Fluctuation effects in melts of symmetric homopolymers, diblock copolymers, and their mixtures

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Zusammenfassung

Korrelationseigenschaften von ternären Homopolymer / Diblock - Copolymer-Schmelzen im Rahmen des Zuganges mit mehreren Ordnungsparametern unter Anwendung der Approximation der zufälligen Phasen. Die kritische Linie, die man im Rahmen dieses Zuganges erhält, stimmt mit der in der Theorie mit einem Ordnungsparameter überein. Der gesamte Konzentrationskorrelator (und folglich die Lifshitz-Linie) stimmt in beiden Theorien überein. Die Betrachtung der Eigenvektoren der Vertex-Matrix zweiter Ordnung zeigt, dass in der Nähe der kritischen Linie nur ein Eigenwert verschwindend klein (kritisch) wird. Der letztere ist verantwortlich für das Crossover von der Ising- zur Brazovskii-Universalitätsklasse. Dieser Umstand rechtfertigt die Benutzung der Theorie mit einem Ordnungsparameter. Der kritische Eigenvektor unterscheidet sich von dem, der vorher in der Literatur benutzt wurde; der Unterschied ist wichtig für die Aufstellung der Fluktuationstheorie. In der ungeordneten Phase weit weg von der kritischen Linie sind zwei Eigenvektoren wichtig für die Aufstellung der Fluktuationstheorie. Die Aufstellung der Fluktuationstheorie mit mehreren Ordnungsparametern (sogar in der Einschleifen-Näherung) erfordert die Berücksichtigung der mikroskopischen Fluktuationen auf hohen Wellenvektoren; ein Problem, das in der Literatur nicht ausreichend untersucht wurde.

Verhaltens der Lifshitz-Linie in ternären Systemen unter Verwendung der Renormierungsgruppenmethode. Es wurde gezeigt, dass in Übereinstimmung mit jüngsten Experimenten von Schwahn et al. die Lifshitz-Linie als Funktion der Temperatur sich nicht monoton verhält. Es konnte festgestellt werden, dass im Grenzfall hoher und tiefer Temperaturen (der letztere Fall entspricht dem Lifshitz-Punkt) die Lifshitz-Linie sich den Mean-Field-Werten nähert. Für moderate Temperaturen wird die Lifshitz-Linie zu größeren Konzentrationen verschoben. Die Verschiebung der Lifshitz-Linie bei großen Temperaturen ist ein Resultat der anwachsenden Fluktuationen im perturbativen Regime, während die nachfolgende Rückkehr zum Mean-Field-Wert mit der weiteren Abnahme der Temperatur das Ergebnis der Renormierung des Vertexes im Regime der starken Fluktuationen ist. Der Höchstwert der Abweichung der Lifshitz-Linie signalisiert den Übergang vom perturbativen zum Fluktuationsregime. Der Wert der unteren kritischen Dimension beeinflußt das Verhalten der Lifshitz-Linie. Zwei mögliche Fälle wurden hierzu untersucht.

Untersuchung der von großen Wellenvektoren herrührenden Fluktuationsbeiträge in der selbst-konsistenten Fluktuationstheorie der reinen Schmelzen symmetrischer Homopolymere bzw. symmetrischer Block-Copolymere. Die Berücksichtigung der Wellenvektor-Abhängigkeit des Vierer-Vertexes hat zur Folge, dass die Einschleifen-Korrektur für große q divergiert, so dass eine spezielle Betrachtung notwendig ist.Es wurde die Anwendbarkeit der Störungsentwicklungen zur Betrachtung der Beiträge von großen q im Falle flexibler Polymere demonstriert. Es wurde gezeigt, dass drei Typen von Fluktuationskorrekturen entstehen: (i) mesoskopische Korrekturen, die von den Skalen, die mit der Größe des Polymers vergleichbar sind, herrühren; (ii) mikroskopische Korrekturen, die der Skala der statistischen Segmentlänge entsprechen und von der Architektur der Polymere unabhängig sind. Das letztere heißt, dass die Fluktuationen für alle Polymerketten, die durch die Gausssche Statistik beschrieben werden, gleich sind; (iii) mikroskopische Korrekturen, die strukturabhängig sind. Das letztere heißt, dass die Fluktuationen davon abhängen, ob Verknüpfungspunkte oder freie Enden vorliegen. Die Unzulänglichkeit der herkömlichen Fredrickson-Helfand-Theorie äußert sich darin, dass in Folge der auf Brazovskii zurückgehenden Approximation zur Berechnung der Integrale, die gesamte Fluktuationskorrektur nur dem mesoskopischen Beitrag entspricht. Es wurden verschiedene Möglichkeiten zur Berücksichtigung der spezifischen Abhängigkeit des Vierer-Vertexes für große q untersucht. Es wurde die selbstkonsistente Dyson-Gleichung unter Berücksichtigung der vollen q-Abhängigkeit und unter Einführung eines Cutoffs von der Größenordnung der Segmentlänge, um die Integrale konvergent zu machen, gelöst.

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Part I

Introduction

Symmetric mixtures of homopolymers [1, 2] and a diblock copolymer, and in particular their properties near the Lifshitz point, have recently been the object of intense theoretical and experimental research. From the experimental point of view the interest is due to discovery of a special fluctuation regime, which was named a "bicontinuous microemulsion phase". It has important practical applications as well as provides a high-molecular analogy to the oil/water/amphiphile mixtures, in which similar phases have been found earlier. A lot of interest has been devoted to mapping the phase diagram of these low molecular systems [3, 4], which also stimulated theoretical investigations and computer simulations[5, 6, 7]. When the relative concentration of diblock is varied in the mixture it provides a realization of transition from the Ising to Brazovskii universality classes, exhibiting an isotropic Lifshitz point (and under certain conditions even a tricritical Lifshitz point), allowing experimental proof of numerical results available for this point from the theory of critical phenomena [8]. We consider theoretically two aspects of these mixtures.

Firstly, although the considered polymer system has four distinct order parameters (concentrations of monomeric units belonging to different types of polymers), almost all theoretical works have been using the simplifying assumption that there is only one relevant order parameter. The same assumption has been used for theoretical and computer modelling of multicomponent oil/water/amphiphile mixtures. We check the validity of this assumption by considering all the order parameters, investigating correlation properties within the Random Phase Approximation and comparing the results with those of a one order-parameter approach.

Secondly, recent scattering experiments on the ternary mixtures discovered the deviation of the behaviour of the Lifshitz line from the mean-field prediction, in particular a non-monotonic behaviour was observed [9, 10, 11, 12]. This phenomenon is all the more interesting because the experiments indicate that the critical line and the disorder line mirror the behavior of the Lifshitz line [13]. No theory was available explaining these new features, which was the motivation behind our developing a RG theory.

We relate a polymer system to parameters of a model phenomenological Hamiltonian. Results obtained for this model have a broad range of applications, as the Lifshitz line appears in a number of systems with competing tendencies for phase separation into bulk or spatially modulated phases. If the appropriate parameter controlling the relative strength of the two tendencies is varied the character of phase separation undergoes a change from bulk phase separation to the phase separation into a spatially modulated phase. The Lifshitz point is known to exist in magnetic systems [14]-[16], liquid crystals,[17] polyelectrolytes,[18]-[19] oil/water/surfactant mixtures,[20] random block-copoly-mers,[21]-[22] mixtures of homopolymers and diblock copolymers [23, 24]. Starting from the pioneering work of Hornreich et al.,[15] who introduced the Lifshitz point and calculated the critical exponents for this class of universality, most of the theoretical effort since has been concentrated on calculating the values of the exponents via application of various renormalization group techniques.[16, 25].

The aim of our consideration is the theoretical description of the behavior of the Lifshitz line with varying temperature. We show that the wavevector dependence of the fluctuation corrections is responsible for the experimentally observable shift of the Lifshitz line. The fluctuation effects will be taken into account within the one-loop renormalization group method. We put special emphasis on the comparison between the theoretically predicted behavior of the Lifshitz line and current experimental results.[9, 10, 11, 12] As we will demonstrate a major factor determining the character of this behavior is the value of the lower critical dimension d_l, a fact which has been little discussed in the literature. It is important to stress that the actual renormalized value of d_l is not known at present. Therefore, since the mean field value $d_l^{mf} = 4$ is close to $d = 3$ — dimension of space of the considered polymer blends, we will theoretically analyze different types of behavior of the Lifshitz line resulting from different possible values of d_l and compare them with the experiment.

While elaborating a multiple order parameter fluctuational theory with full treatment of wavevector dependence of the fourth order vertex we have encountered the problem of divergence of high wavevector contributions in the correction. The pioneering work of Brazovskii [26] simply neglected this divergence taking into account only critical (around q_*) fluctuations, assuming that high-q contributions result in renormalization of transition temperature. The currently standard fluctuational theories of diblock copolymers [27, 28] follow Brazovskii and neglect these contributions; incorrectly, as we argue below. As it turns out the problem of high-q contributions has been little addressed in the literature. To our knowledge it was mentioned only twice.

Holyst and Vilgis [29] considered the self-consistent one-loop corrections in the case of a homopolymer melt and observed the divergence. However, they do not make distinction between renormalization of χ and proper fluctuational contribution and thus introduce a cutoff at a lengthscale of the radius of gyration and count this term as the fluctuational correction. Their idea that the term represents proper fluctuational correction indeed inevitably leads to the choice of the cutoff at the radius of gyration. We argue that this correction is due to small scale renormalization as it is a property of Gaussian statistics (it is the same for all chains) and thus obviously represents renormalization of χ. Hence it is clear that if the cutoff is to be introduced, it must be a microscopic length, the obvious choice being the persistence length, since at this lengthscale the chain loses its Gaussian statistics.

Olmsted and Milner [30] considered fluctuational corrections arising from the effects of different architectures. To that end they perform calculations for two systems: blend of homopolymers, and a multiblock copolymer melt and compare the one-loop corrections. They also report that the correction depends as Λ^3 on the cutoff length and correctly identify the corrections as resulting from microscopic-scale renormalization. They are interested in macrophase separation only and for this case rightly claim that the correction is architecture independent and thus is on the one hand experimentally irrelevant and on the other hand can easily be canceled theoretically by taking the difference for two systems. However all of this is true only for the case when the correction is taken at $q = 0$. It was precisely their case, and they interpret the input of architecture dependent fluctuations as a correction to χ. However as we will show below for final q the microscopic contribution is also architecture dependent, and thus requires special consideration. Furthermore it is clear that for a diblock copolymer melt the correction should be taken at a final q.

From the experimental side the need to modify the classic Fredrickson-Helfand theory [27] is also tangible. Earlier experiments [31, 32] serving to check the predictions of the Fredricskon-Helfand theory [27] claimed good agreement, but actually used some fit parameters as a result of difficulties with relating experimental and theoretical χ. However, quite recent studies [33] directly comparing the values of χ obtained in melts of pure homopolymer and pure diblock copolymer have highlighted the discrepancies between FH theory and experiment. The experiments show that χ obtained by interpreting experimental results from copolymer melt within Leibler theory [34] better fit the values of χ (obtained from homopolymer blends) than analogous interpretation within the fluctuational FH theory. In fact the sign of the fluctuational correction seems to be wrong as is suggested by the measurement of the phase diagram of the ternary system [35]. When using χ determined from the homopolymer blend the transition point for a copolymer melt lies above (in temperature) the mean-field result, while the current fluctuation theories [27, 28] predict that fluctuations stabilise the disorder phase and thus actual transition should lie below the mean-field prediction. Correcting the theory is extremely important as it serves as a basis for taking into account effects of fluctuations in a vast array of industrially important polymer systems containing block copolymers and thus belonging to Brazovskii universality class.

In view of the above indications we consider a pure diblock copolymer melt and make an attempt to develop a self-consistent one-loop theory with the full wavevector dependence of the fourth vertex with correct handling of the high-q contributions.

Part II

Ternary A/B/A-B blends of homopolymers and a copolymer

1. Theoretical background

Our subsequent results are especially closely related to the works [23, 24] which also initiated both theoretical and experimental studies of the ternary systems therefore we first discuss them in some detail and then give overview of other works.

The work [23] has essentially two parts. The first part is based on considering the Flory-Huggins expression for the mixture (in their notations):

$$\frac{F}{T} = \frac{\psi_A}{N} \ln \psi_A + \frac{\psi_B}{N} \ln \psi_B + \frac{\psi_{AB}}{N_{AB}} \ln \psi_{AB} + \chi \psi_a \psi_b \tag{1.1}$$

and subsequent analysis of the phase diagram of this incompressible melt with the use of two order parameters: $\psi = \psi_A + \psi_B$ and $\eta = \psi_A - \psi_B$. This multicomponent system is properly analysed but with respect to stability to macrophase separation only (that is why the authors stress that the analysis is applicable for both random and diblock copolymer). Phase diagrams are constructed and a its peculiarities are discussed. In the second part the RPA theory of the blend is presented. However in this analysis the authors employ only a single order parameter, viz. the concentration of all monomers of type a, which may belong to homopolymer or copolymer: $\psi_a = -\psi_b$ and calculate the correlation function

$$S^{-1}(q) = \frac{S_{aa} + 2S_{ab} + S_{bb}}{S_{aa}S_{bb} - S_{ab}^2} - 2\chi \tag{1.2}$$

The structure factors are well-known [34]

$$\begin{aligned} S_{aa} &= \psi_A N g(1, x) + \psi_{AB} N_{AB} g(1/2, x_{AB}) && (1.3) \\ S_{bb} &= \psi_B N g(1, x) + \psi_{AB} N_{AB} g(1/2, x_{AB}) && (1.4) \\ S_{ab} &= \frac{1}{2} \psi_{AB} N_{AB} \left[g_D(1, x_{AB}) - 2 g_D(1/2, x_{AB}) \right] && (1.5) \end{aligned}$$

By taking the expansion of $S^{-1}(x)$ (1.2) and demanding that the first derivative equals zero the concentration ψ of the Lifshitz point is obtained which separates the sections of the critical line where the transition has micro- or macrophase character. It is established that the case $\alpha = 1$ presents a tricritical Lifshitz point.

The theory presented in [24] is properly many order parameter in both calculation of the correlation properties (using the RPA) and in finding the expansion of the free energy (staring from the Flory-Huggins expression (1.1)). Using incompressibility condition they introduce three order parameters and calculate the all the correlation functions between the order parameters. Rather surprisingly the expression for the full correlator of one of the component $S(q)$ coincides with that found by Broseta-Fredrickson, which means that the critical line (and of course the Lifshitz line) are also the same. The authors however go further and analyse two more special lines: equimaxima line (which they introduce) and a disorder line (much used in low molecular weight mixtures). They calculate the disorder line from the requirement that the full correlator $S(x)$ lose its oscillating character. Actually it is not exactly the experimentally determined line [3]. It was introduced in the experiments on oil/water/amphiphile mixtures based on the so-called Teubner-Strey fit [36] for the scattering function:

$$I(q) \sim (a_2 + c_1 q^2 + c_2 q^4)^{-1} \tag{1.6}$$

which is just an expansion of the correlator up to the fourth order. The correlation function resulting from (1.6) can be easily calculated as

$$G(r) \sim \frac{\sin(r/\lambda)}{r/\lambda} \exp(-r/\xi) \tag{1.7}$$

the disorder line is defined by the condition $\lambda = 0$ (note that the Lifshitz line corresponds to $\lambda = \xi$). Having completed fluctuation analysis the authors use the Flory-Huggins free energy they obtain an expansion of it in order to show that the Lifshitz point at $\alpha = 1$ is also a tricritical point as was indeed found in [23].

It is worthwhile to say that the work of Holyst-Schick represents the only multiple order parameter treatment available in literature. In particular all calculations of the phase diagrams have been conducted with the use of one order parameter ψ_a. The phase diagram of the considered system was first calculated in Ref [37]. They employed the weak-segregation approach with the expansion of the free energy up to the fourth order (ie constructed the theory analogous to Leibler's) and calculated resulting phase diagrams, for different values of relatives lengths of the homopolymers (not necessarily symmetric) and copolymer. However their they considered ordering into a lamellar phase only. All standard phases (bcc, hex, lam) have been considered in Ref [38] using a self-consistent field theory. Dependence of phase diagrams on practically all parameters of the system was investigated. Another approach to understanding the phase behaviour and in particular the nature of the fluctuational "bicontinuous microemulsion" is to look at the modification of the interface between two homopolymer phase upon introduction of a copolymer in the system. Such calculation also within a self-consistent theory was conducted in [39]. Results of Monte-Carlo computer simulations to that effect are reported in [40].

2. Experimental background

Motivated by the theoretical construction of the phase diagrams and in particular prediction of the Lifshitz point [23, 24] in symmetric isoplethic mixtures of homopolymers A and B ($N_A = N_B, \phi_A = \phi_B$) and a symmetric diblock copolymer ($f = 1/2$) experiments realising this system have been started. Of special interest was the region of the Lifshitz point, since the current theoretical idea [35, 10] is that the Lifshitz point exists only in mean-field theory, while in physical reality it must be destroyed by fluctuations due to the fact that mixtures of homopolymers and diblock copolymer melts have different classes of universality (Brazovskii class of universality and Ising one, respectively).The ratio $\alpha = N_A/N_{A-B}$, must be of the order of 2, so that the transition temperature for the whole system as a function of varying concentration of diblock ϕ lie in the same experimental window (as is indeed clear from the mean field equations for homopolymers: $\chi N = 2$ and diblock: $\chi N = 10.495$); in this case $\alpha = 0.208$. Note that within the RPA theory the location (ie ϕ) of the Lifshitz line is determined only by this ratio: $\phi_{LL} = 2\alpha^2/(1 + 2\alpha^2)$.

The first experimental work [35] looked at the properties of a mixture of polyethylene (PE)and poly(ethylenepropylene) (PEP) homopolymers and a corresponding PE-PEP copolymer ($N_{PE} = 392$, $N_{PEP} = 409$, $N_{PE-PEP} = 1925$). The system was studied with Small Angle Neutron Scattering (SANS) and rheological measurements (to determine the phase transition in the diblock-like part of the phase diagram). Surprisingly in this study the authors found no deviations from the mean-field behavior near the Lifshitz point and by looking at the scattering also found the mean-filed value of the critical exponents of the Lifshitz universality class: $\gamma = 1$ and $\nu = 1/4$. (Probably the most important result of the work however (yet which the authors do not appreciate) is the discrepancy between the experimental results and fluctuational theory of purely diblock melt which we will discuss in more detail in Section 9.)

By looking more carefully at the region delineating Ising and Brazovskii classes of universality [11] for the same system a strong deviation from the prediction of the mean-field theory was found. Namely, approximately in the region of ϕ_{LL} no phase transition at all with lowering temperature has been established (by looking at the SANS results). With the use of the transmission electron microscopy on cryoultrimcirotomed section obtained from melts quenched in liquid nitrogen the authors visualised the structure of the melts at different ϕ (Figure 3 of Ref. [11]). In the region of the mean-field Lifshitz Point the structure of the solution was claimed to be that of a bicontinuous microemulsion phase (looking similar to that found low-weight amphiphilic mixtures[41]). Although here and in the following they call it a phase no grounds for that actually exist. So far it has not been rigorously shown that there exists a bicontinuous microemulsion phase, so that it would be better to call it a fluctuation regime. Existence of the channel of microemulsion has been shown to be a generic feature of the ternary mixtures under consideration as it was discovered [12] for various types of monomeric units involved as well as for a wide region of molecular weight (even down to actually oligomeric system $N_A \approx 7$ and $N_{A-B} = 32$).

The most detailed investigation to date of the correlation properties of the ternary mixtures has been conducted by Schwahn et al. [9, 10], also by employing SANS. They conducted detailed study of the phase separation lines, Lifshitz line, critical exponents, behaviour of the maximum of scattering q_*. They confirm results of previous investigation in that they find no phase transition in the vicinity of ϕ_{LL} thus also dub this special fluctuation regime a bicontinuous microemulsion. However they go a little further and also present some suggestions how this regime can be located: they find a jump (or at least an abrupt change) of the value of the maximum of scattering q_* with change of ϕ at constant T (both already at $q_* \neq 0$), which can serve as a border of the "microemulsion phase". Furthermore, when in the behaviour of χ with temperature at constant ϕ certain deviation have been discovered which the authors also attribute to the onset of the "microemulsion phase". The behaviour of q_* as a function of varying T or ϕ has been probed and considerable discrepancies between the experiment and mean-field theoretical predictions discovered. Also these two works investigate the critical exponents γ and ν in the Lifshitz universality class and find deviations from the mean-field values. Interestingly they find even two fluctuational values for each of the exponent, the result validity of which is unclear. However these results are important as provide a rare experimental check of predictions for the isotropic $d = 3$ Lifshitz universality class.

The most important for our subsequent consideration result obtained in [9, 10] is the behaviour of the Lifshitz line. The Lifshitz line is determined the volume fraction ϕ at which the peak in the SANS profiles shifts off the zero value and is thus directly experimentally accessible. It has been found that is contrast to the prediction of the RPA theory that the Lifshitz line is independent of temperature (is simply given by $\phi_{LL} = 2\alpha^2/(1+2\alpha^2)$) experimentally the line was found to exhibit non-monotonic behaviour: deviating to larger ϕ for intermediate temperatures. This feature was the motivation for our studying theoretically the behaviour of the Lifshitz line with temperature in Section III. Further study [13] indicates that this non-monotonic behaviour may be quite a general feature: it is observed not only for LL, but also for the Disorder Line and even for the critical line (which implies re-entrant phase behavior in a small region of ϕ).

Another important feature of the behaviour of the Lifshitz line which is overlooked in the literature is its shift from the mean-field value as a whole to larger ϕ. For example for the Schwahn system the prediction is $\phi_{LL} \approx 0.06$ while experimental value is $\phi_{LL} \approx 0.09$. The same difference of $20 - 40\%$ between the experimental and theoretical results is present in other works ([13] and other). This feature seems to be a physical one and was the motivation behind considering the ternary mixture as a proper many order parameter system; such consideration is presented immediately below, however we were not able to progress beyond the RPA theory and therein this shift of the LL as a whole is absent (in fact results coincide with those of the single order parameter treatment).

