Application of random phase approximation to the dynamics of polymer blends and copolymers

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(Received 18 December 1985)

The dynamics of melts of homopolymer mixtures and copolymers is studied with RPA. The first cumulant and the zeroth-order time moment of the measured dynamic scattering function $S(q,t)$ are expressed in terms of their counterparts in the non-interacting system of bare chains. The qualitative behaviour of these quantities as function of the wave number q and the interaction parameter χ_F are obtained using Rouse dynamics for bare chains, and the results are presented graphically as a guide to the interpretation of dynamic scattering experiments on such systems. The q-dependent threshold for spinodal decomposition in the case of copolymers, and the variation of the growth rate of the mean response with q in the unstable regime are also discussed qualitatively in both systems.

(Keywords: dynamic scattering function; random phase approximation; Rouse dynamics; polymer blends; copolymer melts)

INTRODUCTION

Application of the random phase approximation (RPA) to the dynamics of polymers in solution and bulk is not new. It was used by de Gennes and his collaborators[1,2] to explain scattering from semi-dilute polymer solutions and mixtures of polymers in bulk in terms of the individual scattering factors of the constituents and the interaction parameter. But the implications of RPA in the interpretation of dynamic scattering experiments has not been exploited as extensively as in the case of static experiments[3-8]. In this paper we report some progress in this direction in two cases: melts of homopolymer mixtures and copolymer melts.

We first remark that the structure of the mean field equations for the mean response of an interacting system in terms of the 'bare' response function and perturbing potentials, is the same in static and dynamic calculations when the time-dependent quantities in the latter are Laplace-transformed. Hence, the dynamic response function $\chi(q,s)$ can often be constructed directly from the expression of the static response function $\chi(q)$ by simply replacing the static bare response function $\chi^0(q)$ by the dynamic bare response functions $\chi^0(q,s)$. As an illustration, consider the static structure factor $S_{AA}(q)$ of component A in a melt of two interacting homopolymers A and B. When the incompressibility of the system is assumed it is known that

$$\frac{1}{\phi_A S_{AA}(q,\chi_F)}=\frac{1}{\phi_A S_A^0(q)}+\frac{1}{\phi_B S_B^0(q)}-2\chi_F \qquad (1)$$

where ϕ_A and ϕ_B are the volume fractions of the components with $\phi_A+\phi_B=1$, and χ_F is the Flory interaction parameter. The bare structure factors $S_j^0(q)$ $j=$ A and B, are normalized such that $S_j^0(0)=N_j$, where N_j is the number of statistical units in the jth chain. The statistical units can be chosen to have the same volume $v_A=v_B=1$ by changing the definition of χ_F accordingly. Since we did not take the individual monomers as the statistical units, there is no need to pay special attention to the case of monomers with different volumes[9].

The structure factor $S_{AA}(q,\chi_F)$ of the interacting system, which is the experimentally accessible quantity, will be denoted henceforth by $S(q,\chi_F)$ or simply $S(q)$ when no confusion arises, because, owing to the incompressibility, $S(q)$ could as well be expressed in terms of $S_{BB}(q,\chi_F)$ or $S_{AB}(q,\chi_F)$. This simplification in notation will also be used for the dynamical quantities to be introduced later. Using the relation

$$\phi S(q)=k_B T\chi(q) \qquad (2)$$

between static structure factors and response functions in equation (1) one finds

$$\frac{1}{\chi(q)}=\frac{1}{\chi_A^0(q)}+\frac{1}{\chi_B^0(q)}-2k_B T\chi_F \qquad (3)$$

By replacing the static response functions by the Laplace transform of their dynamic counterparts one obtains the desired expression for the dynamic response function $\chi(q,s)$:

$$\frac{1}{\chi(q,s)}=\frac{1}{\chi_A^0(q,s)}+\frac{1}{\chi_B^0(q,s)}-2k_B T\chi_F \qquad (4)$$

This procedure eliminates repetitious calculations in extending RPA to the dynamics of more complex systems, such as the mixtures of homopolymers in solution.

Equation (4) can be used to express the dynamic structure factor $S(q,\omega)$, or the intermediate scattering

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0032-3861/86/121935-08$03.00
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function $S(q,t)$, which are obtained conventionally in dynamic scattering experiments, in terms of the corresponding bare-chain counterparts and χ_F, as an extension of equation (1) to dynamics. Jannink and de Gennes[1] followed this procedure in 1967 and investigated numerically $S(q,\omega)$ for semi-dilute polymer solutions using the Rouse dynamics to calculate the bare-chain dynamic structure factors $S^0(q,\omega)$ of the constituents. The resulting expression of $S(q,\omega)$ in terms of $S^0(q,\omega)$ and χ_F is very complicated for qualitative discussions.

In this paper we follow a different procedure in which we consider only certain dynamical quantities, such as the first cumulant $\Omega(q)$, that are extracted routinely from the measured $S(q,t)$ or $S(q,\omega)$ in dynamic scattering experiments, and express them, rather than the full $S(q,t)$ or $S(q,\omega)$, in terms of the corresponding bare-chain quantities, such as $\Omega_0(q)$, and χ_F. These expressions are obtained without resorting to particular models for the dynamics of bare chains. In addition to first cumulant, we also consider the time-integral of the normalized $S(q,t)$ and the diffusion coefficient, both in the case of polymer blends and copolymers.

We first consider a mixture of amorphous homopolymers. The case of molten copolymers will be discussed in the next but one section.

MIXTURES OF HOMOPOLYMERS

Theory

In the framework of the linear response theory the Laplace transform of the dynamic scattering function $S(q,t)$ is written as

$$S(q,s)=\frac{1}{s+q^2D(q,s)}S(q) \tag{5}$$

where $S(q)$ is the static structure factor, and $D(q,s)$ is a generalized diffusion coefficient. This equation can be considered as the definition of $D(q,s)$. In polymer solution dynamics, the latter is expressed as[10]

$$D(q,s)=\frac{1}{q^2}[\Omega(q)-M(q,s)] \tag{6}$$

where $\Omega(q)$ is the first cumulant and $M(q,s)$ is the Laplace transform of the memory function $M(q,t)$.

