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Critical dynamics of random copolymer melts

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The transport properties of an A–B random copolymer melt near the order–disorder phase transition are examined by using a mode coupling approach. The key parameters of the model are the volume fraction of type A monomers, f, the Flory χ parameter, and a parameter λ that characterizes the monomer sequence distribution. The equilibrium phase diagram for this model of random copolymers contains a Lifshitz point at $\lambda = \lambda_L$. For $\lambda < \lambda_L$, composition fluctuations first become unstable at finite wavelength and the homogeneous phase separates into microphases, while for $\lambda > \lambda_L$ the fluctuations first become unstable at infinite wavelength giving a binary fluid type transition. Our analysis shows that for $\lambda < \lambda_L$ the Onsager coefficient remains finite as the phase transition is approached, while the viscosity diverges proportional to $\epsilon^{-3/2}$, where $\epsilon = (T - T_c)/T_c$ is the dimensionless difference between the temperature and the critical temperature. For $\lambda > \lambda_L$, there is a very weak divergence in the viscosity, but the Onsager coefficient diverges proportional to $\epsilon^{-1/2}$ for $\epsilon^{-1}(\lambda - \lambda_L) \gg 1$, and proportional to $\epsilon^{-3/4}$ for $\epsilon^{-1}(\lambda - \lambda_L) \ll 1$. The dependence of the Onsager coefficient and viscosity on χ, f and λ are explicitly determined.

1. Introduction

We are delighted to contribute to this special issue of Physica A honoring Professor Kyozi Kawasaki on the occasion of his retirement from Kyushu University. Our article deals with a topic, the critical dynamics of random copolymer melts, that is closely aligned with Professor Kawasaki's past and present research interests. In particular, the present mode coupling analysis is a natural extension of the beautiful framework developed by Professor Kawasaki in his thorough investigations of the critical dynamics of simple fluids. More recently, his pioneering studies of the thermodynamic and transport properties of block copolymers [1] have yielded important new insights into the behavior of these complicated polymeric fluids. We look forward to Professor Kawasaki's continuing outstanding contributions to our field and aspire to his model of scholarship.

In recent years, there has been much interest in the thermodynamics and dynamics of multicomponent polymer melts, including polymer blends and block copolymers [2]. The structure and dynamics of these materials are largely determined by a competition between enthalpic interactions among the dissimilar monomers, which tend to segregate the monomers into different domains, and the entropic forces that promote mixing. An interesting aspect of these polymeric systems is that they can exhibit more than one type of phase transition from a disordered phase to a segregated phase upon lowering the temperature. For example, the familiar phase separation of a binary mixture of homopolymers results in two coexisting homogeneous phases and is of the binary liquid type [2,3]. In the case of block copolymers, where polymerized sequences of two or more distinct monomers are chemically linked together on the same macromolecule, the phase separation results in the formation of spatially periodic domains of mesoscopic extent (a so-called microphase separation). Such phase transitions are of the order-disorder type. A variety of domain geometries, such as lamellar, cylindrical, spherical, and certain bicontinuous structures have been observed experimentally, and most of these have also been predicted theoretically [4].

The thermodynamic properties of random copolymer melts, which contain monomers of more than one type distributed stochastically along each chain, have received much less attention [5,6]. Fredrickson, Milner and Leibler (FML) [6] recently investigated the mean-field phase diagram for a simple model of A–B random copolymer melts (linear chains constructed from two types of monomers, A and B). This model contains three key dimensionless parameters: the volume fraction of type A monomers, f, the Flory χ parameter, χ_F, which determines the strength of the enthalpic repulsion between monomers of types A and B, and a parameter λ $(-1<\lambda<1)$ that describes the correlation among the locations of the A and B monomers along the chain. The case $\lambda=-1$ corresponds to an alternating copolymer where A and B monomers alternate along the backbone of chain, while the opposite limit $\lambda=1$ corresponds to a mixture of type A and type B homopolymers where the monomers are only found adjacent to others of the same type. The intermediate case of $\lambda=0$ corresponds to a truly 'random' copolymer melt for which there are neither ferromagnetic nor antiferromagnetic correlations of A and B along the polymer backbones. For a large range of λ, FML [6] have shown that the model exhibits a phase transition from a homogeneous to an inhomogeneous phase when the Flory χ parameter is $\mathcal{O}(1)$. A particularly interesting feature of the phase diagram is the presence of a multicritical 'Lifshitz' point at $\lambda=\lambda_L$. (The value of λ_L is generally nonuniversal, but for one microscopic model investigated by FML was found to describe chains with a slight alternating tendency, $\lambda_L\approx-0.268$.) For $\lambda>\lambda_L$, the phase transition is of the binary fluid type and the two coexisting phases have a composition difference that is characteristically of $\mathcal{O}(N^{-1/2})$ (N is the degree of polymerisation). In contrast, for $\lambda<\lambda_L$ the phase separation occurs at a finite wavelength and is of the 'microphase separation' type observed in block copolymers.

The reptation dynamics of a highly entangled random copolymer in the melt were very recently considered by Bouchaud and Cates [7]. They found that the reptation time [2] increases in proportion to $\exp(N^{1/2}\chi_F)$, where N is the number of monomers on a chain. Based on this result, they predict a dynamical crossover line for $\chi_F \sim N^{-1/2}$, below which (in temperature) the self-diffusion of long chains in the melt is drastically slowed down. This line would normally be expected to preempt the equilibrium phase transition, which as noted above scales as $\chi_F \sim O(1)$. It is important to emphasize that the Bouchaud–Cates prediction of suppressed self-diffusion does *not* necessarily imply that microphase separation is arrested. Indeed, the collective diffusion events required to produce the typical microphase with a period that is smaller than a chain radius of gyration probably do not involve complete tube renewal.

In the present paper, we use a mode coupling technique to study the effect of concentration and momentum density fluctuations on the *collective* transport properties of a random copolymer melt near its order-disorder or (depending on the value of λ) liquid–liquid phase transition. This analysis is directly applicable to melts of relatively short chains where the diffusion of polymers is governed by Rouse dynamics rather than by reptation, so that the dynamical slowing down mechanism of Bouchaud and Cates is inoperative. Furthermore, because the Bouchard–Cates arguments do not necessarily impact collective diffusion phenomena even for long chains (and particularly for $\lambda < \lambda_L$), we expect that our analysis may have even more general applicability.

The dynamics of our model random copolymer melt are described by using a slight modification of the familiar model H equations that were earlier employed to study the binary fluid transition in simple liquids [8,9] and the microphase separation transition of diblock copolymers [10,11]. We also invoke the FML random copolymer model whose static properties have been investigated in detail elsewhere [6]. Our goal is to determine the dependence of the renormalized transport coefficients, namely the Onsager coefficient and the shear viscosity, on the fraction of A monomers, f, the parameter λ, and the reduced temperature $\epsilon = (T - T_c)/T_c$, where T is the temperature and T_c is the critical temperature. Our main results are that for $\lambda < \lambda_L$, the viscosity diverges proportional to $\epsilon^{-3/2}$, while the Onsager coefficient remains finite as the critical temperature is approached. For $\lambda > \lambda_L$, the divergence in the viscosity is weak, while the Onsager coefficient diverges proportional to $\epsilon^{-1/2}$ for $\epsilon^{-1}(\lambda - \lambda_L) \gg 1$, and proportional to $\epsilon^{-3/4}$ for $\epsilon^{-1}(\lambda - \lambda_L) \ll 1$.

