Dynamical Response of a Single Star Polymer Chain

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ABSTRACT: The initial decay rate $\Omega(\vec{k})$ of the dynamical scattering factor of a single regular star polymer is investigated with the chain conformational renormalization group method up to first order in ϵ. The reduced relaxation rate $\Omega(\vec{k})/k^3$ is expressed as the ratio of the mobility to the static structure factor, and we have analyzed the two contributions separately. At the Gaussian fixed point we have found a qualitatively different result to that of the standard calculation in three dimensions, and the difference comes from the effect of the ϵ-expansion on the mobility. The renormalization group result at the self-avoiding fixed point describes qualitatively well the behavior of $\Omega(\vec{k})/k^3$ observed in neutron scattering experiments for 12-arm stars in a good solvent.

1. Introduction

The understanding of the static and dynamic properties of branched polymers in dilute solutions still remains a challenging problem in polymer physics.[1-8] Regular star polymers, where a number of linear chains with the same molecular weight are joined together by one end at a center, are the simplest branched structure and represent the prototype system used to get insight into the architecture's dependence of the molecular properties. The modern techniques of anionic polymerization allow the synthesis of star molecules, with a number of branches that can vary from 3 to 270.[9,10] This new availability of well-characterized and monodisperse molecules triggered a number of experimental efforts, with the scattering methods being the most useful because of their capacity to probe the density fluctuations in all the different scales.

The structure and dynamics of flexible star polymers in a good solvent were experimentally investigated by Richter et al.[1] using small-angle neutron scattering (SANS) and neutron spin-echo (NSE) spectroscopy, respectively. The scattering intensity $I(k)$ of star polymers with functionality f shows, in a Kratky representation ($I(k)\,k^2$), a pronounced maximum around $kR_g^1 \simeq 1.2$, the height of which increases with f. Here, R_g^1 is the radius of gyration of one arm in the star, and k is the momentum transfer during scattering. The reduced relaxation rates $\Omega(k)/k^3$ of the same stars show a sharp minimum at similar intermediate scales, between the translational diffusion of the whole polymer and the short-scale segmental motion.

This behavior is qualitatively different from that of linear chains. In fact, the scattering data $I(k)\,k^2$ increases monotonically from zero to the high-k plateau limit. On the other hand, the reduced relaxation rate decreases monotonically from the small-k regime ($\Omega(k)/k^3 \sim 1/k$) corresponding to the global translation of the chain to the constant segmental high-k Zimm regime.[11]

From a theoretical point of view, the study of the internal dynamics of polymer chains obeying Gaussian statistics was pioneered by de Gennes[12] and the scattering law $S(k,\omega)$ for dilute linear polymer solutions was obtained from Kirkwood's diffusion equation by Akcasu and Gurol,[13] without preaveraged hydrodynamic interactions. The initial decay rate $\Omega(k)$ of the dynamical scattering factor $S(k,t)$ was calculated for starlike chains by Burchard, Schmidt, and Stockmayer[14] (in the following BSS model), using the same formalism. This model is currently used in the analysis of the experimental data in good solvents.

The theoretical basis of Kirkwood's diffusion equation for the time-dependent distribution function for the chain conformation was critically analyzed by Lee, Baldwin, and Oono.[15] Employing a kinetic level description of both the chain and the solvent, they showed that the diffusion equation could be justified only up to order ϵ ($\epsilon = 4 - d$, with d being the spatial dimensionality), and the renormalization group (RG) approach to order ϵ appears to be the only consistent method to treat Kirkwood's diffusion equation. Corrections up to order ϵ^2 of the kinetic models to include the effect of the solvent velocity fluctuations have been undertaken by Wang and Freed[16] to study long-wavelength low-frequency polymer properties with the Rouse−Zimm model. Nevertheless, the initial decay rate of the dynamical scattering factor was evaluated for linear chains in the Gaussian and self-avoiding fixed points of the theory only up to order ϵ.[15]

The aim of the present work is to investigate the influence of excluded-volume effects on the initial decay rate of the dynamical scattering factor of a single f-branched star polymer

$$\Omega(k) = -\frac{\mathrm{d} \ln I(k,t)}{\mathrm{d}t}\Big|_{t=0} \qquad (1)$$

with the chain conformational renormalization group method[17,18] to first order in ϵ. Here, $I(k,t) = S(k,t)/S(0,0)$ is the normalized dynamical scattering factor. The calculation is a straightforward generalization of ref 15. This paper is organized as follows. In the next section a brief theoretical background is presented. The bare calculation and the renormalization procedure are developed in section 3. The results and a discussion are considered in section 4.

