PHYSICAL REVIEW E VOLUME 60, NUMBER 3 SEPTEMBER 1999

Dynamics of irregular copolymers

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(Received 18 November 1998; revised manuscript received 11 May 1999)

Reptation dynamics of AB copolymers with irregular chemical structure are considered theoretically. It is shown that interactions between A and B monomers could result in a significant slowdown of copolymer dynamics in the disordered (macroscopically homogeneous) state. The dynamical copolymer length N^* showing the crossover to the strongly retarded dynamics is calculated. It is shown that contour-length fluctuations (internal reptation modes) give rise to a strong reduction of the slowdown effect and to a strong increase of N^* which becomes unrealistically high in the case of a genuinely random chemical structure. The following scaling dependence of N^* is predicted for irregular block copolymers: $N^* \propto \delta^{-8}\chi^{-8}n_0^{-8}N_e^3$, where δ is the degree of block polydispersity, χ the Flory AB interaction parameter, and n_0 the mean block length. The strongest dynamical effect of AB interactions is predicted for correlated random copolymers near the critical point related to the formation of microdomain superstructures. [S1063-651X(99)03709-5]

PACS number(s): 61.41.+e

I. INTRODUCTION

Polymers formed by two types of monomers (say, A and B) are known as copolymers. Chemical structures like $[AB]_m$ or $[(A)_{n_A}(B)_{n_B}]_m$ are examples of regular copolymers with all A (and B) blocks of exactly the same length n_A (n_B for B). In practice, however, the block molecular weights are always characterized by some degree of randomness, i.e., block polydispersity. The latter can be characterized by the polydispersity degree $\delta = n_w/n_z - 1$, where n_w and n_z are weight average and number average block lengths [1]. Hence there is a somewhat irregular chemical structure, the extreme example being a completely random sequence of A and B. The latter case is relevant for biopolymers: for example, most proteins can be well described as essentially random sequences of hydrophobic and hydrophilic amino-acid residues.

In this paper we will consider systems of long linear copolymer chains with many blocks per chain ($m \gg 1$) and with *quenched* (frozen) chemical disorder. The latter means that the chemical structure of each chain is fixed. In contrast, annealed (or molten) chemical disorder implies that each sequence of A and B monomers can be rearranged, i.e., the chemical structure can be adjusted to a new chain conformation, say.

Block copolymer melts generally tend to form positional microdomain structures as a result of the tendency for A and B monomers to avoid each other, which can be described by the Flory interaction parameter $\chi = \chi_{AB}$ [2]. These structures were predicted for both regular [3–7] and irregular (in particular, random) copolymers [8–20]. Moreover, in the case of irregular multiblock copolymers, microdomain structures with multiple levels of ordering have been recently predicted [21–23]. These extensive predictions are based on the assumption that the copolymer system is allowed to reach an equilibrium state. In practice polymer dynamics can be rather slow for two reasons: (i) entanglements between long polymer chains giving rise to reptation dynamics [24,25]; (ii) fluctuations of the molecular field associated with the interaction parameter χ. The latter source of slowing down was first recognized in Ref. [26]. They showed that the effect of random molecular field on random copolymers can result in a freezing of long chain molecular motions. Below I show that this slowing down is actually much weaker than that predicted in Ref. [26]; the weaker effect is due to the internal dynamical modes which provide additional averaging out of fluctuations of the interaction energy. This main result is derived both in a simple way using scaling arguments (Sec. IV), and with a quantitative perturbation approach (Sec. V). The results are discussed in Sec. VI. The basic static properties of irregular copolymers are considered in the next section.

II. STATIC PROPERTIES OF IRREGULAR COPOLYMERS

A. Chemical sequence

In the case of chemical disorder (irregularity) the structure of each copolymer chain is not known exactly, and hence must be characterized by probability distributions. Let us consider a system of very long copolymer chains. In this case the effect of their ends on their chemical structure can be neglected. Hence it is reasonable to assume that the probability of an A monomer at position n along a polymer chain is independent of n: $p_A = f$, where f is the gross fraction of A monomers. The probability of B is then $p_B = 1 - p_A = 1 - f$. Let us introduce ‘‘spin’’ variables $\{\sigma_n\}$ at each site along the chain: $\sigma = 1 - f$ if the site is occupied by an A monomer, and $\sigma = -f$ in the case of B. Obviously the average value is zero: $\langle \sigma_n \rangle = 0$. The monomer correlation function,

$$g_n = \langle \sigma_{n_1}\sigma_{n_1+n} \rangle, \tag{1}$$

does not depend on n_1 due to assumed ‘‘uniform’’ chemical structure; g_n must decay at large $|n|$ due to chemical disorder. Obviously $g_0 = f(1-f)$ and $g_n = g_{-n}$. Let us consider a long chain of N monomers. The average number of A monomers there is fN. However, the actual number N_A of A

monomers in this fragment might deviate from the average value. Note that $\Delta N_A = N_A - fN = \Sigma_{n=1}^{N}\sigma_n$. Hence the mean-square fluctuation

$$\langle(\Delta N_A)^2\rangle = \sum_{n_1,n_2}\langle\sigma_{n_1}\sigma_{n_2}\rangle \simeq Ng^*, \tag{2}$$

where g^* is the integrated correlation strength,

$$g^* = \sum_{n=-\infty}^{\infty} g_n . \tag{3}$$

Equation 2 can also be applied to any chain fragment (with N replaced by the fragment length).

Let us consider two important particular irregular structures.

(I) In the case of correlations only between the nearest neighboring ''spins'' we arrive at the so-called correlated random copolymer structure [15–17]. Then

$$g_n = f(1-f)\left(1-\frac{2}{n_0}\right)^{|n|} \tag{4}$$

(this equation can be easily derived using the results of Refs. [15–17], see also Ref. [23]). Here n_0 is a parameter related to the average block lengths: $n_A = n_0/2(1-f)$, $n_B = n_0/2f$. The case $n_0 = 2$ corresponds to a completely random copolymer with no correlations in the chemical sequence. Using Eqs. (3), (4) we get $g^* = f(1-f)(n_0-1)$.

