# Influence of Hydrodynamic Preaveraging on Quasi-Elastic Scattering from Flexible Linear and Star-Branched Macromolecules‡

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ABSTRACT: The first cumulant Γ (initial logarithmic time derivative) of the dynamic structure factor is calculated for linear and star-branched flexible macromolecules by use of a formula due to Akcasu and Gurol, both with and without hydrodynamic preaveraging. To facilitate applications to polydisperse and branched systems, an accurate approximation suitable for use in the cascade branching theory is developed. The relative error in Γ reduced by preaveraging does not exceed 15% for linear chains but can become as large as 40% for regular stars with many rays. This effect, which is largest at intermediate values of the scattering vector **q**, is interpreted as due to the increase of segment density in the branched macromolecule.

In recent years the development of the quasi-elastic light-scattering experiment and the related theory[1] has enhanced the methodology of characterization of macromolecules in solution. Photon-correlation techniques afford more or less direct observation of the dynamic structure factor

$$S(q,t) = \langle \rho^*(0)\rho(t) \rangle \tag{1}$$

$$\rho(t) = \sum_j^N \exp(i\mathbf{q}\cdot\mathbf{r}_j(t)) \tag{2}$$

where $\mathbf{r}_j(t)$ represents the position of the $j$'th scattering element of the dissolved macromolecule at time $t$, and $\mathbf{q}$ is the well-known scattering vector with magnitude

$$q = (4\pi/\lambda) \sin \theta/2 \tag{3}$$

The angular brackets in eq 1 denote an average over a suitable ensemble.

Because of available theoretical capability, special attention is often directed (as in this paper) at the first cumulant,

$$\Gamma = -[\mathrm{d} \ln S(q,t)/\mathrm{d}t]_{t=0} \tag{4}$$

of the structure factor. By suitable approximations for not too long times, such as

$$S(q,t)/S(q,0) \simeq \exp[-\Gamma t + (\Gamma_2/2)^2 t^2] \tag{5}$$[2]

or

$$S(q,t)/S(q,0) \simeq [1 + (\Gamma_2/2)t^2] \exp(-\Gamma t) \tag{6}$$[3]

where $\Gamma_2$ is the second cumulant, it is possible to obtain rather accurate values of Γ from experiment.

A general theoretical formula for Γ within the framework of diffusion theory was derived several years ago by Akcasu and Gurol (hereafter AG),[4] and the theory has recently been reviewed by Akcasu, Benmouna, and Han.[5] The basis of the treatment is the general diffusion theory of Kirkwood[6,7] in the form due to Fixman.[8] If the time-dependent distribution function $\psi(\mathbf{r}^N,t)$ for the set of space coordinates $\mathbf{r}^N$ of the elements of a macromolecule in solution is factored into the form $\psi_{eq}(\mathbf{r}^N)f(\mathbf{r}^N,t)$, where $\psi_{eq}(\mathbf{r}^N)$ is the equilibrium distribution function, the remaining function $f$ obeys the diffusion equation

$$\partial f/\partial t + \mathcal{L}f = 0 \tag{7}$$

with the operator

$$\mathcal{L} = \sum_j^N \sum_k^N (\beta \nabla_j U \cdot \mathbf{D}_{jk} \cdot \nabla_k - \nabla_j \cdot \mathbf{D}_{jk} \cdot \nabla_k); \qquad \beta^{-1} = k_B T \tag{8}$$

Here $U(\mathbf{r}^N)$ is the potential of the mean force among the chain elements, and $\mathbf{D}_{jk}$ is a component of the diffusion tensor. In the model used by Kirkwood and applied in the calculations of AG and of this paper, the hydrodynamic interactions among chain elements, which produce the off-diagonal components of the diffusion tensor, are described by the Oseen formula. We then have[7]

$$\beta\mathbf{D}_{jk} = \delta_{jk}\zeta_j^{-1}\mathbf{1} + (1 - \delta_{jk})(8\pi\eta_0 R_{jk})^{-1}(\mathbf{1} + R_{jk}^{-2}\mathbf{R}_{jk}\mathbf{R}_{jk}) \tag{9}$$

where $\eta_0$ is the solvent viscosity, $\zeta_j$ the friction coefficient for element $j$, and $\mathbf{R}_{jk}$ the vector from element $j$ to element $k$.

Under some circumstances the use of the Oseen interaction produces mathematical troubles (singularities in computed transport coefficients) that have been amply discussed elsewhere[7] but are unlikely to intrude on the present considerations.

Fixman noted that the operator $\mathcal{L}$ was Hermitian with respect to the scalar product

$$(g,\mathcal{L}h) = \int \cdots \int \psi_{eq} g \mathcal{L} h \, \mathrm{d}\mathbf{r}^N \tag{10}$$

where the equilibrium distribution function is of course proportional to $\exp(-\beta U)$. With reliance on the Hermitian property, AG were able to show that the first cumulant is given by

$$\Gamma = (\rho,\mathcal{L}\rho)/(\rho,\rho) \tag{11}$$

where

$$(\rho,\mathcal{L}\rho) = \sum_j^N \sum_k^N \langle (\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{R}_{jk}) \rangle \equiv \sum_j^N \sum_k^N q^2 \phi_{jk}^{\,Q} \tag{12}$$

$$(\rho,\rho) = \sum_j^N \sum_k^N \langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk}) \rangle \equiv \sum_j^N \sum_k^N \phi_{jk}^{\,I} \tag{13}$$

The angular brackets now denote *equilibrium* averages. The denominator of eq 11 is recognized as

$$(\rho,\rho) = \langle \rho^*(0)\rho(0) \rangle = N^2 P(q) \tag{14}$$

where $P(q)$ is the usual particle scattering factor of conventional ("integrated") light scattering.

A noteworthy feature of the AG result, eq 12, is that the Oseen interaction terms, which depend directly on the molecular coordinates, need not always be *preaveraged* over the equilibrium coordinate distribution, as was necessary, for example, by Kirkwood and Riseman[9] and by Zimm[10] in treatment of the intrinsic viscosity. Indeed, AG give an explicit solution for Gaussian chains without

‡ Dedicated to Paul J. Flory on the occasion of his 70th birthday.

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preaveraging, which is reproduced later in this paper (cf. eq 21). However, for sufficiently complex molecular structures the calculation without the preaverage approximation becomes formidable, and resort to preaveraging becomes tempting. In that case, eq 12 is replaced by the approximation

$$(\rho,\mathcal{L}\rho)_{\text{pre}} = \sum_j^N \sum_k^N \langle \mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}\rangle \langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle \equiv q^2 \sum_j^N \sum_k^N \phi_{jk}{}^D \phi_{jk}{}^I \tag{15}$$

The principal object of the present paper is to investigate explicitly the errors that are induced by the preaveraging approximation of $\Gamma$ for typical linear and branched flexible macromolecular systems, with due regard for the effects of polydispersity. At the same time, we introduce an accurate and tractable approximation to the difference between exact and preaveraged results, in a form facilitating computation; thus we were able to give practically reliable predictions avoiding the preaveraging error even for highly branched and polydisperse systems. It may be mentioned that the preaveraging error in some cases may be as high as 40% in the calculation of $\Gamma$.