2. Theoretical Background

The uniform star polymer is represented by a continuous chain with f branches joined together by one

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end at a center located at the origin of a d-dimensional coordinate system. We adopt the minimal model described by the standard Edwards Hamiltonian generalized to consider an f-arm star polymer:[5,19]

$$\mathscr{H}[\vec{c}(\tau)] = \frac{1}{2}\sum_{i=1}^{f}\int_0^{N_0/f} d\tau \left[\frac{d\vec{c}(\tau_i)}{d\tau_i}\right]^2 + \frac{1}{2}v_0\sum_{i=1}^{f}\int_0^{N_0/f}\int_0^{N_0/f} d\tau_i\, d\tau_i'\, \delta[\vec{c}(\tau_i)-\vec{c}(\tau_i')] + \frac{1}{2}v_0\sum_{i=1}^{f}\sum_{j=1}^{f}\int_0^{N_0/f}\int_0^{N_0/f} d\tau_i\, d\tau_j\, \delta[\vec{c}(\tau_i)-\vec{c}(\tau_j)] \quad (2)$$

$$|\tau_i - \tau_i'| \geq a \qquad |\tau_i + \tau_j| \geq a$$

The second term describes interactions on the same arm, whereas the third term describes interactions between arms. In this model, each arm is considered as a continuous chain described by the curve $\vec{c}(\tau)$. The intrinsic variable τ follows the contour of the arm of length N_0/f. N_0 is a microscopic measure of the total chain length, and a is a cutoff distance to avoid the self-interaction of the units. The excluded-volume interaction is considered in an effective way through a δ function pseudopotential of strength v_0.

The dynamics of the molecule is described by Kirkwood's diffusion equation[15]

$$dP/dt = \mathscr{L}_F^* P \quad (3)$$

where P is the time-dependent distribution function for the conformation of the chain $\vec{c}(\tau)$, and the operator $\mathscr{L}_F^*$ is given by

$$\mathscr{L}_F = \int_0^{N_0/f} d\tau_\alpha \int_0^{N_0/f} d\sigma_\beta \left[-\frac{\delta\mathscr{H}}{\delta\vec{c}(\sigma_\beta)} + \frac{\delta}{\delta\vec{c}(\sigma_\beta)}\right] \overleftrightarrow{\mathbf{D}}(\tau_\alpha,\sigma_\beta)\frac{\delta}{\delta\vec{c}(\tau_\alpha)} \quad (4)$$

with

$$\frac{1}{k_B T}\overleftrightarrow{\mathbf{D}}(\tau_\alpha,\sigma_\beta) = \frac{1}{\zeta_0}\delta(\tau_\alpha-\sigma_\beta)\overleftrightarrow{\mathbf{1}} + \overleftrightarrow{\mathbf{T}}(\vec{c}(\tau_\alpha) - \vec{c}(\sigma_\beta)) \quad (5)$$

The hydrodynamic interaction is considered through the Oseen tensor

$$\overleftrightarrow{\mathbf{T}}(\vec{r} - \vec{r}') = \frac{1}{(2\pi)^d}\int d^d k \frac{1}{\eta_0 k^2}\left[\overleftrightarrow{\mathbf{1}} - \frac{\vec{k}\vec{k}}{k^2}\right] e^{i\vec{k}(\vec{r}-\vec{r}')} \quad (6)$$

Here, ζ_0 is the (bare) friction coefficient of the chain unit, and η_0 is the viscosity of the solvent.

From the above description for the polymer dynamics, a formula for the (bare) initial decay rate is derived using projection operator methods,[13,15] expressed in terms of equilibrium statistical averages of the chains

$$\Omega_B(k) = -\frac{\overline{\langle\tilde{\varrho}(\vec{k})\rangle}\,\mathscr{L}_F\tilde{\varrho}(\vec{k})\rangle}{S_B(k)} \quad (7)$$

where the bar denotes complex conjugation, $\tilde{\varrho}(\vec{k})$ is the Fourier transform of the local density at $t = 0$

$$\tilde{\varrho}(\vec{k}) = \sum_{i=1}^{f}\int_0^{N_0/f} d\tau_i\, e^{i\vec{k}\vec{c}(\tau_i)} \quad (8)$$

and $S_B(k)$ is the (bare) static structure factor.[19]