(II) Slightly irregular block copolymer: alternating A and B blocks consisting of n_A and n_B monomers on the average, so that $f = n_A/(n_A+n_B)$. The deviations δn_A (and δn_B) of the actual block lengths from their average values are assumed to be independent. The polydispersity degrees, $\delta_A = \langle\delta n_A^2\rangle/n_A^2$ and $\delta_B = \langle\delta n_B^2\rangle/n_B^2$, are assumed to be small. The correlation function g_n can then be calculated in a straightforward way. The main features are that g_n is a nearly periodic function of n if $|n| \ll 1/\delta$, where $\delta \equiv (\delta_A + \delta_B)/2$, and it decays exponentially for $|n| \gg 1/\delta$. Using Eq. (2) we get

$$g^* = 4\delta f^2(1-f)^2 n_0 ,$$

where $n_0 = (n_A+n_B)/2$ is the mean block length.

B. Microphase separation

Block copolymers are known to form microdomain structures if the interaction parameter is high enough, $\chi > \chi^*$. The relevant order parameter is

$$\psi = (1-f)c_A - fc_B ,$$

where $c_A = c_A(\mathbf{r})$ is the microscopic concentration of A monomers, and c_B is the concentration of B. The incompressibility condition is assumed:

$$c_A + c_B = 1, \tag{5}$$

where the effective monomer volume v (same for both A and B monomers) is set to 1 here and below (yet the v dependence is explicitly shown in some important equations below). Also the standard Flory-Huggins model of AB interactions is adopted: the corresponding excess free energy is

$$\mathcal{F}_{\rm int} = \chi\int c_A c_B d^3r \tag{6}$$

in k_BT units.

The static correlation function (structure factor) is defined as

$$S(q) = \int\langle\psi(0)\psi(\mathbf{r})\rangle e^{-i\mathbf{q}\cdot\mathbf{r}}d^3r, \tag{7}$$

where $\langle\cdot\rangle$ stands for averaging over thermal fluctuations. Using the standard random phase approximation (RPA) approach [27], the fluctuation dissipation theorem [28], and the Flory-Huggins interaction model, Eq. (6), we get the structure factor in the disordered state (see Appendix A):

$$S(q) = \frac{S_0(q)}{1-2\chi S_0(q)}, \tag{8}$$

where $S_0(q)$ is defined in Eq. (A3). For the random copolymer structure, case (I), we get, using Eq. (4) for $n_0 \gg 1$,

$$S_0(q) = \frac{f(1-f)n_0}{1+n_0q^2a^2/2}, \tag{9}$$

in agreement with the results of Refs. [16–18]. Here $a = b/\sqrt{6}$, and b is the statistical segment which is assumed to be the same for A and B blocks.

The mean-field spinodal for the disorder-to-order transition (microphase separation) is defined by the condition $\min[1/S(q)] = 0$. For model (I) (random copolymer) the critical wave vector $q^* = 0$, i.e., the spinodal equation is $2\chi^* S_0(0) = 1$. Taking into account that $S_0(0) = g^*$, we get $\chi^* = 0.5/g^* = 0.5/f(1-f)(n_0-1)$ (for $n_0 \gg 1$ this equation was obtained in Refs. [16,17]). The critical point corresponds to $f = 1/2$ if A and B monomers are geometrically similar (as assumed here). The critical interaction parameter is $\chi^* = 2/(n_0-1)$ [16] in case (I), and $\chi^* \simeq 7.55/n_0$ [5] in case (II) if $n_0 \gg 1$.

Mean-field phase diagrams of multiblock-copolymer melts were predicted in Refs. [17,18] for case (I); the regular case was considered in Ref. [6]. The static mean-field approach is valid outside the critical region around the critical point where fluctuations are important. The fluctuation zone shrinks in the limit of long blocks, $n_0 \to \infty$ [4]. For model (I) the fluctuation zone is defined by the condition

$$|\tau| \lesssim \tau_c = \bar{n}^{-1/4}, \tag{10}$$

where $\tau \equiv 1 - \chi/\chi^*$ is the relative distance to the critical point and $\bar{n} = b^6 n_0/v^2$ [19,20].

III. TUBE MODEL: REPTATION AND INTERNAL MODES

In this section I briefly summarize the well-known concepts of the reptation model [25,29] which are relevant for what follows.

Let us consider a concentrated system (a melt) of long polymer chains. The reptation model assumes that the dynamical effect of entanglements between a polymer chain and its neighbors can be accounted for by a virtual tube enveloping the chain. The tube diameter is $d \simeq 0.9 N_e^{1/2} b$, where N_e is the mean number of monomers per entanglement, and 0.9 stands for $\sqrt{4/5}$ [25]; typically $N_e \sim 50$. The length of the tube axis (primitive chain path) is $L = Nb^2/d$ on the average. The three-dimensional (3D) configurations of the primitive path are assumed to be Gaussian (in analogy with the statistics of polymer chains themselves); in particular, the mean-square distance between two points s and s' of a primitive chain is $\langle r_{ss'}^2 \rangle = (|s-s'|/l_0) b^2$, where

$$l_0 \equiv L/N = b^2/d \simeq 1.1 b N_e^{-1/2}. \tag{11}$$

The reptation can be considered as a 1D diffusion of the chain along its primitive path.

The length of the primitive path is not exactly constant, but rather it fluctuates, giving rise to internal dynamical modes of the reptating chain. Let $s(n,t)$ be the curvilinear coordinate of the nth monomer along the primitive path. The master Langevin equation for reptation with contour-length fluctuations is [25]

$$\zeta_0 \frac{\partial s}{\partial t} = \frac{1}{2a^2} \frac{\partial^2 s}{\partial n^2} + \xi, \quad \frac{\partial s}{\partial n} = l_0 \text{ at } n = 0, N, \tag{12}$$

where $\xi = \xi(n,t)$ is the thermal noise, $\langle \xi \rangle = 0$,

$$\langle \xi(n,t) \xi(n',t') \rangle = 2 \zeta_0 \delta_{nn'} \delta(t-t'), \tag{13}$$

and ζ_0 is the effective monomer friction constant (note that $k_B T$ is the energy unit here). The normal mode analysis of Eqs. (12) leads to the following expansion:

$$s(n,t) = \text{const} + n l_0 + \sum_{p=0}^{N} s_p(t) \cos\left(\frac{\pi p n}{N}\right),$$

where s_0 corresponds to the genuine reptation mode; its dynamics are characterized by the curvilinear diffusion constant $D = 1/N\zeta_0$, the characteristic reptation time is

$$\tau_{\text{rept}} \sim L^2/D. \tag{14}$$

Other amplitudes $s_1, s_2, \ldots$ correspond to the internal Rouse modes. The time associated with the main Rouse mode (s_1) is

