

1. Landau theory for polydisperse copolymer melts

1.1 Introduction

The weak segregation regime

For many monomer pairs A and B the net interaction in an incompressible system is unfavorable, that is, $\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) > 0$, where $\epsilon_{\alpha\beta}$ is the contact energy between a monomer of type α , and a monomer of type β . Consequently, in many cases a polymer system containing two or more monomer types will undergo a phase separation if the interaction strength is increased relative to $k_B T$, which can be achieved simply by lowering the temperature (k_B is Boltzmanns constant). If the different monomer types are chemically bonded in the same chain to form (block) copolymers, the phase separation can give rise to a microscopic structure. Typically, it consists of domains which are alternately rich in A and rich in B . Depending on the degree of separation between A and B , three regimes can be distinguished: the weak segregation regime (WSR), the intermedeate segregation regime^{2,7} (ISR), and the strong segregation regime⁸ (SSR). In the SSR the separation between the A - and the B -monomers is complete, and the only A/B -interactions take place at the thin interfaces between the domains. The chains are strongly stretched⁹ in order to minimize the interfacial area. In the WSR the difference in composition between the A -rich and the B -rich domains is small, and the thickness of the interface is comparable to the size of the domains. The concentration profile is more or less sinusoidal. Due to their limiting character, both the SSR and the WSR allow for analytical calculations. Although traditionally these calculations have a quite different nature, recently succesfull attempts¹⁰ have been made to unify the WSR with the SSR.

Landau theory

In this thesis the phase behavior of polydisperse copolymer melts is studied in the WSR. This phase behavior can be described within the framework of classical statistical mechanics. However, taking into account all microscopic details of its chemical constituents is an impossible task. Fortunately, this is also not necessary. It is known from experiments that

polymer systems having quite different chemical compositions may exhibit very similar behavior. The influence of the microscopic (i.e. on the level of the atoms) details can be caught in a small number of parameters, such as the Flory-Huggins χ -parameter,¹¹ the excluded volume ν per segment (a segment is a flexible piece of chain), and the stiffness of the chain. Apart from these parameters it is the molecular architecture on the level of the blocks which determines the phase behavior. Therefore, a model to explain the phase behavior need not (and should not) take into account the microscopic details. Landau theory¹² has proven to be a useful tool in these cases, because it avoids dealing with the underlying microscopic theory by working with a coarse grained description. We start with giving a rough sketch of the idea underlying the Landau theory.

Since copolymer melts are almost incompressible, we can study them using the canonical ensemble, which assumes constant volume and temperature. In this ensemble, the partition function Z is defined as the integral of the Boltzmann factor $e^{-E/k_B T}$ over the positions and momenta of all particles present in the system. Quite generally, it is possible to factorize Z into a contribution from the momenta, and a contribution from the positions. The integral over the momenta is a function of the temperature, and will not be considered any more, since it is of no use for the determination of the phase behavior. The integral over the positions is called the configurational partition function, and is denoted by Z . The probability that a certain configurational microstate occurs is proportional to its Boltzmann factor $e^{-E/k_B T}$, where E does not include kinetic energy. However, we are not interested in microscopic states, but in coarse grained states. For example, if we study binary blends containing A - and B -particles, we are interested in whether the system is homogeneously mixed, or phase separated, and not in the exact positions of all particles. Each coarse grained state represents a large number of microstates. In order to find the probability of a coarse grained state, one has to add the probabilities (i.e. Boltzmann factors) of all microstates it represents. The coarse grained states are often chosen in such a way that most of the microstates it represents have the same energy content, and, therefore, the same probability of occurrence. In that case the (unnormalized) probability P to find the system in a certain coarse grained state is equal to the Boltzmann factor per microstate, multiplied with the number Ω of microstates, that is,

$$P \propto \Omega e^{-E/k_B T} = e^{-F_L/k_B T} \tag{1.1.1}$$
$$F_L = E - TS, \quad S = -k \ln \Omega$$

The quantity F_L is called the Landau free energy of the coarse grained state (although in fact it is not a free energy in the true sense of the word), and S is its entropy. One can expect that the system will be found in the coarse grained state for which P attains its maximum value. At low temperatures the system prefers a state with low energy, whereas at high temperatures it prefers a state with high entropy. In many cases these two conditions cannot be satisfied simultaneously, and in rising the temperature there could be a phase transition from a low-energy state to a high-entropy state. In order to describe these phase transitions, it is useful to have an expression for the partition function Z . As a first step, write Z as a summation over the coarse grained states s , in the following way:

$$Z = \sum_s e^{-F_L^s/kT} \quad (1.1.2)$$

If it is assumed that the most probable state \tilde{s} (which is the one with the lowest value for F_L) is completely dominant over all other states, the free energy of the system can be approximated by

$$F = -kT \ln \sum_s e^{-F_L^s/kT} \cong F_L^{\tilde{s}} \quad (1.1.3)$$

This is called the saddle point approximation, and the resulting theory is equivalent to mean-field theory. Usually the coarse grained states s are characterized by the value of an *order parameter*. In the most simple case the order parameter is a single variable. In the Ising model, for instance, it is the average magnetization m . For copolymer melts the situation is more complicated, and the order parameter is a function of space,¹³ thus representing infinitely many variables.

The main purpose of this chapter is to derive an expression for the Landau free energy F_L for all sorts of polydisperse block copolymers, the only restriction being that the molecules are linear or tree-like (the study of the phase behavior of ring copolymer melts is much harder, because rings in the melt state do not obey random walk statistics¹⁴). However, there is the restriction that Landau theory is only applicable in the region where the order parameter is small, which, in the case of copolymer melts, corresponds to the region where the interaction-induced separation is small (weak segregation regime, WSR). In the remainder of this introduction we first discuss the choice of the order parameter, and then we present a coarse grained description of block copolymer chains, which ignores the (for our purpose irrelevant)

microscopic details. In paragraph 1.2 we define the so-called correlation functions, which play an important role in the calculation of the Landau free energy in paragraph 1.3. The expression for the Landau free energy obtained in this chapter forms the basis for the rest of this thesis, where it is used to calculate the phase diagram of polydisperse multiblock copolymers in various approximations.

The choice of the order parameter

In Landau theory one has to make a choice for the order parameter. There is not a strict rule which fixes the order parameter for a given system, but generally it should be a slow degree of freedom which comes to equilibrium only after all other degrees of freedom have come to equilibrium. In AB -copolymer melts the usual choice^{13,15} is the concentration profile $\psi(\vec{x})$, which is defined as the deviation of the A -monomer fraction from the average value.

$$\psi(\vec{x}) = \frac{\rho_A(\vec{x})}{\rho} - f \quad (1.1.4)$$

where ρ is the average total monomer density (including the B -monomers). Since incompressibility is assumed throughout (implying a constant density), there is only one independent concentration profile. The profile $\psi(\vec{x})$ as defined in 1.1.4 is not a smooth function. On the length scale corresponding to the size of a monomer, its value fluctuates between $(1-f)$ (if there is an A -monomer present at position \vec{x}) and $-f$ (if there is a B -monomer present at \vec{x}). However, Landau theory does not deal with properties on this length scale, and in fact one should take for $\psi(\vec{x})$ the *coarse grained* profile. Coarse graining means getting rid of short-scale fluctuations, which makes the profile smooth. Technically, coarse graining can be accomplished by introducing a cut-off value Λ for the vectors in Fourier space,¹⁶ that is, by setting the Fourier coefficients $\psi_A(\vec{q})$ for $|\vec{q}| > \Lambda$ equal to zero. The value of Λ should be chosen such that Λ^{-1} is small compared to the radius of gyration¹⁷ of the blocks (which is the characteristic length scale in a block copolymer melt), but on the other hand Λ^{-1} should be large compared to the size of the monomers. Nevertheless, in calculations one usually takes the limit $\Lambda \rightarrow \infty$. This can lead to divergencies in the integrals over Fourier space (see for instance chapter 5), but it will now be clear that these divergencies have no physical meaning.

A coarse grained model for block copolymer melts

Consider a copolymer system containing two chemical building blocks (monomers) A and B . A microscopic description of the (configurational) state of this system would involve giving the position in space of all monomers. Instead, we choose a coarse grained description, which is possible provided that there are long sequences of like monomers present in the molecules. To define the coarse grained state of the chain we proceed as follows. The *persistence length* L_p of the chain is defined as the distance, measured along the chain, over which the directional correlations vanish. Roughly speaking, pieces of chain which are shorter than L_p are stiff, whereas pieces of chain which are longer than L_p are flexible. A piece of chain with length L_p is called a *segment*. On the level of the segments the chain behaves like a random walk (the random walk behavior of chains in the melt will be discussed in paragraph 1.2). In a coarse grained description the chain of monomers can be regarded as a chain of segments. The length of the blocks should be much larger than the lengths of the segments, otherwise the theory described in this thesis is not applicable. Often the *Kuhn segment*¹⁸ is regarded as the building block for the coarse grained chain. It is defined in the following way. Consider a flexible chain. Approximate this chain by a model chain of N freely jointed segments with fixed length a_K , such that the model chain has the same radius of gyration R_g and the same contour length L as the real chain. These conditions fix the values of N and a_K via

$$L = Na_K \quad R_g^2 = \frac{1}{6} Na_K^2 \quad (1.1.5)$$

The thus obtained Kuhn segment length a_K is closely related to the persistence length. In the following it is assumed that the length of a segment is not fixed, but has a Gaussian distribution with root mean square value a , which is often called the *statistical segment length*. Since the segment length is much shorter than the block length, most segments are homogeneous in composition, making it possible to talk about A -segments and B -segments. The coarse grained state of the system can be described by the set of positions of the begin- and end-points of the segments. This coarse grained state contains no microscopic details. All microscopic properties (that is, the properties on the level of the chemical monomers) will be represented by just three parameters ν , a and χ . The parameter ν is the excluded volume per segment, a is the root mean square of the end-to-end distance of a segment, and the χ -parameter gives the effective interaction between the A - and B -segments, which includes both energetic and entropic contributions. Because of incompressibility one interaction parameter is sufficient. This χ -

parameter should be regarded as a phenomenological parameter, the value of which can be determined by experiments.

The fact that the microscopic properties can be dealt with in such a simple way is due to the following.¹⁹ Consider the system of disconnected monomers, which is the same system but without the presence of the chemical bonds. The set of microscopic states corresponding to just one coarse grained state of the polymer system is representative for the whole phase space of the system of disconnected monomers (assuming that most monomer-monomer contacts in the polymer system are between monomers belonging to different chains). Therefore, averaging over the microscopic properties is independent of averaging over the properties of the coarse grained system. In the dynamics of the polymer system this is reflected by the fact that on small timescales the coarse grained configurations of the molecules do not change significantly, whereas the individual monomers have had contacts with many different monomers.

