Abstract

The $n$-vector model and critical exponents in the theory of critical phenomena are introduced and the concept of universality is described. The equivalence between the $n \to 0$ limit and the self-avoiding walk model for polymer chains is shown. Critical behavior of polymer mixtures is described along with the crossover from the mean-field to Ising scaling, substantiated by both simulations and experimental results.
1 Introduction

The behavior of physical systems close to their critical points is collectively dealt with by the theory of critical phenomena. Critical behavior was first observed by Andrews in the 19th century during his study of carbon dioxide gas [1]. He found a point on its $pV$ diagram where the liquid phase became indistinguishable from the gas phase. Nevertheless, even after Curie managed to make a connection between his work on ferromagnetic transition [2] and Andrews’ research, a general framework to describe such phenomena quantitatively was still lacking. The first such attempt came from Landau in 1937 [3], but his theory failed to show quantitative agreement with later research on individual critical systems (for example the two-dimensional Ising model). During following years much work was done to develop a general description but it was not until the renormalization group theory was introduced by Wilson in 1971 [4, 5] that the critical phenomena of different systems could be explained universally. This also means that study of a given physical system near its critical point can yield quantitative predictions of the behavior of some other such system and this is what makes this theory so important.

This seminar serves as a brief overview of the theory of critical phenomena and its application in polymer physics, more precisely polymer melts and solutions. First, the $n$-vector model and critical exponents are introduced, along with the concept of universality. As an interesting theoretical excursion, we show the link between the $n$-vector model and the self-avoiding walk model of polymer chains. Next, we focus on polymer mixtures and phase transition from mixed to phase separated state, where in the vicinity of critical point mean-field scaling transitions into Ising scaling, substantiated by both simulations as well as experimental results.

1.1 $n$-vector model

$n$-vector model is a model of $n$-dimensional unit spin variables on the sites of a $d$-dimensional lattice. We write the Hamiltonian for such system, in analogy with the well known Ising model, as

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i \cdot s_j - \sum_i H \cdot s_i,$$

where $i$ and $j$ are neighbor sites on the lattice (notation $\langle ij \rangle$), $J$ is the coupling constant between two spins, and $H$ is some external field. For some values of $n$, we get well known cases—Ising model, XY model and Heisenberg model for $n = 1, 2$ and 3, respectively. We also define the partition function $Z = \sum_{\{s_i\}} \exp(-\mathcal{H}/k_B T)$.

Now we can introduce some basic quantities that are relevant for our further discussion. The most important one to consider when dealing with critical phenomena is the order parameter. The exact definition of the order parameter is different from system to system but it should always be zero in the disordered phase and nonzero in the ordered phase. In the $n$-vector model, it is a $n$-dimensional vector with examples including magnetization

$$m = \frac{1}{N} \sum_i s_i$$
among others. In the Ising model at high temperatures, the spins will be oriented randomly and magnetization will be zero, and bellow the critical temperature they will be aligned which results in a nonzero magnetization.

Next, we define the spin-spin correlation function as another measure of order in the system

\[ G(\mathbf{r}) = \langle \mathbf{s}(\mathbf{r}) \cdot \mathbf{s}(0) \rangle - \langle \mathbf{s}(0) \rangle^2, \]  

where \( \langle \rangle \) denotes ensemble average over all possible configuration of the system at given temperature, \( \langle A \rangle = \int d\Gamma A(\Gamma) \exp(-\mathcal{H}/k_B T)/\int d\Gamma \exp(\mathcal{H}/k_B T) \). Here, instead of denoting lattice sites by their indices, we rather use the coordinate of the site \( \mathbf{r} \). We also introduce susceptibility as the zero-momentum component of the spin-spin correlation function

\[ S = \sum_\mathbf{r} G(\mathbf{r}) = \sum_\mathbf{r} \left[ \langle \mathbf{s}(\mathbf{r}) \cdot \mathbf{s}(0) \rangle - \langle \mathbf{s}(0) \rangle^2 \right], \]  

where the sum runs over all lattice sites, and second-moment correlation length of order parameter fluctuations

\[ \xi = \left[ \frac{\sum_\mathbf{r} r^2 G(\mathbf{r})}{\sum_\mathbf{r} G(\mathbf{r})} \right]^{1/2}, \]  

with \( r = |\mathbf{r}| \). The correlation length serves as a measure of length scale at which spins on the lattice are correlated as opposed to uncorrelated at greater distances.

