Physics of Polymer solutions and polymer gels

Hauptseminar Porous Medias SS 2021

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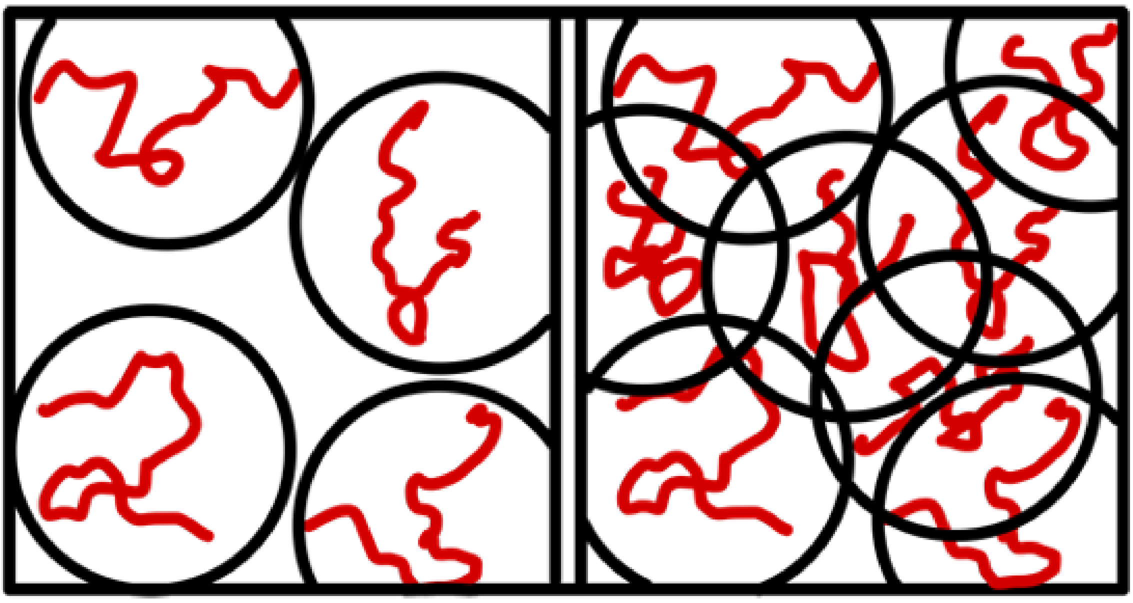

1 Introduction

Polymers are wide spread in nature and thus are of general concern of research throughout different disciplines. They occur in research of new materials for energy conservation, they occur in application that demand highly specialized mechanical property, and they occur in new flexible production technics. But how can they be treated in the perspective of physics, how can there behavior be described or even foreseen, and how general is such a description. In this handout I want to give a summary of the talk "Physics of polymer solutions an polymer gels"from a elaborated and unrestrained perspective.

According to the presentation the topics of this handout are the general treatment of polymer chains in ideal and real fashion. This will lei the theoretical ground for the investigation of polymers in solution. There the core part will be the understanding of the topic-over-spanning phase diagramm. The next thougth that will be added is the bonding of Polymers to form networks and finally polymer gels. Achieving an understanding of polymer gels will be crucial for understanding polymer gels and networks as porous media, which is the topic of the seminar. If not stated otherwise the used source for this handout is the book [2].

2 Polymers

Mr. Staudinger in the 1920 first proposed that polymers could be macromolecules, consisting of N reoccuring monomers that are covalent bonded into the macromolecule. Where the monomers are elementary units but not necessarily periodically reoccurring nor consisting of single atoms. Mostly polymers can be described as long chains of covalent bonded monomers but polymers are not restricted to single branches instead they can have several branches with periodic order or without. Thus to treat all polymers with one general physical model is not yet successful and hardly thinkable. To get an understanding of the physical processes with polymers it shall be enough to treat polymer chains that consist of one backbone branch with 2 ends and one sort of monomers of length l. An example of such a polymer is given by the polylactide polymer from picture 1.

Generally speaking polymers in their solid state are amorphous. Because of that they have a glass transition temperature to get into the molten state. Next to this phases, properly chosen solvent and polymers can form a solution with a variety of phases for different mixing

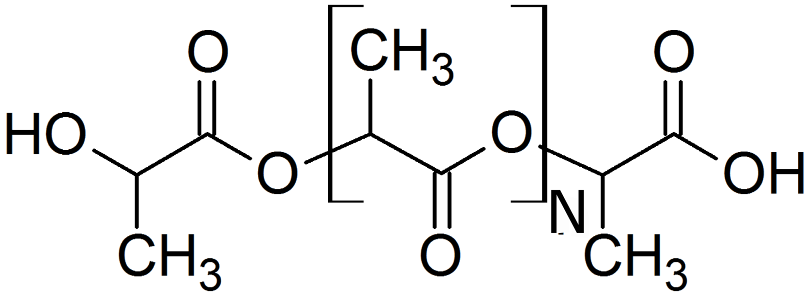

Abbildung 1: [1] The Picture shows a polylactide (PLA) polymer chain in standard chemical convention. The square brackets with the suffix N mean that there are N many monomers like the marked one inside a chain. For standard (PLA) the chain size reaches $N = 1000$.