3. Calculation

3.1. Bare Calculation. To calculate the numerator in eq 7, we introduce explicitly the operator $\mathscr{L}_F$ in the definition and we get

$$L_B(k) = f\vec{k}\vec{k}:\int_0^{N_0/f} d\tau \int_0^{N_0/f} d\sigma \langle\overleftrightarrow{\mathbf{D}}(\sigma,\tau)\, e^{i\vec{k}[\vec{c}(\sigma)-\vec{c}(\tau)]}\rangle + f(f-1)\vec{k}\vec{k}:\int_0^{N_0/f} d\tau \int_0^{N_0/f} d\sigma \langle\overleftrightarrow{\mathbf{D}}(\sigma,\tau)\, e^{i\vec{k}[\vec{c}_i(\sigma)-\vec{c}_j(\tau)]}\rangle \quad (9)$$

$$L_B(k) = fL_{B,l}(k) + f(f-1)L_{B,s}(k) \quad (10)$$

The term containing $\delta\mathscr{H}/\delta\vec{c}(\sigma_\beta)$ in eq 4 was disregarded, because it vanishes after the Gaussian averaging. The first term is the contribution of f independent linear chains,[15] and the second one describes the correlations between different branches of the star architecture.

In the contribution $L_{B,l}(k)$ of each independent arm, a divergence appears due to the hydrodynamic interaction. This divergence is avoided by introducing explicitly a cutoff distance a along the chain, and the final result is

$$L_{B,l}(k) = k_B T\frac{2\theta_0}{\zeta_0}\left[1 + \frac{3\zeta_0}{16\pi^2\eta_0}\ln\frac{N_0}{fa} - \frac{3\zeta_0}{16\pi^2\eta_0} + \frac{3\zeta_0}{16\pi^2\eta_0}V_l(\theta_0)\right] \quad (11)$$

where $\theta_0 = N_0k^2/2f$, and the function $V_l(\theta_0)$ is defined by

$$V_l(\theta_0) = 2\int_0^1 dy \left(\frac{1}{y} - 1\right)\left(A(\theta_0 y) - \frac{1}{2}\right) \quad (12)$$

with

$$A(\theta_0 y) = \frac{1 - e^{-\theta_0 y}}{\theta_0 y} - \frac{e^{-\theta_0 y} - 1 + \theta_0 y}{(\theta_0 y)^2} \quad (13)$$

The result for the interbranch contribution $L_{B,s}(k)$ is completely regular, free of divergences, and its calculation follows closely that of the linear chain. So, we refer the reader to the original ref 15 for details. It reads

$$L_{B,s}(k) = k_B T\frac{2\theta_0}{\zeta_0}\frac{3\zeta_0}{16\pi^2\eta_0}V_s(\theta_0) \quad (14)$$

where

$$V_s(\theta_0) = \int_0^1 dy\, A(\theta_0 y) - \int_1^2 dy\, A(\theta_0 y) + 2\int_1^2 dy \frac{A(\theta_0 y)}{y} \quad (15)$$

The behavior of the functions $V_l(x)$ and $V_s(x)$ is depicted in Figure 1. $V_l(x)$ vanishes at the origin and decreases monotonically up to its asymptotic value

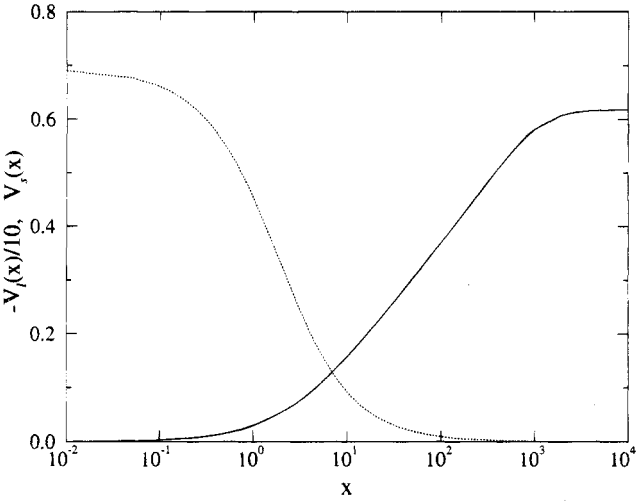

Figure 1. Behavior of the functions $V_l(x)$ (solid line) and $V_s(x)$ (dotted line), defined by eqs 12 and 15, respectively. Note the different vertical scales.

(−6.195) for high x. On the other side, $V_s(x)$ has its maximum value at the origin ($V_s(0) = \ln 2$) and vanishes at infinity.