The linear response function $\chi(q,t)$ is related to $S(q,t)$ by

$$k_BT\chi(q,t)=-\phi\frac{\mathrm{d}S(q,t)}{\mathrm{d}t} \tag{7}$$

Inserting equation (5) into equation (7), we find

$$\frac{1}{k_BT\chi(q,s)}=\frac{1}{\phi S(q)}\left[\frac{s}{q^2D(q,s)}+1\right] \tag{8}$$

This relation holds both for the interacting and bare chains. Hence, substitution of the corresponding expressions for $\chi(q,s)$, $\chi_A^0(q,s)$ and $\chi_B^0(q,s)$ from equation (8) into equation (4) with normalized structure factors, yields

$$\frac{1}{\phi_AS(q)}\left[\frac{s}{q^2D(q,s)}+1\right]=\frac{1}{\phi_AS_A^0(q)}\left[\frac{s}{q^2D_A^0(q,s)}+1\right]+\frac{1}{\phi_BS_B^0(q)}\left[\frac{s}{q^2D_B^0(q,s)}+1\right]-2\chi_F \tag{9}$$

Elimination of the terms involving only the static structure factors which satisfy equation (1), results in the main equation of this paper:

$$\frac{1}{\phi_AS(q)D(q,s)}=\frac{1}{\phi_AS_A^0(q)D_A^0(q,s)}+\frac{1}{\phi_BS_B^0(q)D_B^0(q,s)} \tag{10}$$

In order to display the dependence of $D(q,s)$ on χ_F explicitly, we rewrite this equation as

$$D(q,s)=D_0(q,s)\frac{\chi_F^c(q)-\chi_F}{\chi_F^c(q)} \tag{11}$$

by introducing

$$\chi_F^c(q)=\tfrac{1}{2}\left[\frac{1}{\phi_AS_A^0(q)}+\frac{1}{\phi_BS_B^0(q)}\right] \tag{12}$$

and

$$\frac{1}{D_0(q,s)}=\frac{1}{2\chi_F^c(q)}\left[\frac{1}{\phi_AS_A^0(q)D_A^0(q,s)}+\frac{1}{\phi_BS_B^0(q)D_B^0(q,s)}\right] \tag{13a}$$

We note for clarification of notation that $D(q,s)$ and $D_0(q,s)$ are abbreviations for $D(q,s,\chi_F)$ and $D(q,s,0)$, respectively. In the case of identical chains for which $S_A^0(q)=S_B^0(q)$ and $D_A^0(q,s)=D_B^0(q,s)$, equation (13a) reduces to

$$D(q,s,0)=D_A^0(q,s) \tag{13b}$$

Specific equations relating various dynamical properties of the measured and bare dynamic scattering functions can now be obtained from equation (11) by taking appropriate limits with respect to q and s.

First cumulant

The short time behaviour of $S(q,t)$ is obtained by taking the large-s limit of $D(q,s)$. Assuming that $M(q,t)$ is finite as $t\rightarrow 0$, which is the case in flexible chains, and using

$$\lim_{t\rightarrow 0}M(q,t)=\lim_{s\rightarrow\infty}sM(q,s)$$

provided both limits exist, we find $M(q,s)\rightarrow 0$, and hence $D(q,s)\rightarrow\Omega(q)/q^2$ according to equation (6), as $s\rightarrow\infty$. With this observation equation (11) yields our first specific result

$$\Omega(q)=\Omega_0(q)\frac{\chi_F^c(q)-\chi_F}{\chi_F^c(q)} \tag{14a}$$

where

$$\frac{1}{\Omega_0(q)}=\frac{1}{2\chi_F^c(q)}\left[\frac{1}{\phi_AS_A^0(q)\Omega_A^0(q)}+\frac{1}{\phi_BS_B^0(q)\Omega_B^0(q)}\right] \tag{14b}$$

In these equations $\Omega(q)=\Omega(q,\chi_F)$ is the first cumulant of the dynamic scattering function $S(q,t)$ in the presence of interactions, and $\Omega_A^0(q)$ and $\Omega_B^0(q)$ are the first cumulants of $S_A^0(q,t)$ and $S_B^0(q,t)$ of the bare chains. The $\Omega_0(q)$ denotes $\Omega(q,0)$.

The first observation is that $\Omega(q)$ becomes negative for those spatial modes for which $q>q_c$ where q_c is

determined by $\chi_F^c(q_c)=\chi_F$. This occurs when $\chi_F>\chi_F^c(0)\equiv\chi_F^c$. The threshold value χ_F^c of the interaction parameter corresponds to the spinodal point at a fixed volume fraction, and is given by

$$\chi_F^c=\tfrac{1}{2}\left[\frac{1}{\phi_A N_A}+\frac{1}{\phi_B N_B}\right] \tag{15}$$

Since equation (7), which was used in the derivation of equations (11) and (14), holds only when equilibrium exists, we assume in the following that $\chi_F<\chi_F^c$ and postpone the discussion of the physical implications of $\chi_F>\chi_F^c$ to a later section.

In order to discuss the experimental implications of equation (14), we consider the symmetrical case in which $S_A^0(q)=S_B^0(q)$ and $\Omega_A^0(q)=\Omega_B^0(q)$, and rewrite $\Omega(q)$ as

$$\Omega(q,\chi_F)=\Omega_A^0(q)[1-2\chi_F S_A^0(q)\phi_A(1-\phi_A)]$$

One may use this equation in the interpretation of dynamic scattering experiments on melts of homopolymer mixtures in several ways, assuming that the first cumulant can be extracted from the measured $S(q,t)$ by conventional cumulant analysis[11]. For instance one may plot $\Omega(q,\chi_F)$ for a given q as a function of $\phi_A(1-\phi_A)$ to determine the Flory parameter χ_F, assuming that S_A^0 is known. Since $S_A^0(q)$ can be written as $S_A^0(q)=N_A P(qR_g)$, one may use for $P(x)$ the Debye function, assuming the bare chains obey Gaussian statistics. One may determine χ_F also by plotting $\Omega(q,\chi_F)/\Omega_A^0(q)$, this time as function of $(qR_g)^2$, or even as function of $S_A^0(q)$ at a given volume ratio, provided $\Omega_A^0(q)$ is known *a priori*. A more interesting representation of the data would be to plot the ratio

