The Dynamic Structure Factor of a Star Polymer in a Concentrated Solution

N. Clarke* and T. C. B. Mcleish

Department of Physics, University of Sheffield, Hicks Building, Sheffield S3 7RH, England

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1. Introduction. To describe the dynamics of very long linear polymers in concentrated solutions, de Gennes[1,2] introduced the reptation concept, where it is assumed that the dominant motion of a given polymer, confined to a tube by neighboring polymers, is along the axis of the tube. This model and its refinements have led to many successful predictions about the mechanical properties of polymeric systems.[2,3]

For a star polymer, which consists of many linear "arms", each attached to a common point, reptation is strongly suppressed due to the presence of the star center. However, we may still use the idea that an effective tube of diameter a, and contour length L, surrounds each star arm. Relaxation now occurs by utilizing fluctuations in contour length; an arm retracts down the tube a certain distance and then pushes back out into the surrounding matrix to form a new tube. The center of the star remains essentially fixed in space until one arm has completely relaxed, when it may then diffuse a distance somewhat less than the step length. A complete description of star dynamics should also allow for motion of the branch point;[4] however, for stars with more than three arms it is believed that such a mechanism is negligible[5] during the time taken for an arm to fully relax.

The adoption of such unlikely configurations associated with arm retraction leads to an exponential dependence on the length of an arm of the longest relaxation time.[6-8] The intermediate relaxation times of sections of primitive path along the entangled arm also increase exponentially. For a length of primitive path s ($0 < s < L$) measured from the free end, the relaxation time $t(s)$ is, if the effects of constraint release [this mechanism enables a polymer to relax more quickly due to the motion of surrounding polymers (i.e., the "obstacles" that form the tube also relax with time) than if it were in a fixed network] are included,[8]

$$t(s) = \tau_R \exp\left\{\frac{2\nu}{aL}\left(\frac{s^2}{2} - \frac{s^3}{3L}\right)\right\} \qquad (1.1)$$

where ν is a numerical factor, L is the contour length of the tube surrounding an arm, and τ_R is the Rouse time of a free polymer, which scales as L^2. This model leads to the prediction that the diffusion coefficient of entangled star polymers decreases exponentially with molecular weight. Such behavior has been observed in diffusion experiments of star polymers in a high molecular weight matrix.[6]

The microscopic motion of individual macromolecules may be probed directly by measuring the dynamic structure factor of a labeled polymer,

$$S(\mathbf{q},t) \equiv \frac{1}{N}\sum_m\sum_n \langle \exp\{i\mathbf{q}\cdot(\mathbf{R}_m(t) - \mathbf{R}_n(0))\}\rangle \qquad (1.2)$$

where $\mathbf{q}$ is the difference between the incident and scattered wavevectors, m and n are segments of the labeled polymer, N is the total number of segments (of bond length b), $\mathbf{R}_i(t)$ is the position vector of the ith segment at time t, and $\langle ... \rangle$ denotes an average over configurations. For an ideal (Gaussian) star, with f arms, N and b are related to the parameters of the tube model by $La = (N/f)b^2$, the mean-square end-to-end distance of a star arm. The regime of particular interest is at length scales greater than a, where the effects of entanglements are most apparent.

$S(\mathbf{q},t)$ for a reptating linear chain was calculated first by de Gennes[9] and then more rigorously by Doi and Edwards.[3,10] Their predictions have been verified, at least for "intermediate" times ($\tau_e < t \ll \tau_d$, where τ_e is the Rouse time for the length of polymer between entanglements, and τ_d is the time for a polymer to completely disengage from its original tube), by Higgins et al.[11] and Richter et al.[12] using neutron spin-echo techniques. A recent calculation by des Cloizeaux[13] of the dynamic structure factor for an entangled polymer, during these intermediate time scales, agrees well with the results of refs 11 and 12, lending further support to the tube model.

In the next section we present our calculation of the dynamic structure factor of an entangled star polymer for times greater than τ_R, and for length scales greater than a, based on the relaxation mechanism described above (consequently we expect the results to be valid only when the star has four or more arms). As pointed out by de Gennes[9] even for such length scales there will be some relaxation during the Rouse time, "kinks" (i.e., local deviations from equilibrium) of the chain along the tube will relax, and the density distribution will become even throughout the tube. He termed this regime local reptation, during which the position of the tube remains fixed and $S(\mathbf{q},t)$ decreases by only a small amount. These results will be the same for branched polymers since they do not depend on effects at the end of the chains.