$$\tau_R = \frac{2}{\pi^2} a^2 \zeta_0 N^2. \tag{15}$$

The typical amplitude of the internal motions is

$$|s_1| \sim l_R = b N^{1/2}. \tag{16}$$

The number of monomers per tube segment l_R is $n_R = l_R / l_0$. We assume below that N is large enough so that n_R is much larger than the block size n_0, i.e.,

$$N N_e \gg n_0^2. \tag{17}$$

The spatial scale λ_R associated with the Rouse motions is of the order of the Gaussian size of the segment n_R:

$$\lambda_R \sim b (N N_e)^{1/4}. \tag{18}$$

IV. EFFECT OF *AB* INTERACTIONS: SCALING ESTIMATES

So far we did not take into account the effect of monomer-monomer interactions on the polymer chain dynamics. This effect was proved to be important even for homopolymer chains [30–35]. The special importance of this effect for the dynamics of random copolymers was also recognized recently [26]. Generally the interactions give rise to high potential barriers that strongly suppress (slow down) the reptation motions. Let me first illustrate this idea using the argument presented in Ref. [26].

A. The frozen environment and no internal modes

The relevant molecular field conjugate to the composition order parameter ψ is

$$\mathcal{U} = \frac{\delta \mathcal{F}_{\text{int}}}{\delta \psi} = \text{const} - 2\chi\psi, \tag{19}$$

where the excess free energy of AB interactions, $\mathcal{F}_{\text{int}}$, is defined in Eq. (6), and the const is omitted below.

Consider a copolymer chain which is reptating through a medium of frozen similar chains. The chain conformation is essentially defined by the curvilinear coordinate $x = s(N/2,t)$ of its middle monomer if the chain contour-length fluctuations are neglected. The chain potential energy is $E = E(x)$,

$$E = \sum_{n=1}^{N} \mathcal{U}_n \sigma_n, \tag{20}$$

where $\mathcal{U}_n \equiv \mathcal{U}(\mathbf{r}_n)$ is the molecular potential near the nth monomer. The mean square of E is

$$\langle E^2 \rangle = \sum_{n_1 n_2} \langle \sigma_{n_1} \sigma_{n_2} \rangle \langle \mathcal{U}_{n_1} \mathcal{U}_{n_2} \rangle = 4\chi^2 N \sum_n g_n S_n,$$

where

$$S_n = \langle \psi(\mathbf{r}_{n_1}) \psi(\mathbf{r}_{n_1+n}) \rangle.$$

Let us assume for simplicity the correlated random copolymer structure with $f = 1/2$ and $\chi \lesssim \chi^*/2$. Taking into account that the correlation length along the chemical sequence is roughly the block length n_0, we get $\Sigma_n g_n S_n \sim n_0 S^*$, where $S^* = \langle \Delta \overline{\psi}^2 \rangle$ is the mean square of the composition fluctuation averaged over a block size $r_0 \sim n_0^{1/2} b$: $\overline{\psi} = (1/V_0) \int_{V_0} \psi(\mathbf{r}) d^3 r$, $V_0 \sim r_0^3$. Hence

$$\langle E^2 \rangle \sim \chi^2 N n_0 \langle \Delta \overline{\psi}^2 \rangle. \tag{21}$$

Since the block sizes are nearly statistically independent, the composition must be inversely proportional to the square root of the number $\nu \sim V_0/n_0$ of blocks in the region V_0: $\Delta\overline{\psi} \sim 1/\sqrt{\nu}$, i.e.,

$$\langle \Delta \overline{\psi}^2 \rangle \sim n_0/V_0 \sim b^{-3} n_0^{-1/2}. \tag{22}$$

Thus we get

$$\langle E^2 \rangle \sim \frac{v}{b^3} \chi^2 N n_0^{1/2}. \tag{23}$$

Hence the typical variation of the potential energy is proportional to $\sqrt{N}$, so that the chain has to overcome high potential barriers (the height $\Delta E \sim \sqrt{\langle E^2 \rangle}$) in order to reptate (i.e., to move along the primitive path). [Note that the typical width of a barrier is of the order of the block length: it is easy to show that $E(x)$ and $E(x')$ are nearly uncorrelated if $|x - x'|$ is larger than the block length.] Hence the basic conclusion of Ref. [26] that the reptation motion of long random copolymers drastically slows down: The reptation time must increase exponentially with N if ΔE is large ($N > N^*$),

$$\tau_{\text{rept}}/\tau_{\text{rept}}^{(0)} \sim \exp[\Delta E] \sim \exp[\sqrt{N/N^*}], \tag{24}$$

where $N^* \sim (b^3/v)\chi^{-2} n_0^{-1/2}$ is the crossover copolymer length (corresponding to the onset of a significant slow-down effect) and $\tau_{\text{rept}}^{(0)} \sim L^2 N \zeta_0$ is the priming reptation (disentanglement) time.

B. The effect of internal modes

Let us now allow for the internal Rouse-like dynamics which imply fluctuations of monomer positions along the primitive path on the top of the ‘‘rigid’’ reptation motion along the primitive path. The typical amplitude l_R of these fluctuations (which are present even when the middle monomer position is fixed) is defined by Eq. (16). The effective potential energy of the chain, Eq. (20), must be averaged over these fluctuations (for a given position x of the middle monomer), i.e., $\mathcal{U}_n$ must be replaced by its coarse-grained value $\overline{\mathcal{U}_n}$, the coarsening length along the primitive path being $l_R \sim bN^{1/2}$; $\overline{E} = \Sigma \overline{\mathcal{U}_n} n \sigma_n$. Taking into account that the correlation length for the molecular field $\mathcal{U}$ is roughly equal to the block size r_0 we find $\langle \overline{\mathcal{U}_n^2} \rangle \sim \chi^2 S^*/m_R$, where $m_R \sim \sqrt{NN_e}/n_0$ is the number of independent blobs of size r_0 along the coarsening segment l_R [$m_R \gg 1$ due to condition (17)]. Hence

$$\langle \overline{E^2} \rangle \sim \langle E^2 \rangle \frac{1}{m_R} \sim \frac{v}{b^3} n_0^{3/2} \chi^2 \left(\frac{N}{N_e} \right)^{1/2}. \tag{25}$$

Here $\langle E^2 \rangle$ is defined in Eq. (23). The effective potential barrier $\Delta E \sim [\langle \overline{E^2} \rangle]^{1/2}$ is thus proportional to $N^{1/4}$, i.e., it shows much weaker N dependence than that ($N^{1/2}$) predicted in Ref. [26]. Equation (25) is valid if $N_e < n_0 < \sqrt{NN_e}$.