$$\frac{\Omega(q,\chi_F)}{[1-2\chi_F S_A^0(q)\phi_A(1-\phi_A)]}=\Omega_A^0(q)$$

as function of $(qR_g)^2$ just to obtain the bare cumulant. Such a procedure will shed light onto the bare chain dynamics. For example, if the Rouse dynamics is assumed for the non-interacting chains, then[10-12]

$$\Omega_A^0(q)=\frac{k_B T}{\xi}\frac{q^2}{N_A P_D(qR_g)} \tag{16}$$

where ξ is the friction coefficient per statistical segment. Accordingly one would expect the experimental ratio to behave as $q^2 k_B T/\xi N_A$ when $qR_g\ll 1$, and as $(k_B T/12\xi a^2)(qa)^4$ when $qR_g\gg 1$ and $qa\ll 1$, where 'a' is the statistical step length in Gaussian chain dynamics. Deviations from this behaviour may provide useful information concerning the range of validity of the Rouse model for the dynamics of bare chains.

Markov limit

This limit corresponds to letting q and s approach zero while keeping q^2/s fixed. Experiments in which $qR_g\ll 1$ and $t\to\infty$ such that $q^2t=$ constant can be described by the Markov limit of $D(q,s)$. The constant value of q^2t in these experiments is adjusted such that $S(q,t)$ decays but remains above the noise level during the experimental time scale. This implies $q^2Dt\sim 1$ where D is the diffusion coefficient. The Markov limit of $D(q,s)$ is [13,14]

$$D=D_{sh}-\lim_{q\to 0}\frac{1}{q^2}\int_0^\infty \mathrm{d}t\, M(q,t)$$

where D_{sh} is defined by $\Omega(q)\to q^2 D_{sh}$ as $q\to 0$, and referred to as the short-time diffusion coefficient. The D in the above equation is the long-time diffusion coefficient which is measured experimentally when $qR_g\ll 1$.

Using this limit in equation (11) one obtains

$$D(\chi_F)=D_0\frac{\chi_F^c-\chi_F}{\chi_F^c} \tag{17}$$

where χ_F^c is defined in equation (15), and

$$\frac{1}{D_0}=\frac{1}{2\chi_F^c}\left[\frac{1}{\phi_A N_A D_A^0}+\frac{1}{\phi_B N_B D_B^0}\right] \tag{18}$$

In equation (18) D_A^0 and D_B^0 are the long-time diffusion coefficients of the bare chains. Taking the small-q limit of equation (14) and using $\Omega(q)\to q^2 D_{sh}$ one obtains the same equation as equation (17) for the dependence of the measured short-time diffusion coefficient on the interaction parameter χ_F. But D_{sh} and D may be very different from each other. Equation (17) was written down and discussed before by de Gennes[5].

Mean response time

As another dynamical quantity that might be of interest in the interpretation of the dynamic experiments, we introduce the 'mean response time $T(q)$' through

$$T(q)=\frac{\int_0^\infty \mathrm{d}t\, t\chi(q,t)}{\int_0^\infty \mathrm{d}t\,\chi(q,t)}$$

Using equation (7) one can show that $T(q)$ can be defined equivalently as the zeroth order time-moment of the normalized $S(q,t)$,[15] i.e.

$$T(q)=\frac{1}{S(q)}\int_0^\infty \mathrm{d}t\, S(q,t) \tag{19}$$

This definition indicates how $T(q)$ can be inferred, in principle, from the measurement of $S(q,t)$. Combining equations (5) and (19) we find that $T(q)$ is related to $D(q,s)$ by $T^{-1}(q)=q^2D(q,0)$. Hence equation (11) reduces in the limit of $s\to 0$, to

$$T^{-1}(q,\chi_F)=T_0^{-1}(q)\frac{\chi_F^c(q)-\chi_F}{\chi_F^c(q)} \tag{20}$$

with

$$T_0(q)=\frac{1}{2\chi_F^c(q)}\left(\frac{T_A^0(q)}{\phi_A S_A^0(q)}+\frac{T_B^0(q)}{\phi_B S_B^0(q)}\right) \tag{21}$$

The bare mean response times T_A^0 and T_B^0 appearing in equation (21) are defined by

$$T_A^0(q)=\frac{1}{S_A^0(q)}\int_0^\infty \mathrm{d}t\, S_A^0(q,t)$$

The expressions of the measured $\Omega(q,\chi_F)$, $D(\chi_F)$ and $T(q,\chi_F)$ in terms of the interaction parameter and their bare equivalents, have the same form because they are obtained from the same starting equation (11). Since they represent different aspects of the measured $S(q,t)$, they can be used individually or jointly in the same experiment for the interpretation of dynamic scattering on melts of homopolymer mixtures. In some special cases they are related to each other in a simple way. For example, in q-regions where $S(q,t)$ can be scaled as $S(q,t)=S(q)f[\Omega(q)t]$ where $f(\tau)$ is a known shape function, one finds

$$T(q)=\frac{1}{\Omega(q)}\int_0^\infty \mathrm{d}\tau f(\tau) \tag{22}$$

In such cases, the results of the cumulant analysis yielding $\Omega(q)$, and the zeroth-order time moment of the normalized $S(q,t)$ yielding $T(q)$ can be compared for consistency of the data analysis provided the shape function is known *a priori*.

