

University of Groningen

**Theory of microphase separation in multiple segment-type statistical multiblock copolymers with arbitrary block molecular weight distributions**

Slot, J.J.M.; Angerman, H.J; ten Brinke, G.

*Published in:*  
Journal of Chemical Physics

*DOI:*  
[10.1063/1.477535](https://doi.org/10.1063/1.477535)

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1998

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Slot, J. J. M., Angerman, H. J., & ten Brinke, G. (1998). Theory of microphase separation in multiple segment-type statistical multiblock copolymers with arbitrary block molecular weight distributions. *Journal of Chemical Physics*, 109(19), 8677 - 8700. DOI: 10.1063/1.477535

**Copyright**

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

**Take-down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

*Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.*

# Theory of microphase separation in multiple segment-type statistical multiblock copolymers with arbitrary block molecular weight distributions

J. J. M. Slot<sup>a)</sup>

Department for Physical, Analytical and Computational Chemistry, DSM Research, P.O. Box 18, 6160 MD, Geleen, The Netherlands

H. J. Angerman and G. ten Brinke

Department of Polymer Chemistry and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

(Received 8 June 1998; accepted 11 August 1998)

A Landau free energy is derived for the weak segregation regime (WSR) of melts belonging to a very general class of statistical multiblock copolymers, referred to as "multiple segment-type statistical multiblock copolymers." Copolymer chains in this class consist of sequences of up to  $M \geq 2$  chemically different types of segments, organized into sequences of blocks of varying lengths (molecular weights). The possible sequences of blocks that are encountered in the copolymer chains, as far as their type is concerned, are described by a first-order Markov process, while the block molecular weight distributions of these  $M$  types of blocks are completely arbitrary. The number of blocks per chain is assumed to be large. This class of copolymers is sufficiently general to encompass all industrial relevant bulk statistical multiblock copolymers, such as all known thermoplastic elastomers. The particular free energy considered is just one realization of an even more general Landau free energy which is applicable to the WSR of melts of all conceivable copolymers, including homopolymers and all possible blends. The derivation of this Landau free energy is given in Appendix A. © 1998 American Institute of Physics. [S0021-9606(98)50943-9]

## I. INTRODUCTION

*Statistical multiblock copolymers* also referred to as *polydisperse multiblock copolymers* are an important class of industrially relevant synthetic materials. They are increasingly being used as adhesives, compatibilizers, emulsifiers, and in their bulk form as thermoplastic elastomers (TPE). As the properties of these materials crucially depend on their morphology, both in the molten and solid state, it is in particular their phase-behavior or thermodynamics which is important to understand. This subject has received considerable attention during the last few years in the academic world.<sup>1-8</sup>

The adjectives *statistical* or *polydisperse* refer to both the fact that the overall molecular weight of a chain usually will vary from chain to chain and to the fact that the molecular weight of the various chemically distinct types of blocks that makeup these *multiblock* copolymer chains will vary from block to block within each chain. However, the emphasis in this paper will lie on the latter form of *polydispersity*. The number of chemically distinct types of blocks in principle can be arbitrary, but the focus in the theoretical literature up to now, has been on the important class of so-called *binary* statistical multiblock copolymers, i.e., copolymer systems where the chains comprise of only two chemically different types of blocks. Many of the commercial available thermoplastic elastomers, such as the well-known polyester-co-polyether family of TPE's (e.g., PBT-co-PTHF), fall into this category.

So far basically two important classes of binary statisti-

cal multiblock copolymers were considered, namely uncorrelated or ideal random copolymers and so-called correlated random copolymers.<sup>2,3,7</sup> In the latter class the correlation in the sequences of both types of segments that makeup the copolymer chains is defined by means of a first-order Markov process, i.e., via a  $2 \times 2$  (stochastic) matrix of transition probabilities  $\underline{p}$ , with  $p_{ij}$  defined as the probability of occurrence of a segment of type  $j$  given that the preceding segment is of type  $i$ . In the former class, on the other hand as the name implies, these sequences are uncorrelated (Bernoulli—or zeroth-order Markov process). It is clear that this ideal binary random copolymer system is just a special example of a correlated binary random copolymer system, namely one where  $p_{AA} = p_{BA} \equiv p$  and  $p_{AB} = p_{BB} \equiv q \equiv 1 - p$ . A particularly nice way of treating this class of correlated binary random copolymers was introduced by Fredrickson *et al.*<sup>2</sup> They showed that this class can be parametrized by two parameters, namely the overall  $A$ -segment or  $A$ -monomer fraction  $f$  and the parameter  $\lambda \equiv p_{AA} + p_{BB} - 1$ , being the only nontrivial eigenvalue of  $\underline{p}$  (the other one is 1). This parameter  $\lambda$  varies between  $-1$ , corresponding to an alternating  $AB$ -copolymer and 1, corresponding to a blend of  $A$ - and  $B$ -homopolymers. The region  $-1 < \lambda < 0$  encompasses multiblock copolymers with a tendency towards alternation, while the region  $0 < \lambda < 1$  harbors multiblock copolymers with a tendency towards blockiness. Finally the midpoint  $\lambda = 0$  describes an ideal random copolymer. Binary statistical multiblock copolymers for which the average molecular weight of both types of blocks is not too small correspond to positive  $\lambda$  close to 1. In that case both block

<sup>a)</sup>Electronic mail: Han.Slot@DSM-group.com

molecular weight distributions are always of the exponential or Flory type,<sup>16</sup> i.e.

$$P_i(n) \equiv \frac{1}{\bar{n}_i} \exp\left[-\frac{n}{\bar{n}_i}\right] \quad (i=A,B), \quad (1)$$

where  $\bar{n}_i$  is the average molecular weight of the blocks of type  $i$ . Such a distribution has a *polydispersity*  $D_i \equiv \bar{n}_i^2/\bar{n}_i^2 - 1$ , equal to 1 (corresponding to the more familiar  $\bar{M}_w/\bar{M}_n$  of 2). This situation is typically encountered when these binary statistical multiblock copolymers are synthesized via a *polycondensation polymerization process* starting from a mixture of  $A$ - and  $B$ -monomers. However, in the synthesis of many of the industrial relevant statistical multiblock copolymers, the initial mixture or initial feedstock will also contain prepolymers of the  $A$ - or  $B$ -type with a possible narrow molecular weight distribution which are to be build into the copolymer chains. This can lead to block molecular weight distributions in the final multiblock copolymer system which will deviate from the above mentioned Flory-type distribution. This situation is of course not limited to binary statistical multiblock copolymers and can also occur when the copolymer chains consist of three or more chemically different types of blocks, a class which we will refer to from here on as so-called *multiple segment-type* statistical multiblock copolymers. It is this generic situation which we want to address in the sequel. The rest of the paper is organized as follows. In Sec. II we will describe a *coarse grained* model for these multiple segment-type statistical multiblock copolymer melts which is sufficiently general to encompass all industrial relevant bulk statistical multiblock copolymer systems. In this model the copolymer chains are allowed to consist of sequences of up to  $M \geq 2$  chemically different types of blocks of varying molecular weight, where the possible sequences are described via a first-order Markov process. Then, in Sec. III, we will develop a Landau free energy appropriate for the description of the *weak segregation regime* (WSR) of these multiple segment-type statistical multiblock copolymer melts. In the WSR, i.e., just inside the inhomogeneous region in parameter space where the deviation from homogeneity is still small, this Landau free energy can be expanded in a functional Taylor series in so-called *segmental order-parameter fields*. These segmental order-parameter fields, which are a measure of this deviation from homogeneity, can be approximated in the WSR by simple sinusoidal functions of position in real space. It is in this so-called *first harmonic approximation* (FHA), that we will consider the above mentioned Landau free energy. The coefficients in the Landau expansion are called *vertices*, and it is these vertices which we need to determine. These vertices, as was shown by Leibler for the first time in his seminal paper on diblock melts,<sup>19,20</sup> can be written in terms of so-called *ideal intrachain correlation functions*, which measure the spatial correlations in density of the various types of monomers in the ideal copolymer melt, i.e., when the interactions between the different types of monomers have been switched off. For the systems of interest in this paper, it proves to be sufficient to truncate the Landau expansion after the fourth-order terms. The main part of Sec. III, therefore, will be devoted to the detailed calculation of the second-,

third-, and fourth-order ideal intrachain correlation functions in the FHA. Of course it is known that such a Landau free energy expansion has a limited validity, especially when the FHA is adopted. Its validity is restricted to the WSR and in particular to the immediate vicinity of the locus in the phase diagram where the homogeneous phase becomes unstable. Even in that region the use of the FHA excludes the possibility of studying the occurrence of certain so-called *nonclassical* (inhomogeneous) phases such as the gyroid phase,<sup>10</sup> that were observed in diblock copolymer melts. For the description of such phases it is necessary to consider contributions to the Landau free energy arising from higher Fourier modes (*higher harmonics*) in the expansions of the segmental order-parameter fields.<sup>11</sup> Although strictly speaking the approach which is followed in the present paper goes in fact beyond the FHA, in the sense that certain higher harmonics are accounted for in the expression for the free energy, Eq. (23) in Sec. III, this is not sufficient to describe these nonclassical phases. For these multiple segment-type statistical multiblock copolymer melts it is to be expected<sup>12</sup> that the use of the FHA even becomes more restrictive if the repulsion between unlike blocks were to become larger, especially for systems with  $M > 2$ . But, in this so-called *intermediate to strong segregation regime* (ISR/SSR) the Landau approach is totally inappropriate and other approaches are asked for such as the *self-consistent field theory* (SCFT) method of Matsen en Schick.<sup>13</sup> It is, however, at present unclear how for instance this last method, which has up to now been formulated in particular for diblock and triblock copolymers melts, can be extended to the class of copolymer melts that is of interest here. With this Landau free energy one is thus able to calculate a part of the mean-field phase diagram for multiple segment-type statistical multiblock copolymer melts with specific but arbitrary block molecular weight distributions. In a forthcoming publication<sup>14</sup> this is done for the case of binary statistical multiblock copolymer melts ( $M = 2$ ) with Schultz–Zimm block molecular weight distributions, where more specifically the influence of polydispersity is studied. The particular Landau free energy here obtained is in fact a specific example of a much more general Landau free energy, which can be used to describe the WSR of all conceivable classes of copolymer melts, including homopolymer melts and their blends. This general Landau free energy is derived in detail in Appendix A. Finally, some concluding remarks are given in last section, Sec. IV. In addition there is a second appendix where characteristic functions of multivariate Gaussian distribution functions are calculated, which we will be needing in Sec. III and in Appendix A.

## II. COARSE GRAINED MODEL FOR A MULTIPLE SEGMENT-TYPE STATISTICAL MULTIBLOCK COPOLYMER MELT

In this section we will present a coarse grained model for multiple segment-type statistical multiblock copolymer melts, sufficiently general to encompass all industrial relevant bulk statistical multiblock copolymer systems. As this model is just a particular realization of a model which is described in Appendix A for a general copolymer melt, we

will restrict the discussion in this section mainly to the appropriate description of the various different species of chains which will be present in the system (specification of the sequence distribution) and refer to Appendix A for other details of the model. In this particular model the copolymer chains consist of sequences of up to  $M \geq 2$  chemically different types of segments, labeled by the variable  $\alpha \in \{1, \dots, M\}$  and organized into a sequence of blocks of varying lengths (molecular weights). The length of a block will be denoted by the (continuous) variable  $n$ . The variable  $s$  which is used in Appendix A to label the various species of chains present in the system, is thus in this particular model a condensed notation for a given sequence of block molecular weights of a particular type, i.e.

$$s \equiv \{(n_1, \alpha_1), (n_2, \alpha_2), \dots, (n_{N_b}, \alpha_{N_b})\}, \quad (2)$$

where it is assumed that each copolymer chain consists of a fixed number of blocks  $N_b$ , which will be taken sufficiently large so that the final results are not influenced by this assumption. Next to that the theory becomes particularly simple in this limit. The block molecular weight distributions of these  $M$  types of blocks will be taken *arbitrary* and *statistically independent*, i.e., described by non-negative functions  $P_1(n), \dots, P_M(n)$  with

$$\int_0^\infty dn P_\alpha(n) \equiv 1, \quad \forall \alpha. \quad (3)$$

It is clear from the notation that we will employ a continuous representation for the copolymer chains, i.e., chains will be represented by continuous curves in three-dimension (3D). So, the various blocks [see Eq. (2)] within a chain will be discriminated but not the segments which makeup these blocks. The possible sequences of blocks one encounters in the various chains of the system, as far as their identity (type) is concerned, will be described by a first-order Markov process, i.e., a stochastic process specified by the following  $M \times M$  matrix of transition probabilities

$$\begin{bmatrix} 0 & w_{12} & \dots & w_{1M} \\ w_{21} & 0 & \dots & w_{2M} \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ w_{M1} & w_{M2} & \dots & w_{M,M-1} & 0 \end{bmatrix}, \quad (4)$$

where  $w_{\alpha\beta}$  is the probability that the next block along the chain is of type  $\beta$  given that the current block is of type  $\alpha$ . This matrix  $\underline{w}$  will in general be asymmetric. By construction the diagonal matrix elements are zero because a block in this description is the basic unit and, therefore, a block of a given type can only be followed by a block of one of the other types. Furthermore the sum of the matrix elements in each row will be equal to one, because each block in a chain is always supposed to be followed by another one (at least in the  $N_b \rightarrow \infty$  limit). This means that there will only be  $M(M-2)$  independent matrix elements. This description of the possible block sequences (chains) in terms of a first-order Markov process for their identities in combination with sta-

tistically independent distributions for their lengths is general enough to encompass all relevant industrial statistical multi-block copolymer systems. As in general the matrix elements of  $\underline{w}$  will be determined by the specifics of the underlying polymerization process, we will consider them as input to the theory which is developed here. Similarly the  $M$  molecular weight distributions are arbitrary in the sense that we will leave the functions  $P_1(n), \dots, P_M(n)$  unspecified in this development. Their statistical independence is barely an assumption, because from a chemical point of view, correlations in sequence will only occur at the monomer level. In general the reactivity of a monomer at a chain end is at most influenced by one or two preceding monomers. At the level of the blocks these correlations will have disappeared, especially when the various types of blocks have an average block molecular weight which is not too small. The number  $\rho_s$  of chains of type  $s$  per unit volume will be proportional to the probability of realizing the particular sequence corresponding to  $s$  [Eq. (2)], i.e.

$$\rho_s \equiv \frac{1}{N_b \sum_\alpha w_\alpha^0 \bar{n}_\alpha} w_{\alpha_1}^0 P_{\alpha_1}(n_1) \times w_{\alpha_1 \alpha_2} P_{\alpha_2}(n_2) w_{\alpha_2 \alpha_3} \dots w_{\alpha_{N_b-1} \alpha_{N_b}} P_{\alpha_{N_b}}(n_{N_b}), \quad (5)$$

where the factor in front ensures that the overall segment density is unity, i.e.

$$\sum_s \rho_s N_s \equiv \frac{1}{N_b \sum_\alpha w_\alpha^0 \bar{n}_\alpha} \times \sum_{\alpha_1} \sum_{\alpha_2} \dots \sum_{\alpha_{N_b}} \int_0^\infty dn_1 \dots \int_0^\infty dn_{N_b} w_{\alpha_1}^0 \times P_{\alpha_1}(n_1) w_{\alpha_1 \alpha_2} \dots w_{\alpha_{N_b-1} \alpha_{N_b}} P_{\alpha_{N_b}}(n_{N_b}) \times \left\{ \sum_{k=1}^{N_b} n_k \right\} = 1. \quad (6)$$

In these expressions  $\bar{n}_\alpha$  denotes the average block molecular weight (average length) of the blocks of type  $\alpha$  and  $w_\alpha^0$  the so-called invariant probability of encountering a block of type  $\alpha$  in a chain. This last quantity will be given by the  $\alpha$ th component of the eigenvector of the transposed matrix of transition probabilities  $\underline{w}^T$  belonging to eigenvalue 1, a result which is well known from the theory of Markov chains.<sup>15</sup>

We will end this section by introducing two quantities, which we will need in the next section. The first quantity is the overall fraction  $f_\alpha$  of segments of type  $\alpha$  in the system [see Eq. (A4)]. This quantity can be expressed in terms of the invariant probabilities  $\{w_\alpha^0; \alpha=1, \dots, M\}$  and the average block molecular weights  $\{\bar{n}_\alpha; \alpha=1, \dots, M\}$  in the following way:

$$f_\alpha \equiv \frac{w_\alpha^0 \bar{n}_\alpha}{\sum_\gamma w_\gamma^0 \bar{n}_\gamma}. \quad (7)$$

In the definition of the ideal intrachain correlation functions [see Eqs. (A40) and (A44)–(A47)] the Ising-type variable

$\sigma_{sj}^\alpha$  appears, which indicates whether segment  $j$  in a chain of species  $s$  is of type  $\alpha$ . In the present model this quantity is given by

$$\sigma_{sj}^\alpha \equiv \sum_{k=1}^{N_b} \delta_{\alpha, \alpha_k} \left\{ \theta \left( j - \sum_{l=1}^{k-1} n_l \right) - \theta \left( j - \sum_{l=1}^k n_l \right) \right\}, \quad (8)$$

with  $\theta(j)$  a Heaviside step function. The function within brackets is a block function, which is 0 everywhere except for the  $k$ th block where it attains the value 1. The Kronecker delta symbol, in combination with the sum over the  $N_b$  blocks, simply selects those blocks which are of type  $\alpha$ . With this last result we are in a position to determine the Landau

free energy for such a melt of multiple segment-type statistical multiblock copolymers. This forms the subject of the next section.

### III. LANDAU FREE ENERGY FOR A MELT OF MULTIPLE SEGMENT-TYPE STATISTICAL MULTIBLOCK COPOLYMERS IN THE FIRST HARMONIC APPROXIMATION

As was mentioned in the introduction, the most general form of the Landau free energy for these copolymer melts is derived in Appendix A and is given by the final result (A60), i.e., by

$$\begin{aligned} \frac{F_L}{V} \equiv \min_{\{m_\alpha\}'} & \left\{ \frac{1}{2} \sum_{\alpha\beta} \sum_{\underline{q}} [\bar{g}_{\alpha\beta}^{-1}(\underline{q}) - 2\tilde{\chi}_{\alpha\beta}] m_\alpha(\underline{q}) m_\beta(-\underline{q}) - \frac{1}{6} \sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\xi} \sum_{\underline{q}_1\underline{q}_2} \bar{g}_{\alpha\beta\gamma}(\underline{q}_1, \underline{q}_2, -\underline{q}_1 - \underline{q}_2) \bar{g}_{\gamma\xi}^{-1}(|\underline{q}_1 + \underline{q}_2|) \right. \\ & \times \bar{g}_{\alpha\delta}^{-1}(\underline{q}_1) \bar{g}_{\beta\epsilon}^{-1}(\underline{q}_2) m_\delta(-\underline{q}_1) m_\epsilon(-\underline{q}_2) m_\xi(\underline{q}_1 + \underline{q}_2) + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2\underline{q}_3} \left\{ -\bar{g}_{\alpha\beta\gamma\delta}(\underline{q}_1, \underline{q}_2, \underline{q}_3, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3) \right. \\ & \times \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_3) \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(-\underline{q}_3) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) + [1 - \delta(\underline{q}_1 + \underline{q}_2)] \\ & \times \sum_{\kappa\lambda} \bar{g}_{\alpha\beta\kappa}(\underline{q}_1, \underline{q}_2, -\underline{q}_1 - \underline{q}_2) \bar{g}_{\kappa\lambda}^{-1}(|\underline{q}_1 + \underline{q}_2|) \bar{g}_{\gamma\delta\lambda}(\underline{q}_3, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3, \underline{q}_1 + \underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_3) \\ & \times \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(-\underline{q}_3) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) + [1 - \delta(\underline{q}_1 + \underline{q}_3)] \sum_{\kappa\lambda} \bar{g}_{\alpha\beta\kappa}(\underline{q}_1, \underline{q}_3, -\underline{q}_1 - \underline{q}_3) \\ & \times \bar{g}_{\kappa\lambda}^{-1}(|\underline{q}_1 + \underline{q}_3|) \bar{g}_{\gamma\delta\lambda}(\underline{q}_2, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3, \underline{q}_1 + \underline{q}_3) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_3) \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_3) \\ & \times m_\mu(-\underline{q}_2) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) + [1 - \delta(\underline{q}_2 + \underline{q}_3)] \sum_{\kappa\lambda} \bar{g}_{\alpha\beta\kappa}(\underline{q}_2, \underline{q}_3, -\underline{q}_2 - \underline{q}_3) \bar{g}_{\kappa\lambda}^{-1}(|\underline{q}_2 + \underline{q}_3|) \\ & \times \bar{g}_{\gamma\delta\lambda}(\underline{q}_1, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3, \underline{q}_2 + \underline{q}_3) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_2) \bar{g}_{\beta\xi}^{-1}(\underline{q}_3) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_1) \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_2) m_\xi(-\underline{q}_3) \\ & \times m_\mu(-\underline{q}_1) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) \left. \right\} \\ & + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2} \overline{g_{\alpha\beta}(\underline{q}_1) g_{\gamma\delta}(\underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_1) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_2) \bar{g}_{\delta\nu}^{-1}(\underline{q}_2)} m_\epsilon(-\underline{q}_1) m_\xi(\underline{q}_1) m_\mu(-\underline{q}_2) m_\nu(\underline{q}_2) \\ & + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2} \overline{g_{\alpha\gamma}(\underline{q}_1) g_{\beta\delta}(\underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_1) \bar{g}_{\delta\nu}^{-1}(\underline{q}_2)} m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(\underline{q}_1) m_\nu(\underline{q}_2) \\ & + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2} \overline{g_{\alpha\delta}(\underline{q}_1) g_{\beta\gamma}(\underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_2) \bar{g}_{\delta\nu}^{-1}(\underline{q}_1)} m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(\underline{q}_2) m_\nu(\underline{q}_1) \left. \right\}, \quad (9) \end{aligned}$$

where  $m_\alpha(\underline{q})$  is the (Fourier-transformed) order-parameter field associated with segments of type  $\alpha$ . Due to the assumption of incompressibility (see Appendix A), we have that  $\sum_\alpha m_\alpha(\underline{q}) \equiv 0$  and so only  $M-1$  fields are independent, which we choose to be  $m_1(\underline{q}), \dots, m_{M-1}(\underline{q})$ . The minimization, implied in Eq. (9), is over these  $M-1$  independent fields with the remaining segmental order-parameter field

