Quasielastic scattering from dilute polymer solutions

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(Received 20 March 1984; revised 21 November 1984)

The initial slope $\Omega(q)$ of the time-dependent scattering function and the static structure factor $S(q)$ of macromolecules in good solvents are calculated without using the Gaussian assumption. For $S(q)$, the scaling relation $S(q) \sim q^{-1.7}$ is confirmed in the intermediate q range, whereas no q dependent cross-over behaviour can be observed. The calculation of $\Omega(q)$ reveals a q^3 dependence in this range and no evidence is seen for an exponent apart from 3. The time-dependent scattering function $S(q,t)$ is treated within the framework of the Gaussian assumption. Hydrodynamic as well as excluded volume interactions are incorporated. It has been found that excluded volume effects decrease the decay of the scattering function in comparison with the Gaussian chain.

(Keywords: scattering; polymer solutions; time-dependent scattering function; initial slope; static structure factor; excluded volume; hydrodynamic interaction)

INTRODUCTION

Scattering measurements from dilute polymer solutions are a powerful tool for extracting important experimental data, which characterize the equilibrium and dynamic properties of a single polymer molecule.

Quasielastic scattering experiments have become more and more important in recent years for studying polymer solution dynamics[1,2]. Using laser light as the scattering medium it is possible to search for the dynamics of the polymer molecule as a whole, or, in the case of high molecular weight polymers, to observe the longest relaxational modes of the molecule[3]. Only the recently introduced neutron spin-echo technique[4] permits us to attain a momentum transfer q in the intermediate range (i.e. $qR_g > 1$, where R_g denotes the radius of gyration) with sufficient energy resolution. In both experiments, one measures the static structure factor $S(q)$, the time-dependent scattering function $S(q,t)$ and its initial slope $\Omega(q)$. Therefore, to interpret these measurements it is desirable to have a theory that can predict these quantities over the entire experimental range.

In recent years much attention has been paid to the problem of excluded-volume effects in polymer solution physics. A particular reason for this interest was the discovery of the analogy between polymer physics and the physics of phase transitions. Using methods developed in this latter field a number of scaling relations have been established[5]. However, in some cases, the experimentally found scaling exponents disagree somewhat with the theoretical exponents. There are two conflicting opinions to explain this: firstly, a dynamical exponent is assumed in addition to the static one[5,6], although at present its existence is disputed[7]. Secondly, the differences between experimental and theoretical exponents are explained by the non-uniform expansion of the polymer chain due to excluded-volume effects[8]. These theories are summarized by the synonym 'blob' models[6,8,9].

In this paper, we will investigate the influence of excluded-volume effects, especially of the non-uniform chain expansion, on $S(q)$ and $\Omega(q)$ within the framework of the projection operator formalism.

As opposed to the existing 'blob' theories[6,8–11], which somewhat artificially simulate the non-uniform chain expansion, we employ the distribution functions of segment–segment distances obtained within the framework of the hierarchy equation approach[12,13]. In this way, we may avoid the Gaussian approximation commonly used in other theories and can assess its quality. Additionally, no free parameter need be fitted in our theory.

Our results show an overall $q^{-1.71}$ wave-vector dependence of the static structure factor in the excluded volume case. No cross-over behaviour can be observed. The influence of excluded volume effect on the initial slope is much less dramatic and causes no substantial change in the q dependence in comparison with the Gaussian chain. $S(q,t)$ will be calculated over the entire range of time including both hydrodynamic and excluded volume interactions. The treatment is analogous to De Gennes and Dubois-Violette[14] regarding the time-dependent scattering function in its Gaussian approximation. After introducing normal coordinates we get a closed expression for $S(q,t)$, where only equilibrium correlation functions of these coordinates and their relaxation times occur. These quantities are calculated using the results from the theory of viscoelastic properties, as presented in a previous paper[15].

The results of the calculation show that the decay of the scattering function $S(q,t)$ of excluded volume chains is somewhat weaker than in the unperturbed case. The dominating contribution to this behaviour comes from the centre-of-mass diffusion, whereas the relaxation of the normal modes accounts mainly for the deviation from a simple exponential law.

