Application of Cascade Theory to Calculation of Quasielastic Scattering Functions. 1. Polydisperse, Ideal, Linear Chains in Dilute Solutions

Walther Burchard

Institute of Macromolecular Chemistry, University of Freiburg, Freiburg, West Germany.

Received December 12, 1977

ABSTRACT: The decay constant $\Gamma(q)$ of coherent quasielastic scattering correlation functions is calculated for flexible polydisperse linear chains obeying Schulz–Zimm chain length distributions. The relationships cover the whole region from quasielastic light scattering ($qb \ll 1$) up to coherent quasielastic neutron scattering ($qb \simeq 1$). The calculations take account of hydrodynamic interaction between segments (Zimm model). Identical curves are obtained for all polydispersity parameters $m = (P_w/P_n)^{-1}$ if $\Gamma/q^2 = D_{app}(q)$ is plotted against q. The curves can in a wide range of q be approximated by $\Gamma/q^2 = 0.053q(kT/\eta_0)$. At very large q values deviations from the straight line up to 10% are obtained. At very small q values the curve can be extrapolated toward $q \rightarrow 0$; the resulting intercept is the z-average diffusion constant D_z. A plot of D_{app}/D_z vs. $u^2 = \langle S^2\rangle_z q^2$ yields at low u^2 values a common straight line of slope $1/6$ for all m parameters. Therefore, quasielastic light scattering allows determination of D_z and $\langle S^2\rangle_z$ simultaneously. While the curves D_{app}/D_z as a function of u depend only slightly on polydispersity, D_z has a more pronounced polydispersity dependence. The product $D_z\langle S^2\rangle_z^{1/2}$, directly measurable by means of quasielastic light scattering, varies within 15% when passing from monodisperse to polydisperse chains with $P_w/P_n = 2$. This variation is sufficient for a determination of the polydispersity of large linear macromolecules.

Since the development of theories for the dynamics of flexible polymer chain molecules by Rouse,[1] Bueche,[2] and Zimm[3] and the versatile range of experimental techniques for measuring quasielastic neutron[4] and quasielastic light scattering[5,6] many attempts have been undertaken to calculate the quasielastic scattering functions. The problem was first attacked by Pecora[7,8] and partially solved for fairly small values of $\langle S^2\rangle q^2$,[9] where $\langle S^2\rangle$ is the mean-square radius of gyration and $q = (4\pi/\lambda)\sin\theta/2$ is the value of the scattering vector, with λ the wavelength of the scattering wave in solution and θ the scattering angle. The behavior at large values of $\langle S^2\rangle q^2$, the region of neutron scattering, was calculated by de Gennes[10] and Dubois-Violette and de Gennes[11] who applied a different technique of calculation. Recently, Akcasu and Gurol[12] succeeded in the derivation of equations which cover the full range of q values accessible to quasielastic light and neutron scattering. This result became possible by application of the linear response theory combined with the projection operator technique developed for purposes of polymers by Bixon[13] and Zwanzig[14,15] (also, see Berne et al.[16,17]).

The purpose of the present paper is the derivation of formulas for the decay constant (or line width) in the scattering correlation function for polydisperse systems of ideal linear chains. This is easily performed by means of cascade theory when the formulas derived by Akcasu and Gurol are brought into a slightly different form.

Dynamic Equations for Monodisperse Chains

According to linear response theory[13–16] the time correlation function of a dynamic process is given by

$$\frac{dg_1(t)}{dt} = -\Gamma g_1(t)t + \int_0^t \phi(u)g_1(t-u)\,du \qquad (1)$$

where Γ is called the "frequency" and $\phi(t)$ the "memory" term. Estimates by Zwanzig[14] show that the memory function $\phi(t)$ for Brownian particles is a rapidly decaying correlation function and negligibly small at correlation times larger than 10^{-8} s. Neglecting therefore the memory term, eq 1 can be integrated formally to yield

$$g_1(t) = \exp(-\Gamma t) \qquad (2)$$

where Γ is now the decay constant.