$m_M(\underline{q})$  replaced by  $-\sum_{\alpha=1}^{M-1} m_\alpha(\underline{q})$ . The quantities  $\bar{g}_{\alpha\beta}(\underline{q})$ ,  $\bar{g}_{\alpha\beta\gamma}(\underline{q}_1, \underline{q}_2, -\underline{q}_1 - \underline{q}_2)$  and  $\bar{g}_{\alpha\beta\gamma\delta}(\underline{q}_1, \underline{q}_2, \underline{q}_3, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3)$  are, respectively, the earlier mentioned second-, third-, and fourth-order ideal intrachain correlation functions. The quantities  $g_{\alpha\beta}(\underline{q}_1) g_{\gamma\delta}(\underline{q}_2)$  etc., on the other hand, are a part of the so-called *nonlocal terms*, that are typical for polydisperse copolymer melts and for which one can show in gen-

eral that they vanish once the number of segment types exceeds the number of chain types in the system.<sup>3</sup> These various quantities are defined in Eqs. (A40), (A43), and (A45) in combination with Eqs. (A46) and (A47). To recapitulate

$$\bar{g}_{\alpha\beta}(q) \equiv \sum_s \rho_s g_{\alpha\beta}^s(q, -q),$$

$$\bar{g}_{\alpha\beta\gamma}(q_1, q_2, -q_1 - q_2) \equiv \sum_s \rho_s g_{\alpha\beta\gamma}^s(q_1, q_2, -q_1 - q_2),$$

$$\bar{g}_{\alpha\beta\gamma\delta}(q_1, q_2, q_3, -q_1 - q_2 - q_3) \equiv \sum_s \rho_s g_{\alpha\beta\gamma\delta}^s(q_1, q_2, q_3, -q_1 - q_2 - q_3),$$

$$\overline{g_{\alpha\beta}(q_1)g_{\gamma\delta}(q_2)} \equiv \sum_s \rho_s g_{\alpha\beta}^s(q_1, -q_1)g_{\gamma\delta}^s(q_2, -q_2)$$
(10)

with

$$g_{\alpha\beta}^s(q_1, q_2) \equiv \int_0^{N_s} di \int_0^{N_s} dj \sigma_{si}^\alpha \sigma_{sj}^\beta e^{(a^2 q_1 \cdot q_2 / 6) |i-j|},$$
(11)

$$g_{\alpha\beta\gamma}^s(q_1, q_2, q_3) \equiv \int_0^{N_s} di \int_0^{N_s} dj \int_0^{N_s} dk \sigma_{si}^\alpha \sigma_{sj}^\beta \sigma_{sk}^\gamma \times e^{(a^2/6)\{q_1 \cdot q_2 |i-j| + q_1 \cdot q_3 |j-k| + q_1 \cdot q_3 |i-k|\}},$$
(12)

and

$$g_{\alpha\beta\gamma\delta}^s(q_1, q_2, q_3, q_4) \equiv \int_0^{N_s} di \int_0^{N_s} dj \int_0^{N_s} dk \int_0^{N_s} dl \sigma_{si}^\alpha \sigma_{sj}^\beta \sigma_{sk}^\gamma \sigma_{sl}^\delta \times e^{(a^2/6)\{q_1 \cdot q_2 |i-j| + q_1 \cdot q_3 |i-k| + q_1 \cdot q_4 |i-l|\}} \times e^{(a^2/6)\{q_2 \cdot q_3 |j-k| + q_2 \cdot q_4 |j-l| + q_3 \cdot q_4 |k-l|\}}.$$
(13)

In Eqs. (11)–(13)  $a$  denotes the common statistical segment length. Finally the quantity  $\tilde{\chi}_{\alpha\beta}$  which appears in the second-order contribution to  $F_L$ , is a generalized Flory  $\chi$ -parameter, defined in Eq. (A13). For the following discussion it is convenient to formally rewrite Eq. (9) as a multivariate expansion in the independent segmental order-parameter fields  $m_1(q), \dots, m_{M-1}(q)$ . This can be achieved by applying to

Eq. (9) the transformation  $m_\alpha(q) \rightarrow \sum_{a=1}^{M-1} T_{\alpha a} m_a(q)$  ( $\alpha = 1, \dots, M$ ) where  $T_{\alpha a}$  is an element of the following  $M \times (M-1)$ -matrix:

$$\begin{bmatrix} 1 & 0 & \dots & \dots & 0 \\ 0 & 1 & & & \cdot \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & \cdot \\ \cdot & & & 1 & 0 \\ 0 & \cdot & \cdot & \cdot & 0 & 1 \\ -1 & \cdot & \cdot & \cdot & -1 & -1 \end{bmatrix}.$$
(14)

In the expressions to come we will adopt the convention that Roman indices run from 1 to  $M-1$ , in contrast with Greek indices which run from 1 to  $M$ . The formal result of the application of the above transformation to Eq. (9) can be written as

$$\frac{F_L}{V} \equiv \min_{\{m_a\}} \left\{ \left( \frac{1}{2!} \right) \sum_{ab} \sum_{\underline{q}} \Gamma_{ab}^{(2)}(q) m_a(\underline{q}) m_b(-\underline{q}) + \left( \frac{1}{3!} \right) \sum_{abc} \sum_{\underline{q}_1 \underline{q}_2 \underline{q}_3} \Gamma_{abc}^{(3)}(q_1, q_2, q_3) \times m_a(\underline{q}_1) m_b(\underline{q}_2) m_c(\underline{q}_3) + \left( \frac{1}{4!} \right) \sum_{abcd} \sum_{\underline{q}_1 \underline{q}_2 \underline{q}_3 \underline{q}_4} \Gamma_{abcd}^{(4)}(q_1, q_2, q_3, q_4) \times m_a(\underline{q}_1) m_b(\underline{q}_2) m_c(\underline{q}_3) m_d(\underline{q}_4) \right\}.$$
(15)

The coefficients  $\Gamma_{ab}^{(2)}$ ,  $\Gamma_{abc}^{(3)}$ , and  $\Gamma_{abcd}^{(4)}$  in this expression are known as vertices and their specific form can be inferred from Eq. (9). The second-order vertex  $\Gamma_{ab}^{(2)}(q)$  is given by

$$\Gamma_{ab}^{(2)}(q) \equiv \sum_{\alpha\beta} [\bar{g}_{\alpha\beta}^{-1}(q) - 2\tilde{\chi}_{\alpha\beta}] T_{\alpha a} T_{\beta b},$$
(16)

and the third-order vertex  $\Gamma_{abc}^{(3)}(q_1, q_2, q_3)$  by

$$\Gamma_{abc}^{(3)}(q_1, q_2, q_3) \equiv - \sum_{\alpha\beta\gamma} \sum_{\alpha'\beta'\gamma'} \delta(q_1 + q_2 + q_3) \bar{g}_{\alpha'\beta'\gamma'}(q_1, q_2, q_3) \times \bar{g}_{\alpha'a}^{-1}(q_1) \bar{g}_{\beta'\beta}^{-1}(q_2) \bar{g}_{\gamma'\gamma}^{-1}(q_3) T_{\alpha a} T_{\beta b} T_{\gamma c},$$
(17)

and finally the fourth-order vertex  $\Gamma_{abcd}^{(4)}(q_1, q_2, q_3, q_4)$  [see also Eq. (A45)] by

$$\begin{aligned}
\Gamma_{abcd}^{(4)}(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) \equiv & \sum_{\alpha\beta\gamma\delta} \sum_{\alpha'\beta'\gamma'\delta'} \left[ \delta(\underline{q}_1 + \underline{q}_2 + \underline{q}_3 + \underline{q}_4) \left\{ -\bar{g}_{\alpha'\beta'\gamma'\delta'}(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) + [1 - \delta(\underline{q}_1 + \underline{q}_2)] \right. \right. \\
& \times \sum_{\kappa\lambda} \bar{g}_{\alpha'\beta'\mu}(\underline{q}_1, \underline{q}_2, -\underline{q}_1 - \underline{q}_2) \bar{g}_{\mu\nu}^{-1}(|\underline{q}_1 + \underline{q}_2|) \bar{g}_{\gamma'\delta'\nu}(\underline{q}_3, \underline{q}_4, -\underline{q}_3 - \underline{q}_4) + [1 - \delta(\underline{q}_1 + \underline{q}_3)] \\
& \times \sum_{\kappa\lambda} \bar{g}_{\alpha'\beta'\mu}(\underline{q}_1, \underline{q}_3, -\underline{q}_1 - \underline{q}_3) \bar{g}_{\mu\nu}^{-1}(|\underline{q}_1 + \underline{q}_3|) \bar{g}_{\gamma'\delta'\nu}(\underline{q}_2, \underline{q}_4, -\underline{q}_2 - \underline{q}_4) + [1 - \delta(\underline{q}_1 + \underline{q}_4)] \\
& \times \sum_{\kappa\lambda} \bar{g}_{\alpha'\beta'\mu}(\underline{q}_1, \underline{q}_4, -\underline{q}_1 - \underline{q}_4) \bar{g}_{\mu\nu}^{-1}(|\underline{q}_1 + \underline{q}_4|) \bar{g}_{\gamma'\delta'\nu}(\underline{q}_2, \underline{q}_3, -\underline{q}_2 - \underline{q}_3) \left. \right\} + \delta(\underline{q}_1 + \underline{q}_2) \\
& \times \delta(\underline{q}_3 + \underline{q}_4) \overline{g_{\alpha'\beta'}(q_1) g_{\gamma'\delta'}(q_3)} + \delta(\underline{q}_1 + \underline{q}_3) \delta(\underline{q}_2 + \underline{q}_4) \overline{g_{\alpha'\gamma'}(q_1) g_{\beta'\delta'}(q_2)} + \delta(\underline{q}_1 + \underline{q}_4) \\
& \times \delta(\underline{q}_2 + \underline{q}_3) \overline{g_{\alpha'\delta'}(q_1) g_{\beta'\gamma'}(q_2)} \left. \right] \bar{g}_{\alpha'\alpha}^{-1}(q_1) \bar{g}_{\beta'\beta}^{-1}(q_2) \bar{g}_{\gamma'\gamma}^{-1}(q_3) \bar{g}_{\delta'\delta}^{-1}(q_4) T_{\alpha\alpha} T_{\beta\beta} T_{\gamma\gamma} T_{\delta\delta}. \quad (18)
\end{aligned}$$

From Eq. (16) it follows that  $\Gamma_{ab}^{(2)}(\underline{q}) = \Gamma_{ba}^{(2)}(\underline{q})$ , which means that the set of second-order vertices forms a symmetric matrix. Such a matrix has real eigenvalues and can be diagonalized by an orthogonal matrix  $\underline{\mathcal{S}}(\underline{q})$ , i.e., a matrix for which  $\underline{\mathcal{S}}^{-1}(\underline{q}) \equiv \underline{\mathcal{S}}^T(\underline{q})$ , whose columns are the eigenvectors of  $\Gamma^{(2)}(\underline{q})$ . So, if we introduce a new set of segmental order-parameter fields  $\{\tilde{m}_a(\underline{q})\}$  defined by

$$\tilde{m}_a(\underline{q}) \equiv \sum_b S_{ba}(\underline{q}) m_b(\underline{q}), \quad (19)$$

which we will refer to as *mixed* segmental order-parameter fields, then Eq. (15) can be transformed into

$$\begin{aligned}
\frac{F_L}{V} \equiv & \min_{\{\tilde{m}_a\}} \left\{ \left( \frac{1}{2!} \right) \sum_a \sum_{\underline{q}} \gamma_a^{(2)}(\underline{q}) \tilde{m}_a(\underline{q}) \tilde{m}_a(-\underline{q}) \right. \\
& + \left( \frac{1}{3!} \right) \sum_{abc} \sum_{\underline{q}_1 \underline{q}_2 \underline{q}_3} \tilde{\Gamma}_{abc}^{(3)}(\underline{q}_1, \underline{q}_2, \underline{q}_3) \\
& \times \tilde{m}_a(\underline{q}_1) \tilde{m}_b(\underline{q}_2) \tilde{m}_c(\underline{q}_3) \\
& + \left( \frac{1}{4!} \right) \sum_{abcd} \sum_{\underline{q}_1 \underline{q}_2 \underline{q}_3 \underline{q}_4} \tilde{\Gamma}_{abcd}^{(4)}(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) \\
& \times \tilde{m}_a(\underline{q}_1) \tilde{m}_b(\underline{q}_2) \tilde{m}_c(\underline{q}_3) \tilde{m}_d(\underline{q}_4) \left. \right\}, \quad (20)
\end{aligned}$$

with  $\{\gamma_a^{(2)}(\underline{q}); a=1, \dots, M-1\}$  the eigenvalues of  $\underline{\Gamma}^{(2)}(\underline{q})$ . This last result for  $F_L$  shows that these  $\{\tilde{m}_a(\underline{q})\}$  for each  $a$  and each  $\underline{q}$ , can be interpreted as a kind of quasi-independent *normal modes* of the system, similar say to phonons in real crystals. These modes are only independent as far as the second-order contribution to  $F_L$  is concerned, because through the third- and fourth-order terms they are coupled to each other.

The general idea of the Landau theory of phase transitions,<sup>17</sup> as applied to these copolymer systems, is that for small values of the  $\tilde{\chi}$ -parameters all the eigenvalues  $\{\gamma_a^{(2)}(\underline{q}); a=1, \dots, M-1\}$  will be positive. In that case the second-order contribution will be dominant and we may for-

get the higher order contributions for the moment. If all these eigenvalues are positive then it is clear that the minimum of  $F_L$  is found for  $\tilde{m}_a(\underline{q}) \equiv 0, \forall a$ , and  $\forall \underline{q}$ , which also implies that  $m_a(\underline{q}) \equiv 0, \forall a$ , and  $\forall \underline{q}$ . A result which follows from the fact that  $\underline{\mathcal{S}}(\underline{q})$  is a nonsingular matrix. This minimum by definition corresponds to the homogeneous phase of the system. If now the various  $\tilde{\chi}$ -parameters are increased, for instance, by lowering the temperature when one is dealing with a system of the UCST (upper critical solution temperature) type, one of the eigenvalues  $\gamma_i^{(2)}$  for some  $q_*$  could pass through zero at some stage and eventually become negative. In the Landau theory this so-called soft mode signals the occurrence of a phase transition in which the symmetry of the homogeneous phase will be broken. Due to its rotational invariance, it is an instability of this high-symmetry phase involving all modes associated with a spherical shell of radius  $q_*$  in Fourier space. The corresponding mixed segmental order-parameter field  $\tilde{m}_l(\underline{q}) \equiv \sum_a S_{al}(\underline{q}) m_a(\underline{q})$  is also known as the *strongly fluctuating order-parameter field*.<sup>4</sup> Whenever such an instability occurs, it is of course important also to consider the higher-order terms in  $F_L$ , as they will be necessary to ensure that the new minimum of  $F_L$  is finite. These same higher-order terms will also cause  $q_*$  to shift beyond the transition, as  $q_*$  has to follow from the conditions  $(\partial F_L / \partial q)|_{q=q_*} = 0, (\partial^2 F_L / \partial q^2)|_{q=q_*} > 0$ . The assumption that only one of the eigenvalues of  $\underline{\Gamma}^{(2)}(\underline{q})$  becomes zero at a some stage when say the temperature is lowered of a UCST system is physically correct, as there is no reason to assume that there are degeneracies in the spectrum of  $\underline{\Gamma}^{(2)}(\underline{q})$ , neither caused by symmetry nor accidental by nature. Although one cannot exclude the possibility that other eigenvalues will pass through zero at some later stage, we will assume that when that happens it will be at critical points in the  $\tilde{\chi}$ -parameter space which are located at a finite distance from the critical point where the homogeneous phase becomes unstable. As the low-symmetry phase in general will be space periodic, the sums over the  $q$ 's in Eq. (20) will run over some appropriate reciprocal lattice. To discriminate between a general  $\underline{q}$ -vector and an element of such

a reciprocal lattice, we will use a capitol vector  $\underline{Q}$  for the latter. From the above discussion it is clear that infinitesimally beyond the phase transition all  $\tilde{m}_l(\underline{Q})$  with  $|\underline{Q}|=q_*$  will acquire a nonzero value, whereas all other  $\tilde{m}_a(\underline{Q})$  will remain zero. In the Landau theory each member of this particular set  $\{\tilde{m}_l(\underline{Q}); |\underline{Q}|=q_*\}$  is referred to as a *primary order parameter*, while all other modes  $\tilde{m}_a(\underline{Q})$ , for which  $\gamma_a^{(2)}(\underline{Q})$  remains positive, are referred to as *secondary order parameters*.