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0032–3861/85/081212–07$03.00

THEORETICAL BACKGROUND

The time evolution of a dynamical variable a_k is governed by the following equation of motion (see e.g. ref. 16)

$$\frac{\partial}{\partial t}a_k = -La_k \qquad (1)$$

where the Liouvillian L for polymer molecules in dilute solutions is given by[17]

$$L = -\sum_{j,l=0}^{N-1}[\mathrm{grad}_j(\ln\psi_0)D_{jl}\mathrm{grad}_l + D_{jl}:\mathrm{div}_j\mathrm{grad}_l] \qquad (2)$$

D_{jl} is the generalized diffusion tensor, which contains contributions from segment friction and hydrodynamic interaction (Oseen tensor), and $\psi_0(\vec{R}_0, \ldots, \vec{R}_{N-1})$ represents the equilibrium distribution of the N polymer segments.

For scattering problems, the relevant dynamical variable is the spatially Fourier-transformed segment density[18]

$$\rho_q(t) = \sum_{j=0}^{N-1}\exp(i\vec{q}\vec{R}_j(t)) \qquad (3)$$

The summation runs over all N segments with the position vectors $\vec{R}_j$ in the chain.

Then, the time-dependent scattering function

$$S(\vec{q},t) = \langle\rho_q^*(0)\rho_q(t)\rangle = \sum_{j,l=0}^{N-1}\langle\exp\{i\vec{q}[\vec{R}_j(t) - \vec{R}_l(0)]\}\rangle \qquad (4)$$

(angular brackets denote equilibrium averages) satisfies the following equation of motion[18]

$$\frac{\partial}{\partial t}S(\vec{q},t) = -\Omega(\vec{q})S(\vec{q},t) + \int_0^t K(\vec{q},s)S(\vec{q},t-s)\mathrm{d}s \qquad (5)$$

which is obtained from equation (1) by the Mori projection operator technique[18,19]. $\Omega(\vec{q})$ denotes the relaxation frequency or the initial slope[10,11] of the scattering function $S(\vec{q},t)$. The derivation of equation (5) yields

$$\Omega(\vec{q}) = \frac{\langle\rho_q^*L\rho_q\rangle}{\langle\rho_q^*\rho_q\rangle} \qquad (6)$$

where the denominator of equation (6) is the static structure factor

$$S(q) = \langle\rho_q^*\rho_q\rangle \qquad (7)$$

As seen from equations (6) and (7), $S(\vec{q})$ and $\Omega(\vec{q})$ are given by equilibrium averages, which can be easily calculated (the calculation is described in the following section).

The memory kernel $K(\vec{q},s)$ of equation (5) has a very complicated structure (because $K(\vec{q},s)$ will not be needed here, we refer to ref. 18) and equation (5) seems to be unsuitable for the calculation of $S(\vec{q},t)$. Therefore, a more approximate approach will be given in the following section.

CALCULATION DESCRIPTION

Static structure factor S(q) *and initial slope* Ω(q)

Substitution of equations (2) and (3) into equation (6) yields[18]

$$\Omega(\vec{q}) = \frac{\sum_{j,l=0}^{N-1}\langle D_{jl}\cdot\exp(i\vec{q}\vec{R}_{jl})\rangle:\vec{q}\vec{q}}{\sum_{j,l=0}^{N-1}\langle\exp(i\vec{q}\vec{R}_{jl})\rangle} \qquad (8)$$

where $\vec{R}_{jl}$ is the distance vector between the jth and the lth segment. In order to facilitate the further calculations here we adopt the commonly used preaveraging approximation of the diffusion tensor D_{jl}. The quality of this approximation is discussed in detail in refs. 18, 20 and 21: maximum errors of about 13% result, but no substantial qualitative changes in wavenumber behaviour occur. Equation (8) then reads

$$\Omega(\vec{q}) = \frac{\sum_{l=0}^{N-1}\langle D_{ll}\rangle q^2 + \sum_{j\neq l=0}^{N}\langle D_{jl}\rangle\langle\exp(i\vec{q}\vec{R}_{jl})\rangle q^2}{\sum_{j,l=0}^{N-1}\langle\exp(i\vec{q}\vec{R}_{jl})\rangle} \qquad (9)$$

where the double sum has been split into the part over the diagonal elements of the diffusion tensor, i.e.

$$\langle D_{ll}\rangle = k_{\mathrm{B}}T/\rho \qquad (10)$$

(ρ is the segment friction coefficient and $k_{\mathrm{B}}T$ is the Boltzmann factor), and the off-diagonal part, containing the hydrodynamic interaction in the preaveraged form

$$\langle D_{jl}\rangle = \frac{k_{\mathrm{B}}T}{6\pi\eta_0}\langle 1/R_{jl}\rangle \qquad (11)$$

where η_0 is the viscosity of the solvent.