C. The effect of the molecular field relaxation

Let us now consider a realistic case when a relaxation of the molecular field is allowed in addition to the Rouse dynamics. On the time scales less than τ_R the field relaxation is mainly due to the internal dynamics of surrounding chains. The typical spatial displacement of a monomer due to the Rouse-like curvilinear motions is $\lambda_R \sim b(l_R/l_0)^{1/2} \sim b(NN_e)^{1/4}$. Any block can meet any other block within the fluctuation region $V_R \sim \lambda_R^3$. Hence it is the coarse-grained molecular field (with coarsening volume V_R) that is defining the effective potential barrier. The square of the barrier is thus still defined by Eqs. (21), (22) with V_0 replaced by V_R:

$$(\Delta E)^2 \sim \chi^2 N n_0^2 / V_R \sim \frac{v}{b^3} \chi^2 n_0^2 N^{1/4} / N_e^{3/4}. \tag{26}$$

Note that the barrier is proportional to $N^{1/8}$ (instead of $N^{1/2}$ predicted in Ref. [26]) due to the contour-length fluctuations of all copolymer chains.

It is also important to note that the scaling argument presented in this section is rigorously applicable only in the region where the slow-down effect is small (i.e., $\Delta E \ll 1$). Otherwise interactions can affect (decrease) the amplitude of tube-length fluctuations thus reducing their effect. It is reasonable to assume a scaling dependence of ΔE on N in the genuine asymptotic limit $N \to \infty$: $\Delta E \propto N^z$. Equation (26) implies that $z = 1/8$ while the result of Ref. [26] is $z = 1/2$. It seems reasonable to consider these two values as the lower and the upper boundaries, i.e., $1/8 \leqslant z \leqslant 1/2$ [see also Sec. VI, Eq. (47)].

However, the main qualitative message encrypted in Eq. (26) stays unchanged: tube-length fluctuations considerably reduce the slow-down effect of monomer interactions. In particular, the critical chain length N^* corresponding to the onset of a considerable slow-down effect is very large in many cases (see Sec. VI for a more detailed discussion).

The main results obtained in this section are corroborated by a more accurate quantitative approach considered below.

V. PERTURBATION THEORY

A. Biased reptation with contour-length fluctuations

The force acting on a monomer due to the molecular field, Eq. (19), is equal to $-\sigma \nabla \mathcal{U}$. The master dynamic equation including the effect of this force reads [compare with Eq. (12)]

$$\zeta_0 \frac{\partial s}{\partial t} = \frac{1}{2a^2} \frac{\partial^2 s}{\partial n^2} + f + \xi, \quad \frac{\partial s}{\partial n} = l_0 \ \text{ at } n = 0, N, \tag{27}$$

where $f = f(n,t) = -\sigma_n \partial \mathcal{U} / \partial s$ is the projection of the molecular force onto the primitive path. The mean curvilinear displacement $\Delta s = (1/N) \Sigma_n [s(n,t) - s(n,0)]$ during long enough time t must obey the diffusion law: $\langle \Delta s \rangle = 0$, $\langle \Delta s^2 \rangle = 2Dt$. The rate of the long-scale reptation dynamics is defined by D; in particular, the reptation time is inverse proportional to D [see Eq. (14)].

Let us consider the effect of molecular field fluctuations on the curvilinear diffusion constant D. Using Eqs. (27), (13) we get

$$D=\frac{1}{N\zeta_0}+\left(\frac{1}{N\zeta_0}\right)^2\int_{-\infty}^{\infty}\left\{\langle F(0)\Xi(t)\rangle+\frac{1}{2}\langle F(0)F(t)\rangle\right\}dt, \tag{28}$$

where $F(t)=\Sigma_n f(n,t)$, $\Xi(t)=\Sigma_n\xi(n,t)$ are the total molecular and random forces, correspondingly. Next we take into account the time isotropy implying that

$$\langle\dot{s}(t_1)F(t_2)\rangle=-\langle\dot{s}(-t_1)F(-t_2)\rangle,$$

where $\dot{s}\equiv d(\Delta s)/dt$ is the mean curvilinear velocity: $\dot{s}$ changes its sign when the time is reversed, $t\rightarrow -t$, while F is invariant. (The argument was applied to a similar problem in Ref. [35].) Using Eqs. (27) we get $\dot{s}=F+\xi$. Hence

$$\langle\Xi(0)F(t)+F(0)F(t)\rangle=-\langle\Xi(0)F(-t)+F(0)F(-t)\rangle.$$

Finally, noting that $\langle\Xi(0)F(-t)\rangle\equiv 0$ for $t>0$ since Ξ is a random noise which does not depend on the system history, we obtain

$$\langle\Xi(0)F(t)\rangle=-2H(t)\langle F(0)F(t)\rangle, \tag{29}$$

where $H(t)$ is the Heaviside function ($=0$ for $t<0$, $=1$ for $t>0$). Using Eqs. (28), (29) we find

$$D=\frac{1}{N\zeta_0}[1-\Delta],\quad \Delta=\frac{1}{N\zeta_0}\int_0^{\infty}\langle F(0)F(t)\rangle dt. \tag{30}$$

[Note that the reptation time is inversely proportional to D: $\tau_{\text{rept}}\sim L^2/D$, i.e., $\tau_{\text{rept}}\simeq\tau_{\text{rept}}^{(0)}(1+\Delta)$.] Here Δ is the correction to the curvilinear diffusion constant (which determines the rate of reptation) due to AB monomer interactions. Note that the correction is definitely negative (compare with Ref. [35]), i.e., interactions always slow down the dynamics.

B. The first-order correction

Equations (30) reduce the problem to a calculation of the force correlation function $\langle F(0)F(t)\rangle$, where F is the total projection of the molecular force onto the primitive path of a copolymer chain (which will be referred to as the labeled chain). The force can be written as

$$F=\sum_n f(n,t)=-\sum_n \sigma_n\frac{\partial\mathcal{U}}{\partial s}$$
$$=-\int\Psi(s)\frac{\partial\mathcal{U}}{\partial s}ds=\int\mathcal{U}\frac{\partial\Psi}{\partial s}ds, \tag{31}$$

where $\mathcal{U}=\mathcal{U}(s)\equiv\mathcal{U}(\mathbf{r}(s))=-2\chi\psi(\mathbf{r}(s))$ is the molecular potential at the point s of the primitive path, and $\mathbf{r}(s)$ is the spatial position of this point; $\Psi(s)$ is the one-dimensional "spin" density due to the labeled monomers:

$$\Psi(s)=\sum_n \sigma_n\delta(s-s_n), \tag{32}$$

where $s_n=s(n,t)$ is the curvilinear position of the nth monomer, $n=1,\ldots,N$.