The third- and fourth-order terms in the free energy not only lead to a coupling between the primary order parameters, but also to a coupling between the primary and the secondary order parameters. This last coupling implies that as a consequence of the fact that the primary order parameters will become nonzero beyond the phase transition, this will also happen with the secondary ones, despite the fact that the corresponding second-order terms in  $F_L$  favor a zero value for these secondary order parameters. As we do not want to go beyond fourth-order terms in the primary order parameters in the expansion of  $F_L$ , the only relevant coupling terms are those third-order terms which are linear in the secondary order parameters. These terms can collectively be written in the following way:

$$\frac{1}{2} \sum_a \sum_{\underline{Q}} \Lambda_a^l(\underline{Q}) \sum_{|\underline{Q}_2|=q_*} \sum_{|\underline{Q}_3|=q_*} \tilde{\Gamma}_{all}^{(3)}(\underline{Q}, \underline{Q}_2, \underline{Q}_3) \times \tilde{m}_a(\underline{Q}) \tilde{m}_l(\underline{Q}_2) \tilde{m}_l(\underline{Q}_3), \tag{21}$$

where  $\Lambda_a^l(\underline{Q}) \equiv 1 - \delta_{al} \delta(|\underline{Q}| - q_*)$  restricts the sums over  $a$  and  $\underline{Q}$  to those values which belong to secondary order parameters. Minimization of Eq. (21) combined with quadratic terms in the secondary order parameters in  $F_L$ , therefore, lead to secondary order parameters beyond the transition which are proportional to bilinear products of primary order parameters, i.e.,

$$\Lambda_a^l(\underline{Q}) \tilde{m}_a(\underline{Q}) = - \frac{\Lambda_a^l(\underline{Q})}{2 \gamma_a^{(2)}(\underline{Q})} \sum_{|\underline{Q}_2|=q_*} \sum_{|\underline{Q}_3|=q_*} \tilde{\Gamma}_{all}^{(3)}(-\underline{Q}, \underline{Q}_2, \underline{Q}_3) \times \tilde{m}_l(\underline{Q}_2) \tilde{m}_l(\underline{Q}_3). \tag{22}$$

With the help of this result we can eliminate the secondary order parameters in the expansion of  $F_L$  and retain only an expansion in terms of the primary order parameters. This expansion is given by

---


$$\begin{aligned} \frac{F_L}{V} \equiv \min_{\{\tilde{m}_i\}} & \left\{ \frac{1}{2!} \sum_{|\underline{Q}|=q_*} \gamma_l^{(2)}(q_*) \tilde{m}_l(\underline{Q}) \tilde{m}_l(-\underline{Q}) + \frac{1}{3!} \sum_{|\underline{Q}_1|=q_*} \sum_{|\underline{Q}_2|=q_*} \sum_{|\underline{Q}_3|=q_*} \tilde{\Gamma}_{lll}^{(3)}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3) \tilde{m}_l(\underline{Q}_1) \tilde{m}_l(\underline{Q}_2) \tilde{m}_l(\underline{Q}_3) \right. \\ & + \frac{1}{4!} \sum_{|\underline{Q}_1|=q_*} \sum_{|\underline{Q}_2|=q_*} \sum_{|\underline{Q}_3|=q_*} \sum_{|\underline{Q}_4|=q_*} \left[ \tilde{\Gamma}_{llll}^{(4)}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3, \underline{Q}_4) - 3 \sum_a \sum_{\underline{Q}} \frac{\Lambda_a^l(\underline{Q})}{\gamma_a^{(2)}(\underline{Q})} \right. \\ & \left. \left. \times \tilde{\Gamma}_{all}^{(3)}(\underline{Q}, \underline{Q}_1, \underline{Q}_2) \tilde{\Gamma}_{all}^{(3)}(-\underline{Q}, \underline{Q}_3, \underline{Q}_4) \right] \tilde{m}_l(\underline{Q}_1) \tilde{m}_l(\underline{Q}_2) \tilde{m}_l(\underline{Q}_3) \tilde{m}_l(\underline{Q}_4) \right\}. \tag{23} \end{aligned}$$

Not all of the different space-periodic (crystallinelike) structures that are conceivable in three-dimensions (230 in total) are possible candidates for the low-symmetry phase. The reason for this is that, for instance, the third-order terms in  $F_L$ , due to the presence of the Kronecker delta  $\delta(\underline{Q}_1 + \underline{Q}_2 + \underline{Q}_3)$  [see Eq. (17)], only couple those three primary order parameters for which the sum of the corresponding  $\underline{Q}$ -vectors adds up to zero, i.e., where the three  $\underline{Q}$ -vectors form an equilateral triangle. Similarly the fourth-order terms only couple four modes for which the sum of the four  $\underline{Q}$ -vectors adds up to zero. It is well-known that such combinations of three and/or four  $\underline{Q}$ -vectors, all having length  $q_*$ , only can be constructed in the reciprocal lattice of a limited set of space-periodic structures, such as the body centered cubic (BCC), hexagonally closed packed (HCP), and lamellar microphases.<sup>20,21</sup> They can also be constructed in certain quasi-periodic structures, such as the icosahedral microphase<sup>20</sup> or the so-called *random wave structure*.<sup>2</sup> The

example which we will use in the rest of this section is the BCC (body centered cubic) structure. So, a WSR low-symmetry phase will be characterized by

$$\tilde{m}_l(\underline{Q}) \neq 0, \quad \forall \underline{Q} \in H, \tag{24}$$

where  $H$  denotes the set of  $\underline{Q}$ -vectors of length  $q_*$  which belong to one of these particular reciprocal lattices. For instance for the BCC structure, whose reciprocal lattice is the FCC (face centered cubic) lattice,  $H$  is the set consisting of the following twelve  $\underline{Q}$ -vectors:

$$\begin{aligned} & \pm \frac{q_*}{\sqrt{2}} (1,1,0)^T, & \pm \frac{q_*}{\sqrt{2}} (-1,1,0)^T, \\ & \pm \frac{q_*}{\sqrt{2}} (0,1,1)^T, & \pm \frac{q_*}{\sqrt{2}} (0,1,-1)^T, \\ & \pm \frac{q_*}{\sqrt{2}} (1,0,1)^T, & \pm \frac{q_*}{\sqrt{2}} (1,0,-1)^T. \end{aligned} \tag{25}$$



The ansatz Eq. (24) is known as the first harmonic approximation (FHA). Now, each of the primary order parameters  $\tilde{m}_l(\underline{Q})$  can be characterized by an amplitude  $A_{\underline{Q}}$  and a phase  $\varphi_{\underline{Q}}$ . As the set of primary order parameters needs to be invariant with respect to the symmetry group of the low-symmetry phase, in particular its point-group symmetry (rotations and reflections), it follows that the amplitude  $A_{\underline{Q}}$  for each  $\underline{Q} \in H$  should be the same. Therefore, Eq. (24) can be written more specifically in the following way:

$$\tilde{m}_l(\underline{Q}) \equiv \sqrt{\frac{2}{n}} A \sum_{\underline{Q}' \in H} e^{i\varphi_{\underline{Q}'}} \delta(\underline{Q} - \underline{Q}'), \quad (26)$$

where  $n$  is the number of elements of  $H$ . The factor  $\sqrt{2/n}$  has been introduced for convenience. As  $\tilde{m}_l(-\underline{Q})$  should be the complex conjugate of  $\tilde{m}_l(\underline{Q})$  [to ensure that  $\tilde{m}_l(\underline{x})$  and consequently  $m_l(\underline{x})$  is a real quantity], it follows that the phase of  $-\underline{Q}$  should be minus the phase of  $\underline{Q}$ , i.e.,  $\varphi_{-\underline{Q}} \equiv -\varphi_{\underline{Q}}$ . Equation (26) has to be considered as a trial function for  $\tilde{m}_l(\underline{Q})$  with  $A$ ,  $\{\varphi_{\underline{Q}}\}$  and  $q_*$ , for a given choice of  $H$ , i.e., a given symmetry of the low-symmetry phase, as adjustable parameters whose value follows from a minimization of the Landau free energy with respect to these parameters. If we now substitute Eq. (26) into Eq. (23), the second-order contribution becomes

$$\frac{F_L^{(2)}}{V} \equiv \gamma_l^{(2)}(q_*) A^2, \quad (27)$$

irrespective of the type of low-symmetry phase, i.e., irrespective of  $H$ , while the third-order contribution leads to

$$\frac{F_L^{(3)}}{V} \equiv \frac{\sqrt{2}\zeta\gamma_l^{(3)}(q_*)A^3}{3n\sqrt{n}}, \quad (28)$$

where  $\zeta$  and  $\gamma_l^{(3)}(q_*)$  are defined by

$$\zeta \equiv \sum_{\underline{Q}_1 \in H} \sum_{\underline{Q}_2 \in H} \sum_{\underline{Q}_3 \in H} \delta(\underline{Q}_1 + \underline{Q}_2 + \underline{Q}_3) e^{i(\varphi_{\underline{Q}_1} + \varphi_{\underline{Q}_2} + \varphi_{\underline{Q}_3})} \quad (29)$$

and

$$\gamma_l^{(3)}(q_*) \equiv - \sum_{\alpha\beta\gamma} \bar{g}_{\alpha\beta\gamma}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3) \times z_{\alpha l}(q_*) z_{\beta l}(q_*) z_{\gamma l}(q_*) \quad (30)$$

with

$$z_{\alpha l}(q_*) \equiv \sum_{\beta} \sum_a \bar{g}_{\alpha\beta}^{-1}(q_*) T_{\beta a} S_{\alpha l}(q_*). \quad (31)$$

Although it seems from Eq. (30) that  $\gamma_l^{(3)}$ , through  $\bar{g}_{\alpha\beta\gamma}$ , depends on  $\underline{Q}_1$ ,  $\underline{Q}_2$ , and  $\underline{Q}_3$ , and therefore, should be a part of the summand of Eq. (29), it follows that  $\bar{g}_{\alpha\beta\gamma}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3)$  only depends on the innerproducts of these three  $\underline{Q}$ -vectors [see Eqs. (10) and (12)]. This implies that  $\bar{g}_{\alpha\beta\gamma}$  is independent of the particular triple of  $\underline{Q}$ -vectors considered (as long as they form an equilateral triangle) and consequently that  $\gamma_l^{(3)}$  is independent of the particular structure.  $\zeta$ , on the other hand, does depend on this structure. For instance in the case of the BCC structure, where one can show that on the basis of rotational symmetry either all phases are zero or equal to  $\pi$ ,  $\zeta$  is equal to  $\pm$  (+ when  $\gamma_l^{(3)}$  is negative and  $-$  when  $\gamma_l^{(3)}$  is positive) the number of equilateral triangles of  $\underline{Q}$ -vectors which can be formed within  $H$  [Eq. (25)], i.e.,  $\pm 8 \times 3!$ . Finally the fourth-order contribution can be written as

$$\frac{F_L^{(4)}}{V} \equiv \frac{A^4}{6n^2} \sum_{\underline{Q}_1 \in H} \sum_{\underline{Q}_2 \in H} \sum_{\underline{Q}_3 \in H} \sum_{\underline{Q}_4 \in H} e^{i(\varphi_{\underline{Q}_1} + \varphi_{\underline{Q}_2} + \varphi_{\underline{Q}_3} + \varphi_{\underline{Q}_4})} \gamma_l^{(4)}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3, \underline{Q}_4) \quad (32)$$

with

$$\begin{aligned} \gamma_l^{(4)}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3, \underline{Q}_4) \equiv & \sum_{\alpha\beta\gamma\delta} \left[ \delta(\underline{Q}_1 + \underline{Q}_2 + \underline{Q}_3 + \underline{Q}_4) \left\{ -\bar{g}_{\alpha\beta\gamma\delta}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3, \underline{Q}_4) + \sum_{\lambda\nu} \bar{g}_{\alpha\beta\lambda}(\underline{Q}_1, \underline{Q}_2, -\underline{Q}_1 - \underline{Q}_2) \right. \right. \\ & \times \bar{g}_{\gamma\delta\nu}(\underline{Q}_3, \underline{Q}_4, -\underline{Q}_3 - \underline{Q}_4) [1 - \delta(\underline{Q}_1 + \underline{Q}_2)] [\bar{g}_{\lambda\nu}^{-1}(|\underline{Q}_1 + \underline{Q}_2|) - Y_{\lambda\nu}^l(|\underline{Q}_1 + \underline{Q}_2|)] \\ & + \sum_{\lambda\nu} \bar{g}_{\alpha\beta\lambda}(\underline{Q}_1, \underline{Q}_3, -\underline{Q}_1 - \underline{Q}_3) \bar{g}_{\gamma\delta\nu}(\underline{Q}_2, \underline{Q}_4, -\underline{Q}_2 - \underline{Q}_4) [1 - \delta(\underline{Q}_1 + \underline{Q}_3)] [\bar{g}_{\lambda\nu}^{-1}(|\underline{Q}_1 + \underline{Q}_3|) \\ & - Y_{\lambda\nu}^l(|\underline{Q}_1 + \underline{Q}_3|)] + \sum_{\lambda\nu} \bar{g}_{\alpha\beta\lambda}(\underline{Q}_1, \underline{Q}_4, -\underline{Q}_1 - \underline{Q}_4) \bar{g}_{\gamma\delta\nu}(\underline{Q}_2, \underline{Q}_3, -\underline{Q}_2 - \underline{Q}_3) [1 - \delta(\underline{Q}_1 + \underline{Q}_4)] \\ & \left. \left. \times [\bar{g}_{\lambda\nu}^{-1}(|\underline{Q}_1 + \underline{Q}_4|) - Y_{\lambda\nu}^l(|\underline{Q}_1 + \underline{Q}_4|)] \right\} + \delta(\underline{Q}_1 + \underline{Q}_2) \delta(\underline{Q}_3 + \underline{Q}_4) \overline{g_{\alpha\beta}(q_*) g_{\gamma\delta}(q_*)} \right. \\ & \left. + \delta(\underline{Q}_1 + \underline{Q}_3) \delta(\underline{Q}_2 + \underline{Q}_4) \overline{g_{\alpha\gamma}(q_*) g_{\beta\delta}(q_*)} + \delta(\underline{Q}_1 + \underline{Q}_4) \delta(\underline{Q}_2 + \underline{Q}_3) \overline{g_{\alpha\delta}(q_*) g_{\beta\gamma}(q_*)} \right] \\ & \times z_{\alpha l}(q_*) z_{\beta l}(q_*) z_{\gamma l}(q_*) z_{\delta l}(q_*), \quad (33) \end{aligned}$$

where the matrix  $Y^l(q)$  which appears in this expression is defined by

$$Y_{\alpha\beta}^l(q) \equiv \sum_a \frac{\Lambda_a^l(q)}{\gamma_a^{(2)}(q)} z_{\alpha a}(q) z_{\beta a}(q). \quad (34)$$

In Eq. (33) the four  $\underline{Q}$ -vectors all have the same length  $q_*$  and only give a contribution whenever their sum is equal to zero. Therefore, one can show that  $\gamma_l^{(4)}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3, \underline{Q}_4)$  only depends on the mutual orientation of these four vectors, which can be described by the following three parameters:<sup>20</sup>

$$h_1 \equiv \frac{(\underline{Q}_1 + \underline{Q}_2)^2}{(q_*)^2}, \quad h_2 \equiv \frac{(\underline{Q}_1 + \underline{Q}_3)^2}{(q_*)^2}, \quad h_3 \equiv \frac{(\underline{Q}_1 + \underline{Q}_4)^2}{(q_*)^2}. \quad (35)$$

These three parameters are not all independent as it follows that  $h_1 + h_2 + h_3 = 4$ . Thus Eq. (32) can be rewritten as

$$\frac{F_L^{(4)}}{V} \equiv \frac{A^4}{6n^2} \sum_{\underline{Q}_1 \in H} \sum_{\underline{Q}_2 \in H} \sum_{\underline{Q}_3 \in H} \sum_{\underline{Q}_4 \in H} e^{i(\varphi_{\underline{Q}_1} + \varphi_{\underline{Q}_2} + \varphi_{\underline{Q}_3} + \varphi_{\underline{Q}_4})} \times \gamma_l^{(4)}(q_*; h_1, h_2, h_3), \quad (36)$$

with  $\gamma_l^{(4)}(q_*; h_1, h_2, h_3)$  a complete symmetric function of its last three arguments. If two of these arguments are zero, then the corresponding set of vectors has the form  $(\underline{Q}, \underline{Q}, -\underline{Q}, -\underline{Q})$  and if only one argument is zero, it has the form  $(\underline{Q}_1, -\underline{Q}_1, \underline{Q}_2, -\underline{Q}_2)$ . The corresponding phase factor for these situations,  $\gamma_l^{(4)}(q_*; 0, 0, 4)$  and  $\gamma_l^{(4)}(q_*; 0, h, 4-h)$ , is always equal to +1, as opposite  $\underline{Q}$ -vectors have opposite phases. A phase factor equal to -1 can only occur when all three  $h$ -parameters are nonzero. For the BCC structure one can show, using Eq. (24), that Eq. (36) becomes

$$\frac{F_L^{(4)}}{V} \equiv A^4 \left\{ \frac{1}{24} \gamma_l^{(4)}(q_*; 0, 0, 4) + \frac{1}{3} \gamma_l^{(4)}(q_*; 0, 1, 3) + \frac{1}{6} \gamma_l^{(4)}(q_*; 1, 1, 2) + \frac{1}{12} \gamma_l^{(4)}(q_*; 0, 2, 2) \right\}. \quad (37)$$

From the structure of Eq. (33) it is clear that  $\gamma_l^{(4)}(q_*; h_1, h_2, h_3)$  can be written as

$$\gamma_l^{(4)}(q_*; h_1, h_2, h_3) \equiv -\Phi_1(q_*; h_1, h_2, h_3) + \Phi_2(q_*; h_1) + \Phi_2(q_*; h_2) + \Phi_2(q_*; h_3) \quad (38)$$

with

$$\Phi_1(q_*; h_1, h_2, h_3) \equiv \sum_{\alpha\beta\gamma\delta} \bar{g}_{\alpha\beta\gamma\delta}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3, \underline{Q}_4) \times z_{\alpha l}(q_*) z_{\beta l}(q_*) z_{\gamma l}(q_*) z_{\delta l}(q_*) \quad (39)$$

and

$$\begin{aligned} \Phi_2(q_*; h \neq 0) &\equiv \sum_{\alpha\beta\gamma\delta} \sum_{\lambda\nu} \bar{g}_{\alpha\beta\lambda}(q_*, q_*, \sqrt{h}q_*) \\ &\times \bar{g}_{\gamma\delta\nu}(q_*, q_*, \sqrt{h}q_*) [\bar{g}_{\lambda\nu}^{-1}(\sqrt{h}q_*) \\ &- Y_{\lambda\nu}^l(\sqrt{h}q_*)] z_{\alpha l}(q_*) z_{\beta l}(q_*) z_{\gamma l}(q_*) \\ &\times z_{\delta l}(q_*), \end{aligned}$$

$$\Phi_2(q_*; 0)$$

$$\equiv \sum_{\alpha\beta\gamma\delta} \overline{g_{\alpha\beta}(q_*) g_{\gamma\delta}(q_*)} z_{\alpha l}(q_*) z_{\beta l}(q_*) z_{\gamma l}(q_*) z_{\delta l}(q_*), \quad (40)$$

where  $\bar{g}_{\alpha\beta\gamma}(q_*, q_*, \sqrt{h}q_*)$  is a shorthand notation for  $\bar{g}_{\alpha\beta\gamma}(\underline{Q}_1, \underline{Q}_2, -\underline{Q}_1 - \underline{Q}_2)$  with  $|\underline{Q}_1| = |\underline{Q}_2| = q_*$  and  $\sphericalangle(\underline{Q}_1, \underline{Q}_2)$  given by  $\cos[\sphericalangle(\underline{Q}_1, \underline{Q}_2)] \equiv h/2 - 1$ . The function  $\Phi_1(q_*; h_1, h_2, h_3)$  can still be simplified further by using Eqs. (10) and (13), which leads to

$$\begin{aligned} \Phi_1(q_*; h_1, h_2, h_3) &\equiv \sum_{\alpha\beta\gamma\delta} \sum_s \rho_s \int_0^{N_s} di \int_0^{N_s} dj \int_0^{N_s} dk \int_0^{N_s} dl \sigma_{si}^\alpha \sigma_{sj}^\beta \sigma_{sk}^\gamma \sigma_{sl}^\delta \\ &\times e^{a^2/6\{\underline{Q}_1 \cdot \underline{Q}_2 |i-j| + \underline{Q}_1 \cdot \underline{Q}_3 |i-k| + \underline{Q}_1 \cdot \underline{Q}_4 |i-l|\}} \\ &\times e^{(a^2/6)\{\underline{Q}_2 \cdot \underline{Q}_3 |j-k| + \underline{Q}_2 \cdot \underline{Q}_4 |j-l| + \underline{Q}_3 \cdot \underline{Q}_4 |k-l|\}} \\ &\times z_{\alpha l}(q_*) z_{\beta l}(q_*) z_{\gamma l}(q_*) z_{\delta l}(q_*). \end{aligned} \quad (41)$$

If we now split the quadruple integral in this expression into twenty-four nested quadruple integrals, i.e., for which the integration variables are ordered such as  $i < j < k < l$  etc., one finds after some rearrangements that this set of nested quadruple integrals can be divided into three subsets consisting of eight nested quadruple integrals, such that all nested quadruple integrals within the same subset give the same contribution to  $\Phi_1(q_*; h_1, h_2, h_3)$ . Thus it follows that:

$$\begin{aligned} \Phi_1(q_*; h_1, h_2, h_3) &\equiv 8 \sum_{i=1}^3 \sum_{\alpha\beta\gamma\delta} \sum_s \rho_s \int_0^{N_s} di \int_i^{N_s} dj \int_j^{N_s} dk \int_k^{N_s} dl \sigma_{si}^\alpha \sigma_{sj}^\beta \sigma_{sk}^\gamma \sigma_{sl}^\delta \\ &\times e^{-a^2/6\{(j-i)q_*^2 + (k-j)h_1 q_*^2 + (l-k)h_2 q_*^2\}} z_{\alpha l}(q_*) z_{\beta l}(q_*) z_{\gamma l}(q_*) z_{\delta l}(q_*) \\ &\equiv \Phi_1(q_*; h_1) + \Phi_1(q_*; h_2) + \Phi_1(q_*; h_3). \end{aligned} \quad (42)$$

By a similar split and rearrangement one can show that  $\Phi_2(q_*; 0)$  Eq. (40) is equal to  $\Phi_1(q_*; 0) + 2\Phi_1(q_*; 2)$ , so that finally  $\gamma_\mu^{(4)}(q_*; h_1, h_2, h_3)$  can be written as

$$\gamma_{\mu}^{(4)}(q_*; h_1, h_2, h_3) \equiv \Phi(q_*; h_1) + \Phi(q_*; h_2) + \Phi(q_*; h_3), \quad (43)$$

where  $\Phi(q_*; h)$  is defined by

$$\Phi(q_*; h) \equiv -\Phi_1(q_*; h) + \Phi_2(q_*; h), \quad (h \neq 0), \quad (44)$$

$$\Phi(q_*; 0) \equiv 2\Phi_1(q_*; 2).$$

With this last result, Eq. (37) for the BCC structure reduces to

$$\begin{aligned} \frac{F_L^{(4)}}{V} &\equiv A^4 \left\{ \frac{1}{2} \Phi(q_*; 0) + \frac{2}{3} \Phi(q_*; 1) \right. \\ &\quad \left. + \frac{1}{3} \Phi(q_*; 2) + \frac{1}{3} \Phi(q_*; 3) + \frac{1}{24} \Phi(q_*; 4) \right\} \\ &\equiv A^4 \left\{ -\frac{2}{3} \Phi_1(q_*; 1) + \frac{2}{3} \Phi_1(q_*; 2) - \frac{1}{3} \Phi_1(q_*; 3) \right. \\ &\quad \left. - \frac{1}{24} \Phi_1(q_*; 4) + \frac{2}{3} \Phi_2(q_*; 1) \right. \\ &\quad \left. + \frac{1}{3} \Phi_2(q_*; 2) + \frac{1}{3} \Phi_2(q_*; 3) + \frac{1}{24} \Phi_2(q_*; 4) \right\}. \quad (45) \end{aligned}$$

If we consider all the contributions to the Landau free energy in the first harmonic approximation separately, it is clear that what is left is to determine the following four functions of  $q$  and/or  $h$ :  $\bar{g}_{\alpha\beta}(q)$ ,  $\gamma_1^{(3)}(q)$ ,  $\bar{g}_{\alpha\beta\gamma}(q, q, \sqrt{h}q)$ , and  $\Phi_1(q; h)$ . Other such functions which appear in the free energy, such as  $\gamma_1^{(2)}(q)$ ,  $z_{\alpha l}(q)$ , and  $\Phi_2(q; h)$ , can be determined once we know the first four. Quantities like  $\zeta$  Eq. (29) and the phase-factors in Eq. (36) have to be determined for each low-symmetry phase separately. In the rest of this section we will determine  $\bar{g}_{\alpha\beta}(q)$ ,  $\gamma_1^{(3)}(q)$ ,  $\bar{g}_{\alpha\beta\gamma}(q, q, \sqrt{h}q)$ , and  $\Phi_1(q; h)$  for the particular system of interest, i.e., the melt of multiple segment-type statistical multiblock copolymers with arbitrary block molecular weight distributions.