In coherent quasielastic scattering the dynamic variable of interest is

$$\rho(t) = \sum_{j=1}^{N} \exp(i\mathbf{q}\mathbf{R}_j) \qquad (3)$$

where N is the number of segments (in the sense of the Rouse–Zimm model) in a particle, and $\mathbf{R}_j$ is the position vector of the jth segment from the origin. The value of the scattering vector $\mathbf{q}$ is connected with the scattering angle θ and the wavelength of the primary beam in the solution

$$q = (4\pi/\lambda)\sin\theta/2 \qquad (4)$$

With the dynamic variable of eq 3 the time correlation function of the quasielastic scattering is defined as

$$g_1(t) = \langle\rho(0)\rho^*(t)\rangle/\langle\rho(0)\rho^*(0)\rangle \qquad (5)$$

where the angle brackets denote the ensemble average. The decay constant Γ is given in the notation of projection operators as

$$\Gamma = (\rho,L\rho)/(\rho,\rho) \qquad (6)$$

where explicitly written

$$(\rho,L\rho) = \int_0^\infty (\rho(0)L\rho^*(0))\psi_0\{\mathbf{R}\}\,d\{\mathbf{R}\} \qquad (7)$$

and

$$(\rho,\rho) = \int_0^\infty (\rho(0)\rho^*(0)\psi_0\{\mathbf{R}\}\,d\{\mathbf{R}\} = \langle\rho(0)\rho^*(0)\rangle \qquad (8)$$

The function $\psi_0\{\mathbf{R}\}$ is the equilibrium distribution function ($t = 0$) for the coordinates of the chain and may be expressed as usual by the partition function of the system. Finally L is an operator which was derived by Bixon[13] from Kirkwood's generalized diffusion equation[18]

$$L = \left[\sum_l^N \sum_j^N (kT)^{-1}\nabla_l U\cdot\mathbf{D}_{lj}\cdot\nabla_j - \nabla_l\cdot\mathbf{D}_{lj}\cdot\nabla_j\right] \qquad (9)$$

Equation 8 is related to the particle scattering factor $P_N(q)$ which becomes clear when eq 3 is inserted in eq 8

$$\langle\rho(0)\rho^*(0)\rangle = \sum_l^N \sum_j^N \langle\exp(i\mathbf{q}\cdot[\mathbf{R}_l(0) - \mathbf{R}_j(0)])\rangle = N^2P_N(q) \qquad (10)$$

where the last equality follows directly from the theory of elastic scattering.[19–21]

0024-9297/78/2211-0455$01.00/0

As shown by Bixon[13] relationship 7 can be rearranged without any specification to a model as follows

$$(\rho,L\rho) = \sum_{l\neq j}^{N}\sum^{N} \mathbf{q}\cdot\langle \mathbf{D}_{lj}\exp(i\mathbf{q}\cdot\mathbf{R}_{lj})\rangle\cdot\mathbf{q} + \sum_{l=1}^{N}\mathbf{q}\cdot\langle\mathbf{D}_{ll}\rangle\cdot\mathbf{q} \qquad (11)$$

Here the angle brackets mean the average with respect to the pair distance distribution $P(\mathbf{R}_{lj})$ where $\mathbf{R}_{lj} = \mathbf{R}_l(0) - \mathbf{R}_j(0)$, i.e., at times $t = 0$. The diffusion tensor is defined as

$$\mathbf{D}_{lj} = kT[\mathbf{T}_{lj} - \zeta^{-1}\mathbf{I}\delta_{lj}] \qquad (12)$$

where $\mathbf{T}_{lj}$ is the Oseen tensor which describes the hydrodynamic interaction between segments j and l

$$\mathbf{T}_{lj} = (8\pi\eta_0 R_{lj})^{-1}(\mathbf{I} + \mathbf{R}_l\mathbf{R}_j/R_{lj}^2) \qquad (13)$$

Assuming Gaussian statistics the pair distance distribution is given by

$$P(\mathbf{R}_{lj}) = \left(\frac{3}{2\pi b^2|l-j|}\right)^{3/2}\exp\left(-\frac{3}{2}\frac{|\mathbf{R}_{lj}|^2}{b^2|l-j|}\right) \qquad (14)$$

Akcasu and Gurol were able to perform the required integration in eq 11. Their formula is, however, fairly complicated and is not suited for application to cascade theory or other techniques for calculating averages over a molecular weight distribution. Instead, therefore, the preaveraged diffusion tensor is used, i.e.,

$$\langle\mathbf{D}_{lj}\exp(i\mathbf{q}\cdot\mathbf{R}_{lj})\rangle = \langle\mathbf{D}_{lj}\rangle\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{lj})\rangle \qquad (15)$$

This approximation appears to be justified in the light of the calculations by Akcasu and Gurol who compared the exactly averaged function with that of the preaveraged diffusion tensor. Appreciable deviations were found at values of $qb \sim 1$ only, where b^2 is the mean-square distance between two consecutive segments. In that region the validity of a Gaussian pair distance distribution is doubtful anyway.