2. Model

We consider a cubical box of N_p polymers, each of which has a total of N monomers. The melt is assumed to be incompressible and the monomer volumes (denoted v) are taken to be the same; hence, the total volume of the system is given by $V = vNN_p$. The average volume fraction of monomers of type A is denoted f, the location of monomers along a chain are indexed by Roman indices $n, m, \ldots$, and different chains are identified by the Greek indices $\alpha, \beta, \gamma, \ldots$. We further invoke the traditional Markov model of random copolymerisation [12] that was earlier employed by FML [6]. In this model, the reactivity of an unreacted monomer with a polymer molecule depends only on the type of monomer at the end of the polymer, and four rate constants, k_{KL} ($\{K, L\} = A, B$), suffice to determine the kinetics of the polymer growth. The analysis is further simplified by assuming that the concentrations of monomers and reactive species during the polymerisation process are constant.

It is convenient to define a conditional probability matrix, p_{KL} for $\{K, L\} = A, B$, which is the probability that a monomer of type L on the chain is immediately followed by a monomer of type K. It is easy to see that two of the probabilities can be expressed in terms of the other two by using the following conservation conditions:

$$p_{AA} + p_{BA} = 1\,, \qquad p_{AB} + p_{BB} = 1\,. \tag{2.1}$$

There is a third relationship among the conditional probabilities resulting from the assumption that the concentration of type A monomers remains constant during the growth process, and hence the probability of finding a monomer at any location is f:

$$f = p_{AA} f + p_{AB}(1 - f)\,. \tag{2.2}$$

The above three relations permit us to specify the sequence distribution of monomers in terms of just two parameters, the fraction of monomers, f, and the non-trivial eigenvalue of the p_{KL} matrix, λ, which is given by

$$\lambda = p_{AA} + p_{BB} - 1\,. \tag{2.3}$$

Next, we introduce a random variable $\theta(n, \alpha)$ which is defined to be 1 if the monomer at location n on chain α is type A, and -1 if the same monomer is type B. The moments of $\theta(n, \alpha)$ can be expressed in terms of the two parameters f and λ. We do not go through the derivation of the moments, but refer the reader to FML [6] for further details. In the present analysis, we only require the first two moments, which are

$$\overline{\theta(n, \alpha)} = 2f - 1\,, \tag{2.4}$$

$$\overline{[\theta(n, \alpha) - \overline{\theta(n,\alpha)}][\theta(m, \beta) - \overline{\theta(m, \beta)}]} = 4f(1 - f)\lambda^{|n-m|}\delta_{\alpha\beta}\,, \tag{2.5}$$

where the overbars denote ensemble averages over the sequence distribution.

The microscopic density field, $\phi(n, \alpha; \boldsymbol{x}, t)$, of a monomer on chain α at backbone location n is defined as follows:

$$\phi(n, \alpha; \boldsymbol{x}, t) = \delta(\boldsymbol{x} - \boldsymbol{R}(n, \alpha, t)) , \tag{2.6}$$

where $\boldsymbol{R}(n, \alpha, t)$ is the monomer position. Similarly, the microscopic densities of A and B monomers are given by

$$\phi_{\mathrm{A}}(x, t) = \sum_{\alpha=1}^{N_{\mathrm{P}}} \sum_{n=1}^{N} \left(\phi(n, \alpha; \boldsymbol{x}, t) \frac{1 + \theta(n, \alpha)}{2} \right) , \tag{2.7}$$

$$\phi_{\mathrm{B}}(x, t) = \sum_{\alpha=1}^{N_{\mathrm{P}}} \sum_{n=1}^{N} \left(\phi(n, \alpha; \boldsymbol{x}, t) \frac{1 - \theta(n, \alpha)}{2} \right) . \tag{2.8}$$

In the present analysis, we use the standard microscopic model for copolymer melts [13] and neglect the difference in the segment lengths of the two monomers. The interactions among the monomers are described in terms of a generalized Flory 'chi' parameter [2,6], which is the enthalpy penalty per monomer of A–B contacts relative to A–A and B–B contacts. The Hamiltonian for the melt can be written as

$$\begin{aligned} H = & \frac{3}{2b^2} \sum_{\alpha=1}^{N_{\mathrm{P}}} \sum_{n=1}^{N} |\boldsymbol{R}(n, \alpha) - \boldsymbol{R}(n+1, \alpha)|^2 \\ & + \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}' \, \phi_{\mathrm{A}}(\boldsymbol{x}) \, \chi_{\mathrm{F}}(|\boldsymbol{x} - \boldsymbol{x}'|) \, \phi_{\mathrm{B}}(\boldsymbol{x}') . \end{aligned} \tag{2.9}$$

In this expression, b is the statistical segment length of a monomer and $\chi_{\mathrm{F}}(r)$ is a non-local Flory interaction parameter [6]. The quantity subsequently denoted by χ_{F} is proportional to the spatial integral of $\chi_{\mathrm{F}}(r)$ and is related to the usual Flory parameter χ by the expression $(\chi/v)(b/\sqrt{6})^3$. Our assumption that the melt is incompressible implies that the local concentrations of A and B are permitted to fluctuate, but the sum of the concentrations of the two species is a constant at all points in the melt. This incompressibility condition is conveniently enforced by means of the random phase approximation [2].

3. Mean field calculation of transport coefficients

In the present section, we calculate the dependence of the static and dynamic structure factors and the Onsager transport coefficient on the parameters f, λ, and χ_{F} of the random copolymer model by using a mean field approximation; the effect of fluctuations is analysed in the next section by means of a mode-coupling approach. The static and dynamic structure factors of interest are the equal time and time-displaced density correlation functions:

$$S(n, \alpha; m, \beta; \boldsymbol{x}) = \langle \delta\phi(n, \alpha; \boldsymbol{x}, 0)\, \delta\phi(m, \beta; \boldsymbol{0}, 0) \rangle \,, \tag{3.1}$$

$$S(n, \alpha; m, \beta; \boldsymbol{x}, t) = \langle \delta\phi(n, \alpha; \boldsymbol{x}, t)\, \delta\phi(m, \beta; \boldsymbol{0}, 0) \rangle \,. \tag{3.2}$$

For future reference, we also define the Fourier–Laplace transforms of the static and dynamic structure factors:

$$S(n, \alpha; m, \beta; \boldsymbol{k}) = \int \mathrm{d}\boldsymbol{x}\, \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\, S(n, \alpha; m, \beta; \boldsymbol{x}) \,, \tag{3.3}$$

$$S(n, \alpha; m, \beta; \boldsymbol{k}, \omega) = \int_0^\infty \mathrm{d}t \int \mathrm{d}\boldsymbol{x}\, \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x} + \mathrm{i}\omega t)\, S(n, \alpha; m, \beta; \boldsymbol{x}, t) \,. \tag{3.4}$$