ratios and temperatures. The physics of such polymer solutions, polymer solids or polymer melts are strongly affected by the existence, degree and kind of bonding between polymers. Speaking of bonds the topic of polymer gels is entered. The starting point of polymer physics is the mathematical treatment of the configuration space monomer positions from a flexible polymer. The objective of a treatment is to determine the size of a polymer chain with its N monomers. This is relevant because size can enter multiple (> 6) orders of magnitude and thus dramatically alter the polymer interactions such as friction and many others.

3 Ideal chain

A basic understanding of polymers and their scaling in length with N is achieved by investigating polymer chains with one branch, one monomer type and no interaction of different monomers what so ever. Thus in this simple picture it is enough to imagine only one polymer chain and to ignore nonphysical motion like interpenetration of different monomers. Entering this assumptions there is still a wast number of different models. The most important one is the freely-jointed-chain (FJC). In this model the bond angle between to neighboring polymers is not restricted by any means.
There are two different ways to get mathematically the first grip on polymer chains. One is about random walk theory and one deals with random vectors in 3 dimensions from the beginning.

3.1 Vector approach

We select at first the second approach and start by measuring the length of a polymer using the sum

$$\vec{R}_\mathrm{N} = \sum_{i=1}^{N} \vec{r}_i \tag{1}$$

of the individual monomer vectors $\vec{r}_i$. This approach yields no information about a typical scale of polymer lengths because the length vary between different individual polymers. Thus building the mean value of $\vec{R}_\mathrm{N}$ seems helpful. But building the mean value yields mathematically exact $\langle \vec{R}_\mathrm{N} \rangle = 0$ because the problem is highly isotropic. But the standard deviation of the value $\langle \vec{R}_\mathrm{N} \rangle$ contains the length information and can be calculated with

$$R := \sqrt{\langle \vec{R}_\mathrm{N}^2 \rangle - \langle \vec{R}_\mathrm{N} \rangle^2} = \sqrt{\langle \vec{R}_\mathrm{N}^2 \rangle} = \sqrt{\langle \sum_{i=1}^{N} \vec{r}_i \sum_{j=1}^{N} \vec{r}_j \rangle} = \sqrt{\sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{r}_i \vec{r}_j \rangle}. \tag{2}$$

In this formula it is essential to know the correlation $\langle \vec{r}_i \vec{r}_j \rangle$ between the monomer vectors. But with the expression

$$\vec{r}_i \vec{r}_j = l^2 \cdot \cos(\theta_{ij}) \tag{3}$$

for the dot product and the knowledge of random bond angles θ_{ij} it is visible that the mean value of the cosine results often the value zero in the terms of the sums in calculation 2. But there are exactly N terms where the θ_{ij}-angle is zero due to comparing monomers to itself according to $i = j$. Because of that the calculation yields $R = l \cdot N^{\frac{1}{2}}$. Raising the R to the third power yields a rough estimation of the volume that one of this ideal chains pervades.

3.2 random walk approach

As indicated the final result of this approach is for our purpose the formula $R = l \cdot N^{\frac{1}{2}}$, but the approach derives a hole probability distribution. The starting point of the derivation is the 1 dimensional random walk with step length l. After N steps this yields an end positions x between $-N$ and N from the starting point. The number of pathways to each position follows the binomial distribution $\binom{N}{\frac{N+x}{2}}$ thus the probability distribution emerging the Laplace-experiment is

$$P_{1\mathrm{D}} = \frac{\binom{N}{\frac{N+x}{2}}}{2^N}. \tag{4}$$

By applying the logarithm and approximating the facultys inside the binomial function with the Stirlings-formula $n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n$ a Gaussian-curve is yielded that need to be normalized according to usage as probability distribution. The last step in this approximation is to rescale the x-axis of the Gaussian-curve according to the step length l. The yielded distribution

$$P_{1\mathrm{D}} = (2\pi N l^2)^{-\frac{1}{2}} \exp\left(\frac{-R^2}{2Nl^2}\right) \tag{5}$$

assigns a positive probability density to each position in the 1D space which is physically not thinkable because the polymer chain has a finite length. Thus this approximation is only a good approximation for the most likely states. Also the continuous treatment of the probability is only reasonable for $N >> 1$. The desired result $R = l \cdot N^{\frac{1}{2}}$ is achieved from the standard deviation of the Gaussian-function. Also to expand the Gaussian-function in 3 dimensions is easily achieved. While expanding the length l of a step size need to be carefully revisited because the steps are done in diagonal directions as well. To put this thought in perspective the next section deals with the basic length l.