### A. Determination of $\bar{g}_{\alpha\beta}(q)$

The first quantity we will determine is the second-order ideal intrachain correlation function  $\bar{g}_{\alpha\beta}(q)$ , which is defined in Eqs. (10) and (11). This correlation function can be written as

$$\bar{g}_{\alpha\beta}(q) \equiv \bar{g}_{\alpha\beta}^o(q) + \bar{g}_{\beta\alpha}^o(q),$$

with

$$\bar{g}_{\alpha\beta}^o(q) \equiv \sum_s \rho_s \int_0^{N_s} dj \int_j^{N_s} dj' \sigma_{sj}^{\alpha} \sigma_{sj'}^{\beta} e^{-(a^2 q^2/6)(j'-j)}. \quad (46)$$

The meaning of  $\bar{g}_{\alpha\beta}^o(q)$  is that of the Fourier-transform of the function that describes the spatial correlation between an  $\alpha$ -segment and a  $\beta$ -segment in the copolymer melt in the absence of interactions between the segments, i.e., in the ideal copolymer melt where the chains obey *random walk statistics*. In Eq. (46) the double integral along the chains has been split in two in such a way that the continuous integration-variables  $j$  and  $j'$  have become ordered. This explains the superscript  $o$  in  $\bar{g}_{\alpha\beta}^o(q)$ . If we now substitute Eq. (8) in Eq. (46) and perform the integrations, it is easy to see that this  $\bar{g}_{\alpha\beta}^o(q)$  can be written as the sum of following two parts:

$$\begin{aligned} \bar{g}_{\alpha\beta}^o(y) &\equiv \delta_{\alpha\beta} \sum_s \rho_s \sum_{k=1}^{N_b} \delta_{\alpha, \alpha_k} \int_{n_{k-1}^c}^{n_k^c} dj \int_j^{n_k^c} dj' e^{-y(j'-j)} \\ &\quad + \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \delta_{\alpha, \alpha_k} \delta_{\beta, \alpha_l} \\ &\quad \times \int_{n_{k-1}^c}^{n_k^c} dj \int_{n_{l-1}^c}^{n_l^c} dj' e^{-y(j'-j)}, \quad (47) \end{aligned}$$

where we have introduced the cumulative length  $n_k^c \equiv \sum_{l=1}^k n_l$  and have changed to the variable  $y \equiv a^2 q^2/6$ . The interpretation of this last result is evident. The first part is the contribution to the  $\alpha\beta$ -correlation from the case where an  $\alpha$ -segment  $j$  and a  $\beta$ -segment  $j'$  are located in the same block, while the second part arises from those cases where these segments are located in different blocks with  $j < j'$ . We will now consider each contribution separately. Let us begin with the first term. By shifting the integration variables over  $n_{k-1}^c$  the double integral can easily be calculated

$$\int_0^{n_k} dj \int_j^{n_k} dj' e^{-y(j'-j)} = \frac{n_k}{y} - \frac{1 - e^{-yn_k}}{y^2}, \quad (48)$$

and, therefore, by using Eq. (5) and the definition of the ‘‘sum over  $s$ ’’ [see Eq. (6)], this contribution to Eq. (47) can be written as

$$\begin{aligned} &\delta_{\alpha\beta} \sum_s \rho_s \sum_{k=1}^{N_b} \delta_{\alpha, \alpha_k} \left( \frac{n_k}{y} - \frac{1 - e^{-yn_k}}{y^2} \right) \\ &\equiv \frac{\delta_{\alpha\beta}}{N_b \sum_{\gamma} w_{\gamma}^0} \sum_{k=1}^{N_b} \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_{N_b}} \int_0^{\infty} dn_1 \cdots \\ &\quad \times \int_0^{\infty} dn_{N_b} w_{\alpha_1}^0 P_{\alpha_1}(n_1) w_{\alpha_1 \alpha_2} \cdots w_{\alpha_{N_b-1} \alpha_{N_b}} P_{\alpha_{N_b}}(n_{N_b}) \\ &\quad \times \left[ \delta_{\alpha, \alpha_k} \left( \frac{n_k}{y} - \frac{1 - e^{-yn_k}}{y^2} \right) \right]. \quad (49) \end{aligned}$$

Now by using the property that each row in the matrix of transition probabilities Eq. (4) adds up to one and the fact that each block length distribution is normalized [Eq. (3)], it follows that for a given term in the sum over the  $N_b$  blocks,

say the  $k$ th one, every  $P_{\alpha_l}(n_l)$  with  $l \neq k$  will be integrated to one and every  $w_{\alpha_{l-1}\alpha_l}$  with  $l > k$  will be summed to one. Therefore, we end up with

$$\frac{\delta_{\alpha\beta}}{N_b \sum_{\gamma} w_{\gamma}^0 \bar{n}_{\gamma}} \sum_{k=1}^{N_b} \left\{ \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_{k-1}} w_{\alpha_1}^0 w_{\alpha_1\alpha_2} \cdots w_{\alpha_{k-1}\alpha} \right\} \times \int_0^{\infty} dn P_{\alpha}(n) \left( \frac{n}{y} - \frac{1 - e^{-yn}}{y^2} \right) = \delta_{\alpha\beta} \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left( \frac{\bar{n}_{\alpha}}{y} - \frac{1 - \hat{\alpha}(y)}{y^2} \right)$$

$$\text{with } \hat{\alpha}(y) \equiv \int_0^{\infty} dn e^{-yn} P_{\alpha}(n), \tag{50}$$

where we have made use of Eq. (7) in combination with the fact that the invariant probability  $w_{\beta}^0$  satisfies  $\sum_{\gamma} w_{\gamma}^0 w_{\gamma\beta} \equiv w_{\beta}^0$ , so that each term in the sum over the  $N_b$  blocks simply gives  $w_{\alpha}^0$ , and the whole sum, therefore,  $N_b w_{\alpha}^0$ . This leaves us with the calculation of the second contribution to Eq. (47), which is slightly more involved. By a similar shift of the integration variables and a little algebra it follows that this part can be transformed into:

$$\begin{aligned} & \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \delta_{\alpha,\alpha_k} \delta_{\beta,\alpha_l} \int_0^{n_k} dj \int_0^{n_l} dj' e^{-y(j'-j+n_{l-1}^c-n_{k-1}^c)} \\ &= \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \delta_{\alpha,\alpha_k} \delta_{\beta,\alpha_l} e^{-y(n_{l-1}^c-n_k^c)} \left[ \int_0^{n_k} dj e^{-y(n_k-j)} \right] \left[ \int_0^{n_l} dj' e^{-yj'} \right] \\ &= \frac{1}{N_b \sum_{\gamma} w_{\gamma}^0 \bar{n}_{\gamma}} \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_{N_b}} \int_0^{\infty} dn_1 \cdots \int_0^{\infty} dn_{N_b} w_{\alpha_1}^0 P_{\alpha_1}(n_1) w_{\alpha_1\alpha_2} \cdots w_{\alpha_{N_b-1}\alpha_{N_b}} P_{\alpha_{N_b}}(n_{N_b}) \\ & \times \left\{ \delta_{\alpha,\alpha_k} \delta_{\beta,\alpha_l} \left( \frac{1 - e^{-yn_l}}{y} \right) (e^{-y \sum_{m=k+1}^{l-1} n_m}) \left( \frac{1 - e^{-yn_k}}{y} \right) \right\}. \end{aligned} \tag{51}$$

From the structure of this last expression it is clear that in the contribution for a given pair  $l$  and  $k$  in the double sum over the blocks, all block length distributions  $P_{\alpha_m}(n_m)$  with  $m < k$  and  $m > l$  will be integrated again to one, and all  $w_{\alpha_{m-1}\alpha_m}$  with  $m > l$  summed again to one. Therefore, this last result can be rewritten as

$$\begin{aligned} & \frac{1}{N_b \sum_{\gamma} w_{\gamma}^0 \bar{n}_{\gamma}} \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \left\{ \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_{k-1}} w_{\alpha_1}^0 w_{\alpha_1\alpha_2} \cdots w_{\alpha_{k-1}\alpha} \right\} \\ & \times \left[ \int_0^{\infty} dn_k \left( \frac{1 - e^{-yn_k}}{y} \right) P_{\alpha}(n_k) \right] \sum_{\alpha_{k+1}} w_{\alpha\alpha_{k+1}} \left[ \int_0^{\infty} dn_{k+1} e^{-yn_{k+1}} P_{\alpha_{k+1}}(n_{k+1}) \right] \cdots \\ & \times \sum_{\alpha_{l-1}} w_{\alpha_{l-2}\alpha_{l-1}} \left[ \int_0^{\infty} dn_{l-1} e^{-yn_{l-1}} P_{\alpha_{l-1}}(n_{l-1}) \right] w_{\alpha_{l-1}\beta} \left[ \int_0^{\infty} dn_l \left( \frac{1 - e^{-yn_l}}{y} \right) P_{\beta}(n_l) \right], \end{aligned} \tag{52}$$

which is equal to

$$\begin{aligned} & \frac{1}{N_b \sum_{\gamma} w_{\gamma}^0 \bar{n}_{\gamma}} \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \left( \frac{1 - \hat{\alpha}(y)}{y} \right) \left( \frac{1 - \hat{\beta}(y)}{y} \right) \sum_{\alpha_{k+1}} \sum_{\alpha_{k+2}} \cdots \sum_{\alpha_{l-1}} w_{\alpha}^0 [w_{\alpha\alpha_{k+1}} \hat{\alpha}_{k+1}(y)] \\ & \times [w_{\alpha_{k+1}\alpha_{k+2}} \hat{\alpha}_{k+2}(y)] \cdots [w_{\alpha_{l-2}\alpha_{l-1}} \hat{\alpha}_{l-1}(y)] w_{\alpha_{l-1}\beta} \\ & \equiv \frac{f_{\alpha}}{N_b \bar{n}_{\alpha}} \left( \frac{1 - \hat{\alpha}(y)}{y} \right) \left( \frac{1 - \hat{\beta}(y)}{y} \right) \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} [\underline{\Omega}(y)^{l-k-1} \cdot \underline{w}]_{\alpha\beta} \equiv \frac{f_{\alpha}}{N_b \bar{n}_{\alpha}} \left( \frac{1 - \hat{\alpha}(y)}{y} \right) \left( \frac{1 - \hat{\beta}(y)}{y} \right) \sum_{k=1}^{N_b} \left[ \left\{ \sum_{j=0}^{N_b-k-1} \underline{\Omega}(y)^j \right\} \cdot \underline{w} \right]_{\alpha\beta}, \end{aligned} \tag{53}$$

where we have introduced  $\Omega_{\alpha\beta}(y) \equiv w_{\alpha\beta} \hat{\beta}(y) \equiv \sum_{\gamma} w_{\alpha\gamma} \{\hat{\gamma}(y) \delta_{\gamma\beta}\} \equiv [w \cdot \underline{L}(y)]_{\alpha\beta}$ , which by construction obeys  $|\Omega_{\alpha\beta}(y \neq 0)| < 1$ . Thus for large enough  $N_b$  this last result is approximated by

$$\frac{f_{\alpha}}{N_b \bar{n}_{\alpha}} \left( \frac{1 - \hat{\alpha}(y)}{y} \right) \left( \frac{1 - \hat{\beta}(y)}{y} \right) N_b \left[ \left\{ \sum_{j=0}^{\infty} \Omega_{\alpha\beta}(y)^j \right\} \cdot \underline{w} \right]_{\alpha\beta} \\ = \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left( \frac{1 - \hat{\alpha}(y)}{y} \right) \left( \frac{1 - \hat{\beta}(y)}{y} \right) [\{w^{-1} - \underline{L}(y)\}^{-1}]_{\alpha\beta}. \quad (54)$$

By adding Eqs. (50) and (54) we obtain the following result for  $\bar{g}_{\alpha\beta}^o(y)$  in the limit of large  $N_b$ :

$$\bar{g}_{\alpha\beta}^o(y) = \delta_{\alpha\beta} \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left( \frac{\bar{n}_{\alpha}}{y} - \frac{1 - \hat{\alpha}(y)}{y^2} \right) \\ + \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left( \frac{1 - \hat{\alpha}(y)}{y} \right) \left( \frac{1 - \hat{\beta}(y)}{y} \right) \pi_{\alpha\beta}(y), \quad (55)$$

where we have introduced the particular propagator

$$\pi_{\alpha\beta}(y) \equiv [\{w^{-1} - \underline{L}(y)\}^{-1}]_{\alpha\beta} \\ \text{with } L_{\alpha\beta}(y) \equiv \hat{\alpha}(y) \delta_{\alpha\beta}. \quad (56)$$

## B. Determination of $\gamma_l^{(3)}(q)$

The second quantity we need to determine is  $\gamma_l^{(3)}(q)$ , which is defined for  $q = q_*$  in Eq. (30). With the help of Eqs. (10) and (12) this quantity can be written as

$$\gamma_l^{(3)}(q) \equiv - \sum_{\alpha\beta\gamma} \rho_s \sum_s \rho_s \int_0^{N_s} dj_1 \int_0^{N_s} dj_2 \int_0^{N_s} dj_3 \sigma_{sj_1}^{\alpha} \sigma_{sj_2}^{\beta} \sigma_{sj_3}^{\gamma} \\ \times e^{-(1/2)(a^2 q^2/6)\{|j_1 - j_2| + |j_2 - j_3| + |j_1 - j_3|\}} z_{\alpha l}(q) \\ \times z_{\beta l}(q) z_{\gamma l}(q), \quad (57)$$

where we have made use of the fact that the three  $\underline{Q}$ -vectors in  $\bar{g}_{\alpha\beta\gamma}(\underline{Q}_1, \underline{Q}_2, \underline{Q}_3)$  form an equilateral triangle, so that  $\underline{Q}_1 \cdot \underline{Q}_2 \equiv \underline{Q}_2 \cdot \underline{Q}_3 \equiv \underline{Q}_1 \cdot \underline{Q}_3 \equiv -\frac{1}{2}q^2$  with  $|\underline{Q}_1| = |\underline{Q}_2| = |\underline{Q}_3| = q$ . As Eq. (57) involves a summation over  $\alpha$ ,  $\beta$ , and  $\gamma$  of an expression which is completely symmetric in these indices, it follows that we can split the triple integration along the chain into six triple nested integrations, which all give the same contribution to  $\gamma_l^{(3)}$ , i.e.

$$\gamma_l^{(3)}(y) \equiv -6 \sum_{\alpha\beta\gamma} \sum_s \rho_s \int_0^{N_s} dj_1 \int_{j_1}^{N_s} dj_2 \int_{j_2}^{N_s} dj_3 \sigma_{sj_1}^{\alpha} \sigma_{sj_2}^{\beta} \\ \times \sigma_{sj_3}^{\gamma} e^{-y(j_3 - j_1)} z_{\alpha l}(y) z_{\beta l}(y) z_{\gamma l}(y) \\ \equiv -6 \sum_{\alpha\beta\gamma} \bar{g}_{\alpha\beta\gamma}^o(y, y, y) z_{\alpha l}(y) z_{\beta l}(y) z_{\gamma l}(y), \quad (58)$$

where we introduced again  $y \equiv a^2 q^2/6$ . To calculate  $\bar{g}_{\alpha\beta\gamma}^o(y, y, y)$  we first substitute Eq. (8) and perform the integrations. This results in

$$\bar{g}_{\alpha\beta\gamma}^o(y, y, y) \\ = \sum_s \rho_s \sum_{k=1}^{N_b} \int_{n_{k-1}^c}^{n_k^c} dj_1 \left\{ \int_{j_1}^{n_k^c} dj_2 + \sum_{l>k}^{N_b} \int_{n_{l-1}^c}^{n_l^c} dj_2 \right\} \\ \times \left\{ \int_{j_2}^{n_l^c} dj_3 + \sum_{m>l}^{N_b} \int_{n_{m-1}^c}^{n_m^c} dj_3 \right\} \\ \times \delta_{\alpha, \alpha_k} \delta_{\beta, \alpha_l} \delta_{\gamma, \alpha_m} e^{-y(j_3 - j_1)}. \quad (59)$$

So  $\bar{g}_{\alpha\beta\gamma}^o(y, y, y)$  can be written as the sum of four contributions

$$\bar{g}_{\alpha\beta\gamma}^o(y, y, y) \equiv \delta_{\alpha\beta} \delta_{\beta\gamma} \sum_s \rho_s \sum_{k=1}^{N_b} \delta_{\alpha, \alpha_k} \int_0^{n_k} dj_1 \int_{j_1}^{n_k} dj_2 \int_{j_2}^{n_k} dj_3 e^{-y(j_3 - j_1)} \\ + \delta_{\alpha\beta} \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{m>k}^{N_b} \delta_{\alpha, \alpha_k} \delta_{\gamma, \alpha_m} \int_0^{n_k} dj_1 \int_{j_1}^{n_k} dj_2 \int_0^{n_m} dj_3 e^{-y(j_3 - j_1 + n_{m-1}^c - n_{k-1}^c)} \\ + \delta_{\beta\gamma} \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{m>k}^{N_b} \delta_{\alpha, \alpha_k} \delta_{\beta, \alpha_m} \int_0^{n_k} dj_1 \int_0^{n_m} dj_2 \int_{j_2}^{n_m} dj_3 e^{-y(j_3 - j_1 + n_{m-1}^c - n_{k-1}^c)} \\ + \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \sum_{m>l}^{N_b} \delta_{\alpha, \alpha_k} \delta_{\beta, \alpha_l} \delta_{\gamma, \alpha_m} \int_0^{n_k} dj_1 \int_0^{n_l} dj_2 \int_0^{n_m} dj_3 e^{-y(j_3 - j_1 + n_{m-1}^c - n_{k-1}^c)}, \quad (60)$$

where the original global variables  $j_1$ ,  $j_2$ , and  $j_3$  have been transformed to local block variables. By using the definition of the cumulative length  $n_k^c \equiv \sum_{l=1}^k n_l$  we can factorize the last three triple integrals in Eq. (60) into contributions from each of the separate blocks labeled from  $k$  to  $m > k$ , i.e.,

$$\int_0^{n_k} dj_1 \int_{j_1}^{n_k} dj_2 \int_0^{n_m} dj_3 e^{-y(j_3 - j_1 + n_{m-1}^c - n_{k-1}^c)} \\ = \left[ \int_0^{n_k} dj_1 \int_{j_1}^{n_k} dj_2 e^{-y(n_k - j_1)} \right] \left[ \prod_{i=k+1}^{m-1} e^{-y n_i} \right] \left[ \int_0^{n_m} dj_3 e^{-y j_3} \right] = \left[ -\frac{n_k e^{-y n_k}}{y} + \frac{1 - e^{-y n_k}}{y^2} \right] \left[ \prod_{i=k+1}^{m-1} e^{-y n_i} \right] \left[ \frac{1 - e^{-y n_m}}{y} \right], \quad (61)$$

$$\int_0^{n_k} dj_1 \int_0^{n_m} dj_2 \int_{j_2}^{n_m} dj_3 e^{-y(j_3-j_1+n_{m-1}^c-n_{k-1}^c)} = \left[ \int_0^{n_k} dj_1 e^{-y(n_k-j_1)} \right] \left[ \prod_{i=k+1}^{m-1} e^{-yn_i} \right] \left[ \int_0^{n_m} dj_2 \int_{j_2}^{n_m} dj_3 e^{-yj_3} \right]$$

$$= \left[ \frac{1-e^{-yn_k}}{y} \right] \left[ \prod_{i=k+1}^{m-1} e^{-yn_i} \right] \left[ -\frac{n_m e^{-yn_m}}{y} + \frac{1-e^{-yn_m}}{y^2} \right], \tag{62}$$

and

$$\int_0^{n_k} dj_1 \int_0^{n_l} dj_2 \int_0^{n_m} dj_3 e^{-y(j_3-j_1+n_{m-1}^c-n_{k-1}^c)}$$

$$= \left[ \int_0^{n_k} dj_1 e^{-y(n_k-j_1)} \right] \left[ \prod_{i=k+1}^{l-1} e^{-yn_i} \right] [n_l e^{-yn_l}] \left[ \prod_{i=l+1}^{m-1} e^{-yn_i} \right] \left[ \int_0^{n_m} dj_3 e^{-yj_3} \right]$$

$$= \left[ \frac{1-e^{-yn_k}}{y} \right] \left[ \prod_{i=k+1}^{l-1} e^{-yn_i} \right] [n_l e^{-yn_l}] \left[ \prod_{i=l+1}^{m-1} e^{-yn_i} \right] \left[ \frac{1-e^{-yn_m}}{y} \right]. \tag{63}$$

