Macrophase and Microphase Separation in Random Comb Copolymers

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ABSTRACT: We introduce and analyze three models for comb copolymer melts that allow for randomness in the placement and number of teeth. In the first model the polymers are constructed using a two-parameter Markov process, which links dispersity in the number of teeth with correlations in their placement. In the other two models these two effects are separated so that the dispersity is allowed to vary while tooth–tooth correlations remain fixed. In one such model the tooth placement is uncorrelated, while in the second it is perfectly correlated. The behavior of these models is studied as a function of the dispersity in the number of teeth and the average number of teeth. The results pinpoint the factors that control micro- versus macrophase separation and thereby yield guidelines for controlling the phase behavior of comb copolymer melts.

1. Introduction

The phase behavior of copolymer melts composed of weakly incompatible monomers has been of interest for some time. To illustrate the complexity of these systems, consider a melt of identical copolymers made up of two different monomers, A and B. At high temperatures, thermal fluctuations dominate and the system forms a disordered phase, where the average spatial distribution of As and Bs is uniform. As the temperature is lowered, the monomers of types A and B tend to repel each other. If the monomers were not chemically bonded, one would expect a phase transition of two coexisting phases, at a given temperature, T_0. Since the monomers are chemically linked, this separation is limited and the ordered phase that occurs is one in which there are regions rich in A and regions rich in B, with a length scale determined both by the architecture of the polymers and by the temperature. Such an ordered phase is referred to as a "microphase", and the order–disorder transition that occurs in such a system is referred to as "microphase separation". It is possible to observe many different types of microphases distinguished by geometric orderings, even within one system, such as lamellar phases, hexagonally close-packed cylinders, and body-centered cubic phases.[1]

In practice, it is often difficult or expensive to make melts of identical copolymers or even, if the polymers are allowed to be different in structure, to ensure that they have the same numbers of As and Bs. It is therefore important to understand the effects of randomness on the phase behavior of such systems. In particular, if there is a dispersity in the numbers of A and B within the polymers, then there is a driving force for a separation of As and Bs on macroscopic length scales. Whether such a "macrophase" separation is to two coexisting phases, as it would be if the monomers were unconnected, as suggested recently by Fredrickson, Milner, and Leibler,[2] or of some more complex type,[3] is unclear and will form the basis of a separate study.

There have been a number of studies into the effects of randomness on the phase behavior of linear copolymers.[2–9] Of particular interest here is a study by Fredrickson and co-workers[2] in which they consider a class of random linear copolymers constructed according to a two-parameter Markov process. The two parameters in this process are the average ratio of As to Bs on the chains and the correlation of monomer types along the chain. The study provided clear evidence of a competition between the two types of order-disorder transitions and addressed the nature of the resulting microphases. However, the parameter linked with correlations also controlled the dispersion of the ratio of A to B monomers within the chain. It was not possible to study the effects of varying these quantities independently. In the present study, two models are introduced in which the dispersity and the correlations are independent.

The system examined is composed of comb copolymers. The combs studied are made up of fixed length backbones made of monomer A with fixed length teeth of monomer type B. The randomness comes in the number of teeth and the correlations in the placements of the teeth.

It is shown here that, when the correlations between the teeth are negligible, the average number of teeth and the dispersity play analogous roles: increasing either will favor macrophase separation, while lowering either will favor microphase separation. When the positioning of the teeth is perfectly correlated, however, these two quantities play different roles. Keeping the average number of teeth fixed, it is still possible to pass from microphase to macrophase separation by increasing the dispersity, but a change in the average number of teeth is not sufficient to bring about an analogous change. For the fully correlated system, we observe two different types of microphase separation with different scaling behavior in the average number of teeth.

The remainder of the article is organized as follows. In section 2, we introduce the essentials of the RPA mean-field theory used in this study. In section 3, we look at the class of comb copolymers constructed along the same lines as the linear copolymers of Fredrickson

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et al.[2] and compare the behavior of the two systems. In section 4, we look at the effects of dispersity on combs in which the teeth placements are uncorrelated. In section 5, the effects of dispersity are studied for comb copolymers where the teeth are perfectly spaced. Section 6 is reserved for a summary and concluding remarks.

2. RPA Scattering Function

In this article, we look at the spinodal instability of the homogeneous, or disordered, phase. While in general the spinodal instability is expected to be pre-empted by a first-order transition, due to the high degree of polymerization of polymers, the spinodal and the true transition line are expected to lie close to each other. A full calculation of the transition line would require at least the calculation of the fourth-order terms in the coarse-grained free energy.

In what follows, it is assumed that the polymers considered are Gaussian and that the interaction part of the Hamiltonian is given by[10,11]

$$H_I = -\chi \int d^3r\, \psi^2(\mathbf{r}) \qquad (1)$$

Denoting by f the volume fraction of monomers of type A in the melt, the order parameter ψ is given by $\psi(\mathbf{r}) = (1-f)\varrho_A(\mathbf{r}) - f\varrho_B(\mathbf{r})$, where $\varrho_A(\mathbf{r})$ and $\varrho_B(\mathbf{r})$ are the local densities of A and B. The parameter χ is the Flory–Huggins interaction energy. Since the polymers examined are in a melt, the approximation that the melt is incompressible is made, i.e., $\varrho_A(\mathbf{r}) + \varrho_B(\mathbf{r}) = \varrho$. For convenience we set $\varrho = 1$.

Within the random phase approximation[10,11] the equation for the scattering function, $S(\mathbf{q})$, is given as

$$S(\mathbf{q}) \equiv \langle \psi(\mathbf{q})\psi(-\mathbf{q})\rangle = \frac{W(\mathbf{q})}{T(\mathbf{q}) - 2\chi W(\mathbf{q})} \qquad (2)$$

where

$$W(\mathbf{q}) = S_{AA}(\mathbf{q})S_{BB}(\mathbf{q}) - S_{AB}^{\,2}(\mathbf{q}) \qquad (3)$$

$$T(\mathbf{q}) = S_{AA}(\mathbf{q}) + 2S_{AB}(\mathbf{q}) + S_{BB}(\mathbf{q}) \qquad (4)$$

with the connected correlation functions defined by $S_{\alpha\beta} = \langle \varrho_\alpha(\mathbf{q})\varrho_\beta(-\mathbf{q})\rangle_0 - \langle \varrho_\alpha(\mathbf{q})\rangle_0 \langle \varrho_\beta(-\mathbf{q})\rangle_0$. The average $\langle\cdot\rangle_0$ is over the noninteracting chains, with $\chi = 0$. The argument $\mathbf{q}$ indicates a Fourier transform of the function in real space. Since we are looking for the spinodal instability for a homogeneous phase, the functions of interest will depend only on the modulus of $\mathbf{q}$, and we henceforth drop the vector dependence of the functions.

The spinodal is defined as the value of χ for which $S(q) \to \infty$ for some q_0. The value of q_0^{-1} is a measure of the length scale characteristic of the emergent structure; for macrophase separation the first divergence in S occurs at $q_0 = 0$. For microphase separation there is a finite characteristic length scale; therefore, q_0 is found to be finite and nonzero. As can be seen from eq 2, within the RPA, the maximum in S is at $q = q_0$, independent of χ, and the divergence will occur when $\chi = \chi_s$, given by

$$\chi_S = \frac{T(q_0)}{2W(q_0)} \qquad (5)$$

corresponding to the spinodal instability.

The calculation of the spinodal line requires a calculation of $S_{\alpha\beta}$. In real space,

$$S_{\alpha\beta}(\mathbf{r}-\mathbf{r}') = \frac{c}{N_P}\sum_{i=1}^{N_P}\sum_{j\in\alpha}\sum_{j'\in\beta}\langle \delta(\mathbf{r}_i^j - \mathbf{r})\delta(\mathbf{r}_i^{j'} - \mathbf{r}')\rangle_0 \qquad (6)$$

where N_P is the number of comb copolymers in the system and $c = N_P/V$ is their number density. If N is the average number of monomers per chain, then $c = \varrho/N = 1/N$, where we have set the density to unity. The indices j and j' label the monomers in each comb, with the sums restricted over type α and type β monomers, respectively.

Using the probability distribution that the ends of a Gaussian chain of length M monomers of size a are found at $\mathbf{r}$ and $\mathbf{r}'$,

$$P(\mathbf{r},\mathbf{r}';M) \propto \exp\left(\frac{-3(\mathbf{r}-\mathbf{r}')^2}{2a^2M}\right) \qquad (7)$$

then taking Fourier transforms and using an explicit representation of the delta function, we obtain the following expressions for $S_{\alpha\beta}$:

$$S_{AA}(q) = cN_A^{\,2}\int_0^1\int_0^1 \exp(-q^2R_A^{\,2}|\tau-\tau'|)\, d\tau\, d\tau' \qquad (8)$$

$$S_{AB}(q) = cN_An_B\int_0^1 \exp(-q^2r_B^{\,2}x)\, dx \int_0^1\int_0^1 \overline{p_1(\tau;n_t)} \times \exp(-q^2R_A^{\,2}|\tau-\tau'|)\, d\tau\, d\tau' \qquad (9)$$

$$S_{BB}(q) = cn_B^{\,2}\,\overline{n_t}\int_0^1\int_0^1 \exp(-q^2r_B^{\,2}|\tau-\tau'|)\, d\tau\, d\tau' + cn_B^{\,2}\left(\int_0^1 \exp(-q^2r_B^{\,2}x)\, dx\right)^2 \int_0^1\int_0^1 \overline{p_2(\tau,\tau';n_t)} \times \exp(-q^2R_A^{\,2}|\tau-\tau'|)\, d\tau\, d\tau' \qquad (10)$$

Here, $\bar{\cdot} = (N_P)^{-1}\sum_{i=1}^{N_P}\cdot$, which represents an average over all the polymers in the melt. Since the melt is taken to be in the thermodynamic limit, polymers with different numbers of teeth will appear in the correct proportions. Different realizations of the melt will therefore be statistically identical, and an additional quenched average over different realizations of the melt is not required.