3.3 Kuhn monomer

Dealing with other polymer chain models means to deal with some stiffness or in the sense of formula 2 with some correlation of monomer vectors. For this, one example of model is the freely-rotation-chain (FRC) from the picture 2.

In there the black monomers are oriented with a fixed purple bond angle. The correlation value of two neighboring monomers (d=1) gets $\langle \vec{r}_i \vec{r}_{i+d} \rangle = |\cos(\theta)^d|$. To evaluate the calculation 2 for this model it is useful to introduce

$$C_i = \sum_{j=1}^{N} \langle \vec{r}_i \vec{r}_j \rangle \quad \text{with} \quad R = \sqrt{\sum_{i=1}^{N} C_i} \tag{6}$$

as a intermediate value. Because the polymer is long ($N >> 1$) most of the C_i are calculated for i inside the polymer far away from one end. Because the correlation drops fast with $d = |i - j|$ as distance from the end it is reasonable to assume that C_i is independent from N. In a approximation a mean value C_∞ for C_i is calculated and then pulled out of the sum in calculation 2. This approximations yields

$$R = \sqrt{C'_\infty l^2 \sum_{i=1}^{N}} = \sqrt{C'_\infty l^2 N} = b \cdot N^{\frac{1}{2}}. \tag{7}$$

Here the C prime means that the length of the monomers is pulled out as a factor. Later this factor is then again included into the l two form the new hypothetical Kuhn monomer length

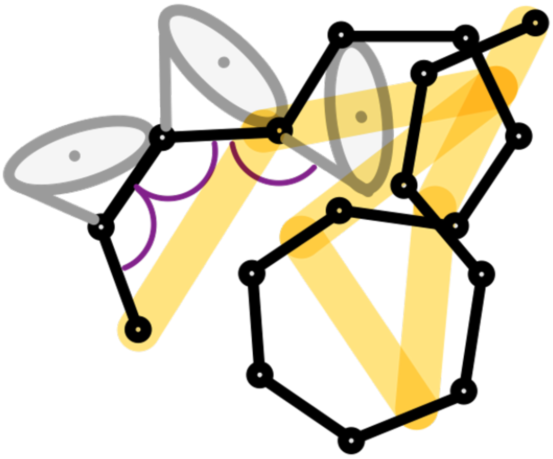

Abbildung 2: This drawing visualizes the restrictions and movements of monomers (black) in FRC-chains. Also Kuhn monomers for the given FRC chain are drawn in yellow.

b. The visualization of b is colored in yellow in picture 2. With this general treatment of making the correlation independent of N all the stiffer models like FRC can then be treated as a FJC with longer monomer lengths b. For FRC carrying out the summation using the geometric series yields

$$C'_\infty = \sum_{j=1}^{\infty} \langle \cos(\theta)^{|i-j|} \rangle \approx \sum_{-\infty}^{j=i-1} \cos(\theta)^{|i-j|} + 1 + \sum_{j=i+1}^{\infty} \cos(\theta)^{|i-j|} \tag{8}$$

$$= 1 + 2\sum_{k=1}^{\infty} \cos(\theta)^k = -1 + 2\sum_{k=0}^{\infty} \cos(\theta)^k \tag{9}$$

$$= -1 + 2\frac{1}{1-\cos(\theta)} = \frac{1+\cos(\theta)}{1-\cos(\theta)}. \tag{10}$$

A general approach in polymer physics is the blob approach. This is essentially a scale separation in length. In the case that follows it is used to approximate the scaling of the stretching force $\vec{f}$ with stretched distance R. A typical polymer under stress is drawn in picture 3.

Here it is visible that in the short regimes the chain behaves like a chain doing a random walk while on the large regime the chain of spheres or blobs is ordered in a nearly straight line. This allows to determine the blob size ξ as a function of the monomers in the blob g to $\xi = bg^{\frac{1}{2}}$ according to the ideal chain scaling. In the large regime the length of the chain becomes $R = \xi \cdot \frac{N}{g}$ where $\frac{N}{g}$ denotes the number of blobs. Motivated by $F = \vec{f} \cdot \vec{s}$ as a formula for the (free) energy the formula for $\vec{f}$ gets $\vec{f} = \vec{\nabla} F$ with the free energy F. The Free energy penalty of the polymer for being stretched is approximated by assigning each lost degree of freedom from the chain the energy $E = \frac{1}{2}kT \approx kT$. The number of lost degrees of freedom is the number of ordered blobs in a row $\frac{N}{g}$. Putting the formulas from the two regimes into the calculation of the free energy

$$F = kT \cdot \frac{N}{g} = kT \cdot \frac{NR^2}{b^2N^2} = kT \cdot \frac{R^2}{b^2N} \tag{11}$$