The (bare) static scattering factor, calculated up to first order in the excluded-volume parameter v_0, was evaluated by us in ref 19 and reads

$$S_B(k) = N_0^2 f(\theta_0)\left[1 + \frac{v_0}{4\pi^2}\left(\theta_0 \frac{f'(\theta_0)}{f(\theta_0)} \ln\frac{N_0}{fa} - f - \frac{f(f-1)}{2}\ln 2 + \frac{g(\theta_0)}{f(\theta_0)}\right)\right] \quad (16)$$

Here, $f(\theta_0)$ is the Benoit function

$$f(\theta_0) = \frac{2}{f}\left[\frac{e^{-\theta_0}}{\theta_0^2} - \frac{1}{\theta_0^2} + \frac{1}{\theta_0}\right] + \frac{f-1}{f}\left(\frac{e^{-\theta_0}-1}{\theta_0}\right)^2 \quad (17)$$

and $g(\theta_0)$ is the regular contribution to the static scattering factor (see Appendix of ref 19 for the full expression). By introduction of the dimensionless parameters

$$u_0 = v_0 L^{\epsilon/2} \quad (18)$$

$$\xi_0 = \frac{\zeta_0}{\eta_0} L^{\epsilon/2} \quad (19)$$

and rearranging the equations above, we finally get

$$\Omega_B(k) = k_B T \frac{2\theta_0}{\zeta_0}\frac{f}{N_0^2 f(\theta_0)}\left[1 + \frac{3}{16\pi^2}\xi_0 \ln\frac{N_0}{fa} - \frac{v_0}{4\pi^2}\theta_0\frac{f'(\theta_0)}{f(\theta_0)}\ln\frac{N_0}{fa}\right]\left[1 + \frac{3}{16\pi^2}\xi_0[-1 + V_l(\theta_0) + (f-1)V_s(\theta_0)]\right]\left[1 + \frac{v_0}{4\pi^2}\left(f + \frac{f(f-1)}{2}\ln 2 - \frac{g(\theta_0)}{f(\theta_0)}\right)\right] \quad (20)$$

This expression is strongly dependent on the cutoff distance a. A renormalization procedure is needed in order to get finite results for the observable quantity $\Omega(k)$ when $a \to 0$.

3.2. Renormalization. At this point, it becomes convenient to introduce the macroscopic scale length L as follows:

$$\ln\frac{N_0}{a} = \ln\frac{N_0}{L} - \ln\frac{a}{L} \quad (21)$$

The microscopic parameters N_0, u_0, and ξ_0 are related to their macroscopic counterparts N, u, and ξ through the multiplicative renormalization constants $\mathbf{Z}_N$, $\mathbf{Z}_u$, $\mathbf{Z}_\xi$, defined by

$$N = \mathbf{Z}_N N_0 \quad (22)$$

$$u = \mathbf{Z}_u u_0 \quad (23)$$

$$\xi = \mathbf{Z}_\xi \xi_0 \quad (24)$$

The initial decay rate Ω is a macroscopic observable, so $\Omega = \Omega_B$. The renormalization of N and u is completely determined by excluded-volume effects and is independent of the topology of the chain. The renormalization factors are given by

$$\mathbf{Z}_N = 1 + \frac{u}{4\pi^2}\ln\left(\frac{L}{a}\right) + \ldots \quad (25)$$

$$\mathbf{Z}_u = 1 - \frac{u}{\pi^2}\ln\left(\frac{L}{a}\right) + \ldots \quad (26)$$

From these results and the choice

$$\mathbf{Z}_\xi = 1 - \frac{u}{4\pi^2}\ln\left(\frac{L}{a}\right) - \frac{3}{16\pi^2}\xi\ln\left(\frac{L}{a}\right) + \ldots \quad (27)$$

the singularities are completely eliminated from the perturbative result of $\Omega_B(k)$ (eq 20). The initial decay rate for the star polymer finally reads

$$\Omega(k) = k_B T \frac{2\theta}{\zeta}\frac{f}{N^2 f(\theta)}\left[1 - \frac{u}{4\pi^2}\theta\frac{f'(\theta)}{f(\theta)}\ln\frac{N}{fL}\right]\left[1 + \frac{3}{16\pi^2}\xi\ln\frac{N}{fL}\right]\left[1 + \frac{3}{16\pi^2}\xi[-1 + V_l(\theta) + (f-1)V_s(\theta)]\right]\left[1 + \frac{u}{4\pi^2}\left(f + \frac{f(f-1)}{2}\ln 2 - \frac{g(\theta)}{f(\theta)}\right)\right] \quad (28)$$

where $\theta = Nk^2/2f$.