Let us assume that Δ is small, i.e., that the effect of interactions for the single-chain reptation dynamics is weak. Then we can neglect the effect of $\mathcal{U}$ on the labeled chain conformation, i.e., decouple $\mathcal{U}$ and Ψ in the first approximation:

$$\langle F(0)F(t)\rangle\simeq\int ds_1ds_2\langle\mathcal{U}(s_1,0)\mathcal{U}(s_2,t)\rangle$$
$$\times\frac{\partial}{\partial s_1}\frac{\partial}{\partial s_2}\langle\Psi(s_1,0)\Psi(s_2,t)\rangle. \tag{33}$$

The positions $\mathbf{r}(s_1)$ and $\mathbf{r}(s_2)$ are independent of the field, hence using Eqs. (19) we get

$$\mathcal{K}(s_2-s_1,t)\equiv\langle\mathcal{U}(s_1,0)\mathcal{U}(s_2,t)\rangle$$
$$=4\chi^2\int\tilde{S}(\mathbf{r},t)G\left(\mathbf{r},\frac{|s_1-s_2|}{l_0}\right)d^3r,$$

where $\tilde{S}(\mathbf{r},t)=\langle\psi(0,0)\psi(\mathbf{r},t)\rangle$ is the dynamic composition correlation function, and the function $G(r,n)$ defined in Eq. (A2) reflects the Gaussian distribution of the vector $\mathbf{r}=\mathbf{r}(s_2)-\mathbf{r}(s_1)$. The field correlation function can also be represented as

$$\mathcal{K}(s,t)=4\chi^2\int S(q,t)\exp\left(-q^2a^2\frac{|s|}{l_0}\right)\frac{d^3q}{(2\pi)^3}, \tag{34}$$

where $S(q,t)=\int\tilde{S}(r,t)e^{-i\mathbf{q}\cdot\mathbf{r}}d^3r$ is the dynamic structure factor calculated in Appendix B. [Note that $S(q,0)$ is equal to the static structure factor $S(q)$ defined in Eq. (7).]

The second correlation function $\mathcal{G}(s_2-s_1,t)=\langle\Psi(s_1,0)\Psi(s_2,t)\rangle$ involved in the righthand side of Eq. (33) can be calculated using the definition, Eq. (32):

$$\mathcal{G}(s,t)=\frac{1}{L}\sum_{n_1n_2}g_{n_2-n_1}\tilde{\rho}(s,n_2,t;0,n_1,0)\simeq\frac{g^*}{L}\int\rho(s,n,t)dn,$$

where the functions $\tilde{\rho}$ and ρ are defined in Appendix B, see Eq. (B3). Using the approximation similar to that introduced in Eq. (B7) we write

$$\mathcal{G}(s,t)\simeq\frac{g^*}{l_0}\frac{1}{\sqrt{2\pi\bar{\beta}}}\exp\left[-\frac{s^2}{2\bar{\beta}}\right], \tag{35}$$

where $\bar{\beta}=\bar{\beta}(t)$ is defined in Eq. (B5). Finally, using Eqs. (30), (33) we get

$$\Delta\simeq-\frac{l_0}{\zeta_0}\int_0^{\infty}dt\int_{-\infty}^{\infty}ds\,\mathcal{K}(s,t)\frac{\partial^2}{\partial s^2}\mathcal{G}(s,t)$$
$$=\frac{4\chi^2g^*}{\zeta_0}\int_0^{\infty}dt\int\frac{d^3q}{(2\pi)^3}S(q,t)I(q,t), \tag{36}$$

where the functions $\mathcal{K}$ and $\mathcal{G}$ are defined in Eqs. (34), (35) and

$$I(q,t) \simeq -\int_{-\infty}^{\infty} e^{-q^2a^2|s|/l_0} \frac{\partial^2}{\partial s^2} \frac{1}{\sqrt{2\pi\overline{\beta}}} \exp\left[-\frac{s^2}{2\overline{\beta}}\right] ds$$

$$= \frac{l_0}{\overline{\beta}^{3/2} q^2 a^2} h\left(\frac{\overline{\beta} q^4 a^4}{2 l_0^2}\right), \tag{37}$$

with

$$h(x) = \sqrt{\frac{8}{\pi}} x [1 - \sqrt{\pi x} e^x \operatorname{erfc} \sqrt{x}].$$

C. The results

Let us first assume that χ is small (i.e., weak AB interactions). The dynamic structure factor $S(q,t) \simeq S_0(q,t)$ is defined in Eq. (B7) in this case. Using Eqs. (36), (37) we then obtain the degree of slow down

$$\Delta \simeq 22.8 \frac{N^{1/4}}{N_e^{3/4}} \frac{v}{b^3} (\chi g^*)^2, \tag{38}$$

where 22.8 stands for

$$\frac{9\sqrt{3}(15)^{3/4}\Gamma(1/4)}{(16)2^{1/4}\pi} \left\{\int_0^{\pi/4} \frac{dx}{(\cos x)^{3/2}}\right\} \left\{\int_0^{\infty} \frac{dx}{[B(x)]^{7/4}}\right\} \tag{39}$$

and the function $B(x)$ is defined in Eq. (B6). The relevant time and spatial scales (that contribute to Δ) are $t \sim \tau_R$ and $1/q \sim \lambda_R \sim b(NN_e)^{1/4}$, see Eq. (18). Equation (39) is valid if $\chi S_0(q_R) \ll 1$, which is equivalent to $\chi \ll \chi^*$ for the correlated random model. For a slightly irregular copolymer the condition reduces to $\chi n_0(\delta + n_0/\sqrt{NN_e}) \ll 1$ which is always valid in the disordered phase since $\delta \ll 1$ and $n_0 \ll \sqrt{NN_e}$ [see Eq. (17)].