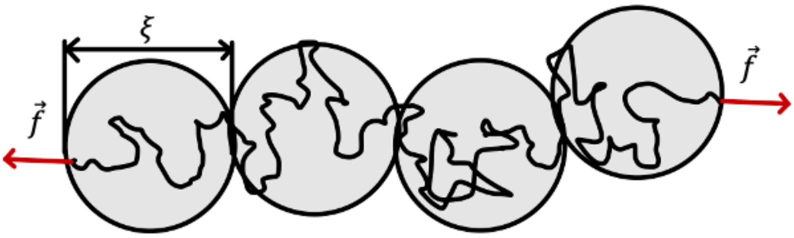

Abbildung 3: In this picture a typical polymer shape under stretching force $\vec{f}$ is drawn. There a assumption of a length scale separation with the critical length ξ is reasonable. This results in the blob approach visualized with the spheres in the drawing.

yields the desired relation for $F(R)$ which allows to calculated $\vec{f} = 2 \cdot \frac{kT}{Nb^2}\vec{R}$ by derivation. It is visible that the force depends linearly on the distance $\vec{R}$ so that the Hooke-law is fulfilled. Also the temperature dependence is determined. Here higher temperatures reinforces the $\vec{f}$ despite the fact that this is against the rule for example in metallic solid bodies.
For the finding of formula 11 it astonishingly wasn't necessary to know the size of ξ. On the one hand the formula then is simple but on the other hand the formula need to be used carefully because in the case that $g > N$ there wouldn't be even one blob. Because of that the formula 11 only is valid for $N > g$ or $R > b^2N$. This minimum size will be called thermal blob size. Here it is reasonable to assume that the lost degrees of freedom needed to elongate to the length R will raise relative to 11 because the gained length decreases when ξ as the blob size is not valid anymore. Therefor the F is assumed to be greater than equation 11 states for $N < g$.

4 Real chain

The mathematical treatment of real chains is in general tedious because the main difference to ideal chains is that the monomers can't possess the same volume, leading to an impossible listing of already blocked position in analytical treatment. But this task is bypassed by the Flory approximation of real chain that will be the goal of the next chapter. To prepare for this calculation it is important to introduce an approximation of the "possessed"volume of one monomer. This thought of blocked volume is expanded to the addition of beneficial distances to the monomer. Blocked and beneficial monomer distances are mathematically expressed by the liklyhood of the occurrences derived from the Boltzmann distribution

$$p = \frac{\mathrm{e}^{-\frac{U(r)}{kT}}}{\sum \mathrm{e}^{-\frac{U(r)}{kT}}}. \tag{12}$$

Blocked distances are the ones where the potential is high and beneficial states are the one where the energy is below zero in other word where the potential has got it's potential well. A plausible and wide spread potential is the Lennard-Jones potential

$$U(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \tag{13}$$

with the parameters A and B that need to be chosen to fit the thickness of the monomer d and the depth of the potential well. In the further treatment unlikely or likely states shall be maped on the positive or negative number line. For this the Mayer-function

$$f(r) = \mathrm{e}^{-\frac{U(r)}{kT}} - 1 \tag{14}$$

with its shifting of -1 of the Boltzmann factor is introduced. The Normalization of the Boltzmann distribution is dropped here because an excluded volume shall be determined. In the blocked area the amplitude of the Mayer-function shall not be below -1 because the excluded volume then would have a numeric weight exceeding it physical volume. On the other end for large distances r $f(r)$ gets zero because no interaction exists and thus no blocked of beneficial states exist. Summing up the Mayer-function over each possible position with a volume integral

$$v = -\int f(r)d^3r \tag{15}$$

the excluded volume per monomer v is yielded. With this sign convention repulsion effects push the excluded volume toward $v > 0$ where attraction contributions aim for $v < 0$.
Also with the introduced formula a temperature dependence of the excluded volume with the Boltzmann-factor is visible. Because of the Lennard-Jones-potential being steep for $r < d$ the blocked volume or the repulsion contribution doesn't alter with temperature that much. On the other hand the potential well loses its dominance with increasing temperature, leading to less attraction effects. If a $U(r)$ is chosen to have no potential well than the temperature doesn't change the excluded volume that much leading to the so called athermal case.
As well as assigning the ideal chain a volume with raising $R = bN^{\frac{1}{2}}$ to the third power, the real chain also pervades a volume. With repulsion effects from $v > 0$ this real chain volume R_F^3 is assumed to be greater than the ideal chain volume R^3. More profound the length R_F should fulfill $R_\mathrm{F} > R^3$ for the same b and N. With this context it is possible to motivate that the chain is stretched when a real chain behavior is assumed. But stretching is assigned to a higher free energy as calculated in 11. Then there need to be another contribution to the free energy so that an elongated chain is beneficial and the equilibrium state. This other energy contribution is approximated using the average number of monomers that overlap with a chosen one. This is approximated with $v \cdot \frac{N}{R_\mathrm{F}^3}$ where the fraction is a rough estimation of the mean monomer density inside the pervaded volume. The total number of occurrences of overlapping is calculated as $v \cdot \frac{N^2}{R_\mathrm{F}^3}$. For each occurrence a monomer needs to choose a different position or bonding angle, hence the degree of freedom is restricted here. This thought yields a formula for the free energy