According to a main postulate in statistical mechanics all microstates in a canonical ensemble have the same a priori probability. This is, however, not applicable for the coarse grained states. In order to find the probability of a coarse grained state one has to integrate over all conformations of the segments. Although a rigorous calculation of this integral is impossible because of the excluded volume, assuming random walk behavior of the chains (see the next paragraph) the segment lengths can be considered as independent, and it is possible to approximate the probability of a coarse grained state by the following expression. Let s denote a molecule type in a polydisperse system. Let m number the molecules of a given type s and let i number the segments in a given chain. Let $\vec{R}_{m,i}^s$ denote the position of the i^{th} segment in the m^{th} molecule. Then the probability to find the system in the coarse grained state $\{\vec{R}_{m,i}^s\}$ is proportional to²⁰

$$P(\{\vec{R}_{m,i}^s\}) \propto \delta(\rho(\{\vec{R}_{m,i}^s\}, \vec{x}) - \nu^{-1}) \prod_{s,m,i} g(\vec{R}_{m,i+1}^s - \vec{R}_{m,i}^s) \quad (1.1.6)$$

where the delta function expresses the incompressibility condition (ρ is the segment density), and $g(\vec{r})$ is the probability that the end-to-end vector of a segment is equal to \vec{r} . Since on the coarse grained level the chain conformations obey random walk statistics, one can take for $g(\vec{r})$ the end-to-end probability distribution of a random walk, which is derived in appendix A:

$$g(\vec{r}) = \left(\frac{3}{2\pi a^2} \right)^{3/2} \exp\left(-\frac{3r^2}{2a^2}\right) \Leftrightarrow g(\vec{q}) = \exp\left(-\frac{a^2 q^2}{6}\right) \quad (1.1.7)$$

Equation 1.1.7 will be used as an a priori probability for the coarse grained model. In the following it is assumed that both monomer types have the same value for a , and the same value for ν . Since a segment contains several monomers, in general we have

$$a \gg \nu^{1/3} \quad (1.1.8)$$

In many theoretical papers the unit of length is chosen such that the excluded volume ν per segment becomes equal to unity. Because of 1.1.8 the statistical segment length a will then be large compared to unity. However, it is possible to rescale the model in such a way that in appropriate units both ν and a become equal to unity. This can be achieved in the following way. Consider a coarse grained model characterized by the parameters χ , ν and a . Replace every segment with k segments, and rescale the parameters according to

$$\chi' = \frac{\chi}{k} \quad \nu' = \frac{\nu}{k} \quad a' = \frac{a}{\sqrt{k}} \quad (1.1.9)$$

The statistical segment length a has been rescaled in such a way that the radius of gyration of the blocks remains the same. The scaling of χ is necessary because χ is the interaction *per segment*. The reason for the rescaling of ν is obvious. Note that after application of the transformation 1.1.9 the block lengths (measured in number of segments per block) are all multiplied by a factor k , that is, $N' = kN$. Strictly speaking the models obtained by taking various values for $k > 1$ are not completely equivalent, but within our coarse graining approximation they can be expected to be equivalent models for the real polymer system (even the fluctuational behavior is independent of k ; see note 21). In the process of refining the segmentation by increasing the value of k , the ratio between $a/\sqrt{\nu}$ and $\nu^{1/3}$ decreases. At a certain value of k this ratio is equal to unity. This shows that without restricting the generality of the considerations it can be assumed that

$$\nu^{1/3} = \left(\frac{1}{6}a^2\right)^{1/2} = 1 \quad (1.1.10)$$

Summarizing, the procedure is first to model the system by choosing the appropriate number of chemical monomers per segment, and to determine the values of the parameters a , ν , and χ . Then, from the class of equivalent models obtained by the refining transformation 1.1.9, that

model is chosen which satisfies condition 1.1.10 for some unit of length. To reduce the number of parameters even more it will also be assumed throughout that the unit of energy is chosen such that $k_B T$, which is roughly speaking the translational kinetic energy per molecule, is equal to unity:

$$k_B T = 1 \quad (1.1.11)$$

Nevertheless, the effect of a change of the temperature on the phase behavior can still be investigated by changing the value of the Flory-Huggins χ -parameter,¹¹ which is temperature dependent.

1.2 Correlation functions

Introduction

The mean-field phase diagram of an AB -copolymer melt can be constructed after deriving an expression for the Landau free energy F_L as a function of the concentration profile ψ (equation 1.1.4). Minimizing this free energy gives the most probable profile. In the weak segregation regime, where ψ is small, it is possible to expand F_L in powers of ψ . The coefficients in this expansion are called the *vertex functions*. These vertex functions can be obtained from the correlation functions in the melt, and these correlation functions can be related to the correlation functions of isolated random walks.¹¹ Therefore, the calculation of correlation functions is an essential ingredient for the following chapters. The correlation functions give information about how the values of ψ at different space points are correlated. In order to explain their physical meaning, we describe qualitatively the second order correlation function for a block copolymer melt. Let f be the average A -monomer fraction in the melt. Then, if \vec{y} denotes any position in space,²² the expectation value of the A -monomer fraction at \vec{y} is equal to f . Now suppose that we measure the A -monomer fraction at a nearby space point \vec{x} (nearby means that the distance between \vec{x} and \vec{y} is of the order of magnitude of the radius of gyration R_g of the blocks). This extra information changes the expectation value for $\psi(\vec{y})$, and this change is described quantitatively by the second order correlation function. The presence of this kind of correlation can be understood as follows. Suppose for the moment that $\psi(\vec{x})$ is larger than average. The A -blocks which are responsible for this, penetrate over a distance R_g through space. Therefore, it is to be expected that the A -monomer fraction at \vec{y} will also be larger than average. This positive correlation, which is characteristic

for block copolymer systems, is called the correlation hole effect.¹³ The correlation disappears if the distance between \vec{x} and \vec{y} becomes too large. The distance at which this occurs is called the correlation length. Since this distance can be much larger than the size of the monomers, the correlation functions in a polymer melt are called *non-local*. These long-range correlations are due to the chain connectivity, and are, therefore, absent in the corresponding system of disconnected monomers, which has the same composition as the polymer system, but where all chemical bonds between the monomers are broken. The short-range correlations (that is, the correlations over a distance corresponding to the size of the monomers) are the same for both systems, provided that in the polymer system most monomer-monomer contacts take place between monomers belonging to different chains. For the calculation of the phase behavior of block copolymer systems only the long-range correlations are important.

The second order correlation function can be studied experimentally by means of a scattering experiment, in the following way. Let the system be irradiated by waves. Then the intensity of the scattered radiation is proportional to $\langle \psi(\vec{q})\psi(-\vec{q}) \rangle$, where $\psi(\vec{q})$ is the Fourier transform of $\psi(\vec{x})$, the brackets denote a thermodynamic average, and $\vec{q} = \vec{q}_{out} - \vec{q}_{in}$ is the momentum transfer. In practice the wavelength of the chosen radiation should be of the same order of magnitude as the size of the structures to be studied. Since the size of the structures in block copolymer systems is of the order of 10 nm , Röntgen or neutron diffraction can be used.

The correlation functions in the melt can be calculated due to the fact that the conformations of polymer molecules in the melt obey random walk statistics.¹¹ To appreciate why this statement is remarkable, consider first an isolated polymer chain in an athermal solution, where the value of the parameter χ describing the effective interaction between the monomers and the solvent molecules is zero. Because of the excluded volume of the monomers, the conformation of the chain is a self-avoiding walk. Since two monomers which are far separated from each other along the chain can still be close to each other in real space, the effect of self-avoidance remains large, no matter how long the chain is (if the walk is regarded as a Markov process, it has order infinity). The excluded volume effect forces the self-avoiding walk to be more open than a random walk: the mean distance travelled by a self-avoiding walk²³ of N steps is proportional to $N^{0.588}$, whereas the mean distance travelled by a random walk is proportional to $N^{0.5}$. Next consider a polymer chain in a melt, which is a rather dense system. Since the chains cannot overlap, they hinder each other enormously. Therefore, it seems that the excluded volume effect is even more important in the melt state than it is for an isolated chain. For each chain the set of possible conformations is still the same as it is for an isolated chain under athermal conditions. For an isolated chain all these self-avoiding walks have the same

probability, but for a chain in the melt the various conformations obtain different weight factors, which is due to the entropy of the remaining chains. Qualitatively, the effect is as follows. If the chain takes on a rather open conformation which is characteristic for an isolated chain, it has a high internal entropy, but at the same time it hinders the other chains considerably, thus decreasing their entropy. If it becomes more crumpled up, its internal entropy decreases, but since it leaves more room for the other chains this decrease is compensated by an increase in *their* entropy. This reasoning shows that in the melt state the chains prefer conformations which are less open than a self-avoiding walk. Flory¹¹ has shown, using simple arguments, that the weight factors of the various self-avoiding walks are such that the set of conformations becomes representative for a random walk. In other words, the effective excluded volume of the monomers is zero, and the conformations of the chains can be considered as random walks. This statement has been verified experimentally,^{24,25} theoretically,²⁶ and by computer simulations.²⁷ It forms the basis for all analysis in this thesis, and without it, analytical calculations on the phase behavior of polymer melts would be impossible.

The presence of the short-range interaction and the incompressibility constraint give rise to correlations between the different chains. However, in this paragraph we ignore these correlations, and calculate the correlation functions of the corresponding *ideal* system,¹⁵ which has no intermolecular correlations. In this (hypothetical) ideal system there are no interactions, and the constraint that the density should be constant is absent. However, the essential feature of chain connectivity is present in the ideal system, and the configurations of the chains obey random walk statistics. Since in the ideal system there are no correlations between monomers belonging to different chains, we need only to calculate the intramolecular correlations. In the next paragraph it is shown how the correlation functions of the ideal system can be used to calculate an expression for the free energy of the incompressible system with interactions.