Let us turn to the case of the correlated random copolymer near its spinodal $\chi = \chi^*(1-\tau)$, where $\chi^* = 0.5/g^* = 0.5/f(1-f)(n_0-1)$ and $\tau \ll 1$. Using Eqs. (B9), (B10), and (B7) we get the generalized susceptibility in this case:

$$\varkappa(p,q) \simeq \frac{g^*}{\tau} \frac{q^2}{q^2 + q_c^2 K(p\tau_R)}, \tag{40}$$

where $q_c^2 = (\pi/2)^{1/2}(l_0/N^{1/2}a^3)(1/\tau)$, and

$$K(x) = x\int_0^{\infty} B(z)^{-1/2} e^{-xz} dz.$$

The dynamic structure factor obtained by substitution of Eq. (40) in Eq. (B8) is then used to calculate Δ [Eq. (36)]:

$$\Delta \simeq C \frac{v}{b^3} \frac{1}{\tau^{3/2}} \frac{N^{1/4}}{N_e^{3/4}} (\chi g^*)^2, \tag{41}$$

where

$$C = \frac{3\sqrt{3}(15)^{3/4}}{2(\pi)^{1/4}} \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} x^{-1} \widetilde{K}(-x) \sqrt{K(x)} dx,$$

$$\widetilde{K}(x) = \int_0^{\infty} B(z)^{-3/2} e^{-zx} dz.$$

Taking into account that $\chi g^* = 0.5(1-\tau)$ and combining the two asymptotic results, Eqs. (38), (41), we get an interpolation valid in the disordered regime, $0 < \tau < 1$:

$$\Delta \simeq 5.7 \frac{v}{b^3} \frac{(1-\tau)^2}{\tau^{3/2}} \frac{N^{1/4}}{N_e^{3/4}}. \tag{42}$$

VI. DISCUSSION

(1) Let us consider first the case of correlated random copolymer with $f = 1/2$ and $\chi < \chi^*/2$. It is precisely this model that was considered in Sec. IV. Comparing Eq. (26) and Eq. (38) we see that $\Delta \sim (\Delta E)^2$ as it should be: the slowdown effect of *low* potential barriers, of height ΔE, must be proportional to $(\Delta E)^2$.

In order to get Δ for the case of quenched molecular field, the dynamic structure factor $S(q,t)$ in Eq. (36) must be replaced by the static structure factor $S(q)$. The result (valid for $N_e < n_0 < \sqrt{NN_e}$) reads $\Delta \sim (v/b^3)\chi^2 n_0^{3/2} N^{1/2} N_e^{-1/2}$ in agreement with Eq. (25) defining $(\Delta E)^2 \sim \langle \overline{E^2} \rangle$.

The case of no contour-length fluctuations (and quenched molecular field) can be treated in a similar way: the correction Δ is still defined by Eqs. (36), (37). The only difference concerns the function $\overline{\beta(t)}$: omitting the contribution of the internal modes with $p = 1,2,\ldots$, i.e., omitting the second term in the righthand side of Eq. (B6), we get $\overline{\beta} = 2t/N\zeta_0$. Thus we get $\Delta \sim (v/b^3) n_0^{1/2} N \chi^2$ in agreement with Eq. (23), i.e., $\Delta \sim (\Delta E)^2$ as expected.

Therefore, we demonstrated that the scaling theory of Sec. IV agrees well with the quantitative results obtained in the preceding section. In particular, both approaches produce the same estimate of the crossover copolymer length N^* for all three dynamical models considered in Sec. IV.

(2) We show that the reptation dynamics slows down due to AB interactions. The relative correction Δ to the curvilinear diffusion constant is defined in Eq. (42) for correlated random copolymers [model (I)], and in Eq. (38) for the slightly irregular case [model (II)]. Both equations can be written as

$$\Delta \simeq \left(\frac{N}{N^*}\right)^{1/4}, \tag{43}$$

where N^* is the crossover copolymer chain length,

$$N^* \simeq (5.7 v/b^3)^{-4} \frac{\tau^6}{(1-\tau)^8} N_e^3 \tag{44}$$

for model (I), and

$$N^* \simeq (22.8 v/b^3)^{-4} [4 f^2 (1-f)^2 \delta n_0 \chi]^{-8} N_e^3 \tag{45}$$

for model (II). Note a significant decrease of N^* for random copolymers in the critical region, i.e., as $\tau = 1 - \chi/\chi^*$ tends to 0. This diverging behavior is a mean-field result, hence a cutoff for this decrease at the boundary of the (static) fluctuation zone, $\tau=\tau_c$, see Eq. (10), i.e., the minimum of N^* attained in the critical regime is (for $f=1/2$)

$$N^*_{\mathrm{min}}\sim\frac{b^3}{v}n_0^{-3/2}N_e^3. \tag{46}$$

(3) Equation (43) is valid if Δ is small, i.e., $N \ll N^*$. In the opposite limit, $N>N^*$, we expect an exponential increase of the diffusion constant as discussed in Sec. IV. Equations (24), (26) imply the following behavior of the reptation time for $N>N^*$: $\tau_{\mathrm{rept}}/\tau_{\mathrm{rept}}^{(0)}\propto\exp[(N/N^*)^z]$ with $z=1/8$. This result, however, is not rigorous: it is based on the implicit assumption that the effective amplitude of the tube-length fluctuations is not affected by AB interactions. This assumption might not be true in the regime $N>N^*$ where these interactions strongly suppress the dynamics. In particular, the effective amplitude of internal modes might be reduced, hence possibly a shift towards the ''rigid'' reptation model considered in Sec. IV A, i.e., the dynamical exponent z is bounded in the range $1/8\leqslant z\leqslant 1/2$. No (scaling) argument is available to get a more accurate estimate of z. The following molecular weight dependence of the reptation time is thus predicted:

$$\ln(\tau_{\mathrm{rept}}/\tau_{\mathrm{rept}}^{(0)})\simeq\begin{cases}\left(\dfrac{N}{N^*}\right)^{1/4}, & N<N^*\\[2ex] \mathrm{const}\times\left(\dfrac{N}{N^*}\right)^{z}, & N>N^*,\quad 1/8\leqslant z\leqslant 1/2\end{cases}, \tag{47}$$

where N^* is defined in Eqs. (44), (45).

(4) The case of a genuine random copolymer ($n_0=2$) in the disordered phase far from the DOT ($\chi\ll\chi^*$) was considered in Ref. [26]. In this case the dynamical crossover defined in Eq. (44) can be represented as (for $f=1/2$)

$$N^*\simeq 0.24\left(\frac{b^3}{v}\right)^4\chi^{-8}N_e^3. \tag{48}$$

A much lower crossover N^* was predicted in Ref. [26]: $N^*\sim\chi^{-2}N_e^{1/2}$. Clearly the latter prediction is an artifact of the rigid-reptation model (see Sec. IV A), which strongly overestimates the slow-down effect of AB interactions.