The problem is now reduced to the calculation of the averages of the exponential factor $\exp(i\vec{q}R_{jl})$ and of the reciprocal segment distance $1/R_{jl}$ in the presence of excluded volume interactions. Until now this has been done in the literature by expressing these averages as averages of the mean square segment distance[10,11]. However, this procedure does make some assumptions, which only hold true in the case of Gaussian chains and whose quality for non-Gaussian chains cannot be appreciated at this theoretical level.

We have overcome this disadvantage by carrying out the averaging excluding these approximations using excluded volume distribution functions provided by a hierarchy equation approach. The system of hierarchy equations of the Fujita–Okita–Norisuye type (see ref. 22) for the segment distance distribution functions is solved with the help of a self-consistent variational method. For a radial symmetric distribution, functions $\psi_0(x_{jl})$ are an ansatz in the form of shifted Gaussian functions as follows:

$$\psi_0(x_{jl})\mathrm{d}x_{jl} = \frac{1}{C}x_{jl}^2\exp[-(px_{jl}^2 + gx_{jl})]\mathrm{d}x_{jl} \qquad (12)$$

The parameters p and g, which have to be determined, are assumed to depend on the strength of the excluded volume interaction, characterized by the parameter

$$z=(3/2\pi b^2)^{3/2}\beta\sqrt{N} \tag{13}$$

as well as on the reduced subchain length $|l-j|/N$ (where C is the normalization factor, b the mean statistical segment length and β the binary cluster integral of the segment–segment interaction). The reduced subchain end-to-end distance x_{jl} is defined by

$$x_{jl}=R_{jl}/\sqrt{\langle R_{jl}^2\rangle_\theta} \tag{14}$$

where the index θ denotes θ-conditions.

In this way, a non-Gaussian, non-uniform expansion theory for the segment distance distribution functions was developed, giving good results for the equilibrium properties of dilute solutions (expansion factors, second virial coefficients, concentration dependence of the expansion factors)[12]. Recently, the distribution functions according to equation (12) were successfully used in an investigation into the effect of the non-uniform chain expansion on the dynamic viscosity also[15]. Working out the averages for $1/R_{jl}$ is a trivial task when using spherical coordinates. For the exponential factor $\exp(i\vec{q}\vec{R}_{jl})$, this procedure is more complicated. After integration over the angular coordinates one gets

$$\langle \exp(i\vec{q}\vec{R}_{jl})\rangle=\frac{4\pi}{Cqb\sqrt{|j-l|}}\int_0^\infty x\sin(qb\sqrt{|j-l|}x)\times\exp(-px^2-gx)\mathrm{d}x \tag{15}$$

with an oscillating factor in the integrand. This latter integration must be done numerically, since the analytical calculation results in complex error functions. For simplicity, we therefore abbreviate the integral in equation (15) by $I(p,g,qb\sqrt{|j-l|})$ in the following formulae (for details see ref. 13). Assuming that the parameters in the distribution function in equation (12) depend on the subchain length only, the double sums in equations (9) and (7) can be replaced by single sums ($m=|j-l|$):

$$\Omega(q)=\frac{k_\mathrm{B}T}{\rho}q^2N\left[1+\frac{8a}{qb}\sum_{m=1}^{N-1}\left(1-\frac{m}{N}\right)\times\alpha_m^{-1}\frac{I(p,q,qb\sqrt{m})}{mC}\right]\Big/S(q) \tag{16}$$

$$S(q)=N\left[1+\frac{8\pi}{qb}\sum_{m=1}^{N-1}\left(1-\frac{m}{N}\right)\frac{I(p,g,qb\sqrt{m})}{C\sqrt{m}}\right] \tag{17}$$

In equation (16), we have introduced the expansion factor

$$\alpha_{jl}^{-1}=\frac{\langle 1/R_{jl}\rangle}{\langle 1/R_{jl}\rangle_\theta} \tag{18}$$

and a hydrodynamic interaction parameter

$$a=\rho/(\sqrt{6\pi}b\eta_0) \tag{19}$$

a is ~ 1 for strong hydrodynamic interactions (non-free-draining case)[15,23]. Equations (16) and (17) are the basis for the numerical calculations.