3. Multiple order-parameter theory of ternary blends: Random Phase Approximation

The system we consider in this part is exactly that considered in the experimental work of Schwahn et al. and theoretical of Broseta-Fredrickson and Holyst-Schick. That is we have a ternary blend: two homopolymers A and B: with degrees of polymerization $N_A = N_B$, and volume fractions of monomers belonging to either of the homopolymers $\phi_A = \phi_B$; and a symmetric ($f = 1/2$) diblock with the degree of polymerization N and volume fraction of diblock monomeric units $\phi_{AB} = 1 - \phi_A - \phi_B$ (due to assumed incompressibility). The system is fully characterized by the following three parameters: $\phi \equiv \phi_{AB}$, N and $\alpha = N_A/N = N_B/N$.

In contrast to the Holyst-Schick theory we will first consider the system with some free vacancies (which can be understood as solvent) and then will obtain the limit of incompressible blend by taking the limit of zero concentration of vacancies. Therefore we consider all four densities of monomeric units:

$$\begin{aligned}
\phi_A(r) &= \phi_A + \psi_A(r) \\
\phi_B(r) &= \phi_B + \psi_B(r) \\
\phi_a(r) &= \frac{\phi_{AB}}{2} + \psi_a(r) \\
\phi_b(r) &= \frac{\phi_{AB}}{2} + \psi_b(r)
\end{aligned} \qquad (3.1)$$

Within the RPA theory the correlation matrix is simply inverse of the matrix of vertices of the second order, ie coefficients in the expansion of the free energy in terms of the concentrations (3.1) (ie coarse-grained free energy). The free energy of the system consists of three types of terms: macromolecular entropic term (we call structural), and two Flory-Huggins lattice-theory terms: short range attraction described interaction via a χ parameter; and hard-core repulsion (or the free energy of solvent).

As is well-known the structural term of the free energy is given by the inverse of the matrix of molecular correlator describing the structure of polymer, which for our system has a block form:

$$\Gamma_{ij}^{str(2)} = \left[G_{ij}^{str(2)}\right]^{-1} \tag{3.2}$$

$$G^{str(2)} = \begin{pmatrix} S_{AA} & 0 & 0 & 0 \\ 0 & S_{AA} & 0 & 0 \\ 0 & 0 & S_{aa} & S_{ab} \\ 0 & 0 & S_{ab} & S_{aa} \end{pmatrix} \tag{3.3}$$

Here we have already made use of the symmetry of the system. The expressions for the correlators are well-known:

$$\begin{aligned} S_{AA} &= \frac{1-\phi}{2}\frac{N}{\alpha} g(\alpha, x) \\ S_{aa} &= \phi N g(\frac{1}{2}, x) \\ S_{ab} &= \phi N h^2(\frac{1}{2}, x) \\ g(f,x) &\equiv \frac{2}{x^2}\left\{fx + \exp(-fx) - 1\right\}, \quad x \equiv \frac{q^2 a^2 N}{6} \\ h(f,x) &= \frac{1}{x}\left\{1 - \exp(-fx)\right\} \end{aligned} \tag{3.4}$$

Taking into account the Flory Huggins free energy [2]

$$F_{FH} = \frac{1}{2}\int \chi_{ij}\phi_i(r_1)\phi_j(r_2)\ dr_1 dr_2 + \int (1 - \sum_i \phi_i(r)) \ln(1 - \sum_i \phi_i(r))\ dr \tag{3.5}$$

we obtain the following matrix of the second vertices

$$\Gamma^{(2)} = \begin{pmatrix} S_{AA}^{-1} + w & \chi + w & w & \chi + w \\ \chi + w & S_{AA}^{-1} + V & \chi + w & w \\ w & \chi + w & \Gamma_{aa} + w & \Gamma_{ab} + \chi + w \\ \chi + w & w & \Gamma_{ab} + \chi + w & \Gamma_{aa} + w \end{pmatrix} \tag{3.6}$$

where $w \equiv (1 - \sum_i \phi_i)^{-1}$ and in order to obtain the incompressible melt we will put in the following $w \to \infty$, and we have introduced obvious notations for the inverse diblock matrix: $\Gamma_{aa} \equiv S_{aa}/(S_{aa}^2 - S_{ab}^2)$ and $\Gamma_{ab} \equiv -S_{ab}/(S_{aa}^2 - S_{ab}^2)$.

Our goal is to investigate the correlational properties and spinodal stability of the system, therefore to proceed we reduce the quadratic in $\phi_i(r)$ term of the free energy to diagonal form by finding the eigenvalues λ_i and eigenvectors of the matrix $\Gamma^{(2)}$:

$$\lambda_i = \begin{pmatrix} \frac{1}{2}\left(S_{AA}^{-1} + \Gamma_d - 2\chi - R\right) \\ \frac{1}{2}\left(S_{AA}^{-1} + \Gamma_d - 2\chi + R\right) \\ \frac{1}{2}\left(S_{AA}^{-1} + (S_{aa} + S_{ab})^{-1}\right) \\ 4w \end{pmatrix} \tag{3.7}$$

$$\begin{pmatrix} -1 & -1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ -\frac{1}{2\chi}(S_{AA}^{-1} - \Gamma_d + R) & -\frac{1}{2\chi}(S_{AA}^{-1} - \Gamma_d - R) & -1 & 1 \\ \frac{1}{2\chi}(S_{AA}^{-1} - \Gamma_d + R) & \frac{1}{2\chi}(S_{AA}^{-1} - \Gamma_d - R) & -1 & 1 \end{pmatrix} \tag{3.8}$$

$$R = \sqrt{4\chi^2 + (S_{AA}^{-1} - \Gamma_d)^2} \tag{3.9}$$

Here the last matrix is composed of the columns of (yet non-renormalized) eigenvectors: ith column corresponding to ith eigenvalue λ_i. In the eigenvectors the number of the line corresponds to the component: 1—A; 2 — B; 3 — a; 4 — b. We have also introduced the notation $\Gamma_d \equiv \Gamma_{aa} - \Gamma_{ab} = (S_{aa} - S_{ab})^{-1}$.

4. Results and Discussion

Let us note that from formulae (3.7) and (3.8) we indeed obtain the incompressibility condition, namely we obtain that the vector $\sum_i \psi_i$ does not fluctuate as the eigenvalue $w \to \infty$. Therefore in the following the fourth eigenvalue and -vector are of no interest to us.

As a first step of the analysis of course we look at the spinodal. As is well known it is given by the equality to zero of an eigenvector. By considering expressions (3.7) and (3.8) we see that only λ_1 can become negative and is thus a spinodal value. Taking into account expression for R it is easy to show that the equation for the spinodal $\lambda_1 = 0$ can be rewritten as

$$\frac{1}{\chi} = S_{AA} + S_{aa} - S_{ab} \tag{4.1}$$

which is the result obtained by Broseta-Fredrickson within one order-parameter approach and by Holyst-Schick by multiple order parameter treatment.

Another important property is the correlation function of chemically identical monomeric units, which may belong either to homopolymer or to copolymer:

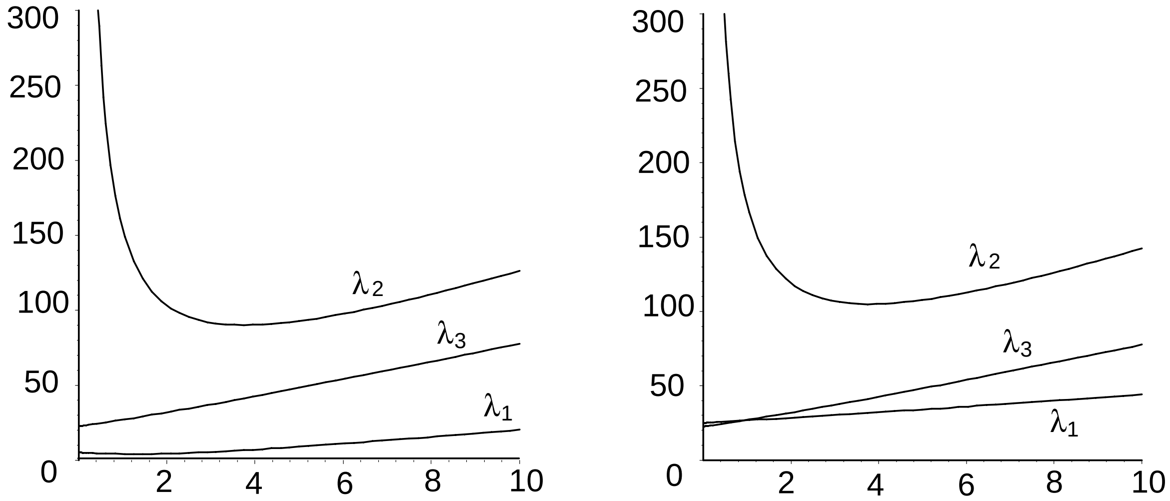

Figure 4.1: Eigenvalues of the vertex matrix for the ternary system of homopolymers and a copolymer. In plot **(a)** the system is close to the spinodal: $\chi N = 10$; in plot **(b)** the system is atherma:l $\chi N = 0$. For both plots $\alpha = 0.2$, $\phi = 0.2$.

$$G(q) = \langle(\phi_a(q) + \phi_A(q))\,(\phi_a(-q) + \phi_A(-q))\rangle = G_{aa}(q) + G_{AA}(q) + 2G_{aA}(q) \quad (4.2)$$

We can obtain the correlation functions by inverting the matrix $\Gamma^{(2)}$. Rather surprisingly the result (given also by Holyst and Schick)

$$G = \frac{1}{2}\frac{S_{AA} + S_{aa} - S_{ab}}{1 - \chi(S_{AA} + S_{aa} - S_{ab})} \quad (4.3)$$

again coincides with that found by the one order parameter theory of BF. The conclusion is that on the level of RPA theories we have not found any difference between the results obtained within the one or multiple order parameter theories.

Let us now analyse the eigenvalues (3.7) in more detail. For illustrative purposes we plot them in Figure 4.1. We take $\alpha = 0.2$, $\phi = 0.2$ and illustrate two important situations: in plot **(a)** $\chi N = 10$, ie the system is near spinodal; whereas plot **(b)** presents the athermal case of $\chi N = 0$.

In order to understand the general behaviour of the eigenvectors with x let us note that $\Gamma_d = (S_{aa} - S_{ab})^{-1}$ is the vertex of a symmetric diblock blend and therefore has a "correlation hole" behaviour: it is $+\infty$ at $x = 0$ and $x = \infty$ and in-between has a minimum. Γ determines the qualitative behaviour of R as can be seen from (3.9). As is well-known S_{AA}^{-1}, S_{aa}^{-1} and S_{ab}^{-1} are all monotonously increasing functions of x. Taking all this into account we obtain the following classification of λ's: λ_1 can be either monotonously increasing or have a minimum at a final x (the change between the two is the Lifshitz line); λ_2 always has a minimum at a final x, whereas λ_3 always monotonously increases with x. As we have mentioned only λ_1 can be negative, while λ_2 and λ_3 always stay positive. Furthermore, the following relations between them exist: $\lambda_1 < \lambda_2$ and $\lambda_3 < \lambda_2$. Importantly there is no inequality for λ_1 and λ_2; they can have various relative magnitudes. All of which leads us to the following conclusions.

Although the system has many order parameters there is only one relevant eigenvalue at the spinodal, viz. λ_1. The minimum of this eigenvalue determines the type of separation: whether it is micro- or macrophase. (Note that this situation is actually not the only in principle possible. Indeed it could be envisaged that two eigenvalues (one always with q_* final and the other always with $q_* = 0$) could be relevant to the stability..) This result justifies using only one order parameter for consideration of the system near the phase transition. This order parameter however must be the eigenvector associated with λ_1. It can be easily found from (3.8): on the spinodal the critical wavevector is $\left\{-1, 1, -\frac{1}{\chi}(S_{AA}^{-1} - \chi), \frac{1}{\chi}(S_{AA}^{-1} - \chi)\right\}$. It is important to note that the usually employed assumption [23, 42] that the order parameter is given by the sum of chemically same monomers, eg $\phi(r) = \phi_A(r) + \phi_a(r)$, leads to the vector $\{-1, 1, -1, 1\}$, which is different from the actual critical vector. Thus although there is indeed only one critical eigenvalue and therefore we can consider one order parameter, that parameter should be found from theory. The right choice of the order parameter should be made for the calculation of the fluctuation corrections. Until now in the literature [42] the $\{-1, 1, -1, 1\}$ vector has always been used (although see [43]).

As we can see directly from Figure 4.1**(b)** for small values of χ two eigenvalues are relevant for fluctuational properties of the system. Although as we have mentioned above the result for the Lifshitz line obtained within the one-parameter Broseta-Fredrickson theory (unexpectedly) coincides with our result, multiple order parameter treatment is essential for correct calculation of the fluctuational effects. We have attempted to conduct a calculation of one-loop fluctuational correction within a proper multiple order parameter approach, however our progress has been checked by the problem of high-q divergency of resulting integrals. We will consider this problem in detail in Part V for the case of a pure diblock melt. Before going to that, however, we consider the behaviour of the Lifshitz Line with changing temperature within the one order-parameter RG approach.

Part III

Lifshitz Line in Ternary Blends

5. Perturbative calculation of the shift of the Lifshitz line

We start from the conventional expansion of the Landau free energy functional

$$H[\psi(\mathbf{q})] = \frac{1}{2}\int_{\mathsf{q}} \psi(-\mathbf{q})G_0^{-1}(\mathbf{q})\psi(\mathbf{q})+\frac{\lambda}{4!}\int_{\mathsf{q}_1}\int_{\mathsf{q}_2}\int_{\mathsf{q}_3} \psi(\mathbf{q}_1)\psi(\mathbf{q}_2)\psi(\mathbf{q}_3)\psi(-\mathbf{q}_1-\mathbf{q}_2-\mathbf{q}_3) \tag{5.1}$$

in powers of the Fourier transform of the order parameter. In particular, for the ternary mixtures under consideration the natural order parameter is the deviation (from the volume averaged) of the concentration of a (or b, since the system is symmetric) monomers. The parameters of the Hamiltonian (5.1) for the polymer system can be obtained from coarse-graining of the corresponding microscopic Hamiltonian.[42] In particular, near the Lifshitz line (to be defined later) the bare correlation function $G_0^{-1}(q)$ can be written as follows:

$$G_0^{-1}(q) = \tau + c_1(\phi)q^2 + c_2 q^4 \tag{5.2}$$

with $\tau \sim (T - T_c)/T$ being the reduced temperature. For the considered ternary mixtures the coefficient $c_1(\phi)$ depends on the concentration of diblock-copolymer ϕ [23, 24, 42] and changes the sign with the variation of ϕ. At sufficiently small values of ϕ the coefficient $c_1(\phi) > 0$ and the system belongs the Ising universality class; at larger concentrations of diblock $c_1(\phi) < 0$ and the system attains the Brazovskii universality class.[26] Within the mean-field theory the Lifshitz point is defined by the two conditions: $\tau = 0$ and $c_1(\phi_{MFLP}) = 0$. More generally, we can introduce the mean-field Lifshitz line as the locus of points in parameter space (ϕ, τ) at which the quadratic term vanishes: $c_1(\phi_{MFLL}(\tau)) = 0$. The Lifshitz line (LL) is easily determined experimentally by considering the position of the peak of the static scattering curve.[11, 12, 9, 10] If we begin increasing the concentration of diblock at constant temperature the LL is determined by the diblock concentration at which the peak in the scattering curve first shifts off the zero wave vector. A noteworthy feature of the considered polymeric system is that the temperature T enters the Hamiltonian (5.1) only via the Flory-Huggins parameter, hence the coefficient $c_1(\phi)$ turns out to be independent of temperature,[23, 24, 42] so that the mean-field position of the LL ϕ_{MFLL} is also temperature independent and is determined solely by the ratio of the molecular weights of the polymers comprising the mixture. This mean-field prediction was not confirmed experimentally. Instead of being constant, the position of the LL was found to vary with temperature, more precisely, it exhibited a non-monotonous behavior, which shows that fluctuations should be taken into account. This is hardly surprising because at the LL, when $c_1(\phi)$ vanishes, the fluctuation corrections in fact become the only input into the renormalized counterpart of c_1 and thus always play a role.

Let us consider the renormalized correlation function. Note, that since our goal is to calculate the deviation of the LL, the renormalized quadratic term vanishes:

$$\begin{aligned} G^{-1}(q) &= \tau_r + l_1(\phi,\tau)q^2 + c_2 q^4 && (5.3)\\ l_1(\phi,\tau) &= c_1(\phi) + \Delta c_1(\tau) = 0 && (5.4)\end{aligned}$$

The shift of the LL (which is temperature dependent due to fluctuation corrections) is denoted by $\Delta c_1(\tau)$. Within the approximation we use in this paper c_2 will not be renormalized. The renormalized parameter l_1 can be found by considering the Dyson equation:

$$\begin{aligned} G^{-1}(q) &= G_0^{-1}(q) - \Sigma(q), && (5.5)\\ \Sigma(q) &= D_1(q) + D_2(q). && (5.6)\end{aligned}$$

We consider in the self-energy $\Sigma(q)$ only the one and two-loop diagrams:

$$\begin{aligned} D_1 &= -\frac{n+2}{6}\lambda \int_{\mathsf{q}} \frac{1}{\tau + c_2 q^4} && (5.7)\\ D_2(q) &= \frac{\lambda^2}{6}\int_{\mathsf{q}_1}\int_{\mathsf{q}_2} \frac{1}{[\tau + c_2 q_1^4][\tau + c_2 q_2^4][\tau + c_2(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q})^4]} && (5.8)\end{aligned}$$

For generality and ease of comparison with known results we have introduced n — the number of components of the order parameter. Note, that for the polymer blends,[9, 10] whose description is the goal of our work, due to the incompressibility condition the order parameter is a scalar, i.e. $n = 1$, as is indeed clear from the Hamiltonian (5.1). The D_1 diagram is q-independent and is therefore of no relevance to the renormalization of c_1. The first correction to it is given by $D_2(q)$. Calculation of $D_2(q)$ is performed easier in the real space. For the experimentally relevant case $d = 3$ we use the r-space representation of the correlation function

$$G(r) = \int \frac{d^3q}{(2\pi)^3}\frac{\exp(iqr)}{\tau + c_2 q^4} = \frac{\xi}{4\pi c_2}\frac{1}{r/\xi}\exp(-r/(\xi\sqrt{2}))\sin\left(r/(\xi\sqrt{2})\right) \qquad (5.9)$$

to rewrite the expression for $D_2(q)$ in terms of $G(r)$ as follows:

$$D_2(q) = \frac{\lambda^2}{6}\int e^{iqr} G^3(r) d^3r \qquad (5.10)$$

where $\xi = (c_2/\tau)^{1/4}$ is the mean-field correlation length. In fact we need only the quadratic term of the diagram in powers of q, which is readily calculated:

$$D_2^{(2)}(q) = -b\frac{\lambda^2\xi^8}{c_2^3}q^2 \qquad (5.11)$$

where $b \approx 0.109\ 10^{-4}$ is a constant. As it is clear from the Dyson equation (5.5) this result gives in fact the shift of the LL:

$$\Delta c_1(\tau) = B\frac{\lambda^2\xi^8}{c_2^3} \tag{5.12}$$

Note, that we have obtained the expression (5.12) within the perturbation theory and therefore it is not valid in the regime of strong fluctuations. However, the scaling behavior of $\Delta c_1(\tau)$ in the regime of strong fluctuations can be obtained from (5.12) by replacing λ with the effective coupling constant λ_r, and understanding under ξ the true correlation length, thus

$$\Delta c_1(\tau) \simeq B\frac{\lambda_r^2(\tau)\xi^8(\tau)}{c_2^3}. \tag{5.13}$$

This formula immediately allows some conclusions about the qualitative behavior of the LL.

First of all, we observe that the correction is positive, which means that on the LL $c_1(\phi) < 0$, i.e. fluctuations shift the LL into the $q_* \neq 0$ region of the mean-field theory. For the homopolymer/diblock copolymer blend that means that LL shifts to greater concentration of diblock, which is in agrement with experiments.[11, 12, 9, 10] Next consider the dependence on temperature. We have two regimes here: perturbative (small correlation lengths, at high temperatures) and scaling (low temperatures, large ξ). In the perturbative regime where the input of fluctuations is small, λ remains practically non-renormalized, so that with lowering temperature $\Delta c_1(\tau)$ should increase simply due to the increase of ξ. In the scaling regime the main effect (as will be shown below) comes from the renormalization of the coupling constant λ_r. In fact in this regime we can obtain the scaling dependence of the correction from the considerations of dimensionality: demanding that the $\Delta c_1(\tau)q^2$ term of the Hamiltonian (5.3) have the same dimensionality in ξ as the c_2q^4 term of the correlation function. If c_2 is not renormalized (as is our case), then

$$\Delta c_1(\tau) \sim \xi^{-2} \tag{5.14}$$

As we can see, in the scaling regime the correction decreases with increasing ξ (i.e. decreasing temperature). Combined with the conclusion made above about the increase of $\Delta c_1(\tau)$ in the perturbative regime we come to conclusion that $\Delta c_1(\tau)$ exhibits a non-monotonous behavior as a function of τ. This behavior is a manifestation of the crossover between the regimes of small and strong fluctuations.

