Hydrodynamic interactions in quasi-elastic light scattering from flexible polymers in solution

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Theoretical calculations of the time correlation function and the mean relaxation time of dynamic light scattering from flexible polymers in dilute solutions have been carried out by use of the Rouse–Zimm model in the non-draining limit. The results have been favourably compared with those predicted assuming free draining in their respective fittings to existing experimental data.

Quasi-elastic light scattering is considered to be a technique which may provide information about intramolecular motions of chain molecules in solution[1]. This information is generally found by use of a method first developed by Pecora[2] applying the Rouse–Zimm model[3] for flexible polymer chains. The method allows the extraction of the largest relaxation times from the Rayleigh spectrum of the scattered light. Other methods of interpretation have recently been proposed in order to understand the role of the rest of the normal motions in the global spectrum. Thus, Saleh *et al.*[4] have computed and studied the scattering time correlation function (Fourier transform of the scattered spectral density) as a whole, and Büldt has made a study of the 'mean relaxation time' (first derivative of the time correlation function at time zero). In both works free draining has been assumed. In this study carry out similar calculations for the non-draining limit in order to find out how hydrodynamic interactions influence the final results. Our results show noticeable differences with respect to the ones obtained in the free draining limit (or Rouse model) and agree more closely with experimental data.

TIME CORRELATION FUNCTION

In this section we report calculations for the scattering time correlation function, $P(\vec{\kappa},t)$ in the non-draining limit of the Rouse–Zimm model. This function can be evaluated from the following expression derived by Pecora[2] by use of the Fokker–Plank equation in normal coordinates:

$$P(\vec{\kappa},t) = \exp(-D\kappa^2 t)Z^{-2}\sum_{j=0}^{Z}\sum_{l=0}^{Z}\exp \quad -\frac{1}{6}\kappa^2\sum_{k=1}^{Z}\langle U_k^2\rangle \times$$

$$[Q_{jk}^2 + Q_{lk}^2 - 2Q_{jk}Q_{lk}\exp(-t/\tau_k)]] \qquad (1)$$

where $\vec{\kappa}$ is the scattering vector, D is the translational diffusion coefficient of the chain, z is the number of statistical segments (each with a length b and a friction coefficient ξ) $\langle u_k{}^2\rangle$ is the mean square equilibrium length, Q_{jl} are eigenvectors of Zimm's matrix equation[3], and τ_k is the kth relaxation time of the chain.

Equation (1) is valid even if hydrodynamic interactions introduced[6] through the Oseen tensor. Therefore, it is possible to evaluate numerically[7] eigenvectors, relaxation times and $\langle u_k{}^2\rangle$ for several values of the hydrodynamic interaction parameter, h, and then to obtain exact results for $P(\vec{\kappa},t)$ in a similar form, as has been done by Perico *et al.* for the intensity of the global spectrum[6]. The results have shown a slight change in the relative contributions of the diffusional term and the internal motions to the total scattered intensity from that obtained in the free draining case, but the main contribution of hydrodynamic interactions is noticeably exerted through D and the τ_k values. In order to study the behaviour of $P(\vec{\kappa},t)$ in the non-draining limit through a simple and systematic procedure, we consider the substitution of the actual $\langle u_k{}^2\rangle$ and eigenvectors, Q_{jl}, by the ones that correspond to free draining, Q_{jl}^R and $\langle u_k^2\rangle$ to be adequate:

$$Q_{jk}^R Q_{lk}^R = \frac{1}{Z} \quad \cos[\pi K(l-j)/Z] + \cos[\pi K(l+j)/Z] \qquad (2)$$

$$\langle U_k^2\rangle = b^2/4\sin^2(\pi K/2Z) \qquad (3a)$$

or*

$$\langle U_k^2\rangle_R = b^2Z^2/\pi^2K^2; K \ll Z \qquad (3b)$$

This substitution avoids a tedious numerical calculation for the exact Q_{jl} and $\langle u_k^2\rangle$ which seems irrelevant to our purposes. In fact this is equivalent to deriving equation (1)

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* The approximation represented by equation (3b) is an adequate one in all instances considered here, because the μ_k values appear in sums whose terms decrease as k increases. The most problematic situation will appear in equation (12), where the approximation leads to a dependence of the type $k^{-1/2}$. However, numerical calculations made by use of both equations (3a) and (3b), show that equation (12) is sufficiently accurate.

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using a matrix, $\underset{\approx}{Q}^R$, whose elements are Q_{jl}^R, for the change to normal coordinates; this is generally regarded as a good approximation[8].

The relaxation times, τ_k, can be approximated in the non-draining limit by[9]:

$$\tau_k = \frac{b^2 \xi Z^2}{\sigma \pi^2 h k_B T} [K^{3/2}(1 - 1/2\pi k)]^{-1} \tag{4}$$

where $k_B T$ is the Boltzmann factor.