In the present analysis, we do not actually prescribe a microscopic dynamics, but simply assume that at long times and for transport over large distances the dynamics of a free (non-interacting) chain can be represented by a single diffusion coefficient, D_0. With this assumption, the static and dynamic structure factors for a free chain are related as follows:

$$S_0(n, \alpha; m, \beta; \boldsymbol{k}, \omega) = \frac{S_0(n, \alpha; m, \beta; \boldsymbol{k})}{-\mathrm{i}\omega + D_0 k^2} \,. \tag{3.5}$$

In a melt where the chains follow Rouse dynamics [2,14], this formula is valid for $k^2Nb^2 \ll 1$ and when the time scale under consideration is large compared to the relaxation time of the internal modes, which is $\mathcal{O}(\xi_0 N^2 b^2/T)$. The diffusion coefficient, D_0, in this regime is of order $(T/N\xi_0)$. In the above expressions, T is the product of the temperature and the Boltzmann constant, and ξ_0 is the monomer friction coefficient. In a highly entangled melt for which the reptation model is applicable, the above assumption requires that $k^2Nb^2 \ll 1$ and that the time scale is large compared to the reptation time, which is $\mathcal{O}(b^2\xi_0 N^3/TN_\mathrm{e})$, where N_e is the number of monomers between entanglements. The diffusion coefficient in the reptation regime is $\mathcal{O}(TN_\mathrm{e}/\xi_0 N^2)$.

For a melt of ideal chains in the absence of interactions, the equilibrium pair distribution function is Gaussian, and the static structure factor is given by

$$S_0(n, \alpha; m, \beta; \boldsymbol{k}) = \frac{1}{V} \exp(-|n - m| k^2)\, \delta_{\alpha\beta} \,. \tag{3.6}$$

Here, the wave vector k has been scaled by $(\sqrt{6}/b)$, where b is the statistical segment length of the monomers, and V is the total volume of the system. Note that in the subsequent analysis, all lengths are scaled by $b/\sqrt{6}$.

There are two types of interactions in the melt that cause deviations from the ideal behaviour – the enthalpic interactions between the monomers of different types, which are modeled by using the non-local Flory 'chi' parameter of (2.9), and the repulsive hard-core interactions among the monomers that are crudely accounted for by requiring the total density at any point to be a constant:

$$\sum_{n,\alpha} \delta\phi(n, \alpha; \boldsymbol{k}, \omega) = 0\,. \tag{3.7}$$

In this expression the index n is summed from 1 to N along a chain, and the index α from 1 to N_p. The structure factor in the presence of interactions is calculated by a linear response procedure as follows. Consider weak perturbing potentials V_A and V_B (respectively conjugate to the densities of type A and B monomers) applied to the monomer at location m of chain β at the position $\boldsymbol{x}'$ and time t'. The change in the density caused by this potential is to linear order given by

$$\delta\phi(n, \alpha; \boldsymbol{x}, t) = -\int_0^\infty \mathrm{d}t' \int \mathrm{d}\boldsymbol{x}'\, \chi(n, \alpha; m, \beta; \boldsymbol{x} - \boldsymbol{x}', t - t')\, V(m, \beta; \boldsymbol{x}', t')\,, \tag{3.8}$$

where we have used the Einstein notation for summation over the repeated indices, and the potential $V(m, \beta; \boldsymbol{x}', t')$ is given by

$$V(m, \beta; \boldsymbol{x}', t') = \tfrac{1}{2}\{[1 + \theta(m, \beta)]V_A(x', t') + [1 - \theta(m, \beta)]V_B(x', t')\}\,. \tag{3.9}$$

The response function, $\chi(n, \alpha; m, \beta; \boldsymbol{x} - \boldsymbol{x}', t - t')$, depends only on the relative distance $(\boldsymbol{x} - \boldsymbol{x}')$ due to translational invariance. Moreover, the response function is causal and thus is non-zero only for $t > t'$. It is convenient to write the above equation in terms of the Fourier–Laplace transforms of the density and potential:

$$\delta\phi(n, \alpha; \boldsymbol{k}, \omega) = -\chi(n, \alpha; m, \beta; \boldsymbol{k}, \omega)\, V(m, \beta; \boldsymbol{k}, \omega)\,. \tag{3.10}$$

Finally, we note that the linear response function is related to the correlation function (structure factor) describing the spontaneous fluctuations in a system at equilibrium by invoking the fluctuation-dissipation theorem:

$$\chi(\boldsymbol{k}, \omega) = T^{-1}[S(\boldsymbol{k}) + \mathrm{i}\omega S(\boldsymbol{k}, \omega)]\,. \tag{3.11}$$

In the random phase approximation [2], the response function is approximated by the ideal (non-interacting) chain response function, but the potentials V_A and V_B are separated into three components: external potentials V_{0A} and V_{0B}; an interaction potential due to the enthalpic interactions among monomers of different species; and a self-consistent potential $U(\boldsymbol{k}, \omega)$ that acts uniformly on all monomers and enforces incompressibility. This separation can be written explicitly as

$$\begin{aligned} V(m, \beta; \boldsymbol{k}, \omega) &= V_0(m, \beta; \boldsymbol{k}, \omega) \\ &+ \tfrac{1}{2} T \chi_F \sum_{l,\gamma} [1 - \theta(m, \beta)\, \theta(l, \gamma)]\, \delta\phi(l, \gamma; \boldsymbol{k}, \omega) + U(\boldsymbol{k}, \omega) , \end{aligned} \tag{3.12}$$

where the external potential $V_0(m. \beta; \boldsymbol{k}, \omega)$ is related to the potentials V_{0A} and V_{0B} in a manner analogous to (3.9) and we employ the shorthand $\chi_F = \chi_F(\boldsymbol{k})$. The above potential is next substituted into (3.10), and the self-consistent potential is calculated by imposing the incompressibility condition (3.7). At this stage, we also perform an average over the possible arrangements of the monomers along the chains by using the correlation functions for the variable $\theta(n, \alpha)$ given in (2.4) and (2.5), the details of which are provided in appendix A. The end result of these steps is expressions for the fluctuations in the densities of species A and B as a function of the applied potentials:

$$\delta\phi_A(\boldsymbol{k}, \omega) = -\chi'(\boldsymbol{k}, \omega)\, [V'_A(\boldsymbol{k}, \omega) - V'_B(\boldsymbol{k}, \omega)] , \tag{3.13}$$

$$\delta\phi_B(\boldsymbol{k}, \omega) = -\chi'(\boldsymbol{k}, \omega)\, [V'_B(\boldsymbol{k}, \omega) - V'_A(\boldsymbol{k}, \omega)] . \tag{3.14}$$

Here, the effective response function, $\chi'(\boldsymbol{k}, \omega)$, *which includes the effect of hardcore repulsions that make the melt incompressible, but not the enthalpic interactions among the monomers of different species*, is given by

$$\begin{aligned} &\chi'(\boldsymbol{k}, \omega) = \\ &\tfrac{1}{4} \sum_{n,\alpha,m,\beta} \chi_0(n, \alpha; m, \beta; \boldsymbol{k}, \omega)\, \overline{[\theta(n, \alpha) - \overline{\theta(n, \alpha)}][\theta(m, \beta) - \overline{\theta(m, \beta)}]} , \end{aligned} \tag{3.15}$$

where

$$\chi_0(n, \alpha; m, \beta; \boldsymbol{k}, \omega) = T^{-1}[S_0(n, \alpha; m, \beta; \boldsymbol{k}) + \mathrm{i}\omega S_0(n, \alpha; m, \beta; \boldsymbol{k}, \omega)] . \tag{3.16}$$