6. Renormalization group study of the Lifshitz line

To describe $\Delta c_1(\tau)$ quantitatively we have to obtain expressions for $\lambda_r(\tau)$ and $\xi(\tau)$ in both the perturbative and scaling regimes. For this purpose we shall employ a renormalization group technique to the first order in ε (one-loop RG). Note, that within this method the parameter c_2 does not renormalize. The renormalization of temperature is described by the one-loop diagram (5.7):

$$D_1 = D_1^a + D_1' = -\frac{n+2}{6}\lambda \int_{\mathsf{q}} \frac{1}{c_2(\mathbf{q}^2)^2} + \frac{n+2}{6}\tau\lambda \int_{\mathsf{q}} \frac{1}{c_2(\mathbf{q}^2)^2(\tau + c_2(\mathbf{q}^2)^2)}, \quad (6.1)$$

The above expression is conventionally split into two parts responsible for additive and multiplicative renormalization of temperature. For dimensions $d > 4$ a cutoff at the upper limit in integration over q in the first term is assumed. These two terms give the critical dimensions of the Lifshitz class of universality. The lower critical dimension d_l is defined as the dimension when the first term logarithmically diverges at small q. The upper critical dimension d_u is the dimension at which the second term logarithmically diverges at small q for zero temperature. A cutoff at the lower limit of integration over $\mathbf{q}$ is implied in Equation (6.1). For the isotropic Lifshitz class of universality we obtain: $d_l^{mf} = 4$ and $d_u^{mf} = 8$. The real experimental system corresponds to $d = 3$ so that we come to conclusion that we are situated below d_l^{mf}. This means that the D_1^a term diverges at small q, i.e. for large correlation lengths and thus no phase transition of the second order is possible at a finite temperature. However, this value for the lower critical dimension is only the mean-field one. Fluctuations renormalize the value of the lower critical dimension. The calculation of the renormalized lower critical dimension is a formidable task, so that the true renormalized value of d_l for the experimental system is actually unknown. Therefore, we will consider below several possibilities.

Going back to renormalization of τ by substituting (6.1) into the Dyson equation we obtain:

$$\begin{aligned} \tau_r &= \tau_a Z_2(\Lambda_{\min}) && (6.2) \\ \tau_a &= \tau - D_1^a Z_2(\Lambda_{\min})^{-1}, && (6.3) \end{aligned}$$

where for purposes of clarity we introduced the temperature with additive term τ_a as well as renormalized temperature τ_r. The quantity $\Lambda_{\min}$ in Equation (6.2-6.3) is the lower cutoff imposed in Equation (6.1) in integration over the momentum $\mathbf{q}$. The RG treatment is based on the following perturbative expression:

$$\tau_r = \tau_a \left(1 - \frac{n+2}{6}\lambda \int_{\mathsf{q}} \frac{1}{c_2(\mathbf{q}^2)^2(\tau + c_2(\mathbf{q}^2)^2)} + ...\right) \quad (6.4)$$

Likewise considering the fluctuation correction to λ for its renormalized counterpart λ_r we obtain:

$$\lambda_r = \lambda \left(1 - \frac{n+8}{6} \lambda \int_{\mathsf{q}} \frac{1}{(\tau + c_2(\mathbf{q}^2)^2)^2} + ... \right) \tag{6.5}$$

These two equations are the starting point to derive the differential equations of the renormalization group for τ_r and λ_r. To do this we introduce a running cutoff Λ at the lower limit of the integrals in (6.4)-(6.5), differentiate both parts of these equations with respect to Λ and replace in the rhs the bare quantities τ and λ through the effective ones. Thus we obtain:

$$\Lambda \frac{\partial \ln \tau_r}{\partial \Lambda} = \frac{n+2}{6} g \tag{6.6}$$

$$\Lambda \frac{\partial}{\partial \Lambda} g = -\varepsilon g + \frac{n+8}{6} g^2 \tag{6.7}$$

where the effective dimensionless coupling constant is defined as follows $g = \bar{\lambda}_r \Lambda^{-\varepsilon}$ with $\varepsilon = 8 - d$, and $\bar{\lambda} = \lambda K_d / c_2^2$, $K_d = S_d/(2\pi)^d$, S_d being the surface of a unit d-dimensional sphere. As can be seen from (6.7) the fixed point of the effective coupling constant, $g = \bar{\lambda}_r \Lambda_{\text{min}}^{-\varepsilon}$, is $g^* = \frac{6}{n+8}\varepsilon$.

Notice that the second equation is independent of τ, therefore we solve it first and then substitute the result $g(\Lambda)$ into the first one. Thus we obtain the solution of the differential equations (6.6)-(6.7):

$$\begin{aligned} \frac{\tau_r}{\tau_a} &= Z_2(\Lambda_{\text{min}}) = \left(1 + \frac{n+8}{6} \frac{\bar{\lambda}}{\varepsilon} \Lambda_{\text{min}}^{-\varepsilon} \right)^{-\frac{\mathsf{n+2}}{\mathsf{n+8}}} && (6.8) \\ \frac{\lambda_r}{\lambda} &= \left(1 + \frac{n+8}{6} \frac{\bar{\lambda}}{\varepsilon} \Lambda_{\text{min}}^{-\varepsilon} \right)^{-1} && (6.9) \end{aligned}$$

Equation (6.8) for τ_r allows us to obtain the critical exponent of the correlation length: $\nu = \frac{1}{4}\left(1 + \frac{n+2}{n+8}\varepsilon\right)$, which is a well-known result.[15, 16] Note, that in this system τ_r is expressed via the temperature with additive shift (RG generalization of Equation (6.3)):

$$\tau_a = \tau + \frac{n+2}{6} \int_{\mathsf{q}} \frac{\lambda_r(q)}{Z_2(q) c_2 q^4} \tag{6.10}$$

Taking into account the renormalization of the coupling constant λ_r and the propagator in the expression of the shift of the critical temperature can be found by considering the higher-order corrections to the self-energy $\Sigma(q)$. It is clear that the infrared behavior of these corrections is controlled by the momentum q, which is the argument of the self-energy $\Sigma(q)$. This demands to write $\lambda_r(q)$ and $Z_2(q)$ under the integral in (6.10) as functions of the external momentum q. The relation (6.10) makes the one-loop RG scheme for renormalization of τ_r and λ_r complete. Now, using the relation between Λ_{min} and ξ (see below) we can obtain from Equation (6.8) $\xi(\tau)$, which substituted into (6.9) will give $\lambda_r(\tau)$. The two dependences substituted in turn into the formula for Δc_1 (5.13) will give our final result — the deviation of the LL from the mean-field value as a function of temperature. In order to find relation between the cutoff wave vector Λ_{min} and the correlation length ξ, one should find the perturbative limit of the RG formulae (6.8) or (6.9) and demand it to be equal to the corresponding diagrams (6.4) or (6.5). Thus it is straightforward to obtain: $\Lambda_{\text{min}} = \xi^{-1}$. Using this relation and introducing reduced variables we can rewrite Equation (6.8)–(6.10) as follows:

$$\frac{\widetilde{\tau}_r}{\widetilde{\tau}_a} \equiv Z_2(\xi) = \left(1 + \widetilde{\lambda}\xi^{\varepsilon}\right)^{-\frac{\mathsf{n+2}}{\mathsf{n+8}}}, \qquad \widetilde{\tau}_a = \widetilde{\tau} + a\int_{\xi^{-1}}^{\infty} \frac{\widetilde{\lambda}_r(q)}{Z_2(q)q^4} q^{d-1} dq \tag{6.11}$$

$$\frac{\widetilde{\lambda}_r}{\widetilde{\lambda}} = \left(1 + \widetilde{\lambda}\xi^{\varepsilon}\right)^{-1} \tag{6.12}$$

where the reduced variables are: $\widetilde{\lambda} \equiv \frac{n+8}{6}\frac{\overline{\lambda}}{\varepsilon}$, $\widetilde{\tau} \equiv \frac{\tau}{c_2}$, and the constant $a \equiv \frac{n+2}{n+8}\varepsilon$. However the relation $\Lambda_{\text{min}} = \xi^{-1}$ is asymptotically correct only in the vicinity of the upper critical dimension $d_u = 8$ and we do not expect it to hold for the considered experimental situation $d = 3$. Therefore, we only know that $\Lambda_{\text{min}} \sim \xi^{-1}$ with the prefactor being unknown. In this situation the constants a and a new constant f (defined via $\widetilde{\lambda} \equiv f\lambda/c_2^2$) become essentially fit parameters of the theory. The expression for $\Delta c_1(\tau)$ in reduced variables reads:

$$\frac{\Delta c_1(\tau)}{c_2 b f^{-2}} = \widetilde{\lambda}_r^2(\widetilde{\tau})\xi^8(\widetilde{\tau}) \tag{6.13}$$

Before solving the system let us make some further comments on the Equation (6.8)-(6.10), in particular discuss the issue of the lower critical dimension. To that end we should consider the scaling of the term responsible for additive renormalization:

$$\Delta\tau \equiv a\int_{\xi^{-1}}^{\infty} \frac{\lambda_r(q)}{Z_2(q)l_2(q)q^4} q^{d-1} dq \sim \xi^{-1/\nu} \tag{6.14}$$

If $d > d_l$ then this integral converges on small q and this addition to temperature can be neglected in the RG calculations as it is does not depend on the correlation length. Note, however that experimentally this correction is still relevant. Since the values of the fluctuation shift of temperature are different in the Ising and Lifshitz classes of universality the temperature of the LP is shifted to lower values then the transition temperature of the Ising class of universality. The situation of the lower critical dimension corresponds to logarithmic divergence of $\Delta\tau$, i.e. $1/\nu = 0$. If $d < d_l$ then the correction diverges at $\xi \to \infty$, which precludes the phase transition at finite temperatures, the transition temperature goes to zero. According to Equation (6.14) we can consider the exponent ν in this case to be formally negative. As we have mentioned above the renormalized value of d_l is not presently known, so we will consider the two possibilities: $d > d_l$ and $d < d_l$. Therefore, it does not make sense to use the exponent ν obtained to order ε, since we do not expect it to be correct for $d = 3$. On the contrary, using the scaling relations (supposed to be correct even for negative ν) we will express the exponents in the equation for $\xi(\widetilde{\tau})$ (6.11) via the exponent ν (generally the exponent η is also necessary, however it is zero in the one-loop approximation). Thus, we arrive at the equation

$$\left(\widetilde{\tau} + a\widetilde{\lambda}\int_{\xi^{-1}}^{\infty}\left(1+\widetilde{\lambda}q^{-\varepsilon}\right)^{-1+(4-1/\nu)/\varepsilon}\frac{q^{d-1}dq}{q^4}\right)^{-1} = \xi^4\left(1+\widetilde{\lambda}\xi^{\varepsilon}\right)^{-(4-1/\nu)/\varepsilon} \qquad (6.15)$$

Its solution $\xi(\widetilde{\tau})$ substituted into (6.12) gives $\widetilde{\lambda}_r(\widetilde{\tau})$ and thus we can obtain the shift of the LL $\Delta c_1(\widetilde{\tau})$ according to (6.13).

The results of numerical evaluation of $\Delta c_1(\widetilde{\tau})$ according to Equation (6.13-6.15) are plotted in Figure 6.1. We have considered two cases: $d > d_l$, $\nu = 1$ — solid line ($\widetilde{\lambda} = 1$, $a = 2$); $d < d_l$, $\nu = -1$ — two dashed curves ($\widetilde{\lambda} = 1$ for both curves; $a = 0.5, a = 2$).

If $d > d_l$ then for all values of parameters a and $\widetilde{\lambda}$ the LL has the qualitative form as the curve plotted in Figure 6.1: with decreasing temperature $\Delta c_1(\widetilde{\tau})$ initially increases (due to increase of ξ as explained above), then for large fluctuations decreases (due to decrease of the renormalized coupling constant λ_r) and the LL ends at a Lifshitz point. Note that the LP occurs at the negative temperatures $\widetilde{\tau}$ due to the finite shift of transition temperature discussed above.

For $d < d_l$ the situation is more complex. At large values of a ($a = 2$ curve of Figure 6.1) the LL goes to $\widetilde{\tau} \to -\infty$, so that no Lifshitz point exists (we may say it is shifted to $\widetilde{\tau} = -\infty$). As can be seen from Figure 6.1 in other respects the LL of this case is qualitatively the same as in the case $d > d_l$. At small values of a ($a = 0.5$ curve of Figure 6.1) two solutions of Equation (6.15) exist at large temperatures (the one corresponding to greater ξ is plotted with the dot curve in Figure 6.1) and no solution at small temperatures. Thus in this case the LL ends in a point at which the correlation length is finite, which indicates that this is a point of the phase transition of the first order. It is not clear however, whether

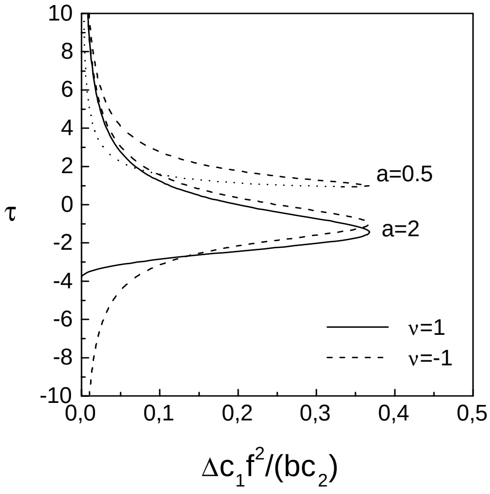

Figure 6.1: Reduced shift of the Lifshitz line $\Delta c_1 f^2/(bc_2)$ as a function of reduced temperature $\widetilde{\tau} = \tau/c_2$. (Here τ and c_2 are parameters of the Hamiltonian (5.1); b is a numerical constant defined in the text; and f is some numerical constant.) The figure illustrates two possible situations: $d > d_l$ ($\nu = 1$) — solid curve (fit parameter $a = 2$); $d < d_l$ ($\nu = -1$) — dash curves ($a = 2, a = 0.5$). For all curves $\widetilde{\lambda} = 1$.

this case represents physical features or is an artifact of approximations of the theory.

Comparing obtained results with the experimental data of Schwahn et al.[9, 10] we observe that the experimental LL has the same qualitative shape. We would like to stress that the present study predicts that the Lifshitz line approaches its mean-field counterpart for high and deep temperatures, the prediction which is also in agreement with experimental behavior of the Lifshitz line.[9, 10] However, on the basis of the current data of Refs. [9, 10] it is not clear which of three cases concerning the value of the lower critical dimension of the system which we have discussed above, actually takes place.

Summarizing, we have calculated the deviation of the LL from the mean-field behavior by taking into account the first fluctuational correction to the c_1 coefficient. The renormalized properties are calculated within the one-loop renormalization group. Our calculations are carried out in the immediate vicinity of the Lifshitz line, so that no crossover to either Ising or Brazovskii universality class is considered. The obtained behavior of the LL qualitatively agrees with that observed in the scattering experiments on ternary homopolymer/diblock-copolymer systems.

The approach we have presented here is based on the Landau-Ginzburg expansion of the free energy with phenomenological parameters λ, c_1, c_2. Of course, this fact restricts a complete quantitative comparison with experiment. However, we point out that despite this the agreement of the behavior of the computed Lifshitz line at high and low temperatures with experimental one is a strong support of the validity of our approach. The major reason for the uncertainty in the complete quantitative comparison with the experiment is due to unknown values of the critical exponents of the Lifshitz universality class. Depending on the value of the lower critical dimension in the renormalized theory the LP exists or it is shifted to infinitely small temperatures. More experiments are needed to determine which of the possibilities actually takes place, which would amount to experimental determination of the lower critical dimension of the system.

Part IV

Fluctuational effects in diblock melts: theoretical and experimental background

7. Fredrickson-Helfand-Brazovskii theory

In this section we will view the constituent elements of the application of the Brazovskii theory [26] to the case of fluctuations in diblock copolymer melt in the weak segregation regime conducted by Fredrickson and Helfand [27]. Special attention will be paid to the approximations used in these theories, since in the following we will try to remove them.

Fredrickson and Helfand considered a diblock copolymer melt under the usual theoretical assumptions: the diblock is monodisperse (and is thus characterized by the number of monomeric units in the diblock N , and the fraction of A monomers f, our work in the following will be concerned with the symmetric case $f = 1/2$), the melt is incompressible (so that can be described by a single order parameter: $\psi(r) = \rho_A(r)/\rho - f$), the values of statistical segments of the A and B monomeric units are the same and are identified with the volume of the monomers entering the Flory-Huggins lattice theory: $v = \rho^{-1} = a^3$. Under these conditions the expression for the coarse-grained Hamiltonian has been obtained by Ohta and Kawasaki [44] and Leibler [34]

$$\begin{aligned} H(\psi) &= \frac{1}{2}\int_q \gamma_2(q,-q)\psi(q)\psi(-q) + \frac{1}{3!}\int_{q_1,q_2} \gamma_3(q_1,q_2,-q_1-q_2)\psi(q_1)\psi(q_2)\psi(-q_1-q_2) + \\ &+ \frac{1}{4!}\int_{q_1}\int_{q_2}\int_{q_3} \gamma_4(q_1,q_2,q_3,-q_1-q_2-q_3)\psi(q_1)\psi(q_2)\psi(q_3)\psi(-q_1-q_2-q_3) \quad (7.1) \end{aligned}$$

As has been noticed already by Leibler [34] melts of diblock copolymers belong to the Brazovskii universality class. Therefore in order to proceed with the description of the fluctuational effects Fredrickson and Helfand simply reduce this Hamiltonian to the model Hamiltonian employed by Brazovskii. Accordingly, since the second vertex

$$\gamma_2(q,-q) = \left[F(x,f) - 2\chi N\right]/N \quad (7.2)$$

is known to have a minimum at q_* and in the vicinity of the spinodal (thus we restrict ourselves to this condition in the weak segregation theory) the peak of the correlation function is very pronounced we may expansion around it instead of the exact expression (7.2):

$$\gamma_2(q,-q) = \overline{\tau} + c^2(q-q_*)^2 \tag{7.3}$$

as it is indeed done in the Brazovskii theory. The next approximation concerns the wavevector dependence of the higher order vertices in (7.1). Generally speaking they depend on the values and orientations of all the vectors. Since in the following, however, due to further approximations only wavevectors equal to q_* will be of interest and the angle dependence is known to be rather small the vertices are taken at $q = q_*$ (for γ_3 there is the single configuration, while for γ_4, they the lamellar symmetry is assumed):

$$\begin{aligned} \gamma_3(q_1,q_2,-q_1-q_2) &\equiv \Gamma_3 & (7.4)\\ \gamma_4(q_1,q_2,q_3,-q_1-q_2-q_3) &\equiv \Gamma_4(0,0) & (7.5)\end{aligned}$$

With these two approximations Fredrickson and Helfand have reduced the coarse-grained Hamiltonian of diblock melt to exactly the Brazovskii one:

$$\begin{aligned} H(\psi) &= \frac{1}{2}\int_q \left[\tau + (q-q_*)^2\right]\psi(q)\psi(-q) + \frac{\mu}{3!}\int_{q_1}\int_{q_2}\psi(q_1)\psi(q_2)\psi(-q_1-q_2) + \\ &+ \frac{\lambda}{4!}\int_{q_1}\int_{q_2}\int_{q_3}\psi(q_1)\psi(q_2)\psi(q_3)\psi(-q_1-q_2-q_3) \qquad (7.6)\end{aligned}$$

As has been shown by Brazovskii in order to obtain the free energy it is necessary consider the equation of state:

$$h(q) = \frac{\delta H(\overline{\psi})}{\delta\overline{\psi}(-q)} \tag{7.7}$$

In the weak approximation regime the usual approximation for the order parameter is to limit consideration to the first harmonics

$$\overline{\psi}(x) = a_n \sum_{k=1}^{n}\left[\exp^{iQ_k x} + \exp^{-iQ_k x}\right] \tag{7.8}$$

with the value $|Q_k = q_*|$ while considering different symmetries with the emerging phases by proper choice of the sets $\{\pm Q_k\}$. This approximation was shown by Brazovskii to lead to the following equation of state:

$$h = ra_n - \theta_n a_n + \eta_n a_n^3 \tag{7.9}$$

and renormalized inverse susceptibility r

$$r = \tau + \frac{d\lambda}{(rN)^{1/2}} + n\lambda a_n^3 \tag{7.10}$$

where we have introduced $d = 3x_*/2\pi$, with the reduced critical wavevector $x_* = q_*^2 N/6$. The coefficient θ_na nd η_n in (7.9) incorporate dependence on μ and λ, respectively, as well as symmetric coefficients. In the process of calculating the inverse susceptibility (7.10) however a very important approximation is made. Indeed the one-loop correction is calculated in the following way

$$\begin{aligned}\frac{\lambda}{2}\int_q \frac{1}{r/N + (q-q_*)^2} &= \frac{\lambda}{4\pi^2}\int_0^\infty \frac{q^2 dq}{r/N + (q-q_*)^2} = \\ &= \frac{\lambda}{4\pi^2} q_*^2 \int_{-\infty}^{\infty} \frac{dq}{r/N + q^2} = \frac{\lambda}{4\pi^2} q_*^2 \frac{\pi}{r^{1/2}} N^{1/2} = \frac{d\lambda}{(rN)^{1/2}}\end{aligned} \tag{7.11}$$

As we can see we some approximation had to be made since the original exact integral diverges at $q \to \infty$. The argument for this "Brazovskii way" of calculating the integral is obviously that we are interested only in the critical fluctuations as only they depend on temperature.. The value of the integral at high q is not influenced by τ, is physically connected with properties of the system at microscopic scales which cannot be described by a coarse-grained theory, and thus amounts to an unimportant (and experimentally irrelevant) renormalization of the transition temperature.