Correlations between monomers

Consider a chain in the ideal system. Since there are no interactions at all between the different chains, the chain can be considered as isolated. Let $\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N$ denote the positions of the monomers marking the beginning or the end of a segment, such that in between the monomers at positions \vec{R}_i and \vec{R}_{i+1} there is only one segment. For shortness we will often refer to the positions $\{\vec{R}_i\}$ as the positions of the segments. The set $\{\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N\}$ is called the configuration of the chain. It involves both the spatial shape of the chain, and the position of its centre of mass. In the ideal system, the random walk statistics is taken as an a priori probability

measure. Let $g(\vec{r})$ be the normalized isotropic probability density that the end-to-end distance of a segment is equal to \vec{r} (appendix A). Then the (unnormalized) probability density on the space of conformations is given by (see also 1.1.6)

$$P(\{\vec{R}_1, \dots, \vec{R}_N\}) = g(\vec{R}_2 - \vec{R}_1) g(\vec{R}_3 - \vec{R}_2) \dots g(\vec{R}_N - \vec{R}_{N-1}) \quad (1.2.1)$$

The integral of P over the phase space of all configurations equals V , which represents the translational freedom of the chain. Although P and the correlation functions to be defined below are probability *densities*, we will call them probabilities for shortness. By definition, the n^{th} order correlation function

$$G_{i_1, \dots, i_n}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \quad (1.2.2)$$

is the probability (normalized to V) that segment number²⁸ i_k is at position \vec{x}_k , for $k = 1, \dots, n$. The peculiar normalization is adopted in order to make the correlation function independent of the size of the system. According to definition 1.2.2, P itself is an N^{th} order correlation function. For the analysis in the WSR we need only⁸⁰ the second, third and fourth order correlation functions. As an example we present the calculation of the fourth order one for the situation that the indices are all different. Suppose that $i < j < k < l$.

$$\begin{aligned} G_{ijkl}(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) &= \int d\vec{R}_1 \dots d\vec{R}_N g(\vec{R}_2 - \vec{R}_1) g(\vec{R}_3 - \vec{R}_2) \dots g(\vec{R}_N - \vec{R}_{N-1}) * \\ & * \delta(\vec{R}_i - \vec{x}_1) \delta(\vec{R}_j - \vec{x}_2) \delta(\vec{R}_k - \vec{x}_3) \delta(\vec{R}_l - \vec{x}_4) \end{aligned} \quad (1.2.3)$$

After the coordinate transformation

$$\begin{aligned} \vec{r}_1 &= \vec{R}_1 \\ \vec{r}_n &= \vec{R}_n - \vec{R}_{n-1} \quad \text{if } n > 1 \end{aligned} \quad \Leftrightarrow \quad \vec{R}_n = \sum_{i=1}^n \vec{r}_i \quad (1.2.4)$$

the correlation function 1.2.3 attains the form

$$\begin{aligned}
G_{ijkl}(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) &= \int d\vec{r}_1 \cdots d\vec{r}_N g(\vec{r}_2) \cdots g(\vec{r}_N) * \\
&* \delta(\vec{r}_1 + \cdots + \vec{r}_i - \vec{x}_1) \delta(\vec{r}_1 + \cdots + \vec{r}_j - \vec{x}_2) * \\
&* \delta(\vec{r}_1 + \cdots + \vec{r}_k - \vec{x}_3) \delta(\vec{r}_1 + \cdots + \vec{r}_l - \vec{x}_4)
\end{aligned} \tag{1.2.5}$$

The vector \vec{r}_1 does not appear as argument for $g(\vec{r})$, because it represents the position of the first segment. Expression 1.2.5 can be simplified by going over to Fourier transforms. Generally, the Fourier transform of a function $f(\vec{x})$ is defined by

$$\begin{aligned}
f(\vec{q}) &= \int d\vec{x} f(\vec{x}) e^{i\vec{q}\cdot\vec{x}} \quad \Leftrightarrow \\
f(\vec{x}) &= \frac{1}{V} \sum_{\vec{q}} f(\vec{q}) e^{-i\vec{q}\cdot\vec{x}} = \frac{1}{(2\pi)^3} \int d\vec{q} f(\vec{q}) e^{-i\vec{q}\cdot\vec{x}}
\end{aligned} \tag{1.2.6}$$

According to this definition, the Fourier transform of the n^{th} order correlation function 1.2.2 for $n = 4$ is given by

$$G_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \int d\vec{x}_1 d\vec{x}_2 d\vec{x}_3 d\vec{x}_4 e^{i\vec{q}_1\cdot\vec{x}_1 + \cdots + i\vec{q}_4\cdot\vec{x}_4} G_{ijkl}(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) \tag{1.2.7}$$

Substituting 1.2.5 into 1.2.7 and using the identity

$$\frac{1}{V} \int d\vec{y} e^{i\vec{q}\cdot\vec{y}} = \delta_K(\vec{q}) \tag{1.2.8}$$

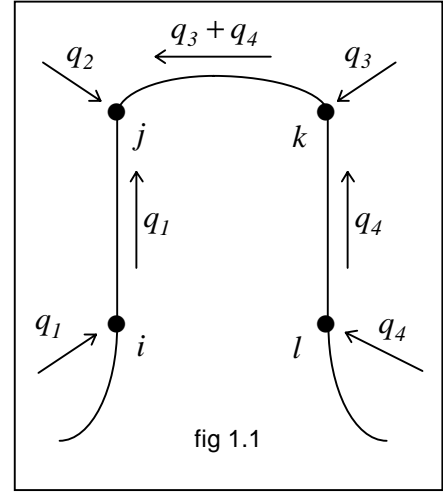
where δ_K is the Kronecker delta (taking on the values 0 or 1), we get

$$\begin{aligned}
G_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) &= V \delta_K(\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4) g^{i-1}(\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4) * \\
&* g^{j-i}(\vec{q}_2 + \vec{q}_3 + \vec{q}_4) g^{k-j}(\vec{q}_3 + \vec{q}_4) g^{l-k}(\vec{q}_4) g(0)^{n-l}
\end{aligned} \tag{1.2.9}$$

Using the normalization $g(\vec{q} = 0) = 1$ this can be rewritten to

$$G_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = V \delta_K(\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4) g^{j-i}(\vec{q}_1) g^{k-j}(\vec{q}_1 + \vec{q}_2) g^{l-k}(\vec{q}_4) \tag{1.2.10}$$

Equation 1.2.10 is only valid if $i < j < k < l$. The result 1.2.10 can be described in the following pictorial way, which makes generalization to higher order correlations straightforward. Through segment i a “current” \vec{q}_1 is flowing into the chain, through segment j a “current” \vec{q}_2 is flowing into the chain, etc (this is just a metaphor). The Kronecker delta ensures that no charge is accumulating. At any point the total sum of all currents must be zero (Kirchhoff’s law). The number of bonds between monomer i and monomer j is equal to $(j-i)$. Through each of these bonds a current \vec{q}_1 is flowing. The expression for the correlation function shows that to each of these bonds a factor $g(\vec{q}_1)$ is assigned. Between segment j and segment k the total current is equal to $\vec{q}_1 + \vec{q}_2$, and each of the $(k-j)$ bonds gets a factor $g(\vec{q}_1 + \vec{q}_2)$, etc. This has been illustrated in fig 1.1.



The correlations between A and B

The notion of correlation function can be generalized to chains consisting of two segment (monomer) types A and B . If $\alpha_i = A$ or B , then the n^{th} order correlation function

$$G_{\alpha_1 \dots \alpha_n}(\vec{x}_1, \dots, \vec{x}_n) \quad (1.2.11)$$

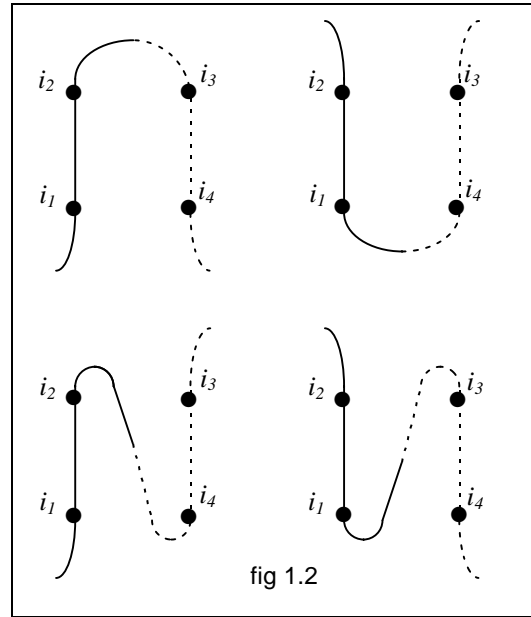
is the probability (normalized to V) that at the point \vec{x}_i a segment of type α_i is present, for $i = 1, \dots, n$. The correlation function 1.2.11 depends on the order in which the A and B monomers are placed along the chain. This AB -sequence can be described by the function σ_i^α , which is defined by

$$\sigma_i^\alpha = \begin{cases} 1 & \text{if segment } i \text{ is of type } \alpha \\ 0 & \text{otherwise} \end{cases} \quad (1.2.12)$$

Using definition 1.2.12, the AB -correlation function 1.2.11 can be written in terms of the correlation function 1.2.2.

$$G_{\alpha_1 \dots \alpha_n}(\vec{x}_1, \dots, \vec{x}_n) = \sum_{i_1 \dots i_n} \sigma_{i_1}^{\alpha_1} \dots \sigma_{i_n}^{\alpha_n} G_{i_1 \dots i_n}(\vec{x}_1, \dots, \vec{x}_n) \quad (1.2.13)$$

Equation 1.2.13 involves a summation over n indices i_1, \dots, i_n . This summation can be split in $n!$ contributions, one contribution corresponding to $i_1 < i_2 < \dots < i_n$, etc. Each of these contributions can be represented by a diagram. This diagram contains k points representing i_1, \dots, i_n . The chain is drawn as a directed line between these points. Fig 1.2 shows the diagrams corresponding to G_{AABB} for a diblock co-polymer. In this case only 4 of the $4!$ diagrams give a contribution (solid line: A-block, dashed line: B-block).



The Fourier transforms of the correlation functions G are proportional to the volume V of the system, and it is convenient to define

$$g_{\alpha_1 \alpha_2 \dots \alpha_n}(\vec{q}_1, \dots, \vec{q}_n) = \frac{1}{V} \delta_K(\vec{q}_1 + \dots + \vec{q}_n) G_{\alpha_1 \alpha_2 \dots \alpha_n}(\vec{q}_1, \dots, \vec{q}_n) \quad (1.2.14)$$

Although the delta function on the right hand side is superfluous (because G itself is zero if the sum of its arguments is not zero), it has been added for clarity. To avoid confusion, note that g , which is given in 1.1.7, denotes the end-to-end distribution function of a single segment, while g denotes the correlation function of the chain as a whole.