It should also be mentioned that susceptibility and also specific heat \( C_H \) are thermodynamic quantities and can also be obtained from derivatives of free energy \( F \): \( S = \partial^2 F/\partial \mathbf{H} \cdot \partial \mathbf{H} \) and \( C_H = \partial^2 F/\partial T^2 \). We can obtain the free energy function from the partition function of the system.

### 1.2 Critical exponents

At the critical point, there exist no length scale characteristic of the system. One can imagine that, starting at infinite temperature and then gradually decreasing it towards the critical temperature \( T_c \), correlated clusters with typical size \( \xi \) start to emerge. The clusters are growing with decreasing temperature until \( \xi \) finally diverges at \( T_c \). From this consideration it follows that at the critical temperature, there is no characteristic lengthscale of the system. This is called scale invariance and it can be shown that it leads to quantities exhibiting power-law behavior.

In general, we should consider three different paths towards the critical point—for \( t > 0 \) and \( t < 0 \) at zero external field \( H = 0 \) and \( |H| \to 0 \) at \( t = 0 \), where \( t = T/T_c - 1 \). The renormalization group theory shows, however, that the critical exponents in first two cases are identical (note that the scaling amplitudes are not) and the third case is not as relevant for our discussion. Therefore, we focus on the temperature dependence of quantities around critical point where we define critical exponents as follows:

\[ C_H \sim |t|^{-\alpha}, \quad S \sim |t|^{-\gamma}, \quad \text{and} \quad \xi \sim |t|^{-\nu} \]  

and the order parameter exponent (only in ordered phase at \( t < 0 \))

\[ m = |m| \sim |t|^\beta. \]  

The spin-spin correlation function exhibits a power-law behavior at critical point \( (H = 0, t = 0, \xi \to \infty) \), where it scales with the distance as

\[ G(\mathbf{r}) \sim \frac{1}{r^{d-2\gamma}}. \]  

There are many relations connecting these exponents. It is customary to consider \( \eta \) and \( \nu \) elementary exponents and derive other as functions of \( \eta \) and \( \nu \). The relations

\[ \alpha + 2\beta + \gamma = 2, \quad \gamma = \nu(2 - \eta), \quad 2 - \alpha = d\nu \quad \text{and} \quad d\nu = 2\Delta_{\text{gap}} - \gamma \]  

can be derived in different ways and are also backed up by the renormalization group theory. In the last equality, we introduced exponent \( \Delta_{\text{gap}} \), which is related to scaling of the "gap" of the partition function (in accordance with Yang-Lee theorem) \[6\]. The last two relations are called hyperscaling relations. Here, we see an explicit dependence on the spatial dimension and there has long been no definite answer if they hold in general because their physical basis is not as firm as with other scaling laws \[7\]. It was shown already in 1970s that hyperscaling is only valid for systems below their upper critical dimension \( d_c \), but even in there some uncertainty prevailed—hyperscaling in polymer systems is thoroughly investigated in Ref. \[7\]. For dimensions higher than \( d_c \), all critical exponents reduce to those of the mean-field theory: \( \eta = 0, \nu = 1/2, \alpha = 0, \beta = 1/2, \) and \( \gamma = 1 \).
1.3 Universality

Some systems exhibit the same behavior around their critical points and can be described with the same model Hamiltonians of the n-vector model. We group them in universality classes where each system in the class has the same, universal values of critical exponents and also some universal amplitude ratios, that is ratios of proportionality constants [from Eqs. (6) and (7)]. This lets us make quantitative predictions of critical behavior of all systems belonging to the same universality class. The best known examples are