These ideal chain structure factors are in turn given by (3.5) and (3.6). Finally, the effective potentials V'_A and V'_B appearing in (3.12) and (3.13) are

$$V'_{\mathrm{A}}(\boldsymbol{k}, \omega) = V_{\mathrm{A}}(\boldsymbol{k}, \omega) + T\chi_{\mathrm{F}}\, \delta\phi_{\mathrm{B}}(\boldsymbol{k}, \omega)\,, \tag{3.17}$$

$$V'_{\mathrm{B}}(\boldsymbol{k}, \omega) = V_{\mathrm{B}}(\boldsymbol{k}, \omega) + T\chi_{\mathrm{F}}\, \delta\phi_{\mathrm{A}}(\boldsymbol{k}, \omega)\,. \tag{3.18}$$

The response function, $\chi'(\boldsymbol{k}, \omega)$, simplifies considerably for cases of $|\lambda|^N \ll 1$, where the identities of the monomers are uncorrelated at separations comparable to the degree of polymerisation. In this situation (which is typical for commercial random copolymers), we have

$$\chi'(\boldsymbol{k}, \omega) = T^{-1} f(1-f)\,\frac{1+\lambda \exp(-k^2)}{1-\lambda \exp(-k^2)}\left(1 + \frac{\mathrm{i}\omega}{-\mathrm{i}\omega + D_0 k^2}\right). \tag{3.19}$$

An interesting feature of the above response function is that it is different in form from the Debye-like functions for homopolymers and block copolymers and it lacks a correlation hole at $\boldsymbol{k} = 0$. There is a correlation hole in a block copolymer melt because the different types of monomers are located at identical positions on different chains, and if we have a monomer located at position n on chain α at the origin, the probability of finding a monomer at position n on a different chain β near to the origin is reduced. However, in a random copolymer, the identities of the chemical species at the same location n on different polymers are uncorrelated and this eliminates the correlation hole in the structure factor.

The response function that takes into account the effect of enthalpic interactions is easily calculated from (3.13), (3.14), (3.17), and (3.18):

$$\chi(\boldsymbol{k}, \omega) = \frac{\chi'(\boldsymbol{k}, \omega)}{1 - 2T\chi_{\mathrm{F}}\chi'(\boldsymbol{k}, \omega)}\,. \tag{3.20}$$

The static and dynamic structure factors can be derived from the above expression as follows. We insert the value of $\chi'(\boldsymbol{k}, \omega)$ from (3.19), carry out a Taylor expansion for small ω and retain terms up to quadratic order. The resulting expression is recast in a form similar to (3.5), and the following static structure factor and generalized diffusion coefficient are read off from this expression:

$$S(\boldsymbol{k}) = \frac{S'(\boldsymbol{k})}{1 - 2\chi_{\mathrm{F}} S'(\boldsymbol{k})}\,, \qquad D(\boldsymbol{k}) = D_0[1 - 2\chi_{\mathrm{F}} S'(\boldsymbol{k})]\,, \tag{3.21}$$

where

$$S'(\boldsymbol{k}) = f(1-f)\frac{1+\lambda\exp(-k^2)}{1-\lambda\exp(-k^2)}\,. \tag{3.22}$$

The advent of a phase transition is signaled by a divergence in the static structure factor. It can be seen from (3.21) that there is a phase transition for $S'(\boldsymbol{k}) = T/(2\chi_F)$; this result is identical to that of FML [6] for our choice of the form of the enthalpic interaction. It is also interesting to note that the diffusion coefficient goes to zero as the structure factor diverges, indicating the familiar Van Hove-type critical slowing down.

To study the relaxation rate of fluctuations, it is convenient to identify the Onsager coefficient $\Lambda(\boldsymbol{k})$ that relates the flux of monomers of either species to the gradient in the respective chemical potential:

$$J_A - J_B = \frac{\Lambda(k)}{T}\,\mathrm{i}\boldsymbol{k}(V_A - V_B)\,. \tag{3.23}$$

The Onsager coefficient is related to the static structure factor and the diffusion coefficient by the expression

$$\Lambda(\boldsymbol{k}) = DS(\boldsymbol{k}) = D_0 S'(\boldsymbol{k})\,, \tag{3.24}$$

where we have used (3.21) for the diffusion coefficient and the structure factor in the second equality. It is interesting to note that the Onsager coefficient is identical to that for a melt in which there are no enthalpic interactions between the monomers because the dependences of the diffusion coefficient and the structure factor on the Flory parameter χ_F cancel each other. Also, the Onsager coefficient is simple in form, and does not diverge or vanish near the critical point in the present mean field approximation.

Our final task in the present section is to discuss the static properties of the model copolymer melt on the basis of the interacting structure factor just computed. This discussion is similar to that in FML, but we include it here for completeness and for reference in the following sections. The expressions for the response function (3.20) and structure factor (3.21) give us the following criterion for phase transition in the melt:

$$2f(1-f)\chi_F(\boldsymbol{k})\frac{1+\lambda\exp(-k^2)}{1-\lambda\exp(-k^2)} = 1\,. \tag{3.25}$$

The above expression is identical to the phase transition criterion obtained by Fredrickson and Milner [6]. Following their lead, it proves convenient to expand the Flory parameter in a Taylor series in the wave number k:

$$\chi_F(\boldsymbol{k}) = \chi_F^{(0)} - \chi_F^{(2)} k^2 . \tag{3.26}$$

The wave number at which the homogeneous phase first becomes unstable depends on the value of λ relative to a critical value, λ_L, which can be identified as an isotropic 'Lifshitz point'. The critical value is given by

$$\lambda_L = -1 + [(1 + 2\kappa_2)^{1/2} - 1]/\kappa_2 , \tag{3.27}$$

where $\kappa_2 \equiv 2f(1-f)\chi_F^{(2)}$. Note that λ_L is generally less than zero. For $\lambda > \lambda_L$, the homogeneous phase first becomes unstable at $k = 0$, signaling a binary liquid phase transition. The spinodal condition for this phase separation is

$$\kappa_0 = \frac{1-\lambda}{1+\lambda} \tag{3.28}$$

where $\kappa_0 = 2f(1-f)\chi_F^{(0)}$. The static susceptibility $\chi(\boldsymbol{k})$ can be approximated near the phase transition by the following Lorentzian form:

$$\chi(\boldsymbol{k}) = \frac{\chi_0}{\xi^{-2} + k^2 + ck^4} , \tag{3.29}$$

$$\chi_0 = 2T^{-1} f(1-f)\kappa_0 \frac{1+\lambda}{1-\lambda} \left(\frac{2\lambda}{(1-\lambda)(1+\lambda)} + \frac{\kappa_2}{\kappa_0} \right)^{-1} , \tag{3.30}$$

$$\xi^{-2} = \frac{1+\lambda}{1-\lambda} \left(\frac{1-\lambda}{1+\lambda} - \kappa_0 \right) \left(\frac{2\lambda}{(1-\lambda)(1+\lambda)} + \frac{\kappa_2}{\kappa_0} \right)^{-1} , \tag{3.31}$$

$$c = \left[\frac{-\lambda}{(1+\lambda)^2} + \frac{2\kappa_2\lambda}{\kappa_0(1+\lambda)(1-\lambda)} + \left(\frac{\kappa_2}{\kappa_0} \right)^2 \right] \left(\frac{2\lambda}{(1-\lambda)(1+\lambda)} + \frac{\kappa_2}{\kappa_0} \right)^{-1} . \tag{3.32}$$

We note that it is necessary to include the $\mathcal{O}(k^4)$ term in the denominator of the response function because the correlation length ξ decreases to zero at $\lambda = \lambda_L$, while $\chi_0 \xi^2$ and $c\xi^2$ remain finite. As will become apparent below, the $\mathcal{O}(k^4)$ term makes a significant contribution to the transport properties for $\lambda \rightarrow \lambda_L$.