Having obtained the equation of state we can obtain the thermodynamic potential using the following identity:

$$\frac{\partial H[\overline{\psi}]}{\partial a_n} = \int_q \frac{\partial H[\overline{\psi}]}{\partial \overline{\psi}(q)} \frac{\partial \overline{\psi}(q)}{\partial a_n} = 2nh \tag{7.12}$$

Within the Brazovskii approach the difference of the free energies of ordered and disordered states (ie $a_n \neq 0$ and $a_n = 0$) can be calculated exactly:

$$\begin{aligned}H[\overline{\psi}] &= \int_0^{a_n} da_n\, 2nh = \\ &= 2n \int_0^{a_n} da\, ra - \frac{2}{3} n\theta_n a_n^3 + \frac{1}{2} n\eta_n a_n^4 \\ &= \frac{1}{2\lambda}(r^2 - r_0^2) + \frac{d}{N^{1/2}}(r^{1/2} - r_0^{1/2}) - \frac{2}{3} n\theta_n a_n^3 + \frac{1}{2} n\eta_n a_n^4\end{aligned} \tag{7.13}$$

It is made possible by the availability of an algebraic equation (7.10) connecting r and a_n. This expression as well as equations (7.9) and (7.10) constitute the closed system of equation of the Brazovskii theory used by Fredrickson Helfand for determination of the phase diagram of a diblock melt. Their mains results are 1). fluctuations leads to a decrease of the transition temperature; 2). the phase diagram changes the topology as compared with the mean-field Leibler diagram. Direct transitions from the disordered to hexagonal and lamellar (even for $f \neq 1/2$) phases are possible.

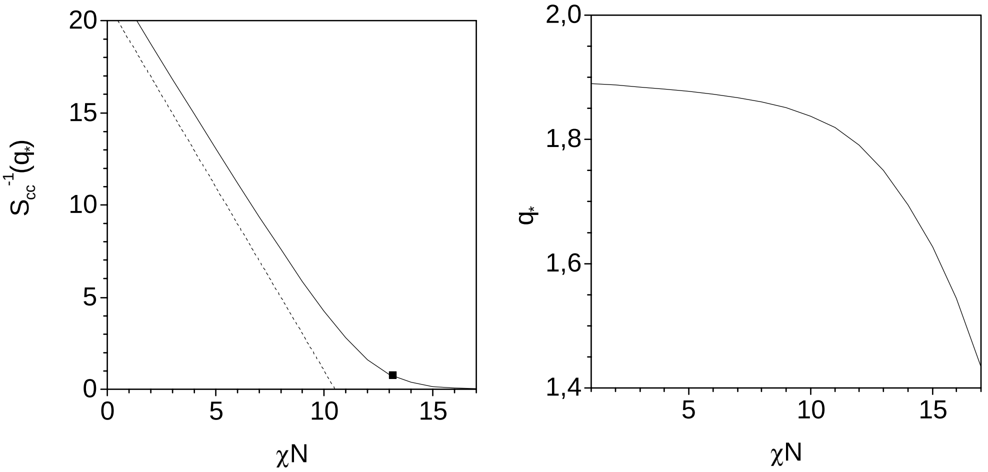

Figure 8.1: **(a)** Inverse susceptibility for a blend of symmetric copolymer with $\overline{N} = 1000$. Dashed line is the Leibler's mean-field line Dot is the transition point to the lamellar phase. **(b)** Peak position of the scattering profile as a function of χN.

Taking an overview of all approximations involved we see that the Fredrickson-Helfand-Bravoskii description is a one-loop self-consistent (Hartree) theory in which the second vertex is approximated at the minimum by eq. (7.3), wavevector dependence of the third and fourth vertices is not taken into account (eqs. (7.4)and (7.5)), and the one-loop integral is calculated by means of a special approximation (7.11) neglecting all fluctuations except the critical ones.

8. Barrat-Fredrickson theory

8.1. Disordered phase

Further refinement of the fluctuational theory was motivated by experiments [45] and computer simulations [46] studying the behaviour of the critical wavevector in the vicinity of the transition point. It was found that q_* deviates from the Leibler values and in particular has other scaling behaviour as a function of N. The mean- field prediction is $q_* \sim N^{-1/2}$, while the exponent found experimentally was considerably larger. In order bring these peculiarities into theoretical description Barrat and Fredrickson [28] considered wavevector dependence of the vertices. That means that in comparison with the FH theory they did not make approximations (7.4) and (7.5) for the vertices, rather considered the original Hamiltonian 7.1 with full vertices. We will follow their work and consider the case of symmetric blend ($f = 1/2$) for which the third vertex is zero and the ordered phase has the lamellar symmetry.

The Brazovksii approach can easily be generalized for the case of wavevector dependent vertex. In the disordered phase the most important property is the concentration-concentration correlating function, which is proportional to the experimentally measurable scattering intensity. In the one-loop self consistent approach the correlator is given by the following Dyson equation

$$S_{cc}^{-1}(q) = \Gamma_2(q) + \frac{1}{2}\int_p \gamma_4(q,p) S_{cc}(p) \tag{8.1}$$

where $\gamma_4(q,p)$ is the spatially averaged vertex:

$$\gamma_4(q,p) \equiv \int_{\mathsf{n}} d\mathbf{n}\ \gamma_4(\mathbf{q}, -\mathbf{q}, p\mathbf{n}, -p\mathbf{n}) \tag{8.2}$$

here $\mathbf{n}$ is a unitary vector and integration is conducted over all orientations of $\mathbf{n}$. Let us emphasize that introduction of $\gamma_4(q,p)$ (instead of taking $\gamma_4(q_*,q_*)$) is the only enhancement of the BF theory, all other approximations are identical with the previous FH one. Accordingly, in order to obtain the fluctuationally renormalised correlator $S_{cc}(p)$ BF use the expansion about the minimum

$$S_{cc}(q) = r + \alpha(q - q_*)^2 \tag{8.3}$$

thus parameterizing the curve. This expression is then substituted into (8.1); with the use of the Brazovskii way the integral in it can be calculated and finally demanding that the right and the left sides of eq. (8.1) coincide in the vicinity of q_* Barrat and Fredrickson obtain three algebraic equations for the three parameters r, α, and q_*.

Results of the solution of these equations are presented in Figure 8.1 (see Figs 2 and 3 of Ref. [28], our results are slightly numerically different from them however; for an unknown reason). In plot (a) we present the dependence of r as a function of χN (the Leibler result is also given for reference). In comparison with the FH theory we observe no qualitative changes; the only difference is a slight shift of the curve to the left of the corresponding FH curve. The qualitative change comes however in the plot (b) of the Figure which illustrates the behaviour of the position of the maximum of the scattering curve with changing χN. Whereas in the FH theory, simply by its construction, the position of the maximum coincides with the Leibler mean-field value $q_* = 1.945$, inclusion of the vertex wavevector dependence leads to considerable decrease of q with increasing χN. An interesting feature of both plots of Figure 8.1 is that r and q_* do not tend to their mean-field values even for $\chi N = 0$. Barrat and Fredrickson claim this to be due to "correlation hole" effect, however as we will show below it is an artifact of the Brazovskii way of integration.

8.2. Transition point

Since we consider a symmetric system the ordered phase can only be a lamellar one. As is conventional in the theories of weak segregation [34, 27] (that is when the system is in a state not far from the critical point) the concentration profile in the ordered phase is assumed to be well-approximated by a single harmonic:

$$\psi(\mathbf{r}) = 2A\cos(\mathbf{q}_l\,\mathbf{r}) \tag{8.4}$$

where q_l is the wavevector of the lamellar structure, which may be in general different from the position of the maximum of the scattering function q_*. Since we used representation (8.4) the free energy is now a function of two parameters A and q_l. Consideration of the derivative of the free energy within the one-loop approximation [26, 47] leads to the following equation of state:

$$\frac{df_m}{d(A^2)} = \Delta(q_l, A) - \frac{1}{2}A^2\gamma_4(q_l, q_l) \tag{8.5}$$

where the inverse susceptibility $\Delta(q, A)$ is determined by the analog of the equation (8.1) for the case of ordered state:

$$\Delta(q, A) = \Gamma_2(q) + A^2\gamma_4(q, q_l) + \frac{c}{2}\int_p \gamma_4(q, p)\Delta^{-1}(p, A) \tag{8.6}$$

Note that $\Delta(q, A = 0) = S_{cc}^{-1}(q)$. (Here, following Barrat and Fredrickson [28] we neglected the angle dependence of the fourth vertex in the second term and replaced it by the orientationally averaged $\gamma_4(q, q_l)$.) Now using equations (8.5) and (8.6) we can obtain coefficients of the expansion of the free anergy in orders of the amplitude of the lamellar phase

$$f_m(A) = \tau(q_l)A^2 + \frac{u(q_l)}{4}A^4 + \frac{w(q_l)}{36}A^6 \tag{8.7}$$

Let us for example show how the calculation of the second coefficient

$$u(q_l) = 2\left.\frac{d^2 f_m(A)}{d(A^2)^2}\right|_{A=0} \tag{8.8}$$

is conducted. Straightforwardly, we obtain from (8.5) the derivative of the free energy

$$\left.\frac{d^2 f_m}{d(A^2)^2}\right|_{A=0} = \Delta'_{A^2}(q_l, A = 0) - \frac{1}{2}\gamma_4(q_l, q_l) \tag{8.9}$$

Now we need the derivative of the susceptibility, which is also straightforwardly obtained from (8.6):

$$\Delta'_{A^2}(q, A=0) = \gamma_4(q, q_l) - \frac{c}{2}\int_p \gamma_4(q_l, p)\Delta^{-2}(p, A=0)\Delta'_{A^2}(p, A=0) \tag{8.10}$$

The equation should be evaluated at $A = 0$, so we use $\Delta(q, A = 0) = S_{cc}^{-1}(q)$ and as in the use preceding section use for $S_{cc}^{-1}(q)$ the approximation (8.3). Again (as indeed throughout all the previous approaches) the evaluation of the integral is carried out by means of the "Brazovskii way of integration":

$$\begin{aligned}
\frac{c}{2}\int_p \gamma_4(q, p)\Delta^{-2}(p, A &= 0)\Delta'(p, A=0) = \frac{c}{2}\gamma_4(q, q_*)\Delta'(q_*, A)\frac{q_*^2}{2\pi^2}\int_{-\infty}^{+\infty}\frac{dp}{(r+\alpha p^2)} = \\
&= \frac{c}{2}\gamma_4(q, q_*)\Delta'(q_*, A=0)\frac{q_*^2}{2\pi^2}\frac{\pi}{2r(r\alpha)^{1/2}} = \qquad (8.11)\\
&= B\gamma_4(q, q_*)\Delta'(q_*, A=0)
\end{aligned}$$

$$B = \frac{6^{1/2}3q_*^2}{4\pi r(r\alpha N)^{1/2}}\frac{v}{a^3} \tag{8.12}$$

This result substituted into the equation (8.10) taken at $q = q_*$ allows us first to obtain $\Delta'_{A^2}(q_*, A = 0)$ and thus obtain the value of the integral; then we take the equation at $q = q_l$ and obtain the expression for $\left.\frac{d^2 f_{\mathrm{m}}}{d(A^2)^2}\right|_{A=0}$ and thus the coefficient $u(q_l)$. Thus we obtain the following values of the coefficients

$$\tau(q_l) = r + \alpha(q_l - q_*)^2 \tag{8.13}$$

$$u(q_l) = \frac{\gamma_4(q_l, q_l) + B\gamma_4(q_l, q_l)B\gamma_4(q_*, q_*) - B\gamma_4(q_l, q_*)^2}{1 + B\gamma_4(q_*, q_*)} \tag{8.14}$$

$$w(q_l) = \frac{9B}{r}\left[\frac{\gamma_4(q_l, q_*)}{1 + B\gamma_4(q_*, q_*)}\right]^3 \tag{8.15}$$

(Note that the expression for B given in the paper of Barrat and Fredrickson [28] contains a misprint). By considering the free energy expansion (8.7) it is clear that the first ordered transition to the lamellar phase takes place when the following two conditions are met

$$u(q_l) < 0 \tag{8.16}$$

$$u^2(q_l) = \frac{16}{9}\tau(q_l)w(q_l) \tag{8.17}$$

Note that the value of q_l is generally not the same as q_* and it should be independently determined from minimisation of the free energy (8.7). However, calculations show that q_l is in fact very close to q_* [28]. This in fact could be expected since the transition to the lamellar phase is known [26, 27] of only weak first order character, ie the properties of the system do not experience considerable changes upon the transition.

In Figure 8.1 the transition point is indicated by a dot. As we can see the transition takes place at smaller value of χN than that predicted by the Fredrickson-Helfand theory (but of course larger than the mean-field Leibler value), which is consistent with the shift of the whole curve in the Figure to smaller χN values. For small enough degrees of polymerisation ($\overline{N} \sim 10^4$) the transition point was found [28] to lie about halfway between the FH and Leibler values (see Figure 4 of Ref. [28]); for larger $\overline{N}$ the values lie closer to FH, both however tend to the mean-field result.

Summarizing the BF theory, we have seen that introduction of wavevector dependence (or rather removing this approximation from the Hartree approach) enables one to obtain new features in the behaviour of q_* (all other changes to the FH theory being qualitative and rather small). The two remaining approximations are representation (8.3) of the correlator (which is rather harmless) and (more importantly) the Brazovskii way of integration. We will demonstrate below that by retaining this feature the wavevector dependence of γ_4 has not been completely taken into account.

9. New experimental findings

In this section we draw attention to two recent experimental papers that put into question the currently accepted theories of melts of diblock copolymer. They were a motivation for our developing the new framework presented in the next part of the dissertation.

The focus of the first work [35] was on investigating the Lifshitz properties in the ternary A/B/A-B melts of two homopolymers and a diblock copolymer. The system was taken to be fully symmetric. Polyethylene (PE) and polyethylene-propylene (PEP) homopolymers with $N_{PE} = 392$ and $N_{PEP} = 409$ and a PE-PEP diblock copolymer with $N_{PE-PEP} = 1925$ were used. The phase diagram of the ternary system was constructed by measuring the transition points for a number of melts with different content of homopolymer fraction, thus the whole range between a pure homopolymer blend and a pure melt of diblock has been scanned. For system with high content of diblock rheological measurements were used for determining the transition point, while for system with high content of homopolymers the Small Angle Neutron Scattering data were used. The obtained results were then compared with the theoretical prediction for the critical line in the whole range of homopolymer concentration.. Results of such a comparison are presented in Figure 2 of Ref. [35]. The theoretical prediction here is obtained within the RPA method as we discussed above. In order to match the theoretical line to experimental phase diagram a dependence $\chi(T)$ is needed. Such a dependence was determined for the corresponding symmetric homopolymer blend using SANS data. The results of a comparison of the RPA result and experimental points in Figure 2 are quite remarkable in that the experimental points lie above (in terms of temperature) the RPA prediction for diblock-like systems. This contradicts the prediction of FH and BF theories that fluctuations should stabilize the disordered phase thus that experimental points should lie in any case below the RPA one. In this connection the authors cautiously note that "the absolute deviation in T_{ODT} between theory and experiment may reflect quantitative failure of the former, although the disparity is barely outside the experimental errors associated with N_{A-B} and N".

However apparently this discrepancy was the motivation behind a comparative study of functions $\chi(T)$ obtained from blends of homopolymers and melts of symmetric copolymers [33]. As the authors note themselves quite remarkably this study is in fact the first of its kind. Previous investigation have focused either on the properties of homopolymers or diblocks, avoiding direct comparison between them. The study again uses PE and PEP polymers. The first step was to obtain $\chi^{mf}_{PE/PEP}(T)$ from the blend of homopolymers by using SANS curves obtained in the disordered state for different temperatures and analysing these data within the RPA theory. The $\chi^{mf}_{PE/PEP}(T)$ obtained in this way was found to be independent of the polymer concentration and linear in T^{-1}. When used to calculate the spinodal and binodal curves of the melt within the Flory-Huggins theory it led to the results consistent with those found experimentally (divergence of susceptibility in SANS). Therefore the Flory-Huggins theory is concluded to be adequate for description of homopolymers.

For interpretation of results obtained from diblock four methods are used. Two of them are based on fitting the experimentally obtained $I^{-1}(q_*)$ against T^{-1} curves with the RPA (taken far from the transition point) or the FH predictions. Functions obtained in this way are denoted as $\chi^{mf}_{PE-PEP}(T)$ and $\chi^{bare}_{PE-PEP}(T)$, respectively. The other two methods are based on measuring transition temperatures for diblocks with different N's and then using the Leibler and FH expressions to obtain:

$$\chi^{ODT,mf}_{PE-PEP}N = 10.495 \tag{9.1}$$

$$\chi^{ODT,fluc}_{PE-PEP}N = 10.495 + 41.0\,\overline{N}^{-1/3} \tag{9.2}$$

All four expressions for diblock χ_{PE-PEP} as well the homopolymer $\chi^{mf}_{PE/PEP}(T)$ are plotted in Figure 8 of Ref. [33]. As the authors correctly note it is reasonable to believe that the homopolymer data present the basis (are closest to the definition of χ) against which results for the diblock should be viewed.

First of all we observe that none of the four diblock dependences actually satisfactorily reproduce the homopolymer results. Another important conclusion is that determination by means of matching the scattering curve gives considerably different results as that by means of changing N: the two sets have different slopes. The better slope have date obtained by changing N's. Probably the most important conclusion though is that for both of these sets results obtained within the RPA lie closer to the homopolymer data (which we suppose to be "true" χ) than those obtained within the FH theory, in complete contrast to expectations. The authors conclude that "a common $\chi(T)$ cannot account for both homopolymer blend and a block copolymer phase behavior based on current theory". In the next section we show that a modification of the existent diblock theory is indeed required.

Part V

Revised theory of fluctuational effects in melts of monodisperse diblock copolymer

10. Preliminary remarks

As is clear from the discussion of the experimental literature there indeed exist a number of indications that the predictions of the original Fredrickson-Helfand theory [27] as well as its modification carried out by Barrat and Fredrickson [28] are in stark disagreement with the experimental results when the χ-parameter used for comparison of the experiment and the theory is determined in an independent way. Indeed, according to the considered experiments the transition temperature lies above the mean-field value of Leibler [34], whereas the both theories predict that the temperature should lower as a result of the presence of fluctuations. These circumstances alone already justify an attempt to improve on the existing theories of the fluctuational effects in the melts of the diblock copolymer. On the other hand, from the theoretical point of view the extension of the previous work, which would eliminate the last approximation of the one-loop self-consistent treatment, is simply straightforward, consisting in full treatment of the p and q-dependence of the fourth vertex $\gamma(q,p)$ appearing in the one-loop integral:

$$S^{-1}(q) = \Gamma_2(q) + \frac{1}{2}\int_p \gamma_4(q,p)\Gamma_2^{-1}(p) \tag{10.1}$$

that is eliminating the approximation of the Brazovskii way of calculating the one-loop integral. In a way the proposed extension may be considered as the next step in the direction taken by Barrat and Fredrickson which improved on the original Fredrickson-Helfand theory by taking into account the q-dependence of the integral. However such a view proves to be more formal than substantial, since as was discussed above taking into account only the q-dependence brought only slight quantitative changes while taking into account of the full dependence will be seen to bring qualitatively new features in the theory. In order to understand their origin let us consider the behaviour of the of the vertex $\gamma_4(q,p)$ as the function of p and q (the function is of course symmetric with respect to their transposition) as well as the plots of the integrand of the Dyson equation (10.1), ie $p^2\gamma_4(q,p)\Gamma_2^{-1}(p)$ for different values of the external impulse q. The behaviour of the vertex $\gamma(p,q)$ is clear from the Figure 10.1. As expected, the vertex diverges

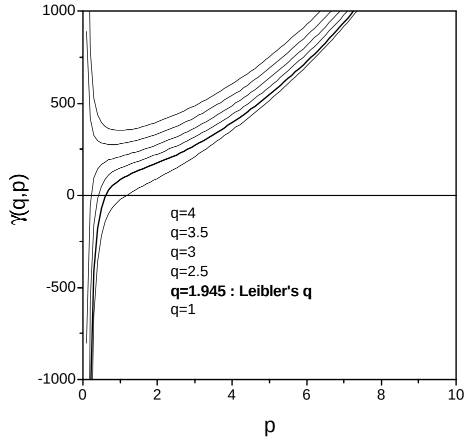

Figure 10.1: The behaviour of the fourth vertex $\gamma_4(p, q)$.

at both small and large impulses: the divergence at small ones being due to the effect of connectivity of blocks in a diblock, while divergence at large ones is a feature of the Gaussian chain. Interestingly, two possible types of the curves are possible: at sufficiently large q the curve tends to $+\infty$ as $p \to 0$, while for smaller q it tends to $-\infty$. This is the situation relevant for our consequent consideration as the Leibler's $q_* = 1.945$ (and considerable vicinity thereof) belongs to this case. (For $q = q_*$ the vertex changes sign at $p \approx 0.63$.) The other important feature of $\gamma(p, q)$ is that it diverges as p^2 for any q. Indeed, as follows from the expression for the Lifshitz entropy of the Gaussian chain [48, 49], $\gamma(p, q)$ has the following asymptotic behaviour [50]: $\gamma(p, q) \sim p^2 + q^2$. Such a behaviour has strong effect on the integral of the one-loop correction as is clear from the Figure 10.2. We see that even for $\chi N = 10$, which is relatively close to the Leibler's mean-field critical point ($\chi N = 10.45$), the "Brazovskii peak" does not dominate the curve, so that calculating the integral in the Brazovskii way seems to be hardly justifiable. Note, that in the Figure we plot $\Gamma^{-1}(q)$, ie, the RPA correlator, which means that for the actual fluctuationally renormalized correlator the picture is even more drastic (as the fluctuations are known to increase the stability of the disordered phase).