- **3-d Ising universality class**: Some well-known transitions belonging to Ising universality class are liquid-vapor transitions and phase separation of ionic fluids and binary mixtures. Polymer mixtures are a part of this last group and will described in Sec. 3. Beside these examples from classical physics, Ising universality class transitions are also expected in high-energy physics. The values of critical exponents are: $\eta = 0.036$, $\nu = 0.630$, $\alpha = 0.110$, $\beta = 0.327$, and $\gamma = 1.237$ [6].

- **3-d XY universality class**: First characterized by ferromagnets or antiferromagnets with easy-plane anisotropy, the most prominent example belonging to this class is the superfluid transition of $^4$He. The possibilities to experimentally investigate this transition have proven to be ideal to test predictions of renormalization group theory.

- **3-d Heisenberg universality class**: This class encompasses transitions of isotropic magnets.

There are also universality classes for n-vector models with $n \geq 4$. This include the O(4) class relevant for quantum chromodynamics and the O(5) class, which might describe the critical behavior of high-$T_C$ superconductors [6].

2 Self-avoiding walk and $n \to 0$ limit

An interesting theoretical insight is gained if one considers the limit $n \to 0$ of the n-vector model—it turns out to be equivalent to the self-avoiding walk (SAW) model of polymer chains. The geometric interpretation of this theoretical generalization follows below, along with derivation. In contrast to the random walk model, the SAW model also takes into account the excluded volume interaction which prohibits self-overlap of monomers in the chain and provides an accurate description of dilute polymer solutions in a good solvent. The scaling law for end-to-end distance $R_e = \sqrt{\langle R_e^2 \rangle}$ of a random walk of $N$ monomers is known to be $R_e \sim N^{1/2}$ [8].

For SAW, scale invariance dictates that end-to-end vector should still have power law dependence but with a different exponent, $R_e \sim N^{\nu_{poly}}$. In the $n \to 0$ limit, we show that this scaling exponent for SAW is exactly the same as the critical exponent for correlation length, $\nu_{poly} = \nu$ [6]. Also scaling exponents for some other quantities in SAW model, e.g., the number of all SAWs of $N$ steps, are the same as ones from theory of critical phenomena [6]. This makes SAW suitable to test predictions of the theory, such as hyperscaling relations, as it can be analyzed both in simulations and experimentally.

To show the equivalence of $n \to 0$ limit and the self-avoiding walk, we first start with the full n-vector model with Hamiltonian $H = -J \sum_{(ij)} s_i \cdot s_j$ [Eq. (1) with $H = 0$]. Consider two spins, $A$ and $B$, on the lattice, with $r$ being the distance between them. Their pair correlation function can be written as

$$G(r) = \langle s_A s_B \rangle = \langle s_A s_B \exp(-H/k_B T) \rangle_0 / \langle \exp(-H/k_B T) \rangle_0,$$

where $\langle X \rangle_0$ is thermal average of the system at infinite temperature, $\langle X \rangle_0 = \int \text{d} \Gamma X(\Gamma) / \int \text{d} \Gamma$. This average is equally weighted over all orientations of each spin. First we calculate the denominator in Eq. (10), which is equal to the partition function of the system (up to a prefactor—normalization) [8]. The exponential can be Taylor-expanded and we get

$$\langle \exp(-H/k_B T) \rangle_0 = \sum_{p=0}^{\infty} \frac{K^p}{p!} \sum_{(ij)} \sum_{(kl)} \cdots \sum_{(mn)} \langle (s_i \cdot s_j)(s_k \cdot s_l) \cdots (s_m \cdot s_n) \rangle_0,$$

where $K = J/k_B T$. Each pair $s_i, s_j \ldots s_m, s_n$ of neighboring spins can be thought of as a bond between two lattice sites so that the expression in brackets corresponds to a cluster composed of $p$ bonds, placed on the lattice in some configuration (bonds might sit on top of one another).
Taking this into account, this expression can be written as
\[
(s_i \cdot s_j)(s_k \cdot s_l) \cdots (s_m \cdot s_n) = (\text{contribution from spin } #1 \text{ on the lattice})
\times (\text{contribution from spin } #2 \text{ on the lattice})
\times \ldots
\] (12)