$$F = kT \cdot v\frac{N^2}{R_\mathrm{F}^3} \tag{16}$$

that is mapped to a real polymer length R_F. Including the free energy contribution from the stretching of the chain yield the total free energy

$$F_\mathrm{tot} = kT \cdot v\frac{N^2}{R_\mathrm{F}^3} + kT \cdot \frac{R^2}{b^2N}. \tag{17}$$

The equilibrium length

$$R_\mathrm{F} = b\left(\frac{\nu}{b^3}\right)^{2\nu-1}N^\nu \tag{18}$$

is now obtained by finding the minimum of F_tot. With this calculation the exponent $\nu = \frac{3}{5}$ is yielded but in experimental observations ν is determined to be $\nu \approx 0.588$. With this result it is shown that real chains following the statistics of self-avoiding-walks (SAW) obey a greater scaling with the monomer number N of the polymer than ideal chains do. But the formula 17 for the total free energy does not include the right scaling of the stretching force for small N. Because the stretching force there is expected to be greater than the formula 11 assumes the equilibrium for R_F is shifted to smaller values and scaling. Below the thermal blob size $v < \frac{R^3}{N^2}$ (or $g < N$ from chapter 2) the scaling is then comparable to the ideal chain scaling $R \approx N^{\frac{1}{2}}$.

5 Polymer solutions

Compared to the previous chapters this chapter adds the interactions of different polymers and the interactions between solvent and the polymers to the observed physics. As a result some new vocabularies need to be introduced. First there is the differentiation between good and poor solvents. According to the Mayer-function, the repulsive interaction between the monomers raises for higher temperature. Then this gets increasingly the dominant energy contribution to the system of polymers and solvent. Because of that the surface area between polymer and solvent doesn't want to be minimized that likely for higher temperatures. Because of that the polymer chain expands and swells inside the solution. For low temperatures this process is very likely reversed so that the polymers tries to minimize its surface to the solvent. In this general discussion the relative energy contributions are relevant. With this the excluded volume definition is reused in polymer solutions.

The second vocabulary is the dilute or semidilute regime of polymer solutions. Because we already attached a volume to each polymer in the solution there is the possibility that the sum of this volume exceeds the experimental volume. In other words there is the possibility that the pervaded volumes overlap an thus lei the basis for dominant polymer interactions in the solution. The semidilute regime is the regime with the overlapping. The dilute regime is the regime where the pervaded volumes don't overlap. To get from the dilute regime to the semidilute regime there is the possibility to change the volume fraction $\phi \in [0, 1]$ of the polymers in the solution. This means that the polymers inside the solution then make up a larger and larger part of the volume.

The physics of polymers in solution is as well determined by the free energy and the minimum of it. By adding solvent to polymers the entropy of mixing S_{mix} make up one contribution to the free energy

$$\Delta F_{mix} = \Delta U + T\Delta S. \tag{19}$$

In an approximation the monomers and solvent molecules are treated as equally shaped cubes that can easily be analytically permuted inside the experiment volume to make up the different mixing states. Mixing nonzero quantities of polymer and solvent will yield several possible combination of the mixed state. Because of that the entropy of a mixed state raises and the mixing process is beneficial in terms of ΔF_{mix} if ΔU is ignored at first. To get a quantitative measurement for the entropy of binary mixing of polymers into solvent the first ansatz is to assume a lattice of cubes with n places filled with $n\phi$ monomers an $n(1-\phi)$ solvent molecules. Before the mixing process the monomers fill up their own volume ending up in $(n\phi)!$ possible configurations. In the following calculations the faculty is neglected. It is assumed that in fact each monomer and solvent molecule can choose between $n\phi$ or $n(1-\phi)$ lattice sites. Also the monomers of the polymer are combined into one element despite the accurate treatment of the polymer volume. This is only completely right in combinatorics if a one dimensional array of the cubes is assumed. In other words the different arrangements of the monomers in the polymer is not kept track of to make the calculation more feasible. In this assumption the entropy gain while mixing for one polymer molecule is given by

$$\Delta S_{\mathrm{P}} = k\ln(n) - k\ln(n(\phi)) = -k\ln(\phi) \tag{20}$$

where

$$\Delta S_{\mathrm{S}} = k\ln(n) - k\ln(n(1-\phi)) = -k\ln(1-\phi) \tag{21}$$

denotes the entropy gain for the solvent molecule. Within the assumption of the neglected facultys the total entropy of mixing is denoted by