The correlation function 1.2.13 can be rewritten in a more familiar form. Let $\rho_\alpha(\{\vec{R}_i\}, \vec{x})$ be the density of monomers of type α at position \vec{x} due to the chain under consideration. It is given by

$$\hat{\rho}_\alpha(\vec{x}) \equiv \rho_\alpha(\{\vec{R}_i\}, \vec{x}) = \sum_i \sigma_\alpha^i \delta(\vec{x} - \vec{R}_i) \quad (1.2.15)$$

where the hat denotes that the density is a function of the configuration $\{\vec{R}_i\}$ of the chain. Using 1.2.15 and the generalization of 1.2.3 to the n^{th} order, equation 1.2.13 can be rewritten as

$$G_{\alpha_1 \dots \alpha_n}(\vec{x}_1, \dots, \vec{x}_n) = \int d\{\vec{R}_i\} P(\{\vec{R}_i\}) \hat{\rho}_{\alpha_1}(\vec{x}_1) \cdots \hat{\rho}_{\alpha_n}(\vec{x}_n) \equiv V \langle \hat{\rho}_{\alpha_1}(\vec{x}_1) \cdots \hat{\rho}_{\alpha_n}(\vec{x}_n) \rangle_0 \quad (1.2.16)$$

The average over the configurations has been normalized to unity, and the subscript 0 indicates that it is defined in the *ideal* system.

The second order correlation function for a homopolymer chain

The most simple, non-trivial example of an (intramolecular) correlation function arises when there is only one monomer type present in the chain. In that case the chain is called a homopolymer. If the chain has N segments, then after combining 1.2.13 with the generalization of 1.2.10, and going over to Fourier transforms, the second order correlation function is given by

$$\begin{aligned} G(\vec{q}_1, \vec{q}_2) &= \sum_{i,j=1}^N G_{ij}(\vec{q}_1, \vec{q}_2) = \\ &= V \delta_K(\vec{q}_1 + \vec{q}_2) \sum_{i,j=1}^N g^{|j-i|}(\vec{q}_1) \equiv V \delta_K(\vec{q}_1 + \vec{q}_2) g(\vec{q}_1) \end{aligned} \quad (1.2.17)$$

For the end-to-end distribution function $g(\vec{q})$ of a single segment we will adopt equation 1.1.7 (do not confuse $g(\vec{q})$ with $g(\vec{q})$)

$$g(\vec{q}) = e^{-\frac{1}{6}a^2q^2} \equiv e^{-x} \quad (1.2.18)$$

The summation representing $g(\vec{q})$ can be split into two parts:

$$g(\vec{q}) = \sum_{i=1}^N 1 + 2 \sum_{i < j=1}^N e^{-x(j-i)} = N + 2 \frac{e^{-(N-1)x} - e^{-x} - N + Ne^x}{(e^x - 1)^2} \quad (1.2.19)$$

The first part is called the self correlation. For large values of the molecule length N this equation can be approximated in the following way. The relevant length scale for the correlation function (i.e. the length scale on which its derivative is of order unity) is the radius of gyration of the chain, which is proportional to

$$R_g \propto \sqrt{N} \quad (1.2.20)$$

Therefore, the relevant values for q scale with N like

$$q \propto \frac{1}{\sqrt{N}} \quad \Rightarrow \quad x \propto \frac{1}{N} \quad (1.2.21)$$

This is the motivation to define a rescaled wave vector y via

$$y \equiv Nx = \frac{1}{6} N a^2 q^2 \quad (1.2.22)$$

The relevant values for y are of order unity. Inserting 1.2.22 into 1.2.19 shows that the dominant contribution to the correlation function is of order N^2 , and after neglecting the lower order terms we get finally

$$g(q) = 2N^2 \frac{e^{-y} + y - 1}{y^2} \quad (1.2.23)$$

This is called the Debye function. The procedure used to approximate 1.2.19 by 1.2.23 is quite general and is also used for block copolymers. In that case, the relevant length scale for the correlation function is not the radius of gyration of the whole molecule, but the radius of gyration of the blocks. The same result 1.2.23 could have been obtained more easily by replacing the summations in 1.2.19 by integrals:

$$g(q) \equiv \int_0^N \int_0^N di dj e^{-x|j-i|} = 2N^2 \frac{e^{-y} + y - 1}{y^2} \quad (1.2.24)$$

It is useless to take along the terms subdominant in N in the calculation of the correlation functions, even if N is small, for the following reason. As will be explained in chapter 5, the free energy can be written as an infinite series of terms. These terms can be ordered with respect to their scaling with N . Usually only the dominant terms, which are proportional to N^{-1} , are taken into account. If the subdominant terms in the calculation of the correlation functions *are* taken into account, then, in order to be consistent, in the free energy expansion one should take into account all terms till order N^{-2} , which proves to be far beyond the accuracy required to calculate phase diagrams in the WSR.

1.3 The Landau free energy for polydisperse copolymer melts

Introduction

In this paragraph we derive an expression for the Landau free energy F_L of polydisperse copolymer melts in terms of the order parameter ψ , which was defined in 1.1.4 as the deviation of the A -monomer fraction from the average value. Since in the WSR the order parameter is small, it is meaningful to expand F_L in a Taylor series. Usually the second and third order contributions to F_L are decreasing functions of the amplitude A of the profile, and in the minimum these terms are balanced by the fourth order contribution, which is usually an increasing function of A . Near the phase transition lines between the various ordered structures these second, third and fourth order terms are of the same order of magnitude, while the fifth and higher order terms are negligible. Therefore, it is sufficient to expand F_L till the fourth order.⁸⁰ As mentioned before, the coefficients in this expansion are called vertex functions. We start from the general expression for the (configurational) partition function Z in the Landau form.

$$Z = \int d\psi e^{-F_L[\psi]} \quad (1.3.1)$$

$$F_L(\psi) \cong \sum_{n=2}^4 \frac{1}{n!} \int d\vec{x}_1 \cdots d\vec{x}_n \Gamma_n(\vec{x}_1, \dots, \vec{x}_n) \psi(\vec{x}_1) \cdots \psi(\vec{x}_n)$$

The vertex functions Γ_n are “non-local,” which means that they couple the values of ψ at different points in space to each other. This non-locality is a consequence of the chain connectivity, and so it is no surprise that the vertex functions Γ_n are related to the correlation functions G_n . Revealing the exact relationship between these objects is the purpose of this paragraph.

Leiblers method for monodisperse copolymers

As an introduction, we will first describe qualitatively how Leibler¹⁵ derived mean-field expressions for the vertex functions of monodisperse diblock copolymers. It is convenient to introduce an auxiliary field $U(\vec{x})$ which acts on the A - and B -monomers in such a way that it

changes the energy content of a copolymer system with profile $\psi(\vec{x})$ by the amount ΔE , which is given by

$$\Delta E = \int d\vec{x} U(\vec{x})\psi(\vec{x}) \quad (1.3.2)$$

Due to the incompressibility we do not need separate fields for the A - and B -monomers. In the presence of the field $U(\vec{x})$, the expression 1.3.1 for the partition function is changed into

$$Z[U] = \int d\psi e^{-\int d\vec{x} U(\vec{x})\psi(\vec{x}) - F_L(\psi)} \quad (1.3.3)$$

$$F[U] = -\ln Z[U]$$

where F_L is the Landau free energy of the system when the external field is absent. By differentiating the free energy $F[U]$ with respect to the external field, one obtains

$$\frac{\partial F[U]}{\partial U(\vec{x})} = \langle \psi(\vec{x}) \rangle \quad (1.3.4)$$

Equation 1.3.3 provides a description of the system in terms of the external field U . Because of the way in which ψ and U are coupled to each other in the exponent of equation 1.3.3 (ψ and U are “conjugated”), it is possible to change the viewpoint, and to go over to a description in terms of ψ . To this end, define the Legendre transform $F'[\psi]$ of the free energy $F[U]$ via

$$F'[\psi] = F[U_\psi] - \int d\vec{x} U_\psi(\vec{x})\psi(\vec{x}) \quad (1.3.5)$$

where U_ψ is the inverse of 1.3.4. The transformation 1.3.5 is called a Legendre transformation. By differentiating 1.3.5 with respect to ψ , one obtains

$$\left. \frac{\partial F'[\psi]}{\partial \psi(\vec{x})} \right|_{\psi=\langle \psi \rangle} = -U(\vec{x}) \quad (1.3.6)$$

which is equivalent to 1.3.4. Since in the real system the external field U is absent, we see from 1.3.6 that the average profile $\langle \psi \rangle$ can be found by minimizing F' . Therefore, it would be useful to have a closed expression for F' (note that F' is the true free energy, not the mean-field free energy). Since equations 1.3.4 and 1.3.6 are each others inverse, the expression for

$F[\psi]$ is known once we have the expression for $F[U]$. It follows directly from 1.3.3 that the coefficients in the Taylor expansion of $F[U]$ around $U = 0$ are (apart from numerical factors) the correlation functions G_n , defined by

$$G_n(\vec{x}_1, \dots, \vec{x}_n) = \langle \psi(\vec{x}_1) \cdots \psi(\vec{x}_n) \rangle \quad (1.3.7)$$

where the brackets denote a thermodynamic average. This average is different from the one used in 1.2.16, which was defined in the (compressible) ideal system, where there are no interactions between the chains. So the problem of finding an expression for $F[U]$ has been reduced to the problem of finding an expression for the correlation functions 1.3.7 in the melt. Up till now, the analysis of the coarse grained system is exact, but in order to find expressions for the correlation functions 1.3.7 Leibler used the mean-field approximation, as follows. In the previous paragraph it was shown how the correlation functions of the corresponding ideal system can be calculated. The interaction and the incompressibility can be accounted for by means of self-consistent fields. In this way, one obtains mean-field expressions for the correlation functions 1.3.7, which, via equations 1.3.4 and 1.3.6, lead to mean-field expressions for the vertex functions. This completes our brief discussion of Leiblers method.