With the use of the preaveraged diffusion tensor eq 11 becomes

$$(\rho,L\rho) = q^2(kT/\zeta)\left[N + (\zeta/\eta_0 b)(1/6^{1/2}\pi^{3/2}) \times \sum_{l\neq j}^{N}\sum^{N}|l-j|^{-1/2}\exp(-q^2b^2|l-j|/6)\right] \qquad (16)$$

Since

$$\int_0^\infty \exp(-\beta^2|l-j|)\,\mathrm{d}\beta = \frac{1}{2}\left(\frac{\pi}{|l-j|}\right)^{1/2} \qquad (17)$$

eq 16 may be written in a form which is more convenient for the calculations below

$$(\rho,L\rho) = q^2(kT/\zeta)\left[N + \frac{2\zeta}{6^{1/2}\pi^2\eta_0 b} \times \int_0^\infty \sum_{l\neq j}^{N}\sum^{N}\exp(-(q^2b^2/6 + \beta^2)|l-j|)\,\mathrm{d}\beta\right] \qquad (18)$$

The three eq 6, 10, and 18 are the starting relationships for the calculation of the average decay constant $\overline{\Gamma}_{\mathrm{QS}}$ observed in quasielastic scattering from polydisperse systems.

Polydisperse Linear Chains

General Relationships. In monodisperse systems the autocorrelation function of a linear chain is a single exponential and can be exhaustively described by the decay constant of eq 6. In polydisperse systems the normalized correlation function is the sum of exponentials[17,22,23]

$$\overline{g_1(t)} = \frac{\Sigma w_N M_N P_N(q)\exp(-\Gamma_N(q)t)}{\Sigma w_N M_N P_N(q)} \qquad (19)$$

where w_N is the weight fraction of chains of molecular weight M_N, particle scattering factor $P_N(q)$, and the decay constant $\Gamma_N(q)$. The function in eq 19 is clearly not a single exponential but has a weaker decaying tail. The *initial* part of the function can still be approximated by an exponential with an average decaying constant $\overline{\Gamma}_{\mathrm{QS}}$ which is found by expansion of the exponentials in eq 19

$$\overline{\Gamma}_{\mathrm{QS}} = \frac{\Sigma w_N M_N P_N(q)\Gamma_N(q)}{\Sigma w_N M_N P_N(q)} \qquad (20)$$

Only the initial part of $\overline{g}_1(t)$ can be described with eq 20 but not the full correlation function which contains further details on the molecular weight distribution w_{N}.

Inserting eq 6 into eq 20 one obtains

$$\overline{\Gamma}_{\mathrm{QS}} = \frac{\Sigma w_N N^{-1}(\rho,L\rho)}{\Sigma w_N N P_N(q)} \qquad (21)$$

where use was made of eq 10. Since for Gaussian chains

$$\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{lj})\rangle = \exp(-q^2b^2|l-j|/6) \qquad (22)$$

one obtains from eq 21 and 18

$$\overline{\Gamma}_{\mathrm{QS}} = \overline{\Gamma}_1 + \overline{\Gamma}_2 \qquad (23)$$

with

$$\overline{\Gamma}_1 = (q^2kT/\zeta)/(P_{\mathrm{w}}P_{\mathrm{z}}(q)) \qquad (24)$$

$$\overline{\Gamma}_2 = [(q^2kT/\zeta)/(P_{\mathrm{w}}P_{\mathrm{z}}(q)]\frac{2\zeta}{6^{1/2}\pi^2\eta_0 b}\int_0^\infty \Sigma\, w_N N^{-1} \times \sum_{l\neq j}^{N}\sum^{N}\exp(-(\beta^2 + q^2b^2/6)|l-j|)\,\mathrm{d}\beta \qquad (25)$$

where the relationship has been used

$$P_{\mathrm{w}}P_{\mathrm{z}}(q) = \sum_{N=1}^{\infty} w_N N^{-1}\sum_{l=1}^{N}\sum_{j=1}^{N}\exp(-(q^2b^2/6)|l-\mathrm{j}|) = \sum_{N=1}^{\infty} w_N N P_N(q) \qquad (26)$$

P_{w} is the weight-average degree of polymerization and $P_{\mathrm{z}}(q)$ the z average of the particle scattering factor. The first term in eq 23 represents the so called Rouse term, and the second term takes account of the hydrodynamic interaction (Zimm term).