Our calculations are restricted to chain models in which each individual "bond" is permitted a Gaussian distribution of lengths and in which there are no directional correlations between neighboring bonds. Further, all sums over chain elements are replaced by integrals. This means that our treatment is devoid of all realism with respect to local chain structure and is therefore incapable of describing scattering at high values of the scattering vector. Formally, our manipulations correspond to the conditions $qb \ll 1$ and $N \gg 1$. This places no practical limitations on the application of our results to scattering of visible light, but it makes them of no use for the treatment of coherent neutron scattering.

## Scattering Function for a Pair of Chain Elements

Since eq 12–15 invoke sums over all pairs of chain elements, it is useful first to consider the scattering functions for a single pair and assess the effect of hydrodynamic preaveraging. The averages prescribed are conveniently done in two stages: The vector $\mathbf{R}_{jk}$ is first averaged over all orientations and subsequently over scalar distances $R_{jk}$. The first stage gives

$$\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle_{\text{or}} = z^{-1}\sin z \tag{16}$$

$$\langle \mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}\rangle_{\text{or}} = q^3(k_B T/\zeta)[\delta_{jk} + (1-\delta_{jk})(\zeta/6\pi\eta_0 z)] \tag{17}$$

$$\langle (\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle_{\text{or}} = q^3(k_B T/\zeta)[\delta_{jk} + (1-\delta_{jk}) \times (\zeta/4\pi\eta_0)(z^{-2}\sin z + z^{-3}\cos z - z^{-4}\sin z)] \tag{18}$$

with

$$z \equiv qR_{jk}$$

Subsequent averaging over a Gaussian distance distribution function, after writing $|j-k| = n$ and $\langle R_{jk}{}^2\rangle = nb^2$, produces the results

$$\phi_n{}^I = \exp(-x^2) \tag{19}$$

$$\phi_n{}^D = (k_B T/\zeta)\delta(n) + [1-\delta(n)]An^{-1/2} \tag{20}$$

$$\phi_n{}^Q = (k_B T/\zeta)\delta(n) + [1-\delta(n)]An^{-1/2}\,{}^3\!/_4 H(x) \tag{21}$$[4]

where

$$x^2 = nb^2q^2/6 \tag{22}$$

$$A = k_B T/(6^{1/2}\pi^{3/2}b\eta_0) \tag{23}$$

$$H(x) = (2x^{-1} + x^{-3})D(x) - x^{-2} \tag{24}$$

$$D(x) = \exp(-x^2)\int_0^x \exp(t^2)\,dt \tag{25}$$

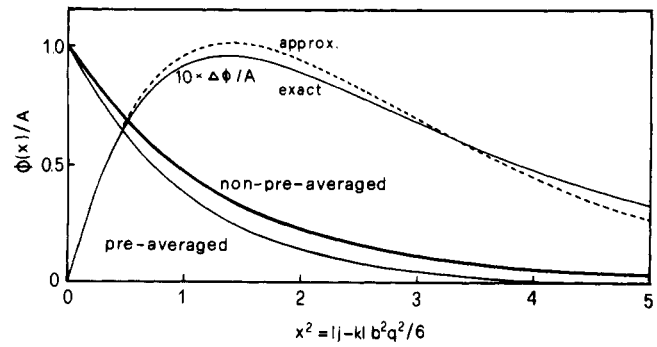


**Figure 1.** Contribution of one scattering pair with a Gaussian distance distribution for $R_{jk}$ to quasi-elastic scattering in the preaverage approximation, light line, and without this approximation, heavy line. The curves labeled "exact" and "approx." represent the difference between the nonpreaveraged and the preaveraged scattering contribution according to eq 18 and 26, respectively. $A = k_b T/(6^{1/2}\pi^{3/2}\eta_0 b|j-k|^{1/2})$.

the last function being the familiar Dawson integral.[11] In the preaveraged approximation, as seen from eq 15, we have simply

$$\phi_{n,\text{pre}}{}^Q = \phi_n{}^D\phi_n{}^I = (k_B T/\zeta)\delta(n) + [1-\delta(n)]An^{-1/2}\exp(-x^2) \tag{26}$$

The two scattering functions of eq 21 and 26 are displayed in Figure 1. The difference $\Delta\phi$ between them is also shown as a curve labeled "exact". A useful simple numerical approximation to this difference function is

$$\Delta\phi_n{}^Q = \phi_n{}^Q - \phi_n{}^D\phi_n{}^I \simeq 0.200An^{-1/2}x^2\exp(-a^2x^2); \quad a^2 = 0.72 \tag{27}$$

and is indicated as the dashed curve labeled "approx." in Figure 1. If values of the first cumulant calculated on the preaveraging approximation are corrected by means of the above numerical approximation, the results generally match the correct nonpreaveraged figures to about 1%, as will be seen later in some examples.

## First Cumulant: General Results

At sufficiently small wave vectors, the observable dynamic effect must come entirely from translational motions, and in that case we have[1]

$$D = \lim_{q\to 0} q^{-2}\Gamma \tag{28}$$

With eq 9 and 12 or 15, we then obtain

$$D = N^{-2}\sum_{j,k}\phi_{jk}{}^D = (k_B T/N\zeta) + (k_B T/6\pi\eta_0 N^2)\sum_{j\neq k}\langle R_{jk}{}^{-1}\rangle \tag{29}$$

which is precisely the equation for $D$ long ago given by Kirkwood.[6] However, it has been known for some time[7] that the Kirkwood equation is in general not exact (exceptions being spherically symmetric systems and, of course, free-draining molecules). When translational and internal motions are coupled, $D$ is not given by the unweighted average of eq 29 except at the very short times reflected in $\Gamma$. For flexible coils the steady-state diffusion coefficient has been calculated[12] to differ from the Kirkwood value by no more than 1.4%, which is probably within the error of most current measurements. In this paper we hereafter ignore this point, reserving more extensive discussion for another occasion.

It should be recalled that for molecules with rigid constraints (e.g., fixed bond lengths or angles) an appropriately modified diffusion tensor is needed.[13]

In the special case of free-draining hydrodynamics, complete neglect of the off-diagonal elements in eq 21 leads directly to

$$\Gamma_{fd} = q^2 k_B T/\zeta NP(q) = q^2 D_{fd}/P(q) \quad (30)$$

where the subscript "fd" stands for "free draining". This simple result was previously obtained by Büldt[14a] for the special case of Rouse (free-draining Gaussian) linear chains,[7,15] starting from Pecora's expression[16] for the complete time-correlation function, but it is here seen to hold for free-draining molecules of any structure.[14b] Hereafter in this paper and in its supplements, we ignore the free-draining contributions. These are physically inconsequential for long chains in dilute solution at low $q$ values such as are accessible in light-scattering measurements, and for very high $q$, such that $bq \ll 1$, our models are useless anyhow because they ignore local chain structure. We thus concentrate on the off-diagonal terms which arise from the hydrodynamic interactions and which depend on polymer architecture and polydispersity, and from now on when we speak of $\Gamma$ we mean the first cumulant after subtraction of the free-draining term.