Time-dependent scattering function S(q,t)

The first attempt at treating this problem was carried out by Pecora[24], who directly solved the generalized diffusion equation for Gaussian chain distribution functions by characterization. Pecora's expressions for $S(q,t)$ were recently reformulated and presented in a much more convenient form by Akcasu, Benmouna and Han (ABH)[11], expanding the time-dependent scattering function into eigenfunctions of the Liouvillian. From this, Han and Akcasu[25] calculated the dynamic structure factor $S(q,\omega)$ in a later work. Another approach to $S(q,t)$ was given by Akcasu and Gurol[18] applying the Mori–Zwanzig projection operator technique[19,16] to the equation of motion for the Fourier-transformed segment density $\rho_q(t)$ (see Theoretical background section). The resulting integro-differential equation (5) is exact but only shifts the mathematical difficulties into the evalutaion of the memory term $K(\vec{q},s)$, which cannot be overlooked even in the case of the Rouse model as shown by several authors[16]. For that reason, the projection operator technique appears unsuitable for the purpose of calculating $S(q,t)$ over the entire time range.

As already mentioned in the introduction we invoke in equation (4) the so-called Gaussian assumption, which means that the average of the exponential is replaced by

$$\langle \exp\{i\vec{q}[\vec{R}_j(t)-\vec{R}_l(0)]\}\rangle \simeq \exp\{-q^2/2\langle[x_j(t)-x_l(0)]^2\rangle\} \tag{20}$$

In equation (20), the wave vector q is assumed to be parallel to the x-axis.

This approximation, used predominantly in literature until now, is equivalent to the factorization of higher moments of the distribution function into second moments. It is exact only for Gaussian segment distribution and appears, at first sight, very inexact for the case of excluded volume chain statistics. However, it may be argued from calculations of the initial slope and the static structure factor (see below), that this approximation does not lead to qualitatively wrong results and therefore we hope that it is also justified for our present purposes. The special advantage of equation (20) is exhibited in calculating $S(q,t)$ via equilibrium correlation functions of the segments' x-coordinates. Removing the square in equation (20) and taking into account that the second moment $\langle x_j^2(t)\rangle$ of the equilibrium distribution function is independent of time we get

$$\langle[x_j(t)-x_l(0)]^2\rangle=\langle x_j^2(0)\rangle+\langle x_l^2(0)\rangle-2\langle x_j(t)x_l(0)\rangle \tag{21}$$

Clearly the time evolution of $S(q,t)$ is determined by the correlation function $\langle x_j(t)x_l(0)\rangle$, whose time dependence can be determined using normal mode analysis. As appropriate normal coordinates the Rouse coordinates were applied; these are a good approximation even in the case of the excluded volume chain distribution as shown in the investigation of viscoelastic properties[15]. We define the transformation matrix

$$Q_{jk}=(2/N)^{1/2}\cos\frac{\pi k}{N}(j+1/2) \tag{22}$$

with

$$x_j=\sum_{k=0}^{N-1}Q_{jk}\xi_k \tag{23}$$

where ξ_k is the component of the kth normal coordinate corresponding to the x coordinate.

Inserting equations (22) and (23) into equation (21) yields

$$\langle [x_j(t)-x_l(0)]^2 \rangle = \sum_{k=0}^{N-1} \langle \xi_k \xi_k \rangle [Q_{jk}^2 + Q_{lk}^2 - 2Q_{jk}Q_{lk}e^{-t/\tau_k}] \tag{24}$$

In the derivation of equation (24) the normal modes relax as[15]

$$\langle \xi_k(0)\xi_k(t) \rangle = \langle \xi_k \xi_k \rangle \cdot \exp(-t/\tau_k) \tag{25}$$

The relaxation times τ_k have been calculated from Bixon's[17] theory, which we extended to the case of linear polymer chains in ref. 15:

$$\tau_k = \frac{\langle \xi_k \xi_k \rangle}{D_k} \tag{26}$$

In equation (26), the average of the normal coordinates is given by

$$\langle \xi_k \xi_k \rangle = -\frac{1}{3N} \sum_{j,l=0}^{N-1} \langle R_{jl}^2 \rangle \cos\frac{\pi k}{N}(j+1/2) \cos\frac{\pi k}{N}(l+1/2) \tag{27}$$

and D_k designates the transformed elements of the preaveraged generalized diffusion tensor

$$D_k = \frac{k_B T}{\rho}\left[1 + \frac{ab}{\sqrt{6\pi N}} \sum_{j\neq l} \langle 1/R_{jl} \rangle \cos\frac{\pi k}{N}(j+1/2) \cos\frac{\pi k}{N}(l+1/2)\right] \tag{28}$$