The sums in eq 25 and 26 are of the general form

$$\sum_{N=1}^{\infty} w_N N^{-1}\sum_{l\neq j}^{N}\sum^{N}\phi_{lj} = \sum_{N=1}^{\infty} w_N N^{-1}\sum_{l\neq j}^{N}\sum^{N}\phi^{|l-j|} \qquad (27)$$

where

$$\phi = \begin{cases}\exp(-q^2b^2/6) & \text{in eq 26}\\ \exp(-(\beta^2 + q^2b^2/6)) & \text{in eq 25}\end{cases}$$

Sums of that kind can be readily evaluated by means of path weighted generating functions as introduced by Kajiwara et al.[24] To this end the chains are represented as rooted trees where any of the repeat units chosen at random may be "planted" as the root of a "tree". These trees from linear chains have, of course, two branches only. Since any of the repeating units have the same chance to become a root, one has to consider the full set of trees where each of the N units of an N-mer has become the root of a tree. Equation 27 can then be rearranged

$$\sum_{N=1}^{\infty} w_N N^{-1}\sum_{l\neq j}^{N}\sum^{N}\phi_{lj} = \sum_{N=1}^{\infty} w_N N^{-1}\sum_{l=1}^{N}\sum_{n=1}^{N} m_{lnN}\phi_n \qquad (28)$$

In this equation at the right l is the running index for the roots, and m_{lnN} the number of units in the n-th generation of an N-meric tree if the repeating unit l was chosen as root. ϕ_n is a function of the length of a path running from a unit in the nth generation to the root, i.e., the number m_{lnN} is weighted according to the path length which corresponds to the distance between two chain elements l and j. The sum of eq 28 is derived by a simple differentiation process of a probability generating function of the type

$$U_0(s) = \sum_{N=1}^{\infty} w_N N^{-1} \sum_{l=1}^{N} s^{\Sigma_{n-1}^{N} m_{lnN}\phi_n} \tag{29}$$

from which one finds

$$U_0'(1) = \left.\frac{\mathrm{d}U_0(s)}{\mathrm{d}s}\right|_{s=1} = \sum_{N=1}^{\infty} w_N N^{-1} \sum_{l=1}^{N} \sum_{n=1}^{N} m_{lnN}\phi_n \tag{30}$$

The path weighted generating function of eq 29 can be constructed from link probabilities by the cascade theory, a technique first discovered by Watson and Galton,[25] forgotten, rediscovered by R. Fisher,[26] further developed by Good,[27,28] and adapted and applied to polymers by Gordon and his coworkers.[29,30] Link probabilities are defined as the probabilities for the formation of a bond between two monomer units. In polycondensates the link probability is equivalent to the extent of reaction, and in addition polymers the link probabilities can be calculated from the kinetic constants.[31]

Linear Chains which Obey the Schulz-Zimm Molecular Weight Distribution

The Schulz-Zimm molecular weight distribution results from an $(m - 1)$-fold convolution of a Schulz-Flory most probable distribution (coupling of m primary chains having the most probable distribution).[32,33] For large chain lengths this distribution has the form

$$w_N = \frac{N^m}{m!} y^{m+1} \exp(-yN) \tag{31}$$

with

$$y = m/P_n = 1 - \alpha \tag{32}$$

In these equations P_n tenotes the number-average degree of polymerization. Here $y^{-1} = P_n/m = P_{n0}$ is the number-average degree of polymerization of the primary chains before coupling which according to Flory is given by[34]

$$P_{n0} = (1 - \alpha)^{-1} \tag{33}$$

where α, briefly called link probability, is the probability that two monomers have reacted.

The path weighted generating function based upon this link probability and the cascade theory has been derived by Franken and Burchard previously.[35] For the derivative the authors obtained

$$U_0'(1) = \phi_0 + \frac{2}{m} \sum_{k=1}^{m} (m - k + \alpha)(1 - \alpha)^{k-1} \times \left[\sum_{i_1=1}^{\infty} \alpha^{i_1-1} \sum_{i_2=1}^{\infty} \alpha^{i_2-1} \ldots \sum_{i_k=1}^{\infty} \alpha^{i_k-1} \phi_{i_1+i_2+\ldots i_k} \right] \tag{34}$$

This equation simplifies considerably under conditions such that

$$\phi_n = \phi^n \tag{35}$$

$$U_0'(1) = \phi_0 + \frac{2}{m} \sum_{k=1}^{m} \frac{m - k + \alpha}{1 - \alpha} \left[\frac{(1 - \alpha)\phi}{1 - \alpha\phi} \right] \tag{36}$$

The term ϕ_0 added here is the weight of the root when the path length is zero.This term vanishes for all weighting functions which can be written as

$$\phi_{lj} = |l - j|^a \tag{37}$$

where a is a rational number.