$$\Delta S = n_{\mathrm{P}}\Delta S_{\mathrm{P}} + n_{\mathrm{S}}\Delta S_{\mathrm{S}} = -k(n_{\mathrm{P}}\ln(\phi) + n_{\mathrm{S}}\ln(1-\phi)) \tag{22}$$

$$= -kn\left(\frac{\phi}{N}\ln(\phi) + (1-\phi)\ln(1-\phi)\right) \tag{23}$$

with the molecule numbers $n_\mathrm{P} = n\frac{\phi}{N}$ of polymers and $n_\mathrm{P} = n\phi$ of solvent. This simplified calculation already results in a positive entropy for all values ϕ as expected. Thus mixing is beneficial to this point. Next is an approximation of the potential energy. Now a different perspective on the matter of excluded volumes is carried out. Taking over the discrete model with monomers and solvent molecules in cubes the inter molecular surface is easily defined. The approach is to assign different kinds of surfaces to different elementary potential energies u_SP, u_PP and u_SS where S again denotes solvent and P monomers. Now that we know what energy each inter molecular surface possesses the task reduces to just sum up all surface energies to get ΔU. Because it is not determined what number of u_SP there are if only ϕ shall be a variable an approximation is made. One face of a monomer has the mean energy $U_\mathrm{P} = u_\mathrm{SP}(1-\phi) + u_\mathrm{PP}\phi$ if ϕ is treated like a probability for the cube type of the other molecule at this face. Of course with that formula is the assumption of periodic boundaries made. With a similar mean energy per face for the solvent a summation over the $z = 6$ (for cubes) faces is conducted. Finally the summation over all cubes yields

$$U = \frac{zn}{2}(U_\mathrm{P}\phi + U_\mathrm{S}(1-\phi)) \tag{24}$$

as a energy of a configuration with the simple ϕ dependence. U is evaluated before and after mixing to receive

$$\Delta U = \chi n\phi(1-\phi)kT \quad \text{with} \quad \chi = \frac{z}{2kT}(2u_\mathrm{SP} - u_\mathrm{PP} - u_\mathrm{SS}). \tag{25}$$

χ is the flory-interaction-parameter and obeys the relation $\chi > 0$ for most combinations of polymer and solvent. With this approximations of the potential energy of mixing and entropy of mixing the free energy reads

$$\Delta F_\mathrm{mix}(\phi) = nkT\left(\frac{\phi}{N}\ln(\phi) + (1-\phi)\ln(1-\phi) + \chi n\phi(1-\phi)\right) \tag{26}$$

according to the Flory-Huggins equation. A figure of it is drawn in picture 4

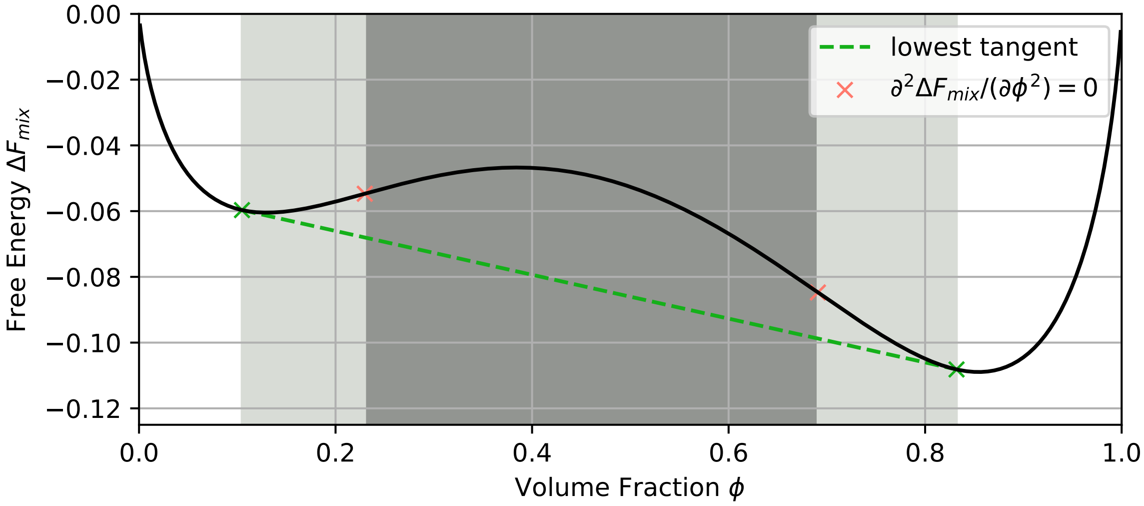

Abbildung 4: This figure presents the characteristic behavior of the $\Delta F_{mix}(\phi)$ for $N = 2$ and $\chi = 2.1$. The parameters are optimized for qualitative understanding. Also the different phases emerging form the curve are marked with background color. The dark regime signals unstable phases and the light grey background signals metastable phases.

