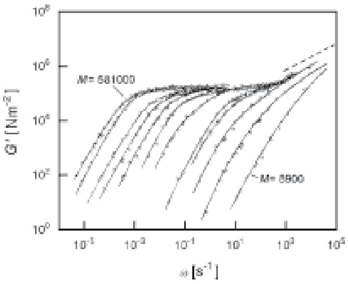

Fig. 6.16. Storage shear moduli measured for a series of fractions of PS with different molar masses in the range $M = 8.9 \times 10^3$ to $5.81 \times 10^5\ \mathrm{g\,mol^{-1}}$. The *dashed line in the upper right corner* indicates the slope corresponding to the power law Eq. (8.82) derived for the Rouse model of the glass transition. Data from Onogi et al. [74]

Fig. 9.3
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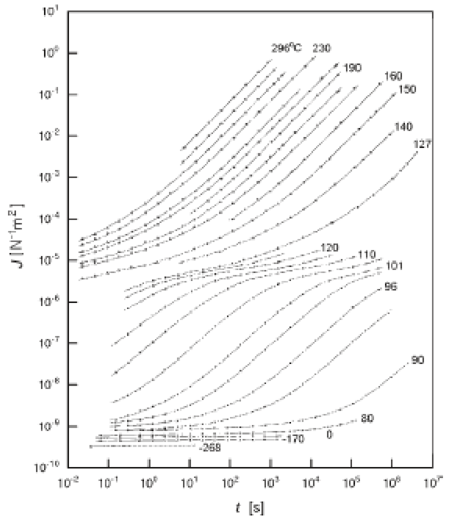

Fig. 6.11. Creep compliance of PS ($\overline{M}_w = 3.85 \times 10^5\ \mathrm{g\,mol^{-1}}$), as measured at the indicated temperatures. Data from Schwarzl [70]

Fig. 9.4
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The internal dynamics is seen at high frequency. There are many more relaxations times related to the motion of parts of the chains as discussed around Eq. 8.24. Importantly, there is power-law behavior. There is no characteristic time (other than the Rouse time, the inverse Rouse time being the lower edge of the scale-invariant regime). The power-law exponent in the relation of G' and G'' versus ω is 1/2, which is linked to the power-law exponent on the left-hand side in Fig. 8.3.

Box 9.1 expands on the relation between random motion an viscoelasticity.

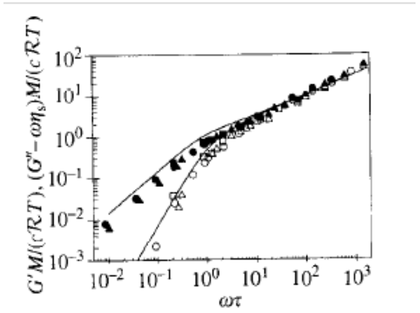

Fig. 8.5
Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus G' and filled symbols are the loss modulus G''. Squares have $c = 0.5\ \mathrm{g\,L^{-1}}$, triangles have $c = 1.0\ \mathrm{g\,L^{-1}}$, and circles have $c = 2.0\ \mathrm{g\,L^{-1}}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).

Fig. 9.5
from Rubinstein/Colby

Box 9.2: Nanorheology

It was repeatedly emphasized that diffusion (more generally: random motion), on the one hand, and viscoelasticity, on the other, were related. There is a technique, which allows to infer the complex viscosity $\tilde{\eta}(\omega)$ and the complex shear modulus $\tilde{G}(\omega)$ from the random motion of a test particle.

According to the Green-Kubo relation, the diffusivity can be written as

$$D = \int_0^\infty \left\langle \mathrm{v}(t)\,\mathrm{v}(t+\tau)_t \right\rangle \mathrm{d}\tau$$

The term in angle brackets is the velocity autocorrelation function. This relation can be extended to finite time:

$$D(t) = \int_0^t \left\langle \mathrm{v}(\tilde{t})\,\mathrm{v}(\tilde{t}+\tau)_{\tilde{t}} \right\rangle \mathrm{d}\tau$$

$D(t)$ can be Fourier-transformed to yield $\tilde{D}(\omega)$. The Stokes-Einstein relation can be extended to this case as

$$\tilde{D}(\omega) = \frac{k_B T}{6\pi\tilde{\eta}(\omega)R}$$

Solve this equation for $\tilde{\eta}(\omega)$:

$$\tilde{\eta}(\omega) = \frac{\tilde{G}(\omega)}{\mathrm{i}\omega} = \frac{k_B T}{6\pi\tilde{D}(\omega)R}$$

Clearly, the viscoelasticity in the vicinity of a probe (usually a small sphere) can be inferred from the sphere’s random motion. These measurements are most interesting, if the motion is complicated (as in Fig. 8.3). Nanorheology can be carried out inside confined spaces (such as biological cells)

10 Glassy polymers

The glassy state is discussed in some length in the course on soft condensed matter. Basically, glasses are supercooled liquids. They are amorphous. Their viscosity is so high that they are solids for all practical purposes.