For further evaluation of equation (25), it is preferable to separate the 'mode' of centre-of-mass diffusion $k=0$ from all the others avoiding divergences in $\langle \xi_k \xi_k \rangle$ as well as in τ_k. Taking into consideration equations (27) and (25) one finds from the limit $k \longrightarrow 0$ the expression $2D_0 t$ for the diffusion 'mode' and hence together with equations (20) and (4) the final result for the time-dependent scattering function is

$$S(q,t) = \exp(-D_0 q^2 t) \sum_{j,l=0}^{N-1} \left\{ \frac{q^2}{2} \sum_{k=1}^{N-1} \langle \xi_k \xi_k \rangle \times [Q_{jk}^2 + Q_{lk}^2 - 2Q_{jk}Q_{lk} \exp(-t/\tau_k)] \right\} \tag{29}$$

where D_0 is the familiar diffusion coefficient of Kirkwood[22], which in our notation reads as

$$D_0 = \frac{k_B T}{N\rho}\left[1 + \frac{ab}{\sqrt{6\pi N}} \sum_{j\neq l} \langle 1/R_{jl} \rangle \right] \tag{30}$$

In the case of Gaussian chains, equation (29) is already known from previous literature[11,24,27].

RESULTS

Static structure factor

Some computation results of the static structure factor are shown in *Figures 1–3*. In *Figure 1*, the static structure factor is plotted double-logarithmically *versus* the reduced wavenumber qb for a chain of 1000 segments. It is clear that $S(q)$ behaves in the intermediate range as a power law of the form $S(q) \sim q^{-\alpha}$. α has the value 2, if no excluded volume is present, i.e. Gaussian-chain behaviour (full line in *Figure 1*). The exponent α alters to 1.71, if excluded volume effects are acting (curve for $z=3$ in *Figure 1*). This corresponds to the scaling results, which give an exponent of $1/\nu = 1.7$ for $\nu = 0.59$ in the excluded-volume case[1]. Contradictory to the existing 'blob' theories[8,9] the present results exhibit no cross-over behaviour in the intermediate q range.

In order to examine this further, the static structure factor $S(q)$ was also calculated by using the commonly applied Gaussian approximation, (equation (20)). Equation (17) then reads

$$S(q) = N\left[1 + 2\sum_{m=1}^{N-1}\left(1 - \frac{m}{N}\right)\exp\left(\frac{q^2 b^2}{6} m\alpha_m^2\right)\right] \tag{31}$$

where α_{jl}^2 is the expansion factor of the mean square segmental distance calculated with the help of the distribution function (12). The results are displayed in *Figure 2* in comparison with the 'exact' results for $z=1$. The differences between these two kinds of calculation are about 20% at a maximum. Apart from these quantitative deviations, the 'approximated' curve also differs somewhat qualitatively from the 'exact' curve in such a way that a q-dependent cross-over behaviour is indicated. This behaviour is indicated by the thin guide lines in *Figure 2*. For small q, the slope is about $\alpha \approx 1.7$, while it tends to Gaussian chain behaviour for greater q ($\alpha \approx 1.9$). This behaviour was shown by the various 'blob' theories using the Gaussian approximation, also. Therefore it may be concluded that the cross-over behaviour as predicted by these theories may be a result of this approximation (equation (31)).

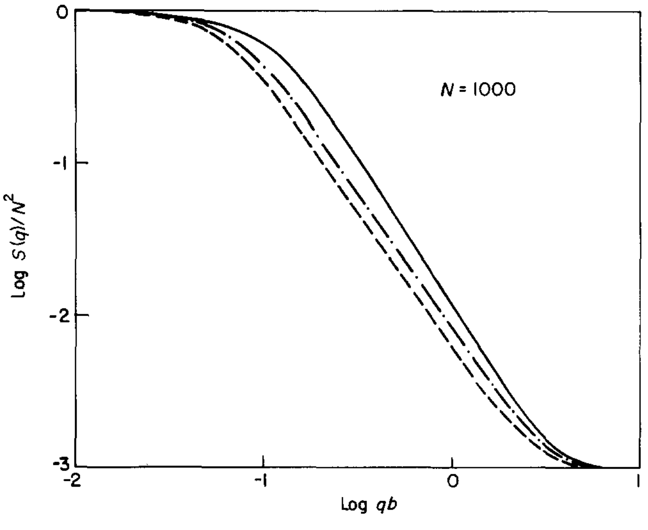

Figure 1 Logarithmic plot of the static structure factor *versus* the reduced wavenumber qb for various strengths of the excluded volume interaction: (———): $z=0$; (—·—·—): $z=1$; (———): $z=3$