Table I
Values of the Constants $c(k)$ in Equation 45 for Different k Values

k	$c(k)$	k	$c(k)$
1	1.000	5	1.365
2	1.000	6	1.475
3	1.124	7	1.576
4	1.250		

Insertion of $\phi = \exp(-q^2b^2/6)\exp(-\beta^2)$ in eq 36 yields for $\bar{\Gamma}_{QS}$ defined in eq 23

$$\bar{\Gamma}_{QS} = (q^2kT/\zeta)/(P_wP_z(q)) \left[1 + 2\zeta/(6^{1/2}\pi^2\eta_0 b) \times \frac{2}{m} \sum_{k=1}^{m} \frac{m - k + \alpha}{1 - \alpha} \int_0^{\infty} \left(\frac{(1 - \alpha)Z\exp(-\beta^2)}{1 - \alpha Z\exp(-\beta^2)} \right)^k \mathrm{d}\beta \right] \tag{38}$$

with the abbreviation

$$Z = \exp(-q^2b^2/6) \tag{39}$$

The relationship for $P_wP_z(q)$ is obtained for $\beta = 0$, and P_w is found from eq 38 for $\beta = q = 0$. The latter relationships were calculated previously[35] and are listed below together with P_n and the polydispersity P_w/P_n

$$P_wP_z(q) = 1 + \frac{2}{m} \sum_{k=1}^{m} \frac{m - k + \alpha}{1 - \alpha} \left(\frac{(1 - \alpha)Z}{1 - \alpha Z} \right)^k \tag{40}$$

$$P_w = (m + \alpha)/(1 - \alpha) \tag{41}$$

$$P_n = m/(1 - \alpha) \tag{42}$$

$$P_w/P_n = 1 + \alpha/m = 1 + 1/m \tag{43}$$

Finally the translational diffusion constant is obtained from eq 37 by setting $q = 0$ in $\bar{\Gamma}_{QS}/q^2$, i.e., $Z = 1$

$$D_z = \frac{kT}{P_w\zeta} \left[1 + 2\zeta/(6^{1/2}\pi^2\eta_0 b) \times \frac{2}{m} \sum_{k=1}^{m} \frac{m - k + \alpha}{1 - \alpha} \int_0^{\infty} \left(\frac{(1 - \alpha)\exp(-\beta^2)}{1 - \alpha\exp(-\beta^2)} \right)^k \mathrm{d}\beta \right] \tag{44}$$

Computations

The integral in eq 38 can be approximated by

$$\int_0^{\infty} \left[\frac{(1 - \alpha)Z\exp(-\beta^2)}{1 - \alpha Z\exp(-\beta^2)} \right]^k \mathrm{d}\beta = \frac{(1 - \alpha)^k}{k} \left[\frac{1.5c(k)}{(1 - \alpha Z)^{k-0.5}} - 1.1 \right] \tag{45}$$

where the constants $c(k)$ are listed in Table I. The approximation is valid within 0.1% for the k values given in the table if $0.875 \leq \alpha Z \leq 1.0$. For larger k values $c(k)$ is no longer a constant but depends slightly on the magnitude of αZ, and the integrals have to be evaluated numerically. With the approximation of eq 45 one has

$$\frac{\bar{\Gamma}_{QS}}{q^2kT/\zeta} = (P_wP_z(q))^{-1} \left[1 + \frac{2\zeta}{6^{1/2}\pi^2\eta_0 b} \times \frac{2}{m} \sum_{k=1}^{m} \frac{m - k + \alpha}{1 - \alpha} \frac{(1 - \alpha)^k}{k} \left(\frac{1.57c(k)}{(1 - \alpha Z)^{k-0.5}} - 1.1 \right) \right] \tag{46}$$

and

$$D_z = \frac{kT}{P_w\zeta} \left[1 + \frac{2\zeta}{6^{1/2}\pi^2\eta_0 b} \frac{2}{m} \sum_{k=1}^{m} \frac{m - k + \alpha}{1 - \alpha} \times \left(\frac{1.57c(k)}{k(1 - \alpha)^{-0.5}} - 1.1 \frac{(1 - \alpha)^k}{k} \right) \right] \tag{47}$$

For large P_w the link probability is $\alpha \sim 1$, and the second

Table II
Variation of the Constants K_s and K_{pw} with the Parameter $m = (P_w/P_n - 1)^{-1}$ [a]

P_w/P_n	m	K_s	K_{pw}
2.0	1	0.0918	0.1836
1.5	2	0.0884	0.1874
1.333	3	0.0864	0.1892
1.25	4	0.0852	0.1905
1.20	5	0.0844	0.1914
1.167	6	0.0838	0.1920
1.143	7	0.0832	0.1921
1.0	∞	0.0800	0.1960