For each ϕ with $\frac{\partial^2 \Delta F_{\text{mix}}(\phi)}{\partial \phi^2} > 0$ the solution is stable in the sense that the solution doesn't split up in subvolumes V_1 and V_2 with different $\phi_{1,2}$. This is because

$$\Delta F_{\text{mix}}(\phi_{1,2}) = V_1 \cdot \Delta F_{\text{mix}}(\phi_1) + V_2 \cdot \Delta F_{\text{mix}}(\phi_2) \tag{27}$$

sits on the secant of the curve $\Delta F_{\text{mix}}(\phi)$ for slight fluctuations obeying $\phi_1 < \phi < \phi_2$. In general there are also metastable regimes that occur when $\frac{\partial^2 \Delta F_{\text{mix}}(\phi)}{\partial \phi^2} > 0$ acts against phase separation but there are $\phi_1 < \phi < \phi_2$ for which $\Delta F_{\text{mix}}(\phi_{1,2})$ on the secant is lower than $\Delta F_{\text{mix}}(\phi)$.
Because the Flory-interaction-parameter χ has an extra temperature dependence included the dominance between ΔS and ΔUresulting in formula 26 changes and leads to the end of existence of the unstable and metastable phases for large temperatures T. In Figure 5 a phase diagram is shown that visualizes the existence or nonexistence of unstable or metastable states for given temperature T and volume fractions ϕ. This way the first two phases in diagram 5 in grey colors are already explained. Here it need to be mentioned that the phase diagram is