It is useful to define the inverse function s_t, of eq 1.1, i.e., the length of arm s that has relaxed at time t ($\tau_R < t < t(L)$). If we ignore constraint release, the s^3 term of eq 1.1 disappears, and we have a closed expression for s_t,

$$s_t = \left[\frac{aL}{\nu}\ln\left(\frac{t}{\tau_R}\right)\right]^{1/2} \qquad (1.3)$$

For $t < \tau_R$ no relaxation by arm retraction has taken place; hence, $s_t = 0$. This is only valid in the ideal case of a star polymer in a fixed network; if we use the expression for $t(s)$ given by eq 1.1, then s_t is the solution to a cubic equation; however, in the calculation that follows the exact form of s_t is unimportant, and the results we obtain are general.

We see in s_t the qualitative difference between the mechanisms of arm retraction and reptation. At time t there is essentially no relaxation for segments closer to the branch point than s_t while those further away are fully relaxed. In a reptating linear polymer the relaxation of different segments of the molecule are not as widely separated in time.

2. Calculation. The dynamic structure factor for a symmetric star polymer with f arms of equal primitive path length, L, may be written as the sum of two terms,

$$S(\mathbf{q},t) = fS_{11}(\mathbf{q},t) + f(f-1)\,S_{12}(\mathbf{q},t) \qquad (2.1)$$

where the first term on the right-hand side represents scattering from segments on the same arm and the second term scattering from segments on different arms,

$$S_{11}(\mathbf{q},t) = \frac{N}{f^2L^2}\int_0^L ds_1 \int_0^L ds_1' \langle \exp\{i\mathbf{q}\cdot(\mathbf{R}(s_1,t) - \mathbf{R}(s_1',0))\}\rangle \qquad (2.2)$$

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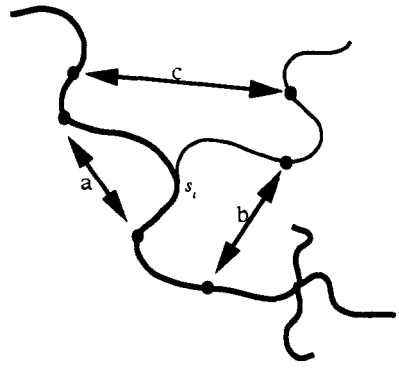

Figure 1. Illustration of the different contributions to the single-arm dynamic scattering function at some time t, when a length s_t of an arm has relaxed. For scattering from pairs of types a and b we are led to eq 2.7, but for scattering from pairs of type c eq 2.9 holds.

and

$$S_{12}(\mathbf{q},t) = \frac{N}{f^2L^2}\int_0^L ds_1 \int_0^L ds_2' \langle \exp\{i\mathbf{q}\cdot(\mathbf{R}(s_1,t) - \mathbf{R}(s_2',0))\}\rangle \tag{2.3}$$

where N is the total number of segments in the star. In eqs 2.2 and 2.3 we have transformed from segment indices (m, n), used in eq 1.2, to length indices (s, s'), which are a measure of distance along the primitive path, i.e.,

$$\sum_m \rightarrow \frac{N_e}{a}\int_0^L ds; \qquad \sum_n \rightarrow \frac{N_e}{a}\int_0^L ds'$$

where N_e is the number of Rouse segments between entanglements, such that

$$L = \left(\frac{N/f}{N_e}\right)a \tag{2.4}$$

The conformation of the primitive path is assumed to be Gaussian at all times; hence[3]

$$\langle \exp\{i\mathbf{q}\cdot(\mathbf{R}(s,t) - \mathbf{R}(s',0))\}\rangle = \exp\left\{-\frac{1}{2}\sum_{\alpha=x,y,z} q_\alpha^2 \langle (R_\alpha(s,t) - R_\alpha(s',0))^2\rangle\right\} \tag{2.5}$$