At high $q$, but with the restriction $qb \ll 1$ that we impose on all our calculations, large unperturbed Gaussian molecules of any structure obey the asymptotic relation

$$\lim_{q\to\infty} q^{-3}\Gamma = k_B T/(16\eta_0) \quad (31)$$

This result, which is independent of polydispersity, branching, or ring formation, is first derived in the next section for the special case of linear chains and is then later generalized in Appendix I. Thus there is a range of $q$ values over which no information about molecular structure can be obtained from measurements of $\Gamma$. The corresponding expression for preaveraged chains has long been known[17] and contains a factor $1/(6\pi)$ in place of $1/16$.

## Monodisperse Linear Chains

Save for the replacement of a sum by an integral and a numerical refinement, the results of this section are contained in the work of AG.[4] For linear Gaussian chains, after substituting eq 21 in eq 12 and converting the double sum to an integral, we have

$$(\rho,\mathcal{L}\rho) = q^2 \int_0^N \phi_n^Q 2(N-n)\, dn = 3q^2 AN^{3/2}u^{-3} \int_0^u H(x)(u^2 - x^2)\, dx \quad (32)$$

where

$$u^2 \equiv b^2 q^2 N/6 = q^2\langle S^2\rangle \quad (33)$$

in which $\langle S^2\rangle$ represents the mean square radius of gyration. Integration by parts leads to

$$(\rho,\mathcal{L}\rho) = (3q^2 AN^{3/2}/(2u^3))[u + D(u) + 2(u^2-1)G(u)] \quad (34)$$

where

$$G(u) \equiv \int_0^u x^{-1} D(x)\, dx \quad (35)$$

The static structure factor, long ago given by Debye,[18] is

$$(\rho,\rho) = 2N^2 u^{-4}[u^2 - 1 + \exp(-u^2)] \quad (36)$$

Thus from eq 34 and 36 we obtain

$$\Gamma/q^2 = (3Au/(4N^{1/2})) \times [u + D(u) + 2(u^2-1)G(u)]/[u^2 - 1 + \exp(-u^2)] \quad (37)$$

Evaluation of the translational diffusion coefficient from eq 28 yields the well-known Kirkwood–Riseman expression

$$D = 8A/(3N^{1/2}) = 16k_B T/((6\pi)^{3/2}\eta_0 bN^{1/2}) \quad (38)$$

which may be substituted into eq 37 to give the alternative form

$$\Gamma/(q^2 D) = (9u/32) \times [u + D(u) + 2(u^2-1)G(u)]/[u^2 - 1 + \exp(-u^2)] \quad (39)$$

Limiting forms for small and large wave vectors are of special interest. For small $u$, we need the expansions

$$D(u) = u - (2u^3/3) + (4u^5/15) - \ldots$$

$$G(u) = u - (2u^3/9) + (4u^5/75) - \ldots$$

which in eq 39 lead to

$$\Gamma/(q^2 D) = 1 + (13u^2/75) + \ldots \quad (40)$$

At large $u$, the dominant term within the square brackets of the numerator in eq 37 is proportional to $u^2 G(u)$, and so (cf. Appendix I)

$$\lim_{q\to\infty} q^{-3}\Gamma = (k_B T/(4\eta_0\pi^{3/2}))G(\infty) = k_B T/(16\eta_0) \quad (41)$$

a result quoted earlier and observed to be independent of chain size and topology. The numerical coefficient in the above result is somewhat higher than an earlier numerical estimate of 0.055.

In similar fashion, the first cumulant for linear Gaussian chains with preaveraged hydrodynamic interactions is found to be

$$\Gamma_{pre}/(q^2 D) = (3\pi^{1/2}u/16)[(2u^2 - 1)\,\mathrm{erf}(u) + 2\pi^{1/2}u\exp(-u^2)]/[u^2 - 1 + \exp(-u^2)] \quad (42)$$

In this case the expanded form for low $q$ is

$$\Gamma_{pre}/(q^2 D) = 1 + (2u^2/15) + \ldots \quad (43)$$

and the asymptotic relation is

$$\lim_{q\to\infty} q^{-3}\Gamma_{pre} = k_B T/(6\pi\eta_0) \quad (44)$$

For numerical evaluation of $\Gamma$, direct use of the correct eq 37 involves a rather long computation of the double integral $G(u)$. Thus even for monodisperse chains it is economical and convenient to calculate $\Gamma_{pre}$ from eq 42 and then apply the approximation $\Gamma = \Gamma_{pre} + \Delta\Gamma$, where the correction term follows from the use of eq 27 in eq 12. The result is

$$\Delta\Gamma/(q^2 D) = 0.0375\pi^{1/2}ua^{-3}[(2u^2 - 3a^{-2})\,\mathrm{erf}(au) + 6a^{-1}\pi^{1/2}u\exp(-a^2u^2)]/[u^2 - 1 + \exp(-u^2)] \quad (45a)$$

or

$$\Delta\Gamma/\Gamma_{pre} = 0.100a^{-3}[(2u^2 - 3a^{-2})\,\mathrm{erf}(au) + 6a^{-1}\pi^{-1/2}u\exp(-a^2u^2)]/[(2u^2 - 1)\,\mathrm{erf}(u) + 2\pi^{-1/2}u\exp(-u^2)] \quad (45b)$$

with $a^2 = 0.72$. For small $u$, eq 45a gives exactly the difference $u^2/25$ between the exact eq 40 and the approximate eq 43. Asymptotically, the approximation leads to

$$\lim_{q\to\infty} q^{-3}(\Gamma_{pre} + \Delta\Gamma) = 0.0617k_b T/\eta_0 \quad (46)$$

which is about 1% below the exact value. In Figure 2 the exact and preaveraged values of $\Gamma/(q^2 D)$ are plotted against u, and the correction term $\Delta\Gamma/\Gamma$ is shown on the same figure.

## Polydisperse Linear Chains

Linear polymers obeying Schulz–Zimm chain-length distributions[19,20] have been treated in an earlier paper,[21] and here it is necessary only to add the correction term.

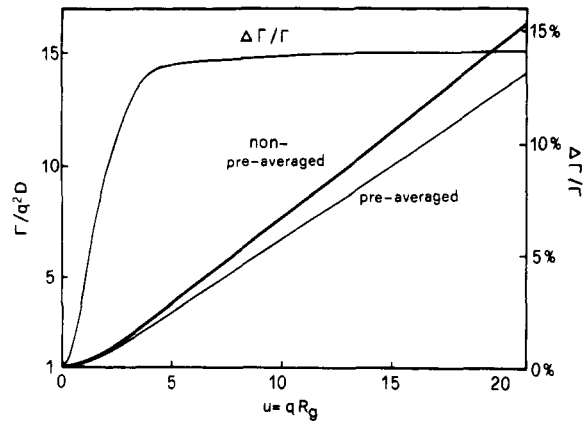


**Figure 2.** Influence of hydrodynamic preaveraging on the angular dependence of the first cumulant Γ and the relative error $\Delta\Gamma/\Gamma$ for monodisperse linear flexible chains. $R_g = \langle S^2\rangle^{1/2}$ is the radius of gyration.