The difference between the full integrand of the one-loop correction (10.1) and the integrand used in the Brazovskii way is further illustrated in Figure 10.3(a) where we plot both of them (for the same value of $\chi N = 10$). Under the Brazovskii- way curve we understand the following function: $q_*^2 \gamma(q_*, q_*)/(\tau + \alpha(p - q_*)^2)$, with the necessary parameters found from $\Gamma(q)$ (note again that this is the RPA value). We would like to note three points in connection with the

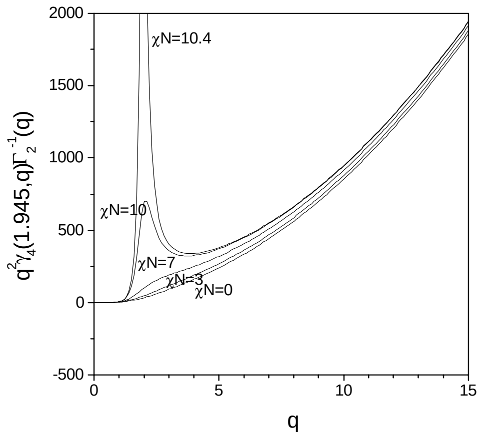

Figure 10.2: The integrand of the one-loop fluctuational correction. Note that here the correlator $\Gamma^{-1}(q)$ is the RPA one.

Figures 10.3 (a) and (b):

— 1. Brazovskii way overestimates input of the contributions at momenta smaller than the peak as it neglects the strong decrease of the vertex at these values. However, this overestimation seems to be rather small, so that it seems to lead only to small quantitative correction to the previous theories. Furthermore, the plots suggest that this overestimation at small q may be compensated by the underestimation visible at $q > q_*$ so that they practically cancel each other. On the other hand the Figure 10.3(b) suggests the effect of fluctuations at smaller than q_* momenta may be to decrease the value of the correction. We will discuss this point further in the section devoted to comparing the fluctuational corrections of homopolymers and diblocks.

However, the $q > q_*$ region of the plots, where the full integrand diverges as $\sim q^2$, but the Brazovskii expression (simply by its construction) converges as $\sim q^{-2}$ poses more fundamental questions, viz. what is the meaning of the fluctuational correction here, ie whether we should distinguish between different types of the corrections when we take the full integral. A remarkable feature of the Brazovskii way (employed in both Fredrickson-Helfand and Barrat-Fredrickson theories) is that it accounts for the critical fluctuations only, so that the whole one-loop correction is considered as a fluctuational correction due to critical (relatively large-scale) fluctuations. Thus by construction we have only one χ which is the same for the RPA and fluctuational treatment. As we can se from the plots of Figure 10.3 in the full calculation of the integral the situation is more complicated. It is intuitively clear that we have two types of fluctuations: relatively large scale

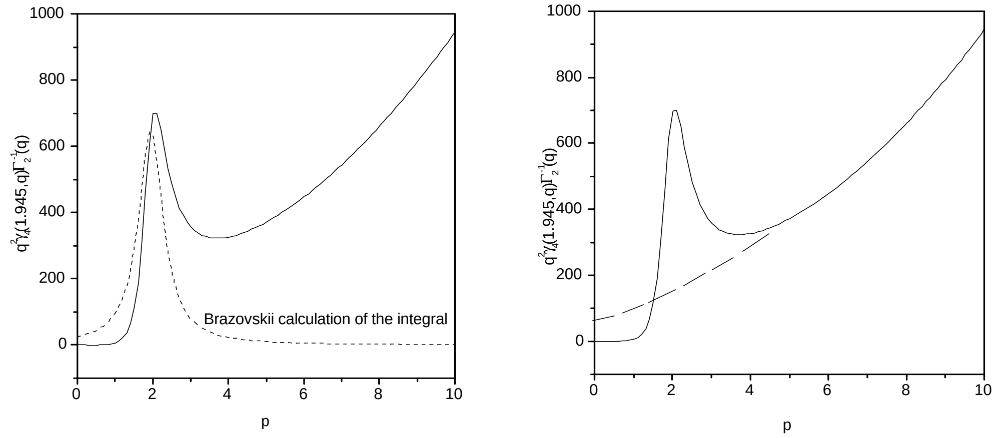

Figure 10.3: **(a)** Brazovskii (dashed curve) and full integrands of the one-loop correction. **(b)** Illustration of the idea that the fluctuations at small q give negative input into the integral.

"correlation-hole" fluctuations leading to the appearance of the peak in the curve; and small-scale (microscopic) fluctuations manifesting itself as the divergence of the integral, which correspond to the renormalization of the properties of the chain on microscopic scales and which thus should results in some renormalization of χ. The broad features which this distinguishing brings to the comparison of the Brazovskii and full treatment can be formulated thus (two further points):

— 2. If we naively draw an imaginative line (Figure 10.3(b)) serving to delineate the fluctuational contributions to the renormalization of χ (below the dash line) and regular "correlational-hole" fluctuations, then we can see that the Brazovskii way (in which all fluctuations are "correlation-hole") seriously overestimates the value of these "correlation-hole" fluctuations. Note, however, that this observation alone can lead only to quantitative corrections to the previous theories, and, of course, it cannot change the sign of the correction as seems to be suggested by the experiments.

— 3. If we want to treat the integral completely we are forced to consider the large q area of the integral and thus renormalization of χ. As we will see when trivial renormalization of χ is taken care of, the non-trivial fluctuational corrections are different for homopolymer and diblock. Indeed relating corrections for a homopolymer blend and a diblock copolymer melt obtained within the one-loop (self-consistent) theory is one of the main topics of this work.

So far we have presented the reasons justifying the attempt to consider the full integral. Now we outline the ideas how we tried (and in most cases failed) to carry out this consideration. The immediate problem is this: the one-loop integral is diverging, so that we should contrive a means of calculating it. Four ways will be discussed in detail in the following sections:

—1. *Referent system.* Departing from the idea of extracting microscopic and macroscopic fluctuational corrections we try to find a referent system for which the microscopic input would be the same as for the considered system of diblock. If such a system was found this would let us subtract the input the one-loop of the referent system from the one-loop correction for he diblock and thus treat the converging remaining part as purely due to "correlation hole" (however the whole treatment would be referent-system dependent, of course). This way, apart from being physically lucid, would provide the possibility of direct experimental check of the theory. Motivated by experiments we look at the blends of symmetric homopolymers in the next section. However, no suitable referent system was found, the findings nevertheless being instructive.

—2. *Substraction of the asymptotics.* We can calculate the asymptotic behaviour of the integral (analytically or numerically) and then subtract the necessary terms making the integral convergent. The asymptotic terms are then calculated by means of introducing a cutoff at a microscopic scale. This method is discussed in Section 12. Its flaw lies in the fact that such calculation cannot be employed in the self-consistent solution of the Dyson equation, as the self-consistisation procedure couples large and small momenta and this method is suitable only for small external momenta of the integral where the asymptotics make sense. The failure of the method indeed can be traced to the fact that we supply no physical way to distinguish (even approximately) microscopic and macroscopic contributions to the integral.

— 3. *Quadratic cutoff.* In this way we introduce a quadratic cutoff for the vertex function

$$\gamma_{cut}(q,p) = \begin{cases} \gamma(q,p), \text{ for } q,p < \Lambda \\ 0, \text{ for } q,p > \Lambda \end{cases} \tag{10.2}$$

and simply solve the integral equation (10.1) for $S(q)$. The results are presented in Section 12. We encounter here no problems in the solution, but instead (as we provide here no idea of separating the two fluctuational contributions) face problems of the interpretation of the obtained results, in particular relating the bare χ_{bare} used in this calculation with the experimentally measurable χ, for example that measured for a homopolymer blend.

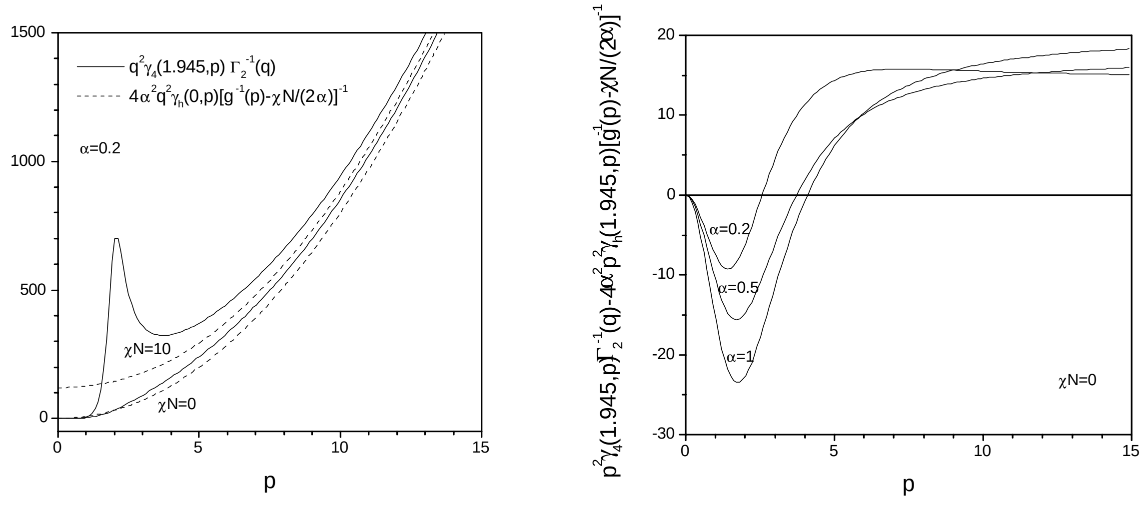

Figure 11.1: **(a)** Integrands of the one-loop corrections for the diblock (solid line) and the homopolymer (dash line). **(b)** Difference of these integrands for different lengths of the homopolymer.

11. Large$-p$ behaviour of the one-loop integrands

11.1. Direct comparison of diblock and homopolymer

As was mentioned in the previous section the easiest and most physically desirable way of getting rid of the divergence of the one-loop correction (10.1) is to find a suitable reference system, which would have the same high-q behaviour as the diblock system. The natural selection for such a reference system is a symmetric blend of homopolymers of equal length ($\phi_A = \phi_B$, $N_A = N_B$) as this system on the one hand is the simplest from the theoretical point of view and on the other hand has been the focus of recent experimental efforts [33]. We will take the diblock length as the reference length and express homopolymer's length through it: $N_A = \alpha N$, as well as reduce momenta by it for both systems, so that we have the same variables.

So we have the following Dyson equations for the two systems. For the diblock system:

$$
\begin{aligned}
S^{-1}(q) &= \Gamma_2(p) + \frac{1}{2}\frac{6^{3/2}}{N^{1/2}}\frac{v}{a^3}\int_p \gamma_4(q,p)\Gamma_2^{-1}(p) \qquad (11.1)\\
\Gamma_2(p) &= F(p) - 2\chi N \qquad (11.2)
\end{aligned}
$$

Here v is the volume of the monomeric unit (volume of the cell in the Flory lattice theory) and a is the statistical segment length of the diblock copolymer. The prefactor $6^{3/2}/N^{1/2}$ is the consequence of reducing the momenta by the radius of gyration of the diblock:$q \equiv \tilde{q}aN^{1/2}/6^{1/2}$. The whole expression is understood to have been already multiplied by N as is in particular clear the expression for $\Gamma_2(p)$ and the prefactor of the fluctuational correction. Analytical expressions for functions $F(p)$ (which is of course the conventional Leibler [34] function) and $\gamma_4(q,p)$ can be found in Appendix B.

For the homopolymer system analogously (the equation already multiplied by N and the wavevector reduced also by R_g of the diblock):

$$\begin{aligned} S_h^{-1}(q) &= \Gamma_h(p) + \frac{1}{2}\frac{6^{3/2}}{N^{1/2}}\frac{v}{a^3}\int_p 4\alpha^2\gamma_h(q,p)\left(g^{-1}(x_p,\alpha) - \frac{\chi N/\alpha}{2}\right)^{-1} && (11.3) \\ \Gamma_h(p) &= 4\alpha g^{-1}(x_p,\alpha) - 2\chi N && (11.4) \end{aligned}$$

Analytical expressions for calculation of $\gamma_h(q,p)$ are found in Appendices A and B. Note that the prefactor v/a^3 is the same provided we consider diblock and homopolymer synthesized from chemically the same monomers.

In Figure 11.1(a) we plot the integrands (up to unimportant numerical coefficients, which is however the same for the two systems) of the one-loop fluctuational corrections for the systems of diblocks and homopolymers. Note that the fluctuational corrections depend on the external momentum q, so that we have to make a choice of their values. We choose the critical momenta for the relative systems (which also represent experimentally relevant values), ie for homopolymers we take $q = 0$, while for diblock it is the Leibler's $q_* = 1.945$. Two important points in connection with the plot are worth mentioning.

Firstly, we observe that the large-p behaviour of the integrands is different, so that the homopolymer (at least of this length, ie α) cannot be taken as the referent system, ie the difference of the two corrections will still be a divergent integral. This means that we cannot consider the renormalization (by which we mean fluctuational corrections resulting from large-q (ie microscopic) fluctuations) of the parameter χ to be the same for homopolymers and diblocks and thus irrelevant for experiments (as is usually done in the current theoretical literature where the large-p corrections are simply neglected on the strength of similar arguments), rather that the renormalization is different and should be somehow taken into account. The fact that despite the polymers being chemically the same (ie the ratio v/a^3 is the same), the renormalization is still different, unequivocally indicates that it is architecture (structure) dependent. The other way to view it is to attribute the difference to the end-effects and/or the effects of junction points in the case of diblock copolymer.

Secondly, let's consider the $p < p_*$ region of the plot. By comparing the curves for $\chi N = 10$ we see that the effect of fluctuations of diblock at $p \leq 1.5$ is to decrease the fluctuation correction relative to the correction of the homopolymer. Therefore if we somehow succeed in establishing a referent system based on a homopolymer one than the fluctuational input of the diblock-specific fluctuations measured relative to the referent system (let's say a line similar to the homopolymer one, but lying a little higher so that it has the same large-p asymptotic as the diblock curve) seems to consist of two parts. One is the usually considered critical input of momenta around q_* and it is positive. The other is due to smaller p's (in our picture $p \leq 1.5$) and it is negative. Numerically the two inputs seem to be of comparable values (the more so, when we take into account that we have to make the Dyson equation self-consistent, which will further decrease the height of the peak). The interplay of the two inputs may result in a negative sign of the overall effect. This would provide explanation for the experimental findings discussed in the previous part.

The unsuitability of the homopolymer for the role of a referent system for the diblocks is further illustrated in Figure 11.1(b). Here we plot the difference of the integrands for the same external $q = q_*$; and present curves for different α's. Again we clearly see that the asymptotics of the diblock and homopolymer integrands are different. Interestingly, despite the fact that $\alpha = 1/2$ represents "a system of broken blocks" (all the blocks have been disconnected) and $\alpha = 1$ may also be expected to be a special referent system ($\alpha = 1$ represents a singular point for the ternary systems of diblock/homopolymers [38]) here these values are obviously not special. Indeed the behaviour for all values of α is qualitatively the same. Again we observe that for relatively small p the difference of the integrands is negative: relative to homopolymer fluctuations specific for diblock lead to negative contributions.

11.2. Homopolymers

In this subsection we will consider the large-p behaviour of the homopolymer system which was used as a would-be reference system in preceding subsection, ie the symmetric blend of homopolymer chains of equal lengths $N_A = N_B = \alpha N$. We will focus our attention on the diverging terms of the one-loop integral and will clarify their origin. Particularly simple results are obtained for the important case of external momentum $q = 0$. Note this special case is the most important one also from the experimental point of view since $q = 0$ is the critical wavevector for the blend of homopolymers. Therefore determination of χ from the measurements of the transition temperature (as it was done e.g. in [33]) also in effect relies on measuring the value of the correlation function (scattering intensity) at $q = 0$.

11.2.1. External momentum $q = 0$

In this case as is shown in the Appendix A the one-loop correction takes the following form

$$\frac{c}{2}\int_p 8\, g^{-1}(x_p,\alpha)\left(g^{-1}(x_p,\alpha)-\frac{\chi N}{2\alpha}\right)^{-1} \equiv \frac{c}{2}\int_p I_h(q=0,p) \tag{11.5}$$

where $g(x,\alpha)$ is the conventional Debye function and we introduced a notation for the prefactor of the integral connected with the reduction of the variables: $c = \frac{v}{a^3}\frac{6^{3/2}}{N^{3/2}}$ and introduced notation $I_h(q=0,p)$. We can immediately extract diverging terms of the integral by taking the series (although it does not strictly speaking exist because of the exp functions) at $p \to \infty$

$$I_h(q=0,p) = 8 + 8\frac{\chi N}{p^2} + O(p^{-4}) \tag{11.6}$$

Using this result we can extract the infinite terms from the integral and attribute them to the renormalization of χ. If we write the Dyson equation for the homopolymer

$$\begin{aligned} S_h^{-1}(0) &= \Gamma_2^h(0) + \frac{1}{2}\frac{v}{a^3}\int_{\widetilde{p}} \Gamma_4^h(q,-q,p,-p)\left[\Gamma_2^h(p)\right]^{-1} && (11.7)\\ S_h^{-1}(0) &= \left(2S_A^{-1}(0) - 2\widetilde{\chi}\right) + \frac{c}{2}\int_p I_h(q=0,p) && (11.8)\end{aligned}$$

then we can obtain a converging integral, while the two diverging integrals incorporating into the definition of the renormalized χ-parameter χ introduced instead of the bare parameter $\widetilde{\chi}$:

$$\begin{aligned} S_h^{-1}(0) &= 2S_A^{-1}(0) - 2\chi + \frac{c}{2}\int_p \left\{ I_h(q=0,p) - 8 - 8\frac{\chi N}{p^2}\right\} && (11.9)\\ 2\chi &= 2\widetilde{\chi} - \frac{c}{2}\int_p 8 - \frac{c}{2}\int_p 8\frac{\chi N}{p^2} && (11.10)\end{aligned}$$

Here we are immediately faced with the question whether we should write the bare or renormalized χ in the converging integral in the Dyson equation (11.9) and indeed in the definition of χ itself (11.10). Let us write here and in the following the renormalized one, as the physical intuition suggests and postpone the discussion why we do so.

The conducted renormalization of χ requires some comments. We are able to say that it is indeed renormalization (rather than fluctuational correction) since the two integrals in (11.10), as can be easily checked, do not depend on N and

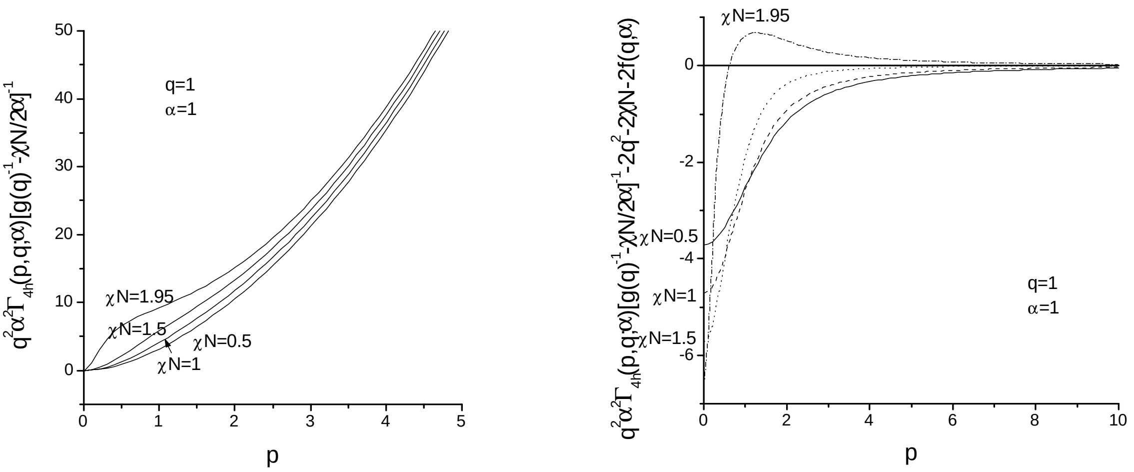

Figure 11.2: **(a)** Integrand of the one-loop correction for a homopolymer blend. **(b)** The integrand minus the asymptotics giving the diverging part of the integrand.

thus only on microscopic parameters v/a^3 (contained in c) and χ, and other details of microscopic structure of the chain, which guide the choice of the cutoff length making the integrals converging. These two integrals are the same for any chain having Gaussian statistics regardless of macroscopic architecture (diblock, star-copolymer, ...) of the chains and thus can indeed be considered a renormalization.

11.2.2. External momentum q arbitrary

In this case we should take the full expression for the fourth vertex of the homopolymer which is given in Appendices A and B. The one-loop correction in this case reads

$$\frac{c}{2}\int_p 4\alpha^2\gamma_h(q,p;\alpha)\left(g^{-1}(x_p,\alpha)-\frac{\chi N/\alpha}{2}\right)^{-1}\equiv\frac{c}{2}\int_p I_h(q,p) \qquad (11.11)$$

With a little computational effort it is also not impossible to obtain the expansion (although strictly speaking it does not exist (again due to exp's)) of this function in powers of p at $p\longrightarrow\infty$, this time for an arbitrary value of the external impulse

q:

$$I_h(q,p) = 8 + \frac{8\chi N}{p^2} + \frac{8f(q,\alpha)}{p^2} + O(p^{-4}) \qquad (11.12)$$

$$f(q,\alpha) = 4q^2/3 + 2/\alpha - 2g^{-1}(q,\alpha)h(q,\alpha) - 2\alpha q^2 g^{-2}(q,\alpha)\gamma_3(q,\alpha)/3 \qquad (11.13)$$

where the new functions are

$$\begin{aligned} h(x,\alpha) &\equiv \frac{1-exp(-\alpha x)}{x}, \quad x \equiv q^2 && (11.14) \\ \gamma_3(x,\alpha) &\equiv \frac{2}{x}\left(g(x,\alpha) - \alpha h(x,\alpha)\right) && (11.15) \end{aligned}$$

In fact, the most important features of the function $f(q,\alpha)$ are captured by its asymptotics:

$$f(q,\alpha) \rightarrow \begin{cases} \frac{13}{9}q^2, & q \rightarrow 0 \\ q^2, & q \rightarrow \infty \end{cases} \qquad (11.16)$$

so that actually we can think of it simply as q^2 for all q's.