Also, for large values of h, we can take[8]:

$$D = \frac{2^{7/2} k_B T}{3 \xi Z} h \tag{5}$$

Considering equations 1–5, we obtain:

$$P(\vec{\kappa},t) = \exp\ (-t/T_R) Z^2 \sum_{j=0}^{Z} \sum_{l=0}^{Z} \exp \left\{ \sum_{k=1}^{Z} - \frac{2x}{\pi^2 k^2} \times \right.$$

$$\left[\cos^2 \frac{\pi k j}{Z} + \cos^2 \frac{\pi k l}{Z} - [\cos \pi k (l - j)/Z + \right.$$

$$\left. \left. \cos \pi k (l + j)/Z] \exp \left[- \frac{3\pi^2 K^{3/2}(1 - 1/2\pi k)}{2^{7/2} x} \frac{t}{T_R} \right] \right] \right\}$$

where T_R represents the relaxation time for the diffusional translation of the chain:

$$1/T_R = D\kappa^2 \tag{7}$$

and x is the scattering parameter defined by:

$$x = \kappa^2 R_G^2 \tag{8}$$

(R_G^2 is the mean-square radius of gyration of the Gaussian coil, $R_G^2 = (1/6) z b^2$).

Using equation (6) we have calculated $P(\vec{\kappa},t)$ numerically as a function of t/T_R for several values of the parameter x; z was taken to be 20 or 50 and, in some cases, we extended the calculation up to $z = 100$. A reasonable convergence of $P(\vec{\kappa},t)$ with z has been found in this range.

The results are shown in *Figures 1* and *2*, where squared relative intensities for $P(\vec{\kappa},t)$ with respect to the value at time zero, (magnitudes accessible from homodyne experimental techniques) have been plotted *versus* t/T_R. These curves have been compared with the ones obtained for the free draining limit[4] and with experimental results for polystyrene in two different solvents[9], reported by Hendrix *et al.* An easy comparison between both types of theoretical curves and the experimental points can be carried out by taking into account the fact that in all cases smaller values of x correspond to less steep curves.

From these Figures, it can be seen that the curves are sensitive to hydrodynamic interactions and tend to flatten out for large values of x. In this region a fair agreement is observed between our curves (non-draining limit) and experimental points which correspond to similar values of x. Therefore, the non-draining limit is shown to be significantly more applicable than the Rouse model to explain the experimental behaviour of the time correlation function. For lower values of x, the differences between both draining limits become smaller and the experimental points agree more closely with one limit or with the other, depending on the solvent.

MEAN RELAXATION TIME

The mean relaxation time, T^*, has been defined by Büldt[5] to be:

$$1/T^* = - \lim_{t \to 0} \frac{dP(\vec{\kappa},t)}{dt} \tag{9}$$

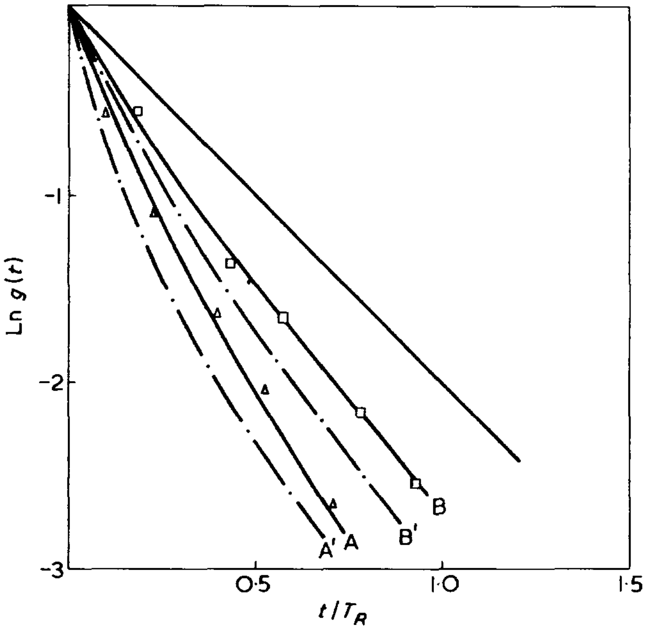

Figure 1 $\ln[P(\vec{\kappa},t)/P(\vec{\kappa},0)]^2$ *versus* t/T_R for several values of x. The curves represent theoretical results for the non-draining (——) and the free draining (— · — ·) limits: A, $x = 15$; B, $x = 6$; A′, $x = 10$; *B*′, $x = 6$. The points correspond to measurements of polystyrene in toluene reported in ref 10: □, $x = 6.0$; △, $x = 12.2$. The unlabelled straight line corresponds to the theoretical behaviour for the case $x = 0$