The first term in S_{BB} is the average correlation within a tooth, and the second term is the average correlation between teeth. N_A is defined as the number of monomers in the backbone (of type A), whereas n_B is the number of monomers in each tooth (of type B). The overall number of monomers of type B will vary from comb to comb and can only be specified as an average, $\overline{N_B} = n_B\overline{n_t}$, where n_t is the number of teeth in the comb. The parameters $R_A^2 = N_Aa^2/6$ and $r_B^2 = n_Ba^2/6$ are the squared radii of gyration for the backbone and each tooth, respectively. The function $p_1(x;n_t)$ is the probability of finding a tooth at a fraction x of the distance along the backbone from one end, conditional on the comb having n_t teeth. The term $p_2(x,y;n_t)$ is a similarly defined function, giving the probability of finding simultaneously a tooth at position x and y.

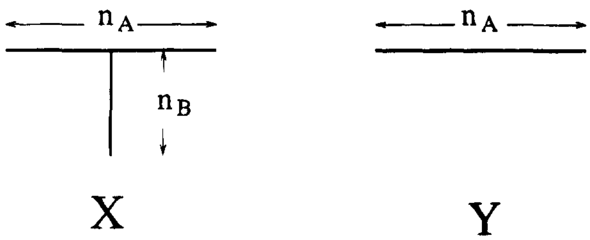

Figure 1. Building blocks for the construction of combs using the two-parameter Markhov process.

Evaluating eqs 8–10 leads to

$$S_{AA} = \frac{2cN_A^{\ 2}}{q^4 R_A^{\ 4}}(\exp(-q^2 R_A^{\ 2}) + q^2 R_A^{\ 2} - 1) \quad (11)$$

$$S_{AB} = \frac{cN_A n_B(1 - e^{-q^2 r_B^2})}{q^2 r_B^{\ 2}} \int_0^1 \int_0^1 \overline{p_1(\tau;n_t)} \times \exp(-q^2 R_A^{\ 2}|\tau - \tau'|)\, d\tau\, d\tau' \quad (12)$$

$$S_{BB} = \frac{2cn_B^{\ 2}\, \overline{n_t}}{q^4 r_B^{\ 4}}(\exp(-q^2 r_B^{\ 2}) + q^2 r_B^{\ 2} - 1) + \frac{cn_B^{\ 2}(1 - e^{-q^2 r_B^2})^2}{q^4 r_B^{\ 4}} \int_0^1 \int_0^1 \overline{p_2(\tau,\tau';n_t)} \times \exp(-q^2 R_A^{\ 2}|\tau - \tau'|)\, d\tau\, d\tau' \quad (13)$$

In order to calculate $S(q)$ it is necessary therefore to calculate $p_1(x;n_t)$ and $p_2(x,y;n_t)$ for the different forms of randomness. The probabilities p_1 and p_2 are normalized according to

$$\int_0^1 p_1(x;n_t)\, dx = n_t \quad (14)$$

$$\int_0^1 p_2(x,y;n_t)\, dx\, dy = n_t(n_t - 1) \quad (15)$$

3. Markov Process Construction of Comb Copolymers

In this section, a two-variable Markov process is used, similar to that used by Fredrickson et al.,[2] in order to construct our ensemble of combs. These combs are formed by the combination of two types of building blocks, shown in Figure 1, which we will label X and Y. X is a section of backbone comprising n_A monomers of type A and a tooth of n_B monomers of type B extending from the center of the backbone fragment. Y, on the other hand, is simply a section of backbone n_A monomers in length. Each comb is composed of $n = N_A/n_A$ units of either type X or Y. Below we will need the radius of gyration of a backbone segment, r_A, given by $r_A^2 = R_A^2/n$.

We define f_t as the fraction of units that are of type X, i.e., the ratio of teeth present to the maximum number of teeth possible. The method of construction is as follows. The first section of a comb is chosen to be of type X with probability f_t and of type Y with probability $1 - f_t$. All subsequent units are added according to the probability matrix $\mathbf{M}_{\alpha,\beta} = p_{\alpha\beta}$, where α is the type of unit to be added and β is the type of the previous unit. While this matrix specifies four probabilities, since a unit must be added at each stage, the restrictions $p_{XY} + p_{YY} = 1$ and $p_{XX} + p_{YX} = 1$ reduce the set to two independent probabilities. The Markov process is defined in terms of two parameters: f_t, already introduced, and $\lambda = p_{XX} + p_{YY} - 1$, which is a measure of the length over which blocks of a particular type are correlated, or the correlation length. There are two limits, $\lambda = -1$ and $\lambda = 1$, in which the positions of the teeth are highly correlated. If $\lambda = -1$ then $p_{XX} = p_{YY} = 0$. In this case, every time an additional section is added it must be of a different type than the previous, giving rise to a melt of identical comb copolymers with $n/2$ teeth all perfectly spaced. This is the system studied by Benoit and Hadziiannou[12] and Shinozaki, Jasnow, and Balazs.[13] If, on the other hand, $\lambda = 1$, then $p_{XX} = p_{YY} = 1$, and once the first section is placed, all subsequent sections must be of the same type. This gives rise to either perfect linear homopolymers or combs with n evenly spaced teeth. The fraction of combs in the melt is then just f_t. The condition $\lambda = 0$ corresponds to the least correlated case, where each section is chosen independently, that is, without reference to the previous sections.

In order to relate f_t to p_{XX} and p_{YY}, we must determine the probability that a given unit chosen at random is of type X. On the one hand this is just f_t; on the other hand, this is the sum of the probabilities that the unit is of type X given that the previous unit is of type X and that the previous unit is of type Y. Putting these probabilities together yields

$$f_t = f_t p_{XX} + (1 - f_t)(1 - p_{YY}) \quad (16)$$

Using the definition of λ we have

$$p_{XX} = f_t(1 - \lambda) + \lambda \quad (17)$$

$$p_{YY} = 1 - f_t(1 - \lambda) \quad (18)$$

The probability matrix, in terms of f_t and λ becomes

$$\mathbf{M} = \begin{pmatrix} f_t(1 - \lambda) + \lambda & f_t(1 - \lambda) \\ (1 - f_t)(1 - \lambda) & 1 - f_t(1 - \lambda) \end{pmatrix} \quad (19)$$

Defining the variable σ_i for the ith unit in the chain so that $\sigma_i = 1$ if the ith section is of type X and $\sigma_i = 0$ if it is of type Y, then the probability that the sections i and j ($i \neq j$) both contain a tooth is given by $\langle \sigma_i \sigma_j \rangle$, or in terms of $\mathbf{M}$

$$\langle \sigma_i \sigma_j \rangle = f_t(1 \quad 0)\mathbf{M}^{|i-j|}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (20)$$

By diagonalizing the matrix $\mathbf{M}$, eq 20 may be evaluated to give

$$\langle \sigma_i \sigma_j \rangle = f_t^{\ 2} + f_t(1 - f_t)\lambda^{|i-j|} \quad (21)$$

Correlations fall off exponentially with a length scale determined by λ, as stated above. Since the probability that section i, chosen at random, is of type X is simply f_t, then one can write $\overline{n_t}$, $\overline{p_1(x;n_t)}$, and $\overline{p_2(x,y;n_t)}$ in terms of the Markov process as follows:

$$\overline{n_t} = f_t n \quad (22)$$

$$\overline{p_1(x;n_t)} = f_t \sum_{i=1}^{n} \delta(i(n_A/n) - (n_A/2n) - x) \quad (23)$$

$$\overline{p_2(x,y;n_t)} = (f_t^{\ 2} + f_t(1 - f_t)\lambda^{|i-j|}) \sum_{i=1}^{n} \sum_{j=1}^{n} \delta(i(n_A/n) - (n_A/2n) - x)\delta(j(n_A/2) - (n_A/2n) - y) \quad (24)$$

Substituting into eqs 11–13

$$\frac{S_{AA}\overline{n_t}}{N} = \frac{2f_t f^2}{n f_p^{\,2} q^4 r^4}\{e^{-n f_p q^2 r^2} + n f_p q^2 r^2 - 1\} \quad (25)$$

$$\frac{S_{AB}\overline{n_t}}{N} = \frac{2f^2 f_t^{\,2}}{n f_p^{\,2} q^4 r^4}(1 - e^{-(1-f_p)q^2 r^2}) \times \left\{n - e^{-f_p q^2 r^2/2}\left(\frac{1 - e^{-f_p n q^2 r^2}}{1 - e^{-f_p q^2 r^2}}\right)\right\} \quad (26)$$

$$\frac{S_{BB}\overline{n_t}}{N} = \frac{2f^2 f_t^{\,2}}{f_p^{\,2} q^4 r^4}\{e^{-(1-f_p)q^2 r^2} + (1 - f_p)q^2 r^2 - 1\} + \frac{2f^2 f_t^{\,3}}{f_p^{\,2} n q^4 r^4}(1 - e^{-(1-f_p)q^2 r^2})^2 \frac{e^{-f_p q^2 r^2}}{1 - e^{-f_p q^2 r^2}} \times \left(n - 1 - e^{-f_p q^2 r^2}\left(\frac{1 - e^{-(n-1)f_p q^2 r^2}}{1 - e^{-f_p q^2 r^2}}\right)\right) + \frac{2f^2 f_t^{\,2}(1 - f_t)}{f_p^{\,2} n q^4 r^4}(1 - e^{-(1-f_p)q^2 r^2})^2 \frac{\lambda e^{-f_p q^2 r^2}}{1 - \lambda e^{-f_p q^2 r^2}} \times \left(n - 1 - \lambda e^{-f_p q^2 r^2}\left(\frac{1 - \lambda^{n-1} e^{-(n-1)f_p q^2 r^2}}{1 - \lambda e^{-f_p q^2 r^2}}\right)\right) \quad (27)$$

where $r^2 \equiv r_A^{\,2} + r_B^{\,2}$, f is the volume fraction of A type monomers, and $f_p \equiv n_A/(n_A + n_B)$. It should be noted that f, f_t, and f_p are related through $f = f_p/(f_p + f_t - f_t f_p)$.