Near the phase transition, we can set $\kappa_0 = (1-\lambda)/(1+\lambda) - \epsilon$, where ϵ is a small (positive) parameter that is proportional to the difference between the temperature and the critical temperature. For this situation, χ_0 and ξ have the following expressions that are correct to leading order in ϵ:

$$\chi_0 = T^{-1} f(1-f) \left[\frac{2\lambda}{(1+\lambda)(1-\lambda)} + \kappa_2 \left(\frac{1+\lambda}{1-\lambda} \right) \right]^{-1} , \tag{3.33}$$

$$\xi = \epsilon^{-1/2}\left(\frac{2\lambda}{(1+\lambda)^2} + \kappa_2\right)^{1/2} . \tag{3.34}$$

For $\lambda < \lambda_{\mathrm{L}}$, the instability occurs at a non-zero value of $k = k_0$, indicating a microphase separation transition:

$$\exp(-k_0^2) = \frac{\lambda_{\mathrm{L}}}{\lambda} \tag{3.35}$$

and the spinodal condition for this phase transition is

$$\kappa_0' = \frac{1-\lambda_{\mathrm{L}}}{1+\lambda_{\mathrm{L}}} , \tag{3.36}$$

where $\kappa_0' = \kappa_0 - \kappa_2 k_0^2$. Near the phase transition, we find that the susceptibility has the following form:

$$\chi(k) = \frac{\chi_0}{\xi^{-2} + (k-k_0)^2} , \tag{3.37}$$

where

$$\chi_0 = T^{-1} f(1-f)\left(\frac{-2k_0^2\lambda_{\mathrm{L}}(1-\lambda_{\mathrm{L}})}{\kappa_0(1+\lambda_{\mathrm{L}})^3}\right)^{-1} , \tag{3.38}$$

$$\xi^{-2} = \left[\left(\frac{1-\lambda_{\mathrm{L}}}{1+\lambda_{\mathrm{L}}} - \kappa_0'\right)\left(\frac{-2k_0^2\lambda_{\mathrm{L}}(1-\lambda_{\mathrm{L}})}{(1+\lambda_{\mathrm{L}})^3}\right)^{-1}\right] \tag{3.39}$$

and where we have used $\kappa_2 = -2\lambda_{\mathrm{L}}\kappa_0/[(1+\lambda_{\mathrm{L}})(1-\lambda_{\mathrm{L}})]$. The parameter λ_{L} is less than zero, and therefore the above expressions for χ_0 and ξ are always positive in the homogeneous phase. When the system is very close to the phase transition, we have $\kappa_0' = (1-\lambda_{\mathrm{L}})/(1+\lambda_{\mathrm{L}}) - \epsilon$, where ϵ is again an appropriate reduced temperature. In this case, the parameter χ_0 is still given by (3.38), while ξ reduces to

$$\xi = \epsilon^{-1/2}\left(\frac{-2k_0^2\lambda_{\mathrm{L}}(1-\lambda_{\mathrm{L}})}{(1+\lambda_{\mathrm{L}})^3}\right)^{1/2} . \tag{3.40}$$

4. Renormalised transport coefficients

Near the line of critical points at $f = 1/2$ and parameterized above for different λ, the Onsager coefficient and the viscosity of the melt may be significantly modified by nonlinear couplings between concentration fluctuations and transverse momentum density fluctuations. This coupling is studied by using the model H system of equations of Hohenberg and Halperin [8], which were previously employed to study the critical dynamics near the gas–liquid and binary fluid critical points. These equations describe the variation in the concentration field $\psi(\boldsymbol{x}, t)$ and the transverse momentum density, $\boldsymbol{j}(\boldsymbol{x}, t)$. In the present case of a random copolymer melt, $\psi(\boldsymbol{x}, t)$ is the difference in the concentrations of the two species $(\delta\phi_{\mathrm{A}}(\boldsymbol{x}, t) - \delta\phi_{\mathrm{B}}(\boldsymbol{x}, t))$, and we replace the momentum density by the velocity field of the incompressible melt $\boldsymbol{v}(\boldsymbol{x}, t)$. A calculation similar to ours was carried out by Sachdev [15] for viscous relaxation in metallic glasses, but in his case the order parameter is not a conserved quantity, and therefore the results are slightly different. In Fourier representation, the model H equations are

$$\frac{\partial\psi(\boldsymbol{k}, t)}{\partial t} = -\Lambda_0 k^2 \frac{\delta H}{\delta\psi(-\boldsymbol{k})} + \mathrm{i}\rho^{-1} \int \frac{\mathrm{d}\boldsymbol{k}'}{2\pi^3} \boldsymbol{k}' \cdot \frac{\delta H}{\delta \boldsymbol{v}(\boldsymbol{k}' - \boldsymbol{k})} \psi(\boldsymbol{k}') + \zeta(\boldsymbol{k}, t) , \tag{4.1}$$

$$\begin{aligned}\frac{\partial \boldsymbol{v}(\boldsymbol{k}, t)}{\partial t} = \boldsymbol{T}_k \cdot \bigg(&-\eta_0 k^2 \frac{\delta H}{\delta \boldsymbol{v}(-\boldsymbol{k})} \\ &- \mathrm{i}\rho^{-1} \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3} (\boldsymbol{k} - \boldsymbol{k}')\psi(\boldsymbol{k} - \boldsymbol{k}') \frac{\delta H}{\delta\psi(-\boldsymbol{k}')} + \boldsymbol{\mu}(\boldsymbol{k}, t)\bigg) .\end{aligned} \tag{4.2}$$

Here, Λ_0 and η_0 are the bare transport coefficients; the λ and f dependence of Λ_0 were derived in the previous section. It should be noted that η_0, as defined here, is (ν_0/ρ), where ν_0 is the kinematic viscosity and ρ is the mass density, while the transport coefficient Λ_0 has units of χD_0, where χ is the susceptibility and D_0 is the diffusion coefficient. The effective Hamiltonian of the system, H, can be adequately represented by a quadratic approximation near equilibrium:

$$H = \frac{1}{2} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3} [\psi(-\boldsymbol{k})\, \chi^{-1}(\boldsymbol{k})\, \psi(\boldsymbol{k}) + \rho \boldsymbol{v}(-\boldsymbol{k}) \cdot \boldsymbol{v}(\boldsymbol{k})] . \tag{4.3}$$