**Table I**
**Coefficients in Equations 47-52**

| $k$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $C_k$ | 1 | 1/2 | 0.3747 | 0.3125 | 0.2730 | 0.2458 | 0.2251 |

For long chains, and with $qb \ll 1$, eq 40, 46, and 52 of ref 21 give

$$\Gamma_{pre}/(q^2D_z) = P_z(q)^{-1}\sum_{k=1}^{m} B_{mk}C_k(1 + v^2)^{1/2-k}/\sum_{k=1}^{m} B_{mk}C_k \quad (47)$$

$$P_z(q) = 2m^{-1}\sum_{k=1}^{m} B_{mk}(1 + v^2)^{-k} \quad (48)$$

$$D_z = 4k_BT(m + 2)^{1/2}\Gamma(m + 3)/(9\pi^{3/2}\eta_0\langle S^2\rangle_z^{1/2}\Gamma(m + 2)) = 2Ab\langle S^2\rangle_z^{-1/2}(m + 2)^{1/2}(6m^2)^{-1/2}\sum_{k=1}^{m} B_{mk}C_k \quad (49)$$

where $m$ is the index of the Schulz-Zimm ("gamma") distribution, such that the z average mean square radius of gyration is given by

$$\langle S^2\rangle_z = b^2P_w(m + 2)/(6(m + 1)) \quad (50)$$

in which $P_w$ is the weight-average degree of polymerization. Further,

$$v^2 = q^2\langle S^2\rangle_z/(m + 2) = u^2/(m + 2) \quad (51)$$

so that we preserve the definition of

$$u^2 \equiv q^2\langle S^2\rangle_z \quad (33')$$

in terms of measurable quantities. The numerical coefficients $C_k$ are listed in Table I, and $B_{mk} = 1 - (m + 1)^{-1}k$.

For the correction term, with the aid of eq 27 and a differential operation (cf. Appendix II), we obtain

$$\Delta\Gamma/\Gamma_{pre} = 0.100v^2\sum_{k=1}^{m} B_{mk}(2k - 1)C_k(1 + 0.72v^2)^{-1/(2-k)}/\sum_{k=1}^{m} B_{mk}C_k(1 + v^2)^{1/(2-k)} \quad (52)$$

In Figure 3, the dependence of this correction term on the polydispersity is shown for several values of the index $m$ and is seen to decrease slightly with increasing polydispersity (lower $m$).

To obtain the exact nonpreaveraged value of Γ for the small scattering angles, it is easiest to insert the expanded forms of eq 34 and 36 into the general relation

$$\Gamma = \sum w_N N^{-1}(\rho,\mathcal{L}\rho)_N/\sum w_N N P_N(q) \quad (53)$$

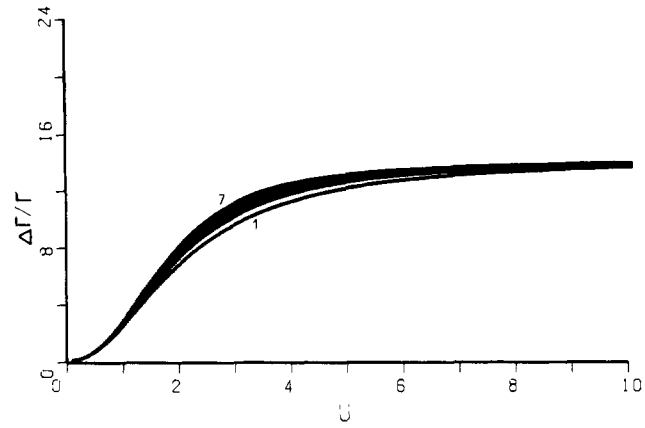


**Figure 3.** Influence of polydispersity on the relative error $\Delta\Gamma/\Gamma$ of the first cumulant introduced by the preaverage approximation. $m = (P_w/P_n - 1)^{-1}$ is the polydispersity parameter, where $P_w$ and $P_n$ are the weight and number average degrees of polymerization.

After performing the averages over a Schulz-Zimm distribution $w_N$ with index $m$, we find

$$\Gamma/(q^2D_z) = 1 + \frac{(13m + 32)}{75(m + 2)}u^2 + \ldots \quad (54)$$

The corresponding maneuver with the preaveraged result yields

$$\Gamma_{pre}/(q^2D_z) = 1 + \frac{(4m + 11)}{30(m + 2)}u^2 + \ldots \quad (55)$$

## Regular Monodisperse Stars

If a star molecule with a total of $N$ segments consists of $f$ identical rays, each of length $N_1 = N/f$, the required results are easily expressed in terms of those for linear chains by the formula

$$L(\text{star}) = f(f - 1)L(2N_1)/2 - f(f - 2)L(N_1) \quad (56)$$

where $L(N_1)$ is the expression for either $(\rho,\mathcal{L}\rho)$ or $(\rho,\rho)$ of a linear chain of length $N_1$ (i.e., a single ray) and $L(2N_1)$ is that of two coupled rays. The above relation is easily understood from the fact that there are $f(f - 1)2$ pairs of sums comprising two rays, but if these are simply added together the scattering contribution from single rays is then counted $f(f - 2)$ times too often. Since eq 56 is restricted to monodisperse regular stars, we use it only to check calculations and prefer to rely on an alternative equation previously derived by one of us,[22,23] which for long rays (inconsequential scattering contribution from the branch point itself) is

$$q^{-2}(\rho,\mathcal{L}\rho) = 2\sum_{n}^{N_1}(N_1 - n)\phi_n^Q + (f - 1)\sum_{n}^{N_1}\sum_{k}^{N_1}\phi_{n+k}^Q \quad (57)$$

with a corresponding expression for $(\rho,\rho)$ involving $\phi_n^I$. It is seen that for $f - 1$ this equation reduces to the correct result for linear chains.