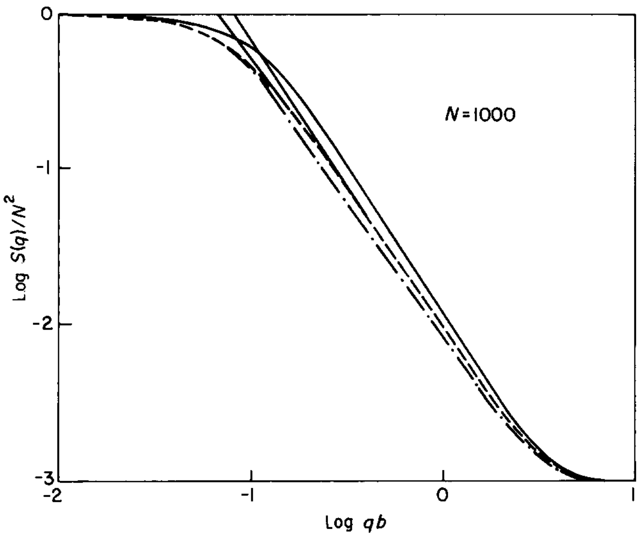

Figure 2 Comparison of the exact and the approximate calculations of the static structure factor: (———), $z=0$; (– · – · –), $z=1$, exact calculation from equation (17); (– – –), $z=1$, approximate calculation from equation (31)

In *Figure 3*, the static structure factor $S(q)$ is plotted double-logarithmically *versus* the mean radius of gyration. The calculated curves for $z=0$ and $z \neq 0$ are not identical because of the non-uniform chain expansion. Note that $S(q)$ of an excluded-volume chain is somewhat larger than for a Gaussian chain. This corresponds well with experimental results from light scattering[28,29] and contradicts the theoretical prediction of Ohta, Oono and Freed[30] and Witten and Schäfer[31]. The differences are likely to arise from the restriction to first-order ε-perturbation theory for $S(q)$ by these authors.

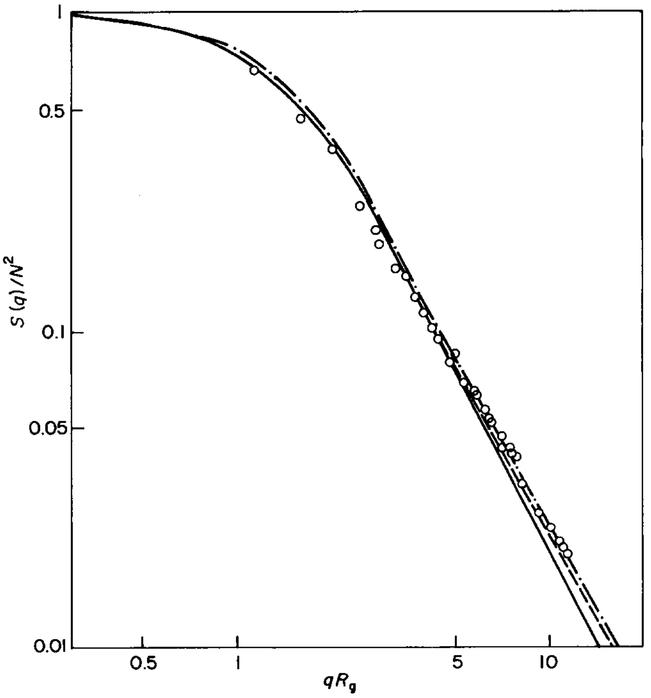

Figure 3 Comparison of experimental and theoretical results for $S(q)$ in dependence of the reduced wavenumber qR_g (R_g is the mean radius of gyration). Experimental data from ref. 28. (———): $z=0$; (– – –): $z=1$; (– · – · –): $z=3$