Now we state without proof that the moments \( \langle s_{\alpha_1} s_{\alpha_2} \cdots s_{\alpha_v} \rangle_0 \) with \( \alpha_1 \ldots \alpha_v \) components of \( n \)-dimensional spin \( s \) vanish in the limit \( n \to 0 \) [8], except the second moment where
\[
\langle s_{\alpha_1} s_{\alpha_2} \rangle_0 = \delta_{\alpha_1 \alpha_2}.
\] (13)

We need the average of the expression in Eq. (12) and get different moments \( \langle s_{\alpha_1} s_{\alpha_2} \cdots s_{\alpha_v} \rangle \) for each spin, with \( v \) the number of repetitions of respective spins in the product on the left-hand side of the equation. From Eq. (13) it follows that the only nonzero terms that we obtain are from spins (lattice sites) where exactly two bonds from our cluster meet, any other number of contacts of bonds on some lattice site gives a moment that is 0. The only clusters where this is true for each spin are closed-loop SAWs on the lattice. Considering Eq. (12), contribution of each such SAW of \( w \) connected spins can be calculated as
\[
\langle (s_1 \cdot s_2)(s_2 \cdot s_3) \cdots (s_w \cdot s_1) \rangle_0 = \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_w} \langle s_{1\alpha_1} s_{1\alpha_1} \rangle_0 \langle s_{2\alpha_2} s_{2\alpha_2} \rangle_0 \cdots \langle s_{w\alpha_w} s_{w\alpha_w} \rangle_0
\]
\[
= \sum_{\alpha_w} \delta_{\alpha_w \alpha_w} = n,
\] (14)

where each sum runs over all \( n \) components of each spin; on going into second row we used Eq. (13) and in the last step we just calculated the trace of the unit matrix. This means that each loop contributes a factor of \( n \) and in limit the \( n \to 0 \) we get factor 0. The only remaining term in Eq. (11) is therefore the \( p = 0 \) term and denominator yields 1.

Now we need the numerator in Eq. (10). Similarly to Eq. (11), we get
\[
\langle s_{Ax} s_{Bx} \exp(-\mathcal{H}/kBT) \rangle_0 = \sum_{p=0}^{\infty} K_p \sum_{\langle ij \rangle} \sum_{\langle kl \rangle} \cdots \sum_{\langle mn \rangle} \langle s_{Ax}(s_i \cdot s_j)(s_k \cdot s_l) \cdots (s_m \cdot s_n)s_{Bx} \rangle_0.
\] (15)

With the same reasoning as above, we see that the only surviving clusters are SAWs from lattice site \( A \) to site \( B \). In the bracket in Eq. (15), a similar calculation to the one from Eq. (14) gives us a contribution of 1 for each SAW [8]. This leaves us with
\[
\lim_{n \to 0} G(r) = \sum_N K^N c_N(r),
\] (16)

where we introduced \( c_N(r) \) as the number of \( N \)-step SAWs with end-to-end vector \( r \). Note that the factor \( 1/p! \) from Eq. (15) got canceled out when we took into account the number of assignments \( \langle ij \rangle \langle kl \rangle \cdots \langle mn \rangle \) to each walk (\( p! \) permutations). This equation gives a connection between the theory of critical phenomena and polymer physics.