Finally the first triple integral in Eq. (60) only involves an nested integration over the  $k$ th block and leads to

$$\int_0^{n_k} dj_1 \int_{j_1}^{n_k} dj_2 \int_{j_2}^{n_k} dj_3 e^{-y(j_3-j_1)} = \frac{n_k(1+e^{-yn_k})}{y^2} - \frac{2(1-e^{-yn_k})}{y^3}. \tag{64}$$

Recalling again the definition of  $\rho_s$  Eq. (5) and that of the ‘‘sum over  $s$ ’’ [see Eq. (6)] it is easy to see, in analogy with Eqs. (49) and (50), that the first contribution to Eq. (60) results in

$$\delta_{\alpha\beta} \delta_{\beta\gamma} \sum_s \rho_s \sum_{k=1}^{N_b} \delta_{\alpha,\alpha_k} \left[ \frac{n_k(1+e^{-yn_k})}{y^2} - \frac{2(1-e^{-yn_k})}{y^3} \right]$$

$$\equiv \frac{\delta_{\alpha\beta} \delta_{\beta\gamma}}{N_b \sum_{\gamma} w_{\gamma}^0 \bar{n}_{\gamma}} \sum_{k=1}^{N_b} \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_{N_b}} \int_0^{\infty} dn_1 \cdots \int_0^{\infty} dn_{N_b} w_{\alpha_1}^0 P_{\alpha_1}(n_1) w_{\alpha_1 \alpha_2} \cdots w_{\alpha_{N_b-1} \alpha_{N_b}} P_{\alpha_{N_b}}(n_{N_b})$$

$$\times \left[ \delta_{\alpha,\alpha_k} \left( \frac{n_k(1+e^{-yn_k})}{y^2} - \frac{2(1-e^{-yn_k})}{y^3} \right) \right]$$

$$= \frac{\delta_{\alpha\beta} \delta_{\beta\gamma}}{N_b \sum_{\gamma} w_{\gamma}^0 \bar{n}_{\gamma}} \sum_{k=1}^{N_b} \left\{ \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_{k-1}} w_{\alpha_1}^0 w_{\alpha_1 \alpha_2} \cdots w_{\alpha_{k-1} \alpha} \right\} \int_0^{\infty} dn P_{\alpha}(n) \left( \frac{n_k(1+e^{-yn_k})}{y^2} - \frac{2(1-e^{-yn_k})}{y^3} \right)$$

$$= \delta_{\alpha\beta} \delta_{\beta\gamma} \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left[ \frac{\bar{n}_{\alpha}}{y^2} - \frac{\hat{\alpha}'(y)}{y^2} - \frac{2(1-\hat{\alpha}(y))}{y^3} \right] \quad \text{with} \quad \hat{\alpha}'(y) \equiv - \int_0^{\infty} dn n e^{-yn} P_{\alpha}(n). \tag{65}$$

The remaining three contributions to Eq. (60) can be determined using Eqs. (61)–(63) and following a similar set of steps which led from Eq. (51) to (55). The result for each contribution can simply be obtained by the following prescription. Start with the Kronecker delta with the ‘‘lowest’’ block index, i.e.,  $\delta_{\alpha,\alpha_k}$  in all three contributions. This Kronecker delta implies that the term which depends on  $n_k$  should be averaged over  $P_{\alpha}(n)$ . Then ‘‘propagate’’ to the next Kronecker delta in line by replacing for instance  $\delta_{\alpha,\alpha_k} \sum_{l>k}^{N_b} [\prod_{i=k+1}^{l-1} e^{-yn_i}] \delta_{\beta,\alpha_l}$ , in the limit of  $N_b \rightarrow \infty$ , by the propagator  $\pi_{\alpha\beta}(y)$  Eq. (56), followed by averaging the term depending on  $n_l$  over  $P_{\beta}(n)$ . Repeat if necessary this propagation step until the last Kronecker delta is encountered. Finally multiply the resulting expression by  $w_{\alpha}^0/N_b \sum_{\gamma} w_{\gamma}^0 \bar{n}_{\gamma} \equiv f_{\alpha}/N_b \bar{n}_{\alpha}$ , originating from  $\rho_s$  Eq. (5), and cancel the  $N_b$  in the denominator by the dummy sum over the blocks  $\sum_{k=1}^{N_b}$  which is still left. The final result for  $\bar{g}_{\alpha\beta\gamma}^o(y,y,y)$ , therefore, becomes

$$\bar{g}_{\alpha\beta\gamma}^o(y,y,y) = \delta_{\alpha\beta} \delta_{\beta\gamma} \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left[ \frac{\bar{n}_{\alpha}}{y^2} - \frac{\hat{\alpha}'(y)}{y^2} - \frac{2(1-\hat{\alpha}(y))}{y^3} \right] + \delta_{\alpha\beta} \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left[ \frac{\hat{\alpha}'(y)}{y} + \frac{1-\hat{\alpha}(y)}{y^2} \right] \pi_{\alpha\gamma}(y) \left[ \frac{1-\hat{\gamma}(y)}{y} \right]$$

$$+ \delta_{\beta\gamma} \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) \left[ \frac{\hat{\beta}'(y)}{y} + \frac{1-\hat{\beta}(y)}{y^2} \right] - \frac{f_{\alpha}}{\bar{n}_{\alpha}} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) [\hat{\beta}'(y)] \pi_{\beta\gamma}(y) \left[ \frac{1-\hat{\gamma}(y)}{y} \right]. \tag{66}$$

### C. Determination of $\bar{g}_{\alpha\beta\gamma}(q, q, \sqrt{h}q)$

This third-order ideal intrachain correlation function appears in the fourth-order coefficient  $\gamma_l^{(4)}(q; h_1, h_2, h_3)$  [see Eqs. (38) and (40) with  $q=q_*$ ] in the Landau free energy  $F_L$  and is a shorthand notation for  $\bar{g}_{\alpha\beta\gamma}(Q_1, Q_2, -Q_1-Q_2)$  with

$|\underline{Q}_1| = |\underline{Q}_2| = q$  and  $\sphericalangle(\underline{Q}_1, \underline{Q}_2)$  given by  $\cos[\sphericalangle(\underline{Q}_1, \underline{Q}_2)] \equiv h/2 - 1$ . As the length of  $\underline{Q}_3 \equiv -\underline{Q}_1 - \underline{Q}_2$  is given by  $\sqrt{h}q$ , it follows that  $\underline{Q}_1 \cdot \underline{Q}_2 \equiv (h/2 - 1)q^2$  and  $\underline{Q}_2 \cdot \underline{Q}_3 \equiv \underline{Q}_1 \cdot \underline{Q}_3 \equiv -(h/2)q^2$ . Thus by using Eqs. (10) and (12) and changing again to the variable  $y$ ,  $\bar{g}_{\alpha\beta\gamma}(y, y, hy) \equiv \bar{g}_{\alpha\beta\gamma}(q, q, \sqrt{h}q)$  can be written as

$$\bar{g}_{\alpha\beta\gamma}(y, y, hy) \equiv \sum_s \rho_s \int_0^{N_s} dj_1 \int_0^{N_s} dj_2 \int_0^{N_s} dj_3 \sigma_{sj_1}^\alpha \sigma_{sj_2}^\beta \sigma_{sj_3}^\gamma e^{-y\{(1-h/2)|j_1-j_2| + (h/2)|j_2-j_3| + (h/2)|j_1-j_3|\}}. \quad (67)$$

If we now split the triple integral into six triple nested integrals according to  $j_1 < j_2 < j_3$  etc., we obtain

$$\bar{g}_{\alpha\beta\gamma}(y, y, hy) \equiv \bar{g}_{\alpha\beta\gamma,1}^o(y, y, hy) + \bar{g}_{\beta\alpha\gamma,1}^o(y, y, hy) + \bar{g}_{\gamma\beta\alpha,2}^o(y, y, hy) + \bar{g}_{\gamma\alpha\beta,2}^o(y, y, hy) + \bar{g}_{\alpha\gamma\beta}^o(y, y, y) + \bar{g}_{\beta\gamma\alpha}^o(y, y, y), \quad (68)$$

where  $\bar{g}_{\alpha\gamma\beta}^o(y, y, y)$  is given by Eq. (66) with  $\beta$  and  $\gamma$  interchanged and where  $\bar{g}_{\alpha\beta\gamma,1}^o(y, y, hy)$  and  $\bar{g}_{\alpha\beta\gamma,2}^o(y, y, hy)$  are defined by

$$\bar{g}_{\alpha\beta\gamma,1}^o(y, y, hy) \equiv \sum_s \rho_s \int_0^{N_s} dj_1 \int_{j_1}^{N_s} dj_2 \int_{j_2}^{N_s} dj_3 \sigma_{sj_1}^\alpha \sigma_{sj_2}^\beta \sigma_{sj_3}^\gamma e^{-y\{j_2-j_1+h(j_3-j_2)\}} \quad (69)$$

and

$$\bar{g}_{\alpha\beta\gamma,2}^o(y, y, hy) \equiv \sum_s \rho_s \int_0^{N_s} dj_1 \int_{j_1}^{N_s} dj_2 \int_{j_2}^{N_s} dj_3 \sigma_{sj_1}^\alpha \sigma_{sj_2}^\beta \sigma_{sj_3}^\gamma e^{-y\{j_3-j_2+h(j_2-j_1)\}}. \quad (70)$$

The determination of  $\bar{g}_{\alpha\beta\gamma,1}^o(y, y, hy)$  proceeds along the same lines as that of  $\bar{g}_{\alpha\beta\gamma}^o(y, y, y)$  in the last subsection. First we substitute the expressions for the  $\sigma$ 's, Eq. (8) into Eq. (69) and perform the trivial integrations over the Heaviside step functions originating from these  $\sigma$ 's. The result is a sum of four contributions similar to Eq. (60), i.e.

$$\begin{aligned} \bar{g}_{\alpha\beta\gamma,1}^o(y, y, hy) &\equiv \delta_{\alpha\beta} \delta_{\beta\gamma} \sum_s \rho_s \sum_{k=1}^{N_b} \delta_{\alpha, \alpha_k} \int_0^{n_k} dj_1 \int_{j_1}^{n_k} dj_2 \int_{j_2}^{n_k} dj_3 e^{-y\{j_2-j_1+h(j_3-j_2)\}} \\ &+ \delta_{\alpha\beta} \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{m>k}^{N_b} \delta_{\alpha, \alpha_k} \delta_{\gamma, \alpha_m} \int_0^{n_k} dj_1 \int_{j_1}^{n_k} dj_2 \int_0^{n_m} dj_3 e^{-y\{j_2-j_1+h(j_3-j_2)+h(n_{m-1}^c - n_{k-1}^c)\}} \\ &+ \delta_{\beta\gamma} \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{m>k}^{N_b} \delta_{\alpha, \alpha_k} \delta_{\beta, \alpha_m} \int_0^{n_k} dj_1 \int_0^{n_m} dj_2 \int_{j_2}^{n_m} dj_3 e^{-y\{j_2-j_1+h(j_3-j_2)+n_{m-1}^c - n_{k-1}^c\}} \\ &+ \sum_s \rho_s \sum_{k=1}^{N_b} \sum_{l>k}^{N_b} \sum_{m>l}^{N_b} \delta_{\alpha, \alpha_k} \delta_{\beta, \alpha_l} \delta_{\gamma, \alpha_m} \int_0^{n_k} dj_1 \int_0^{n_l} dj_2 \int_0^{n_m} dj_3 e^{-y\{j_2-j_1+h(j_3-j_2)+n_{l-1}^c - n_{k-1}^c + h(n_{m-1}^c - n_{l-1}^c)\}}. \end{aligned} \quad (71)$$

Then each of the triple nested integrals is evaluated and the result for the last three of them is written as a product of terms belonging to separate blocks labeled from  $k$  to  $m > k$  [similar to Eqs. (61)–(63)]. Having derived these factorizations we can again apply the prescription, described at the end of the last subsection, to obtain the final expression for  $\bar{g}_{\alpha\beta\gamma,1}^o(y, y, hy)$ , which reads

$$\begin{aligned} \bar{g}_{\alpha\beta\gamma,1}^o(y, y, hy) &= \delta_{\alpha\beta} \delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{\bar{n}_\alpha}{hy^2} - \frac{1+h}{h^2y^3} + \frac{\hat{\alpha}(hy)}{h^2(1-h)y^3} - \frac{\hat{\alpha}(y)}{(1-h)y^3} \right] + \delta_{\alpha\beta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1}{hy^2} + \frac{\hat{\alpha}(y)}{(1-h)y^2} - \frac{\hat{\alpha}(hy)}{h(1-h)y^2} \right] \\ &\times \pi_{\alpha\gamma}(hy) \left[ \frac{1-\hat{\gamma}(hy)}{hy} \right] + \delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) \left[ \frac{1}{hy^2} + \frac{\hat{\beta}(y)}{(1-h)y^2} - \frac{\hat{\beta}(hy)}{h(1-h)y^2} \right] \\ &- \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) \left[ \frac{\hat{\beta}(hy) - \hat{\beta}(y)}{(1-h)y} \right] \pi_{\beta\gamma}(hy) \left[ \frac{1-\hat{\gamma}(hy)}{hy} \right]. \end{aligned} \quad (72)$$

We do not have to determine  $\bar{g}_{\alpha\beta\gamma,2}^o(y, y, hy)$  Eq. (70) separately, as it is easy to see that it is equal to  $\bar{g}_{\alpha\beta\gamma,1}^o(\tilde{y}, \tilde{y}, \tilde{h}\tilde{y})$  with  $\tilde{y} \equiv hy$  and  $\tilde{h} \equiv 1/h$ . This identification obviously breaks down for  $h=0$ , but this case is excluded anyhow [see Eq. (40)]. Therefore, it follows that:

$$\begin{aligned} \bar{g}_{\alpha\beta\gamma,2}^o(y,y,hy) = & \delta_{\alpha\beta}\delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{\bar{n}_\alpha}{hy^2} - \frac{1+h}{h^2y^3} + \frac{\hat{\alpha}(hy)}{h^2(1-h)y^3} - \frac{\hat{\alpha}(y)}{(1-h)y^3} \right] + \delta_{\alpha\beta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1}{hy^2} + \frac{\hat{\alpha}(y)}{(1-h)y^2} - \frac{\hat{\alpha}(hy)}{h(1-h)y^2} \right] \\ & \times \pi_{\alpha\gamma}(y) \left[ \frac{1-\hat{\gamma}(y)}{y} \right] + \delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(hy)}{hy} \right] \pi_{\alpha\beta}(hy) \left[ \frac{1}{hy^2} + \frac{\hat{\beta}(y)}{(1-h)y^2} - \frac{\hat{\beta}(hy)}{h(1-h)y^2} \right] \\ & - \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(hy)}{hy} \right] \pi_{\alpha\beta}(hy) \left[ \frac{\hat{\beta}(hy)-\hat{\beta}(y)}{(1-h)y} \right] \pi_{\beta\gamma}(y) \left[ \frac{1-\hat{\gamma}(y)}{y} \right]. \end{aligned} \tag{73}$$

This last result in combination with Eqs. (72), (66), and (68) completes the determination of  $\bar{g}_{\alpha\beta\gamma}^o(y,y,hy)$ .

### D. Determination of $\Phi_1(q;h)$

The final quantity which we need to determine is  $\Phi_1(q;h)$ , which is also part of  $\gamma_l^{(4)}(q;h_1,h_2,h_3)$  as shown in Eqs. (43) and (44). It is defined for  $q=q_*$  in Eq. (42) and can be written as

$$\Phi_1(y;h) \equiv 8 \sum_{\alpha\beta\gamma\delta} \bar{g}_{\alpha\beta\gamma\delta}^o(y;h) z_{\alpha l}(y) z_{\beta l}(y) z_{\gamma l}(y) z_{\delta l}(y) \tag{74}$$

with

$$\bar{g}_{\alpha\beta\gamma\delta}^o(y;h) \equiv \sum_s \rho_s \int_0^{N_s} dj_1 \int_{j_1}^{N_s} dj_2 \int_{j_2}^{N_s} dj_3 \int_{j_3}^{N_s} dj_4 \sigma_{sj_1}^\alpha \sigma_{sj_2}^\beta \sigma_{sj_3}^\gamma \sigma_{sj_4}^\delta e^{-y\{j_2-j_1+h(j_2-j_3)+j_3-j_4\}}. \tag{75}$$

This  $\bar{g}_{\alpha\beta\gamma\delta}^o(y;h)$  can be determined in the same way as  $\bar{g}_{\alpha\beta\gamma}^o(y,y,y)$  or  $\bar{g}_{\alpha\beta\gamma,1}^o(y,y,hy)$  in the last two subsections, albeit at the expense of a bit more algebra. For instance when the expressions for the  $\sigma$ 's (8) are substituted in Eq. (75) and we integrate over the Heaviside step-functions appearing in these  $\sigma$ 's, we end up with the following result:

$$\begin{aligned} \bar{g}_{\alpha\beta\gamma\delta}^o(y;h) \equiv & \sum_s \rho_s \sum_{k=1}^{N_b} \int_{n_{k-1}^c}^{n_k^c} dj_1 \left\{ \int_{j_1}^{n_k^c} dj_2 + \sum_{l>k}^{N_b} \int_{n_{l-1}^c}^{n_l^c} dj_2 \right\} \left\{ \int_{j_2}^{n_l^c} dj_3 + \sum_{m>l}^{N_b} \int_{n_{m-1}^c}^{n_m^c} dj_3 \right\} \\ & \times \left\{ \int_{j_3}^{n_m^c} dj_4 + \sum_{p>m}^{N_b} \int_{n_{p-1}^c}^{n_p^c} dj_4 \right\} \delta_{\alpha,\alpha_k} \delta_{\beta,\alpha_l} \delta_{\gamma,\alpha_m} \delta_{\delta,\alpha_p} e^{-y\{j_2-j_1+h(j_2-j_3)+j_3-j_4\}}, \end{aligned} \tag{76}$$

which leads to a sum of eight contributions instead of six as in Eq. (60) or Eq. (71). In evaluating this quantity we have to consider the situation where  $h$  is equal to 1 separately, because in that case the argument of the exponential does not depend on  $j_3$ . We can determine  $\bar{g}_{\alpha\beta\gamma\delta}^o(y;h)$  for general  $h$  and subsequently take the limit of  $h \rightarrow 1$ , but it is just as easy to take  $h = 1$  in Eq. (76) and redo the calculation. The result for  $h \neq 1$  in the limit of  $N_b \rightarrow \infty$  reads