The transverse projection operator, $(T_k)_{ij} = \delta_{ij} - \hat{k}_i \hat{k}_j$, appearing in (4.2) selects the transverse component of the vector in the brackets, since the component of $\boldsymbol{v}(\boldsymbol{k})$ in the direction of $\boldsymbol{k}$ is zero due to incompressibility. The Gaussian white noise sources for the concentration and momentum density fields, ζ and μ, have zero mean, and their autocorrelations are chosen so as to satisfy the fluctuation–dissipation theorem:

$$\langle \zeta(\boldsymbol{k}, t)\, \zeta(\boldsymbol{k}', t')\rangle = 2T(2\pi)^3 k^2 \Lambda_0 \delta(\boldsymbol{k} + \boldsymbol{k}')\, \delta(t - t')\,, \tag{4.4}$$

$$\langle \mu_i(\boldsymbol{k}, t)\, \mu_j(\boldsymbol{k}', t')\rangle = 2T(2\pi)^3 k^2 \eta_0 \delta(\boldsymbol{k} + \boldsymbol{k}')\, \delta(t - t')\, \delta_{ij}\,. \tag{4.5}$$

The model H equations ((4.1) and (4.2)) have been approximately solved by Siggia, Hohenberg and Halperin [9] using a self-consistent one-loop expansion, and neglecting the frequency dependence of η and Λ (Kawasaki approximation). The renormalised transport coefficient and viscosity are given by

$$\Lambda(\boldsymbol{k}) = \Lambda_0 + T\rho^{-2} k^{-2} \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3}\, \chi(\boldsymbol{k}')\, \frac{\boldsymbol{k} \cdot \boldsymbol{T}_{\boldsymbol{k}'} \cdot \boldsymbol{k}}{\eta(\boldsymbol{k}' - \boldsymbol{k})\, (\boldsymbol{k}' - \boldsymbol{k})^2 + \Lambda(\boldsymbol{k}')\, \chi^{-1}(\boldsymbol{k}')\, \boldsymbol{k}'^2}\,, \tag{4.6}$$

$$\eta(\boldsymbol{k}) = \eta_0 + \frac{T\rho^{-2} k^{-2}}{2} \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3} \times \frac{\chi(\boldsymbol{k}' - \boldsymbol{k})[\chi^{-1}(\boldsymbol{k}') - \chi^{-1}(\boldsymbol{k}' - \boldsymbol{k})](\boldsymbol{k}' \cdot \boldsymbol{T}_{\boldsymbol{k}} \cdot \boldsymbol{k}')}{[\Lambda(\boldsymbol{k}')\, \chi^{-1}(\boldsymbol{k}')\, \boldsymbol{k}'^2 + \Lambda(\boldsymbol{k}' - \boldsymbol{k})\, \chi^{-1}(\boldsymbol{k}' - \boldsymbol{k})\, (\boldsymbol{k}' - \boldsymbol{k})^2]}\,. \tag{4.7}$$

First, we consider the case $\lambda < \lambda_{\mathrm{L}}$, where the phase separation occurs at a finite value of k. In this regime, the susceptibility $\chi(\boldsymbol{k})$ has a peak at k_0, and can be approximated by the Lorentzian form in (3.37). Close to the phase transition, this Lorentzian has a narrow width and it is a good approximation to replace $\Lambda(\boldsymbol{k})$ by its value at $k = k_0$ and the viscosity η by its value at $k = 0$. With this simplification the above equations reduce to a pair of simultaneous equations for $\Lambda(k_0)$ and $\eta(k = 0)$:

$$\Lambda = \Lambda_0 + \lim_{k \to k_0} T\rho^{-2} k^{-2} \eta^{-1} \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3}\, \chi(\boldsymbol{k}')\, \frac{\boldsymbol{k} \cdot \boldsymbol{T}_{\boldsymbol{k}'} \cdot \boldsymbol{k}}{(\boldsymbol{k}' - \boldsymbol{k})^2}\,, \tag{4.8}$$

$$\eta = \eta_0 + \lim_{k \to 0} \frac{T\rho^{-2} k^{-2}}{4\Lambda} \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3}\, \frac{\boldsymbol{k}' \cdot \boldsymbol{T}_{\boldsymbol{k}} \cdot \boldsymbol{k}'}{(\boldsymbol{k}')^2 [\chi(\boldsymbol{k}')]^{-2}}\, [\chi^{-1}(\boldsymbol{k}') - \chi^{-1}(\boldsymbol{k}' - \boldsymbol{k})]\,. \tag{4.9}$$

The above equations can be reduced to one-dimensional quadratures by inserting the Lorentzian form of the susceptibility (3.37):

$$\Lambda = \Lambda_0 + \frac{T\rho^{-2}\chi_0\xi}{4\pi^2\eta}\int_0^\infty \frac{\mathrm{d}x}{1+(x-l)^2} \times \left(\frac{(x+l)^2(x-l)^2}{4l^3x}\log\left|\frac{(x-l)}{(x+l)}\right| + \frac{x^2+l^2}{2l^2}\right), \tag{4.10}$$

$$\eta = \eta_0 + \frac{T\rho^{-2}\chi_0\xi}{60\pi^2\Lambda}\left(\frac{l}{2} + \frac{(5+l^2)(\pi + 2\arctan l)}{4}\right), \tag{4.11}$$

where $l = k_0\xi$ and $x = k'\xi$. We note that the integrand in (4.10) is proportional to x^{-2} for $x \to \infty$, so no high wave number cut-off proves necessary.

The expressions for the transport coefficients (4.10) and (4.11) can be written more compactly as two simultaneous equations of the form

$$\Lambda - \Lambda_0 = \frac{A}{\eta}, \qquad \eta - \eta_0 = \frac{B}{\Lambda}, \tag{4.12}$$

where the constants A and B can be read off from (4.10) and (4.11). The above equations can solved for the renormalised transport coefficients:

$$\Lambda = \Lambda_0 + \frac{1}{2\eta_0}\left[-(B - A + \eta_0\Lambda_0) \pm \sqrt{(B - A + \eta_0\Lambda_0)^2 + 4A\eta_0\Lambda_0}\right], \tag{4.13}$$

$$\eta = \eta_0 + \frac{1}{2\Lambda_0}\left[-(A - B + \Lambda_0\eta_0) \pm \sqrt{(A - B + \Lambda_0\eta_0)^2 + 4B\Lambda_0\eta_0}\right]. \tag{4.14}$$

In the limit of small Λ_0, the above equations can be simplified to the following form:

$$\text{for } B > A \qquad \Lambda - \Lambda_0 = \frac{A\Lambda_0}{B - A}, \quad \eta - \eta_0 = \frac{B - A}{\Lambda_0}, \tag{4.15}$$

$$\text{for } B < A \qquad \Lambda - \Lambda_0 = \frac{A - B}{\eta_0}, \quad \eta - \eta_0 = \frac{B\eta_0}{A - B}. \tag{4.16}$$

In the above expressions, both A and B are proportional to the correlation length ξ (at fixed l), but the ratio (B/A) remains finite, and therefore only the terms proportional to $A - B$ diverge near the critical line. We see that Λ has a critical contribution for $B < A$, while the renormalized viscosity is of the same magnitude as the bare viscosity in this regime. On the other hand, for $B > A$ we find that the viscosity η is significantly modified by slow concentration fluctuations, while the Onsager coefficient remains close to its bare value. A numerical integration of (4.10) and (4.11) shows that $B > A$ for $k_0\xi > 2.02$.