Initial slope

The wavenumber behaviour of $\Omega(q)$ for Gaussian chains in the free-draining and the non-free-draining cases is well known since the pioneering work of De Gennes and Dubois–Violette[14]: in the first case, we find a q^4 dependence and a q^3 one in the second. This different q behaviour is reflected by the lower curves ($a=1$ is the non-free-draining case) in *Figure 4*. The other curves are the results of the excluded-volume chain calculated by equations (16) and (17). Evidently, no significant changes of the slopes of the curves can be stated in the intermediate range for $z \neq 0$. The following relations are found by a regression analysis:

$$\Omega(q)=0.066\frac{k_B T}{b^3}(qb)^{2.98} \qquad \text{for } z=1 \qquad (32a)$$

$$\Omega(q)=0.071\frac{k_B T}{b^3}(qb)^{3.00} \qquad \text{for } z=3 \qquad (32b)$$

There is no difference between the q dependence of $\Omega(q)$ in the Gaussian and in the excluded-volume case. This is in agreement with the experimental results, where a q^3 behaviour (within the experimental errors) is always found[32,33]. The conclusions of Daoud and Jannink[6], who extracted a dynamic exponent 2.85 from $\Omega(q)$ measurements, must therefore once more be in some doubt. Furthermore, a cross-over behaviour in $\Omega(q)$ is not observed. Benmouna and Akcasu[10] reached the same conclusion in the frame of their 'blob' concept also. The agreement between equation (32b) and Benmouna and Akcasu's adequate formulae is surprisingly good. Furthermore, equation (32a) corresponds well with experimental results from quasielastic neutron scattering by Ewen *et al.*[33]. *Figure 4* also shows the influence of the Gaussian approximation (31) on the initial slope $\Omega(q)$ (dotted line). The differences are not as high as in $S(q)$ (about 15%) and reveal no other qualitative behaviour other than the 'exact' calculation.

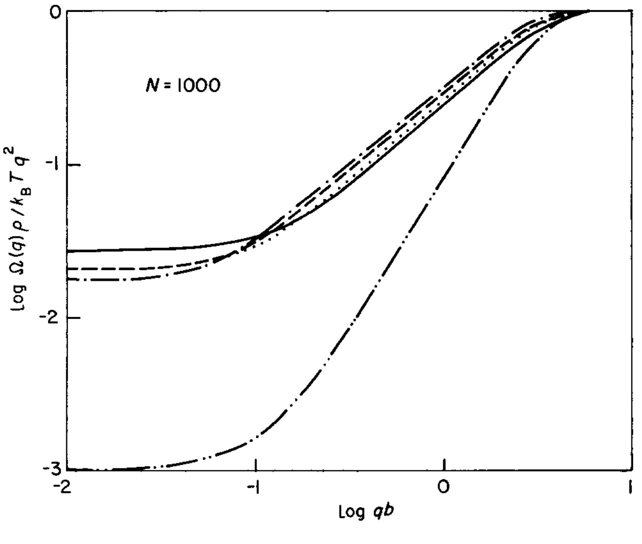

Figure 4 Logarithmic plot of the initial slope *versus* the reduced wavenumber qb for various excluded volume and hydrodynamic interaction parameters: (– · · – · · –), $a=z=0$; (———), $a=1$, $z=0$; (– – –), $a=z=1$; (– · – · –), $a=1$, $z=3$; (· · · ·), $a=z=1$ and Gaussian approximation

Time-dependent scattering function

Some results of the calculation according to equation (29) are shown in *Figure 5*: the logarithm of the normalized scattering function is plotted against the reduced time Ωt. Calculations were performed in the free-draining ($a=0$) and the non-free-draining ($a=1$) limits, respectively, likewise varying the excluded volume parameter z in both cases. For numerical reasons, our calculations are restricted to one hundred statistical segments per chain and therefore representative reduced wavenumbers qb were chosen as $qb=0.5$ and 1. It can be clearly seen from *Figure 5* and equation (29) that the shape of the scattering function is far from a single exponential in all cases. The reason is the relaxation of the normal modes. For Gaussian chains, this was previously shown by the theories of ABH[11], and Freire, de la Torre and Escudero[27] and has been confirmed by neutron spin-echo experiments[32,34]. An exponential law is only found for very small ($qR_g \ll 1$) and large ($qb \gg 1$) wavenumbers, where information is obtained from the motion of the whole molecule or from the statistical segments respectively. In both cases, the graph of the scattering function is close to the thin straight line in *Figure 5*, i.e. $S(q,t)=S(q)\exp(-\Omega(q)t)$.

