DYNAMIC LIGHT SCATTERING FROM POLYMER SOLUTIONS: THE SUBTRACTION TECHNIQUE

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

Correlation functions measured in dynamic light scattering on polymer solutions often contain a strong sharp decay which obscures and renders difficult a reliable analysis of other decay processes. We demonstrate that this problem can be circumvented by performing a two-step inverse Laplace transformation. The strong component obtained in the first step is subtracted from the correlation function which is then re-analyzed in the second step. We illustrate this technique on semidilute solutions of polystyrene in cyclohexane and tetrahydrofuran.

The existence of slow decays in the correlation functions obtained in dynamic light scattering from semidilute solutions has been reported in many cases, in particular for solutions that are close to the *theta* temperature. We have demonstrated[1] several years ago that these slow modes exist also for a semidilute solution in a good solvent (polystyrene in toluene), but that they have a vanishingly small amplitude. The detailed analysis of these modes in both types of solvents has always been obscured and rendered difficult by the dominant dynamic process of semidilute solutions – the cooperative diffusion. The presence of this mode has two effects: (i) under good solvent conditions, the amplitude of the cooperative diffusion represents more than 90% of the total signal so that the amplitude of the slow mode is very weak; (ii) the peak of cooperative diffusion in the decay times spectra is very narrow, almost equivalent to a δ-function. It was shown[2] that the presence of such sharp components introduces nonphysical oscillations into the inverse Laplace transform of the correlation function that could be erroneously interpreted as significant peaks. This has been called the δ-effect[3].

We demonstrate in this contribution that this problem can be circumvented by a two-step Laplace inversion: after the first inversion, the sharp component is subtracted from the original correlation function and the resulting subtracted correlation function is inverted again. This technique is then applied to selected data obtained on semidilute solutions in both good and *theta* solvents.

THEORETICAL

In dynamic light scattering, the intensity correlation function $g^2(t)$ is measured, which is related to the field correlation function $g^1(t)$ by the Siegert relation,

$$g^2(t) = 1 + \beta \mid g^1(t) \mid^2 \quad . \tag{1}$$

Here, β is an experimental coherence factor. From the field correlation function, the distribution of relaxation times $A(\tau)$ of the scattered light can be obtained, using the following relation:

$$g^1(t) = \int A(\tau) \exp(-t/\tau) \, d\tau \quad . \tag{2}$$

Since Eq. (*2*) represents a Laplace transformation, one has to perform an inverse Laplace transformation of this equation in order to extract $A(\tau)$ from $g^1(t)$. The ill-conditioned nature of this task led to the development of a variety of regularization techniques used to ensure a stable solution to the inversion of Eq. (*2*); for a recent review, see e.g., ref.[4]. Here, we apply a non-linear fitting routine REPES (refs[2,4]) operating directly on the intensity correlation function $g^2(t)$. This program is similar to the widely used program CONTIN (ref.[5]) which, however, inverts the field correlation function $g^1(t)$.

As outlined in the introduction, the inverse Laplace transformation suffers from a particular problem when a strong narrow component is present in the distribution of decay times. The δ-effect observed on experimental data is illustrated in Fig. 1, reproduced from ref.[4], on simulated distributions. In Fig. 1, as well as in subsequent figures showing a distribution function of decay times, the “equal-area representation” is used: when the axis of decay times τ is logarithmic, the quantity $\tau A(\tau)$ has to be plotted on the vertical axis to ensure that two peaks of mathematically equal amplitude also visually look like having the same area.

The subtraction procedure involves the elimination of a relaxation component from the relaxation-time distribution spectrum. The position (τ_d) and amplitude (A_d) of the relaxation must have been identified in a previous analysis (with REPES). In order to subtract the influence of this relaxation at each lag-time, the $g^2(t)$ values must first be converted to $g^1(t)$ values, followed by the subtraction of $A_d \exp(-t/\tau_d)$ and subsequent re-conversion to $g^2(t)$. Thereafter, the corrected corelation spectrum may be analyzed with REPES without the disturbing δ-effect.