Since the correlation length ξ diverges at the transition temperature, the regime $k_0\xi > 2.02$ is the important regime near the phase transition, and in this regime the Onsager coefficient remains close to its bare value while the divergence in the viscosity can be calculated by inserting (3.38) and (3.40) for χ_0 and ξ into (4.11):

$$\eta = \eta_0 + \frac{f(1-f)\rho^{-2}\epsilon^{-3/2}}{120\pi\Lambda_0}\left(\frac{-2k_0^6\lambda_L(1-\lambda_L)}{(1+\lambda_L)^3}\right)^{1/2}, \tag{4.17}$$

where $k_0^2 = \log(\lambda/\lambda_L)$.

The broken line in fig. 1 shows the variation of the function $c_\eta \propto (\eta - \eta_0)\Lambda_0\epsilon^{3/2}$ with λ. Here, the Lifshitz point has been fixed at $\lambda_L = -0.268$ in accordance with the results of FML for a specific random block copolymer model [6], and the ordinate has been scaled so that $c_\eta = 1$ at $\lambda = -1$. From (4.17) we see that c_η is 0 at $\lambda = \lambda_L$, and increases in proportion to $[\log(\lambda/\lambda_L)]^{3/2}$ for $\lambda < \lambda_L$.

At this point, it is useful to compare the above results with those obtained by Fredrickson and Helfand [10] for the rheology of diblock copolymers near the microphase separation transition. Near the critical temperature the parameter χ_0 does not diverge, while the mean field correlation length ξ increases in proportion to $\epsilon^{-1/2}$, where ϵ is the reduced temperature introduced earlier. From the above calculations, we see that the Onsager coefficient does not diverge as the transition temperature is approached, while the viscosity diverges in proportion to $\epsilon^{-3/2}$. Both of these results are consistent with the findings of Fredrickson and Helfand [10] for diblock copolymer melts. Indeed, apart from numerical factors, the critical transport properties of a diblock

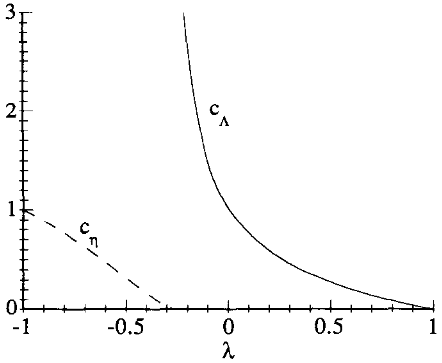

Fig. 1. The variation of the functions $c_\Lambda \propto \epsilon^{1/2}\eta_0(\Lambda - \Lambda_0)$ and $c_\eta \propto \epsilon^{3/2}\Lambda_0(\eta - \eta_0)$ with the sequence distribution parameter λ. The Lifshitz point has been fixed at $\lambda_L = -0.268$ and the ordinate has been normalised so that $c_\Lambda = 1$ at $\lambda = 0$, and $c_\eta = 1$ at $\lambda = -1$.

copolymer melt are very similar to those of a random copolymer melt with a strong tendency for alternation, $\lambda \ll \lambda_L$.

Next, we analyze the dynamical behavior of a random copolymer melt with $\lambda > \lambda_L$. For such monomer correlations, the system first becomes unstable at $k = 0$ and the phase transition is in the same universality class as a binary liquid transition. The renormalised transport coefficient and viscosity for this type of transition have been calculated previously [8], and it has been found that the divergence in the viscosity is very weak ($\eta \propto (T - T_c)^{-1/19}$), while there is a strong divergence in the Onsager coefficient as the critical temperature T_c is approached. It has been observed in experiments [9] that the value of η never rises by more than 20%–30% above its bare value η_0, and as a result it is a reasonably good approximation to neglect the divergence in the viscosity and replace it by a constant when calculating the divergence in the Onsager coefficient. With this approximation, the renormalised Onsager coefficient is given by

$$\Lambda = \Lambda_0 + \frac{T\rho^{-2}\chi_0\xi}{6\pi\eta_0}, \tag{4.18}$$

where we have substituted the Lorentzian form for the susceptibility (3.29) into (4.6) and have neglected the second term in the denominator of the latter expression due to the strong divergence in the structure factor. The term proportional to k^4 in the expression for the susceptibility (3.29) has also been neglected in deriving (4.18). It can be easily seen that (4.10) for the transport coefficient reduces to the above equation in the limit $k_0 \to 0$ or $l \to 0$. Inserting (3.33) and (3.34) for χ_0 and ξ respectively, we obtain

$$\Lambda = \Lambda_0 + \frac{f(1-f)\rho^{-2}\epsilon^{-1/2}}{6\pi\eta_0}\left[\left(\frac{2\lambda}{(1+\lambda)^2} + \kappa_2\right)^{-1/2}\frac{1-\lambda}{1+\lambda}\right]. \tag{4.19}$$

The above equation predicts that the Onsager coefficient increases as $\epsilon^{-1/2}$ as the critical point is approached, consistent with the mean-field value of the correlation length exponent employed here, $\nu = 1/2$. The solid line in fig. 1 is a plot of the λ dependence of (4.19). The function plotted in the figure, $c_\Lambda \propto \epsilon^{1/2}\eta_0(\Lambda - \Lambda_0)$, is defined as the quantity in the square brackets of (4.19). The renormalisation of the Onsager coefficient apparently vanishes at $\lambda = 1$ (which corresponds to homopolymers), because the value of the Flory chi parameter at the phase transition is proportional to $(1-\lambda)/(1+\lambda)$ (see 3.28) and this vanishes at $\lambda = 1$. However, we have neglected terms proportional to λ^N in calculating the correlation functions, which is not valid in the extreme vicinity of $\lambda = 1$. By retaining the neglected terms, the factor of $(1-\lambda)/(1+\lambda)$ in (4.19) is replaced by a finite quantity that is $\mathcal{O}(1/N)$ for $\lambda = 1$.

A more interesting behaviour is exhibited in the limit $\lambda \rightarrow \lambda_L$, where the Onsager coefficient appears to diverge. This is because the correlation length ξ in (3.34) is proportional to $\epsilon^{-1/2}(\lambda - \lambda_L)^{1/2}$, and the value of the Onsager coefficient depends on the nature of the two limiting processes $\epsilon \rightarrow 0$ and $\lambda \rightarrow \lambda_L$. For $\epsilon^{-1}(\lambda - \lambda_L) \gg 1$, (4.19) gives the correct value for the Onsager coefficient, but for $\epsilon^{-1}(\lambda - \lambda_L) \ll 1$ the term proportional to c in the expression for the susceptibility (3.29) (which was neglected in deriving (4.19)) becomes important and (4.19) is no longer valid. In this limit, we can neglect the $\mathcal{O}(k^2)$ term in the expression for the susceptibility, and obtain the following expression for the Onsager coefficient:

$$\Lambda = \Lambda_0 + \frac{f(1-f)\rho^{-2}\epsilon^{-3/4}}{6\sqrt{2}\pi\eta_0} \frac{1-\lambda_L}{1+\lambda_L} \left(\frac{-\lambda_L(1-\lambda_L)}{(1+\lambda_L)^3} \right)^{-1/4} . \tag{4.20}$$

In deriving the above equation, we have set $\lambda = \lambda_L$, $\kappa_0 = (1-\lambda_L)/(1+\lambda_L) + \epsilon$ and $\kappa_2 = -2\lambda_L\kappa_0/[(1-\lambda_L)(1+\lambda_L)]$ in (3.33), (3.34) and (3.32) and neglected the $\mathcal{O}(k^2)$ term in the denominator of (3.29). Thus, we find that the Onsager coefficient increases proportional to $\epsilon^{-3/4}$ for $\epsilon^{-1}(\lambda - \lambda_L) \ll 1$, implying that the collective diffusion coefficient should exhibit an unusual critical slowing down, $D \sim \epsilon^{1/4}$, very near the Lifshitz point.