First, we consider the contribution from a single arm. At time t, for all segments closer to the branch point than s_t, our model implies that

$$\langle \mathbf{R}(s,t)\rangle = \langle \mathbf{R}(s,t=0)\rangle \tag{2.6}$$

We can identify three types of scattering pairs depending on the relative positions of s, s', and s_t, illustrated in Figure 1. For $\{s > s_t$, all s' (type a in Figure 1)$\}$ and $\{s < s_t, s' > s_t$ (type b in Figure 1)$\}$ the mean-square distance between s and s' has not changed from its value at $t = 0$.

$$\langle (R_\alpha(s,t) - R_\alpha(s',0))^2\rangle = \langle (R_\alpha(s,t=0) - R_\alpha(s',0))^2\rangle = \frac{a}{3}|s - s'| \tag{2.7}$$

Hence, these scattering pairs contribute no time dependence to the dynamic structure factor. For $\{s < s_t, s' < s_t$ (type c in Figure 1)$\}$ the mean-square distance between s and s' is greater than at t=0.

$$\begin{aligned}\langle (\mathbf{R}(s,t) - \mathbf{R}(s',0))^2\rangle &= \langle [(\mathbf{R}(s,t) - \mathbf{R}(s_t,t)) + (\mathbf{R}(s_t,0) - \mathbf{R}(s',0))]^2\rangle \\ &= \langle (\mathbf{R}(s,t) - \mathbf{R}(s_t,t))^2\rangle + \langle (\mathbf{R}(s_t,0) - \mathbf{R}(s',0))^2\rangle - \\ &\quad 2\langle (\mathbf{R}(s,t) - \mathbf{R}(s_t,t))\cdot(\mathbf{R}(s_t,0) - \mathbf{R}(s',0))\rangle \end{aligned} \tag{2.8}$$

However, $\langle(\mathbf{R}(s,t)-\mathbf{R}(s_t,t))\rangle$ and $\langle(\mathbf{R}(st,0)-\mathbf{R}(s',0))\rangle$ are uncorrelated, so the third term on the right-hand size is zero, and we have

$$\begin{aligned}\langle (R_\alpha(s,t) - R_\alpha(s',0))^2\rangle &= \langle (R_\alpha(s,t) - R_\alpha(s_t,t))^2\rangle + \langle (R_\alpha,(s_t,0) - R_\alpha(s',0))^2\rangle \\ &= \frac{a}{3}(|s_t - s| + |s_t - s'|)\end{aligned} \tag{2.9}$$

It is scattering from these pairs that leads to the decay of $S(\mathbf{q},t)$. Inserting eqs 2.7 and 2.9 into eq 2.2, we have

$$\begin{aligned}S_{11}(\mathbf{q},t) &= \frac{N}{f^2L^2}\int_0^{s_t} ds[\int_0^{s_t} ds' \exp\{-u(2s_t - s - s')\} + \int_{s_t}^L ds' \exp\{-u|s - s'|\}] + \frac{N}{f^2L^2}\int_{s_t}^L ds \int_0^L ds' \exp\{-u|s - s'|\} \\ &= \frac{N}{f^2L^2u^2}[1 + 2\exp\{-Lu\} - 4\exp\{-s_tu\} + \exp\{-2s_tu\} + 2u(L - s_t)]\end{aligned} \tag{2.10}$$

where

$$u = aq^2/6$$

For scattering from different arms eq 2.6 is true for all $t < t(L)$; there is no decay of this part of the scattering function during this time; hence,

$$\begin{aligned}S_{12}(\mathbf{q},t) &= S_{12}(\mathbf{q},t=0) \\ &= \frac{N}{f^2L^2}\int_0^L ds \int_0^L ds' \exp\{-u(s + s')\} \\ &= \frac{N}{f^2L^2u^2}[1 - 2\exp\{-Lu\} + \exp\{-2Lu\}]\end{aligned} \tag{2.11}$$

Combining eqs 2.10 and 2.11, we obtain for the total scattering function of an f-arm star, for times less than the total disengagement time,

$$\begin{aligned}S(\mathbf{q},t) = \frac{N}{fL^2u^2}[f + 2(2 - f)\exp\{-Lu\} - 4\exp\{-s_tu\} + \exp\{-2s_tu\} + 2u(L - s_t) + (f - 1)\exp\{-2Lu\}]\end{aligned} \tag{2.12}$$

This is illustrated, at various times during the relaxation, for a four-arm star in Figure 2. In Figure 3 we have plotted $\ln S(\mathbf{q},t)$ against $(a/\nu L)\ln(t/\tau_R)$, again for a four-arm star, for different q values, with s_t given by eq 1.3. For $t < \tau_R$, s_t=0 and hence eq 2.12 reduces to the static structure factor for a Gaussian f-arm star, first calculated by Benoit.[14] It can be seen from eq 2.12 that the time dependence of s_t only affects the rate at which the structure factor decays and not its general form.