For $q \to 0$, eq 57 leads to a diffusion coefficient

$$D = (8A/(3N^{1/2}))(2^{1/2} + f)(2^{1/2} - 1)f^{-1/2} \quad (58)$$

which is a well-known result[24] for stars. The exact first cumulant for regular stars will not be written here but could be found via eq 34 and 56. The preaveraged result (cf. Appendix III for some details) is found to be

$$\Gamma_{pre} = q^2DP(q)^{-1}3\pi^{1/2}(4w)^{-1}[(2 - f) + 2^{1/2}(f - 1)]^{-1}\{(1 - (2w)^{-1})\,\text{erf}(w) + (w\pi^{1/2})^{-1}e^{-w} + (f - 1)/2[(2 - (2w)^{-1})(\text{erf}(w2^{1/2}) - \text{erf}(w))(2w^2)^{-1}\,\text{erf}(w) + (w\pi^{1/2})^{-1}2(2^{-1/2}e^{-2w^2} - e^{-w^2})]\} \quad (59)$$

where the particle scattering factor is given by[25-27]

$$P(q) = (2/fw^2)[1 - w^{-2}(1 - e^{-w^2}) + (f - 1)(1 - e^{-w^2})^2/(2w^2)] \quad (60)$$

with

$$w^2 = b^2q^2N/6 = fq^2\langle S^2\rangle/(3f - 2) = fu^2/(3f - 2)$$

The correction term is

$$\Delta\Gamma = q^2DP(q)^{-1}3\pi^{1/2}(4w)^{-1}[(2 - f) + 2^{1/2}(f - 1)]^{0.100a^{-3}} \times \{(1 - (2a^2w^2)^{-1}3)\ \mathrm{erf}(aw) + (aw\pi^{1/2})^{-1}3e^{-a^2w^2} + (f - 1)[(1 - (4a^2w^2)^{-1}3)(\mathrm{erf}(aw2^{1/2}) - \mathrm{erf}(w)) + (4a^2w^2)^{-1}3\ \mathrm{erf}(aw) + (aw\pi^{1/2})^{-1}3(2^{-1/2}e^{-2a^2w^2} - e^{-a^2w^2})]\} \quad (61)$$

where $a^2 = 0.72$ as before. At small scattering angles, expansions yield

$$\Gamma_{pre}/(q^2D) = 1 + \left(\frac{1}{3} - \frac{f}{5(3f - 2)}\frac{3f + 2^{1/2}f - 2}{f + 2^{1/2}}\right)u^2 + \ldots \quad (62)$$

$$\Gamma/(q^2D) = 1 + \left(\frac{1}{3} - \frac{4f}{25(3f - 2)}\frac{3f + 2^{1/2}f - 2}{f + 2^{1/2}}\right)u^2 + \ldots \quad (63)$$

and for large $q$ the asymptotic behavior is again that of eq 46.

## Polydisperse Stars

The rays are now distributed in length according to the standard exponential or "most probable" law. Again from previous work[22,23] we have

$$q^{-2}(\rho,\mathcal{L}\rho) = (1 + \alpha)\sum_1^\infty \alpha^{n-1}\phi_n{}^Q + (f - 1)(1 - \alpha)\sum_{n=1}^\infty\sum_{k=1}^\infty \alpha^{n+k-2}\phi_{n+k}{}^Q \quad (64)$$

with an analogous formula for $(\rho,\rho)$. Here $\alpha$ is a reaction probability, such that the number-average chain length of a ray is $(1 - \alpha)^{-1}$. The translational diffusion coefficient and the weight-average degree of polymerization of the stars follow if $\phi_n{}^Q$ is replaced by $\phi_n{}^D$ and $\phi_n{}^I$ by unity, respectively, in eq 64.

With these operations, the diffusion coefficient is found to be

$$D_z = \pi^{1/2}A(f + 3)/(2(f + 1)^{1/2}p_w{}^{1/2}) = (k_BT/2\pi\eta_0)(f/6)^{1/2}(f + 3)(f + 1)^{-3/2}\langle S^2\rangle_z{}^{-1/2} \quad (65)$$

where

$$\langle S^2\rangle_z = b^2P_wf/(f + 1)^2 \quad (66)$$

The first cumulant and the correction term take the relatively simple forms

$$\Gamma_{pre}/(q^2D_z) = (1 + y^2)^{1/2}[1 + 4y^2(f + 3)^{-1}]/[1 + 2y^2(f + 1)^{-1}] \quad (67)$$

$$\Delta\Gamma/\Gamma_{pre} = \frac{0.100y^2(1 + y^2)^{3/2}(1 + 3f + 4a^2y^2)}{(1 + a^2y^2)^{5/2}(3 + f4y^2)} \quad (68)$$

and the particle scattering factor is[27]

$$P_z(q) = 1 + 2y^2(f + 1)^{-1}/(1 + y^2)^2 \quad (69)$$

where

$$y^2 = u^2(f + 1)/6f = q^2\langle S^2\rangle_z(f + 1)/6f$$

Table II
Coefficient of the Initial Slope of the First Cumulant as a Function of $u^2$ [a]

| model | $C_{pre}$ | $C$ |
|---|---|---|
| linear chains | | |
| $m = 1$ | 1/6 = 0.1666 | 1/5 = 0.2000 |
| $m = \infty$ | 2/15 = 0.1333 | 13/75 = 0.1733 |
| regular stars | | |
| $f = 1$ | 2/15 = 0.1333 | 13/75 = 0.1733 |
| $f = \infty$ | 1/25.6 = 0.0391 | 1/10.2 = 0.0979 |
| polydisperse stars | | |
| $f = 1$ | 1/6 = 0.1666 | 1/5 = 0.2000 |
| $f = \infty$ | 1/12 = 0.0893 | 2/15 = 0.1333 |

[a] $\Gamma = D_zq^2(1 + Cu^2 - \ldots)$ for limiting cases of linear chains and regular and polydisperse star macromolecules. The suffix "pre" denotes the coefficient in the preaverage approximation.

For the correct and approximate expressions at small angles we now have

$$\Gamma/(q^2D_z) = 1 + \frac{(2f^2 + 11f - 1)}{15f(f + 3)}u^2 + \ldots \quad (70)$$

and

$$\Gamma_{pre}/(q^2D_z) = 1 + \frac{(f^2 + 8f - 1)}{12f(f + 3)}u^2 + \ldots \quad (71)$$

## Discussion

The results presented above show considerable diversity, and the discussion here is confined to the influence of the hydrodynamic preaveraging approximation. The application of the results to the estimation of branching and polydispersity from light-scattering data will be treated in a future paper.[28]

Some limiting cases are of special interest. These are the monodisperse linear chains ($m = \infty$) and polydisperse linear chains with a most probable length distribution ($m = 1$). For the star molecules the values $f = 1$ (linear chains) and $f = \infty$ are characteristic marginal cases for the effect of branching and polydispersity. Table II gives a list of the coefficients $C$ in $\Gamma = D_zq^2(1 + Cu^2 - \ldots)$, where the suffix "pre" denotes the coefficient in the preaverage approximation.

One notices three general effects. First, in any case the initial slope is larger in the correct nonpreaveraged case than in the preaveraged approximation. Second, polydispersity causes an *increase* of the coefficient $C$. Third, branching causes a *decrease* of $C$, but this decrease is highly overestimated in the preaverage approximation.