Using the formula (11.12) we can rewrite the one-loop correction in the following way:

$$S_h^{-1}(q) = \left[2S_A^{-1}(q) - 2\chi\right] + \frac{c}{2}\int_p \left\{ I_h(q=0,p) - 8 - 8\frac{\chi N}{p^2} - \frac{8f(q,\alpha)}{p^2} \right\} + \frac{c}{2}\int_p \frac{8f(q,\alpha)}{p^2} \qquad (11.17)$$

Note that the renormalization of χ is exactly the same as before. The novelty is the q-dependent integral which obviously represents fluctuational corrections (rather than renormalization of χ) due to end effects. The calculation of the term requires introduction of a cutoff length. The correction is absent for $q = 0$, but then monotonically increases with the increase of q. Note that this term is also N-independent and thus (in this simplest system there are no other parameters describing the chain as a whole) depends only on microscopics:

$$\frac{c}{2}\int_p \frac{8f(q,\alpha)}{p^2} \sim \frac{v}{a^3}\frac{1}{N^{3/2}}q^2 \int_{p=0}^{N^{1/2}} 1 \sim \frac{v}{a^3}\tilde{q}^2 \qquad (11.18)$$

where we used the natural choice of the cutoff as the statistical segment length a, i.e. $\tilde{p} \sim 1$, $p \equiv \tilde{p}R_g \sim N^{1/2}$. We cannot call this correction a renormalization of χ because it depends on q, while by its very physical sense χ should be the same for all systems with the same chemical composition, that is why the last term of in (11.17) represents a proper fluctuational correction, resulting however from microscopic details of the chain, rather than from the mesoscopic fluctuation of chains, described by the second term (11.17).

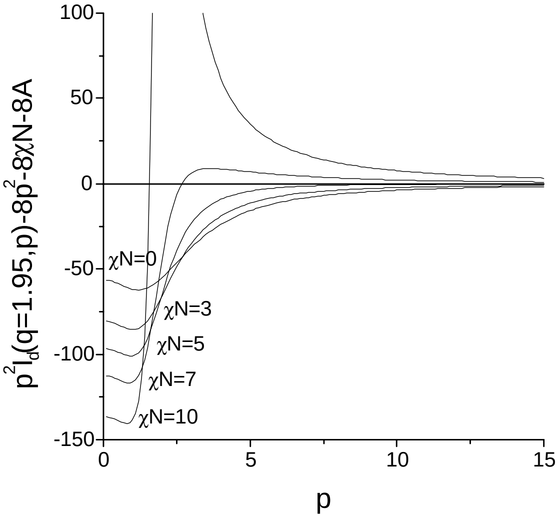

Figure 11.3: The integrand of the one-loop correction of diblock melt minus its divergent terms.

Finally, let us consider the mesoscopic fluctuations term in more details. To that end in Figure 11.2(a) we have plotted the integrand of the fluctuational correction for different χN and in plot (b) the corresponding converging part of it. Looking at the plot of the integrand we observe that it equals zero at $p = 0$ and as expected diverges as p^2 (it is a feature of the Gaussian statistics of the chain) at large p. The integrand after the substraction of the diverging terms indeed converges at large p. However we observe that this integral, which we thought to represent a "mesoscopic fluctuational correction" has considerable input at small p; in fact most of the input comes from the vicinity of $p = 0$. Yet this contribution is spurious as it comes from the terms $8\chi N$ and $8f(q, \alpha)$ which are only asymptotics at large p, and are absolutely irrelevant at small p. Since the value of the integral as we can see directly from Figure 11.2(b) is determined by the values at small p, we conclude that this substraction of divergencies does not make sense as it leads to wrong account of fluctuational corrections at small p.

11.3. Diblocks

We take the one-loop integral for diblock

$$\frac{1}{2}\frac{v}{a^3}\frac{6^{3/2}}{N^{3/2}}\int_p \gamma_4(q,p)\left[F(q) - 2\chi N\right]^{-1} \equiv \frac{c}{2}\int_p I_d(q,p) \qquad (11.19)$$

and extract diverging terms from it. Since the analytical formulae seem to be formidable in the case of diblock we do everything numerically. Thus we arrive at the following expansion

$$I_d(q,p) = 8 + \frac{8\chi N}{p^2} + \frac{8A(q)}{p^2} + O(p^{-4}) \tag{11.20}$$

where the newly introduced function $A(q)$ has been numerically found to have the following asymptotics:

$$A(q) = \begin{cases} 1 + \frac{4}{q^2}, & q \to 0 \\ 3 + q^2, & q \to \infty \end{cases} \tag{11.21}$$

First of all we see that the first two terms in the expansion (11.20) are exactly the same as in the case of homopolymer. As we mentioned before they are a property of a Gaussian statistics of the chain and that is why we treat them as a renormalization of χ. The diblock specific fluctuational renormalization is described by the last term:$8A(q)/p^2$. As in the case of homopolymers this terms does not depend on N and thus describes effects of microscopic structure of the chain.

The essential difference lies in the behaviour of the term as described by the asymptotics of $A(q)$ (11.21). Whereas the homopolymer function $f(q) = 0$ the diblock function $A(q)$ diverges for both $q = 0$ and $q = \infty$. Obviously the new singularity at $q = 0$ is due to the effect of connectivity of blocks in a copolymer; put otherwise due to the junction points of the blocks. The singular behaviour of $A(q)$ should have been expected since the second and fourth vertex are also singular at $q = 0$. The familiar divergence at $q = \infty$ obviously describes the end effects just as in the case of homopolymer. (Note that the asymptotic of the function at $q \to \infty$ is the same, viz. q^2).

It is also worthwhile to consider the mesoscopic fluctuational correction for the case of diblock. In Figure 11.3 we plot the integrand of this correction, ie original one-loop integral minus all diverging terms (the corresponding curves of $I_d(q = 1.945, p)$ can be observed in Figure 10.2). Again we see that for the values of χN not very close to the critical value the most part of the input into the integral comes from the area of small p where the original correction is actually almost zero. Again this contribution is due to the first two terms in (11.20) and again the result is spurious, since they do not make sense at small p. Therefore substraction of the diverging terms from the integral to make it convergent is an unsatisfactory way since leads to a wrong value of the mesoscopic fluctuational correction.

12. Solution of the Dyson equation

We return to the problem of the diblock melt. Drawing on the results of the preceding section we can now discuss the various ways the evaluation of the Dyson equation (10.1) with full integration should be conducted. The immediate problem is how to make a physical approximation for the apparently diverging integral of the first correction. First we explain why the various variants of the calculation through the substraction of the asymptotics fail, and then give account of the results and arising problems of the self-consistent solution of the Dyson equation with a cutoff.

12.1. Substraction of the asymptotics

Non-existence of a reference system.

As we have mentioned before the most physically desirable way of solving the problem would be to find a reference system having the same high$-q$ behaviour as the considered diblock system. However now it is clear that no such system can exist, because, as we have shown above, the high$-q$ behaviour of the one-loop correction for diblocks and homopolymers is essentially different and is determined be the details of microscopic structure such as end-effects and the effects connected with existence of juncture points in diblocks (although large parts of the correction are the same for all chains with Gaussian statistics and thus can be considered to be an experimentally irrelevant renormalization of a purely theoretical bare χ-parameter to an experimentally measurable χ).

Substraction of the high$-p$ asymptotic.

We can suggest another way of getting rid of the divergence: we calculate (analytically or numerically) the asymptotics of the integrand and simply subtract the diverging part from it. Thus we obtain a converging integral which can be used in making the equation self-consistent and a diverging part, which is then made finite with the help of the introduction of a physical cutoff. Apart from the problem of giving a physical sense (ie relating to experiment) of the subtracted portion, this method is unacceptable due to two physical reasons.

First, as we have seen above for both the cases of homopolymer and diblock, it would lead to an emergence of considerable spurious contributions at relatively small wavevectors, while this region is actually the most important for homopolymers and for diblocks it is important in view of the comparison with homopolymers. Note that this reason is due to the fact that among diverging terms there are terms independent of the impulse of integration, rather than terms of the kind e.g. p^2.

Secondly, it is simply physically inconsistent since there is no physical sense to

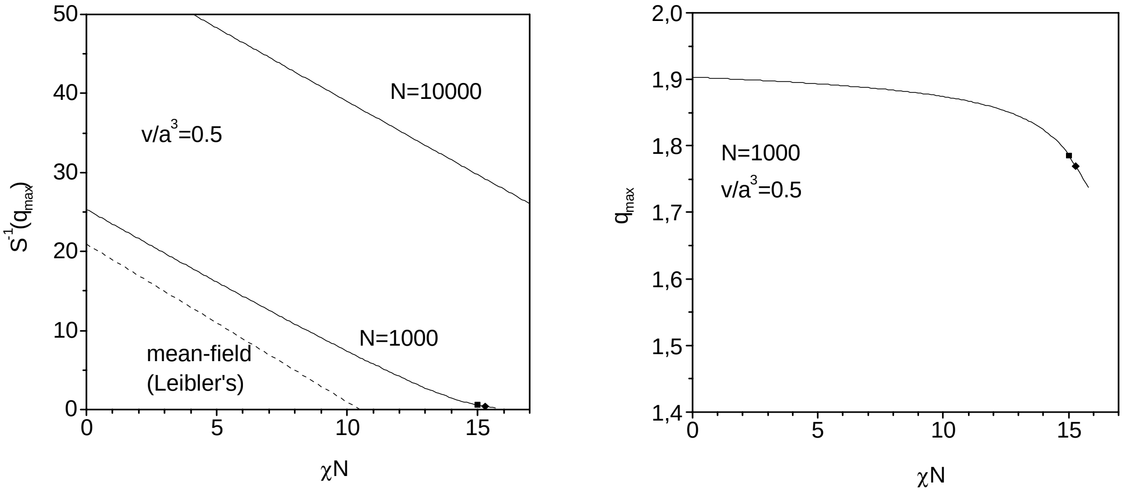

Figure 12.1: **(a)** Inverse of the maximum value of the correlation ($\sim$ to scattering intensity) function. (Dash line is the corresponding curve for the Leibler's mean-field case) **(b)** Position of the maximum of scattering function. Square dots in the both plots (smaller χN) indicates transition to the lamellar phase calculated according to the integral formulae; diamond point (at larger χN) — according to the Barrat-Fredrickson formulae.

calculate a high-p asymptotic at the values of external impulse q which are already sufficiently large. Practically this means that if we try to obtain an asymptotic of the integrand at external impulse $q \sim \Lambda$, (where Λ is the cutoff wavelength) we have to go to $p \gg q$, however it does not make physical sense to go beyond the cutoff length since we will al the same conduct integration only up to Λ, where this asymptotic works poorly.

Ultimately, both reasons are due to the fact that we use the notion of distinguishing contributions from low and high momenta (when we find asymptotic we find value at *large* momenta) yet do not provide a mechanism responsible for implementing it, so that in the first case the terms from large p show up at small p quite uninvited, while in the second case the small and large values are coupled simply through the vertex $\gamma_4(q, p)$.

12.2. Cutoff

In view of the above arguments, the best way to estimate the integral in the Dyson equation seems to be to introduce a cutoff and do not make any other approximations after that just solving the integral equation. For simplicity we take the square cutoff

$$\gamma_{cut}(q,p) = \begin{cases} \gamma_4(q,p), \text{ for } q,p < \Lambda \\ 0, \text{ for } q,p > \Lambda \end{cases} \tag{12.1}$$

Other forms of the cutoff are of course possible (for example

$$\gamma_{cut}(q,p) = \gamma_4(q,p)\exp(-(q^2+p^2)/\Lambda^2) \tag{12.2}$$

looks especially graceful) however the difference between them is only quantitative and thus immaterial for the following discussion. The cutoff length should be chosen as the length where the chain statistics begin to show essential deviation from Gaussian one. The natural choice is thus the persistence length. However, for simplicity we will estimate it as $l_p/a \sim (v/a^3)^{-1}$, so that we arrive at (all variables reduced by R_g):

$$\Lambda = \frac{v}{a^3}\left(\frac{N}{6}\right)^{1/2} \tag{12.3}$$

In the following we always use $v/a^3 = 0.5$.

In accordance with the Brazovskii approach we write the equation (10.1) self-consistently, which involves writing the renormalized (rather than RPA) correlator $S(q)$ in the integral. Thus in reduced variables we obtain the following integral equation for the function $S(q)$:

$$S^{-1}(q) = [F(q) - 2\chi N] + \frac{1}{2}\frac{v}{a^3}\frac{6^{3/2}}{N^{1/2}}\int_p \gamma_{cut}(q,p)S(p) \tag{12.4}$$

Let us note, that due to introduction of cutoff we have now two independent variables: N and v/a^3 (or even three, if we keep the persistence length as the cutoff), whereas in the previous theories [27, 28] there is only one combination of parameters: $\overline{N} \equiv N(v/a^3)^{-2}$.

Equation (12.4) is not a Fredholm integral equation and therefore the best way to solve seems to be via iterations. Indeed we used this way and found that the simple iterational scheme nicely converges to a single solution for small enough χN (in fact when $S^{-1}(q_{\max})$ is not very small) but ceases to converge for larger χN (ie when $S^{-1}(q_{\max}) \approx 0$). The problem is not physical and lies of course in the value of the step of numerical integration of the integral, which must be made sufficiently small, however here we are limited by time. Application of the Seidel iteration technique (when we use the newest available values of $S(q)$ all the time) broadens the region of χN where the scheme converges and was found to be the best among a number other techniques tried. We employ it with the use of changing integration step whose value is defined by $S^{-1}(q)$. Results of numerical solution are presented in Figure 12.1.

First we consider the behaviour of the position of the maximum scattering intensity as a function of χN, which is plotted In Figure 12.1(b). As we can see the qualitative behaviour of $q_{\max}$ is the same as is found in the theory of Barrat and Fredrickson [28], ie the wavevector is always smaller than the Leibler's critical value $q_* = 1.945$ (even for $\chi N = 0$) and monotonously decreases with the increase of χN. However, on a quantitative level, our values of $q_{\max}$ are somewhat larger.

In Figure 12.1(a) we present results for the inverse value of the scattering function $S(q)$ at maximum for two values of the degree of polymerisation: $N = 1000$ and $N = 10000$. We see that the slope of the curves is about the same as that of the Leibler's curve and that (as expected) they lie above the mean-field Leibler's curve. However the main conclusion from the Figure is clear: the values of χN used in the Figure are not experimentally relevant (crystal clear is this from the $N = 10000$ curve). Just by solving the equation (12.4) iteratively we took into account fluctuations at all momenta (even considerably large) but did not separate contributions leading to renormalization of χ from the genuinely diblock-specific contributions. Therefore by not making any approximations (except introduction of cutoff) at the beginning we ended up with the problem of relating χ entering the Dyson equation (12.4) to some experimentally relevant χ (for example that measured in the homopolymer system). How to carry out such a relating however turns out to be a tricky business (if at all possible), therefore before turning to it we consider in the next subsection the determination of the transition point.

13. Transition point

We will consider two ways of determining the point of the first order transition to the lamellar phase. The first is direct application of the results of the Barrat-Fredrickson theory considered in Section 8. Once we determine the correlation function $S^{-1}(q)$ from our theory (full treatment of $\gamma_4(q,p)$) we can use then for it approximation (8.3) and thus their formulae (8.13)–(8.17) for determination of the transition point. Based on their result that the lamellar wavevector q_l is very close to the position of the maximum of scattering q_* immediately before the transition here and below we will work in the approximation $q_l = q_*$.

However, as we have discussed in Section 8 the formulae of Barrat-Fredrickson theory are based on the calculation of the derivatives of the correlation function using the Brazovskii way of calculating the one-loop integral and are not applicable if we want to keep full treatment of momenta in $\gamma_4(q,p)$. However their approach is quite suitable for such a treatment. Indeed the expressions for the the equation of state (8.5) and the susceptibility in the ordered phase (8.6) use no approximations regarding dependence on p and q. We will follow their theory and determine the transition through obtain the expansion of the free energy (8.7) in powers of A.

In order to obtain the coefficients of the expansion:

$$\tau(q_l) = \left.\frac{df_m(A)}{d(A^2)}\right|_{A=0} = \Delta(q_l, A=0) = S^{-1}(q_*) \tag{13.1}$$

$$u(q_l) = 2\left.\frac{d^2 f_m(A)}{d(A^2)^2}\right|_{A=0} = 2\left[\Delta'(q_l) - \frac{1}{2}\gamma_4(q_l, q_l)\right] \tag{13.2}$$

$$w(q_l) = 6\left.\frac{d^3 f_m(A)}{d(A^2)^3}\right|_{A=0} = 6\Delta''_{A^2}(q_l) \tag{13.3}$$

we have to know the correlation function given by the usual Dyson equation (we write it here for completeness)

$$S^{.-1}(q) = \Gamma_2(q) + \frac{c}{2}\int_p \gamma_4(q,p)S(p) \tag{13.4}$$

as well as the first and second derivative of the susceptibility at $A = 0$, which are given by the following integral equations:

$$\Delta'(q) = \gamma_4(q, q_l) - \frac{c}{2}\int_p N\gamma_4(q,p)S^2(p)\Delta'(p) \tag{13.5}$$

$$\Delta''_{A^2}(q) = c\int_p \gamma_4(q,p)S^3(p)\left[\Delta'_{A^2}(p)\right]^2 - \frac{c}{2}\int_p N\gamma_4(q_l,p)S^2(p)\Delta''_{A^2}(p) \tag{13.6}$$

As we can see in order to obtain the transition point without neglecting at any point the q-dependence of the vertex we have to solve subsequently three integral equations (13.4),(13.5) and (13.6), then taking the obtained functions at $q_l = q_*$ (our approximation) we obtain the coefficients (13.1)–(13.2) and thus with the use of the formulae (8.16)–(8.17)are able to determine the first order transition point. Note that solving the three integral equations is simplified by the fact that they all are of exactly the same type and as it turns out are nicely solved by the iteration scheme used for determination of $S(q)$ (the first equation), which was discussed above.

Transition points determined according to the described two methods are presented in Figure 12.1. We indicate the BF-like transition point by a diamond (it lies at larger χN) and the point calculated within the full treatment of $\gamma_4(q,p)$ by the square (smaller χN).

We can see that taking into account full dependence of $\gamma_4(q,p)$ leads to a slightly lower (in terms of χN, ie higher in terms of temperature) value of the transition point. However the difference between the values obtained within the two treatments (approach is in fact the same) is rather small. If we take into account that the BF approach based on the expansion of the free energy (rather than complete determination of the free energy as it was done in [27]) is approximate (yet the only possible if we want to consider all momenta) and that the reported difference between the two methods if we work within the FH assumptions is 8% [47], than the 2% difference between the values of the transition point found here can obviously be neglected; Barrat-Fredrickson method can always be safely used.

This insensitivity to the method can be understood as a consequence of two circumstances: the phase transition is controlled by the behaviour of the correlation function around q_*; the transition is of weakly first order character, so that the correlation function does not considerably change upon the transition and thus coupling of different momenta is here unimportant. Which means that once we have found $S(q)$ (and we use the same in both methods) we can safely determine the transition point by looking at the properties of it around the critical wavevector q_*. Precisely because of this determination of the transition point is not specifically affected by taking into account the high-q behaviour of $\gamma_4(q,p)$. That is, the transition point of course lies on the curve $S^{-1}(q_*)$, so in this sense just as in the disordered phase we face the problem of relating theoretical and bare χ, however the value of $S^{-1}(q_*)$ at the transition point is insensitive to whether we take into account full dependence of $\gamma_4(q,p)$ or not.

14. Relating the theory to experiment: going over from χ to χ_{exp}.

We consider now again disordered phase. As we could immediately see from Figure 12.1 the results obtained so far are not directly comparable with experiment, ie the χ-parameter used in the Figure is some theoretical and not experimentally measurable property. The reason for this is of course that in the process of solving the Dyson integral equation we considered the whole one-loop integral to give fluctuational correction, while in fact, as we have discussed for the cases of diblocks and homopolymers, it makes physical sense to distinguish in this integral three separate contributions, viz., trivial renormalization of Gaussian chain statistics (it is the same for homopolymers and diblock, ie is independent the architecture); high-q (microscopic) fluctuational corrections due to end effects and effects connected with junction points in diblock; and low-q (mesoscopic) fluctuational effects, ie the usually considered effects defined by the behaviour of the chains on the scales of the radius of gyration of the chains (Brazovskii fluctuations). We will consider in this section two seemingly possible ways of relating the developed theory to experiment.

Simple subtraction of trivial Gaussian renormalization.

In order to be able to compare results with experiment we have to subtract the

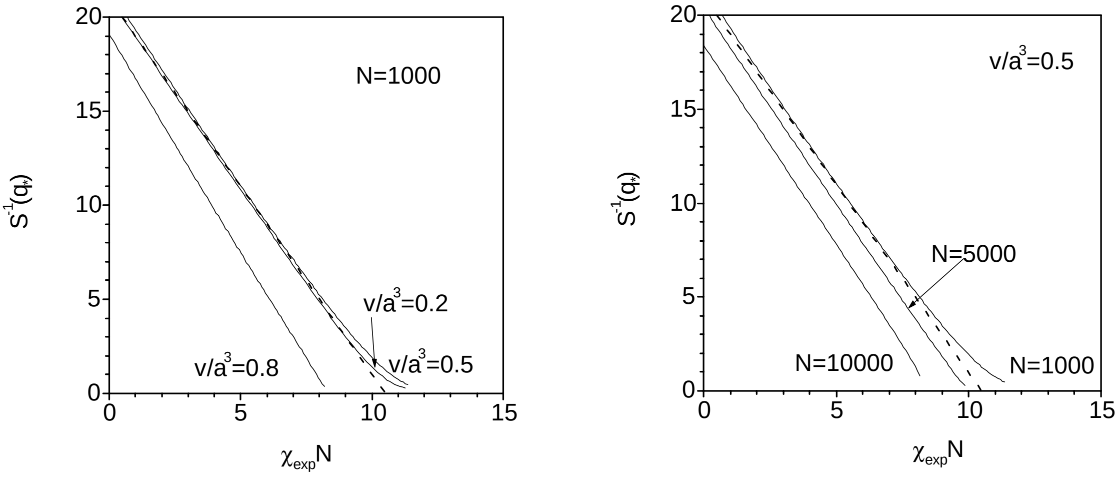

Figure 14.1: Inverse of the scattering function peak intensity as a function of renormalized $\chi_{\rm exp}N$ obtained from the analytical asymptotics of the correction for the homopolymer blend. (Dash line is the mean-field Leibler's result.)

trivial Gaussian renormalization of χ. This claim rests on the above shown fact that for $q = 0$ for the blend of (symmetric) homopolymers the only large-q correction is the trivial Gaussian renormalization; some mesoscopic corrections are also present (which are to be treated by the Renormalization Group method in this case), they are known to be small however, and we oversee them. Since measurements of χ are usually conducted by observing the properties of homopolymers at $q = 0$ (by measuring the scattering or measuring the transition point) we come to the claim that if we subtract the trivial renormalization we will obtain the results in terms of $\chi_{\rm exp}$ as measured in the experiments on homopolymers.