Let us estimate N^* assuming monomer parameters which are typical for conventional flexible copolymers: $\chi\lesssim 0.1$, $b^3/v\sim 2$, and $N_e\sim 50$. Then [using Eq. (48)] $N^*\gtrsim 10^{14}$, corresponding to astronomically high copolymer molecular weights of $M^*\gtrsim 10^{16}$. Obviously the ''freezing'' transition (at M^*) is never accessible for conventional random copolymers; the dynamical effect of AB interactions is always weak in this case. Also any fraction of ''impurities'' of a different chemical nature in the homopolymer sequence could not possibly strongly affect homopolymer dynamics (unless the ''foreign'' monomers are strongly interacting as in ionomers).

However, N^* decreases dramatically as the interaction parameter χ is increased; this conclusion is corroborated by recent computer simulations [36] which reveal a quasifrozen behavior of long random copolymer chains for $\chi_{\mathrm{eff}}\sim 2$ when reptation dynamics are imposed (note that N_e is forced to be of the order 1 in simulations).

(5) The situation with irregular *block* copolymers is somewhat different: the dynamical effect of interactions is amplified here. For symmetric correlated random copolymers [model (I), $f=1/2$] at $\chi=0.5\chi^*$ (i.e., halfway to the microphase separation transition) we get, using Eq. (44), $N^*\simeq 3.8\times 10^{-3}(b^3/v)^4N_e^3\sim 8000$. Similarly for slightly irregular copolymers [model (II)] at $\chi=\chi^*$ we get (for $f=1/2$ and assuming the block polydispersity degree of $\delta=0.25$)

$$N^*\simeq 2.3\times 10^{-8}\left(\delta\frac{\chi}{\chi^*}\right)^{-8}\left(\frac{b^3}{v}\right)^4N_e^3, \tag{49}$$

i.e., $N^*\sim 3000$. Therefore the ''freezing'' transition must be quite accessible experimentally in the case of irregular block copolymers. The strongest slow-down effect is predicted near the microphase separation critical point and for high block polydispersity. In particular, for a random correlated copolymer with ''block size'' $n_0\sim N_e$ we get using Eq. (46), $N^*\sim 1000$ (for $N_e\sim 50$).

(6) Another feature of irregular block copolymers that was predicted recently [21–23] is their ability to form secondary microdomain structures. These structures are stable if the number of blocks per chain is high enough, $N>N_c=n_0\delta^{-3}$. The structures are easily accessible dynamically if N is lower than N^*. Hence the condition $N_c<N^*$. Using Eq. (49) with $b^3/v\sim 2$ and $N_e\sim 50$ we rewrite this condition as $\delta<0.5n_0^{-1/5}$ which is not strongly restrictive (for a typical $n_0\sim 200$ it reduces to $\delta<0.2$). Thus the secondary structures are indeed accessible if the degree of block polydispersity is not too high. On the other hand, the secondary structures predicted in correlated random copolymers (with $\delta=1$) necessarily fall into the regime $N\gg N^*$ of retarded dynamics. It is not clear whether they are dynamically accessible or not. The answer depends primarily on the value of the dynamical exponent z [see Eq. (47)] which is not known.

(7) It is interesting to compare the degree of slow down, Δ, predicted here for copolymers with the similar correction Δ_h for homopolymers [32,33,35],

$$\Delta_h\simeq 1.14\frac{v}{b^3}\frac{N^{1/4}}{N_e^{3/4}}. \tag{50}$$

Note that Δ_h is due to fluctuations of the molecular field conjugate to the total monomer density, while Δ reflects the effect of AB interactions, i.e., that of the molecular field conjugate to composition. The density fluctuations are also present in the copolymer system, hence the total degree of slow down for copolymers is $\Delta^*=\Delta+\Delta_h$. Let us consider case (II) of slightly irregular copolymers ($f=1/2$). Using Eqs. (38), (50) we get $\Delta/\Delta_h\simeq 70(\delta\chi/\chi^*)^2$. Hence the copolymer effect is important if $\delta\chi/\chi^*\gtrsim 0.1$; it is totally dominating if $\delta\chi/\chi^*\sim 1$, i.e., for correlated random copolymers near the critical point.

VII. CONCLUSIONS

(1) The effect of interactions between monomers of different kinds (A and B) on the reptation dynamics in copoly-

mer melts is considered both with a scaling argument and with a quantitative approach. A significant slowing down of the dynamics at high copolymer molecular weights, $N>N^*$, is predicted in a qualitative agreement with the results of Ref. [26].

(2) It is shown that contour-length fluctuations (internal reptation modes) which were neglected in Ref. [26] result in a considerable reduction of the slow-down effect.

(3) In particular, the dynamical effect of AB interactions is usually weak for random copolymers with uncorrelated sequence (unless the chain is ''astronomically'' long).

(4) The dynamical crossover chain length N^* is predicted to be strongly dependent on the degree of block polydispersity δ, the interaction parameter χ, and the number of monomers per entanglement N_e: $N^* \propto \delta^{-8}\chi^{-8}N_e^3$ in contrast to a much weaker dependence predicted in Ref. [26].

(5) The strongest slow-down effect is predicted for irregular *block* copolymer with high block polydispersity near the critical point for microphase separation ($\chi \simeq \chi^*$). In this case the regime of strongly retarded dynamics (where the reptation time increases exponentially with N: $\ln \tau_{\mathrm{rept}} \propto N^z$) is likely to be accessible both experimentally and by computer simulations.

(6) The following range for the dynamical exponent z corresponding to the genuine asymptotic limit $N\to\infty$ is proposed: $1/8 \leqslant z \leqslant 1/2$, where the upper boundary is the Bouchaud and Cates result [26].

ACKNOWLEDGMENT

The work was supported by EPSRC Grant No. GR/L37694.