A renormalization group equation for $\Omega(k)$ can be written following the standard procedure[17] as

$$\left[L\frac{\partial}{\partial L} + \beta(u)\frac{\partial}{\partial u} + \beta_h(u,\xi)\frac{\partial}{\partial \xi} + \gamma_N(u)N\frac{\partial}{\partial N}\right]\Omega(k) = 0 \quad (29)$$

where

$$\gamma_N(u) = L\frac{\partial \ln \mathbf{Z}_N}{\partial L}\Big|_{N_0,v_0,a} \quad (30)$$

and

$$\beta(u) \equiv L\frac{\partial u}{\partial L}_{N_0,v_0,a} = \frac{u}{\pi^2}\left[\frac{\pi^2\epsilon}{2} - u\right] + \ldots \quad (31)$$

$$\beta_h(u,\xi) \equiv L\frac{\partial \xi}{\partial L}\Big|_{v_0,\zeta_0,a} = \xi\left[\frac{\epsilon}{2} - \frac{3}{16\pi^2}\xi - \frac{1}{4\pi^2}u\right] + \ldots \quad (32)$$

The fixed points $u = u^*$ and $\xi = \xi^*$ are the zeros of the Gell-Mann−Low functions $\beta(u)$ and $\beta_h(u,\xi)$. Four

fixed points are found, and they are

$$\text{(a)} \qquad u^* = 0, \quad \xi^* = 0$$

$$\text{(b)} \qquad u^* = \frac{\pi^2}{2}\epsilon, \quad \xi^* = 0$$

$$\text{(c)} \qquad u^* = 0, \quad \xi^* = \frac{8}{3}\pi^2\epsilon$$

$$\text{(d)} \qquad u^* = \frac{\pi^2}{2}\epsilon, \quad \xi^* = 2\pi^2\epsilon$$

The fixed points a and b belong to the free-draining cases. The fixed points with $u^* = 0$ belong to Gaussian statistics, and those with $u^* = \pi^2\epsilon/2$ represent the self-avoiding limit. As the free-draining limit is meaningless in dilute solution theory, we will consider only the cases c and d.

At the fixed points, the renormalization group equation reduces to

$$\left[L\frac{\partial}{\partial L} + \gamma^* N\frac{\partial}{\partial N}\right]\Omega(k) = 0 \tag{33}$$

where $\gamma^* = \gamma_N(u^*)$. From the general solution of this equation and dimensional analysis, we get a scaling law for $\Omega(k)$

$$\Omega(k) = N^{-(4-\epsilon)\nu} G_f(N^\nu k) \tag{34}$$

$G_f(z)$ being a well-behaved function of z.

With the introduction of the scaling variable

$$\hat{\theta} = \frac{Nk^2}{f2}\left(\frac{N}{fL}\right)^{u^*/4\pi 2} \tag{35}$$

and the exponentiation of the contributions coming from the fixed points, $\Omega(k)$ can be expressed as

$$\Omega(k) = k_B T\left[\frac{N}{f}\left(\frac{N}{fL}\right)^{2(\nu-1/2)}\right]^{-d/2} \frac{2\hat{\theta}}{\eta_0\xi^* f f(\hat{\theta})} \times \exp\left[\frac{3\xi^*}{16\pi^2}(-1 + V_1(\hat{\theta}) + (f-1)V_s(\theta))\right] \times \exp\left[\frac{u^*}{4\pi^2}\left(f + \frac{f(f-1)}{2}\ln 2 - \frac{g(\hat{\theta})}{f(\hat{\theta})}\right)\right] \tag{36}$$

where $\nu = {}^1/_2$ for the Gaussian fixed point c and $\nu = {}^1/_2(1 + \epsilon/8)$ for the self-avoiding fixed point d.

In order to get universal behavior of Ω, independent of the microscopic details, it is useful to introduce a new dimensionless variable y. It is proportional to $k^2R_g^2$, where R_g^2 is the mean-square radius of gyration of the star polymer

$$y = \frac{1}{4}\frac{3f}{3f-2}k^2R_g^{\,2} \tag{37}$$

We note that the factor $(3f - 2)/f$ accounts for the relation between the unperturbed mean-square radius of gyration of one arm to that of the whole star.