How large the error is for stars with many rays may be seen from Figure 4a,b. While in the preaverage approximation a differentiation between a star of 10 or 100 rays appeared to be easy, it now becomes hardly possible from the correct nonpreaveraged cumulant. The polydisperse stars show similar behavior to that of the regular stars and are not shown here. The relative error $\Delta\Gamma/\Gamma$ introduced by the preaverage approximation is given in Figures 5 and 6 for the regular and polydisperse stars, respectively. The error is not significantly different from that of the linear chains as long as the ray number is less than 4. For stars with more rays, however, the error can become considerable and reach values up to 32 and 40% for the regular and polydisperse stars, respectively. In all cases $\Delta\Gamma/\Gamma$ approaches the limiting value of linear chains, as it should, although this asymptote may not in all cases be attainable by experiment.

The curves in Figures 5 and 6 exhibit a striking maximum in the region of $u = 4$–$8$ which becomes very pro-

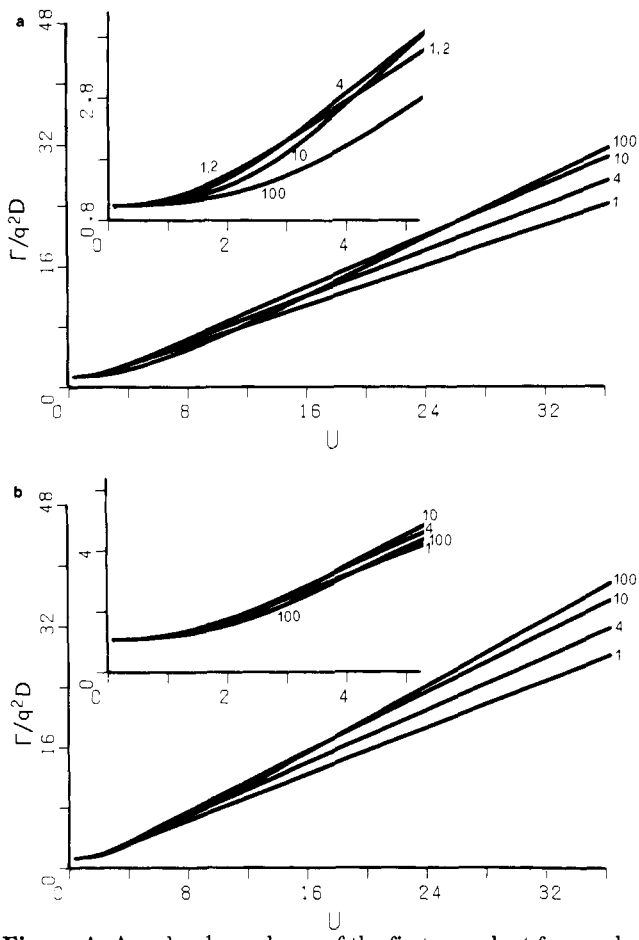


**Figure 4.** Angular dependence of the first cumulant for regular stars (a) in the preaverage approximation, (b) without hydrodynamic preaveraging. $f$ is the number of rays per star molecule and $u = q\langle S^2\rangle^{1/2}$. Insert: behavior at small $u$.

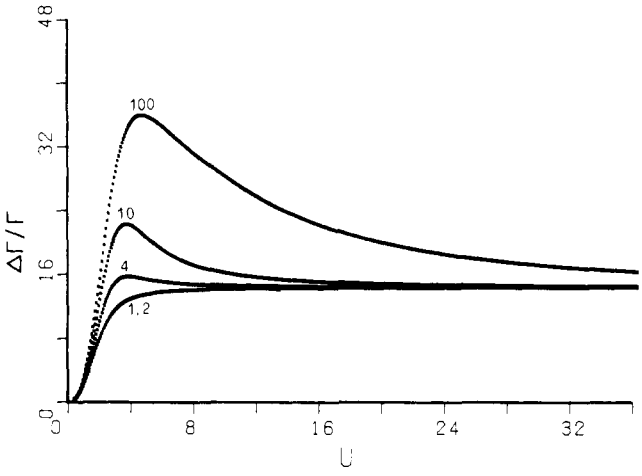


**Figure 5.** Relative error $\Delta\Gamma/\Gamma$ for regular stars.

nounced for stars with many rays. For a better understanding of this surprising effect it will be useful to recall the equation for the balance of the frictional forces, which reads, for the $i$'th chain element of velocity $\mathbf{u}_i$,

$$\zeta\mathbf{u}_i = \mathbf{F}_i + \zeta\sum_{j\neq i}^{N}\mathbf{T}_{ij}\mathbf{F}_j \qquad (72)$$

where

$$\mathbf{T}_{ij} = (8\pi\eta_0 R_{ij})^{-1}(1 - \delta_{ij})(1 + R_{ij}^{-2}\mathbf{R}_{ij}\mathbf{R}_{ij}) \qquad (73)$$

is the Oseen tensor for the hydrodynamic interaction and

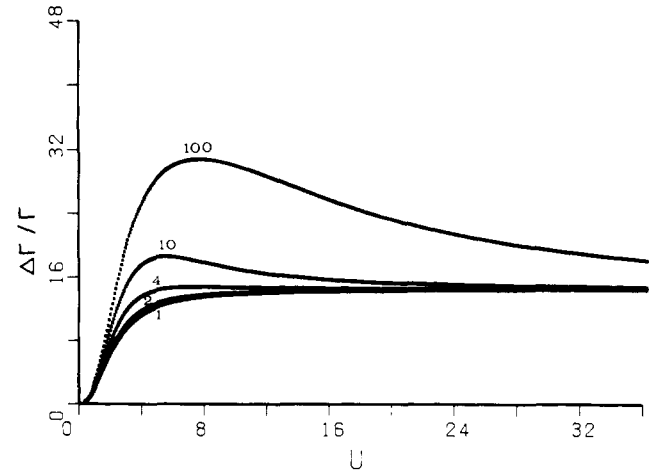


**Figure 6.** Relative error $\Delta\Gamma/\Gamma$ for polydisperse stars.

$\zeta$ is the frictional coefficient of an isolated chain element. The first term of the right-hand side of eq 72 represents the frictional force of the isolated chain element (no hydrodynamic interaction, HI), and the second term gives the additional force arising from the HI with the other $N - 1$ chain elements of the macromolecule. Obviously this additional force depends on how many chain elements are found on the average in a shell of thickness $dr$ at a distance $r$ apart from a unit selected at random, or in other words, on the local density in that shell. The difference between the preaveraged and nonpreaveraged HI can be expected to be large where the HI is also high.