[a] The values for the monodisperse case were taken from Yamakawa.[36]

term in eq 46 and 47 is large compared to 1. Hence

$$\frac{\overline{\Gamma}_{QS}}{q^2} \equiv D_{app}(q) = \frac{D_z \sum_{k=1}^{m} \left(\frac{m+1}{k} - 1\right) c(k) \left(\frac{1-\alpha}{1-\alpha Z}\right)^{k-0.5}}{P_z(q) \sum_{k=1}^{m} \left(\frac{m+1}{k} - 1\right) c(k)} \qquad (48)$$

and

$$D_z = \frac{kT}{\eta_0} 0.1299 \langle S^2 \rangle_z^{-1/2} \frac{2}{m(m+1)} \times \left(\frac{m+2}{6}\right)^{1/2} \sum_{k=1}^{m} \left(\frac{m+1}{k} - 1\right) c(k) \qquad (49)$$

$$D_z = \frac{kT}{\eta_0} K_s(m) \langle S^2 \rangle_z^{-1/2} \qquad (49')$$

or

$$D_z = \frac{kT}{b\eta_0} K_{pw}(m) P_w^{-1/2} \qquad (50)$$

with

$$K_{pw}(m) = \left(\frac{6(m+1)}{m+2}\right)^{1/2} K_s(m) \qquad (51)$$

Here use has been made of a relationship for the mean-square radius of gyration derived previously[35]

$$\langle S^2 \rangle_z = b^2/6 \frac{(m+1)(m-1+3\alpha)}{(1-\alpha)(m+\alpha)} \rightarrow b^2/6 \frac{m+2}{1-\alpha} \qquad (52)$$

The values of K_{pw} and K_s are listed in Table II for various m values.

Discussion

Angular Dependence of the Decay Constant. A fairly simple relationship is obtained from eq 48 for the case $m = 1$, which represents the most probable molecular weight distribution.

$$\frac{\overline{\Gamma}_{QS}}{q^2} = D_{app}(q) = \frac{D_z}{P_z(q)} \left(\frac{1-\alpha}{1-\alpha Z}\right)^{1/2} = D_z P_z(q)^{-1/2} \left(\frac{1+\alpha}{1+\alpha Z}\right)^{1/2} \alpha Z \rightarrow D_z P_z(q)^{-1/2} \qquad (53)$$

The arrow indicates the limit of large degrees of polymerization ($\alpha \sim 1$) and fairly small q values. In that limit the particle scattering factor is[35,33]

$$P_z(q) = (1 + \langle S^2 \rangle_z q^2/3)^{-1} \qquad (54)$$

and thus with eq 53

$$D_{app}(q) = D_z(1 + \langle S^2 \rangle_z q^2/3)^{+1/2} \qquad (55)$$

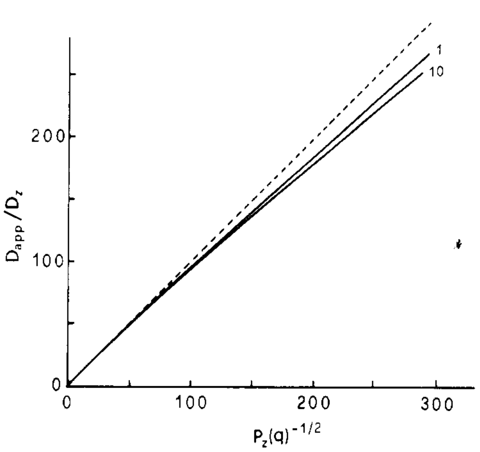

Figure 1. Plot of D_{app}/D_z against $P_z(q)^{-1/2}$ for chains of different polydispersity. $D_{app} = \overline{\Gamma}_{QS}/q^2$ is an apparent diffusion constant, $D_z = D_{app}$ ($q = 0$) is the z average of the translatory diffusion constant, and $P_z(q)$ is the z average of the particle scattering factor. $m = (P_w/P_n - 1)^{-1}$ is a parameter describing polydispersity. Dotted line: direct proportionality with $P_z(q)^{-1/2}(P_w = 10^6)$.

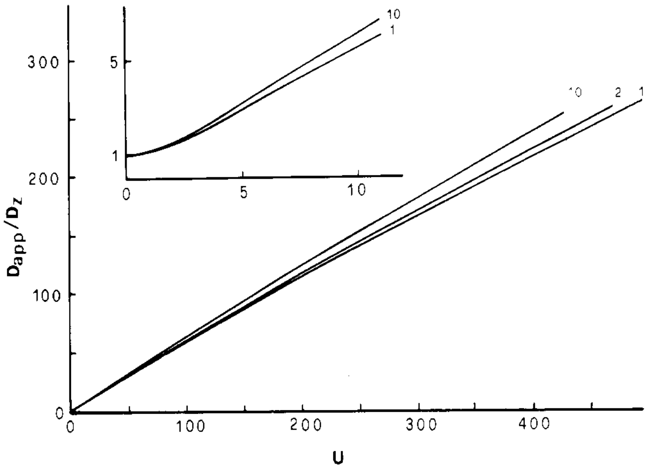

Figure 2. Plot of D_{app}/D_z as a function of $u = \langle S^2 \rangle_z^{1/2} q$ for chains of different polydispersity; insert: behavior at small u values (light scattering region) ($P_w = 10^6$).