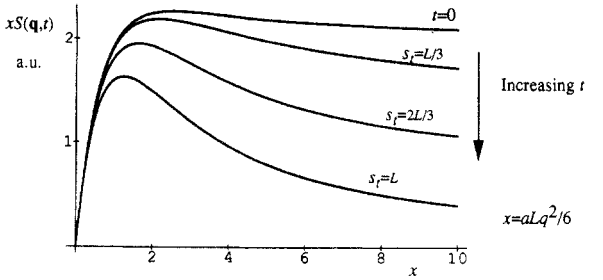

Figure 2. Kratky plot of the dynamic scattering function from a four-arm star of path length L, at various times. Note that the time intervals between each curve are not equal and that the time dependence of s_t only affects the rate at which the structure factor decays and not its general form.

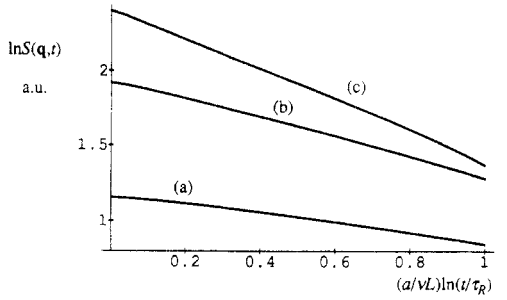

Figure 3. Plot of ln $S(\mathbf{q},t)$ against $(a/\nu L)\ln(t/\tau_R)$ for a four-arm star, at different scattering vectors, (a) $q^2R_g^2 = 1.5$, (b) $q^2R_g^2 = 3$, and (c) $q^2R_g^2 = 5$, for $\tau_R < t < t_{max}$, where t_{max} is the time required for complete relaxation of an arm. R_g is the radius of gyration of an arm given by[3] $R_g^2 = aL/6$. We have used eq 1.3 for the relaxation spectrum of segments of an arm, so that $t_{max} = t(L) = \tau_R \exp\{\nu L/a\}$.

As stated in the introduction the process of arm retraction without any diffusive motion of the branch point is a good approximation for the dynamics of the molecule for $t < t(L)$, and $f > 3$. For times greater than $t(L)$ branch point motion must be considered, the arm relaxes by simple diffusion, and we have

$$S(\mathbf{q},t) = \frac{N}{fL^2u^2}\exp\{-D_s ut\}[\exp\{-Lu\} - 1]^2 \quad (2.13)$$

where D_s is the self-diffusion coefficient for the center of mass of the star, which is of the form[5]

$$D_s \propto \tau_R^{-1}\exp\{-\nu L/a\} \quad (2.14)$$

The functionality of the stars, f, only enters the diffusion coefficient as a prefactor and not an exponent; viscosity[15] and diffusion[16] experiments seem to verify this result. Equation 2.13 is also valid at shorter times when it is a small perturbation on the structure factor, eq 2.12.

3. Discussion. We have shown that the time evolution of $S(\mathbf{q},t)$ for an entangled star polymer in the regime $t < t(L)$, during which the star center remains fixed, is very complex and certainly nonexponential; in fact the decay exhibits "pseudo" power law behavior (see Figure 3) due to the terms which are exponentials of logarithmic functions. In the limit $q \to 0$, and for $t < t(L)$, $S(\mathbf{q},t) \to N$, which is unsurprising since at these wavevectors the star looks like a fixed particle in space, and the scattering intensity is just proportional to the total scattering from the particle.

The dynamic scattering function from a single arm, eq 2.10, will also be applicable to any "dangling" end in a network or of a branched polymer, i.e., any situation where one end is essentially fixed in space, but the rest of the polymer is free to explore available configurations.

With present neutron scattering techniques it is not possible to access the time scales required to test eq 2.12; however, knowledge of $S(\mathbf{q},t)$ is important as it contains dynamic information about the polymers and is known to be related to the correlation function of bulk density fluctuations in concentrated solutions.[17]

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