Whether the homogeneous state is unstable to microphase or macrophase separation is determined by the location of the maximum of $S(q;\chi = 0)$. If this occurs at $q = 0$, then the system will be unstable to macrophase separation. If, however, the maximum occurs at a finite q, then the system is unstable to microphase separation.

In Figure 2, we plot phase diagrams as a function of λ and f_t, the fraction of teeth present, which pinpoint whether the first transition is microphase separation or macrophase separation. Equations 17 and 18, coupled with $0 \le p_{XX}, p_{YY} \le 1$, impose a restriction on the range of allowed values for f_t for $\lambda < 0$. We have chosen for these figures $f_p = 1/4$, $1/2$, and $3/4$, respectively. In Figures 3 and 4, we show representative plots for the scattering function for $f_p = 0.5$, $f_t = 0.5$, $\lambda = -0.5$, and $\lambda = 0.5$, respectively.

In this section, the Markov construction method for combs, analogous to that used by Fredrickson et al.[2] for random block copolymers, has been presented. The behavior of the spinodal is found to be qualitatively similar to the block copolymer case, in that there is a region where microphase separation is the first instability and a region in which macrophase separation is the first instability. The existence of these regions persists for all values of n. This may be seen, for example from Figure 3 and 4, where there exists a definite limit as n is increased, which remains in the microphase and macrophase separation regions, respectively.[14] A detailed calculation of the phase diagrams would require a knowledge of higher order terms in the effective Hamiltonian.

4. Uniform Random Copolymer Combs

In this and the following section, two alternative simple models are introduced in which the randomness in the number of teeth may be varied without affecting the correlations in the tooth placement. In this section, we consider the case where the tooth placement is

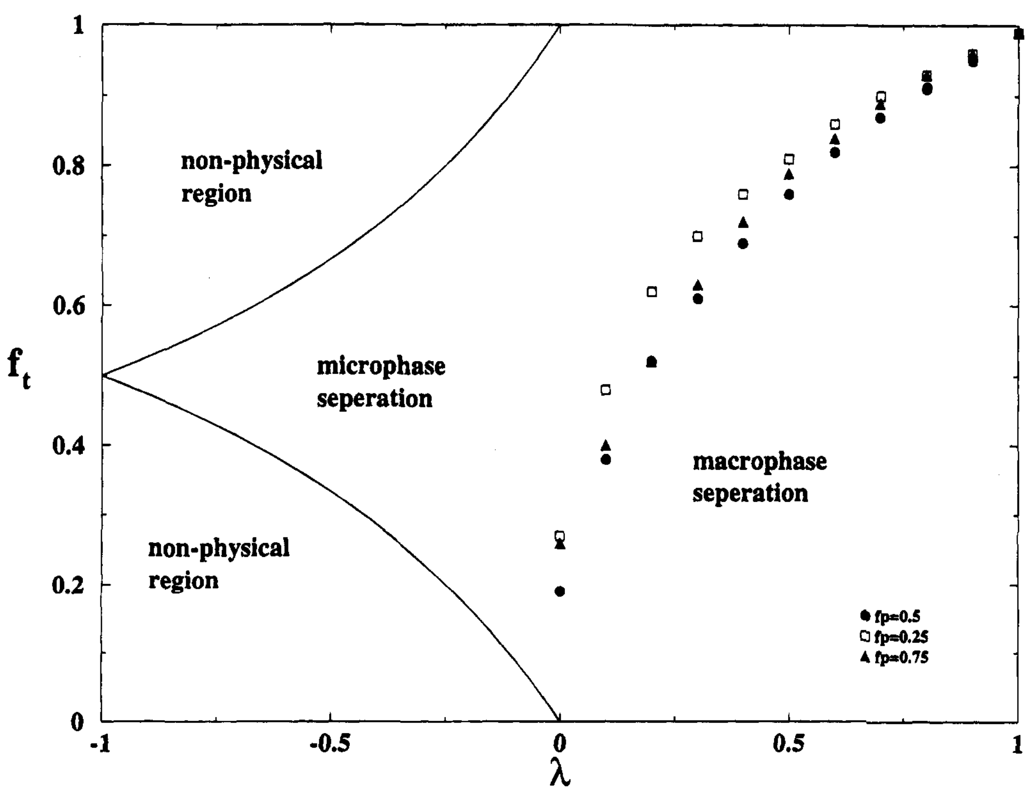

Figure 2. f_t plotted against λ showing the regions in which the homogeneous phase is unstable to microphase and macrophase separation.

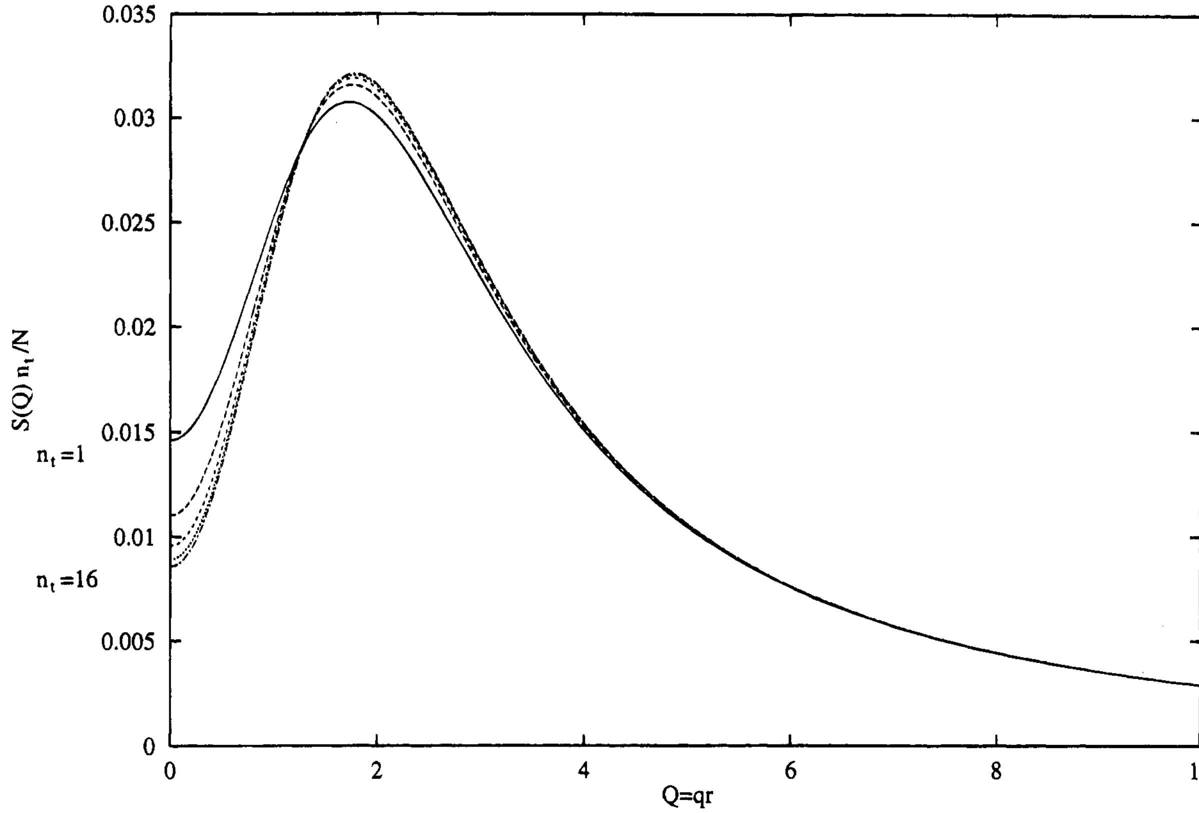

Figure 3. Plot of the scattering function for Markov combs, $f_t = 0.5$, $f_p = 0.5$, and $\lambda = -0.5$ for average numbers of teeth of 1, 2, 4, 8, and 16.

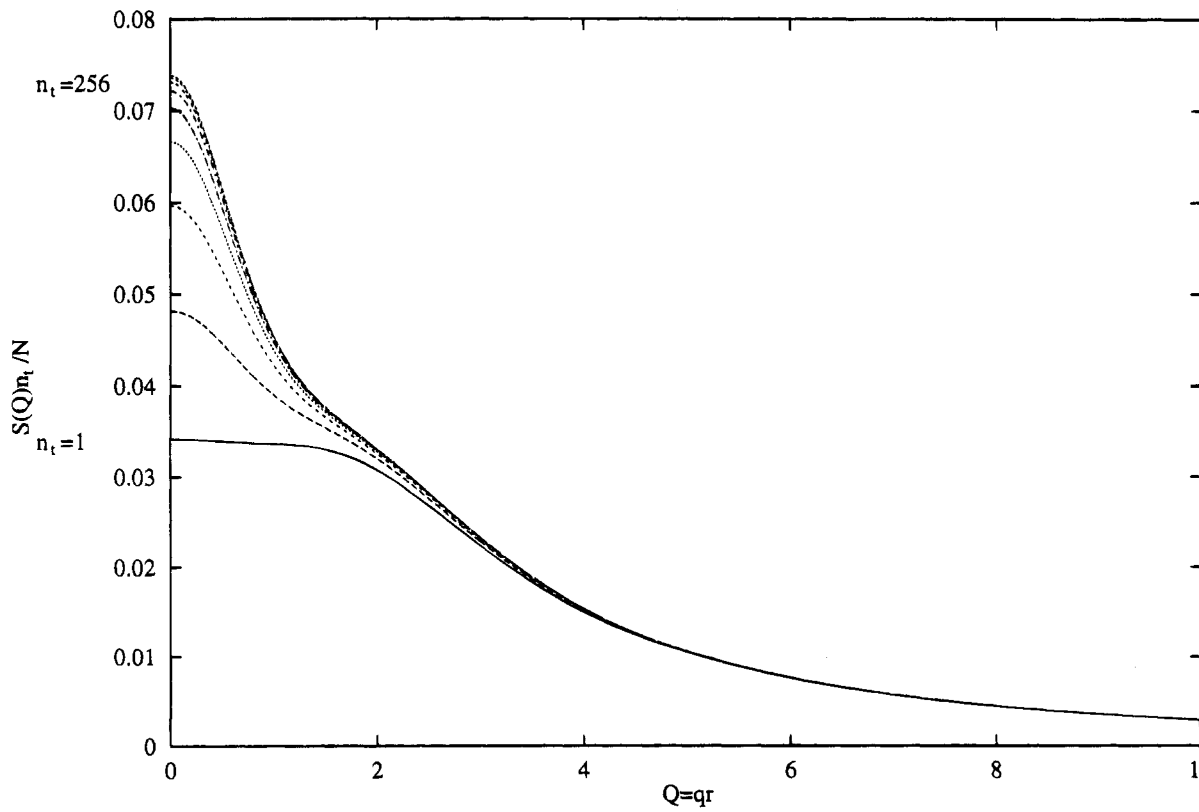

Figure 4. Plot of the scattering function for Markov combs, $f_t = 0.5$, $f_p = 0.5$, and $\lambda = 0.5$ for average numbers of teeth between 1 and 256 in powers of 2.