Taking the scaling law for susceptibility \( S \sim |t|^{-\gamma} \) into account and defining the total number of SAWs of length \( N \), \( c_N = \sum_r c_N(r) \), we can calculate that it scales as \( c_N \sim N^{(\gamma-1)} \) in the vicinity of the critical point \( t \to 0 \) [6]. With this in mind we can further calculate
\[
\lim_{n \to 0} \sum_r r^2 G(r) = \sum_r \sum_N r^2 K^N c_N(r) = \sum_N K^N c_N R_e^2(N) \sim t^{-\gamma-2\nu_{\text{poly}}},
\] (17)

where we have used the scaling relation for the end-to-end distance \( R_e \sim N^{\nu_{\text{poly}}} \). Considering the definition [Eq. (5)] and the scaling relation for correlation length \( \xi \sim |t|^\nu \), we see that \( \nu = \nu_{\text{poly}} \)—scaling exponent for self-avoiding walks is the same as critical exponent for correlation length in \( n \to 0 \) limit. Do note, however, that scaling laws for polymer chains are asymptotic for \( N \to \infty \); for finite-size chains, corrections should be applied [6, 7].

The \( n \to 0 \) limit constitutes its own universality class which encompasses all walk models that considers excluded volume interaction. Among other well-known polymer chain models, the bead-rod model and continuum Edwards model are also included in this class. Most commonly, Monte Carlo simulations are used to get
the values of scaling exponents. The best currently known algorithm to generate an ensemble of self-avoiding walks is the pivot algorithm, where new configuration is obtained by rotation of a sub-chain of existing SAW around a random axis by a random angle. Such move is accepted if the generated configuration is again a SAW. In 1995, Li, Madras, and Sokal obtained $\nu = 0.5877(6)$ [7]. In 2010, Clisby managed to further improve the algorithm and with it in 2016, along with Dünweg, found that $\nu = 0.5875900(40)$ [9].

3 Critical behavior of polymer mixtures

As an example of critical behavior we present the mean-field to Ising crossover in polymer mixtures. The topic is significant in materials research where blending polymers to get the desired properties can be of great importance. Research on polymer mixtures also provides a better understanding of fundamental concepts in statistical physics, such as phase diagrams and phase transitions. Although the crossover itself might not be the focus of recent research, it provides valuable insight into the physics of polymers, specifically polymer mixtures, which is often omitted from undergraduate curriculum.

Most research on this topic was done in 1990s [10, 11, 12]. First predicted theoretically, it was observed in simulations as well as experiments that for binary mixtures of polymers where both compounds $A$ and $B$ have the same chain length ($N_A = N_B = N$), the critical exponents very close to critical temperature of the system, where system transitions from mixed to phase separated state, change from mean-field values to those of the Ising model (for $N \to \infty$). However, before we can further describe this crossover, one should first get some insight into critical behavior of such systems. This is provided by the Flory–Huggins theory.

3.1 Flory–Huggins theory

Flory–Huggins theory uses classical mean-field arguments and thermodynamics to describe polymer mixtures and solutions. Consider two kinds of polymers $A$ and $B$, with degrees of polymerization (chain lengths) $N_A$ and $N_B$ respectively. Monomers are points on a lattice and cannot overlap (SAW). We now define volume fraction $\phi_i$ for both kinds of monomers ($i = A, B$) as the ratio between the number of sites occupied by monomers of the same species and the number of all lattice sites.

Now we consider interaction between monomers. If there is some monomer on an adjacent lattice site to another monomer, the system gains energy $\epsilon_{AB}$ or $\epsilon_{BB}$ in case the monomers are the same species or $\epsilon_{AB}$ if they are different. The probabilities of such contacts between monomers are equal to volume fractions. The free energy per lattice site of these two-component systems can be written as

$$\frac{f}{k_B T} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi.$$  \hspace{1cm} (18)