In the first paper²⁹ dealing with the generalization of Leiblers theory to polydisperse melts, it was shown that the correct procedure involves the averaging of the ideal correlation functions over the various molecule types present in the system. However, an important contribution to the fourth order vertex function was missed. To obtain the complete expression for the fourth order vertex, several methods are available. One of these methods will be presented in detail further on, but first we discuss briefly two alternative methods: the replica trick,³⁰ and the detailed densities.³¹

The generalization to polydisperse block copolymer melts: quenched average and replica trick

In a polydisperse copolymer system several molecule types are present. If s denotes a molecule type (i.e. a finite sequence of A 's and B 's), and if ρ_s denotes the *number* density of molecules of type s , then the composition of the melt is fixed completely by the set $\{\rho_s\}$. Clearly, the probability that a randomly chosen molecule is of type s is proportional to ρ_s . Since for the determination of the phase behavior the chemical bonds are considered to be irreversible, any molecule is a *fixed* realization of the probability distribution $\{\rho_s\}$. Therefore, there is a quenched (i.e. frozen) disorder present in the chains of these systems. The concept of disorder

is well known from the study of spin glass systems.^{30,32} In these systems, magnetic atoms are present in a matrix. The nature of their pair interaction (ferro- or para-magnetic) is a very sensitive function of their mutual distance. Since the positions of the magnetic atoms are random and quenched, so are their interactions, and the system can be described by an Ising model with interaction strengths J_{ij} which are, for each i and j , fixed random numbers (chosen according to some appropriate distribution $P(J_{ij})$). The problem is to find an expression for the free energy of such disordered systems. To make the discussion general, let x denote the set of quenched variables, and let y denote the set of free variables. For the Ising model $x = \{J_{ij}\}$ and $y = \{\sigma_i\}$, where $\sigma_i = \pm 1$ is the spin at lattice site i ; whereas for a chain from a polydisperse copolymer melt $x = s$ (its AB -sequence), and y is its configuration $\{\vec{R}_i\}$. Let $P(x_0)$ denote the probability that $x = x_0$ in a realization of the system. In principle, the free energy of such a quenched system could be obtained by calculating the partition function after taking a representative realization \bar{x} of the quenched variables, that is

$$F_{\bar{x}} = -\ln \int dy e^{-H_{\bar{x}}(y)} = -\ln Z_{\bar{x}} \quad (1.3.8)$$

where H is the Hamiltonian. If the system is self-averaging,³⁰ then the free energy density $F_{\bar{x}}/V$ is independent of \bar{x} , once the volume V of the system is large enough (this statement can be made more precise). This means that the properties of the system are reproducible, despite the randomness. Although 1.3.8 gives the expression for the free energy of a quenched system, it does not provide a direct means of calculating it. However, since all representative realizations of x give the same value for F_x , averaging the free energy over the randomness will not change its value, so

$$F_{quenched} = F_{\bar{x}} = \int dx P(x) F_x = -\langle \ln Z_x \rangle \quad (1.3.9)$$

This is called a quenched average. It is important to note that this way of averaging gives other results than the so-called annealed average, which is defined by

$$F_{annealed} = -\ln \langle Z_x \rangle \quad (1.3.10)$$

and which leads to the free energy of a system in which the variables x are not quenched, but change in time according to $P(x)$. Due to the presence of the logarithm, the average in 1.3.9 cannot be obtained in a straightforward way. The logarithm can, however, be rewritten as follows:³³

$$F_{quenched} = -\langle \ln Z_x \rangle = -\lim_{n \rightarrow 0} \frac{\langle Z_x^n \rangle - 1}{n} = \lim_{n \rightarrow 0} F_n \quad (1.3.11)$$

The chain of identities in 1.3.11 is called the replica trick. The quantity Z_x^n is the partition function of n non-interacting replicas of the system, which all have exactly the same realization x of the quenched disorder (i.e. n identical chains in the case of a polydisperse copolymer). However, the averaging induces coupling between the replicas, and so $\langle Z_x^n \rangle$ may contain interreplica terms. Strictly speaking, the quantity F_n has only meaning for positive integer values of n , and taking the limit $n \rightarrow 0$ is, therefore, a rather tricky business. If the procedure outlined above is applied to polydisperse copolymer melts, and the free energy is expanded till fourth order in the concentration profile ψ , one obtains a sum of two parts.^{34,35,36} The first part can be obtained by replacing in the Leibler expressions the single-chain correlation functions by their averages, i.e.

$$g_{\alpha_1 \dots \alpha_n} \rightarrow \sum_s \rho_s g_{\alpha_1 \dots \alpha_n}^s \quad (1.3.12)$$

The second part, which is a contribution to the fourth order coefficient, is called the non-local term. Its expression contains the peculiar average³⁵

$$\sum_s \rho_s g_{\alpha\beta}^s g_{\gamma\delta}^s \quad (1.3.13)$$

which involves the second order correlation functions of two replicas (i.e. two chains having the same AB -sequence s). Its precise form will be given further on, but first we discuss an alternative way to arrive at the same expression for the free energy, without the use of replicas.

Detailed densities

Since in polydisperse copolymer melts as considered here there is no replica symmetry breaking,³⁷ it is possible to arrive at the correct expression for the free energy without the use of replicas. As a first example we discuss shortly the so-called detailed densities approach, which was introduced in ref 31 by Erukhimovich and Dobrynin. In the detailed densities approach, the concentration profiles $\psi_{s\alpha}(\vec{x})$ of monomers of type $\alpha = A/B$ belonging to a molecule of type s are taken as independent thermodynamic variables. These profiles $\psi_{s\alpha}(\vec{x})$ are called detailed densities. Generalizing the method used by Leibler, it is possible to write

down a mean-field expression for the free energy in terms of the detailed densities. The lowest (second) order contribution F_2 to this free energy has the form³¹

$$F_2 = \frac{1}{2V} \sum_{\vec{q}} \sum_{\substack{s_1, \alpha_1 \\ s_2, \alpha_2}} \gamma_2(q) \psi_{s_1, \alpha_1}(\vec{q}) \psi_{s_2, \alpha_2}(-\vec{q}) \quad (1.3.14)$$

where in the generalized second order vertex matrix $\gamma_2(q)$ the incompressibility has been taken into account by assigning an infinite free energy to profiles $\psi_{s\alpha}(\vec{x})$ which do not satisfy the incompressibility constraint

$$\sum_{s, \alpha} \psi_{s\alpha}(\vec{q}) = 0 \quad (1.3.15)$$

As long as all eigenvalues of the (symmetric and real) matrix $\gamma_2(q)$ are positive for all values of $q \geq 0$, the homogeneous state is stable against infinitesimal fluctuations. Therefore, the spinodal condition is that one of the eigenvalues of $\gamma_2(q_*)$ becomes zero for some value of q_* . The corresponding eigenvector $E(q_*)$, having components $E_{s\alpha}(q_*)$, is called the strongly fluctuating field, and in composition space the spinodal decomposition proceeds along its direction. In the WSR in the microphase separated state, the dominant Fourier components $\langle \psi_{s\alpha} \rangle(\vec{q})$ will be present for vectors \vec{q} with length q_* , and they will be proportional to the strongly fluctuating field (for the correlated random copolymer to be analyzed in chapter 3, 4 and 5 this is not completely true, since $q_* = 0$ for this system. However, the procedure can easily be adapted to cover this system as well). If the free energy is expanded in powers of the strongly fluctuating field, then one arrives at the same expression for the free energy as by using the replica trick, including the non-local term. This is because the strongly fluctuating field is a better choice for the order parameter in a Landau description of a polydisperse copolymer system than the A -monomer concentration profile. The advantage of the detailed densities approach is that the expression for the strongly fluctuating field gives information about how much each molecule type separately contributes to the arising profile ψ ; see for instance ref 39. The detailed densities approach will be used in chapter 4 in order to examine phase coexistence in polydisperse copolymer melts.

The generalization of the FLM-method

Although the use of replicas or detailed densities leads to the correct expression for the free energy, here we will follow a different route. The derivation presented further on is a generalization of the calculation of the free energy as developed by Fredrickson, Leibler and Milner (FLM) in ref 40 for the special case of correlated random multiblock copolymers. In ref 40, after writing down a formal general equation for the partition function, all further manipulations were done within this particular model, until an approximate expression for the free energy was found. The FLM-method can be generalized to give the expression for the free energy for block copolymers having a general architecture and sequence distribution. Before presenting this generalization, we need a number of definitions.

Preliminaries

A molecule type s is defined as a finite sequence $(\alpha_1, \alpha_2, \dots, \alpha_n)$ of segment types $\alpha_i = A/B$. If ρ_s is the number of molecules of type s per unit of volume, and N_s is the number of segments per molecule of type s , then

$$\sum_s \rho_s N_s = \frac{l}{v} = l \quad (1.3.16)$$

See equation 1.1.10. The set $\{\rho_s\}$, which describes completely the composition of the system, is called the monomer sequence distribution. In order to be able to describe the state of the polymer system we number the molecules of a given type s with the label m

$$m = 1, 2, \dots, n_s \quad n_s = \rho_s V \quad (1.3.17)$$

where n_s is the total number of molecules of type s in the system. If $\vec{R}_{m,i}^s$ denotes the position of segment i in molecule m of type s , then $\{\vec{R}_{m,i}^s\}$ fixes the coarse grained state of the system. Remember that $\{\vec{R}_{m,i}^s\}$ is not a microscopic state: all coarse grained states have different probabilities even if there is no interaction present. As explained in paragraph 1.1, the probability of the coarse grained state $\{\vec{R}_{m,i}^s\}$ is proportional to the integral over the conformations of the segments, and assuming random walk statistics it is given by (see equations 1.1.6, 1.1.7 and 1.1.10, and appendix A)

$$e^{-H_0(\{\vec{R}_{m,i}^s\})} = \prod_s \prod_{m=1}^{n_s} \frac{1}{V} \prod_{i=1}^{N_s-1} \frac{1}{(4\pi)^{3/2}} e^{-\frac{1}{4}(\vec{R}_{m,i+1}^s - \vec{R}_{m,i}^s)^2} \quad (1.3.18)$$

where H_0 is called Edwards Hamiltonian.²⁰ Expression 1.3.18 is only valid for configurations having constant density $\rho = 1$. All other configurations have probability zero. The factor $1/V$ is included for normalization: it accounts for the probability to find the centre of mass of the chain (s, m) at a certain place in the volume V . The exponential gives the probability for the relative positions of the monomers. In order to be able to write the partition function in the form 1.3.1, we have to find an expression for the profile ψ as a function of the configuration $\{\vec{R}_{m,i}^s\}$. As a first step define the state function (a state function is a function of $\{\vec{R}_{m,i}^s\}$)

$$\rho_A(\{\vec{R}_{m,i}^s\}, \vec{x}) = \sum_{s,m,i} \sigma_{s,i}^\alpha \delta(\vec{x} - \vec{R}_{m,i}^s) \quad (1.3.19)$$

For shortness, we denote state functions with a hat, for instance

$$\hat{\rho}_A(\vec{x}) \equiv \rho_A(\{\vec{R}_{m,i}^s\}, \vec{x}) \quad (1.3.20)$$