uncorrelated. In particular each comb is constructed as follows. Onto a backbone of a fixed number, N_A, of monomers of type A, n_t teeth are placed at random, where $n_t \geq 0$ and is chosen from a truncated Gaussian distribution

$$p(n_t)\mathrm{d}n_t = \frac{2\exp[-(n_t - n_0)^2]/\sigma^2}{\sigma\sqrt{\pi}\,\mathrm{erfc}(-n_0/\sigma)}\mathrm{d}n_t \qquad (28)$$

The parameters n_0 and σ are the mean and width for

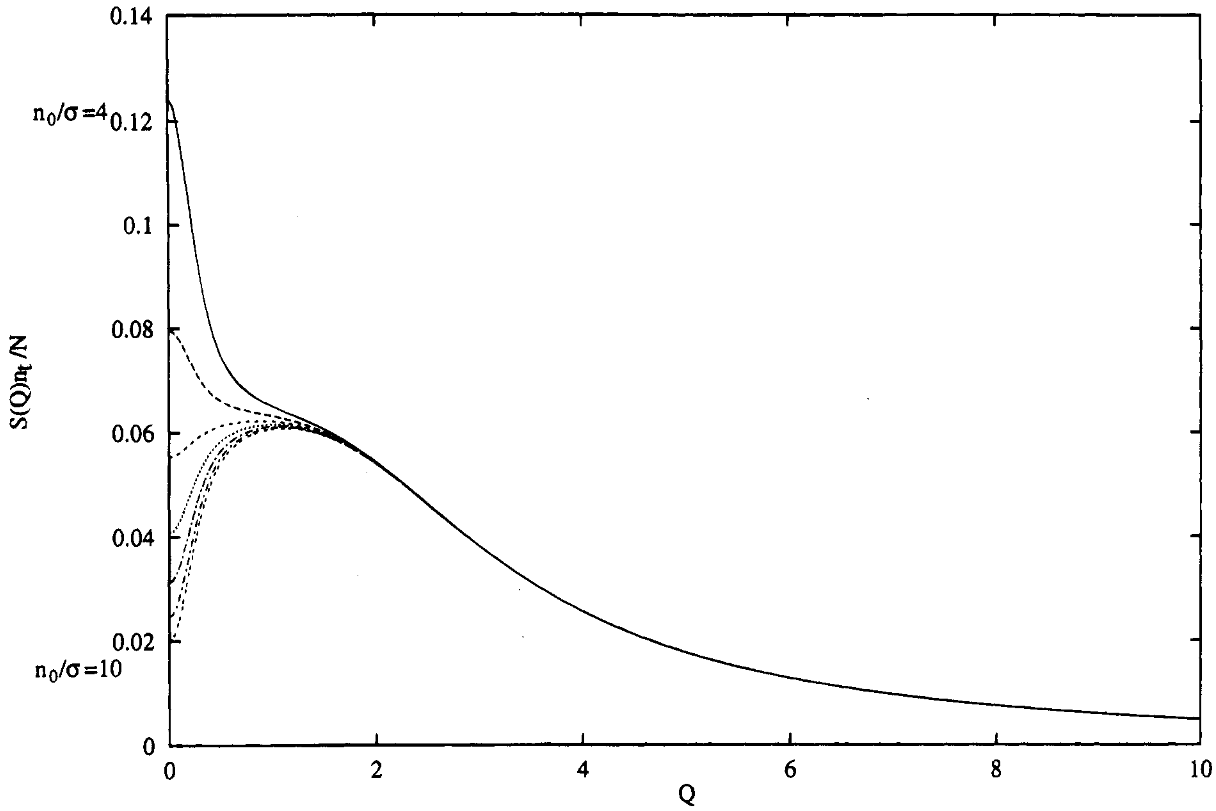

Figure 5. Plot of the scattering function for combs with uncorrelated tooth placement for values of n_0/σ = 4, 5, 6, 7, 8, 9, and 10. f = 0.5, and the average number of teeth is 64.

the untruncated Gaussian distributions. The true mean will be slightly shifted from n_0 since $n_t < 0$ is excluded. Each tooth may be placed anywhere on the backbone with a uniform probability distribution. This leads to $p_1(x;n_t) = n_t$ and $p_2(x,y;n_t) = n_t(n_t - 1)$.

Performing the integrals in eqs 11–13 we find

$$\frac{S_{AA}(q)\overline{n_t}}{N} = \frac{2}{\overline{n_t}q^4r^4}\{e^{-\overline{n_t}fq^2r^2} + \overline{n_t}fq^2r^2 - 1\} \quad (29)$$

$$\frac{S_{AB}(q)\overline{n_t}}{N} = \frac{2(1 - e^{-(1-f)q^2r^2})}{\overline{n_t}fq^6r^6}\{e^{-\overline{n_t}fq^2r^2} + \overline{n_t}fq^2r^2 - 1\} \quad (30)$$

$$\frac{S_{BB}(q)\overline{n_t}}{N} = \frac{2}{q^4r^4}\{e^{-(1-f)q^2r^2} + (1-f)q^2r^2 - 1\} + 2\left(\frac{\overline{n_t(n_t-1)}}{(\overline{n_t})^2}\right)\frac{(1 - e^{-(1-f)q^2r^2})^2}{\overline{n_t}f^2q^8r^8}\{e^{-\overline{n_t}fq^2r^2} + \overline{n_t}fq^2r^2 - 1\} \quad (31)$$

Again $r^2 \equiv r_A^2 + r_B^2$, but here we have chosen a slightly different definition of $r_A^2 \equiv R_A^2/\overline{n_t}$. It follows directly from the probability distribution defined in eq 28 that

$$\overline{n_t} = n_0\left\{\left(\frac{\sigma}{n_0}\right)\frac{e^{-(n_0/\sigma)^2}}{\sqrt{\pi}\,\mathrm{erfc}(-n_0/\sigma)} + 1\right\} \quad (32)$$

and

$$\overline{n_t(n_t - 1)} = n_0^2\left\{\frac{1}{2}\left(\frac{\sigma}{n_0}\right)^2 + \left(\frac{n_0 - 1}{n_0}\right)\left(\frac{\sigma}{n_0}\right)\frac{e^{-(n_0/\sigma)^2}}{\sqrt{\pi}\,\mathrm{erfc}(-n_0/\sigma)} + \frac{(2n_0 - 1)}{n_0}\right\} \quad (33)$$

Note from eq 32 that n_t/σ, which can provide a measure of the relative dispersity in the number of teeth, is a function of the ratio n_0/σ.

Figure 5 shows plots of $S(Q)\overline{n_t}/N$ against Q, where $Q = qr$, for different values of n_0/σ for a system of combs with an average number of teeth $\overline{n_t}$ = 64 and $f = 1/2$. As n_0/σ decreases, the relative dispersion in the number of teeth increases (see eq 32), and the type of phase separation observed changes from microphase to macrophase. This behavior is due to the fact that at large values of σ, the melt contains combs that are predominantly rich in A (few teeth), as well as combs that are predominantly rich in B (many teeth). This disparity in composition facilitates macrophase separation. The companion dependence on the number of teeth is shown in Figure 6. It is shown that the first instability in the homogeneous phase may also be changed from microphase separation to macrophase separation by increasing the mean number of teeth, keeping n_0/σ constant. Increasing the number of teeth increases the number of incompatible B components and again promotes macrophase separation.

The specific form for the probability distribution function, $p(n_t)$, is chosen to enable comparison with section 5 below. In the present case, the only parameters that enter into the calculation of $S(q)$ are the

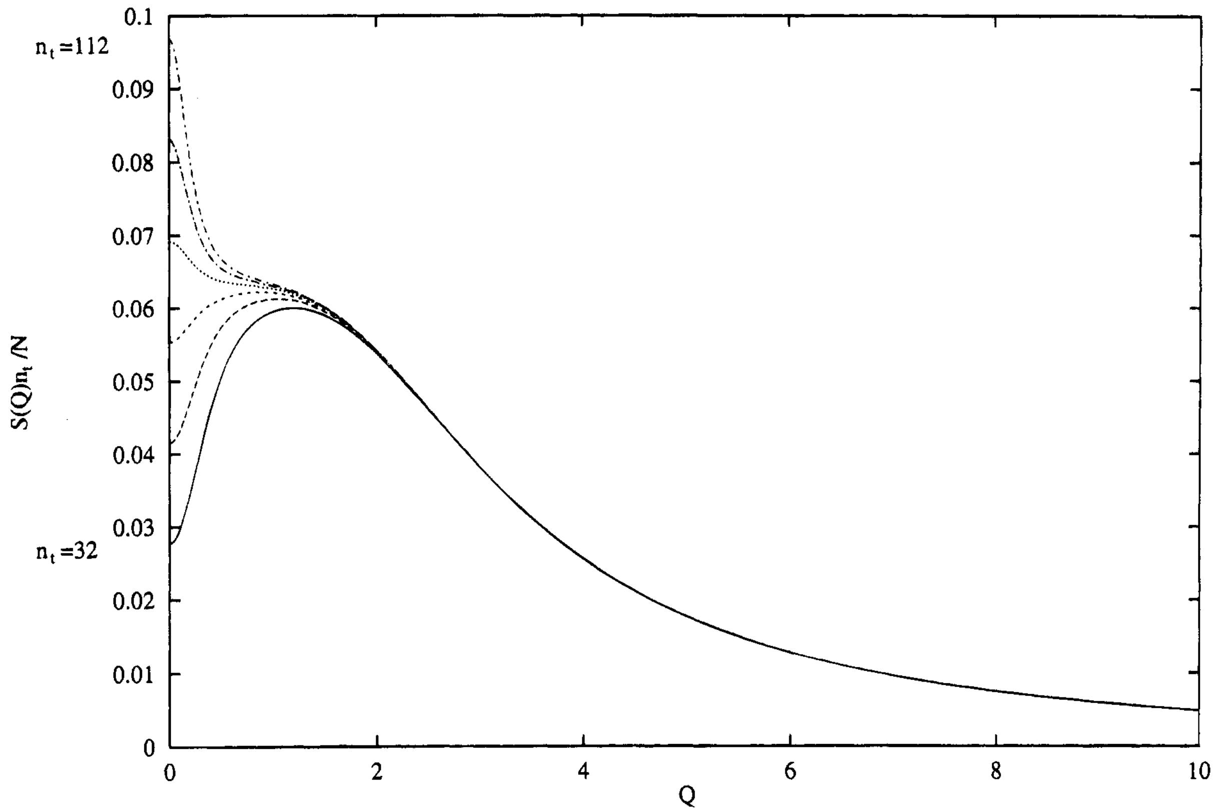

Figure 6. Plot of the scattering function for combs with different numbers of teeth. n_0/σ = 6.0.