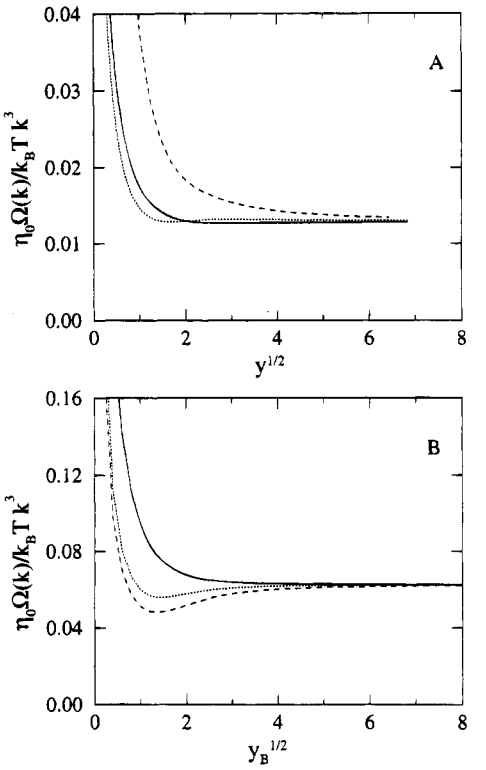

Figure 2. Reduced relaxation rates for linear (solid line), 5-arm (dotted line), and 12-arm (dashed line) regular stars. (A) Renormalization group method at the Gaussian fixed point and (B) results of the BSS model. The RG result for f = 12 does not show a minimum at intermediate scales.

In terms of y we find a universal relation for $\eta_0\Omega(k)/k_BTk^d$, which for $\epsilon = 1$ and for the Gaussian limit c is

$$\frac{\eta_0\Omega(k)}{k_BTk^3} = \frac{3\sqrt{2}}{16\pi^2}\frac{y^{-1/2}}{ff(y)}\exp\left[-\frac{1}{4} - \frac{1}{4}y\frac{f'(y)}{f(y)}\right] \times \exp\left[\frac{1}{2}(-1 + V_l(y) + (f-1)V_s(y))\right] \tag{38}$$

whereas for the self-avoiding limit d, it is

$$\frac{\eta_0\Omega(k)}{k_BTk^3} = \frac{\sqrt{2}}{4\pi^2}\frac{y^{-1/2}}{ff(y)}\exp\left[-\frac{1}{4} - \frac{1}{4}y\frac{f'(y)}{f(y)}\right] \times \exp\left[\frac{1}{8}\left(\frac{g'(0)}{f'(0)} - \frac{g(0)}{f(0)}\right)\left(1 + y\frac{f'(y)}{f(y)}\right)\right]\exp\left[\frac{3}{8}(-1 + V_l(y) + (f-1)V_s(y))\right]\exp\left[\frac{1}{8}\left(f + \frac{f(f-1)}{2}\ln 2 - \frac{g(y)}{f(y)}\right)\right] \tag{39}$$

Equations 38 and 39 are the main results of this paper.[20]

4. Results and Discussion

Our results for the nondraining Gaussian fixed point (eq 38) are shown in Figure 2A for functionalities f = 1, 5, and 12. The reduced relaxation rate for the linear chain is a monotonically decreasing function of y, whereas the 5-arm star displays a weak minimum at $y^{1/2} \simeq 1.6$. Nevertheless, this minimum disappears for the 12-arm star.

The pattern displayed by these Gaussian chains is even qualitatively different to that obtained from the BSS model[4] in three dimensions. We reproduce, in Figure 2B, the results of BSS as a function of $y_B^{1/2} = kR_g^1$. In these cases, the 5-arm star also develops a minimum at $y_B^{1/2} \simeq 1.4$, and the minimum is enhanced

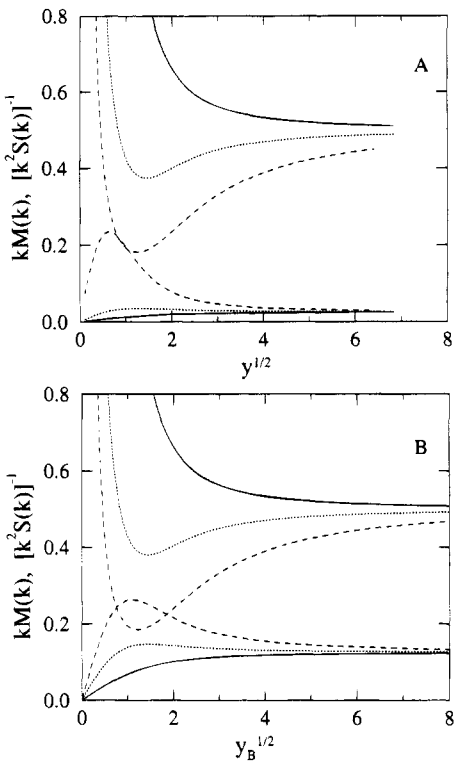

Figure 3. Static ($[k^2S(k)]^{-1}$) and dynamical ($kM(k)$) contributions to the reduced relaxation rates in the Gaussian fixed point of the RG method (A) and in the Gaussian BSS model (B). The lines are as in Figure 2. The curves corresponding to $kM(k)$ vanish at the origin.