The first two terms have entropic origin while the last describes the free energy of mixing [13]. $\chi$ is the Flory–Huggins parameter

$$\chi = \frac{z \epsilon}{2k_B T},$$  \hspace{1cm} (19)

with $\epsilon = 2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}$ and $z$ being the coordination number of the lattice. We expect that for large values of $\chi$, $AB$ contacts are penalized (lead to higher energy of the system) and we expect separation of polymers. To describe this we write the free energy of both the mixed and phase separated state of the system—separation occurs when the free energy of the separated state is lower. The calculation shows that this happens for values of $\chi$ higher than some critical value $\chi_C$. This also implies a critical temperature $T_C$. In the dense limit ($\phi_A + \phi_B = 1$), the result for $T_C$ of symmetric mixtures ($N_A = N_B$) is written as

$$k_B T_C = \frac{z \epsilon N}{4}.$$  \hspace{1cm} (20)

and predicts a scaling linear in $N$.

The phase diagram of a symmetric polymer mixture in the dense limit ($\phi_A = \phi$, $\phi_B = 1 - \phi$) is sketched in Fig. 1. Below the critical temperature (i.e., at large $\chi$) the system undergoes a phase transition from mixed to phase separated state. In thermodynamic equilibrium, the dividing line for this transition is the binodal (blue solid line). It is calculated as the extreme case for which the free energy of phase separated state is lower than that of the mixed state. The system, however, is only absolutely unstable towards phase separation in the region where the free energy of the mixed state (Eq. 18) is concave. This gives the condition for the spinodal (red dashed curve): $df^2/d\phi^2 = 0$ [14].
Figure 1: Phase diagram of symmetric polymer mixture of polypropylene (PP) and head-to-head polypropylene (hhPP), calculated within the Flory–Huggins theory. Below the critical temperature (i.e., at large $\chi$), the system transitions to phase separated state, separated from stable mixed state by binodal (blue solid line). Below the spinodal (red dashed line), the mixed state is meta-stable and above the spinodal it is unstable. Adapted from Ref. [15].

3.2 Scaling crossover

The Flory–Huggins theory assumes constant volume fractions across the whole system. It does not take into consideration thermal composition fluctuations that are intrinsic to any multi-component system at finite temperatures. In case of strong thermal fluctuations that appear near the critical point, the mean-field approach ceases to describe the critical behavior and other scaling models are needed. It turns out the system transitions to 3d-Ising critical behavior that describes simple binary fluids. To a good approximation, this crossover is controlled by only one variable, $t/Gi$ [11]. Gi is the Ginzburg number and is used to estimate the boundary between weak and strong thermal fluctuations [13]. In an interval around the critical point $|t|/Gi \ll 1$, the system exhibits Ising critical scaling while for $|t|/Gi \gg 1$ the exponents are that of the mean-field theory. In the crossover region, neither scaling is correct and the exponents smoothly transition from one case to another [11].

The crossover behavior is not limited only to polymer mixtures—it is also present in simple binary fluids already mentioned. Nevertheless, relatively large Ginzburg numbers (e.g. Gi = 0.014 for CO$_2$ or Gi = 0.025 for H$_2$O [11]) make them imperfect for studying of such crossover. In polymer mixtures, the Ginzburg number depends on degree of polymerization of both components. For symmetric mixtures, this yields Gi $\propto$ 1/$N$ [13] and we see that by increasing the chain length one can make Ginzburg number arbitrarily small.

Scaling crossover can be investigated both by simulations and experiments. As a common approach in polymer physics, one uses Monte Carlo simulations to examine the phase space of the system [11]. Experimentally, scattering methods, especially small angle neutron scattering (SANS), are very suitable to study properties of polymer blends [10, 12, 13].