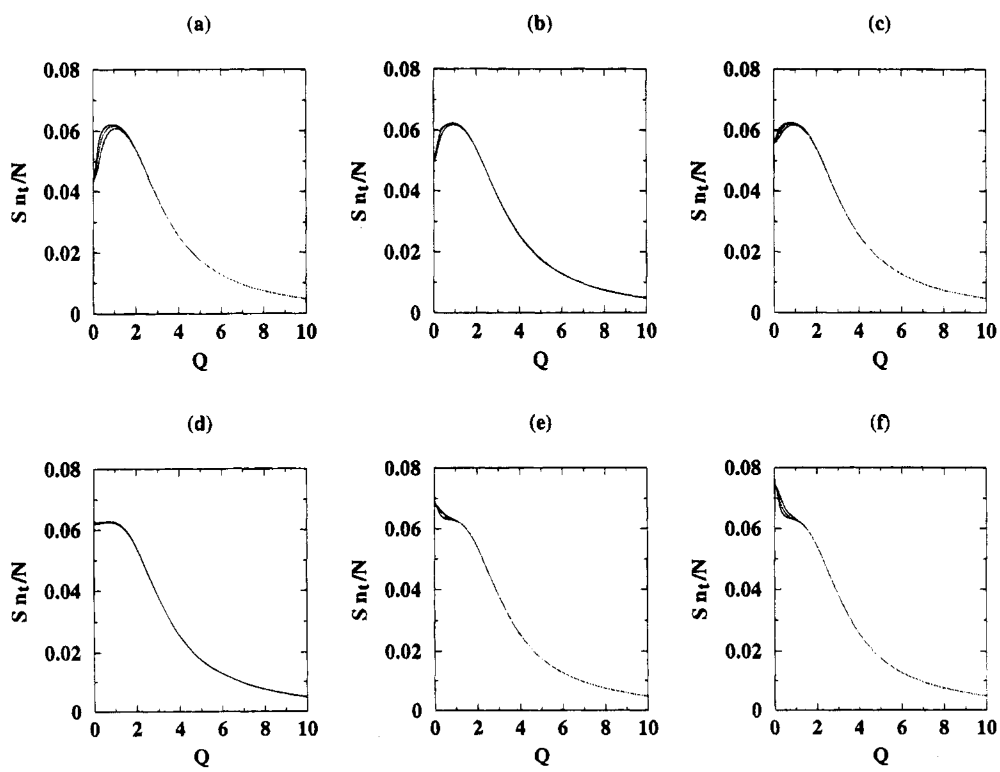

Figure 7. Plot of the scattering function for values of C between 0.7 (a) and 1.2 (f) in equal steps, with n_t = 32, 64, and 128.

average number of teeth, $\overline{n_t}$, and the variance in the number of teeth,

$$v = \frac{\overline{n_t^2}}{(\overline{n_t})^2} - 1 \qquad (34)$$

which is an appropriate measure of dispersity. All the results could be expressed in these terms.

In the limit $q \to 0$ the above eqs 29–33 give rise to the following expression for $S(q)$:

$$\frac{S(q \to 0)\overline{n_t}}{N} = \overline{n_t}\frac{f^2(1-f)^2 v}{1 + v(1-f)^2} \qquad (35)$$

It may be seen from eq 35 that if $v \propto 1/\overline{n_t}^{\omega}$, $S(q \to 0)\overline{n_t}/N$ will diverge with the number of teeth if ω

< 1, will go to zero as $\overline{n_t} \to \infty$ if $\omega > 1$, and will reach a finite, nonzero, value only if $\omega = 1$. In many real situations, the variance behaves as $v = C/\overline{n_t}$, which largely removes the dependence on the average number of teeth. In this case, the existence of micro- or macrophase separation depends on the precise value of the constant, C. One may well imagine that different chemical compositions of the monomers A and B, as well as the specifics of construction, may lead to different values for C. Figure 7 a–f shows the dependence of $S(q)$ on C for chains of $\overline{n_t} = 32$, 64, and 128. Figure 7a corresponds to $C = 0.7$ and Figure 7f corresponds to $C = 1.2$ with equal steps in C in between, showing the change from micro- to macrophase separation as C in increased.

In Figure 7 it may be seen that as $\overline{n_t}$ is increased, the peak in $S(Q)$ moves to smaller values of Q. This is a feature of the uniform distribution. The scaling behavior of this displacement with n_t was previously studied for all values of f by Shinozaki et al.[13]

In summary, for polymers in which the teeth are positioned at random with an uncorrelated uniform distribution, the roles of the dispersity and the average number of teeth are analogous. By keeping one of these variables fixed and varying the other, the nature of the ordering can change from macro- to microphase separation.

5. Regularly Spaced Random Copolymer Combs

In this section we consider the case in which the teeth are perfectly correlated and are spaced a distance x_0 from their neighbors. In this case, the minimum number of teeth is still zero, but there is a maximum given by $n_{max} = N_A a/x_0$. Each comb is constructed with n_t teeth, chosen from a Gaussian distribution with the constraint that $0 \geq n_t \geq n_{max}$. The Gaussian distribution is given by

$$p(n_t) = A^{-1} e^{-(n_t - n_0)^2/\sigma^2} \tag{36}$$

with

$$A = \sum_{n_t=0}^{n_{max}} e^{-(n_t - n_0)^2/\sigma^2} \tag{37}$$

The first tooth is placed at a distance x_1 from one end of the backbone and then the teeth are all placed at a distance x_0 from their neighbors. For each value of n_t, x_1 is chosen at random with a uniform probability on the interval $[0, N_A a - (n_t - 1)x_0]$.

These construction rules give

$$p_1(x) = \int_0^{1-n_t z_0} \sum_{i=0}^{n_t-1} \delta(z_1 + i z_0 - x)\, dz_1 \tag{38}$$

$$p_2(x,y) = \int_0^{1-n_t z_0} \sum_{i=0}^{n_t-1} \sum_{j\neq i=0}^{n_t-1} \delta(z_1 + i z_0 - x)\delta(z_1 + j z_0 - y)\, dz_1 \tag{39}$$

where r is defined as in the previous section, $z_0 = x_0/N_A a$ is the normalized distance between teeth, and $z_1 = x_1/N_A a$ measures the amount of bare backbone before the first tooth (normalized by the total length of backbone). Note that for fixed values of N_A, z_1 *increases* as $z_0 n_t$ is *decreased*.

Substituting back into eqs 11–13

$$\frac{S_{AA}\overline{n_t}}{N} = \frac{2}{\overline{n_t} q^4 r^4}\{e^{-\overline{n_t} f q^2 r^2} + \overline{n_t} q^2 r^2 - 1\} \tag{40}$$

$$\frac{S_{AB}\overline{n_t}}{N} = 2\frac{(1 - e^{-(1-f)q^2 r^2})}{\overline{n_t} q^4 r^4}\left\{\overline{n_t} - \overline{\left[\frac{1 + e^{-f\overline{n_t}(1+z_0)q^2r^2} - e^{-f\overline{n_t}(1-(n_t-1)z_0)q^2r^2} - e^{-n_t z_0 f\overline{n_t} q^2 r^2}}{f\overline{n_t} q^2 r^2 (1 - (n_t - 1)z_0)(1 - e^{-f\overline{n_t} z_0 q^2 r^2})}\right]}\right\} \tag{41}$$

$$\frac{S_{BB}\overline{n_t}}{N} = \frac{2}{q^4 r^4}\{(1 - f)q^2 r^2 + e^{-(1-f)q^2 r^2} - 1\} + \frac{2e^{-f\overline{n_t} z_0 q^2 r^2}(1 - e^{-(1-f)q^2 r^2})^2}{\overline{n_t} q^4 r^4 (1 - e^{-f\overline{n_t} z_0 q^2 r^2})^2}\{(\overline{n_t} - 1)(1 - e^{-f\overline{n_t} z_0 q^2 r^2}) + e^{-f\overline{n_t} z_0 q^2 r^2}(\overline{[e^{-(n_t-1)z_0 \overline{n_t} f q^2 r^2}]} - 1)\} \tag{42}$$

The averages over the number of teeth were done by performing the sums numerically.

In the model described in this section, there are two sources of randomness. The first comes from the number of teeth, and the second from the position of the teeth on the backbone, described by the probability functions p_1 and p_2. It is instructive to examine first the effect of tooth placement, for a fixed number of teeth, and then to introduce dispersity in the number of teeth.