$$\begin{aligned} \bar{g}_{\alpha\beta\gamma\delta}^o(y;h) = & \delta_{\alpha\beta}\delta_{\beta\gamma}\delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{\bar{n}_\alpha}{hy^3} - \frac{1+2h}{h^2y^4} + \frac{\hat{\alpha}(hy)}{h^2(1-h)^2y^4} - \frac{(3-2h)\hat{\alpha}(y)}{(1-h)^2y^4} + \frac{\hat{\alpha}'(y)}{(1-h)y^3} \right] + \delta_{\alpha\beta}\delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1}{hy^3} \right. \\ & - \frac{\hat{\alpha}(hy)}{h(1-h)^2y^3} + \frac{(2-h)\hat{\alpha}(y)}{(1-h)^2y^3} - \frac{\hat{\alpha}'(y)}{(1-h)y^2} \left. \right] \pi_{\alpha\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right] + \delta_{\alpha\beta}\delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1}{hy^2} - \frac{\hat{\alpha}(hy)}{h(1-h)y^2} \right. \\ & + \frac{\hat{\alpha}(y)}{(1-h)y^2} \left. \right] \pi_{\alpha\gamma}(hy) \left[ \frac{1}{hy^2} - \frac{\hat{\gamma}(hy)}{h(1-h)y^2} + \frac{\hat{\gamma}(y)}{(1-h)y^2} \right] + \delta_{\beta\gamma}\delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) \left[ \frac{1}{hy^3} - \frac{\hat{\beta}(hy)}{h(1-h)^2y^3} \right. \\ & + \frac{(2-h)\hat{\beta}(y)}{(1-h)^2y^3} - \frac{\hat{\beta}'(y)}{(1-h)y^2} \left. \right] + \delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) \left[ \frac{\hat{\beta}(hy)-\hat{\beta}(y)}{(1-h)y} \right] \pi_{\beta\gamma}(hy) \left[ \frac{1}{hy^2} - \frac{\hat{\gamma}(hy)}{h(1-h)y^2} \right. \\ & + \frac{\hat{\gamma}(y)}{(1-h)y^2} \left. \right] + \delta_{\alpha\beta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1}{hy^2} - \frac{\hat{\alpha}(hy)}{h(1-h)y^2} + \frac{\hat{\alpha}(y)}{(1-h)y^2} \right] \pi_{\alpha\gamma}(hy) \left[ \frac{\hat{\gamma}(hy)-\hat{\gamma}(y)}{(1-h)y} \right] \pi_{\gamma\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right] \\ & + \delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) \left[ \frac{\hat{\beta}(hy)}{(1-h)^2y^2} - \frac{\hat{\beta}(y)}{(1-h)^2y^2} + \frac{\hat{\beta}'(y)}{(1-h)y} \right] \pi_{\beta\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right] \\ & + \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) \left[ \frac{\hat{\beta}(hy)-\hat{\beta}(y)}{(1-h)y} \right] \pi_{\beta\gamma}(hy) \left[ \frac{\hat{\gamma}(hy)-\hat{\gamma}(y)}{(1-h)y} \right] \pi_{\gamma\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right], \end{aligned} \tag{77}$$

and for  $h = 1$



$$\begin{aligned}
\bar{g}_{\alpha\beta\gamma\delta}^o(y;1) = & \delta_{\alpha\beta}\delta_{\beta\gamma}\delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{\bar{n}_\alpha}{y^3} - \frac{3(1-\hat{\alpha}(y))}{y^4} - \frac{2\hat{\alpha}'(y)}{y^3} + \frac{\hat{\alpha}''(y)}{2y^2} \right] + \delta_{\alpha\beta}\delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y^3} + \frac{\hat{\alpha}'(y)}{y^2} - \frac{\hat{\alpha}''(y)}{2y} \right] \\
& \times \pi_{\alpha\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right] + \delta_{\alpha\beta}\delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y^2} + \frac{\hat{\alpha}'(y)}{y} \right] \pi_{\alpha\gamma}(y) \left[ \frac{1-\hat{\gamma}(y)}{y^2} + \frac{\hat{\gamma}'(y)}{y} \right] + \delta_{\beta\gamma}\delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \\
& \times \pi_{\alpha\beta}(y) \left[ \frac{1-\hat{\beta}(y)}{y^3} + \frac{\hat{\beta}'(y)}{y^2} - \frac{\hat{\beta}''(y)}{2y} \right] - \delta_{\gamma\delta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) [\hat{\beta}'(y)] \pi_{\beta\gamma}(y) \left[ \frac{1-\hat{\gamma}(y)}{y^2} + \frac{\hat{\gamma}'(y)}{y} \right] \\
& - \delta_{\alpha\beta} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y^2} + \frac{\hat{\alpha}'(y)}{y} \right] \pi_{\alpha\gamma}(y) [\hat{\gamma}'(y)] \pi_{\gamma\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right] + \delta_{\beta\gamma} \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \\
& \times \pi_{\alpha\beta}(y) \left[ \frac{1}{2} \hat{\beta}''(y) \right] \pi_{\beta\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right] + \frac{f_\alpha}{\bar{n}_\alpha} \left[ \frac{1-\hat{\alpha}(y)}{y} \right] \pi_{\alpha\beta}(y) [\hat{\beta}'(y)] \pi_{\beta\gamma}(y) [\hat{\gamma}'(y)] \pi_{\gamma\delta}(y) \left[ \frac{1-\hat{\delta}(y)}{y} \right].
\end{aligned} \tag{78}$$

#### IV. CONCLUDING REMARKS

Summarizing, in this work we developed a Landau theory which can be used to determine the phase behavior (stability of possible microphases) of melts belonging to a very general class of statistical multiblock copolymers, referred to as multiple segment-type statistical multiblock copolymers, within the weak segregation regime (WSR). This class of copolymers, which is sufficiently general to cover all industrial relevant bulk statistical multiblock copolymers such as all known thermoplastic elastomers, is characterized by chains containing a large number of blocks, of which there are  $M \geq 2$  chemically different types. Each chemically different type of block is assumed to have a (normalized) molecular weight distribution  $P_\alpha(n)$  ( $\alpha = 1, \dots, M$ ) which can have any shape. The possible sequences of blocks which are encountered in these copolymer chains are, as far as their type is concerned, described by a first-order Markov process, i.e., by a matrix of transition probabilities  $\underline{w}$  Eq. (4). Furthermore there is no correlation in length (molecular weight) between different blocks within a copolymer chain, nor between blocks belonging to different chains. As blocks are sequences of segments, there are  $M$  chemically different types of segments present in the system. Interactions between unlike segments within a chain or between unlike segments belonging to different chains are taken to be pairwise and described in the usual way by a set of  $\frac{1}{2}M(M-1)$  Flory  $\chi$ -parameters. As the melt is assumed to be incompressible, this Landau theory is formulated in terms of  $M-1$  independent segmental order-parameter fields  $m_\alpha(\underline{x})$  ( $\alpha = 1, \dots, M-1$ ). These segmental order-parameter fields are coarse grained deviations of microscopic segment densities from their values in the homogeneous state. In the WSR, i.e., just inside the inhomogeneous region in parameter space where the segmental order-parameter fields are still "small," the Landau free energy  $F_L$  can be written as a functional Taylor expansion in these fields, or more precisely their Fourier-transforms  $m_\alpha(\underline{q})$  ( $\alpha = 1, \dots, M-1$ ). These segmental order-parameter fields can be approximated in the WSR by simple sinusoidal function of position in real space. This approximation is known as the first harmonic approximation (FHA).

The coefficients of  $F_L$  in this FHA are known as vertices and the main object of this work was to determine these vertices. This can be done analytically as these vertices can be written in terms of so-called ideal intrachain correlation functions, which measure spatial correlations in density of the various types of segments in the ideal copolymer melt, i.e., when the interactions between the different types of segments have been switched off.

The general expression of this Landau free energy  $F_L$  was derived in Appendix A using a coarse grained model for a general copolymer melt by methods of statistical mechanics. It involves the most general description of a polymer melt in that it encompasses all possible regular and statistical copolymers, including homopolymers and all possible blends. This derivation is a generalization of the one given by Fredrickson *et al.*<sup>2</sup> for the binary correlated random copolymer system and avoids the use of replica methods to cope with the quenched disorder in the copolymer chains.

As the current theory is genuine mean-field theory, fluctuations in the various order-parameter fields are neglected. It is known, however, that these fluctuations are important in certain statistical multiblock copolymers.<sup>9</sup> Thus it is to be expected that this will also be the case for the more general class of statistical multiblock copolymers which is considered in this work. These so-called fluctuation corrections will be considered in future work.

#### ACKNOWLEDGMENTS

H.J.A. and G. ten B. gratefully acknowledge Professor I. Erukhimovich, Moscow State University, for stimulating discussions on this work. J.J.M.S. likes to thank the board of DSM Research for their permission to publish this work. All three authors would like to thank the referee for his comments concerning the applicability of the first harmonic approximation.

#### APPENDIX A: FORMAL DERIVATION OF A LANDAU FREE ENERGY FOR A GENERAL COPOLYMER MELT

In this Appendix we will present a formal derivation of a Landau free energy for a general copolymer melt. General in

the sense that the copolymer chains may consist of arbitrary sequences of monomers or segments of which there are  $M$  chemically different sorts present. So, both the composition distribution and the sequence distribution as well as the overall length (molecular weight) distribution of the system are left arbitrary. This encompasses all possible regular and statistical copolymer systems (binary, ternary, etc.), but also homopolymers and all conceivable blends of these systems (homopolymer–homopolymer, homopolymer–copolymer, etc.). A related derivation for copolymer systems for which the sequence distribution of the segments is described by Markovian statistics has been given by Panyukov and Kuchanov,<sup>3</sup> but in contrast to this derivation our derivation does not rely upon the use of the replica method<sup>22</sup> and is more general as far as the sequence distribution of the segments is concerned. In fact our derivation is a generalization of the one given by Fredrickson *et al.*<sup>2</sup> for the binary correlated random copolymer system.

To describe this general copolymer melt we will employ the typical coarse graining one usually encounters in polymer physics.<sup>18</sup> Consider a melt of  $n_c$  copolymer chains in a volume  $V$ . As these chains consist of arbitrary sequences of up to  $M$  chemically different types of monomers, the number of possible chains is astronomically large. To denote the various different species of chains present in the system, we will use the label  $s$ . Each chain belonging to species  $s$ , of which there are  $n_s$  present, will consist of  $N_s$  monomers or segments. A *segment*, also and interchangeably referred to as a *monomer*, consists of a piece of the real polymer chain (a number of real monomers) chosen in such a way that the chain will behave as random walk on the scale of such a segment. In other words at that scale the chain will appear to be *flexible*, whereas at smaller scales it will be *stiff*. These  $M$  chemically different segments will be labeled by Greek lowercase symbols  $\alpha, \beta$ , etc. running from 1 to  $M$  and we will assume without loss of generality that the statistical segment lengths (Kuhnian lengths) of these various segments are all equal and denoted by  $a$ . To specify a given chain species  $s$ , Ising-type variables  $\sigma_{si}^\alpha$  will be introduced with  $\alpha = 1, \dots, M$  and  $i = 1, \dots, N_s$  in such a way that  $\sigma_{si}^\alpha \equiv 1$  when segment  $i$  is of type  $\alpha$  and  $\sigma_{si}^\alpha \equiv 0$  otherwise. The conformations of the  $n_s$  chains belonging to species  $s$  will be specified by the begin and the end positions of the corresponding segments that make up these chains, i.e., the set of three-dimensional vectors  $\{\mathbf{R}_{mi}^s\}_{mi}$  with  $m = 1, \dots, n_s$  defined with respect to some origin  $O$  in  $V$ . The total set of these vectors, i.e.,  $\{\mathbf{R}_{mi}^s\}_{smi}$  defines a configurational *microstate* of the whole system. Such a microstate will be denoted by  $\gamma$ . A function  $G$  which depends on these microstates, i.e., a so-called *state variable*, will be written as  $\hat{G} \equiv G(\gamma)$ . Examples of important state variables which we will need later on are the *microscopic  $\alpha$ -segment density*  $\hat{\rho}_\alpha(\underline{x})$ , defined for each  $\underline{x} \in V$  by

$$\hat{\rho}_\alpha(\underline{x}) \equiv \sum_{smi} \sigma_{si}^\alpha \delta(\underline{x} - \mathbf{R}_{mi}^s), \quad (\text{A1})$$

and the *overall microscopic segment density*  $\hat{\rho}(\underline{x})$  through

$$\hat{\rho}(\underline{x}) \equiv \sum_\alpha \hat{\rho}_\alpha(\underline{x}) = \sum_{smi} \delta(\underline{x} - \mathbf{R}_{mi}^s). \quad (\text{A2})$$

By integrating these densities over  $V$  we obtain, respectively, the total number of  $\alpha$ -segments  $N_\alpha$  and the overall number of segments  $N$  in the system. This last number can be either written as  $\sum_\alpha N_\alpha$  or as  $\sum_s n_s N_s$ . Thus the fraction of  $\alpha$ -segments is given by  $f_\alpha \equiv N_\alpha/N$ . Without loss of generality we will choose our length scale in such a way that each segment has a unit volume and therefore that  $N \equiv V$ . In that case it follows that:

$$\frac{1}{V} \int_V d^3x \hat{\rho}(\underline{x}) \equiv 1, \quad (\text{A3})$$

and that  $f_\alpha$  can be written as

$$f_\alpha \equiv \frac{1}{V} \int_V d^3x \hat{\rho}_\alpha(\underline{x}). \quad (\text{A4})$$

In order to account approximately for the effect of excluded volume due to the repulsive nature of the intrachain and interchain potentials at short distances, we will assume that the system is *incompressible*, i.e., that the overall microscopic segment density is not only equal to 1 “globally,” as in Eq. (A3), but also “locally,” that is  $\hat{\rho}(\underline{x}) \equiv 1, \forall \underline{x} \in V$ . As our aim is to derive a Landau free energy for this copolymer melt of  $M$  quasi-components,<sup>3</sup> we need to define a set of  $M$  *order parameters* or actually  $M$  *order-parameter fields* to describe the possible *inhomogeneous phases* of the system and to be able to calculate their free energy. These order parameter fields can be defined by coarse graining the following set of *microscopic order-parameter fields*

$$\hat{\psi}_\alpha(\underline{x}) \equiv \hat{\rho}_\alpha(\underline{x}) - f_\alpha, \quad (\alpha = 1, \dots, M). \quad (\text{A5})$$

It is clear that due to the incompressibility assumption only  $M - 1$  of these fields will be independent, as it follows that:

$$\sum_\alpha \hat{\psi}_\alpha(\underline{x}) \equiv 0. \quad (\text{A6})$$

The interactions between the various segments in this copolymer melt can be described in terms of these microscopic order-parameter fields. This can be shown in the following way. Under the assumption that segment–segment interactions are pairwise additive, the total interaction energy  $\hat{U}$  of the system is given by

$$\hat{U} \equiv \frac{1}{2} \sum_{\alpha\beta} \sum_{smi} \sum_{tlj} \sigma_{si}^\alpha \sigma_{tlj}^\beta u_{\alpha\beta}(\mathbf{R}_{mi}^s - \mathbf{R}_{tlj}^t), \quad (\text{A7})$$

where  $u_{\alpha\beta}(\underline{x})$  is the interaction potential between a segment of type  $\alpha$  and a segment of type  $\beta$ , which is assumed to be short ranged in space. Although formally this last expression contains “self-energy” terms, i.e., terms with  $\alpha = \beta, s = t, l = m$ , and  $i = j$ , we will not bother to explicitly exclude them in the notation used in Eq. (A7). It is easy to see that this total interaction energy  $\hat{U}$  can be written in terms of the specific microscopic segment densities  $\hat{\rho}_\alpha(\underline{x})$  [Eq. (A1)] as

$$\hat{U} \equiv \frac{1}{2} \sum_{\alpha\beta} \int_V d^3x \int_V d^3y u_{\alpha\beta}(\underline{x} - \underline{y}) \hat{\rho}_\alpha(\underline{x}) \hat{\rho}_\beta(\underline{y}), \quad (\text{A8})$$

which for a short-ranged  $u_{\alpha\beta}(\underline{x})$  becomes

$$\hat{U} \equiv \frac{1}{2} \sum_{\alpha\beta} \epsilon_{\alpha\beta} \int_V d^3x \hat{\rho}_\alpha(\underline{x}) \hat{\rho}_\beta(\underline{x}) \quad (\text{A9})$$

with

$$\epsilon_{\alpha\beta} \equiv \int_V d^3x u_{\alpha\beta}(\underline{x}). \quad (\text{A10})$$

By eliminating one of the  $\hat{\rho}$ 's, say  $\hat{\rho}_M$ , from Eq. (A9) using  $\sum_\alpha \hat{\rho}_\alpha(\underline{x}) \equiv 1$  and substituting  $\hat{\rho}_\alpha(\underline{x}) \equiv \hat{\psi}_\alpha(\underline{x}) + f_\alpha$ , one ends up, apart from a constant term, with

$$\hat{U} \equiv \frac{1}{2} \sum_{\alpha\beta} \{ \epsilon_{\alpha\beta} - \epsilon_{\alpha M} - \epsilon_{\beta M} + \epsilon_{MM} \} \int_V d^3x \hat{\psi}_\alpha(\underline{x}) \hat{\psi}_\beta(\underline{x}), \quad (\text{A11})$$

where the accent implies that both sums run from 1 to  $M-1$ . In terms of the set of Flory  $\chi$ -parameters<sup>16</sup> between the different segments, i.e.

$$\chi_{\alpha\beta} \equiv \epsilon_{\alpha\beta} - \frac{\epsilon_{\alpha\alpha} + \epsilon_{\beta\beta}}{2} \quad \text{with} \quad \chi_{\alpha\alpha} = 0, \quad \forall \alpha, \quad (\text{A12})$$

this  $\hat{U}$  can finally be written as

$$\begin{aligned} \hat{U} &\equiv \frac{1}{2} \sum_{\alpha\beta} \{ \chi_{\alpha\beta} - \chi_{\alpha M} - \chi_{\beta M} \} \int_V d^3x \hat{\psi}_\alpha(\underline{x}) \hat{\psi}_\beta(\underline{x}) \\ &\equiv - \sum_{\alpha\beta} \tilde{\chi}_{\alpha\beta} \int_V d^3x \hat{\psi}_\alpha(\underline{x}) \hat{\psi}_\beta(\underline{x}). \end{aligned} \quad (\text{A13})$$

For the binary case ( $M=2$ ), the only remaining  $\tilde{\chi}$ -parameter,  $\tilde{\chi}_{11}$ , then reduces to the more familiar  $\chi_{12}$ . Having introduced the interaction energy of the copolymer melt, the final ingredient we need before we can write down the system's partition function  $Z$ , is the Hamiltonian  $\hat{H}_0$  of the system in absence of these interactions. As unperturbed chains in a melt obey random walk statistics, this  $\hat{H}_0$  can be defined via the following normalized statistical weight belonging to an ensemble of Gaussian chains

$$e^{-\hat{H}_0} \equiv \prod_s \prod_{m=1}^{n_s} \left\{ \frac{1}{V} \prod_{i=1}^{N_s-1} g(\underline{R}_{m,i+1}^s - \underline{R}_{m,i}^s) \right\}, \quad (\text{A14})$$

with  $g(\underline{x}) \equiv (3/2\pi a^2)^{3/2} \exp(-3x^2/2a^2)$ . In this expression there is a factor  $1/V$  to account for the center-of-mass position of each of the  $n_c$  chains. This brings us to the starting point of the derivation of a Landau free energy, namely the system's partition function  $Z$  or more precise the system's configurational partition function  $Z$ , i.e., the sum of the Boltzmann weights over all allowed states of the system. The set of all allowed states furnishes the so-called state space or configuration-space  $\Gamma$  of the system, which in this case is given by

$$\Gamma \equiv \{ \{ \underline{R}_{mi}^s \}_{smi} | \hat{\rho}(\underline{x}) = 1, \quad \forall \underline{x} \in V \}. \quad (\text{A15})$$

As we are ultimately only interested in differences in free energy between possible inhomogeneous phases of the system, all combinatorial terms will be left out of this partition function since they only lead to constant terms in the free energy. With this in mind  $Z$  becomes

$$Z \equiv \prod_{smi} \int_V d^3R_{mi}^s \delta(1 - \hat{\rho}) e^{-\hat{H}_0} e^{\sum_{\alpha\beta} \tilde{\chi}_{\alpha\beta} \int_V d^3x \hat{\psi}_\alpha(\underline{x}) \hat{\psi}_\beta(\underline{x})}. \quad (\text{A16})$$

In this coarse grained description incompressibility, which is due to interactions at the molecular level, has to be explicitly accounted for via a delta function. Given this partition function, the first thing we will do is transform it, in four steps, into a form which is more suitable for further analysis. The first step involves a formal shift of the state variable dependence of the second exponential in Eq. (A16). This is done by introducing the following functional decomposition of the identity into  $Z$ :

$$\prod'_v \int D\psi_v \delta(\psi_v - \hat{\psi}_v) = 1, \quad (\text{A17})$$

where  $\int D\psi$  denotes a functional integration over the scalar field  $\psi$ , and leads to

$$\begin{aligned} Z &= \prod'_v \int D\psi_v e^{\sum_{\alpha\beta} \tilde{\chi}_{\alpha\beta} \int_V d^3x \psi_\alpha(\underline{x}) \psi_\beta(\underline{x})} \\ &\quad \times \prod_{smi} \int_V d^3R_{mi}^s e^{-\hat{H}_0} \delta(1 - \hat{\rho}) \prod'_\lambda \delta(\psi_\lambda - \hat{\psi}_\lambda). \end{aligned} \quad (\text{A18})$$