According to Pekeris[29] and Debye and Bueche[30] a normalized space correlation function $\gamma(r)$ can be calculated from the particle scattering factor

$$\gamma(r) = (2\pi)^{-3}\int_0^\infty [P_z(q)\ (qr)^{-1}\sin qr]4\pi q^2\,dq \qquad (74)$$

The quantity $4\pi\gamma(r)\ r^2\ dr$ is the probability of finding another chain element in the shell volume $4\pi r^2\ dr$ if a randomly selected element was located at $r = 0$. Consequently

$$G(r)\ dr = P_w 4\pi\gamma(r)\ r^2\ dr \qquad (75)$$

is the local density in that shell, where $P_w$ is the weight average degree of polymerization. For the polydisperse stars the Fourier transformation can be carried out analytically with the result

$$G(r) = f^{-1}(f+1)(\langle S^2\rangle_z/12b^2)^{1/2}c^2x[2 + cx(f-1)/2]e^{-cx} \qquad (76)$$

with

$$c^2 = 6f/(f+1); \qquad x^2 = r^2/\langle S^2\rangle_z$$

Figure 7 shows this function for $f = 1$, 4, 10, and 100. One notices that around $x = 0.5$–$0.8$ the density in a shell of thickness $\Delta r = b/12^{1/2}$ is drastically increased with the number of attached star rays, and in that region the error of the hydrodynamic preaveraging should have its largest effect, which at least qualitatively corresponds to the observed maximum of $\Delta\Gamma/\Gamma$. At large $x$, i.e., at small $u$, the difference in density between the various stars and the linear chain becomes negligibly small, and $\Delta\Gamma/\Gamma$ goes to zero; the nonpreaveraged and the preaveraged HI yield the same result, i.e., identical values for the translational diffusion coefficient.

The smallest radius physically possible is $r_{min} = b/12^{1/2}$, which is the radius of gyration of a one-dimensional rigid bond. Within this volume one should find one chain ele-

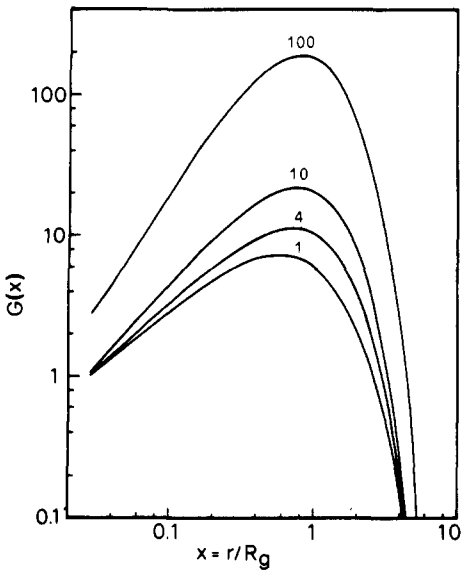


**Figure 7.** Density correlation function $G(x)$ as a function of the relative distance $x = r\langle S^2\rangle_z^{-1/2}$ for polydisperse star molecules with $\langle S^2\rangle_z^{1/2}/b = 10$. The figures at the curves denote the number $f$ of rays per molecule.

ment only, namely the unit selected at random. For $b^2/\langle S^2\rangle_z \ll 1$ we find from eq 76

$$G(r_{min}) \simeq 1 + \frac{f-1}{4}\left[\frac{b^2}{S^2_z}\frac{f}{2(f+1)}\right]^{1/2} \quad (77)$$

which gives $G(r_{min}) \simeq 1$ only if either $f = 1$ (linear chain) or if $b^2/\langle S^2\rangle_z$ is a very small number. In the example of Figure 7 a value of $b/\langle S^2\rangle_z^{1/2} = 10$ was chosen, and in this case one finds for $f = 10$ $G(r_{min}) = 1.152$, but for $f = 100$ one has $G(r_{min}) = 2.746$. This result is an obvious deficiency of the Gaussian chain model which in principle allows the presence of several units at the same place because of the neglect of the finite volume of the repeating unit. Of course, for small $b/\langle S^2\rangle_z^{1/2}$ the mean density of segments is low, and the overcrowding effect plays no significant role. For high segment densities, i.e., many rays of short length, the overcrowding of segments becomes important and must no longer be neglected, even under $\Theta$ conditions.

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## Appendix I. Asymptotic Behavior at large $q$

We need at large $u$ the value of $G(u)$ defined in eq 35:

$$G(\infty) = \int_0^\infty x^{-1}D(x)\,dx = \int_0^\infty x^{-1}\exp(-x^2)\int_0^x \exp(t^2)\,dt\,dx$$

Putting $t = \alpha x$, we have

$$G(\infty) = \int_0^\infty \exp(-x^2)\int_0^1 \exp(\alpha^2x^2)\,d\alpha\,dx = \int_0^1 d\alpha\int_0^\infty \exp[-x^2(1-\alpha^2)]\,dx = (\pi^{1/2}/2)\int_0^1 (1-\alpha^2)^{-1/2}\,d\alpha = \pi^{3/4}/4 \quad (A1)$$

which with eq 37 leads to eq 41.

To find general asymptotic behavior at large $q$ for any structure, we observe that the sumand $\phi_{jk}^Q$ of eq 12 at high $q$ decays to very small values before $|i-k|$ from almost any $j$ reaches a limit imposed by the particular molecular structure. The limit can therefore be made as large as we please, and so in this case

$$(\rho,\mathcal{L}\rho) = q^2\sum_j^N\sum_k^N\ldots \to q^2N\sum_{n=1}^\infty 2\phi_n^Q = (3q^2AN/2)\int_0^\infty H(x)\,n^{-1/2}\,dn = 3(6)^{1/2}NAqb^{-1}\int_0^\infty H(x)\,dx \quad (A2)$$

Integration by parts gives

$$\int_0^\infty H(x)\,dx = G(\infty) \quad (A3)$$

and this, together with the asymptotic form of eq 36, leads to the limiting value of $\Gamma$, eq 41.

## Appendix II. The Correction Term

The correction term describes the difference in the first cumulant between the nonpreaveraged and the preaveraged HI and is given by

$$\Delta\Gamma = \frac{\Delta(\rho,\mathcal{L}\rho)}{(\rho,\rho)} = (\rho,\rho)q^2A/5\sum_j^N\sum_k^N y^2|j-k|^{1/2}e^{-a^2y^2|j-k|} \quad (A4)$$

with $y^2 = b^2q^2/6$ and $A = k_BT/(6^{1/2}\pi^{3/2}b\eta_0)$. Obviously the right-hand side can also be written as

$$\Delta\Gamma = (\rho,\rho)q^2A/5\;\partial/\partial a^2\,(\sum_j^N\sum_k^N|j-k|^{-1/2}e^{-a^2y^2|j-k|}) \quad (A5)$$

According to eq 15 and 26 we have

$$\Gamma_{pre} = (\rho,\rho)q^2A\sum_j^N\sum_k^N|j-k|^{-1/2}e^{-y^2|j-k|}$$

Hence

$$\Delta\Gamma/\Gamma_{pre} = \frac{1}{5}\,\frac{\partial/\partial a^2\,(\sum_j^N\sum_k^N|j-k|^{-1/2}e^{-a^2y^2|j-k|})}{\sum_j^N\sum_k^N|j-k|^{-1/2}e^{-y^2|j-k|}} \quad (A6)$$

and the correction term is obtained from $\Gamma_{pre}$ by replacing $(\rho,\mathcal{L}\rho)y^2$ by $a^2y^2$ followed by differentiation with respect to $a^2$. Equation A6 is quite general and can be applied to any Gaussian chain model. Sometimes, however, it is easier to perform the required summation, or the corresponding integration, directly.