As can be seen from *Figure 5* the time-dependent scattering function is clearly affected by the excluded volume interactions, i.e. excluded volume effects cannot entirely be absorbed in $\Omega(q)$. For the free-draining limit (hypothetical for dilute solutions), the decay of $S(q,t)$ is, in the excluded volume case, for small wavenumbers ($qb \lesssim 0.8$) weaker and for greater wavenumbers ($qb \gtrsim 0.8$) stronger than for Gaussian chains. The reason for this 'cross-over' is difficult to explain from equation (29). It may be, however, explained as an effect of the $\Omega(q)$-reduced representation. The differences are, in any case, small and of less interest.

If the hydrodynamic interaction is included, the decay of the scattering function changes more dramatically than in the former case. This can be explained by the dominating influence of the diffusion term (first factor in equation (29)) of $S(q,t)$. Excluded volume effects cause a decrease in the decay of the scattering function because the increasing chain dimensions due to excluded volume swelling are accomplished by a diminishing of the molecular centre-of-mass diffusion.

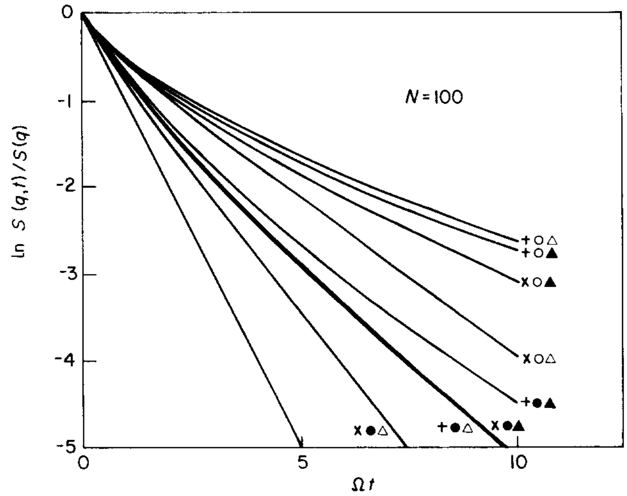

Figure 5 Logarithm of the normalized time-dependent scattering function *versus* the reduced time Ωt for various wavenumbers (×), $qb=0.5$; (+), $qb=1$; and parameters of hydrodynamic (○), $a=0$; (●), $a=1$; and excluded volume interaction (△), $z=0$; (▲), $z=3$. The thin line designates the exponential law

SUMMARY AND CONCLUSION

Here we have been concerned with the calculation of some physical quantities characterizing the scattering process in dilute polymer solutions above the theta temperature. The static structure factor is clearly influenced by excluded-volume effects: the wavenumber behaviour changes from q^{-2} to the scaling behaviour $q^{-1.7}$, but no wavenumber cross-over could be observed. The cross-over ascertained by some previous theories seems to be a result of the use of the Gaussian approximation.

The initial slope $\Omega(q)$ is much less affected by excluded-volume effects than the static structure factor $S(q)$. No significant change in the q dependence between Gaussian and excluded-volume chains could be found. The differences lie within the numerical errors and allow no extraction of an exponent apart from 3 in the q dependence. This corresponds to the experiments. Furthermore, from our calculations no evidence can be found for the existence of a dynamic exponent, because all experimental findings can be explained in full by the supposition of non-uniform chain expansion due to excluded-volume effects. Nevertheless, this question is still unsettled, but if such an exponent exists at all, it would be very close to 3 and would be practically speaking indistinguishable.

The coherent time-dependent scattering function $S(q,t)$ is calculated for macromolecules in good solvents. For this purpose, it was necessary to use the scattering function in its Gaussian approximation. It may be seen from our calculations that excluded volume effects influence the strength of the decay and the shape of the time-dependent scattering function in the $\Omega(q)t$ representation also. The main contribution, which alters the decay of the scattering function compared with the Gaussian chain, comes from the translational diffusion term in $S(q,t)$, whereas the relaxation of the normal modes is responsible for changes in its shape. Whether the excluded volume influence on $S(q,t)$ is correctly estimated by using the Gaussian assumption cannot be evaluated at this theoretical level. We can conceive that our present work is a first attempt at treating the problem of excluded volume effects for $S(q,t)$ and gives qualitatively correct results as discussed earlier in this paper. In order to clarify the quantitative accuracy of the theory some further experimental work seems desirable specifically in the higher Ωt range. In this limit, however, the problem of the long-time diffusion coefficient as mentioned by Fixman[35] and more recently by Akcasu[36] must be taken into consideration by an improved theory.

ACKNOWLEDGEMENT

We are grateful to Professor G. Helmis for his helpful discussions and stimulating interest.

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