5. Discussion

In the present paper we have analysed the critical dynamics of a simple model of random copolymer melts. An unusual feature of this model is the existence of an isotropic Lifshitz point that delineates competing tendencies for liquid-liquid separation or microphase separation. Our analysis is based on a mean-field description of the static properties of the model and on a Kawasaki-type approximation for the mode-coupled dynamics.

For $\lambda < \lambda_L$, which corresponds to copolymers with a tendency for alternation of type A and B monomers, the phase transition is of the order-disorder type (microphase separation). In such cases we find, in accordance with previous work [10,11], that the shear viscosity exhibits a strong critical anomaly, $\eta \sim \epsilon^{-3/2}$, while the Onsager coefficient for collective diffusion is essentially unaffected by mode couplings. We note that in principle one should also incorporate the effects of fluctuations on the static properties of the model, which for $\lambda < \lambda_L$ is in the Brazovskii universality class [16]. However, as fluctuations can be shown to induce a weak first order character to the phase transition, the primary effect of such corrections are simply to cut-off the viscosity anomaly at the transition [10].

In the case of $\lambda > \lambda_L$, describing copolymers with a tendency for blockiness, two types of critical dynamics are possible. Not too near the Lifshitz point, i.e. $\epsilon^{-1}(\lambda - \lambda_L) \gg 1$, we find critical dynamics essentially identical with that predicted for binary fluids (model H) [8]. In such cases the Onsager coefficient has a power law divergence, which in the present mean-field description of the statics is given by $\Lambda \sim \epsilon^{-1/2}$, and the shear viscosity has a very weak power law divergence that we have not bothered to reproduce [9].

Finally, in the close vicinity of the Lifshitz point, $\epsilon^{-1}(\lambda - \lambda_L) \ll 1$, we find the unusual prediction that the Onsager coefficient has an even stronger divergence, $\Lambda \sim \epsilon^{-3/4}$, when computed within the Kawasaki approximation. This would imply an anomalous diffusivity of the form $D \sim \epsilon^{1/4}$, which could be tested in various types of time-resolved scattering experiments.

While our model is still quite crude and the analysis somewhat oversimplified, we believe that the calculations summarized here should capture the qualitative dynamical behavior of real laboratory random copolymers. We look forward to the availability of high quality experimental data on this fascinating class of complex disordered fluids.

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Appendix A

The equations for the dynamics of the two species in a random copolymer melt are derived by averaging the dynamical equations for the microscopic concentration fields over the sequence distributions of the monomers. We start with the linear response formula for the fluctuation in the density as a function of the applied potential, (3.10). In the random phase approximation [2], the response function is that for a non-interacting, Gaussian chain, but the potential consists of three parts – the applied potential $V_0(m, \beta; \boldsymbol{k}, \omega)$, which is given by a formula similar to (3.9), an external potential $U(\boldsymbol{k}, \omega)$ to enforce incompressibility and an additional component due to enthalpic interactions between the monomers (3.12):

$$\phi(n,\alpha;\boldsymbol{k},\omega) = -\sum_{m,\beta}\chi_0(n,\alpha;m,\beta;\boldsymbol{k},\omega)\Big(V_0(m,\beta;\boldsymbol{k},\omega)+U(\boldsymbol{k},\omega) + \tfrac{1}{2}T\chi_{\mathrm{F}}\sum_{l,\gamma}[1-\theta(m,\beta)\,\theta(l,\gamma)]\,\delta\phi(l,\gamma;\boldsymbol{k},\omega)\Big)\,. \tag{A.1}$$

The self-consistent potential $U(\boldsymbol{k},\omega)$ is calculated from the above equation by enforcing the incompressibility condition, (3.7):

$$U(\boldsymbol{k},\omega) = -\Big(\sum_{n,\alpha,m,\beta}\Big\{\chi(n,\alpha;m,\beta;\boldsymbol{k},\omega)\Big(V(m,\beta;\boldsymbol{k},\omega) + \tfrac{1}{2}T\chi_{\mathrm{F}}\sum_{l,\gamma}[1-\theta(m,\beta)\,\theta(n,\gamma)]\delta\phi(l,\gamma;\boldsymbol{k},\omega)\Big)\Big\}\Big) \Big/ \sum_{n,\alpha,m,\beta}\chi(n,\alpha;m,\beta;\boldsymbol{k},\omega)\,, \tag{A.2}$$

where we have dropped the zero subscripts for simplicity. The above potential is next inserted into (A1), and we multiply this by [1/2] $[1+\theta(n,\alpha)]$ and [1/2] $[1-\theta(n,\alpha)]$ and trace over (n,α) to derive equations for the densities of species A and B respectively, which are given in (3.13) and (3.14). The response function χ' is the sum of two contributions – the first, χ_1, is a natural consequence of the correlations in an ideal, non-interacting melt,

$$\chi_1 = \tfrac{1}{4}\sum_{n,\alpha,m,\beta}[1+\theta(n,\alpha)]\chi_0(n,\alpha;m,\beta;\boldsymbol{k},\omega)\,[1+\theta(n,\beta)]\,, \tag{A.3}$$

while the second, χ_2, emerges from the incompressibility constraint:

$$\chi_2 = -\Big(\sum_{n,\alpha,m,\beta,k,\gamma,l,\nu}[1+\theta(n,\alpha)]\chi_0(n,\alpha;k,\gamma;\boldsymbol{k},\omega)\,\chi_0(m,\beta;l,\nu;\boldsymbol{k},\omega) \times[1+\theta(m,\beta)]\Big)\Big/\sum_{k,\gamma,l,\nu}\chi_0(k,\gamma;l,\nu;\boldsymbol{k},\omega)\,. \tag{A.4}$$

When the above contributions are averaged over the distributions of monomers, the terms that are either independent of $\theta(n,\alpha)$, or that are dependent on the first moment, $\overline{\theta(n,\alpha)}$, sum to zero, and we are left with the terms that are proportional to the second cumulant, $\overline{[\theta(n,\alpha)-\overline{\theta(n,\alpha)}][\theta(m,\beta)-\overline{\theta(m,\beta)}]}$. It can easily be verified that the term proportional to the second cumulant in χ_2 is $\mathcal{O}(1/N_{\mathrm{p}})$ smaller than the equivalent term in χ_1, and can therefore be neglected in the thermodynamic limit. This leaves us with the term in χ_1 that is proportional to the second cumulant of θ, which is given in (3.15).

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