by increasing the functionality. In both schemes, the reduced relaxation rate achieves a constant value at high y, independent of functionality. However, the renormalization group method predicts a limiting value approximately 4 times lower than that of the BSS model. This behavior agrees with that expected from our knowledge of the linear chain.[20]

We investigate the differences shown by both methods by plotting separately, in Figure 3, the static and dynamical contribution to $\Omega(k)$. In fact, the reduced relaxation rates can be written as

$$\frac{\eta_0\Omega(k)}{k_BTk^3} = \frac{kM(k)}{k^2S(k)} \tag{40}$$

This equation defines the mobility $M(k)$. From the known limiting behaviors of $\Omega(k)$ and $S(k)$, it follows that $M(k) \to$ constant when $k \to 0$ and $M(k) \sim k^{-1}$ as $k \to \infty$. At intermediate scales, $M(k)$ must depend on the chain structure. As a matter of fact, $kM(k)$ increases monotonically from 0 to the high-k plateau for Gaussian linear chains. This behavior is reproduced by both our RG result and the BSS model (f = 1 and 2). When the number of arms is increased, a maximum at $y^{1/2} \simeq 1.4$ develops, showing the effect of the chain topology. Both methods give the same qualitative behavior, but the RG calculation displays a higher maximum than the BSS model.

The reason for the quantitative discrepancy in the results given by both methods lies in the influence of the first-order ϵ-expansion on multiarm polymer chain properties. The properties calculated for f = 1 or f = 2 agree exactly with each other, demonstrating the consistency of the partial contributions from intra- and interarm quantities, i.e., the functions V_1 and V_s defined by eqs 12 and 15, respectively. It is the strong (exponential) increase (dependence) of the mobility at large and intermediate scales with the number of arms that causes the ϵ-expansion to display anomalous behavior. A similar trend is shown by the translational friction coefficient of regular stars as treated with the Kirkwood–Riseman method. Here, either the classical Stockmayer–Fixmann result[21] or a more accurate numerical solution of the integral equations in three dimensions[22] predicts a slow decrease of the ratio h ($=f_b/f_l$) of the friction coefficient of branched and linear chains of the same molecular weight. In fact, the methods give $h = 0.669$ or $h = 0.763$, respectively, for stars with 10 arms. The (naive) first-order ϵ-expansion predicts for the same system $h = 0.140$, an extremely small value. The predictions are even worse for other topologies, such as stars with loops instead of linear chains emerging from the center.[22]

Since the domain of validity of the (naive) first-order ϵ-expansion seems to shrink as f grows, an appropriate resummation of the resulting series would be necessary to account properly for the influence of the large f limit on the physical observables. This strategy was employed by Ohno[6] in the calculation of critical exponents for self-avoiding many-arm star polymers. Nevertheless, no attempts have been made even for the simplest dynamical calculations, and we postpone this point for further study.

On the other hand, both models give quantitatively the same behavior of $[k^2S(k)]^{-1}$ at each functionality (the difference is less than 5%, as was demonstrated in ref 19). Hence, the strong difference in $\Omega(k)/k^3$ for 12-arm stars in our method with respect to low functionality stars or to the 12-arm BSS stars is completely due to the mobility factor. Note that separately both the mobility and the structure factor are qualitatively similar in the two methods, but their product gives different curves.

The reduced relaxation rates for self-avoiding linear and 5-arm star polymers are plotted in Figure 4A. As expected, our calculation agrees with the original result of Lee, Baldwin, and Oono for the self-avoiding linear chain. Our 5-arm star develops a minimum followed by a maximum before achieving its asymptotic high-k value.