STABILITY CONSIDERATIONS

The homogeneous state of the mixture becomes unstable when $\chi_F>\chi_F^c$, and the system tends to a new overall heterogeneous equilibrium state although locally the system may be stable since $\chi_F<\chi_F^c(q)$ for $q>q_c$. In this case the response function $\chi(q,s)$ of the interacting mixture can not be expressed in terms of $S(q,t)$ which is an equilibrium time correlation function. However, the mean response $\delta\phi_A(q,t)$ of the interacting system to a time-dependent external potential $U_A(q,t)$ can still be expressed as

$$\delta\phi_A(q,s)=-\chi(q,s,\chi_F)U_A(q,s) \tag{23}$$

within the framework of the mean field theory. The expression of $\chi(q,s,\chi_F)$ in equation (4) can be written as

$$\chi(q,s)=\frac{\chi_0(q,s)}{1-2k_BT\chi_F\chi_0(q,s)} \tag{24}$$

where $\chi_0(q,s)$ is defined by

$$\frac{1}{\chi_0(q,s)}=\frac{1}{\chi_A^0(q,s)}+\frac{1}{\chi_B^0(q,s)} \tag{25}$$

Equation (24) suggests an interpretation of the interacting system as a closed-loop feedback network (cf. *Figure 1*) with $\chi_0(q,s)$ and $2\chi_Fk_BT$ being the forward and feedback transfer functions. The stability of the system is determined by the algebraically largest root of the characteristic equation

$$1=2k_BT\chi_F\chi_0(q,s) \tag{26}$$

The roots are real because the dynamics of the interacting system are governed by diffusion, and are overdamped. Each discrete root of this equation corresponds to an exponential term in the mean response $\delta\phi_A(q,t)$. It is of course possible that $\chi_0(q,s)$ may contain

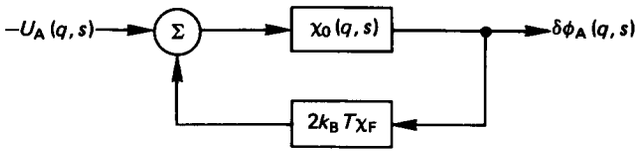

Figure 1 Interpretation of RPA as a feedback network for stability analysis

branch-cuts in the complex s-plane, so that $\delta\phi_A(q,t)$ cannot be expressed as sum of exponentials. However, we shall not be concerned with this question, and assume that there is a discrete root $s=\alpha(q,\chi_F)$ that changes sign when χ_F is increased. The threshold of instability is determined by $\alpha(q,\chi_F)=0$, i.e.

$$1=2k_BT\chi_F\chi_0(q,0)$$

This equation yields either the critical value $\chi_F^c(q)$ of the interaction parameter χ_F as function of q (see equation (12)), or q_c as function of χ_F, such that the asymptotic growth rate of $\delta\phi_A(q,t)$ is negative for $q>q_c$ and positive for $q<q_c$. This equation is of course identical to $\chi_F=\chi_F^c(q)$ where $\chi_F^c(q)$ was introduced in equation (12).

The bare response functions in equation (25) can still be expressed in terms of their corresponding equilibrium time correlation functions (cf. equations (7) and (8)). Hence, using equation (8) in equations (25) and (26) one can rewrite the characteristic equation as

$$\alpha(q,\chi_F)=q^2D_0(q,\alpha)\frac{\chi_F-\chi_F^c(q)}{\chi_F^c(q)} \tag{27}$$

where $D_0(q,\alpha)$ was defined in equation (13). Several conclusions can be drawn from this form of the characteristic equation: In the case of $\chi_F<\chi_F^c$ where the homogeneous state is an equilibrium state, the right hand side of equation (27) can be identified as the generalized diffusion coefficient $-q^2D(q,\alpha,\chi_F)$ of the interacting system (cf. equation (11)). Then, equation (27) becomes $\alpha+q^2D(q,\alpha,\chi_F)=0$, which is the denominator in equation (5). One concludes that the relaxation spectra of $S(q,t,\chi_F)$ and the mean response $\delta\phi_A(q,t)$ are the same. This result is also a consequence of a more general property that $S(q,t)$ satisfies the linearized macroscopic equations for the mean response. More specific conclusions are: (1) Since $\chi_F^c(q\to\infty)=\infty$, $\alpha\to-q^2D_M$ in the large q-limit with $D_0(\infty,\alpha)=D_M$, implying relaxation through segmental diffusion. Here D_M^{-1} is a weighted combination of the inverse segmental diffusion coefficients of the bare chains (cf. equation (18)). (2) Since $\alpha\to0$ as $q^2\to0$, the growth rate of the long wavelength spatial modes is given by the Markov limit of equation (27):

$$\alpha\to q^2D_0\left(\frac{\chi_F}{\chi_F^c}-1\right) \tag{28}$$

where D_0 is a combination of the long-time diffusion coefficients of the bare chains (cf. equation (18)). (3) The growth rates of the spatial modes with $q\approx q_c$ follows from $q^2D_0(q,0)=T_0^{-1}(q)$ as

$$\alpha\to T_0^{-1}(q)\frac{\chi_F-\chi_F^c(q)}{\chi_F^c(q)} \tag{29}$$

where $T_0(q)$ is a weighted average of the bare mean response times (cf. equation (21)). Equation (29) reduces to equation (28) when $q_c \to 0$. (4) When χ_F is very large, equation (27) yields, with $q^2 D_0(q,\alpha\to\infty)=\Omega_0(q)$,

$$\alpha \to \Omega_0(q)\frac{\chi_F-\chi_F^c(q)}{\chi_F^c(q)} \tag{30}$$

where $\Omega_0(q)$ is defined by equation (14b).

Figure 2 shows the q-regions for the stable and unstable modes, as well as the qualitative behaviour of the growth rate as function of q, when $\chi_F \approx \chi_F^c$. The latter implies that both the cut-off q_c and the growth rate are small so that $\alpha \simeq q^2 D_0[\chi_F-\chi_F^c(q)]/\chi_F^c(q)$. For simplicity we consider the case of identical chains where $\chi_F^c(q)=\chi_F^c/P_D(\kappa)$ with $P_D(\kappa)$ being the Debye function and $\kappa=(qR_g)^2$. The solid curve is plotted using $\chi_F^c/\chi_F=2/3$ in

$$\alpha(q,\chi_F) \simeq q^2 D_0\left(P_D(\kappa)\frac{\chi_F}{\chi_F^c}-1\right) \tag{31}$$

The behaviour of $\alpha(\kappa,\chi_F)$ can be explained analytically by approximating $P_D(\kappa)$ as $1-\kappa/3$. Then the cut-off wave number q_c is given by

$$q_c^2 R_g^2 = 3\left[1-\frac{\chi_F^c}{\chi_F}\right]$$

and $\alpha(\kappa,\chi_F)$ becomes a parabola for $q \leqslant q_c$ with a maximum growth rate

$$\alpha_{max}=\tfrac{1}{2}D_0 q_{max}^2\left[\frac{\chi_F}{\chi_F^c}-1\right]$$

where $q_{max}=q_c/2^{1/2}$ is the mode with the maximum growth rate.