Besides $\hat{\rho}_A$, we will need the following state functions as well:

$$\hat{\rho}(\vec{x}) = \hat{\rho}_A(\vec{x}) + \hat{\rho}_B(\vec{x}) \quad \hat{\psi}_A(\vec{x}) = \hat{\rho}_A(\vec{x}) - f \quad \psi_B(\vec{x}) = \hat{\rho}_B(\vec{x}) - I + f \quad (1.3.21)$$

where f denotes the fraction of A -monomers. According to its definition, $\hat{\psi}_A$ is a sum of delta spikes. Only after coarse graining will it correspond to the order parameter. This coarse grained profile is denoted by $\psi_A(\vec{x})$, which, in an incompressible system, satisfies

$$\psi_A(\vec{x}) = -\psi_B(\vec{x}) \equiv \psi(\vec{x}) \quad (1.3.22)$$

The interaction energy

As already explained in paragraph 1.1, the physics on the level of the monomers can be treated independently from the physics on the level of the coils. As a consequence, the mean-field free energy can be written as a sum of two parts:⁴² one part coming from the short-ranged interaction (quantified by the χ -parameter), and another part coming from the long-ranged chain connectivity. In order to obtain the first part, the Flory-Huggins expression,¹¹ which is valid if the profile is flat, is taken as a starting point.

$$E = n\chi\rho_A\rho_B = \frac{\chi}{\nu} V\rho_A\rho_B \quad (1.3.23)$$

where $n = V/\nu$ is the number of segments in the system. If the profile is not flat (i.e. if ρ_A is a function $\rho_A(\vec{x})$ of space), then the multiplication with V should be replaced by an integral. Since we have

$$\rho_A = f + \psi, \quad \rho_B = 1 - f - \psi \quad (1.3.24)$$

the generalization of 1.3.23 is

$$E = -\frac{\chi}{\nu} \int d\vec{y} \psi^2(\vec{y}) + E_0 \quad (1.3.25)$$

where E_0 is an unimportant constant, which is omitted from now on. In arriving at 1.3.25 use has been made of the fact that the integral of ψ over space is zero. Equation 1.3.25 can be simplified even more. Via the substitution $\vec{x} = \vec{y}/\nu^{1/3}$ we go over to length units in which the excluded volume ν is unity (see equation 1.1.10), and the final expression for the interaction energy is

$$E = -\chi \int d\vec{x} \psi^2(\vec{x}) \quad (1.3.26)$$

This is analogous to the Ising model, where the average magnetization m is the order parameter, J is the interaction strength, and the interaction energy is given by $E = -Jm^2$. In the literature the Flory-Huggins parameter χ is often defined for the situation where the excluded volume ν of the segments is 100 cm^3 per mole. The value to be used in 1.3.26 has to be corrected for this, according to

$$\chi = \frac{\nu\chi_{\text{literature}}}{100 \text{ cm}^3 / \text{mole}} \quad (1.3.27)$$

Since the value of χ is a combination of energetic and entropic contributions which depend on the details on the low-molecular level, it is most convenient to regard χ as a phenomenological parameter which has to be determined experimentally.

The partition function

At this point all preliminary work has been done, and we can write down the expression for the configurational partition function Z in the Landau description (see 1.1.2):

$$Z = \int d\psi e^{\chi_I \psi^2} \int d\vec{R}_{m,i}^s e^{-\hat{H}_0} \delta(I - \hat{\rho}) \delta(\psi - \hat{\psi}) \quad (1.3.28)$$

The integral over ψ is a functional integral, that is,

$$\int d\psi \equiv \int D\psi(\vec{x}) = \int \prod_{\vec{x}} d\psi(\vec{x}) \quad (1.3.29)$$

We make no distinction in notation between a functional integral and a normal integral; the difference will be clear from the context. The Edwards Hamiltonian \hat{H}_0 taking into account the chain connectivity has been defined in 1.3.18. Since the incompressibility is due to interactions on the molecular level, it has to be incorporated in an artificial way via the delta function $\delta(I - \hat{\rho})$. This delta function can be rewritten in the following way:

$$\begin{aligned} \delta(I - \hat{\rho}) &= \prod_{\vec{x}} \delta(I - \hat{\rho}(\vec{x})) = \prod_{\vec{x}} \left(\frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} dJ_1(\vec{x}) \exp[iJ_1(\vec{x})(I - \hat{\rho}(\vec{x}))] \right) \infty \\ &\left(\prod_{\vec{x}} \int_{-\infty}^{\infty} dJ_1(\vec{x}) \right) \left(\prod_{\vec{x}} \exp[iJ_1(\vec{x})(I - \hat{\rho}(\vec{x}))] \right) \infty \int dJ_1 \exp\left[i \int d\vec{x} J_1(\vec{x})(I - \hat{\rho}(\vec{x})) \right] \\ &\Rightarrow \delta(I - \hat{\rho}) \infty \int dJ_1 e^{i \int J_1(I - \hat{\rho})} \\ &\delta(\psi - \hat{\psi}) \infty \int dJ_2 e^{i \int J_2(\psi - \hat{\psi})} \end{aligned} \quad (1.3.30)$$

where the symbol ∞ means that the equality is valid up to a factor which is independent of the configuration $\{\vec{R}_{m,i}^s\}$. Using 1.3.30 and taking as many factors as possible out of the integral over the configurations leads to (in the following the symbol ∞ will be replaced by the symbol $=$ because constant multiplication factors in the partition function have no influence on the final results)

$$Z = \int d\psi e^{\chi \int \psi^2} \int dJ_1 dJ_2 e^{i \int (J_1 + J_2) \psi} \int d\vec{R}_{m,i}^s e^{-\hat{H}_0} e^{-i \int (J_1 \hat{\rho} + J_2 \hat{\psi})} \quad (1.3.31)$$

Rewriting $\hat{\rho}$ and $\hat{\psi}$ in terms of $\hat{\rho}_A$ and $\hat{\rho}_B$ via

$$\begin{aligned} \hat{\rho} &= \hat{\rho}_A + \hat{\rho}_B \\ \hat{\psi} &= \frac{1}{2} \hat{\psi}_A - \frac{1}{2} \hat{\psi}_B = \frac{1}{2} (\hat{\rho}_A - \hat{\rho}_B) + \frac{1}{2} - f \end{aligned} \quad (1.3.32)$$

and introducing the shorthand notation

$$\langle \hat{A} \rangle_0 \equiv \int d\vec{R}_{m,i}^s e^{-\hat{H}_0} \hat{A} \quad (1.3.33)$$

leads to

$$Z = \int d\vec{R}_{m,i}^s e^{\chi \int \psi^2} \int dJ_1 dJ_2 \exp^{i \int (J_1 + J_2 \psi + (f - \frac{1}{2}) J_2)} \left\langle e^{-i \int (J_1 (\hat{\rho}_A + \hat{\rho}_B) + \frac{1}{2} J_2 (\hat{\rho}_A - \hat{\rho}_B))} \right\rangle_0 \quad (1.3.34)$$

After the substitution

$$J_A = J_1 + \frac{1}{2} J_2 \quad J_B = J_1 - \frac{1}{2} J_2 \quad (1.3.35)$$

1.3.34 can be rewritten as

$$Z = \int d\psi e^{\chi \int \psi^2} \int dJ_A dJ_B e^{i \int \sum f_\alpha J_\alpha + i \int \sum J_\alpha \psi_\alpha} \left\langle e^{-i \int \sum J_\alpha \hat{\rho}_\alpha} \right\rangle_0 \quad (1.3.36)$$

where $\psi_A \equiv \psi$ and $\psi_B \equiv -\psi$. Following ref 40, we define \tilde{J}_α in the following way

$$\tilde{J}_\alpha(\vec{x}) = J_\alpha(\vec{x}) - \frac{1}{V} \int d\vec{y} J_\alpha(\vec{y}) \quad \Leftrightarrow \quad \tilde{J}_\alpha(\vec{q}) = (1 - \delta_K(\vec{q})) J_\alpha(\vec{q}) \quad (1.3.37)$$

The right hand equation shows clearly that one variable is lost in this way. However, the integrand of 1.3.36 does not depend on this variable and can be written in terms of \tilde{J}_α .

$$Z = \int d\Psi e^{\chi \int \Psi^2} \int dJ_A dJ_B e^{i \int \tilde{J}_\alpha \Psi_\alpha - G} \quad G = -\ln \left\langle e^{-i \int \tilde{J}_\alpha \hat{\rho}_\alpha} \right\rangle_0 \quad (1.3.38)$$

G is the free energy of a compressible system of non-interacting random walk chains in the presence of an external field $i \tilde{J}_\alpha$. Since in such a system the chains are independent of each other, the expression for G can be factorized in contributions from the different chains:

$$G = -\sum_{s,m} \ln \int d\vec{R}_{m,i}^s e^{-i \int \tilde{J}_\alpha \hat{\rho}_\alpha^{s,m}} \frac{1}{V} \prod_i g(\vec{R}_{m,i+1}^s - \vec{R}_{m,i}^s) \quad (1.3.39)$$

$$\hat{\rho}_\alpha^{s,m}(\vec{x}) = \sum_i \sigma_{s,i}^\alpha \delta(\vec{x} - \vec{R}_{m,i}^s)$$

Different chains (labeled with m) having the same architecture s are present in the same external field. Therefore, they all have the same free energy and G can be rewritten as

$$G = -V \sum_s \rho_s \ln \left\langle e^{-i \int \tilde{J}_\alpha \hat{\rho}_\alpha^s} \right\rangle_0 \equiv -V \overline{\ln \langle e^{-i\epsilon} \rangle_0} \quad (1.3.40)$$

The bar represents the average over all chains: $\bar{A} = \sum_s \rho_s A_s$. The thermodynamic average $\langle \dots \rangle_0$ in 1.3.40 is now an average over the configurations of a *single* chain, and it includes a factor V^{-1} . The expression for G can be expanded in powers of ϵ . In the weak segregation regime it is sufficient to expand till the fourth order. Using $\langle \epsilon \rangle_0 = 0$ one obtains

$$\frac{G}{V} = \frac{1}{2} \overline{\langle \epsilon^2 \rangle_0} - \frac{i}{6} \overline{\langle \epsilon^3 \rangle_0} - \frac{1}{24} \overline{\langle \epsilon^4 \rangle_0} + \frac{1}{8} \overline{\langle \epsilon^2 \rangle_0^2} \quad (1.3.41)$$

The first term on the right hand side of 1.3.41 can be written as (use 1.2.24 in the second step, and 1.2.14 in the third step)

$$\begin{aligned} \overline{\langle \epsilon^2 \rangle_0} &= \sum_{\alpha\beta} \int d\vec{x} d\vec{y} \tilde{J}_\alpha(\vec{x}) \tilde{J}_\beta(\vec{y}) \sum_s \rho_s \langle \hat{\rho}_\alpha^s(\vec{x}) \hat{\rho}_\beta^s(\vec{y}) \rangle_0 = \\ &= \sum_{\alpha\beta} \int d\vec{x} d\vec{y} \tilde{J}_\alpha(\vec{x}) \tilde{J}_\beta(\vec{y}) \sum_s \rho_s \frac{1}{V} G_{\alpha\beta}^s(\vec{x}, \vec{y}) = \sum_{\alpha\beta} \int d\vec{x} d\vec{y} \tilde{J}_\alpha(\vec{x}) \tilde{J}_\beta(\vec{y}) \overline{g_{\alpha\beta}(\vec{x}, \vec{y})} \end{aligned} \quad (1.3.42)$$