The second step involves substitution of the following functional spectral representations for the  $M$  "delta-functions" in the above expression

$$\begin{aligned} \delta(1 - \hat{\rho}) &\equiv \int DI_0 e^{i \int_V d^3x I_0(\underline{x}) \{1 - \hat{\rho}(\underline{x})\}} \\ \delta(\psi_\alpha - \hat{\psi}_\alpha) &\equiv \int DI_\alpha e^{i \int_V d^3x I_\alpha(\underline{x}) \{ \psi_\alpha(\underline{x}) - \hat{\psi}_\alpha(\underline{x}) \}} \\ &\quad (\alpha = 1, \dots, M-1), \end{aligned} \quad (\text{A19})$$

resulting in

$$\begin{aligned} Z &= \prod'_v \int D\psi_v e^{\sum_{\alpha\beta} \tilde{\chi}_{\alpha\beta} \int_V d^3x \psi_\alpha(\underline{x}) \psi_\beta(\underline{x})} \\ &\quad \times \int DI_0 \prod'_\lambda \int DI_\lambda e^{i \int_V d^3x \{ I_0(\underline{x}) + \sum'_\alpha I_\alpha(\underline{x}) \psi_\alpha(\underline{x}) \}} \\ &\quad \times \prod_{smj} \int_V d^3R_{mj}^s e^{-\hat{H}_0} e^{-i \int_V d^3x \{ I_0(\underline{x}) \hat{\rho}(\underline{x}) + \sum'_\alpha I_\alpha(\underline{x}) \hat{\psi}_\alpha(\underline{x}) \}}. \end{aligned} \quad (\text{A20})$$

In the third step the auxiliary integration fields  $I_0(\underline{x})$ ,  $I_1(\underline{x}), \dots, I_{M-1}(\underline{x})$  are transformed to new fields  $J_1(\underline{x}), \dots, J_M(\underline{x})$ , defined in the following way:

$$\begin{aligned} J_\alpha(\underline{x}) &\equiv I_\alpha(\underline{x}) + I_0(\underline{x}) \quad (\alpha = 1, \dots, M-1) \\ J_M(\underline{x}) &\equiv I_0(\underline{x}). \end{aligned} \quad (\text{A21})$$

Using this isometric transformation and Eqs. (A2), (A5), and (A6) it is easily verified that the following two identities hold:

$$I_0(\underline{x}) \hat{\rho}(\underline{x}) + \sum'_\alpha I_\alpha(\underline{x}) \hat{\psi}_\alpha(\underline{x})$$

$$= J_M(\underline{x}) + \sum_{\alpha} J_{\alpha}(\underline{x}) \hat{\rho}_{\alpha}(\underline{x}) - \sum_{\alpha} f_{\alpha} J_{\alpha}(\underline{x}), \tag{A22}$$

$$I_0(\underline{x}) + \sum_{\alpha} I_{\alpha}(\underline{x}) \psi_{\alpha}(\underline{x}) = J_M(\underline{x}) + \sum_{\alpha} J_{\alpha}(\underline{x}) \psi_{\alpha}(\underline{x}),$$

and, therefore, that  $Z$  can be written as

$$Z = \prod_{\nu} \int D\psi_{\nu} e^{\sum_{\alpha\beta} \tilde{\chi}_{\alpha\beta} \int_V d^3x \psi_{\alpha}(\underline{x}) \psi_{\beta}(\underline{x})} \\ \times \prod_{\lambda} \int DJ_{\lambda} e^{i \sum_{\alpha} \int_V d^3x \{ J_{\alpha}(\underline{x}) [\psi_{\alpha}(\underline{x}) + f_{\alpha}] \}} \\ \times \langle e^{-i \sum_{\alpha} \int_V d^3x J_{\alpha}(\underline{x}) \hat{\rho}_{\alpha}(\underline{x})} \rangle_0. \tag{A23}$$

In this expression  $\langle \dots \rangle_0$  denotes an average with respect to the unperturbed ensemble of chain conformations defined by  $\hat{H}_0$ , i.e.

$$\langle \hat{A} \rangle_0 \equiv \prod_{smi} \int_V d^3R_{mi} e^{-\hat{H}_0 \hat{A}}. \tag{A24}$$

The last step in the transformation of  $Z$  boils down to rewriting the integrand of Eq. (A23) using the fields  $\tilde{J}_1(\underline{x}), \dots, \tilde{J}_M(\underline{x})$ , defined by<sup>2</sup>

$$\tilde{J}_{\alpha}(\underline{x}) \equiv J_{\alpha}(\underline{x}) - \frac{1}{V} \int_V d^3y J_{\alpha}(\underline{y}) \quad (\alpha = 1, \dots, M). \tag{A25}$$

It is easy to see that the use of these new fields in conjunction with Eq. (A4) will eliminate the term in Eq. (A23) involving  $f_{\alpha}$ . Thus we finally end up with

$$Z = \prod_{\nu} \int D\psi_{\nu} e^{\sum_{\alpha\beta} \tilde{\chi}_{\alpha\beta} \int_V d^3x \psi_{\alpha}(\underline{x}) \psi_{\beta}(\underline{x})} \\ \times \prod_{\lambda} \int DJ_{\lambda} e^{i \sum_{\alpha} \int_V d^3x \tilde{J}_{\alpha}(\underline{x}) \psi_{\alpha}(\underline{x}) + G}, \tag{A26}$$

with  $G$  defined by

$$G \equiv \ln \langle e^{-i \sum_{\alpha} \int_V d^3x \tilde{J}_{\alpha}(\underline{x}) \hat{\rho}_{\alpha}(\underline{x})} \rangle_0. \tag{A27}$$

In order to be able to extract a Landau free energy from Eq. (A26), we will need to analyze this last quantity a bit further. This part, however, forms the essence of the whole derivation of this free energy. From the definition of  $\langle \dots \rangle_0$ , Eq. (A24), in combination with Eq. (A14) it follows that:

$$G \equiv \ln \prod_{sm} \int_V d^3R_{m1} \dots \int_V d^3R_{mN_s} \frac{1}{V} \\ \times \prod_{j=1}^{N_s-1} g(R_{m,j+1}^s - R_{mj}^s) e^{-i \sum_{\alpha} \int_V d^3x \tilde{J}_{\alpha}(\underline{x}) \hat{\rho}_{\alpha}^{sm}(\underline{x})}, \tag{A28}$$

where use has been made of the decomposition

$$\hat{\rho}_{\alpha}(\underline{x}) \equiv \sum_{sm} \hat{\rho}_{\alpha}^{sm}(\underline{x})$$

with

$$\hat{\rho}_{\alpha}^{sm}(\underline{x}) \equiv \sum_i \sigma_{si}^{\alpha} \delta(\underline{x} - R_{mi}^s). \tag{A29}$$

This can also be written as

$$G = \sum_{sm} \ln \int_V d^3R_{m1} \dots \int_V d^3R_{mN_s} \frac{1}{V} \\ \times \prod_{j=1}^{N_s-1} g(R_{m,j+1}^s - R_{mj}^s) e^{-i \sum_{\alpha} \int_V d^3x \tilde{J}_{\alpha}(\underline{x}) \hat{\rho}_{\alpha}^{sm}(\underline{x})}. \tag{A30}$$

From a closer inspection of this last expression it becomes clear that because of the  $N_s$ -fold integration over the  $R$  variables (which, therefore, have become dummy variables), each term in the sum over  $m$  for a given chain type  $s$ , i.e., each term in the sum over all chains of a given type in the system, gives the same contribution to  $G$ . Therefore,  $G$  becomes

$$G = \sum_s n_s \ln \int_V d^3R_1 \dots \int_V d^3R_{N_s} \frac{1}{V} \\ \times \prod_{j=1}^{N_s-1} g(R_{j+1} - R_j) e^{-i \sum_{\alpha} \int_V d^3x \tilde{J}_{\alpha}(\underline{x}) \hat{\rho}_{\alpha}^s(\underline{x})}, \tag{A31}$$

where  $\hat{\rho}_{\alpha}^s(\underline{x})$  is defined by

$$\hat{\rho}_{\alpha}^s(\underline{x}) \equiv \sum_i \sigma_{si}^{\alpha} \delta(\underline{x} - R_i), \tag{A32}$$

which clearly is equal to

$$G = \sum_s n_s \ln \langle e^{\hat{\omega}_s} \rangle_0$$

with

$$\hat{\omega}_s \equiv -i \sum_{\alpha} \int_V d^3x \tilde{J}_{\alpha}(\underline{x}) \hat{\rho}_{\alpha}^s(\underline{x}). \tag{A33}$$

Now by introducing the number density of chains of type  $s$ ,  $\rho_s \equiv n_s/V$  it follows that  $G$  can be written as:

$$G \equiv V \sum_s \rho_s \ln \langle e^{\hat{\omega}_s} \rangle_0 \equiv V \langle \ln \langle e^{\hat{\omega}} \rangle_0 \rangle_d. \tag{A34}$$

In this last expression the second average with subscript  $d$  is a disorder average, i.e., an average over the quenched disorder in the copolymer chains. More important this quenched average involves the logarithm of a quantity proportional to the partition function, as can be seen from Eqs. (A26) and (A34), and therefore, it is the free energy that is being averaged over the disorder. To calculate the average of the logarithm of the partition function one can resort to the replica method,<sup>22</sup> but this is not necessary for the kind of quenched disorder one encounters in statistical copolymer systems, as will be shown now.

As the Landau free energy for this system involves an expansion up to the fourth order in the order-parameter fields  $\{\psi_{\alpha}(\underline{x})\}$ , the thing to do is to expand  $G$  up to the fourth order in  $\hat{\omega}$ . The reason for this step will become clear in the process. The result is

$$\begin{aligned} \frac{G}{V} \approx & \frac{1}{2} \langle \langle \hat{\omega}^2 \rangle_0 \rangle_d + \frac{1}{6} \langle \langle \hat{\omega}^3 \rangle_0 \rangle_d + \frac{1}{24} \langle \langle \hat{\omega}^4 \rangle_0 \rangle_d \\ & - \frac{1}{8} \langle \langle \hat{\omega}^2 \rangle_0^2 \rangle_d, \end{aligned} \quad (\text{A35})$$

where we have used the fact that  $\langle \hat{\omega} \rangle_0 = 0$ , a result which is easily derived with a little bit of algebra. Let us first consider the second-order term. By using Eq. (A33) it follows that:

$$\begin{aligned} \frac{1}{2} \langle \langle \hat{\omega}^2 \rangle_0 \rangle_d \equiv & -\frac{1}{2} \sum_{\alpha\beta} \int_V d^3x \int_V d^3y \tilde{J}_\alpha(\underline{x}) \tilde{J}_\beta(\underline{y}) \\ & \times \sum_s \rho_s \langle \hat{\rho}_\alpha^s(\underline{x}) \hat{\rho}_\beta^s(\underline{y}) \rangle_0, \end{aligned} \quad (\text{A36})$$

which by invoking the Fourier-representation of  $\hat{\rho}_\alpha^s(\underline{x})$  Eq. (A32), i.e.

$$\hat{\rho}_\alpha^s(\underline{x}) \equiv \frac{1}{V} \sum_{\underline{q}} \sum_j \sigma_{sj}^\alpha e^{i\underline{q} \cdot (\underline{x} - \underline{R}_j)}, \quad (\text{A37})$$

can be written as

$$\begin{aligned} \frac{1}{2} \langle \langle \hat{\omega}^2 \rangle_0 \rangle_d \equiv & \frac{(-i)^2}{2V^2} \sum_{\alpha\beta} \sum_{\underline{q}\underline{q}'} \tilde{J}_\alpha(\underline{q}) \tilde{J}_\beta(\underline{q}') \\ & \times \sum_{jj'} \sum_s \rho_s \sigma_{sj}^\alpha \sigma_{sj'}^\beta \langle e^{-i(\underline{q} \cdot \underline{R}_j + \underline{q}' \cdot \underline{R}_{j'})} \rangle_0, \end{aligned} \quad (\text{A38})$$

where  $\tilde{J}_\alpha(\underline{q})$  is the Fourier-transform of  $\tilde{J}_\alpha(\underline{x})$ . The unperturbed ensemble average which appears in this expression, i.e.,  $\langle e^{-i(\underline{q} \cdot \underline{R}_j + \underline{q}' \cdot \underline{R}_{j'})} \rangle_0$ , is a two-point characteristic function of a multivariate Gaussian distribution function and is calculated in Appendix B. It is equal to

$$\langle e^{-i(\underline{q} \cdot \underline{R}_j + \underline{q}' \cdot \underline{R}_{j'})} \rangle_0 \equiv \delta(\underline{q} + \underline{q}') e^{-(a^2 q^2/6)|j-j'|}. \quad (\text{A39})$$

In this last expression the delta function is in fact a Kronecker delta symbol because due to the finiteness of the volume  $V$ , the allowed wave vectors form a discrete set. This Kronecker delta symbol expresses the translational invariance of the system. Now by introducing

$$\begin{aligned} G_{\alpha\beta}^{(2)}(\underline{q}_1, \underline{q}_2) & \equiv \delta(\underline{q}_1 + \underline{q}_2) \sum_s \rho_s g_{\alpha\beta}^s(\underline{q}_1, \underline{q}_2) \\ & \equiv \delta(\underline{q}_1 + \underline{q}_2) \bar{g}_{\alpha\beta}(\underline{q}_1), \end{aligned}$$

$$\text{with } g_{\alpha\beta}^s(\underline{q}_1, \underline{q}_2) \equiv \sum_{jj'} \sigma_{sj}^\alpha \sigma_{sj'}^\beta e^{(a^2 \underline{q}_1 \cdot \underline{q}_2/6)|j-j'|}, \quad (\text{A40})$$

this second-order contribution to  $G$  becomes

$$\frac{1}{2} \langle \langle \hat{\omega}^2 \rangle_0 \rangle_d \equiv \frac{(-i)^2}{2V^2} \sum_{\alpha\beta} \sum_{\underline{q}_1 \underline{q}_2} G_{\alpha\beta}^{(2)}(\underline{q}_1, \underline{q}_2) \tilde{J}_\alpha(\underline{q}_1) \tilde{J}_\beta(\underline{q}_2). \quad (\text{A41})$$

The third-order and the two fourth-order contributions to  $G$  can also be written in such a form, namely as

$$\begin{aligned} \frac{1}{6} \langle \langle \hat{\omega}^3 \rangle_0 \rangle_d & \equiv \frac{(-i)^3}{6V^3} \sum_{\alpha\beta\gamma} \sum_{\underline{q}_1 \underline{q}_2 \underline{q}_3} G_{\alpha\beta\gamma}^{(3)}(\underline{q}_1, \underline{q}_2, \underline{q}_3) \\ & \times \tilde{J}_\alpha(\underline{q}_1) \tilde{J}_\beta(\underline{q}_2) \tilde{J}_\gamma(\underline{q}_3), \end{aligned} \quad (\text{A42})$$

with

$$\begin{aligned} G_{\alpha\beta\gamma}^{(3)}(\underline{q}_1, \underline{q}_2, \underline{q}_3) & \equiv \delta(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) \sum_s \rho_s g_{\alpha\beta\gamma}^s(\underline{q}_1, \underline{q}_2, \underline{q}_3) \\ & \equiv \delta(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) \bar{g}_{\alpha\beta\gamma}(\underline{q}_1, \underline{q}_2, -\underline{q}_1 - \underline{q}_2) \end{aligned} \quad (\text{A43})$$

and

$$\begin{aligned} \frac{1}{24} \langle \langle \hat{\omega}^4 \rangle_0 \rangle_d - \frac{1}{8} \langle \langle \hat{\omega}^2 \rangle_0^2 \rangle_d & \equiv \frac{(-i)^4}{24V^4} \sum_{\alpha\beta\gamma\delta} \sum_{\underline{q}_1 \underline{q}_2 \underline{q}_3 \underline{q}_4} G_{\alpha\beta\gamma\delta}^{(4)}(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) \\ & \times \tilde{J}_\alpha(\underline{q}_1) \tilde{J}_\beta(\underline{q}_2) \tilde{J}_\gamma(\underline{q}_3) \tilde{J}_\delta(\underline{q}_4), \end{aligned} \quad (\text{A44})$$

where  $G_{\alpha\beta\gamma\delta}^{(4)} \equiv G_{\alpha\beta\gamma\delta}^{(4)reg} - G_{\alpha\beta\gamma\delta}^{(4)nl}$  with

$$\begin{aligned} G_{\alpha\beta\gamma\delta}^{(4)reg}(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) & \equiv \delta(\underline{q}_1 + \underline{q}_2 + \underline{q}_3 + \underline{q}_4) \sum_s \rho_s g_{\alpha\beta\gamma\delta}^s(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) \\ & \equiv \delta(\underline{q}_1 + \underline{q}_2 + \underline{q}_3 + \underline{q}_4) \bar{g}_{\alpha\beta\gamma\delta}(\underline{q}_1, \underline{q}_2, \underline{q}_3, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3), \end{aligned}$$

and

$$\begin{aligned} G_{\alpha\beta\gamma\delta}^{(4)nl}(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) & \equiv \delta(\underline{q}_1 + \underline{q}_2) \delta(\underline{q}_3 + \underline{q}_4) \sum_s \rho_s g_{\alpha\beta}^s(\underline{q}_1, \underline{q}_2) g_{\gamma\delta}^s(\underline{q}_3, \underline{q}_4) \\ & + \delta(\underline{q}_1 + \underline{q}_3) \delta(\underline{q}_2 + \underline{q}_4) \sum_s \rho_s g_{\alpha\gamma}^s(\underline{q}_1, \underline{q}_3) g_{\beta\delta}^s(\underline{q}_2, \underline{q}_4) \\ & + \delta(\underline{q}_1 + \underline{q}_4) \delta(\underline{q}_2 + \underline{q}_3) \sum_s \rho_s g_{\alpha\delta}^s(\underline{q}_1, \underline{q}_4) g_{\beta\gamma}^s(\underline{q}_2, \underline{q}_3) \\ & \equiv \delta(\underline{q}_1 + \underline{q}_2) \delta(\underline{q}_3 + \underline{q}_4) \overline{g_{\alpha\beta}(\underline{q}_1) g_{\gamma\delta}(\underline{q}_3)} \\ & + \delta(\underline{q}_1 + \underline{q}_3) \delta(\underline{q}_2 + \underline{q}_4) \overline{g_{\alpha\gamma}(\underline{q}_1) g_{\beta\delta}(\underline{q}_2)} + \delta(\underline{q}_1 + \underline{q}_4) \\ & \times \overline{\delta(\underline{q}_2 + \underline{q}_3) g_{\alpha\delta}(\underline{q}_1) g_{\beta\gamma}(\underline{q}_2)}. \end{aligned} \quad (\text{A45})$$

In this last result  $G_{\alpha\beta\gamma\delta}^{(4)nl}(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4)$  has been symmetrized. This contribution to  $G_{\alpha\beta\gamma\delta}^{(4)}$  is a part of the so-called *nonlocal term*, which is typical for polydisperse copolymer melts and which vanishes once the number of segment types  $M$  exceeds the number of chain types in the system.<sup>3</sup> Both the quantities  $g_{\alpha\beta\gamma}^s(\underline{q}_1, \underline{q}_2, \underline{q}_3)$  and  $g_{\alpha\beta\gamma\delta}^s(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4)$  involve higher order Gaussian characteristic functions (see Appendix B) and are given by

$$g_{\alpha\beta\gamma}^s(\underline{q}_1, \underline{q}_2, \underline{q}_3) \equiv \sum_{ijk} \sigma_{si}^\alpha \sigma_{sj}^\beta \sigma_{sk}^\gamma e^{(a^2/6)\{q_1 \cdot q_2|i-j| + q_2 \cdot q_3|j-k| + q_1 \cdot q_3|i-k|\}}$$

$$(A46)$$

and

$$g_{\alpha\beta\gamma\delta}^s(\underline{q}_1, \underline{q}_2, \underline{q}_3, \underline{q}_4) \equiv \sum_{ijkl} \sigma_{si}^\alpha \sigma_{sj}^\beta \sigma_{sk}^\gamma \sigma_{sl}^\delta e^{a^2/6\{q_1 \cdot q_2|i-j| + q_1 \cdot q_3|i-k| + q_1 \cdot q_4|i-l| + q_2 \cdot q_3|j-k| + q_2 \cdot q_4|j-l| + q_3 \cdot q_4|k-l|\}}$$

$$(A47)$$

The functions  $\bar{g}_{\alpha\beta}(q)$ ,  $\bar{g}_{\alpha\beta\gamma}(q_1, q_2, -q_1 - q_2)$  and  $\bar{g}_{\alpha\beta\gamma\delta}(q_1, q_2, q_3, -q_1 - q_2 - q_3)$  are, respectively, referred to as second-, third- and fourth-order ideal intrachain correlation functions, because they are density correlation functions of an ideal copolymer melt, i.e., a melt where the interactions between segments have been switched off. As the partition function  $Z$ , Eq. (A26) involves a functional integration over the  $J$  fields, while the three contributions to  $G$  Eqs. (A41)–(A43) all involve the  $\tilde{J}$  fields, we need to transform  $G$  to the former kind of fields. This is most easily done by recalling that from the definition of  $\tilde{J}_\alpha(\underline{x})$  [Eq. (A25)], it follows that:

$$\tilde{J}_\alpha(\underline{q}) \equiv J_\alpha(\underline{q}) - J_\alpha(\underline{0}) \delta(\underline{q}), \quad (A48)$$

in other words  $\tilde{J}_\alpha(\underline{q}) \equiv J_\alpha(\underline{q})$  for  $\underline{q} \neq \underline{0}$  and  $\tilde{J}_\alpha(\underline{0}) \equiv 0$ . Therefore, by restricting the sum over  $\underline{q}$  in expressions (A41)–(A43) to  $\underline{q} \neq \underline{0}$ , we can simply change the  $\tilde{J}$ 's herein to  $J$ 's. Symbolically we now can write the expression for  $G$  as

$$\frac{G}{V} \equiv -\frac{1}{2} G_{ab}^{(2)} v_a v_b + \frac{i}{6} G_{abc}^{(3)} v_a v_b v_c + \frac{1}{24} G_{abcd}^{(4)} v_a v_b v_c v_d, \quad (A49)$$

where we have introduced *composite labels*  $a \equiv (q \neq 0, \alpha)$ ,  $b \equiv (q \neq 0, \beta)$  etc. and where  $v_a \equiv J_\alpha(q)/V$ . Furthermore the Einstein summation convention has been used. By Fourier transforming all the integrals involving the  $\psi$  fields and making use of the fact that according to the definition of  $\tilde{\chi}_{\alpha\beta}$  [see Eq. (A13)]  $\tilde{\chi}_{MM} \equiv 0$ , the partition function  $Z$ , Eq. (A26) can be written as

$$Z \equiv \prod_c' \int Dm_c e^{V\{\tilde{\chi}_{ab} m_a m_b\}} Z_G[\underline{m}], \quad (A50)$$

with  $\tilde{\chi}_{ab} \equiv \tilde{\chi}_{\alpha\beta} \delta(q_1 + q_2)$ ,  $m_a \equiv \psi_\alpha(-\underline{q})/V$  and

$$Z_G[\underline{m}] \equiv \prod_h \int Dv_h e^{V\{im_a v_a - (1/2)G_{ab}^{(2)} v_a v_b + (i/6)G_{abc}^{(3)} v_a v_b v_c + (1/24)G_{abcd}^{(4)} v_a v_b v_c v_d\}}. \quad (A51)$$