From this equation it follows for small q

$$D_{app}(q) = D_z(1 + \langle S^2 \rangle_z q^2/6 + \ldots) \qquad (56)$$

and for large q

$$D_{app}(q) \rightarrow D_z \langle S^2 \rangle_z^{+1/2} 3^{-1/2} q \qquad (57)$$

With eq 49′ this can also be written as

$$D_{app}(q) \rightarrow \frac{kT}{\eta_0} 0.053 q \qquad (58)$$

The same q dependence has been derived previously for infinitely long monodisperse chains by Dubois-Violette and de Gennes,[11] by Freed et al.,[37] and by Akcasu and Gurol,[12] but with the slightly larger constant of 0.055. The smaller value is probably the consequence of the preaveraged Oseen tensor approximation, since Akcasu–Gurol found with monodisperse chains also a slightly lower curve (their Figure 2) when using the preaverage approximation. We did not succeed in deriving the corresponding numerical constants for chains of intermediate polydispersity ($m > 1$). Numerical calculations show, however, no noticible change of the constant.

The relationships of eq 53 to eq 58 suggest similar behavior for chains with $m > 1$, i.e., Schulz–Zimm distributions.[32,33]

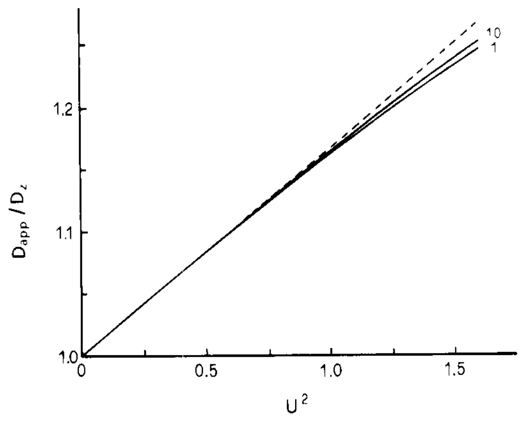

Figure 3. Dependence of D_{app}/D_z as a function of $u^2 = \langle S^2\rangle_z q^2$ for chains of different polydispersity. Dotted line: initial slope $1/6$ ($P_w = 10^6$).

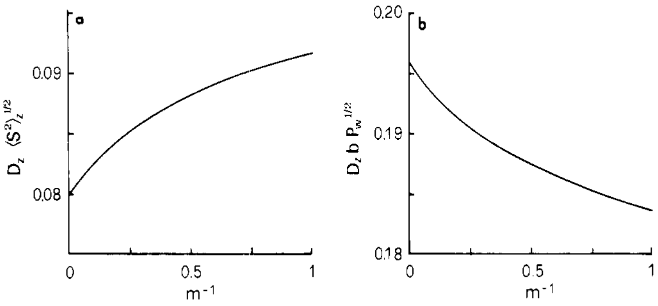

Figure 4. Variation of (a) $D_z\langle S^2\rangle_z^{1/2}$ with polydispersity and (b) $D_z b P_w^{1/2}$ with polydispersity. $m = (P_w/P_n - 1)^{-1}$. Ordinates in units of kT/η_0 where η_0 is the solvent viscosity.

Figure 1 shows a plot of D_{app}/D_z against $P_z(q)^{-1/2}$. One finds small deviations from the simple $P_z(q)^{-1/2}$ dependence to lower values, and these deviations are slightly more pronounced for monodisperse ($m \gg 1$) than for polydisperse chains ($m = 1$). The plot of D_{app}/D_z against $u = \langle S^2\rangle_z^{1/2}q$ on the other hand gives for the various m values a deviation in the opposite direction. The lines are almost linear but bend down slightly for large u values (neutron scattering region). In that region a correction term similar to eq 53 becomes effective; the deviations are, however, not larger than 10%. At low u values (light-scattering region) the curves show an upturn as expected from eq 55. A plot of D_{app}/D_z against u^2 in Figure 3 gives a common curve for all m values with a clearly linear initial part. The slope is $1/6$.