The correlation functions $g_{\alpha\beta}^s(\vec{x}, \vec{y})$ were defined and discussed in the previous paragraph. Going over to Fourier transforms the expression for G becomes

$$\begin{aligned}
G = & \frac{1}{2V} \sum_{\vec{q}_1 \vec{q}_2} \sum_{\alpha\beta} \tilde{J}_\alpha(\vec{q}_1) \tilde{J}_\beta(\vec{q}_2) \sum_s \rho_s g_{\alpha\beta}^s(\vec{q}_1, \vec{q}_2) + \\
& - \frac{i}{6V^2} \sum_{\vec{q}_1 \vec{q}_2 \vec{q}_3} \sum_{\alpha\beta\gamma} \tilde{J}_\alpha(\vec{q}_1) \tilde{J}_\beta(\vec{q}_2) \tilde{J}_\gamma(\vec{q}_3) \sum_s \rho_s g_{\alpha\beta\gamma}^s(\vec{q}_1, \vec{q}_2, \vec{q}_3) + \\
& - \frac{1}{24V^3} \sum_{\vec{q}_1 \vec{q}_2 \vec{q}_3 \vec{q}_4} \sum_{\alpha\beta\gamma\delta} \tilde{J}_\alpha(\vec{q}_1) \cdots \tilde{J}_\delta(\vec{q}_4) \sum_s \rho_s g_{\alpha\beta\gamma\delta}^s(\vec{q}_1, \cdots, \vec{q}_4) + \\
& + \frac{1}{8V^3} \sum_{\vec{q}_1 \vec{q}_2 \vec{q}_3 \vec{q}_4} \sum_{\alpha\beta\gamma\delta} \tilde{J}_\alpha(\vec{q}_1) \cdots \tilde{J}_\delta(\vec{q}_4) \sum_s \rho_s g_{\alpha\beta}^s(\vec{q}_1, \vec{q}_2) g_{\gamma\delta}^s(\vec{q}_3, \vec{q}_4)
\end{aligned} \tag{1.3.43}$$

In the summations over \vec{q} , the terms corresponding to $\vec{q} = 0$ give no contribution, because $\tilde{J}(\vec{q} = 0) = 0$; see 1.3.37. Since $\tilde{J}(\vec{q}) = J(\vec{q})$ for $\vec{q} \neq 0$, one can rewrite 1.3.43 by removing the tildes over the J 's, and at the same time restricting the summations to non-zero values of \vec{q} . For instance, the first term in 1.3.43 becomes

$$\frac{1}{2V} \sum_{\vec{q}_1 \vec{q}_2}^* \sum_{\alpha\beta} J_\alpha(\vec{q}_1) J_\beta(\vec{q}_2) \sum_s \rho_s g_{\alpha\beta}^s(\vec{q}_1, \vec{q}_2) \tag{1.3.44}$$

where the star denotes that the summation is restricted to $\vec{q} \neq 0$. We now return to equation 1.3.38 for the configurational partition function Z . The functional integral over the fields $J(\vec{x})$ can be replaced by an integral over the Fourier components $J(\vec{q})$. Since the integrand does not depend on $J(\vec{q} = 0)$, the integration over this variable gives just a constant (though infinite) factor in front of the partition function. In order to make the notation more transparent, the following abbreviations are used:

$$a = (\alpha, \vec{q})^*$$

$$y_a = \frac{J_\alpha(\vec{q})}{V}$$

$$x_a = \frac{-i\Psi_\alpha(-\vec{q})}{V}$$

$$\begin{aligned}
 P_{ab} &= \sum_s \rho_s g_{\alpha_1 \alpha_2}^s(\vec{q}_1, \vec{q}_2) \\
 P_{abc} &= -i \sum_s \rho_s g_{\alpha_1 \alpha_2 \alpha_3}^s(\vec{q}_1, \vec{q}_2, \vec{q}_3) \\
 P_{abcd} &= -\sum_s \rho_s g_{\alpha_1 \alpha_2 \alpha_3 \alpha_4}^s(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) + \\
 &\quad + \sum_s \rho_s g_{\alpha_1 \alpha_2}^s(\vec{q}_1, \vec{q}_2) g_{\alpha_3 \alpha_4}^s(\vec{q}_3, \vec{q}_4) \\
 &\quad + \sum_s \rho_s g_{\alpha_1 \alpha_3}^s(\vec{q}_1, \vec{q}_3) g_{\alpha_2 \alpha_4}^s(\vec{q}_2, \vec{q}_4) \\
 &\quad + \sum_s \rho_s g_{\alpha_1 \alpha_4}^s(\vec{q}_1, \vec{q}_4) g_{\alpha_2 \alpha_3}^s(\vec{q}_2, \vec{q}_3)
 \end{aligned} \tag{1.3.45}$$

Again, the star in $(\alpha, \vec{q})^*$ denotes that $\vec{q} \neq 0$. The object P_{abcd} has been defined in such a way that it is symmetric in a, b, c and d . As shown in the previous paragraph, the Fourier transforms of the correlation functions appearing in 1.3.45 are zero unless the sum of their arguments is zero, i.e.

$$g_{\alpha_1 \alpha_2 \dots \alpha_n}^s(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_n) = \delta_K(\vec{q}_1 + \vec{q}_2 + \dots + \vec{q}_n) g_{\alpha_1 \alpha_2 \dots \alpha_n}^s(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_n) \tag{1.3.46}$$

In the following the delta function appearing in 1.3.46 will be written down explicitly for clarity, although strictly speaking this is superfluous. Moreover, we will write

$$g_{\alpha\beta}^s(\vec{q}_1, \vec{q}_2) = \delta_K(\vec{q}_1 + \vec{q}_2) g_{\alpha\beta}^s(q_1) \tag{1.3.47}$$

where q_l is the length of the vector \vec{q}_l . In terms of the abbreviations introduced in 1.3.45, the expression 1.3.38 for the partition function becomes

$$\begin{aligned}
 Z &= \int d\psi e^{\chi \int \psi^2} \int d\{y_a\} e^{-V \sum x_a y_a - \frac{1}{2} V \sum P_{ab} y_a y_b - \frac{1}{6} V \sum P_{abc} y_a y_b y_c - \frac{1}{24} V \sum P_{abcd} y_a y_b y_c y_d} \equiv \\
 &\equiv \int d\psi e^{-F_L}
 \end{aligned} \tag{1.3.48}$$

where the summations run over $a, b, c,$ and d . The integral over y_a will be calculated by the saddle point method⁴³. That is, we make the approximation

$$\begin{aligned}
 & -\ln \int dy_a e^{-V \sum x_a y_a - \frac{1}{2} V \sum P_{ab} y_a y_b - \frac{1}{6} V \sum P_{abc} y_a y_b y_c - \frac{1}{24} V \sum P_{abcd} y_a y_b y_c y_d} = \\
 & = V \sum_a x_a \tilde{y}_a + \frac{1}{2} V \sum_{ab} P_{ab} \tilde{y}_a \tilde{y}_b + \frac{1}{6} V \sum_{abc} P_{abc} \tilde{y}_a \tilde{y}_b \tilde{y}_c + \frac{1}{24} V \sum_{abcd} P_{abcd} \tilde{y}_a \tilde{y}_b \tilde{y}_c \tilde{y}_d
 \end{aligned} \tag{1.3.49}$$

where \tilde{y}_a is determined by the condition that it maximizes the integrand. The saddle point approximation 1.3.49 is exact in this situation. Solving the maximization condition for \tilde{y}_a iteratively and substituting this back into 1.3.48 gives the final expression for the Landau free energy F_L truncated to fourth order.

$$\begin{aligned}
 F_L &= \sum_{n=2}^4 \frac{1}{n!} \int d\vec{x}_1 \cdots d\vec{x}_n \Gamma_n(\vec{x}_1, \dots, \vec{x}_n) \psi(\vec{x}_1) \cdots \psi(\vec{x}_n) = \\
 &= \sum_{n=2}^4 \frac{1}{n!} \frac{1}{V^n} \sum_{\vec{q}_1 \cdots \vec{q}_n} \Gamma_n(\vec{q}_1, \dots, \vec{q}_n) \psi(\vec{q}_1) \cdots \psi(\vec{q}_n)
 \end{aligned} \tag{1.3.50}$$

where the term 1.3.26 accounting for the interaction energy

$$E = \chi \int d\vec{x} \psi^2(\vec{x}) = \frac{\chi}{V} \sum_{\vec{q}} \psi(\vec{q}) \psi(-\vec{q}) \tag{1.3.51}$$

has been absorbed into the second order vertex function. The vertices Γ_n are given by (remember that the bar denotes an average over all molecules types: $\bar{A} \equiv \sum_s \rho_s A_s$)

$$\Gamma_2(\vec{q}_1, \vec{q}_2) = V \delta_K(\vec{q}_1 + \vec{q}_2) \left[\frac{\overline{g_{AA}}(q_1) + 2\overline{g_{AB}}(q_1) + \overline{g_{BB}}(q_1)}{\overline{g_{AA}}(q_1) \overline{g_{BB}}(q_1) - \overline{g_{AB}}(q_1) \overline{g_{AB}}(q_1)} - 2\chi \right] \tag{1.3.52}$$

$$\Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3) = -V \delta_K(\vec{q}_1 + \vec{q}_2 + \vec{q}_3) \sum_{\alpha\beta\gamma} \overline{g_{\alpha\beta\gamma}}(\vec{q}_1, \vec{q}_2, \vec{q}_3) z_\alpha(q_1) z_\beta(q_2) z_\gamma(q_3) \tag{1.3.53}$$

$$\Gamma_4(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \Gamma_4^{reg}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) + \Gamma_4^{nl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) \quad (1.3.54)$$