Figure 2 also shows $\alpha(q\to\infty,\chi_F)=-q^2 D_M$ where D_M is the diffusion coefficient of a statistical segment in a bare chain. This limit is of course outside the validity of the above approximation, because $D_0(q,s)$ cannot be approximated by its Markov limit for large q.

The kinetics of spinodal decomposition were recently studied by Pincus[16] and Binder[17] using a thermodynamic approach.

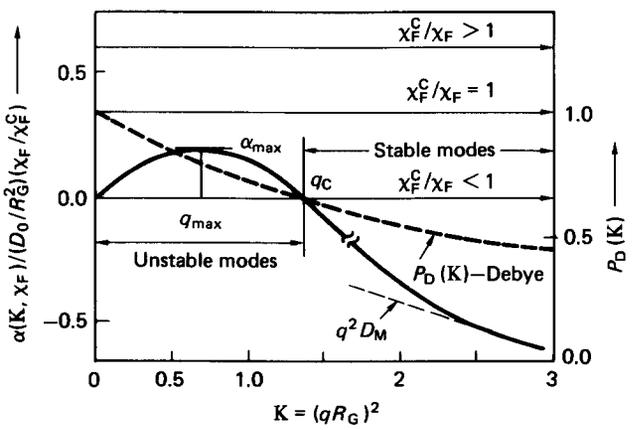

Figure 2 Qualitative behaviour of the growth rate of the mean response, and the stability regions of the spatial modes for homopolymer mixtures in melt

COPOLYMER MELTS

General results

The static structure factor $S_{AA}(q)=S_{BB}(q)=-S_{AB}(q)$ of melts of copolymers consisting of two species A and B was calculated previously[4]:

$$\frac{1}{\phi_A S_{AA}}=\frac{\phi_A S_A^0+\phi_B S_B^0+2(\phi_A\phi_B)^{1/2}S_{AB}^0}{\phi_A S_A^0 \phi_B S_B^0-\phi_A\phi_B(S_{AB}^0)^2}-2\chi_F \tag{32}$$

where $S_{ij}^0(q)$ are the bare structure factors with the normalization $S_{ii}^0(0)=(N_i N_j)^{1/2}$ where N_i and N_j are the number of monomers of the ith and jth sections of a given copolymer. The prescription described in the introduction yields the dynamic response function $\chi(q,s,\chi_F)$ of the interacting copolymers as

$$\frac{1}{\chi(q,s)}=\frac{\chi_T^0(q,s)}{\chi_A^0(q,s)\chi_B^0(q,s)-[\chi_{AB}^0(q,s)]^2}-2\chi_F k_B T \tag{33}$$

where $\chi_T^0=\chi_A^0+\chi_B^0+2\chi_{AB}^0$. This equation can be written in a compact form in matrix notation:

$$\chi^{-1}(q,s)=\underline{m}^T[\underline{\underline{\chi}}^0(q,s)]^{-1}\underline{m}-2\chi_F k_B T \tag{34}$$

where $\underline{m}=\mathrm{col}[1,-1]$, $\underline{m}^T$ is its transpose, and $\underline{\underline{\chi}}^0(q,s)$ is

$$\underline{\underline{\chi}}^0(q,s)=\begin{bmatrix}\chi_A^0 & \chi_{AB}^0\\ \chi_{BA}^0 & \chi_B^0\end{bmatrix} \tag{35}$$

The case of copolymer melts differs from that of melts of mixtures because of the presence of the off-diagonal terms $\chi_{AB}^0(q,s)$. These terms account for the dynamic coupling between the two parts of the copolymers. The dynamic quantities of the interacting system can be related to those of the bare chains in a similar way as in mixtures by using matrix notation only with minor changes. These modifications are pointed out in the following.

Equation (5), for the bare dynamic scattering function, becomes

$$\underline{\underline{S}}^0(q,s)=[s\underline{\underline{I}}+q^2\underline{\underline{D}}^0(q,s)]^{-1}\underline{\underline{S}}^0(q) \tag{36}$$

where the static structure matrix $\underline{\underline{S}}^0$ has matrix elements $\phi_A S_A^0$, $\phi_B S_B^0$ and $(\phi_A\phi_B)^{1/2}S_{AB}^0$. The generalized diffusion matrix $\underline{\underline{D}}^0(q,s)$ is related to the first cumulant matrix $\underline{\underline{\Omega}}^0(q)$ and the memory matrix $\underline{\underline{M}}^0(q,s)$ by $q^2\underline{\underline{D}}^0=\underline{\underline{\Omega}}^0-\underline{\underline{M}}^0$ (cf. equation (6)). Using the extension of equation (7) to matrices, we find

$$k_B T\underline{\underline{\chi}}^0=q^2\underline{\underline{D}}^0[s\underline{\underline{I}}+q^2\underline{\underline{D}}^0]^{-1}\underline{\underline{S}}^0 \tag{37}$$

Since $\chi(q,s)$ is a scalar, we still use equations (5) and (8) to introduce $D(q,s)$. The procedure leading to equation (11) yields, in this case

$$D(q,s)=D_0(q,s)\frac{\chi_F^c(q)-\chi_F}{\chi_F^c(q)} \tag{38}$$

where

$$\frac{1}{D_0(q,s)}=\frac{1}{2\chi_F^c(q)}\underline{m}^T[\underline{\underline{D}}^0(q,s)\underline{\underline{S}}^0(q)]^{-1}\underline{m} \tag{39}$$

$$\chi_F^c(q)=\tfrac{1}{2}\underline{m}^T[\underline{\underline{S}}^0(q)]^{-1}\underline{m} \tag{40}$$