We analyze the influence of the excluded volume on $\Omega(k)/k^3$ through its contributions to the mobility and static scattering factors, which are plotted in Figure 4B. It appears that the contribution from the mobility is similar to our RG calculation at the Gaussian fixed point. The only difference comes from the numerical value of the renormalized friction coefficient ξ^*, at the self-avoiding fixed point. However, the excluded-volume interaction has a dramatic influence on the scattering factor of the stars.[19] The functionality f enters implicitly in the definition of the regular function $g(y)$ (eqs 3.7 and 3.9 of ref 19), which appears in the exponent of our eq 39. It collects contributions from diagrams with weights f, f(f − 1), f(f − 1)(f − 2), and f(f − 1)(f − 2)(f − 3) and restricts the validity of the first-order RG static structure factor to self-avoiding stars of low functionality. In spite of this, the picture emerging from our RG calculations in the self-avoiding limit is clearly different from that obtained with Gaussian star chains by Burchard et al.[14] Actually, our picture agrees qualitatively with the tendency shown by numerical simulations of low functionality stars[3] and by experiments on 12-arm polystyrene star molecules in good solvent[1b] (see Figure

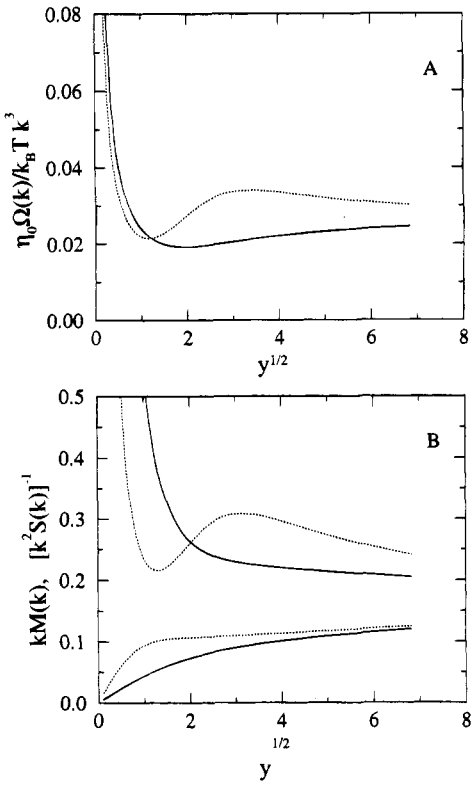

Figure 4. (A) Reduced relaxation rate for linear (solid line) and 5-arm (dotted line) star molecules at the self-avoiding nondraining fixed point of renormalization group theory. (B) Static ($[k^2S(k)]^{-1}$) and dynamical ($kM(k)$) contributions to the reduced relaxation rates. The first quantities are scaled by a factor $^1/_3$ and the second ones by 3.

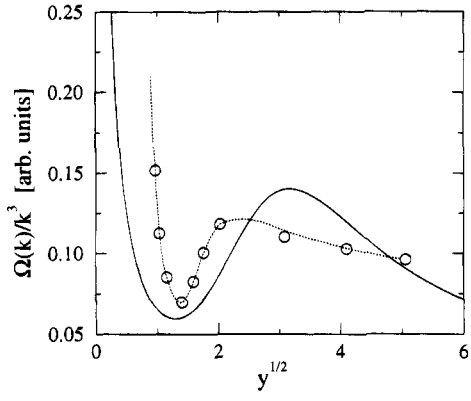

Figure 5. Reduced relaxation rate for a 12-arm star in the self-avoiding fixed point (solid line) and the experimental finding of ref 1b (circles). Quantitative agreement is not expected at this functionality.

5). These experiments reveal a maximum following the expected minimum, and this maximum is above the asymptotic limit.

In conclusion, the renormalization group theory describes the slowing down of the relaxation density fluctuations of self-avoiding stars at intermediate scales and its approach to the asymptotic limit in qualitative agreement with numerical simulations and experiments. Nevertheless, at the present stage, it applies only to low functionality star polymers. Extension of the theory to order ϵ^2 and an appropriate treatment for many-arm stars[6] are necessary before a quantitative comparison with experiments could be made.

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References and Notes

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(20) Our function $V_1(x)$ is shifted with respect to that defined by Lee et al. in ref 15, so we have $V_1(0) = 0$ instead of -0.5. On the other hand, their definition of the static structure factor for a Gaussian chain is half of the Debye function. Hence, our $f(x)$ is twice theirs. At the self-avoiding fixed point the expression

$$\frac{1}{4} - \frac{1}{8}\left(\frac{g'(0)}{f'(0)} - \frac{g(0)}{f(0)}\right) \tag{41}$$

equals 37/96 for f = 1, which replaces the coefficient $n = 0.156$ in eq 5.4 of ref [15]. The difference arises from an additional term ln $(2\pi)/8$ introduced erroneously by the authors in the change of variables $\hat{\theta}$ to y.
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