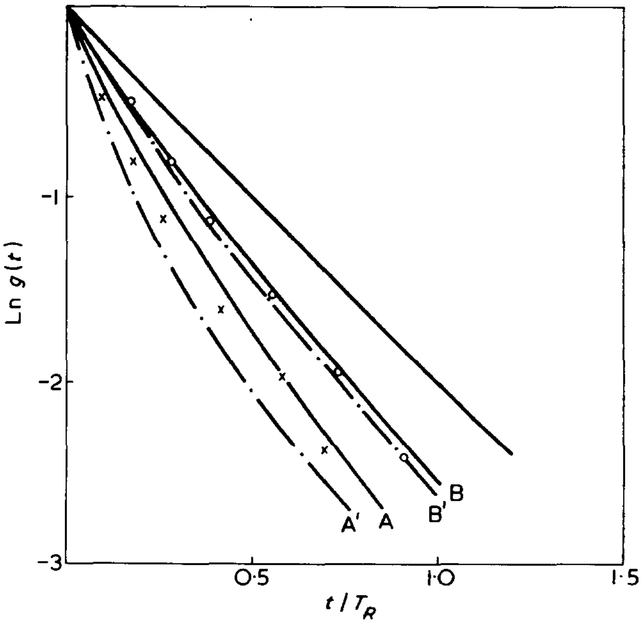

Figure 2 As *Figure 1*, with experimental points corresponding to polystyrene in cyclohexane. A, $x = 10$; B, $x = 5$; A′, $x = 8$; *B*′, $x = 4$. Points: ○, $x = 3.4$; X, $x = 9.6$

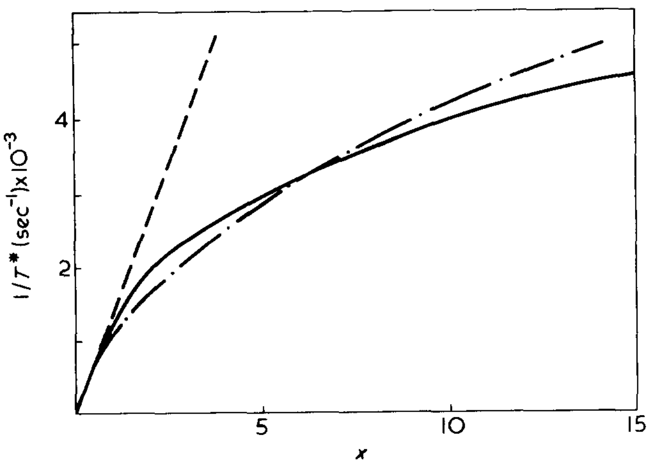

Figure 3 $1/T^*$ *versus* x for a coil in the free draining (— — —) and non-draining (——) limits compared with the curve predicted in ref 5 for a rod with the same translational diffusion coefficient (– · – ·) ($D = 10^{-7}$ cm^2/sec). Dr for the rod is 300 sec^{-1}

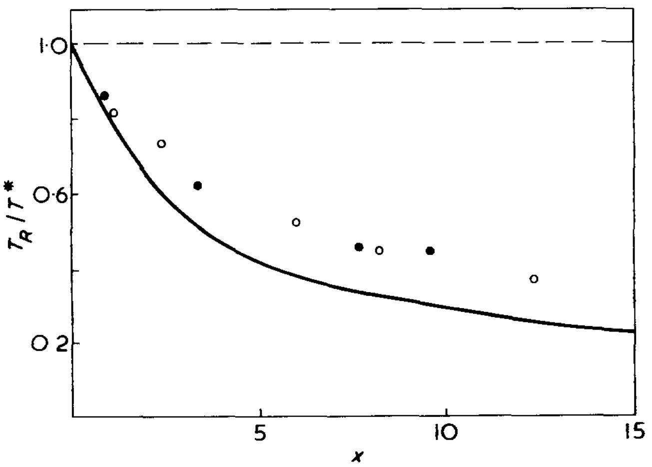

Figure 4 Comparison between the curve T_R/T^* *versus* x predicted for the non-draining limit (———) and the values obtained from the experimental points of ref 10 for polystyrene in toluene (○) and Cyclohexane (●). The free draining assumption leads to T_R/T^*, (— — —)

From equations (6) and (9), the following expression is derived for the non-draining limit:

$$T_R/T^* = P(x) + \frac{3}{2^{7/2}} R \tag{10}$$

where $P(x)$ is the integrated form factor, i.e. for a Gaussian coil:

$$P(x) \equiv P(\vec{\kappa},0) = \frac{2}{x^2}(e^{-x} - 1 + x) \tag{11}$$

and

$$R = Z^{-2} \sum_{j=0}^{Z} \sum_{l=0}^{Z} e^{-x|j-l|/Z} \sum_{k=1}^{Z} K^{-1/2}(1 -$$

$$1/2\pi k) \left[\cos\frac{\pi k(l+j)}{Z} + \cos\frac{\pi k/l - j)}{Z} \right] \tag{12}$$