The results can be summarized as follows: (1) The apparent diffusion constant $\overline{\Gamma}_{QS}/q^2$, or the line width $\overline{\Gamma}_{QS}(q)$, exhibits almost no dependence on polydispersity and chain length at medium and large values of the scattering vector q. The change due to polydispersity lies within 4% when passing from monodisperse to polydisperse chains with most probable molecular weight distribution. (2) At small q values a linear slope is obtained when D_{app} is plotted against q^2; the intercept gives the translational diffusion constant D_z, and the initial slope is $1/6\langle S^2\rangle_z$.

Translational Diffusion Constant. The z average of the diffusion constant D_z shows a more pronounced dependence on polydispersity. This influence is contained in the dependence of K_{pw} and K_s, respectively, shown graphically in Figure 4. Of the two constants, K_s is of particular interest. Its value can directly be determined from the product of the intercept and the initial slope of the quasielastic light-scattering measurements

$$K_s(m) = (\eta_0/kT)D_z\langle S^2\rangle_z^{1/2} \qquad (49'')$$

The variation of this constant with polydispersity is not larger than 15%. In view of the high accuracy of quasielastic light-scattering measurements eq 49″ provides therefore a good method for the determination of the polydispersity P_w/P_n of linear chains.

Acknowledgment. Financial support by Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References and Notes

(1) P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272 (1953).
(2) F. Bueche, *J. Chem. Phys.*, **22**, 603 (1954).
(3) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
(4) T. Springer, *Springer Tracts Mod. Phys.*, **64**, 1 (1972).
(5) H. Z. Cummins and H. L. Swinney, *Prog. Opt.*, **8**, 133 (1970).
(6) H. Z. Cummins and E. R. Pike, Ed., "Photon Correlation and Light Beating Spectroscopy", Plenum Press, New York, N.Y., 1974.
(7) R. Pecora, *J. Chem. Phys.*, **40**, 1604 (1964).
(8) R. Pecora, *J. Chem. Phys.*, **43**, 1562 (1965).
(9) R. Pecora, *J. Chem. Phys.*, **49**, 1032 (1967).
(10) P.-G. de Gennes, *J. Appl. Phys.*, **3**, 37 (1967).
(11) E. Dubois-Violette and P.-G. de Gennes, *J. Appl. Phys.*, **3**, 181 (1967).
(12) Z. Akcasu and H. Gurol, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1 (1976).
(13) M. Bixon, *J. Chem. Phys.*, **58**, 1459 (1973).
(14) R. Zwanzig, *J. Chem. Phys.*, **60**, 2717 (1974).
(15) R. Zwanzig, *Annu. Rev. Phys. Chem.*, **16**, 67 (1965).
(16) B. J. Berne and D. Forster, *Annu. Rev. Phys. Chem.*, **22**, 563 (1971).
(17) B. J. Berne and R. Pecora, "Dynamic Light Scattering", Wiley, New York, N.Y., 1976.
(18) See also: M. Fixamn and W. H. Stockmayer, *Annu. Rev. Phys. Chem.*, **20**, 407 (1970).
(19) P. Debye, *Ann. Phys. (Paris)*, **46**, 809 (1915).
(20) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
(21) L. van Hove, *Phys. Rev.*, **95**, 249 (1954).
(22) G. Brehm and V. Bloomfield, *Macromolecules*, **8**, 290 (1975).
(23) B. Chu, "Laser Light Scattering", Academic Press, New York, N.Y., 1974.
(24) K. Kajiwara, W. Burchard, and M. Gordon, *Br. Polym. J.*, **2**, 110 (1970).
(25) H. W. Watson and F. Galton, *Educ. Times*, **19**, 103 (1873).
(26) R. A. Fisher, "The Genetical Theory of Natural Selection", Oxford University Press, 1930; 2nd ed, Dover Publications, New York, N.Y., 1958, p 80 ff.
(27) I. J. Good, *Proc. Cambridge Philos. Soc.*, **45**, 360 (1948).
(28) I. J. Good, *Proc. R. Soc. London, Ser. A*, **272**, 54 (1963).
(29) M. Gordon, *Proc. R. Soc. London, Ser. A* **268**, 240 (1962).
(30) M. Gordon, K. Kajiwara, and A. Charlesby, *Eur. Polym. J.*, **11**, 385 (1975), and literature cited therein.
(31) Ch. Wolf and W. Burchard, *Makromol. Chem.*, **177**, 2519 (1976).
(32) G. V. Schulz, *Z. Phys. Chem. (Leipzig)*, **43**, 25 (1939).
(33) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
(34) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(35) I. Franken and W. Burchard, *Macromolecules*, **6**, 848 (1973).
(36) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, p 272.
(37) K. Freed, S. F. Edwards, and M. Warner, *J. Chem. Phys.*, **64**, 5132 (1976).