4 Simulations

As a more realistic representation, bond fluctuation model is used to describe flexible polymers. In this lattice model, each monomer is represented by a cube (in 3-d) and so blocking 8 lattice positions from further occupa-
tion (excluded volume interaction), and with effective bonds in between monomers from a set of allowed vectors (lengths between 2 and $\sqrt{10}$) [11]. Figure 2 illustrates this model on a two-dimensional lattice. During each Monte Carlo step, we attempt to translate one monomer along one of the axes by one lattice spacing. To apply this model to polymer mixtures, we again define interaction energies between monomers $\epsilon_{AA}(r)$, $\epsilon_{BB}(r)$, and $\epsilon_{AB}(r)$. Note that now these energies depend on the distance between monomers. Usually, further limitations are introduced so that only monomers close to each other interact, which lets us change the effective coordination number $z_{\text{eff}}$ of the lattice. One such choice of interaction is $\epsilon_{AA} = \epsilon_{BB} = 0$, $\epsilon_{AB} = \epsilon$ and with monomers only interacting if they are within distance 2 on the lattice (smallest possible). This choice gives $z_{\text{eff}} = 5$ and was also used to obtain all of the simulation results discussed below.

![Figure 2: Bond fluctuation model on a 2-d lattice. Here, each monomer (blue dots) effectively blocks 4 lattice positions. Bonds are represented by blue solid lines. Also shown is a possible Monte Carlo displacement move, where one monomer is translated by one lattice spacing. Adapted from Ref. [16].](image)

When using this model in simulations it is also common to describe symmetric polymer mixtures in a semi-grand canonical ensemble. Here, the number of all polymer chains stays constant but chains can change identity ($A \leftrightarrow B$) which allows differentiation of an otherwise homogeneous system. To incorporate this into the Monte Carlo algorithm, one should add a move that executes such a change, beside the displacement already mentioned above. In both cases, the Metropolis criterion must be considered for acceptance or rejection of the move. An important parameter for Monte Carlo simulations of symmetric polymer blends is also the difference in chemical potential $\Delta \mu = \mu_A - \mu_B$, with $\mu_A$ and $\mu_B$ the chemical potentials of monomers of species $A$ and $B$, respectively. In a semi-grand canonical ensemble, it is independent of temperature. At the critical point this difference vanishes (because of symmetry) and $\Delta \mu = 0$. To study the region around the critical point where $\Delta \mu \neq 0$, one uses histogram reweighting of results obtained for $\Delta \mu = 0$—each point of the probability histogram obtained from Monte Carlo simulation at $\Delta \mu = 0$ is multiplied with an appropriate factor, which gives results equivalent to performing the simulation at a given nonzero $\Delta \mu$ [11].

The main observable in studying scaling crossover is the order parameter

$$m = \frac{\Delta M}{M},$$

with $M = M_A + M_B$ and $\Delta M = M_A - M_B$, where $M_A$ and $M_B$ are numbers of $A$ and $B$-type chains, respectively. First, the determination of critical point is needed and for this we exploit finite-size scaling effects. Scaling relations [Eqs. (6) and (7)] are valid for systems in the thermodynamic limit, i.e. of infinite size. For finite size systems, correlation length is limited by the system size $L$ which makes also other critical properties size dependent at $T_C$. However, if we now define cumulants $U_{kl}^{ij} = \langle |m|^k \rangle^j / \langle |m|^l \rangle^j$ with $kl = ij$, one can show that at critical temperature they are independent of system size. This allows us to determine critical temperature from simulations of different system sizes plotted as function of temperature (Fig. 3a). Using this technique for different chain lengths $N$, we see that it asymptotically approaches scaling linearly with $N$ and so confirms prediction from Flory–Huggins theory (Fig. 3b). Nevertheless, it should be noted that the prefactor to this scaling that we get from simulations is different from the one in Eq. (20) which shows that Flory–Huggins theory is not best suited for quantitative predictions of critical temperature.
The mean-field to Ising crossover can be observed in size-dependences of the simulated system which is thoroughly discussed in Ref. [11]. To limit the scope of the present discussion, the focus here is on thermal crossover, which can be also experimentally observed. In order to avoid significant size effects, the size of simulation box needs to be as large as possible—for the results shown here (Fig. 4), this means $160^3$ (this limit was imposed by the available computing power at the time). Finite size effects were assumed to be negligible at this system size. The results are plotted in dependence to variable $Nt$ for better representation—chains of different lengths have different Ginzburg numbers, so their behavior in the same temperature interval falls into different parts of crossover. The mean-field and Ising power-law scaling are indicated by straight lines. Simulation data shows good qualitative agreement with theoretical predictions, aside from short chains, where there are obvious discrepancies. We can also see that even for chain with $N = 512$, the mean-field regime was still not reached. With the help of renormalization group theory, it can be calculated that the crossover spans over several decades in $|t|/G_i$, as opposed to approximately two decades of data in variable $N|t|$ investigated by the presented simulation.
5 Experimental results