The characteristic equation describing the stability of the interacting system is obtained from equation (26) by using $\chi_0^{-1}(q,s)=\underline{m}^{\mathrm{T}}[\underline{\chi}^0(q,s)]^{-1}\underline{m}$, and the growth rate is found as

$$\alpha(q,\chi_{\mathrm{F}})=q^2D_0(q,\alpha)\frac{\chi_{\mathrm{F}}-\chi_{\mathrm{F}}^{\mathrm{c}}(q)}{\chi_{\mathrm{F}}^{\mathrm{c}}(q)} \tag{41}$$

These equations are identical in form to their counterparts in the case of mixtures. The difference between them lies in the definitions of $D_0(q,s)$ and $\chi_{\mathrm{F}}^{\mathrm{c}}(q)$. Various q and s limits of equations (38) and (41) can be investigated in a similar manner. Here we discuss the short time and Markov limits to draw some physical conclusions relevant to dynamic scattering experiments on copolymer melts. The mean response time is left out because its discussion does not add anything new.

First cumulant

The large-s limit of equations (38) and (39) defines the first cumulants:

$$\Omega(q)=\Omega_0(q)\frac{\chi_{\mathrm{F}}^{\mathrm{c}}(q)-\chi_{\mathrm{F}}}{\chi_{\mathrm{F}}^{\mathrm{c}}(q)} \tag{42}$$

with

$$\frac{1}{\Omega_0(q)}=\frac{1}{2\chi_{\mathrm{F}}^{\mathrm{c}}(q)}\underline{m}^{\mathrm{T}}[\underline{\underline{\Omega}}^0(q)\underline{\underline{S}}^0(q)]^{-1}\underline{m} \tag{43}$$

In order to proceed further we must specify the static structure matrix $\underline{\underline{S}}^0(q)$ and the first cumulant matrix $\underline{\underline{\Omega}}^0(q)$ for the bare chains. For simplicity we consider symmetrical copolymers for which $\phi_{\mathrm{A}}=\phi_{\mathrm{B}}=1/2$, $N_{\mathrm{A}}=N_{\mathrm{B}}=N_{1/2}$, $S_{\mathrm{A}}^0(q)=S_{\mathrm{B}}^0(q)=N_{1/2}P_{1/2}$ and $S_{\mathrm{AB}}^0(q)=N_{1/2}[2P_{\mathrm{T}}(q)-P_{1/2}(q)]$ where $P_{1/2}(q)$ and $P_{\mathrm{T}}(q)$ are taken to be the Debye functions for the half and full chains respectively. Substitution of these into equation (40) yields

$$\chi_{\mathrm{F}}^{\mathrm{c}}(q)=1/N_{1/2}(P_{1/2}-P_{\mathrm{T}}) \tag{44}$$

The product $\underline{\underline{\Omega}}^0(q)\underline{\underline{S}}^0(q)$ in equation (43) can be expressed, in the framework of the linear response theory, as

$$\underline{\underline{\Omega}}^0(q)\underline{\underline{S}}^0(q)=\langle\underline{\delta\phi}\,\mathscr{L}^0\underline{\delta\phi}^{\mathrm{T}}\rangle \tag{45}$$

where $\underline{\delta\phi}=\mathrm{col}[\delta\phi_{\mathrm{A}},\delta\phi_{\mathrm{B}}]$ and $\mathscr{L}^0$ is a time-independent operator that describes the dynamics of the bare chains[10,11]. The $\delta\phi_j(q)$ are the fluctuations in the volume fractions of the jth type of monomers. If the Rouse model is adopted to describe the dynamics of the bare chains, one finds from equation (45)

$$\underline{\underline{\Omega}}^0(q)\underline{\underline{S}}^0(q)=q^2\frac{k_{\mathrm{B}}T}{\xi}\begin{bmatrix}\phi_{\mathrm{A}} & 0\\ 0 & \phi_{\mathrm{B}}\end{bmatrix} \tag{46}$$

Substitution of equations (44) and (46) into equation (42) yields

$$\Omega(q,\chi_{\mathrm{F}})=q^2\frac{k_{\mathrm{B}}T}{2N_{1/2}\xi}\frac{1-\chi_{\mathrm{F}}N_{1/2}(P_{1/2}-P_{\mathrm{T}})}{P_{1/2}-P_{\mathrm{T}}} \tag{47}$$

Although perhaps too simplistic, this expression displays some interesting qualitative features of the dynamics of copolymer melts.

Firstly, it shows that the small-q limit of $\Omega(q,\chi_{\mathrm{F}})$ does not vanish. Using $P_{1/2}-P_{\mathrm{T}}\rightarrow(qR_{\mathrm{gT}})^2/6$ as $q\rightarrow 0$, we find

$$\Omega(q,\chi_{\mathrm{F}})\rightarrow\frac{3k_{\mathrm{B}}T}{N_{1/2}\xi R_{\mathrm{gT}}^2} \tag{48}$$

where R_{gT} is the radius of gyration of the full chain. This result is interesting because $\Omega(q,\chi_{\mathrm{F}})$ vanishes as q^2 in the case of mixtures (cf. equation (16) and the subsequent discussion) implying the translational diffusion of the entire molecule during the initial relaxation of long-wave spatial inhomogeneities. In the case of copolymer melts the maximum spatial inhomogeneity is of the order of $R_{\mathrm{gT}}/2$ and hence the initial relaxation of long-wave density inhomogeneities is due to local motions, and independent of q whenever $qR_{\mathrm{gT}}\ll 1$.

Secondly, equation (47) yields, in the large-q limit where $qR_{\mathrm{gT}}\gg 1$,

$$\Omega(q,\chi_{\mathrm{F}})=\frac{3k_{\mathrm{B}}T}{N_{1/2}\xi R_{\mathrm{gT}}^2}\frac{(qR_{\mathrm{gT}})^4}{12} \tag{49}$$

which is the usual q^4-behaviour of the internal motions in the Rouse dynamics. In the still higher q-regions where $qa\geqslant 1$, $\Omega(q,\chi_{\mathrm{F}})\rightarrow q^2(k_{\mathrm{B}}T/\xi)$, which corresponds to the segmental diffusion. However, this limit cannot be obtained from equation (43) when $S(q)$ is approximated by the Debye function, as is the case in equation (47).