$$\begin{aligned} \Gamma_4^{reg}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = V\delta_K(\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4) \sum_{\alpha\beta\gamma\delta} \left[\overline{-g_{\alpha\beta\gamma\delta}}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) + \right. \\ \sum_{\mu\nu} \overline{g_{\alpha\beta\mu}}(\vec{q}_1, \vec{q}_2, -\vec{q}_1 - \vec{q}_2) \overline{g_{\mu\nu}^{-1}}(\vec{q}_1 + \vec{q}_2) \overline{g_{\gamma\delta\nu}}(\vec{q}_3, \vec{q}_4, -\vec{q}_3 - \vec{q}_4) + \\ \sum_{\mu\nu} \overline{g_{\alpha\beta\mu}}(\vec{q}_1, \vec{q}_3, -\vec{q}_1 - \vec{q}_3) \overline{g_{\mu\nu}^{-1}}(\vec{q}_1 + \vec{q}_3) \overline{g_{\gamma\delta\nu}}(\vec{q}_2, \vec{q}_4, -\vec{q}_2 - \vec{q}_4) + \\ \left. \sum_{\mu\nu} \overline{g_{\alpha\beta\mu}}(\vec{q}_1, \vec{q}_4, -\vec{q}_1 - \vec{q}_4) \overline{g_{\mu\nu}^{-1}}(\vec{q}_1 + \vec{q}_4) \overline{g_{\gamma\delta\nu}}(\vec{q}_2, \vec{q}_3, -\vec{q}_2 - \vec{q}_3) \right] * \\ * z_\alpha(q_1) z_\beta(q_2) z_\gamma(q_3) z_\delta(q_4) \end{aligned} \quad (1.3.55)$$

$$\begin{aligned} \Gamma_4^{nl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = V\delta_K(\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4) \sum_{\alpha\beta\gamma\delta} \left[\delta_K(\vec{q}_1 + \vec{q}_2) \delta_K(\vec{q}_3 + \vec{q}_4) * \right. \\ * \left(\overline{g_{\alpha\beta}(q_1) g_{\gamma\delta}(q_3)} - \sum_{\mu\nu} \overline{g_{\alpha\beta\mu}}(\vec{q}_1, \vec{q}_2, -\vec{q}_1 - \vec{q}_2) \overline{g_{\mu\nu}^{-1}}(\vec{q}_1 + \vec{q}_2) \overline{g_{\gamma\delta\nu}}(\vec{q}_3, \vec{q}_4, -\vec{q}_3 - \vec{q}_4) \right) + \\ + \delta_K(\vec{q}_1 + \vec{q}_3) \delta_K(\vec{q}_2 + \vec{q}_4) * \\ * \left(\overline{g_{\alpha\gamma}(q_1) g_{\beta\delta}(q_2)} - \sum_{\mu\nu} \overline{g_{\alpha\gamma\mu}}(\vec{q}_1, \vec{q}_3, -\vec{q}_1 - \vec{q}_3) \overline{g_{\mu\nu}^{-1}}(\vec{q}_1 + \vec{q}_3) \overline{g_{\beta\delta\nu}}(\vec{q}_2, \vec{q}_4, -\vec{q}_2 - \vec{q}_4) \right) + \\ + \delta_K(\vec{q}_1 + \vec{q}_4) \delta_K(\vec{q}_2 + \vec{q}_3) * \\ * \left(\overline{g_{\alpha\delta}(q_1) g_{\beta\gamma}(q_2)} - \sum_{\mu\nu} \overline{g_{\alpha\delta\mu}}(\vec{q}_1, \vec{q}_4, -\vec{q}_1 - \vec{q}_4) \overline{g_{\mu\nu}^{-1}}(\vec{q}_1 + \vec{q}_4) \overline{g_{\beta\gamma\nu}}(\vec{q}_2, \vec{q}_3, -\vec{q}_2 - \vec{q}_3) \right) \left. \right] * \\ * z_\alpha(q_1) z_\beta(q_2) z_\gamma(q_3) z_\delta(q_4) \end{aligned} \quad (1.3.56)$$

where the superscript *reg* stands for *regular*, and the superscript *nl* for *non-local*; see the next section for an explanation. The quantity $z_\alpha(q)$ is defined by

$$z_\alpha(q) = \bar{g}_{\alpha A}^{-1}(q) - \bar{g}_{\alpha B}^{-1}(q) \quad (1.3.57)$$

This completes the calculation of the Landau free energy of a polydisperse copolymer melt in the WSR. Since the Fourier transforms of the vertex functions are proportional to the volume V , it is convenient to define, in analogy with the correlation functions,

$$\gamma_n(\vec{q}_1, \dots, \vec{q}_n) = \frac{1}{V} \delta_K(\vec{q}_1 + \dots + \vec{q}_n) \Gamma_n(\vec{q}_1, \dots, \vec{q}_n) \quad (1.3.58)$$

where the delta function on the right hand side is in fact superfluous, but has been added for clarity.

The non-local term

The contribution Γ_4^{nl} given by 1.3.56 is called the non-local term. It was first derived by Shakhnovich and Gutin³⁴ for the special case of uncorrelated random copolymers, and later in the most general form by Panyukov and Kuchanov.^{35,36} One can show generally that the non-local term is identically zero if the number of molecule types does not exceed the number of monomer types. For instance, if there are two monomer types present the non-local term vanishes for monodisperse copolymers, and for two-component blends. In polydisperse copolymers, however, its presence can be of crucial importance. For instance for random copolymers, which form the subject of the following three chapters, the non-local term is even the dominant contribution to the fourth order vertex, and together with the second order vertex it is responsible for the strong temperature dependence of the period of the microstructure, which is characteristic for these systems.³⁶

The phrase *non-local term* was introduced in refs 35, 36 and originates from the study of uncorrelated random copolymers. For uncorrelated random copolymers there is no correlation between the chemical identity of the monomers along the chain. The probability that the neighbor of a randomly picked monomer is of type A or B is independent of the chemical identity of the monomer picked. A representative chain can be constructed by drawing monomers one by one from a large reservoir containing disconnected A - and B -monomers in the ratio $f : 1-f$, and connecting them. The block lengths in the random copolymer chains

thus obtained are of order unity. For a melt of these chains, the second order vertex, the third order vertex, and the regular part of the fourth order vertex contain only the self-correlations G_{ii} , G_{iii} , and G_{iiii} , since the contributions coming from G_{ij} , G_{ijk} , and G_{ijkl} cancel if the indices are not all equal. As a consequence, apart from the non-local term, the vertices of the random copolymer coincide with the vertices of a low-molecular mixture of disconnected A - and B -monomers. These vertices could be obtained in an alternative way by expanding the Flory-Huggins expression for the entropy of mixing in a Taylor series. The non-local term, however, is different for these systems: it is zero for the low-molecular mixture, and proportional to $1/(q_1^2 + q_2^2)$ for the random copolymer. Therefore, if the Landau free energy of the random copolymer is expanded to fourth order, the non-local term is the only part which contains correlations between different monomers of the same chain, and so it accounts for the chain connectivity; hence the name “non-local term.” There is an easy physical explanation for the fact that only the self-correlation survives in the calculation of the regular vertices for the uncorrelated random copolymer. We will return to this in chapter 3, where it is shown that an analogous (though slightly more complicated) situation exists for the *correlated* random copolymer. The peculiarity that the chain connectivity is only present in the non-local term is only strictly true for uncorrelated random copolymers: for general polydisperse melts *all* vertices are non-local. However, we stick to the convention and use the name “non-local term” generally.

Although 1.3.54, 1.3.55 and 1.3.56 present the conventional way to split Γ_4 into two contributions, it is a bit unnatural, because if for instance $\vec{q}_1 + \vec{q}_2 = 0$, then the term involving the two third order correlation functions is added to Γ_4^{reg} , and subsequently subtracted from Γ_4^{nl} . Therefore, the problems arising due to the fact that $\overline{g_{\mu\nu}}(q=0)$ may not be invertible are artificial. Conventionally, these problems are dealt with by taking the limit

$$\begin{aligned} \gamma_4^{non-local}(q, q') &\equiv \\ &\equiv \lim_{\vec{p} \rightarrow 0} \sum_{\alpha\beta\gamma\delta} \left(\overline{g_{\alpha\beta}(q)g_{\gamma\delta}(q')} - \sum_{\mu\nu} \overline{g_{\alpha\beta\mu}(\vec{q}_1, \vec{q}_2, \vec{p})g_{\mu\nu}^{-1}(p)g_{\gamma\delta\nu}(\vec{q}'_1, \vec{q}'_2, \vec{p})} \right) z_\alpha(q)z_\beta(q)z_\gamma(q')z_\delta(q') \\ &|\vec{q}_1| = |\vec{q}_2| = q \quad |\vec{q}'_1| = |\vec{q}'_2| = q' \quad \vec{q}_1 + \vec{q}_2 = \vec{q}'_1 + \vec{q}'_2 = -\vec{p} \end{aligned} \quad (1.3.59)$$

The advantage of splitting the fourth order vertex like $\Gamma_4 = \Gamma_4^{reg} + \Gamma_4^{nl}$ is that in this way the part Γ_4^{reg} is a continuous function.

The mean-field approximation

By now we arrived at an expression for the configurational partition function Z of the form

$$Z = \int d\psi e^{-F_L(\psi)} \quad (1.3.60)$$

If the Landau free energy $F_L(\psi)$ is minimized by the profile $\tilde{\psi}$, then $\tilde{\psi}$ gives the dominant contribution to Z . Although $\tilde{\psi}$ is the *most probable* profile, it is not necessarily the *average* profile, because profiles other than $\tilde{\psi}$ can also give a contribution to the integral in 1.3.60. However, in a first approximation one could ignore all profiles other than $\tilde{\psi}$ and investigate the consequences.¹⁵ In this approximation the profile $\tilde{\psi}$ is assumed to be completely dominant, and the statistical weight of all other profiles is strictly zero. This assumption is justified if any experimental measurement of the profile gives $\tilde{\psi}$ as a result. In other words, this approximation is correct if the profile is static, not fluctuating, and the instantaneous fluctuations $\delta\psi(\vec{x}, t) \equiv \psi(\vec{x}, t) - \langle\psi(\vec{x})\rangle$ where t represents time can be ignored. Therefore, this approximation is equivalent to the mean-field approximation, and the mean-field free energy can be obtained by calculating the integral 1.3.60 with the saddle point method:

$$F_{mean-field} = -\ln \int d\psi e^{-F_L[\psi]} \Big|_{saddle\ point} = F_L[\tilde{\psi}] \quad (1.3.61)$$

According to equation 1.3.61, the mean-field free energy coincides with the Landau free energy. For most physical systems, the mean-field approximation is rather crude. For copolymer melts, however, it can be made arbitrary accurate by increasing the (average) block length N in the system. For homopolymer blends it can be shown that the error in the free energy due to the mean-field approximation has relative magnitude N^{-1} , for monodisperse multiblock copolymers it has relative magnitude $N^{-1/3}$ (ref 44), and for correlated random copolymers, which have rather polydisperse blocks, it has relative magnitude $N^{-1/4}$ (refs 45, 46). Summarizing, once the block lengths are large enough, the mean-field approximation is quite reasonable for block copolymer melts.