To study the crossover scaling in polymer mixtures, the most commonly used method is small-angle neutron scattering, followed by small-angle neutron scattering and time-averaged light scattering. A schematic sketch of the SANS experiment can be seen in Fig. 5. The behavior of the system is investigated by determining the structure factor at zero scattering vector \( S(0) \) which acts as a susceptibility and obeys the same scaling law [Eq. (6)]. To obtain \( S(0) \), a wide range of scattering \( S(q) \) is examined. The expression for \( S(q) \) can be expanded in the Zimm approximation for small values of \( q \) which yields \( S^{-1}(q) = S^{-1}(0) + Cq^2 \) (\( C \) depends only on composition of the melt) and makes it easy to calculate \( S^{-1}(0) \) and study its scaling [13].

Figure 5: Sketch of the SANS experiment. Measured is the scattering intensity in dependence to the scattering vector \( q \), \( S(q) \). Ref. [17].

The results from two different experiments can be seen in Fig. 6. Solid lines in both panels represent Ising (Fig. 6a and b) and mean-field (Fig. 6b) scaling laws, while solid lines are calculated according to crossover function for susceptibility. We see it shows excellent agreement with experimental results—nevertheless, we will not pursue the crossover formalism in this seminar any further. Note also that reduced temperature is defined a bit differently here, \( \tau = 1 - T_C/T \). On the left graph with the data for a mixture of deuterated polybutadiene (dPB) and polystyrene (PS), we see that the experimentally determined structure factor \( S(0) \) really scales with Ising value of critical exponent \( \gamma \), up to the vicinity of the Ginzburg number (indicated by the arrow). The mean-field scaling coincides with crossover function line for \( t \gg G_i \). Inverse structure factor being 0 at \( T_C \) is expected as correlation length—and with it \( S(0) \)—diverges. Figure 6b shows the results for two different polymer mixtures of dPB and PS, with 7 and 54% vinyl contents for the PB component. In the temperature window examined, the two systems are in different parts of their respective crossover regions and have therefore different scaling exponents, between the values for mean-field and Ising model. The crossover range for these two mixtures is rather large, 13 K in contrast to the order of 1 K for some other mixtures [13].

6 Conclusions

Critical phenomena plays a significant role in different areas of physics, with polymer physics being no exception. First, we got familiar with the \( n \)-vector model and some basic quantities of the theory of critical phenomena. Discussed was the \( n \to 0 \) limit and how it relates to self-avoiding walk. Further, we described polymer mixtures and their scaling crossover originating in strong thermal composition fluctuations near the critical point. Explained was the Monte Carlo simulation of such systems and experimental investigation through small angle neutron scattering. We saw that the results of both simulation as well as experiments confirmed the crossover behavior.

On many occasions, we did not dive into the details of underlying physical description and only introduced most fundamental concepts needed to understand the phenomena. For further insight into the theory of critical phenomena or behavior of polymer melts, there exist numerous review articles, such as Refs. [6] and [13], respectively, also indicating strong activity in the field.
Figure 6: Temperature dependence of inverse structure factor in polymer mixtures at zero scattering vector $S(0)$. Dashed lines indicate mean-field and Ising model asymptotic scaling laws. Solid line represents theoretical crossover model fit which shows good agreement with experiments. Panel a is adapted from Ref. [12] whereas panel b is adapted from Ref. [13].

References