We have derived an approximate analytical expansion (equation A3) for R as a function of x. The expression is contained in the Appendix, together with some details of the procedure. It has been verified that R exhibits a weak dependence on x. Although it is only for large values of x that the first few terms of the expansion can be taken as a good approximation, the most important contribution to the smaller ones in equation (10) comes from the term $P(x)$. This has been confirmed by the satisfactory agreement between the numerical results for $1/T^*$ obtained by the use of equation (A3), and those given by the direct computation of equation (12) for values of z up to 50 with $x \leqslant 2$. *Figure 3* shows the comparison between our results for $1/T^*$ and those previously obtained by Büldt[5] for a rod and a coil in the free draining limit. If the non-draining limit is supposed to hold for the coil, it is observed that noticeably different trends for coil- and rod-shaped molecules are present only for very large values of x.

From the experimental points utilized below, it is possible to make a preliminary estimate of the behaviour of $1/T^*$. Measuring the slope at $t = 0$ of the curves formed by the points in *Figures 1* and *2* and some others taken from ref 10, i.e.:

$$(1/T^*)_{\text{exp}} = \lim_{t\to 0} \frac{d[\ln P^2(\vec{\kappa},t)/P^2(\vec{\kappa},o)]}{d(t/T_R)} \tag{13}$$

we obtain

$$T_R/T^* = (1/T^*)_{\text{exp}} P(x)/2 \tag{14}$$

The comparison between experimental and theoretical values is shown in *Figure 4*. We should keep in mind that for the free draining limit Büldt obtained $T_R/T^* = 1$. The convenience of taking the non-draining limit to explain these experimental results is thus once again demonstrated.

APPENDIX

As a first approximation (neglecting the contribution of the term in $k^{-3/2}$), the sums over k in equation (12) are of the type:

$$\sum_{k=1}^{Z} k^{-1/2} \cos\frac{\pi nk}{Z} \simeq \text{Re} \sum_{k=1}^{\infty} k^{-1/2} \exp\left(\frac{i\pi nk}{Z}\right) \tag{A1}$$

(The substitution of Z by infinity in the upper limit is a good approximation for $n > 2$; it produces small distribution for $n = 1$ and $n = 2$, which do not significantly affect the final results.)

The sum on the right-hand side of equation (A1) is just the analytic continuation in the complex plane of the polylogarithm[10] of order $1/2[\exp(i\pi n/z)]$. This term is expanded in a Lindelöf series[10] and, taking the real part, we find:

$$\sum_{k=1}^{\infty} k^{-1/2} \cos\frac{\pi kn}{Z} = \left(\frac{Z}{zn}\right)^{1/2} - 1.46 + 0.126\left(\frac{n}{Z}\right)^2 + \theta\left(\frac{n}{Z}\right)^4 \tag{A2}$$

The double sum remaining in equation (12) can be transformed into a double integral without any significant loss of accuracy and, after some straight-forward algebra, we arrive at the results:

$$R = \left(\frac{2}{x}\right)^{1/2} \gamma\left(\frac{1}{2},x\right) - 4.24\left(\frac{1}{x}\right)^{3/2} \gamma\left(\frac{3}{2},x\right) +$$

$$e^{-x}\left[-\frac{2.83}{x} + \theta(x^{-2})\right] - \frac{2.92}{x} + \frac{5.86}{x^2} + \theta'(x^{-3}) \quad \text{(A3)}$$

Where $\gamma(a,z)$ is the incomplete gamma function, defined by:

$$\gamma(a,z) = \int_0^z e^{-t} t^{a-1} dt$$

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REFERENCES

1 Berne, B. J., and Pecora, R. 'Dynamic Light Scattering', Wiley, New York, 1976
2 Pecora, R. *J. Chem. Phys.* 1968, **49**, 1032 and earlier papers referenced therein
3 Zimm, B. H. *J. Chem. Phys.* 1956, **24**, 269
4 Saleh, B. and Hendrix, J. *Chem. Phys.* 1976, **12** 25
5 Büldt, G. *Macromolecules* 1976, **9**, 606
6 Perico, A., Piaggio, P. and Cuniberti, C. *J. Chem. Phys.* 1975, **62**, 2690
7 Perico, A., Piaggio, P. and Cuniberti, C. *J. Chem. Phys.* 1975, **62**, 4911
8 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, 1971 (Chapter VI)
9 Hendrix, J., Saleh, B., Gnädig, K. and de Maeyer, L. *Polymer* 1977, **18**, 10
10 Applequist, J. *J. Chem. Phys.* 1969, **50**, 600