Finally, equation (47) predicts that $\Omega(q,\chi_{\mathrm{F}})$ can become negative for a range of q-values when the interaction parameter exceeds a threshold value $\chi_{\mathrm{F}}^{\mathrm{c}}$ given by

$$\chi_{\mathrm{F}}^{\mathrm{c}}=N_{1/2}^{-1}[P_{1/2}(q_{\mathrm{c}})-P_{\mathrm{T}}(q_{\mathrm{c}})]^{-1} \tag{50}$$

where q_{c} maximizes $P_{1/2}(q)-P_{\mathrm{T}}(q)$. Numerically, $(q_{\mathrm{c}}R_{\mathrm{gT}})^2\simeq 3.7934$ and $P_{1/2}(q_{\mathrm{c}})-P_{\mathrm{T}}(q_{\mathrm{c}})\simeq 0.19057$. When $\chi_{\mathrm{F}}>\chi_{\mathrm{F}}^{\mathrm{c}}$ there are two roots $q_{\mathrm{c}1}$ and $q_{\mathrm{c}2}$ of

$$\chi_{\mathrm{F}}^{\mathrm{c}}=\chi_{\mathrm{F}}\eta(q) \tag{51}$$

where

$$\eta(q)=\frac{P_{1/2}(q)-P_{\mathrm{T}}(q)}{P_{1/2}(q_{\mathrm{c}})-P_{\mathrm{T}}(q_{\mathrm{c}})} \tag{52}$$

The spatial modes in the range $q_{\mathrm{c}1}\leqslant q\leqslant q_{\mathrm{c}2}$ are unstable when $\chi_{\mathrm{F}}>\chi_{\mathrm{F}}^{\mathrm{c}}$. It is interesting that the mode corresponding to $qR_{\mathrm{gT}}\approx 2$ (more precisely, 1.9476) becomes unstable first when the spinodal point $\chi_{\mathrm{F}}=\chi_{\mathrm{F}}^{\mathrm{c}}$ is reached, in contrast with the melt of mixture of homopolymers where the mode $q=0$ becomes unstable first. This behaviour may also be attributed to the fact that the spatial inhomogeneities in copolymer melts are local involving distances of the order of $R_{\mathrm{gT}}/2$.

In *Figure 3* we have plotted the normalized first cumulant

$$\frac{\Omega(q,\chi_{\mathrm{F}})}{(k_{\mathrm{B}}T\chi_{\mathrm{F}}^{\mathrm{c}}/2\xi R_{\mathrm{gT}}^2)}=\kappa\left[\frac{1}{\eta(q)}-\frac{\chi_{\mathrm{F}}}{\chi_{\mathrm{F}}^{\mathrm{c}}}\right]$$

as function of $\kappa=q^2R_{\mathrm{gT}}^2$ and for $\chi_{\mathrm{F}}/\chi_{\mathrm{F}}^{\mathrm{c}}=0$, 0.65 and 1.0. The predicted approach of $\Omega(q,\chi_{\mathrm{F}})$ to a constant in the

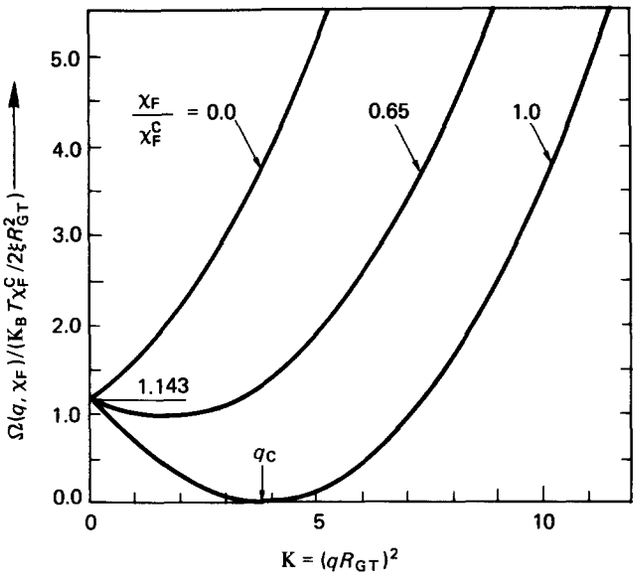

Figure 3 Expected behaviour of the first cumulant in copolymer melts as function of the interaction parameter χ_F, and qR_{gT}

small-q limit may not be observed experimentally. One reason is that the intensity of the scattered beam decreases because $S(q,t)$ vanishes as q is decreased. The second reason is that the conditions of a dynamic scattering experiment correspond to the Markov limit when $qR_{gT} \ll 1$, and hence the cumulant analysis yields the long-time diffusion coefficient rather than the first cumulant. Therefore, one would more likely expect a bending towards the origin, even if it were feasible to extend the experimental q-range to $qR_{gT} \ll 1$. The most suitable q-region in an experiment to observe the behaviour depicted in the Figure is around $qR_{gT} \approx 2$ where the cumulant analysis yields the first cumulant, and where $\Omega(q,\chi_F)$ is expected to attain its minimum in the case of incompatible species. This region is also favourable from the point of view of signal intensity.

Markov limit

Since it corresponds to the long-time diffusion of the bare copolymers, the matrix $\underline{\underline{D}}^0(q,s)$ in equation (39) is diagonal in the Markov limit. The diagonal elements representing the long-time diffusion coefficients of the two-parts of a copolymer molecule are equal to each other, and to the diffusion coefficient of the entire molecule. The off-diagonal terms are zero because the two parts of a copolymer diffuse together, and the relative distance between their centre of masses remains finite as $t \to \infty$. From equations (38) and (39) we find $D(\chi_F) = D$, i.e. the long-time diffusion coefficient is not affected by the interaction between the two arms of the copolymer.