In Figure 8a, we plot the scattering functions for combs with 16 teeth. The seven cases considered are $z_0 n_t = 0.7$, 0.75, 0.8, 0.85, 0.9, 0.95, and 1.0. Two peaks are observed at two different values of $Q = qr$. The first, at $Q = Q_1$, is absent when $z_0 n_t = 1.0$, but increases, and becomes the dominant peak, as $z_0 n_t$ is decreased. The second peak, at $Q = Q_2$, remains fixed with changing $z_0 n_t$. When this second peak is dominant, it gives rise to an instability to a microphase, as previously noted by Shinozaki et al.[13] and Benoit and Hadziiannou.[12] The length scale for this peak is provided by the intertooth distance. The peak at Q_1 arises from the positional randomness of the cluster of teeth along the backbone. The length scale for this peak is given by the amount of bare backbone on either side of the cluster of teeth. This increases as $z_0 n_t$ is decreased, and the corresponding peak is seen to grow. In Figure 8a the scattering function is shown for $n_t = 16$. The two peaks are not very well separated, but as may be seen in Figure 8b, the two peaks become more distinct as the number of teeth is increased (here $n_t = 100$). The increase in the number of teeth also enhances the value of $z_0 n_t$ for which the peak at Q_1 becomes dominant.

In Figure 9a, the scattering functions for small numbers of teeth and $z_0 n_t = 0.7$ are shown. Again, for comparison, Figure 9b shows scattering functions for larger numbers of teeth (here $z_0 n_t = 0.9$). It can be seen that this new peak gains in importance relative to the old one as the number of teeth is increased. In Figure 10, we show the scattering functions for $z_0 n_t = 0.5$ and $n_t = 4$, 8, 16, 24, 32, and 48. Here the value of $z_0 n_t$ is

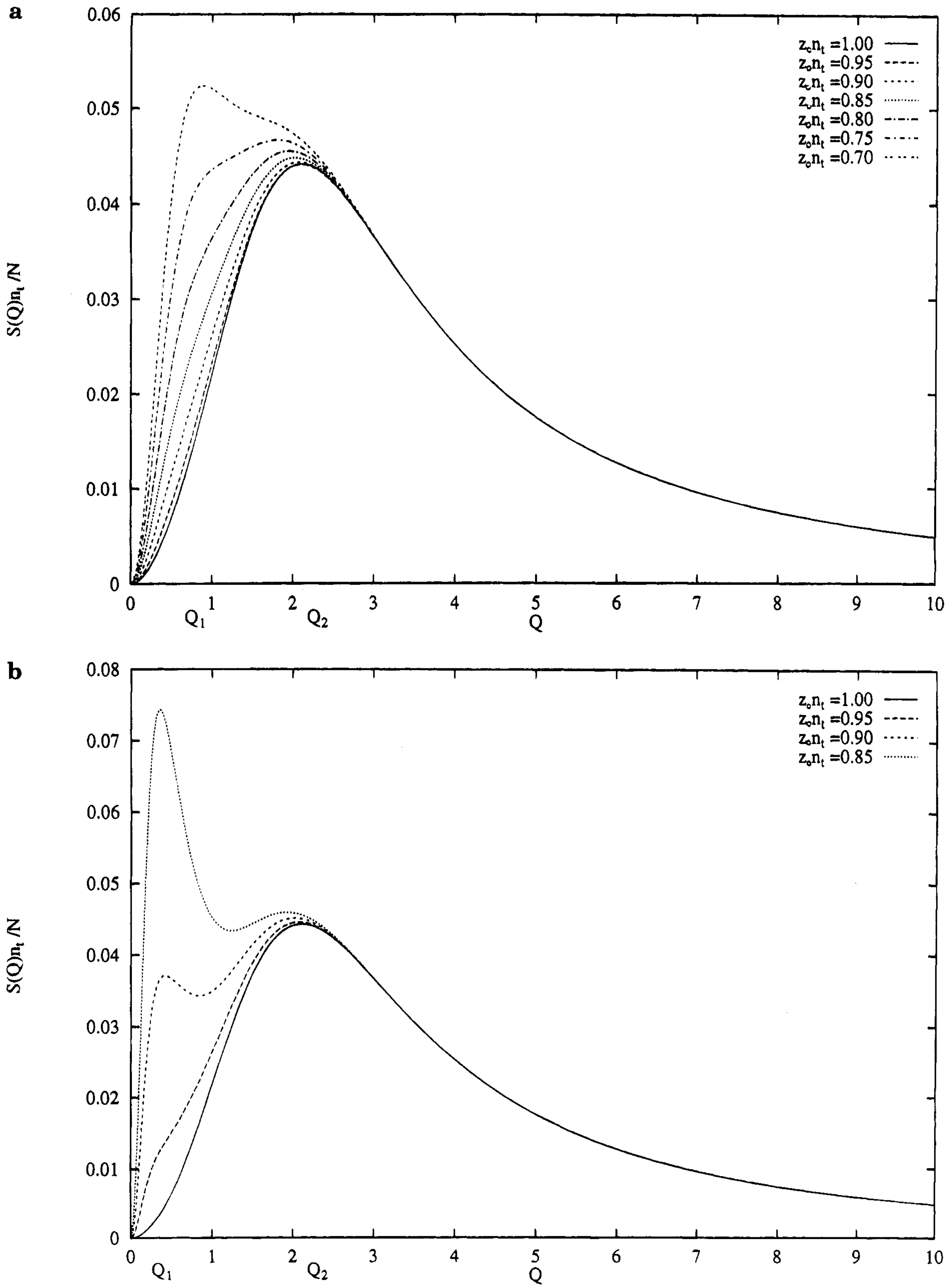

Figure 8. Plot of the scattering function for a regularly spaced comb with (a) 16 teeth and (b) 100 teeth and different values of z_0n_t.

sufficiently low (and, hence, z_1 is sufficiently high) that the peak at Q_2 essentially vanishes. To gain more information about the character of the peak at Q_1, we plotted $S(Q)/N$ against $Qn_t^{1/2}$. As n_t is increased, the plots rapidly fall to a limiting curve. From this limiting scaling behavior, it may be seen that for the new microphase at Q_1, the ensemble of teeth effectively appear as a single tooth. Note that changing the number of teeth only weakly affects the scattering function away from the peak.

These observations imply that the important parameter in determining which form of microphase wins is the amount of bare backbone on either end relative to the intertooth spacing. If this is large, then the teeth

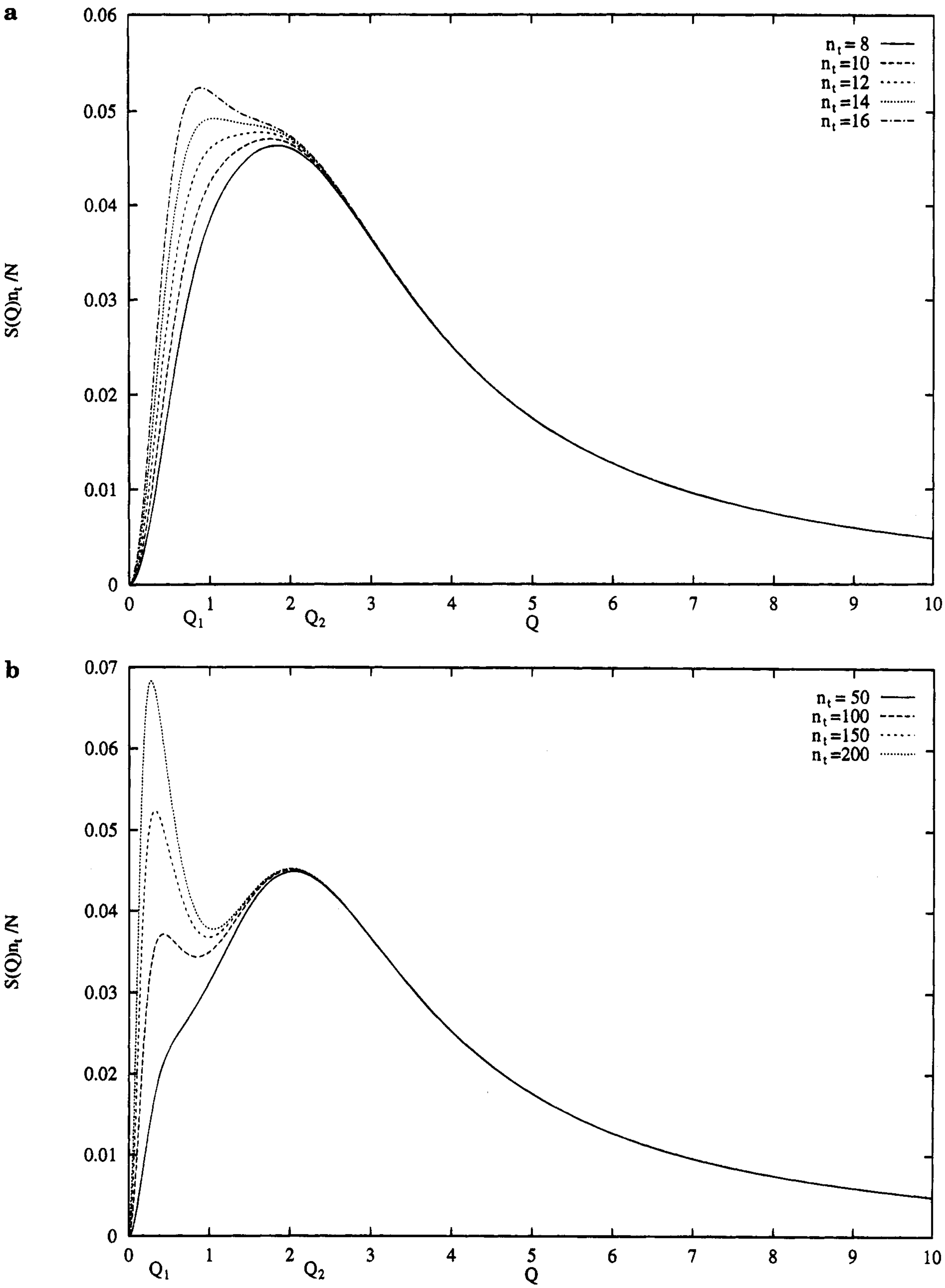

Figure 9. Plot of the scattering function for combs with (a) $z_0 n_t$ = 0.7 for small numbers of teeth and (b) $z_0 n_t$ = 0.9 for large numbers of teeth; no dispersity.

are seen as a single effective tooth whose position is uniformly distributed as in the previous section.