Polymeric glasses fit into this framework, but are special in a few ways. First, atactic polymers often have "frozen disorder" at the level of the individual chains. In polymers with a zigzag carbon backbone, side groups can point either to the "right" or to the "left". The way in which this happens is called "tacticity". With random tacticity of polymethyl methacrylate (PMMA) or polystyrene (PS), crystallization is impossible. There is no well-ordered energetic ground state, which would not be reached only because the nucleation would be too slow.

A second special feature of polymers is that they hardly ever crystallize completely.[43] They are always partially amorphous. The problem is best explained using Fig. 11.2. In order for the lamella to form, the chain must fold back. These areas are often amorphous. Chain ends are also often not integrated into the crystallites.

A third special feature also results from the chain topology. Polymeric glasses (such as the atactic PMMA, Plexiglas) tend to not suffer brittle fracture because the chains prevent this. The failure behavior under mechanical load is complicated and interesting. There is a yield stress at which irreversible plastic deformation occurs without immediate fracture. This has advantages from a technical point of view. On the other hand, the yield stress is lower than the corresponding stress in metals. Polymer glasses are inferior to metals in terms of rigidity, strength, and surface hardness.

Materials which appear to glassy, may be true glasses, but may also contain nanocrystallites. This is tolerable as long as the ordered areas are nanoscopically small. Crystallites are usually birefringent and the refractive indices differ between the different orientations and, also, between crystalline phase and the amorphous phase. The crystallites scatter light (as we know from ceramics being white). However, the scattering efficiency scales as d^6 with d the size of the scattering object. Nanocrystallites do not cause the material to become cloudy. PET used for bottles is semi-crystalline. The advantage of semi-crystallinity here is both the mechanical strength and the reduced gas permeability (low oxygen permeability, in particular).

The gradual solidification and gradual softening of partially amorphous substances is of much practical importance. (Steel also softens before it melts and can be forged in this state.)

There is much talk of the glass transition being “universal”. Polymer scientists have disputed that for polymers. The way, in which the degrees of freedom freeze in, is complicated, interesting, and specific to the polymer under study. Polymer glasses mostly appear as amorphous in x-ray scattering, but they have intriguing and important local order.

Remember

- From a structural point of view, glasses are supercooled liquids.
- Polymer glasses not usually are ideal glasses. They are more complicated (and more interesting).
- The glass transition is a kinetic transition. The supercooled liquid falls out of thermodynamic equilibrium at the glass temperature.
- Polymers are often partially amorphous (semi-crystalline).
- Polymers, which appear to be glassy to the eye, may contain nanoscopic crystallites.

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[43] Single crystals *have* been grown from polymers. This is difficult. These single crystals have no technical application.

11 Semi-crystalline polymers

Most structural polymers (polyethylene, polypropylene) are semi-crystalline. Most synthetic fibers are semi-crystalline. Crystallinity implies good stiffness and strength. The degree of crystallization can be controlled within certain limits by the number of branches. Branching reduces the degree of crystallization. Low-density polyethylene (LDPE) and high-density polyethylene (HDPE) differ in this regard. HDPE has fewer branches and therefore has a larger volume fraction of crystallites.