The expression for the trivial renormalization has been found in Section 11.2, formula (11.10):

$$2\chi_{\rm exp} = 2\chi - \frac{c}{2}\int_p 8 - \frac{c}{2}\int_p 8\frac{\chi N}{p^2} \tag{14.1}$$

where everything is written in reduced variables, accordingly $c = \frac{v}{a^3}\frac{6^{3/2}}{N^{3/2}}$. Taking the expression for the cutoff we arrive at the following results:

$$c_1 \equiv \frac{c}{2}\int_p 8 = \frac{2}{3\pi^2}\left(\frac{v}{a^3}\right)^4 \tag{14.2}$$

$$c_2 \equiv \frac{c}{2}\int_p \frac{8N}{p^2} = \frac{12}{\pi^2}\left(\frac{v}{a^3}\right)^2 \tag{14.3}$$

$$2\chi_{\text{exp}} = 2\chi - c_1 - c_2\chi \tag{14.4}$$

Note that in this formula in the r.h.s. of the equation we use the bare value χ, whereas the spirit of the self-consistent Brazovskii approach suggests that we should use fluctuationally renormalized values when calculating the correction. By doing so we arrive at the final expression:

$$2\chi_{\text{exp}} = \frac{2\chi - c_1}{1 + c_2/2} \equiv 2\chi - \tilde{c}_2\chi - \tilde{c}_1 \tag{14.5}$$

For example for $v/a^3 = 0.5$ and $N = 1000$ we obtain the following numerical values:

$$\begin{aligned} c_1 &\approx 0.00422, \quad \tilde{c}_1 = \frac{c_1}{1 + c_2/2} \approx 0.00366 && (14.6) \\ c_2 &\approx 0.304, \quad \tilde{c}_2 = \frac{c_2}{1 + c_2/2} \approx 0.264 && (14.7) \end{aligned}$$

The most representative curves of replotting inverse scattering at the peak $S^{-1}(q_*)$ with the use of χ_{exp} calculated according to (14.5) are presented in Figure 14.1. As we mentioned before due to the existence of cutoff we have now two independent parameters (even three if we take into consideration the persistence length): N and v/a^3 and we vary them independently in the plots of Figure 14.1. The most striking result is that some curves lie to the left of the Leibler's mean-field line (shown by dash line); the result absolutely impossible in the previous theories.

The dependence of the curves on v/a^3 (at a fixed N) turns out to be not monotonous as is illustrated by plot (a) of Figure 14.1. In contrast, the dependence of the curves on N (at a fixed $v/a^3 = 0.5$) as illustrated by plot (b) turns out to be monotonous. For smaller values of N the curve lies very close to the mean-field curve (practically indistinguishable for smaller χN). Note that the Fredrickson-Helfand curve is considerably shifted to the right for any value of χN (which is obviously a spurious result of not making a distinction between the renormalization of χ and mesoscopic fluctuational correction), while in the more sophisticated theory of Barrat and Fredrickson the curve lies closer to the Leibler line. It seems that our result, that the fluctuational curve is practically indistinguishable from the Leibler line at smaller χ makes even more physical sense.

With the increase of N the curve monotonously shifts to the left of the Leibler curve. As we have already mentioned this is a qualitatively new result, peculiar to our approach. However its value is undermined by the fact that (as we checked numerically) this shift is indeed monotonous for all values of N, ie this shift has no limit and the curve shifts to infinitely small χN with the increase of N. This result seems to be unphysical and by itself casts a shadow of doubt on the results obtained within this approach. Moreover, we can question the validity of the presented way of relating the theoretical results to experiments on the following grounds.

We solved the self consistent Dyson equation just by introducing the cutoff in the vertex and solving the integral equation for all values of wavevectors. By doing this we subjected to the self-consistisation procedure also the high-q behaviour of the correlator for the system of diblock. However when relating to the system of homopolymers immediately above we used the RPA asymptotics of the homopolymer (in fact trivial Gaussian renormalization) correlator at high-q. Therefore it seems physical that in relating we should use also the asymptotic behaviour obtain from the solution of the self-consistent Dyson equation with one-loop diagram, ie analogously as it was done for homopolymers. It may be argued that the blends of homopolymers belong to the Ising class of universality and the proper way to account for fluctuation is application of the renormalization group method. However, we are interested here in the modification of the high-q behaviour of the correlator which has nothing to do with the RG, but is important for relating the homopolymer and diblock systems, as this modification has been conducted for the diblock system. (As we mentioned above we do not pay any attention to the RG fluctuations at small values of q.) Therefore we suggest the second way of relating the results to experiments.

Obtaining the renormalization of χ via solution of self-consistent one-loop integral equation for homopolymers.

In this method we solve the integral equation (12.4) with the vertex also cut off according to the formula (12.1) but for homopolymers. Then we make an assumption that all the fluctuations contained in the one-loop correction can be considered to be due to high-q (microscopic) corrections, ie contributing to renormalization of χ. In order to extract the coefficients of the renormalization (14.4) we plot the value of the correction against χN and approximate the plot by a line (it turns out to be quite a good approximation). As we know renormalization of χ must indeed be independent of N, so that carrying out the procedure for different N we obtain the estimate of the accuracy of our approach. For example for $v/a^3 = 0.5$ we obtain:

$N = 1000 :\ c_1 = 2,75897\ 10^{-3}$, $c_2 = 0,05886 \quad (1,3548410^{-7}; 1,2191410^{-4})$
$N = 5000 :\ c_1 = 2.70535\ 10^{-3}$, $c_2 = 0,05545$
$N = 10000$: $c_1 = 2.69928\ 10^{-3}$, $c_2 = 0,05507$

(In brackets we indicated the errors of the coefficients; the linear fits have been obtained using the least squares method.) We see that the coefficients indeed display a rather weak dependence on N, which lends support to our approach. This dependence is caused by the inaccurate description of the small-q region of

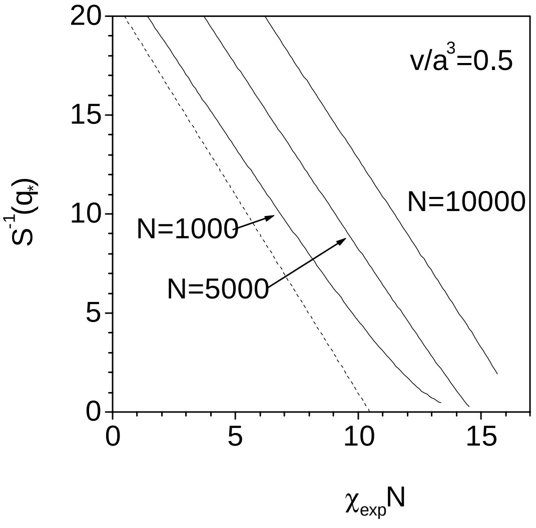

Figure 14.2: Inverse of the scattering function peak intensity as a function of renormalized $\chi_{\mathrm{exp}}N$ obtained from the self-consistent one-loop approximation for the homopolymer blend.

the correlator by the high-q asymptotic; and by the coupling of different momenta in the process of solving the integral equation self-consistent.

We use the obtained coefficients c_1 and c_2 for obtaining the renormalised χ_{exp} according to formula (14.4) and replot the inverse of the scattering at peak using this χ_{exp}. Results for different N are presented in Figure 14.2. Interestingly curves for all N lie sufficiently far from the Leibler mean-field curve. Moreover, in contrast to the expectation that they should approach it as N increases, they in fact monotonously shift to the right of the curve with the increase of N. This behaviour also seems to be quite unphysical and thus the approach is also inadequate.

Summarising, having solved the integral solution with the sole assumption of the cutoff, but without any physical ideas about isolating the input of renormalization of χ right from the start, we find that the two proposed ways of relating the obtained results to experiment do not seem to be satisfactory as is indicated by the results for large enough values of N.

15. Discussion and Outlook

The parameter of the perturbation theory expansion.

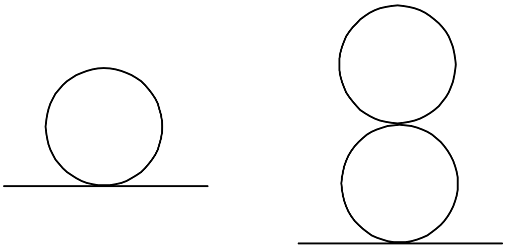

Figure 15.1: Diagrammatic representation of the one- and two-loop integrals

Let us see the high-q behaviour of the higher order diagrams, ie let us obtain the parameter of the perturbation theory associated with the divergence of the integrals at high q. For simplicity let us obtain estimates for homopolymers for zero external impulse. As we know the vertex has the following asymptotic behaviour at large momenta:

$$\gamma_h(q,p) \sim q^2 + p^2 \tag{15.1}$$

The asymptotic of the binary correlator is known to be $\sim q^2$. Thus we obtain the following estimates of the one- and two-loop diagrams (their diagrammatic representations are given in Figure 15.1).

One-loop:

$$I_1(q=0) \sim \frac{1}{\overline{N}^{1/2}} \int_p \frac{\gamma_h(q=0,p)}{p^2} \sim \frac{1}{\overline{N}^{1/2}} \int_{p=0}^{\Lambda} p^2\, dp\, \frac{p^2}{p^2} \sim \frac{1}{\overline{N}^{1/2}} \int_{p=0}^{\Lambda} p^2\, dp \sim \frac{1}{\overline{N}^{1/2}} \Lambda^3 \tag{15.2}$$

Two-loop:

$$\begin{aligned} I_2(q \;\; &= \;\; 0) \sim \frac{1}{\overline{N}} \int_{p_1} \int_{p_2} \frac{\gamma_h(q=0,p_1)\gamma_h(p_1,p_2)}{\left(p_1^2\right)^2 p_2^2} \sim \frac{1}{\overline{N}} \int_{p_1=0}^{\Lambda} \int_{p_2=0}^{\Lambda} p_1^2\, dp_1\, p_2^2\, dp_2 \frac{p_1^2(p_1^2+p_2^2)}{\left(p_1^2\right)^2 p_2^2} \sim \\ &\sim \;\; \frac{1}{\overline{N}} \int_{p_1=0}^{\Lambda} \int_{p_2=0}^{\Lambda} (p_1^2+p_2^2)\, dp_1 dp_2 \sim \frac{1}{\overline{N}} \Lambda^4 \end{aligned} \tag{15.3}$$

Comparing the expressions we see that the perturbation series parameter is (we use expression (12.3) for the cutoff Λ) reads:

$$\left[\frac{1}{\overline{N}^{1/2}}\right] \Lambda \sim \left[\frac{1}{N^{1/2}} \frac{v}{a^3}\right] \frac{v}{a^3} N^{1/2} \sim \left(\frac{v}{a^3}\right)^2 \tag{15.4}$$

(Although we conducted the calculation for $q = 0$ the result can be shown in fact to hold for arbitrary value of q.) Naturally this parameter is independent of N, as it describes renormalization of the chain on microscopic scales. On the

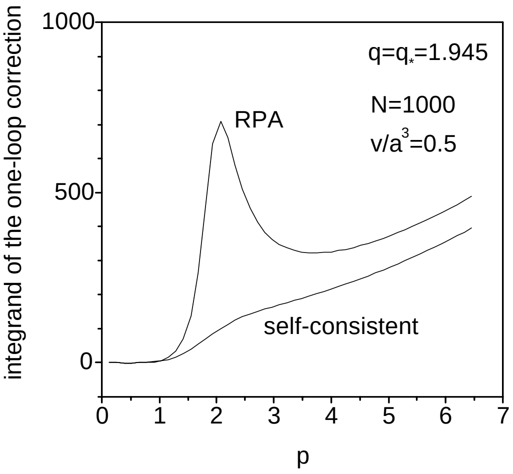

Figure 15.2: Integrands of the one-loop correction for the two cases: 1). when the correlator is the RPA one; 2). the correlator is found from one-loop self-consistent Dyson equation.

other hand the only microscopic parameter describing the chain is indeed v/a^3. Since the parameter v/a^3 is known to be at least < 0.5 for real polymer chains we can claim that our theory, based on the application of the perturbation approach makes sense even for the description of high-q fluctuations.

Let us analyse the obtained result closer. The important consequence is that we can indeed consider the high-q contributions due to junction points and end-effects in diblocks only on the level of the one-loop diagram and can calculate the corresponding additional inputs relative to the homopolymer case. However all this discussion actually concerns only high-q behavior, whereas we are interested in obtaining the whole range of q, while solving the equation.

Coupling of low- and large-q contributions.

In order to gain intuitive understanding of the problem let us view the plots of the one-loop integrand with the RPA correlator and its fluctuationally renormalized counterpart (ie with the correlator found from the solution of the Dyson equation); such plots are presented in Figure 15.2. We see that since in the process of solution we do not make any distinction between the origin of the fluctuational correction the largest contribution is the trivial renormalization of Gaussian chain and as a result the whole self-consistent curve lies considerably lower than the RPA one. Intuitively it is clear that it is wrong. Following physical intuition one would expect that the trivial renormalization should be taken care of separately, ie somehow while solving the equation we should self-consist χ separately. In the Figure, accordingly we would expect the high-q regions to remain practically the same while the critical fluctuations to be affected considerably, and primarily by the critical fluctuations. However how to formalize this idea is currently unclear.

Overview of obtained results.

We have put forward the problem of considering full q-dependence in the fluctuational theories of homopolymers and diblocks and discussed in depth issues related to such theories. One of the most important results obtained by considering the asymptotics of homopolymers and diblocks is demonstration that the fluctuational correction (one-loop or higher order diagrams) consists of three inputs which theoretically should be treated separately: low-q mesoscopic correction; and two types of high-q fluctuational corrections: trivial Gaussian (which is the same for all polymer chains having Gaussian statistics) and microscopic correction due to architecture (end-effects, junctions points, etc). As has been shown such a distinction should be made to relate the theoretical results to experiments and we suggested that it may lead to the inversion of the sign of the mesoscopic correction relative to the previous fluctuational theories which did not make such a distinction, treating the whole one loop integral as a mesoscopic fluctuational input. By considering the parameter of the perturbation theory we proved the validity of the perturbation approach for not extremely flexible polymer chains, as is the case experimentally.

Consistent formal implementation of this new ideological framework, however, turned out to be tricky. We have considered several apparent possibilities..

— 1). The simplest solution would have been to find a system having the same high-q asymptotic behaviour as the considered diblock system; then having subtracted the fluctuational correction of that system we would have obtained a Fredrickson-Helfand-like correction which could then be treated self-consistently. However we have demonstrated that there exists no such auxiliary system, which is of course due to existence of architecture-dependent input in the one-loop.

— 2). We subtract the asymptotics of the one-loop integrand and obtain converging expression. Then we treat this converging expression self-consistently in a FH fashion while use a cutoff (or simply some phenomenological constants to be experimentally found) to evaluate the diverging part. However this way also proves wrong since substraction of asymptotics leads to appearance of spurious (and at the same time relatively large) contributions at $q \approx 0$, correct description of this region being crucial to the theory. Without introducing any mechanism separating high and low momenta we cannot subtract the high-q asymptotic of the integrand, since the asymptotic contains independent terms of p, which are large at small p.

— 3). Another variant of the previous approach is not to try to isolate an

FH like contribution to be treated self-consistently, but to solve the equation self-consistently simply using this subtraction for estimation of the integral. This is also impossible since for large enough wavevectors there is no asymptotic behaviour on the scale of the cutoff length. The cause of this is exactly as above the absence of mechanism separating high- and low-q regions.

Having been unable to separate the contributions before self-consistisation (essential for description of mesoscopic fluctuations) we proceeded further by not making any assumptions except cutting off the vertex on a microscopic scale and solved the integral equation. Thus we did not solve the problem, rather put off the solution, since obtained results are obviously not directly applicable to experiments, as they contain the renormalization of χ. The two suggested methods of relating the results to experiments (one based on the RPA expression for the homopolymer and the other on its self-consistent version obtained analogously to the diblock) seem to be yield unphysical results. We obtain unphysical monotonous shift (to the left or to the right (depending on the method) of the mean-field Leibler curve) of the inverse scattering at peak with the increasing N. As importantly (as discussed immediately above in relation with Figure 15.2), the whole procedure of solving the integral equation without preliminary isolation of different fluctuational inputs seems to be erroneous. It seems that trivial renormalization (and possibly microscopic architecture-dependent too) should be given special treatment, while only mesoscopic input should be found from self-consistent solution of the Dyson equation.

Outlook.

The only missing (and seemingly *sine qua non*) ingredient seems to be the frequently mentioned mechanism (and physical understanding thereof) allowing us to treat high- and low-q contributions to the one-loop integral separately. If that mechanism is available we could easily solve the problem by applying for example the method 2 described above. In all other respects the new theoretical framework is well defined and indeed capable of delivering the newly experimentally observed result of fluctuational corrections destabilising the disordered phase.

Part VI

Conclusions

In the present work we considered a number of fluctuational effects in the ternary mixtures of homopolymers/copolymer as well as addressed the problem of a correct description of microscopic scale fluctuational contributions in diblock copolymer melts.

In **Part II** the **correlation properties of ternary homopolymer/diblock copolymer melts** are considered within the Random Phase Approximation in which all densities of monomeric units are treated as independent order parameters. Surprisingly the critical line obtained within this approach coincides with that of a one-order parameter theory. The expressions for the full concentration correlator (and consequently the Lifshitz line) are also equivalent. Consideration of the eigenvectors of the second order vertex matrices shows that near the critical line only one critical eigenvalue exists which is alone responsible for the change from the Ising to Brazovskii universality class. This also justifies use of only one order parameter near the critical line. However the critical eigenvector was found to be different from that previously assumed in the literature; this difference is important for construction of the fluctuation theory. Far from the critical line in the disordered phase two eigenvalues were found to be of physical relevance, their separate treatment being important for the fluctuation theory. However construction of a proper multiple order parameter fluctuation theory (even the simplest one-loop one) requires taking into account high wavevector (microscopic) fluctuations, the problem which has been little addressed in the literature.

In **Part III** the **behaviour of the Lifshitz line with changing temperature in the ternary systems** is investigated within the one-loop Renormalisation Group method. We employ the standard ϕ^4 Landau Hamiltonian with the use of only one order parameter and obtain expressions for renormalizes parameters of the Hamiltonian which are valid in both perturbation and RG regimes. The Lifshitz line has been shown to exhibit the non-monotonic behaviour with changing temperature, which agrees with recent experimental observations of Schwahn et al. The Lifshitz line has been found to have the mean-field value at very large and very small (or at the Lifshitz point) temperatures and deviate from it to larger concentrations of diblock at intermediate temperatures. The deviation at large temperatures has been shown to be a result of growing fluctuations in the perturbation regime, while the subsequent return to the mean-field value with lowering temperature is due to the onset of an RG fluctuational regime in which the vertex strongly renormalizes. Thus the peak deviation of the Lifshitz line signals a change from the perturbative to a fluctuation regime. The value of the lower critical dimension was found to be important for the behaviour and two possible cases have been investigated.

In **Part V** treatment of **large wavevector contributions in the self-consistent one-loop fluctuational theory** for the pure melts of symmetric homopolymers or symmetric diblock copolymer was considered. It was shown that when the wavevector dependence of the fourth vertex is taken into account the one-loop correction integral diverges at large q so that special treatment of this divergence is required. Applicability of the perturbation expansion for the treatment of large-q contributions has been shown for flexible polymer chains. The necessity to distinguish three types of contributions in the correction: mesoscopic (arising from fluctuations at large (ie of the order of the radius of chains) scales); microscopic Gaussian (arising from microscopic (of the order of the statistical segment of the chain) scale fluctuations, but the architecture independent, ie the same for all chains having Gaussian statistics), and microscopic structure dependent (microscopic scale fluctuations, but structure specific to such features as end-point or junction points) has been established. Based on this classification inadequacy of the standard Fredrickson-Helfand theory has been demonstrated, since as a result of Brazovskii way of integration, it treats the whole fluctuational contribution as due to mesoscopic fluctuations. Several ways to take into account the specific large wavevector dependence of the vertex have been explored. In particular the self-consistent Dyson equation was solved with full treatment of the dependence and with the cutoff at the segment length to make the integral divergent. However this approach seems to be unsatisfactory as the results obtained within it are unphysical and objections to self-consistent treatment of the large-q contributions conducted in this approach may be raised. Correct treatment of large-q contribution in the fluctuational correction remains yet to be elaborated.