APPENDIX A: STATIC STRUCTURE FACTOR

First note that

$$\psi(\mathbf{r}) = \sum_a \sigma_a \delta(\mathbf{r}-\mathbf{r}_a), \tag{A1}$$

where a indexes all monomers in the system, and σ_a is the ''spin'' variable related to the monomer type defined just above Eq. (1). Hence the correlation function of the ideal system of copolymer chains (when all interactions of monomers are switched off) is

$$\langle \psi(0)\psi(\mathbf{r})\rangle = \frac{1}{V}\sum_{ab} \langle \sigma_a\sigma_b\rangle G_{ab}(r),$$

where $G_{ab}(\mathbf{r})$ is the probability density that monomer b is located at $\mathbf{r}$ provided that monomer a is at the origin. Taking into account that σ variables for different chains are not correlated and using Eq. (1) we get

$$\langle \psi(0)\psi(\mathbf{r})\rangle = \frac{1}{N}\sum_{n_1n_2} g_{n_2-n_1}G_{n_1n_2}(r) = \sum_{n=-\infty}^{\infty} g_n G(r,|n|),$$

where N is the total number of monomers per chain which is assumed to be large ($N\to\infty$), $n=n_2-n_1$, and

$$G(r,n) = (4\pi n a^2)^{-3/2}\exp\left(-\frac{r^2}{4na^2}\right) \tag{A2}$$

is the end-to-end vector distribution for a chain fragment consisting of n monomers, $a=b/\sqrt{6}$, and b is the statistical segment of copolymer chains. Hence using Eq. (7) we get the ideal structure factor

$$S_0(q) = \sum_{n=-\infty}^{\infty} g_n e^{-q^2a^2|n|}. \tag{A3}$$

Next we note that fluctuations of total monomer density $c = c_A + c_B$ are uncorrelated with the order parameter ψ. In fact, consider a fluctuation δc induced by, say, an external field conjugate to c. The field does not distinguish between A and B monomers. Hence all the monomers must be distributed in the same way (in the limit $N\to\infty$), and so $\delta c_A = f\delta c$, $\delta c_B = (1-f)\delta c$, i.e., $\psi \equiv 0$.

Therefore the incompressibility [see condition (5)] must not affect the statistics of ψ fluctuations, i.e., Eq. (A3) also holds for an incompressible copolymer system if the Flory interaction parameter is set to null, $\chi=0$. Accounting for the effect of χ in a standard self-consistent way [27] we get

$$1/S(q) = 1/S_0(q) - 2\chi.$$

This last equation is equivalent to Eq. (8).

APPENDIX B: DYNAMIC STRUCTURE FACTOR

The definition of the dynamic structure factor is analogous to Eq. (7):

$$S(q,t) = \int \langle \psi(0,0)\psi(\mathbf{r},t)\rangle e^{-i\mathbf{q}\cdot\mathbf{r}} d^3r.$$

Let us first calculate $S_0(q,t)$ corresponding to $\chi=0$. Using the definition and Eq. (A1) we get

$$S(q,t) = \frac{1}{N}\sum_{n_1n_2} \langle \sigma_{n_1}\sigma_{n_2}\rangle \langle \exp[i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)]\rangle, \tag{B1}$$

where n_1, n_2 index all monomers of a copolymer chain, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of the monomers n_1 and n_2. The decoupling here is due to the fact that the chain dynamics is independent of the chemical sequence since $\chi=0$. The first correlation factor in Eq. (B1) is just $g_{n_2-n_1}$; the second factor is

$$\langle \exp[i\mathbf{q}(\mathbf{r}_1-\mathbf{r}_2)]\rangle = \int \tilde{\rho}(s_2,n_2,t;s_1,n_1,0) \times \exp(-q^2a^2|s_2-s_1|/l_0)\,ds_2, \tag{B2}$$

where $\tilde{\rho}(s_2,n_2,t;s_1,n_1,0)$ is the probability that the monomer n_2 is located at s_2 at the moment t provided that the monomer n_1 was at s_1 at $t=0$. The typical values of $n_2 - n_1$ are determined by the spin correlation function, i.e., the block length: $|n_2-n_1| \lesssim n_0$. On the other hand, the typical curvilinear displacement is of the order of l_R [see

Eq. (16)]: $s=s_2-s_1\sim l_R$, i.e., $|s|\gg|n_2-n_1|l_0$. Hence $\tilde{\rho}(s_2,n_2,t;s_1,n_1,0)$ in Eq. (B2) can be substituted by $\tilde{\rho}(s_2,n_1,t;s_1,n_1,0)\equiv\rho(s_2-s_1,n_1,t)$. The latter distribution function can be easily calculated using Eqs. (12), (13), i.e., the Rouse curvilinear dynamics of the monomers. The result is (see, e.g., Ref. [29])

$$\rho(s,n,t)=\frac{1}{\sqrt{2\pi\beta}}\exp\left[-\frac{s^2}{2\beta}\right], \tag{B3}$$

where

$$\beta=\beta(n,t)=\frac{4}{\pi^2}Na^2\left\{\frac{t}{\tau_R}+2\sum_{p=1}^{\infty}p^{-2}[1-e^{-tp^2/\tau_R}]\times\cos^2\left(\frac{\pi p n}{N}\right)\right\}$$

and the Rouse time τ_R is defined in Eq. (15). Using Eqs. (B1)–(B3) we get

$$S_0(q,t)=\frac{g^*}{N}\int\varphi\left(\frac{\beta(n,t)q^4a^4}{2l_0^2}\right)dn,$$

where

$$\varphi(x)=e^x\operatorname{erfc}\sqrt{x}. \tag{B4}$$

The mean-square displacement β shows a weak dependence on n; hence it is reasonable to approximate $\beta(n,t)$ by its average value

$$\overline{\beta}(t)=\frac{1}{N}\int\beta(n,t)dn=\frac{4}{\pi^2}Na^2B(t/\tau_R), \tag{B5}$$

where

$$B(x)=x+\sum_{p=1}^{\infty}p^{-2}[1-e^{-p^2x}], \tag{B6}$$

leading to

$$S_0(q,t)\simeq g^*\varphi\left(\frac{\overline{\beta}(t)q^4a^4}{2l_0^2}\right). \tag{B7}$$

An analysis shows that the typical error implied by this approximation is less than 7%.

The effect of AB interactions can be taken into account in a standard way using the general dynamic RPA approach [37,38]. The result is

$$S(q,t)=\frac{1}{2\pi i}\int_{-i\infty}^{i\infty}\frac{\varkappa(0,q)-\varkappa(p,q)}{p}e^{pt}dp, \tag{B8}$$

where

$$\varkappa(p,q)=\{1/\varkappa_0(p,q)-2\chi\}^{-1}, \tag{B9}$$

and

$$\varkappa_0(p,q)=S_0(q)-p\int S_0(q,t)e^{-pt}dt. \tag{B10}$$

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