We now consider what happens once dispersity in the number of teeth is introduced. Since the effects are more pronounced the larger the average number of teeth, in the following relatively large numbers of teeth are considered, probably outside the realms of experimental systems. Figure 11 shows the scattering functions for 100 teeth, $z_0\overline{n_t}$ = 0.9 and different values of n_0/σ. In all these figures, f = 0.5. As the width of the dispersity is increased, n_0/σ is decreased, and it may be seen that the peak at Q_1 is enhanced, as well as the

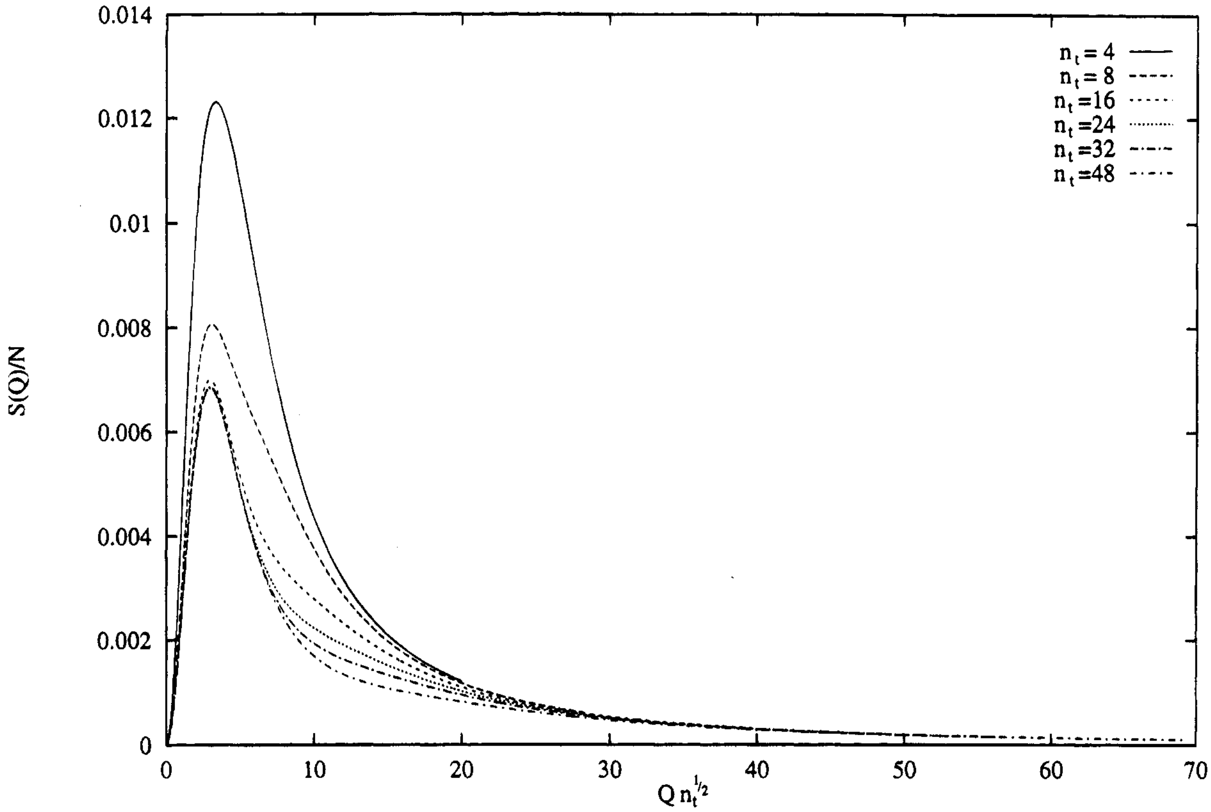

Figure 10. Plot of the scattering function for combs with $z_0 n_t = 0.5$, different numbers of teeth, and no dispersity.

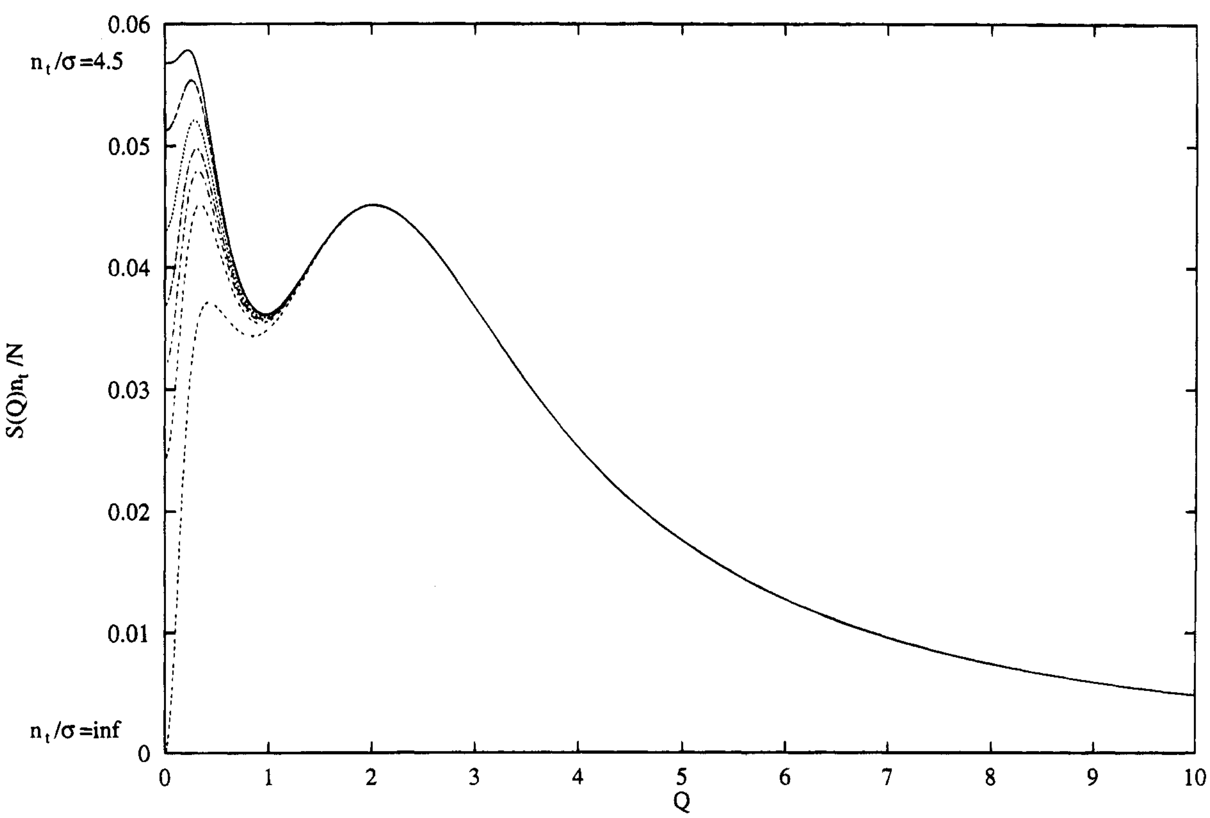

Figure 11. Plot of the scattering function for regularly spaced combs with an average of 100 teeth and n_0/σ = 4.5, 5, 6, 7, 8, 9, and 10, $z_0 n_t = 0.9$.

value of $S(0)$. For some width of the distribution, this peak dominates over the usual peak at Q_2 and the homogeneous phase changes to being unstable to this new microphase. As the dispersity is increased further, the homogeneous system becomes unstable to macrophase separation.

Figure 12 shows the effect of changing the number of teeth while keeping $n_0/\sigma = 10.0$. In contrast to the previous section, increasing the number of teeth will not cause an instability to microphase separation to change into an instability to macrophase separation. This is because, while there is a dispersity in the amount of B

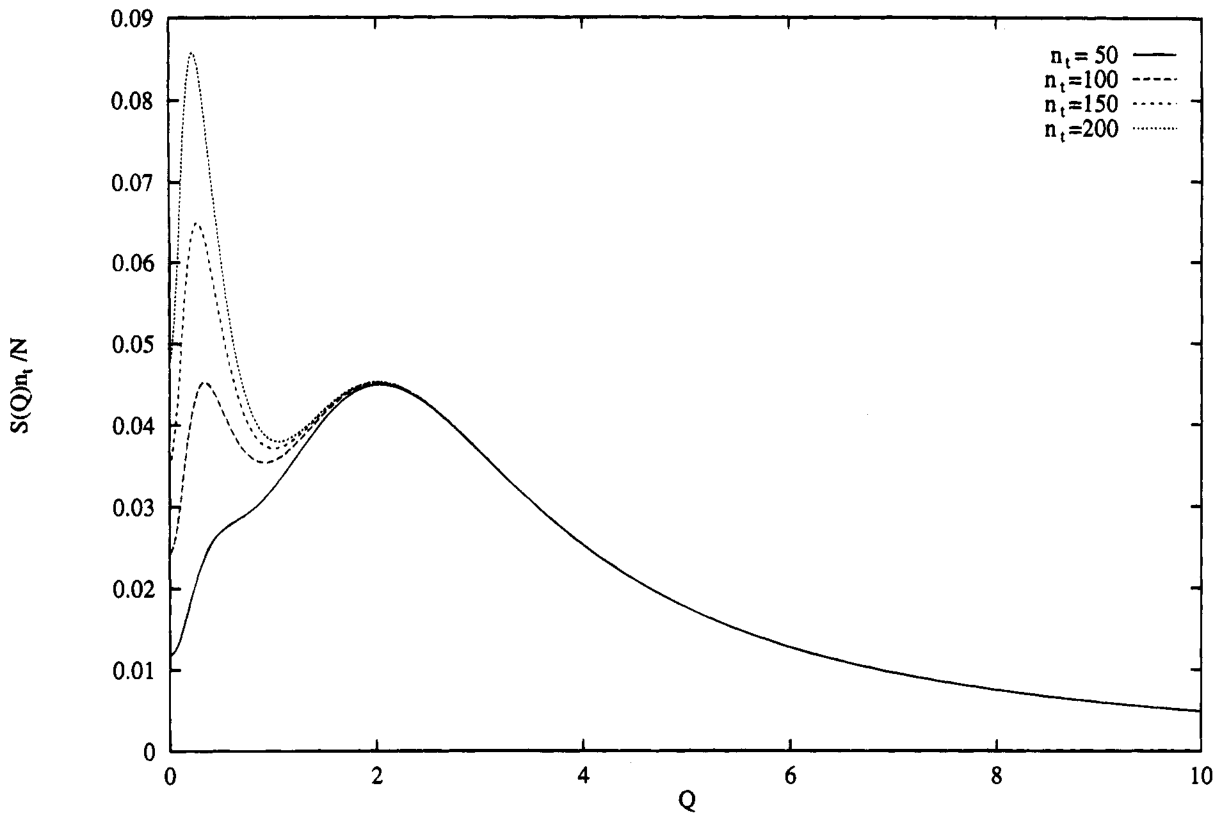

Figure 12. Plot of the scattering function for regular combs with n_0/σ = 10.0, changing the number of teeth.