For polydisperse chains the parameter $v$ is used which is related[27] to $y^2$ and $\langle S^2\rangle_z$ by the relationships $y^2 = v^2(1-\alpha)$ and $\langle S^2\rangle_z = b^2(m + 2/(6(1-\alpha))$.

## Appendix III. Integrals in Equation 57 for $\Gamma_{pre}$ and $\Delta\Gamma$

On solving eq 56 for the regular stars some integrals occur which are not familiar. These are, for $\Gamma_{pre}$

$$I = \int_0^N (N-n)n^{-1/2}e^{-y^2n}\,dn = y^{-1}\pi^{1/2}N[(1-1/2w^2)\,\mathrm{erf}(w) + (w\pi^{1/2})^{-1}e^{-w^2}]$$

$$w^2 = y^2N \quad (A7)$$

$$II = \int_0^N\int_0^N (n+m)^{-1/2}e^{-y^2(n+m)}\,dn\,dm$$

and for $\Delta\Gamma$

$$\text{III} = \int_0^N n^{1/2}(N-n)e^{-a^2y^2n}\,dn = \pi^{1/2}N/(y^2a^3)[(1-3/2a^2w^2)\,\text{erf}(aw) + 3/(aw\pi^{1/2})e^{-a^2w^2}] \tag{A8}$$

$$\text{IV} = \int_0^N \int_0^N (n+m)^{1/2}e^{-a^2y^2(n+m)}\,dn\,dm$$

The evaluation of I and III is straightforward. For II, we first substitute $m^* = n + m$ which gives

$$\text{II} = \int_0^N dn \int_0^{n+N} (m^*)^{-1/2}e^{-y^2m^*}\,dm^* = y^{-1}\pi^{1/2}\int_0^N \text{erf}(y(n+m)^{1/2})\,dn - y^{-1}\pi^{1/2}\int_0^N \text{erf}(yn^{1/2})\,dn$$

A change of variables leads to

$$\text{II} = y^{-3}2\pi^{1/2}\int_0^{y(2N)^{1/2}} t\,\text{erf}(t)\,dt - 2\int_0^{y(N)^{1/2}} t\,\text{erf}(t)\,dt \tag{A9}$$

and with the known integral[11]

$$\int \text{erf}(t')\,dt' = t\,\text{erf}(t) + \pi^{-1/2}e^{-t^2}$$

one finds after partial integration

$$2\int t\,\text{erf}(t')\,dt' = (t^2 - \tfrac{1}{2})\,\text{erf}(t) + t\pi^{-1/2}e^{-t^2} \tag{A10}$$

Thus,

$$\text{II} = y^{-3}\pi^{1/2}\{(2w^2 - \tfrac{1}{2})[\text{erf}(2^{1/2}w) - \text{erf}(w)] + \tfrac{1}{2}\,\text{erf}(w) + [w(2/\pi)^{1/2}e^{-2w^2} - 2w^{-1/2}e^{-w^2}]\} \tag{A11}$$

By the same kind of substitutions and partial integration, the last integral becomes

$$\text{IV} = (ay)^{-5}\pi^{1/2}\{(a^2w^2 - \tfrac{3}{4})[\text{erf}(2^{1/2}aw) - \text{erf}(aw)] + \tfrac{3}{4}\,\text{erf}(aw) + [aw(2/\pi)^{1/2}e^{-a^2w^2} - 2aw^{-1/2}e^{-a^2w^2}]\} \tag{A12}$$

With these four integrals the equations for $\Gamma_{pre}$ and $\Delta\Gamma$ are verified after some tedious but elementary rearrangements.

## Appendix IV. Derivation of Equations 65-68 for Polydisperse Stars

We are interested in large star molecules. The weight average degree of polymerization is[27] $P_w = (f+\alpha)/(1-\alpha)$. Therefore, $1-\alpha$ is a small quantity and $\alpha$ can be well approximated by

$$\alpha \simeq e^{-(1-\alpha)}$$

Inserting now the expressions for $\phi_n{}^Q$ and $\phi_n{}^I$ into eq 57 and passing to integrals we get

$$\Gamma_{pre} = q^2A\left\{2\int_0^\infty n^{-1/2}e^{-(1-\alpha+\xi^2)n}\,dn + (f-1)(1-\alpha)\int_0^\infty\int_0^\infty (n+k)^{-1/2}e^{-(1-\alpha+\xi^2)(n+k)}\,dn\,dk\right\} \Big/ \left\{2\int_0^\infty e^{-(1-\alpha+\xi^2)n}\,dn + (f-1)(1-\alpha)\left[\int_0^\infty e^{-(1-\alpha+\xi^2)n}\,dn\right]^2\right\} \tag{A13}$$

All integrals in this equation are well known, and we find

$$\Gamma_{pre} = q^2A\pi^{1/2} \times \frac{2(1-\alpha+\xi^2)^{-1/2} + [(f-1)(1-\alpha)/2](1-\alpha+\xi^2)^{-3/2}}{2(1-\alpha+\xi^2) + (f-1)(1-\alpha)(1-\alpha+\xi^2)^{-2}} \tag{A14}$$

and after slight rearrangements

$$\Gamma_{pre} = q^2A\pi^{1/2}(1-\alpha)^{1/2}(1+y^2)^{1/2}\,\frac{2(1+y^2)+(f-1)/2}{2(1+y^2)+(f-1)} \tag{A15}$$

where we have used the abbreviations

$$y^2 = b^2q^2/(6(1-\alpha)) = u^2(f+1)/(6f)$$

$$\xi^2 = y^2(1-\alpha)$$

$$x^2 = nb^2q^2/6$$

From eq A15 we immediately get an expression for the diffusion coefficient

$$D_z = A\pi^{1/2}(1-\alpha)^{1/2}(f+3)/(2(f+1)) \tag{A16}$$

which with $P_w$ gives eq 65 of the text. Combination with eq A15 yields the result of eq 67. Similarly one finds for

$$\Delta\Gamma = 0.200q^2A\xi^2\left\{2\int_0^\infty n^{1/2}e^{-(1-\alpha+a^2\xi^2)n}\,dn + (f-1)\times(1-\alpha)\int_0^\infty\int_0^\infty (n+e)^{1/2}e^{-(1-\alpha+a^2\xi^2)(n+k)}\,dn\,dk\right\} \Big/ \{2(1-\alpha+\xi^2)^{-1} + (f-1)(1-\alpha)(1-\alpha+\xi^2)^{-2}\} \tag{A17}$$

Again the integrals are readily solved, and with eq A15 one finds eq 68 of the text.

$$\Delta\Gamma = 0.100\Gamma_{pre}y^2\frac{(1+y^2)^{3/2}}{(1+a^2y^2)^{5/2}}\,\frac{2(1+a^2y^2)+3(f-1)/2}{2(1+y^2)+(f-1)/2}$$

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