Appendix A

A. The one-loop fluctuational correction of the symmetric homopolymer blend

In this Appendix we present formulae for the calculation of one-loop correction of the symmetric blend of homopolymers A and B of the same length $N_A (= N_B)$. As we are interested in comparing our results with the calculations for the diblock case we measure the length relative to the length of the diblock: $N_A = \alpha N$, where N is the relative length (in our case of the diblock). The blend is fully symmetric, ie the volume fractions $\phi_A = \phi_B = 1/2$. We will give results for the general case of arbitrary external momenta p and q and for the important special case of the external momentum $q = 0$, for which the expressions turn out to be particularly simple. We will not provide here expressions for the so-called molecular correlators, since the corresponding expressions coincide with that of the diblock and can be found in Appendix B.

The Dyson equation with the one-loop correction reads

$$S^h(q) = \Gamma_2^h(q) + \frac{1}{2} v \int_p \Gamma_4^h(q, -q, p, -p) \left[\Gamma_2^h(p)\right]^{-1}$$

$$\frac{1}{2} \int_p \Gamma_4^h(q, -q, p, -p) \left[\Gamma_2^h(p)\right]^{-1} = \frac{1}{2} \int_p \left[2\Gamma_{AAAA}(p, -p, q, -q)\right] \left(2S_A^{-1}(p) - 2\chi\right)^{-1}$$

$$\begin{aligned}
S_A(q) &= \frac{\phi_A}{N_A} N_A^2 g(x_A) = \frac{\phi_A}{N_A} N^2 g(x, \alpha) = \frac{1}{2}\frac{N}{\alpha} g(x, \alpha) \\
\text{where } x_A &\equiv \frac{q^2 a^2 N_A}{6} \text{ and } x \equiv \frac{q^2 a^2 N}{6} \\
g(x, \alpha) &= \frac{2}{x^2}(\alpha x + \exp(-\alpha x) - 1)
\end{aligned}$$

$$\begin{aligned}
\Gamma_{AAAA}(p, -p, q, -q) &= \tilde{\gamma}_{AAAA}(p, -p, q, -q) S_A^{-1}(p) S_A^{-1}(p) S_A^{-1}(q) S_A^{-1}(q) \\
\gamma_{AAAA}(p, -p, q, -q) &= -G_{AAAA}(p, -p, q, -q) + \\
&\quad G_{AAA}(p, -p, 0) S_A^{-1}(0) G_{AAA}(0, q, -q) + \\
&\quad G_{AAA}(p, q, -p-q) S_A^{-1}(p+q) G_{AAA}(p+q, -p, -q) + \\
&\quad G_{AAA}(p, -q, -p+q) S_A^{-1}(p-q) G_{AAA}(p-q, -p, q)
\end{aligned}$$

Now we want to extract from the expressions $\tilde{\gamma}_{AAAA}(p, -p, q, -q)$ and $S_A^{-1}(p)$ dependence on N and $\phi_A = 1/2$ and obtain dimensionless expressions in terms of reduced wavevectors and $\alpha = N_A/N$.

$$\begin{aligned}
G_{AAAA}(p,-p,q,-q) &= \frac{\phi_A}{N_A}\widetilde{g}_{AAAA}(\widetilde{p},-\widetilde{p},\widetilde{q},-\widetilde{q}) = \frac{1}{2}\frac{N^3}{\alpha}g_{AAAA}(p,-p,q,-q;\alpha) \\
G_{AAA}(p,q,-p-q) &= \frac{\phi_A}{N_A}\widetilde{g}_{AAA}(\widetilde{p},\widetilde{q},-\widetilde{p}-\widetilde{q}) = \frac{1}{2}\frac{N^2}{\alpha}g_{AAA}(p,q,-p-q;\alpha)
\end{aligned}$$

Here under $\widetilde{p}$ (and $\widetilde{q}$) we understand original momenta and under $\widetilde{p} \equiv pR_g = p(aN^{1/2}/6^{1/2})$ their reduced counterparts. Expressions for $g_{AAAA}(p,-p,q,-q;\alpha)$ and $g_{AAA}(p,q,-p-q;\alpha)$ are presented in Appendix B.

$$\begin{aligned}
\gamma_{AAAA}(p,-p,q,-q) &= \frac{1}{2}\frac{N^3}{\alpha}\gamma_{AAAA}(p,-p,q,-q;\alpha) \\
\Gamma_{AAAA}(p,-p,q,-q) &= \widetilde{\gamma}_{AAAA}(p,-p,q,-q)S_A^{-1}(p)S_A^{-1}(p)S_A^{-1}(q)S_A^{-1}(q) = \\
&= \frac{8\alpha^3}{N}\gamma_{AAAA}(p,-p,q,-q;\alpha)g^{-2}(p,\alpha)g^{-2}(q,\alpha)
\end{aligned}$$

Thus we finally obtain for the one-loop correction

$$\begin{aligned}
&= \frac{1}{2}\int_p [2\Gamma_{AAAA}(p,-p,q,-q)]\left(2S_A^{-1}(p) - 2\chi\right)^{-1} \\
&= \frac{1}{2}\int_p \left[2\frac{8\alpha^3}{N}\gamma_{AAAA}\left[g^{-1}\right]^4\right]\left(2\left[\frac{1}{2}\frac{N}{\alpha}g(x_p,\alpha)\right]^{-1} - 2\chi\right)^{-1} = \\
&= \frac{1}{2}\int_p 4\alpha^2\left[\gamma_{AAAA}\left[g^{-1}\right]^4\right]\left(g^{-1}(x_p,\alpha) - \frac{\chi N/\alpha}{2}\right)^{-1} = \\
&= \frac{1}{2}\int_p 4\alpha^2\gamma_h(q,p;\alpha)\left(g^{-1}(x_p,\alpha) - \frac{\chi N/\alpha}{2}\right)^{-1}
\end{aligned}$$

where we have introduced the following notation:

$$\gamma_h(q,p;\alpha) \equiv \gamma_{AAAA}(p,-p,q,-q;\alpha)g^{-2}(p,\alpha)g^{-2}(q,\alpha)$$

A.1. The case of external momentum $q = 0$

In this case all expression simplify considerably:

$$\begin{aligned}
\Gamma_{AAAA}(0,0,q,-q) &= \widetilde{\gamma}_{AAAA}(0,0,q,-q)S_A^{-1}(0)S_A^{-1}(0)S_A^{-1}(q)S_A^{-1}(q) \\
\widetilde{\gamma}_{AAAA}(0,0,q,-q) &= -G_{AAAA}(0,0,q,-q) + G_{AAA}(0,0,0)S_A^{-1}(0)G_{AAA}(0,q,-q) + \\
&\quad G_{AAA}(0,q,-q)S_A^{-1}(q)G_{AAA}(q,0,-q) + \\
&\quad G_{AAA}(0,-q,q)S_A^{-1}(q)G_{AAA}(-q,0,q)
\end{aligned}$$

$$
\begin{aligned}
&= -G_{AAAA}(0,0,q,-q) + G_{AAA}(0,0,0)S_A^{-1}(0)G_{AAA}(0,q,-q) + \\
&\quad 2G_{AAA}(0,q,-q)S_A^{-1}(q)G_{AAA}(q,0,-q) \\
&= 2G_{AAA}(0,q,-q)S_A^{-1}(q)G_{AAA}(q,0,-q) = 2N_A^2 S_A(q) \\
\Gamma_{AAAA}(0,0,q,-q) &= 2N_A^2 S_A(q)S_A^{-2}(0)S_A^{-2}(q) = 2N_A^2 S_A^{-1}(0)S_A^{-1}(0)S_A^{-1}(q) = \frac{2}{\phi_A^2}S_A^{-1}(q) \\
S_A(0) &= \phi_A N_A, \qquad G_{AAAA}(0,0,q,-q) = N_A^2 S_A(q), \qquad G_{AAA}(0,0,0) = \phi_A N_A^2
\end{aligned}
$$

So that the one-loop correction takes the final form

$$
\begin{aligned}
&= \frac{1}{2}\int_{\widetilde{p}} [2\Gamma_{AAAA}(p,-p,q,-q)] \left(2S_A^{-1}(q) + S_B^{-1}(q) - 2\chi\right)^{-1} = \\
&= \frac{1}{2}\int_{\widetilde{p}} \left[2\frac{2}{\phi_A^2}S_A^{-1}(q)\right] \left(2S_A^{-1}(q) - 2\chi\right)^{-1} = \\
&= \frac{1}{2}\int_{\widetilde{p}} \left[2\frac{2}{(\frac{1}{2})^2}\left[\frac{1}{2}\frac{N}{\alpha}g(x_p,\alpha)\right]^{-1}\right] \left(2\left[\frac{1}{2}\frac{N}{\alpha}g(x_p,\alpha)\right]^{-1} - 2\chi\right)^{-1} = \\
&= \frac{1}{2}\int_{\widetilde{p}} 8\, g^{-1}(x_p,\alpha)\left(g^{-1}(x_p,\alpha) - \frac{\chi N}{2\alpha}\right)^{-1}
\end{aligned}
$$

Appendix B

B. The fourth vertex function of the diblock melt

In this Appendix we list the program (in Pascal language) which was used to calculate the value of the fourth vertex of the diblock melt numerically. The expressions mainly follow the work [51]

```
----------------------------------------------------------------------------------------
function vsq(p1,p2:vector):extended; {Vector Sum sQuared}
begin
 vsq:=sqr(p1[1]+p2[1])+sqr(p1[2]+p2[2])+sqr(p1[3]+p2[3]);
end;

function vsq3(p1,p2,p3:vector):extended;{Vector Sum sQuared 3 vecs}
begin
 vsq3:=sqr(p1[1]+p2[1]+p3[1])+sqr(p1[2]+p2[2]+p3[2])+sqr(p1[3]+p2[3]+p3[3]);
end;

function vmq(p:vector):extended; {vector’s module squared}
begin
 vmq:=sqr(p[1])+sqr(p[2])+sqr(p[3]);
```

```
end;

function g(x,f:extended):extended;
begin
 if abs(f*x)>1e-7 then
                        if x*f<1e3 then g:=2*(x*f+exp(-x*f)-1)/(x*x)
                                  else g:=2*(x*f-1)/(x*x)
                   else g:=f*f*(1-f*x/3+sqr(f*x)/12-sqr(f*x)*f*x/60);
end;

function h(x,f:extended):extended;
begin
 if abs(f*x)>1e-7 then
                        if f*x<1e3 then h:=(1-exp(-x*f))/x
                                       else h:=1/x
                    else h:=f*(1-f*x/2+sqr(f*x)/6-sqr(f*x)*f*x/24);
end;

function gam3(x,f:extended):extended;
begin
 if abs(f*x)>1e-7 then gam3:=2*(g(x,f)-f*h(x,f))/x
                 else gam3:=f*f*f*(1/3-f*x/6+sqr(f*x)/20-sqr(f*x)*f*x/90);
end;

function gam4(x,f:extended):extended;
begin
 if abs(f*x)>1e-7 then
        if f*x<1e3 then gam4:=(3*gam3(x,f)-f*exp(-x*f)*g(-x,f))/(2*x)
                   else gam4:=(3*gam3(x,f)-2*f/(x*x))/(2*x)
        else gam4:=f*f*f*f*(1/12-f*x/20+sqr(f*x)/60-sqr(f*x)*f*x/252);
end;

function del3(x,f:extended):extended;
begin
 if abs(f*x)>1e-7 then
                 if f*x<1e3 then del3:=(1-(1+f*x)*exp(-x*f))/(x*x)
                            else del3:=1/(x*x)
           else del3:=f*f*(1/2-f*x/3+sqr(f*x)/8-sqr(f*x)*f*x/30);
end;

function del4(x,f:extended):extended;
```

```
begin
 if abs(f*x)>1e-7 then
       if f*x<1e3 then del4:=(h(x,f)-f*(1+f*x/2)*exp(-x*f))/(x*x)
                   else del4:=h(x,f)/(x*x)
       else del4:=f*f*f*(1/6-f*x/8+sqr(f*x)/20-sqr(f*x)*f*x/72);
end;

function J3(x1,x2,f:extended):extended;
begin
 if abs(x1-x2)>1e-7 then J3:=(g(x1,f)-g(x2,f))/(x2-x1)
                    else J3:=gam3((x1+x2)/2,f);
end;

function G3aaa(q1,q2,q3:vector; f:extended):extended;
var
 z,x1,x2,x3:  extended;
begin
 x1:=vmq(q1);
 x2:=vmq(q2);
 x3:=vmq(q3);
 z:=J3(x1,x2,f);
 z:=z+J3(x1,x3,f);
 G3aaa:=z+J3(x2,x3,f);
end;

function K3(x1,x2,f:extended):extended;
begin
 if abs(x1-x2)>1e-7 then K3:=(h(x1,f)-h(x2,f))/(x2-x1)
                    else K3:=del3((x1+x2)/2,f);
end;

function ksi2(q1,q2:vector; f:extended):extended;
var x1,x2,x12:extended;
begin
 x1:=vmq(q1);
 x2:=vmq(q2);
 x12:=vsq(q1,q2);
 ksi2:=K3(x1,x12,f)+K3(x2,x12,f)
end;

function G3abb(q1,q2,q3:vector; f:extended):extended;
```

```
   var x1:extended;
   begin
    x1:=vmq(q1);
    G3abb:=h(x1,f)*ksi2(q2,q3,1-f);
   end;

   function J4(x1,x2,y,f:extended):extended;
   begin
    if abs(x1-x2)>1e-7
               then J4:=(J3(x1,y,f)-J3(x2,y,f))/(x2-x1)
               else if abs((x1+x2)/2-y)>1e-7
               then J4:=( J3((x1+x2)/2,y,f)-J3((x1+x2)/2,(x1+x2)/2,f)
)/((x1+x2_)/2-y)
               else J4:=gam4((x1+x2+y)/3,f);
   end;

   function G4aaaa(q1,q2,q3,q4:vector; f:extended):extended;
   var z,x1,x2,x3,x4,x12,x13,x23:  extended;
   begin
    x1:=vmq(q1);
    x2:=vmq(q2);
    x3:=vmq(q3);
    x4:=vmq(q4);

    x12:=vsq(q1,q2);
    x13:=vsq(q1,q3);
    x23:=vsq(q2,q3);

    z:=J4(x1,x12,x4,f);
    z:=z+J4(x1,x23,x2,f);
    z:=z+J4(x1,x13,x2,f);
    z:=z+J4(x3,x23,x4,f);
    z:=z+J4(x3,x13,x4,f);
    z:=z+J4(x1,x23,x3,f);
    z:=z+J4(x1,x12,x3,f);
    z:=z+J4(x2,x23,x4,f);
    z:=z+J4(x2,x12,x4,f);
    z:=z+J4(x2,x13,x3,f);
    z:=z+J4(x2,x12,x3,f);

    G4aaaa:=z+J4(x1,x13,x4,f);
```

```
   end;

   function G4aabb(q1,q2,q3,q4:vector; f:extended):extended;
   begin
    G4aabb:=ksi2(q1,q2,f)*ksi2(q3,q4,1-f);
   end;

   function K4(x1,x2,y,f:extended):extended;
   begin
    if abs(x1-x2)>1e-7
                then K4:=(K3(x1,y,f)-K3(x2,y,f))/(x2-x1)
               else if abs((x1+x2)/2-y)>1e-7
                   then K4:=( K3((x1+x2)/2,y,f)-K3((x1+x2)/2,(x1+x2)/2,f)
)/( (x1+x2)/2-y )
                    else K4:=del4((x1+x2+y)/3,f);
   end;

   function ksi3(q1,q2,q3:vector; f:extended):extended;
   var z,x1,x2,x3,x12,x23,x13,x123:extended;
   begin
    x1:=vmq(q1);
    x2:=vmq(q2);
    x3:=vmq(q3);

    x12:=vsq(q1,q2);
    x13:=vsq(q1,q3);
    x23:=vsq(q2,q3);

    x123:=vsq3(q1,q2,q3);

    z:=K4(x1,x12,x123,f)+K4(x2,x12,x123,f);
    z:=z+K4(x2,x23,x123,f)+K4(x3,x23,x123,f);

    ksi3:=z+K4(x1,x13,x123,f)+K4(x3,x13,x123,f);
   end;

   function G4aaab(q1,q2,q3,q4:vector; f:extended):extended;
   var x4:extended;
   begin
    x4:=vmq(q4);
    G4aaab:=ksi3(q1,q2,q3,f)*h(x4,1-f);
   end;
```

```
function G3(i1,i2,i3:byte; q1,q2,q3:vector; f:extended):extended;
begin
 if (i1=1) and (i2=1) and (i3=1) then G3:=G3aaa(q1,q2,q3,f);
 if (i1=2) and (i2=2) and (i3=2) then G3:=G3aaa(q1,q2,q3,1-f);
 if (i1=1) and (i2=1) and (i3=2) then G3:=G3abb(q3,q2,q1,1-f);
 if (i1=1) and (i2=2) and (i3=1) then G3:=G3abb(q2,q1,q3,1-f);
 if (i1=1) and (i2=2) and (i3=2) then G3:=G3abb(q1,q2,q3,f);
 if (i1=2) and (i2=1) and (i3=1) then G3:=G3abb(q1,q2,q3,1-f);
 if (i1=2) and (i2=2) and (i3=1) then G3:=G3abb(q3,q2,q1,f);
 if (i1=2) and (i2=1) and (i3=2) then G3:=G3abb(q2,q1,q3,f);
end;

function Gamma(q1,q2,q3,q4:vector; f:extended):extended;
var i,j,k,l:byte;
 y,z:extended;
 psi:array[1..4,1..2] of extended;
 G4:array[1..2,1..2,1..2,1..2] of extended;

 function det(x:extended):extended;
 var z,f2,f3,f4:extended;
 begin
     f2:=f*f;
     f3:=f2*f;
     f4:=f3*f;
     if x>1e-7 then det:=g(x,f)*g(x,1-f)-sqr(h(x,f)*h(x,1-f))
                 else
             begin
                     z:=(-13*f3/30+2*f2/3-11*f/18+7/30+13*f4/90)*f2*x*x*x;
                     z:=z+(-1/2+10*f/9-5*f2/6+f3/3-f4/9)*f2*x*x;
                     z:=z+2*(1-2*f+f2)*f2*x/3;
                     det:=z;
             end;
end;

 function S(i1,i2:byte; x:extended):extended;
 begin
 if i1=i2 then
             if i1=1 then S:=g(x,f)
                     else S:=g(x,1-f)
         else S:=h(x,f)*h(x,1-f)
 end;
```

```
 function T4(i1,i2,i3,i4:byte; q1,q2,q3,q4:vector):extended;
 var x12,detv,zt:extended;
 m,n:byte;
 q12,mq12:vector;
 si:array[1..2,1..2] of extended;
 begin
     x12:=vsq(q1,q2);
     if x12>1e-8 then
             begin
                q12[1]:=q1[1]+q2[1];
                q12[2]:=q1[2]+q2[2];
                q12[3]:=q1[3]+q2[3];
                mq12[1]:=-q12[1];
                mq12[2]:=-q12[2];
                mq12[3]:=-q12[3];
                detv:=det(x12);
                si[1,1]:=g(x12,1-f)/detv;
                si[2,2]:=g(x12,f)/detv;
                si[1,2]:=-h(x12,f)*h(x12,1-f)/detv;
                si[2,1]:=si[1,2];
                zt:=0;
                for m:=1 to 2 do
                    for n:=1 to 2 do
   zt:=zt+G3(i1,i2,m,q1,q2,mq12,f)*si[m,n]*G3(n,i3,i4,q12,q3,q4,f);
                T4:=zt;
        end
         else
        begin
           T4:=S(i1,i2,vmq(q1))*S(i3,i4,vmq(q3));
        end;
 end;

procedure um(x:extended; var p1,p2:extended);
begin
   p1:=( g(x,1-f)+h(x,f)*h(x,1-f) )/det(x);
   p2:=-( g(x,f)+h(x,f)*h(x,1-f) )/det(x);
end;

begin
 G4[1,1,1,1]:=G4aaaa(q1,q2,q3,q4,f);
```

```
 G4[2,2,2,2]:=G4aaaa(q1,q2,q3,q4,1-f);
 G4[1,1,2,2]:=G4aabb(q1,q2,q3,q4,f);
 G4[2,2,1,1]:=G4aabb(q1,q2,q3,q4,1-f);
 G4[1,2,1,2]:=G4aabb(q1,q3,q2,q4,f);
 G4[2,1,2,1]:=G4aabb(q1,q3,q2,q4,1-f);
 G4[1,2,2,1]:=G4aabb(q1,q4,q3,q2,f);
 G4[2,1,1,2]:=G4aabb(q1,q4,q3,q2,1-f);
 G4[1,1,1,2]:=G4aaab(q1,q2,q3,q4,f);
 G4[1,1,2,1]:=G4aaab(q1,q2,q4,q3,f);
 G4[1,2,1,1]:=G4aaab(q1,q4,q3,q2,f);
 G4[2,1,1,1]:=G4aaab(q4,q2,q3,q1,f);
 G4[2,2,2,1]:=G4aaab(q1,q2,q3,q4,1-f);
 G4[2,2,1,2]:=G4aaab(q1,q2,q4,q3,1-f);
 G4[2,1,2,2]:=G4aaab(q1,q4,q3,q2,1-f);
 G4[1,2,2,2]:=G4aaab(q4,q2,q3,q1,1-f);

 um(vmq(q1),psi[1,1],psi[1,2]);
 um(vmq(q2),psi[2,1],psi[2,2]);
 um(vmq(q3),psi[3,1],psi[3,2]);
 um(vmq(q4),psi[4,1],psi[4,2]);

 z:=0;
 for i:=1 to 2 do
 for j:=1 to 2 do
 for k:=1 to 2 do
 for l:=1 to 2 do
     begin
         y:=-G4[i,j,k,l];
         y:=y+T4(i,j,k,l,q1,q2,q3,q4);
         y:=y+T4(i,k,j,l,q1,q3,q2,q4);
         y:=y+T4(i,l,k,j,q1,q4,q3,q2);

         z:=z+y*psi[1,i]*psi[2,j]*psi[3,k]*psi[4,l]
     end;
 Gamma:=z;
end;
```

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