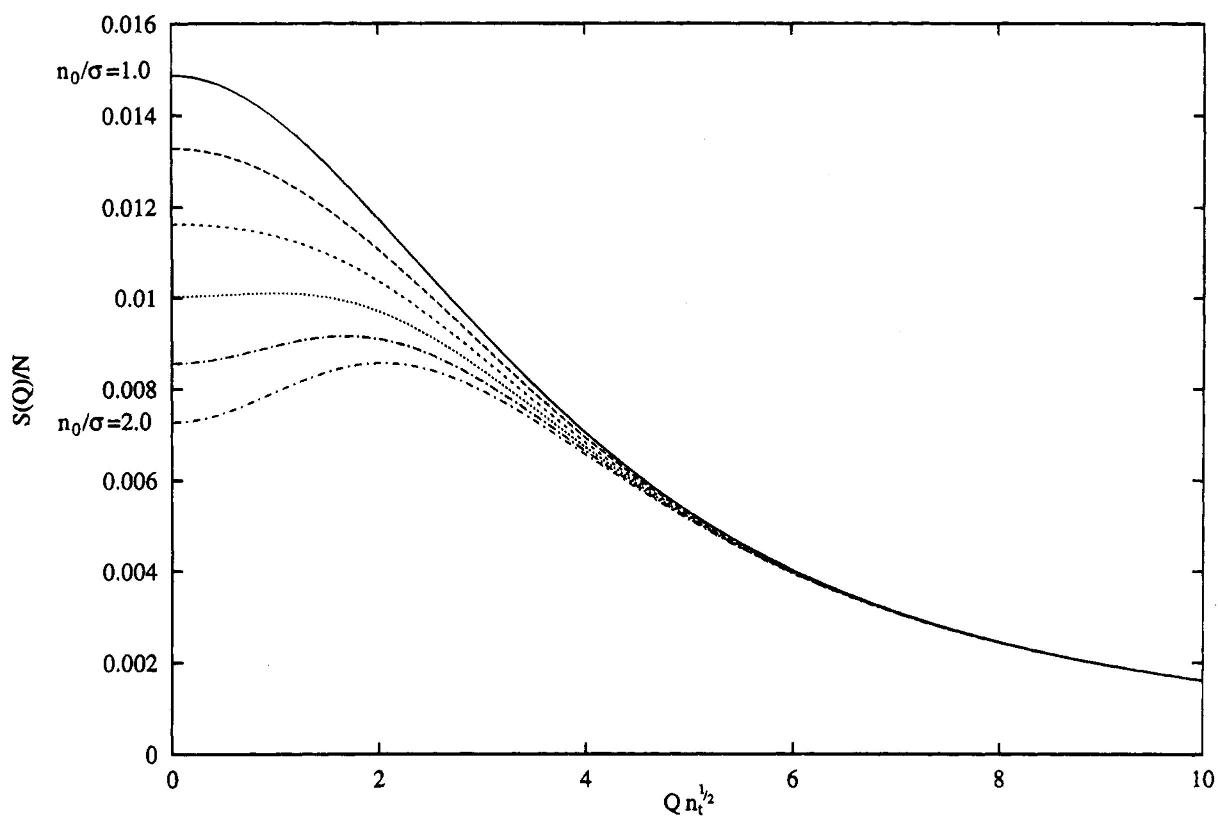

Figure 13. Plot of the scattering function for a regularly spaced comb, average number of teeth = 100, $z_0 n_t$ = 0.5, and values of n_0/σ = 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0.

type monomer in the combs, the peak at Q_1 behaves as if there were only one tooth. As the number of teeth is increased, both $S(0)$ and $S(Q_1)$ scale in the same way.

Figures 13 and 14 show the figures equivalent to Figures 11 and 12, with an appropriate choice of scaling variables, but for $z_0\overline{n_t}$ = 0.5. Again, the crossover from micro- to macrophase separation may only be effected by changing n_0/σ and not by increasing the number of teeth.

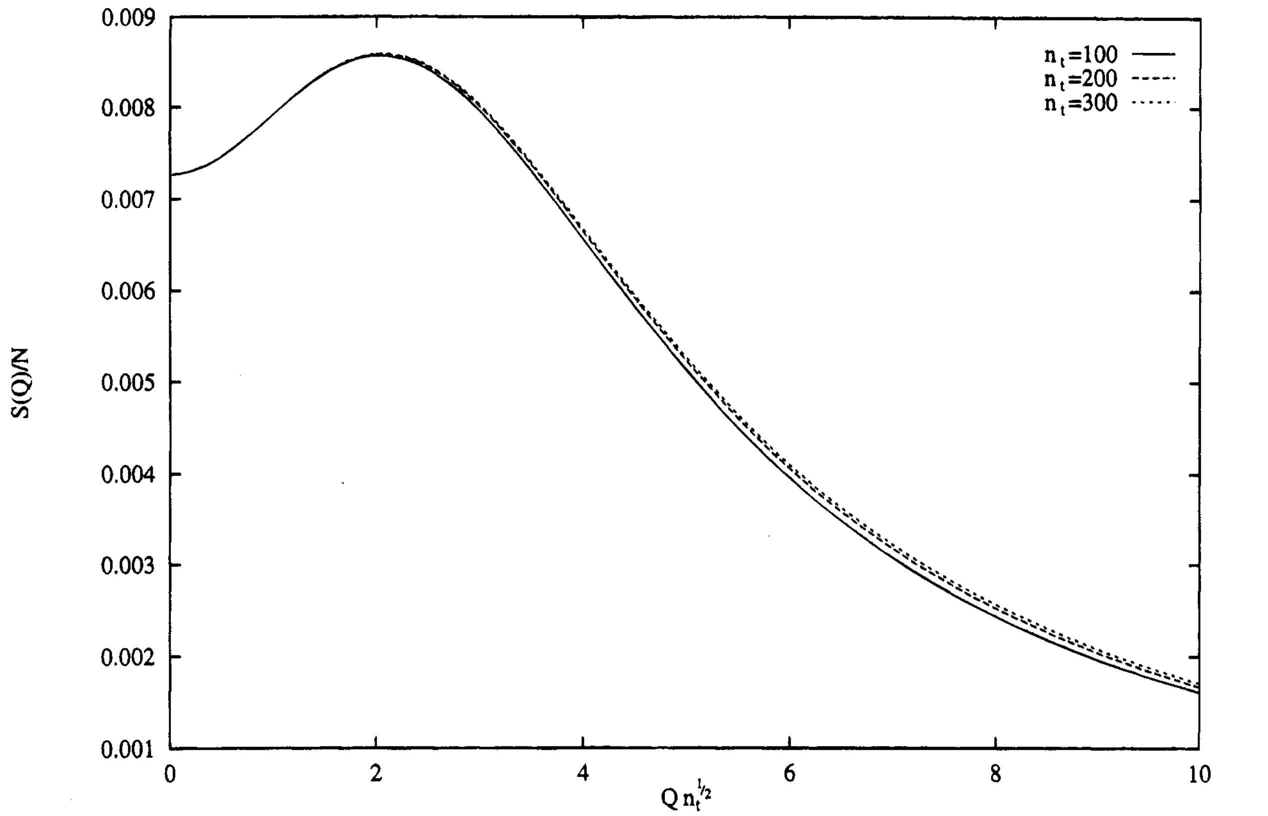

Figure 14. Plot of the scattering function for a regularly spaced comb, $z_0 n_t = 0.5$, $n_0/\sigma = 2.0$, and different numbers of teeth.

6. Conclusions

In this article we have presented results for the instabilities of the homogeneous phase for a two-parameter Markov process construction of comb copolymers. In addition, we introduce two models, corresponding to two limiting cases in the intertooth correlation, in which the dispersity in the number of teeth appears as an independent parameter. In the case where the comb copolymers were constructed with uncorrelated tooth placements, both the width of the distribution in the number of teeth and the average number of teeth play an important part in determining whether the homogeneous phase was unstable to microphase or macrophse separation.

A very correlated tooth placement (at least in the context of the model presented here) led to a more complex situation. For cases where, on average, the comb had a large percentage of the backbone covered with teeth, it was possible to observe two forms of microphase separation, as well as macrophase separation, as the dispersity was changed. For a narrow distribution, the usual microphase separation is observed. For larger dispersities, a second microphase separation is seen, similar to that which would be observed for a one-tooth comb with a uniform distribution of tooth placement. As the dispersity is increased further, the system becomes unstable to macrophase separation.

For lower backbone coverages, the usual microphase separation was supressed in favor of the "effective one-tooth" microphase separation. In all cases, this reduction of the correlated sequence of teeth to one effective tooth made the transition to macrophase separation insensitive to the number of teeth present; no matter how many teeth were placed on the backbone, their correlation makes them behave as one.

It would be of interest to see how the gradual weakening of the correlations between teeth wash out this "one-tooth" behavior, as well as to investigate the nature of the phase separation transitions which occur. These topics form the basis of future work.

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