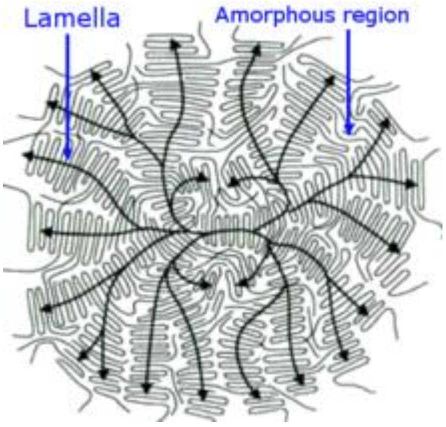

Fig. 11.1
When polymers crystallize, amorphous regions always remain.
en.wikipedia.org/wiki/Crystallization_of_polymers

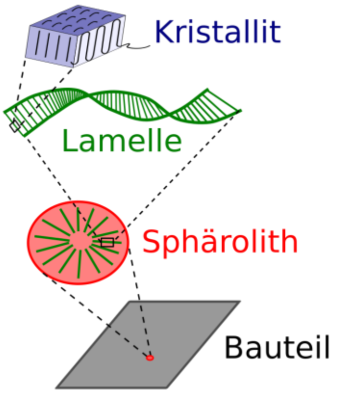

Fig. 11.2
On the texture of semi-crystalline polymers.
en.wikipedia.org/wiki/Crystallization_(polymer)

Crystallization can be induced and controlled by stretching. Stretching leads to an alignment of the chains and facilitates crystallization. The process is rather complicated. Elastomers can crystallize locally and reversibly in the stretched state. When the elastomer returns to the unstretched state, the crystallites melt.

Sometimes polymers (such as polyethylene, PE, and polypropylene, PP) crystallize into lamellae (Fig. 11.2). These lamellae have an edge. Because more space is required at the edge than in the center, the lamellae have a tendency to twist. Sometimes the lamellae grow outwards from a center and then form spherulites.

<u>Remember</u>

- Semi-crystalline polymers often contain lamellae and spherulites.
- Crystallization can be induced by stretching.

12 Fracture mechanics

The fracture mechanics of polymers is peculiar and of much practical importance (Fig. 11.1). Fig. 11.2 illustrates, how crazing contributes to the deformation beforce fracture. Fig. 12.3 shows the structure of high-impact polystyrene. Soft inclusions of polybutadiene stop crack propagation.

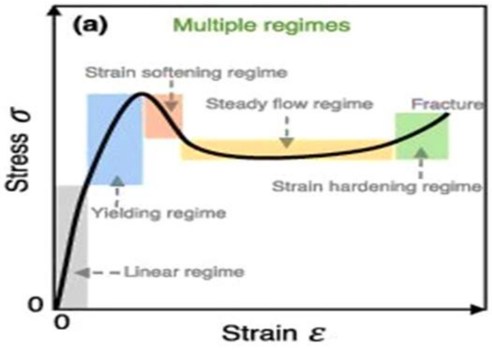

Fig. 12.1
Polymers are deformed before they break
behinpolymerco.com/en/tensile-test-in-polymers/

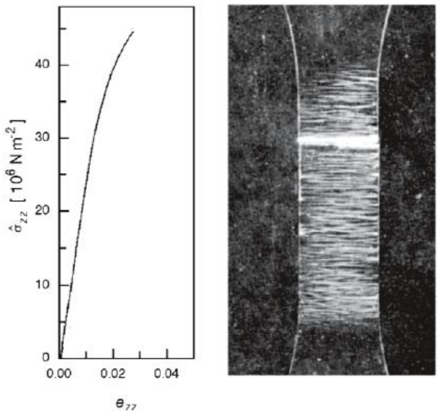

Fig. 10.3. Stress-strain curve of a sample of PS and photograph showing crazes

Fig. 12.2
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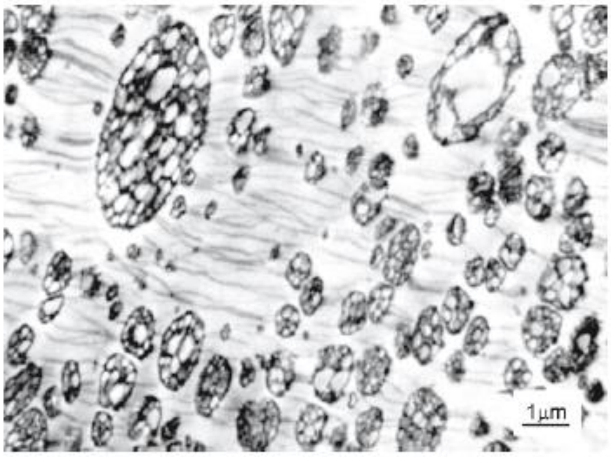

Fig. 10.39. Electron micrograph of a stained microtomed section of HIPS, showing crazes running between the elastomeric precipitates. From Kambour [133]

Fig. 12.3
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