For large values of the system's volume  $V$ ,  $Z_G[\underline{m}]$  can be evaluated with the well-known *saddle-point method*, i.e., approximating  $Z_G[\underline{m}]$  by

$$Z_G[\underline{m}] \approx e^{V\Omega[\underline{m}]}, \quad (A52)$$

where  $\Omega[\underline{m}]$  is the stationary value of  $im_a v_a + (G[\underline{v}]/V)$  with respect to the set of  $v$ 's for which the absolute value is the smallest. This stationary point is a solution of the following set of equations:

$$im_a - G_{ab}^{(2)} v_b + \frac{i}{2} G_{abc}^{(3)} v_b v_c + \frac{1}{6} G_{abcd}^{(4)} v_b v_c v_d = 0, \quad \forall a. \quad (A53)$$

Which in vector notation becomes

$$i\underline{m} - \underline{G}^{(2)} \cdot \underline{v} + \frac{i}{2} \underline{G}^{(3)} : \underline{v}\underline{v} + \frac{1}{6} \underline{G}^{(4)} : \underline{v}\underline{v}\underline{v} = \underline{0}. \quad (A54)$$

As we ultimately want to arrive at a Landau free energy as an expansion up to the fourth order in the  $m$  fields, we only need to solve this last vector equation iteratively for  $\underline{v}$  up to the third order in  $\underline{m}$ . One can easily verify that the solution is given by

$$\underline{v} = i\underline{G}^{(2)-1} \cdot \underline{m} - \frac{i}{2} \underline{G}^{(2)-1} \cdot \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) + \frac{i}{2} \underline{G}^{(2)-1} \cdot \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) \cdot \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m}) \times (\underline{G}^{(2)-1} \cdot \underline{m}) - \frac{i}{2} \underline{G}^{(2)-1} \cdot \underline{G}^{(4)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) + O(m^4). \quad (A55)$$

If we now substitute this result back into  $\Omega[\underline{m}]$ , then after some rearrangement we end up with

$$\Omega[\underline{m}] \approx -\frac{1}{2} \underline{G}^{(2)-1} : \underline{m}\underline{m} + \frac{1}{6} \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) + \frac{1}{24} \underline{G}^{(4)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) \times (\underline{G}^{(2)-1} \cdot \underline{m}) - \frac{1}{8} \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) \cdot \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}). \quad (A56)$$

Given this approximation to  $Z_G[\underline{m}]$ , i.e., Eq. (A52) with Eq. (A56), the partition function  $Z$  thus becomes

$$Z \approx \prod_a' \int Dm_a e^{V\{\tilde{\chi}:\underline{m}\underline{m} + \Omega[\underline{m}]\}} \quad (\text{A57})$$

The Landau free energy, that is the free energy of the system within the *mean-field approximation*, can be obtained by again applying the saddle-point method, but now to approximately evaluate this last set of functional integrals. If we write this result as

$$Z \approx e^{-F_L}, \quad (\text{A58})$$

then this  $F_L$  (in units of  $k_B T$ ) will be the Landau free energy we are looking for and equal to

$$\begin{aligned} \frac{F_L}{V} \equiv \min_{\underline{m}'} \{ & \frac{1}{2} [\underline{G}^{(2)-1} - 2\tilde{\chi}] : \underline{m}\underline{m} - \frac{1}{6} \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) \\ & - \frac{1}{24} \underline{G}^{(4)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) + \frac{1}{8} \underline{G}^{(3)} : (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{G}^{(3)} : \\ & \times (\underline{G}^{(2)-1} \cdot \underline{m})(\underline{G}^{(2)-1} \cdot \underline{m}) \} \}. \quad (\text{A59}) \end{aligned}$$

The minimization in this expression is over the  $M-1$  independent order-parameter fields, which we choose to be  $m_1(\underline{q}), \dots, m_{M-1}(\underline{q})$ , with the remaining dependent order-parameter field,  $m_M(\underline{q})$ , expressed via  $m_M(\underline{q}) \equiv -\sum_{\alpha=1}^{M-1} m_\alpha(\underline{q})$ . If we now use the definitions of  $\underline{G}^{(2)}$  [Eq. (A40)],  $\underline{G}^{(3)}$  [Eq. (A43)], and  $\underline{G}^{(4)} \equiv \underline{G}^{(4)reg} - \underline{G}^{(4)nl}$  [Eq. (A45)], this Landau free energy can be transformed into

$$\begin{aligned} \frac{F_L}{V} \equiv \min_{\{m_\alpha\}'} \{ & \frac{1}{2} \sum_{\alpha\beta} \sum_{\underline{q}} [\bar{g}_{\alpha\beta}^{-1}(\underline{q}) - 2\tilde{\chi}_{\alpha\beta}] m_\alpha(\underline{q}) m_\beta(-\underline{q}) - \frac{1}{6} \sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\xi} \sum_{\underline{q}_1\underline{q}_2} \bar{g}_{\alpha\beta\gamma}(\underline{q}_1, \underline{q}_2, -\underline{q}_1 - \underline{q}_2) \bar{g}_{\gamma\xi}^{-1}(|\underline{q}_1 + \underline{q}_2|) \\ & \times \bar{g}_{\alpha\delta}^{-1}(\underline{q}_1) \bar{g}_{\beta\epsilon}^{-1}(\underline{q}_2) m_\delta(-\underline{q}_1) m_\epsilon(-\underline{q}_2) m_\xi(\underline{q}_1 + \underline{q}_2) + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2\underline{q}_3} \left\{ -\bar{g}_{\alpha\beta\gamma\delta}(\underline{q}_1, \underline{q}_2, \underline{q}_3, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3) \right. \\ & \times \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_3) \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(-\underline{q}_3) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) + [1 - \delta(\underline{q}_1 + \underline{q}_2)] \\ & \times \sum_{\kappa\lambda} \bar{g}_{\alpha\beta\kappa}(\underline{q}_1, \underline{q}_2, -\underline{q}_1 - \underline{q}_2) \bar{g}_{\kappa\lambda}^{-1}(|\underline{q}_1 + \underline{q}_2|) \bar{g}_{\gamma\delta\lambda}(\underline{q}_3, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3, \underline{q}_1 + \underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_3) \\ & \times \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(-\underline{q}_3) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) + [1 - \delta(\underline{q}_1 + \underline{q}_3)] \\ & \times \sum_{\kappa\lambda} \bar{g}_{\alpha\beta\kappa}(\underline{q}_1, \underline{q}_3, -\underline{q}_1 - \underline{q}_3) \bar{g}_{\kappa\lambda}^{-1}(|\underline{q}_1 + \underline{q}_3|) \bar{g}_{\gamma\delta\lambda}(\underline{q}_2, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3, \underline{q}_1 + \underline{q}_3) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_3) \\ & \times \bar{g}_{\gamma\mu}^{-1}(\underline{q}_2) \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_3) m_\mu(-\underline{q}_2) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) + [1 - \delta(\underline{q}_2 + \underline{q}_3)] \\ & \times \sum_{\kappa\lambda} \bar{g}_{\alpha\beta\kappa}(\underline{q}_2, \underline{q}_3, -\underline{q}_2 - \underline{q}_3) \bar{g}_{\kappa\lambda}^{-1}(|\underline{q}_2 + \underline{q}_3|) \bar{g}_{\gamma\delta\lambda}(\underline{q}_1, -\underline{q}_1 - \underline{q}_2 - \underline{q}_3, \underline{q}_2 + \underline{q}_3) \\ & \times \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_2) \bar{g}_{\beta\xi}^{-1}(\underline{q}_3) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_1) \bar{g}_{\delta\nu}^{-1}(|\underline{q}_1 + \underline{q}_2 + \underline{q}_3|) m_\epsilon(-\underline{q}_2) m_\xi(-\underline{q}_3) m_\mu(-\underline{q}_1) m_\nu(\underline{q}_1 + \underline{q}_2 + \underline{q}_3) \\ & + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2} \overline{g_{\alpha\beta}(\underline{q}_1) g_{\gamma\delta}(\underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_1) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_2) \bar{g}_{\delta\nu}^{-1}(\underline{q}_2)} m_\epsilon(-\underline{q}_1) m_\xi(\underline{q}_1) m_\mu(-\underline{q}_2) m_\nu(\underline{q}_2) \\ & + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2} \overline{g_{\alpha\gamma}(\underline{q}_1) g_{\beta\delta}(\underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_1) \bar{g}_{\delta\nu}^{-1}(\underline{q}_2)} m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(\underline{q}_1) m_\nu(\underline{q}_2) \\ & + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \sum_{\epsilon\xi\mu\nu} \sum_{\underline{q}_1\underline{q}_2} \overline{g_{\alpha\delta}(\underline{q}_1) g_{\beta\gamma}(\underline{q}_2) \bar{g}_{\alpha\epsilon}^{-1}(\underline{q}_1) \bar{g}_{\beta\xi}^{-1}(\underline{q}_2) \bar{g}_{\gamma\mu}^{-1}(\underline{q}_2) \bar{g}_{\delta\nu}^{-1}(\underline{q}_1)} m_\epsilon(-\underline{q}_1) m_\xi(-\underline{q}_2) m_\mu(\underline{q}_2) m_\nu(\underline{q}_1), \quad (\text{A60}) \end{aligned}$$

where we have symmetrized the terms involving the two third-order ideal intrachain correlation functions. Notice that the sums over the various  $\underline{q}$ 's in this last expression are no longer restricted to  $\underline{q} \neq \underline{0}$ . This is allowed and causes no

problem, even though one can show that  $\bar{g}(\underline{q})$  is singular (not invertible) at  $\underline{q} = \underline{0}$  for the infinite system, due to the fact that by definition  $m_\alpha(\underline{0}) = \psi_\alpha(\underline{0})/V \equiv 0, \forall \alpha$ . However, in the second term of the first fourth-order contribution to Eq.

(A60), the term  $\bar{g}_{\kappa\lambda}^{-1}(|q_1 + q_2|)$  appears, which is even undefined for  $q_2 = -q_1 \neq 0$ , let alone  $q_1 = q_2 = 0$ . This is the reason why we introduced the factor  $1 - \delta(q_1 + q_2)$  in this contribution to  $F_L$ .

**APPENDIX B: CHARACTERISTIC FUNCTIONS OF MULTIVARIATE GAUSSIAN DISTRIBUTION FUNCTIONS**

The subject of this Appendix is the calculation of the following type of average over the ensemble of unperturbed chain conformations

$$C_m(j_1, \dots, j_m) \equiv \langle e^{-i \sum_{l=1}^m q_l \cdot R_{j_l}} \rangle_0, \tag{B1}$$

with  $q_1, q_2, \dots, q_m$   $m$  arbitrary wave vectors,  $\{j_1, \dots, j_m\} \subset \{1, 2, \dots, N\}$   $m$  arbitrary segment labels, and where  $\langle \dots \rangle_0$  is defined by Eqs. (A14) and (A24). An example of such an average is given by Eq. (A39). As this ensemble is described by a multivariate Gaussian distribution function [see Eq. (A14)], this average is in fact an  $m$ -point correlation function or more precisely an  $m$ -point characteristic function of this multivariate Gaussian distribution function. Explicitly this correlation function is given by

$$C_m(j_1, \dots, j_m) \equiv \frac{1}{V} \int_V d^3 R_1 \dots \int_V d^3 R_N \prod_{j=1}^{N-1} \left( \frac{3}{2\pi a^2} \right)^{3/2} \times e^{-(3/2a^2)(R_{j+1} - R_j)^2} e^{-i \sum_{l=1}^m q_l \cdot R_{j_l}}. \tag{B2}$$

By introducing the following isometric change of variables:

$$u_1 \equiv R_1 \\ u_j \equiv R_j - R_{j-1} \quad (j = 2, \dots, N), \tag{B3}$$

the argument of the product of the exponentials in the integrand of Eq. (B2) becomes

$$-\frac{3}{2a^2} \sum_{j=2}^N u_j^2 - i \sum_{l=1}^m q_l \cdot \sum_{k=1}^{j_l} u_k. \tag{B4}$$

The second term can be written as

$$-i \sum_{l=1}^m q_l \cdot \sum_{k=1}^{j_l} u_k \equiv -i u_1 \cdot \sum_{l=1}^m q_l - i \sum_{l=1}^m q_l \cdot \sum_{k=2}^N \theta(j_l - k) u_k \\ = -i u_1 \cdot \sum_{l=1}^m q_l - i \sum_{k=2}^N \left[ \sum_{l=1}^m \theta(j_l - k) q_l \right] \cdot u_k, \tag{B5}$$

where  $\theta(n)$  is a Heaviside step function. If we now ‘‘complete the square’’ by combining the last term of Eq. (B5) with the first term of Eq. (B4), therefore, Eq. (B4) can be written as

$$-i u_1 \cdot \sum_{l=1}^m q_l - \frac{3}{2a^2} \sum_{j=2}^N \left[ u_j + \frac{ia^2}{3} \sum_{l=1}^m \theta(j_l - j) q_l \right]^2 \\ - \frac{a^2}{6} \sum_{j=2}^N \sum_{k=1}^m \sum_{l=1}^m q_k \cdot q_l \theta(j_k - j) \theta(j_l - j). \tag{B6}$$

It is easy to verify that

$$\sum_{j=2}^N \theta(j_k - j) \theta(j_l - j) \equiv \min\{j_k, j_l\} - 1, \tag{B7}$$

therefore,  $C_m$  becomes

$$C_m(j_1, \dots, j_m) \\ \equiv \left( \frac{3}{2\pi a^2} \right)^{3(N-1)/2} e^{(a^2/6) \sum_{k=1}^m \sum_{l=1}^m [\min\{j_k, j_l\} - 1] q_k \cdot q_l} \frac{1}{V} \\ \times \int_V d^3 u_1 e^{-i u_1 \cdot \sum_{l=1}^m q_l} \prod_{k=2}^N \int_V d^3 u_k \\ \times e^{-(3/2a^2) \sum_{j=2}^N [u_j + (ia^2/3) \sum_{l=1}^m \theta(j_l - j) q_l]^2} \\ = \delta \left( \sum_{l=1}^m q_l \right) e^{-(a^2/6) \sum_{k=1}^m \sum_{l=1}^m \min\{j_k, j_l\} q_k \cdot q_l}, \tag{B8}$$

because each of the  $N - 1$  Gaussian integrals cancels one factor  $(3/2\pi a^2)^{3/2}$  in front and the integral over  $u_i$  vanishes unless the sum over the  $m$   $q$ -vectors is equal to zero, in which case the integral cancels the factor  $V$  in the denominator. The fact that the delta function causes  $\sum_{l=1}^m q_l = 0$  is the reason that the  $-1$  in Eq. (B7) vanishes from the argument of the exponent in Eq. (B8). Similarly by using this same condition it follows that:

$$\sum_{k=1}^m \sum_{l=1}^m \min\{j_k, j_l\} q_k \cdot q_l \\ = \sum_{k=1}^m j_k q_k^2 + \sum_{k=1}^m \sum_{l \neq k}^m \min\{j_k, j_l\} q_k \cdot q_l \\ = - \sum_{k=1}^m \sum_{l \neq k}^m [j_k - \min\{j_k, j_l\}] q_k \cdot q_l \\ = - \sum_{k=1}^m \sum_{l > k}^m |j_k - j_l| q_k \cdot q_l. \tag{B9}$$

This last step follows from the observation that for a given pair  $(k, l)$  with  $l \neq k$  one either has that  $j_k \leq j_l$ , in which case  $j_k - \min\{j_k, j_l\} = 0$  or  $j_k > j_l$  leading to  $j_k - \min\{j_k, j_l\} = j_k - j_l$ . With this last result  $C_m$  can finally be written as

$$C_m(j_1, \dots, j_m) = \delta \left( \sum_{l=1}^m q_l \right) e^{(a^2/6) \sum_{k=1}^m \sum_{l > k}^m |j_k - j_l| q_k \cdot q_l}, \tag{B10}$$



which for instance for  $m=2$  reduces to Eq. (A39) and which is being used with  $m=3$  and 4 in Eq. (A46), (A47), and in Sec. III.

- <sup>1</sup>H. Benoit and G. Hadziioannou, *Macromolecules* **21**, 1449 (1988).
- <sup>2</sup>G. H. Fredrickson, S. T. Milner, and L. Leibler, *Macromolecules* **25**, 6341 (1992).
- <sup>3</sup>S. V. Panyukov and S. I. Kuchanov, *J. Phys. II* **2**, 1973 (1992).
- <sup>4</sup>I. Erukhimovich and A. V. Dobrynin, *Macromol. Symp.* **81**, 253 (1994).
- <sup>5</sup>H. J. Angerman, G. Hadziioannou, and G. ten Brinke, *Phys. Rev. E* **50**, 3808 (1994).
- <sup>6</sup>C. D. Sfatos, A. M. Gutin, and E. I. Shakhnovich, *Phys. Rev. E* **51**, 4727 (1995).
- <sup>7</sup>H. J. Angerman, G. ten Brinke, and I. Erukhimovich, *Macromolecules* **29**, 3255 (1996).
- <sup>8</sup>S. I. Kuchanov and S. V. Panyukov, *Comprehensive Polymer Science, Second Supplement*, edited by G. Allen (Pergamon, Oxford, 1996), chap. 13, pp. 441–496.
- <sup>9</sup>H. J. Angerman, G. ten Brinke, and I. Erukhimovich, *Macromolecules* **31**, 1958 (1998).
- <sup>10</sup>See for instance M. F. Schulz, F. S. Bates, K. Almdal, and K. Mortensen, *Phys. Rev. Lett.* **73**, 86 (1994).
- <sup>11</sup>V. E. Podneks and I. W. Hamley, *JETP Lett.* **64**, 617 (1996); I. W. Hamley and V. E. Podneks, *Macromolecules* **30**, 3701 (1997).
- <sup>12</sup>For example in the SSR of ABC triblock copolymer melts, lamellar phases can never be treated in the first harmonic approximation. The problem is that the lamellae order in the sequence  $ABCBABCBA\cdots$  and hence the period of the  $B$ -rich domains is twice that of the  $A$ - and  $C$ -rich domains. See M. W. Matsen, *J. Chem. Phys.* **108** (2), 785 (1998).
- <sup>13</sup>M. W. Matsen and M. Schick, *Phys. Rev. Lett.* **72**, 2660 (1994).
- <sup>14</sup>H. J. Angerman, G. ten Brinke, and J. J. M. Slot, *The European Physical Journal B* (submitted).
- <sup>15</sup>N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
- <sup>16</sup>P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
- <sup>17</sup>L. D. Landau, *Phys. Z. Sowjetunion* **11**, 26 (1937); [Translated in *JETP* **7**, 19 (1937)]; J. C. Toledano and P. Toledano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987), Vol. 3.
- <sup>18</sup>I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, *Rev. Mod. Phys.* **50**, 683 (1978).
- <sup>19</sup>P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- <sup>20</sup>L. Leibler, *Macromolecules* **13**, 1602 (1980).
- <sup>21</sup>S. Alexander and J. McTague, *Phys. Rev. Lett.* **41**, 702 (1978).
- <sup>22</sup>E. I. Shakhnovich and A. M. Gutin, *J. Phys. (Paris)* **50**, 1843 (1989).