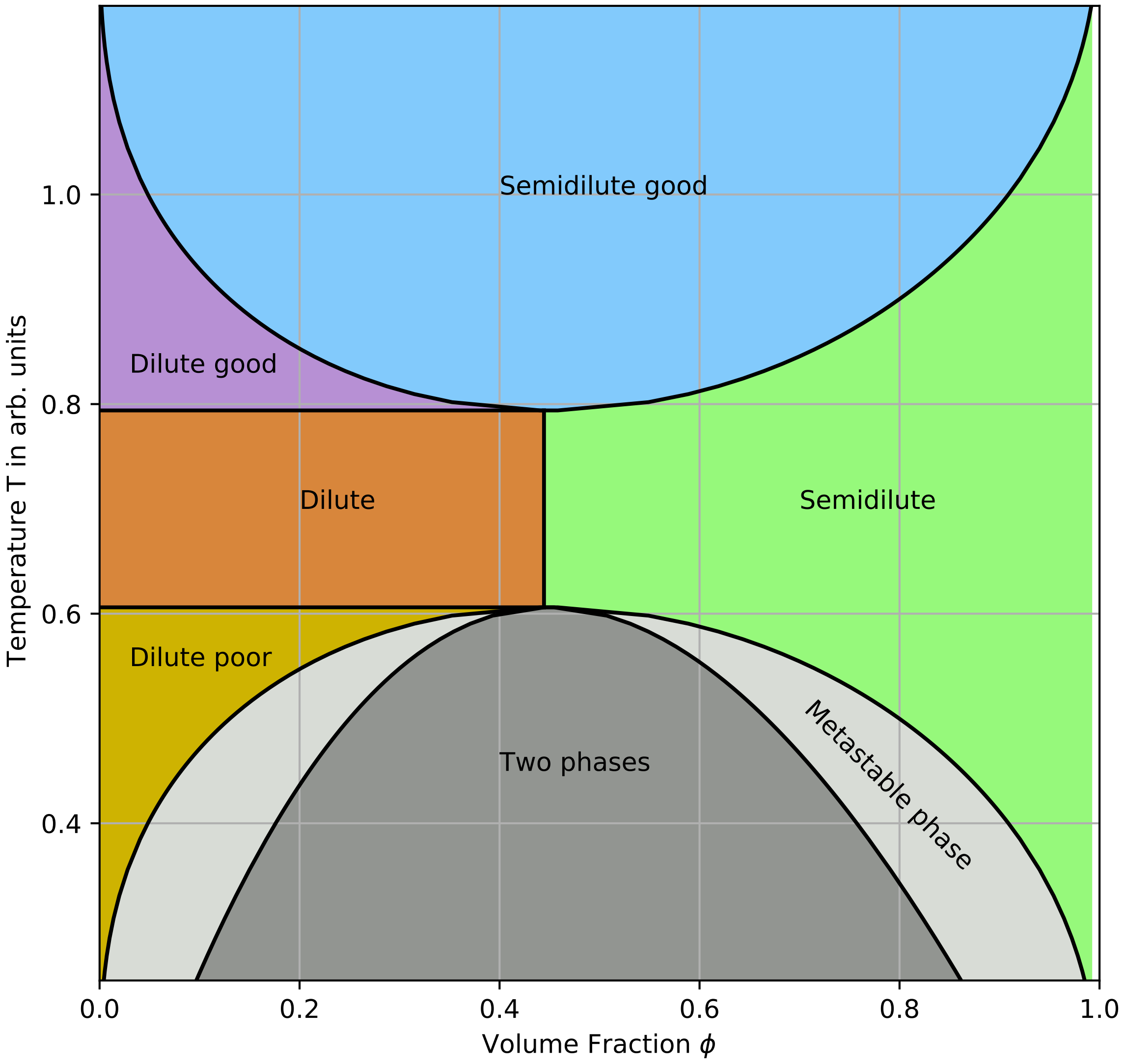

Abbildung 5: It is shown a phase diagram for different polymer solution states under different conditions for the temperature T and the volume fraction ϕ. The phase borders emerge form underlying changes in the length scaling of polymers with N, phase separation effects and conditions for overlapping of polymer volumes.

based on 26, with the parameters $N = 2$ and $\chi \in [0.8, 4.5]$. Thus the parameters are optimized for visual clarity not for physical plausibility. For low temperatures or in the poor solvent regime the energy penalty emerging from SP surfaces forces the polymers to from globules with a length scaling of essentially $R = N^{\frac{1}{3}}$ because the monomers fill out the volume of a sphere. The sphere serves the largest volume for the lowest surface with the solvent. This length scaling rule is characteristic for the dilute poor regime in 5. For higher temperatures the relative energy penalty on PS-surfaces is reduced. A counteracting energy contribution is the Flory energy of overlapping monomers. Taking both into account the scaling law in the dilute regime is comparable to the ideal chain $R = bN^{\frac{1}{2}}$ especially for the θ-temperature this is valid. In the dilute good regime the repulsive forces of the SAW takes over and yields the scaling law of real chains $R = b\left(\frac{\nu}{b^3}\right)^{2\nu-1} N^{\nu}$ above the thermal blob size and proportional to $N^{\frac{1}{2}}$ below the thermal blob size. When Investigating the semidilute regimes for higher ϕ the interaction between the polymers need to be taken into account. The first notion on the phase diagram 5 is that the semidilute regime exists for lower volume fractions the better the solvent gets. This is because the same amount of polymers pervade and possess more volume in the swollen state inside the good solvent. The interactions between the chains lead to the fact that not only the excluded volume of the own monomers act on the length scaling, but also the excluded volumes of foreign monomers act on the length scaling. Because of that the scaling proportional to N^{ν} changes to the smaller $N^{\frac{1}{2}}$ above the correlation blob size ξ_C with the condition

$$\xi_C = b\left(\frac{b^3}{v}\right)^{\frac{2\nu-1}{3\nu-1}} \phi^{\frac{-\nu}{3\nu-1}}. \tag{28}$$

For the semidilute regime in good solvents three different scalings of R with N emerge. At the phase diagram border to the normal semidilute regime in figure 5 the intermediate scaling regime disappears because the correlation blob shrinks with ϕ at and below the thermal blob size. Thus in the semidilute regime there is only a single scaling similar to the ideal chain scaling.

6 Polymer gels

The last part of the handout want to quickly introduce the topic polymer gels, to motivate that these materials can be treated as porous media. The one aspect that emerges in this topic compared to the polymer solutions is that polymers in the polymer gel are interconnected to a degree that the the network extends into macroscopic length scales. These connections can be of physical nature like the pure physical entanglement of two polymer chains into a helix. Also charged monomers,... in the polymer can form a connection inside the the network. On the other hand chemical bonds mostly covalent bonds can form the interconnections. The differentiation into weak connections and strong connections is made with the argument that for example H-bonds between monomers can be released while entanglement in a helix is a rigid connection. The connection type has a strong effect on the dynamical processes inside the gel. While for weak connections it is possible two rearrange the material in macroscopic lengths with no limit but the needed time to do so, for strong connections the rearrangement is restricted to the initial given connections. Further rearrangement will break the polymer chains and alter the average N of the polymers. In either of the connection types a critical fraction of made connection p_C from the polymers is needed so that the gel pervades the hole experimental volume. Of course when $1 > p_C$ there are possibilities for polymers to not be connected to the gel because some possible connections aren't made. These left out polymers then form the sol of more or less mobile polymers and polymer bunches. The 3D landscape of areas of gel and sol then fills the observed structure like a porous media does.

7 Literatur

[1] `https://commons.wikimedia.org/wiki/File:PLA_from_lactic_acid_%26_lactide.png`

[2] Michael Rubinstein and Ralph H. Colby, Polymer Physics Oxford University Press, 2003