Growth rates

The discussion of the growth rate $\alpha(q,\chi_F)$ of the mean response, given by the characteristic equation differs from the investigation of the various q and s limits of $D(q,s,\chi_F)$ using equation (38), because q and s are independent variables in the latter, whereas equation (41) determines $\alpha(q,\chi_F)$ for each q. Since the long time behaviour of the mean response is governed by the algebraically largest root of the characteristic equation, we look for roots near zero. For small-q, there is a root that vanishes with q^2. It is obtained by taking the Markov limit of equation (41) as $\alpha = -q^2 D$ where D is the long-time diffusion coefficient of a copolymer. It is independent of χ_F because $\chi_F^c(q)$ diverges as $q \to 0$. For $\chi_F > \chi_F^c$, equation (41) has positive roots for modes $q_{c1} < q < q_{c2}$ (see *Figure 4*). Around the instability threshold where $\chi_F \approx \chi_F^c$, these roots can be approximated by

$$\alpha(q,\chi_F) = T^{-1}(q)\frac{\chi_F - \chi_F^c(q)}{\chi_F^c(q)}$$

where $T(q) = [q^2 D_0(q,0)]^{-1}$ and denotes the mean response time of the noninteracting chains. In the large-q limit, $\alpha = -q^2 D_M$ corresponding to segmental diffusion.

Figure 4 depicts the qualitative behaviour of $\alpha(q,\chi_F)$ as a function of $\kappa = q^2 R_{gT}^2$. The solid curve is plotted in the symmetrical case using

$$\alpha(q,\chi_F) = (\chi_F D_0/\chi_F^c R_{gT}^2)\kappa\left[\eta(\kappa) - \frac{\chi_F^c}{\chi_F}\right]$$

with $\chi_F^c/\chi_F = 0.8$. In this expression $D_0(q,\alpha)$ is approximated by the constant D_0 for all values of q. Without explicit knowledge of bare chain dynamics to calculate $D_0(q,s)$ it is not possible to investigate the variation of $\alpha(q,\chi_F)$ more precisely.

SUMMARY AND DISCUSSIONS

The main point in this paper was the derivation of an equation for the generalized diffusion coefficient $D(q,s)$ of the interacting polymers in melt, in terms of $D^0(q,s)$ of the bare chains, starting from the expression of the dynamic response function obtained in RPA. Taking proper limits of $D(q,s)$ as function of q and s in this equation, specific relationships were obtained between various dynamic quantities of the interacting and bare systems. In particular the first cumulant $\Omega(q,\chi_F)$, mean response time $T(q,\chi_F)$ and the long-time diffusion coefficient $D(\chi_F)$ are studied since they can be inferred from the measured $S(q,t)$ by the conventional data analysis. The expressions of these quantities in terms of their bare counterparts are not based on any particular model for the dynamics of the bare chains, so that they can be used to extract

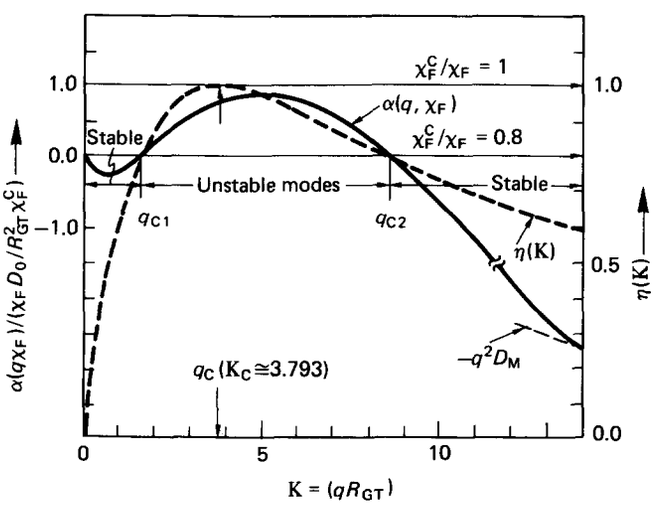

Figure 4 Qualitative behaviour of the growth rate of the mean response, and the stability regions of the spatial modes for copolymer melts

information to test the validity of the different models. We have occasionally used the Rouse dynamics for bare chains to illustrate the application of the general results, and to explore the expected qualitative behaviour of the above dynamical quantities as function of wave number q and the interaction parameter χ_F, in the cases of melts of a mixture of two homopolymers and copolymer melts. The physical content of our results in the former case is essentially the same as those discussed by Brochard and de Gennes[2] when homopolymers are compatible. In the case of copolymer melts, new and somewhat interesting qualitative results are obtained concerning the q-dependence of the first cumulant of $S(q,t)$ and the growth rate $\alpha(q,\chi_F)$ of the mean response (cf. *Figures 3* and *4*), specially in the case of incompatible species. We think it would be interesting to test these qualitative preidctions experimentally. The threshold of instability of the dynamic properties as function of q and the interaction parameter is the same for all of them, and determined by the behaviour of the static structure factor $S(q,\chi_F)\phi_A = (1/2)[\chi_F^c(q) - \chi_F]^{-1}$. Thermodynamics enters in the description of the interacting system only through χ_F parameter.

We would like to emphasize that our specific results based on the Rouse dynamics, and the qualitative curves presented in the Figures are only meant to be a guide to experimental studies. Our main purpose in this work was to explore the implications of RPA in the dynamics of polymer blends systematically, using the formalism of the linear response theory without trying to assess its validity.

ACKNOWLEDGEMENTS

One of us (A.Z.A.) expresses his gratitude to the University of Strasbourg I for appointing him as a Guest Professor for 3 months, and to Professor G. Weill, the Director of Centre de Recherches sur les Macromolecules (C.R.M.) for providing him with the opportunity of collaboration with the scientist at the centre. He also gratefully acknowledges the invitation by the National Science Council, Republic of China, to the National Tsing-Hua University as a Guest Professor for 3 months where the final version of this manuscript was completed. Also one of us (M.B.) thanks the C.R.M. for giving him the opportunity of participating in the research leading to this manuscript.

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