EXPERIMENTAL

A dilute stock solution of polystyrene (molecular weight M_w = 3.84 . 10^6, Toyo Soda) in cyclopentane (Fluka) was prepared and optically cleared by centrifugation. The solution was transferred into a dust-free light scattering cell and evaporated. On a vacuum line, known amounts of either cyclohexane or tetrahydrofuran (THF) were condensed into the cells which were then sealed in a dry ice–ethanol mixture under vacuum. The exact resulting concentration of the solutions was determined by weighing. The polystyrene/cyclohexane solution had a concentration of 0.064 g/ml, the polystyrene/THF solution had a concentration of 0.08 g/ml.

The dynamic light scattering apparatus consists of a home-built goniometer with a Hammamatsu R843 photomultiplier, an ALV5000 correlator and an Ar laser (Coherent Innova 70) as a light source. The data were accumulated in a personal computer and treated off-line.

The solution cells were placed in a temperature-controlled sample holder, with accessible temperature range from –140 to +150 °C. The temperature was controlled by electrical heating acting against a cold source provided by a flow of nitrogen vapour obtained by boiling liquid nitrogen. The accuracy of temperature control is 0.1 °C.

RESULTS AND DISCUSSION

Theta Solvent

Figure 2 shows correlation functions obtained for a semidilute solution of polystyrene (M_w = 3.84 . 10^6) in cyclohexane, at a concentration c = 0.064 g/ml and a scattering angle of 90°, and at various temperatures including the *theta* temperature T_Θ = 35 °C. They all exhibit the classical slow mode reported in several instances earlier[6], in addi-

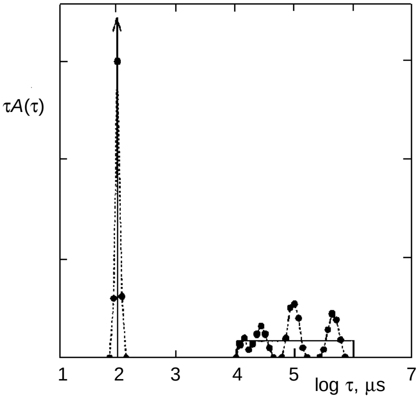

FIG. 1

Recovery (●) by CONTIN with IQUAD = 1 of simulated distribution function of decay times consisting of a δ-function and a rectangular broad component (full line). From refs[2,4]

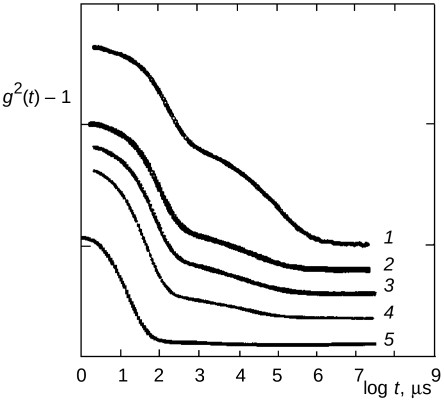

FIG. 2

Intensity correlation functions obtained for the polystyrene/cyclohexane solution at the angle of 90° and at the temperatures: *1* 29, *2* 35, *3* 40, *4* 50, *5* 80 °C tion to the fast decay located in the vicinity of $\tau = 100$ μs which corresponds to the cooperative diffusion. The relative amplitude of the slow mode decreases, as temperature is increased away from the *theta* temperature. The distributions of decay times obtained from the full correlation functions are displayed in Fig. 3. The slow part of the spectrum of decay times exhibits at all temperatures a collection of irregularly positioned peaks. It has been shown[7] that the longest of these relaxation times corresponds well to the longest viscoelastic relaxation time τ_R determined from rheological measurements. It has been speculated before[8] that, because of the δ-effect in the inverse Laplace transformation, the remaining structure of the slow relaxations is not real and that the correct picture consists of one broad relaxation peak representing other internal relaxations of the polymer chains faster than the longest one.

After subtraction of the sharp component corresponding to cooperative diffusion and re-analysis of the data, we obtain a modified distribution of decay times for the slow mode, shown in Fig. 4. A more consistent structure now emerges with only 2 or 3 peaks apparent at any temperature. In particular the fast component in this subtracted spectrum of decay times varies systematically with temperature (more than corresponds to the change in viscosity) and will be important in comparison with the good solvent system discussed below.

Good Solvent

It is well known that, to a first approximation, correlation functions obtained on a semidilute solution in good solvent are single exponential[9]. Figure 5 shows, for several

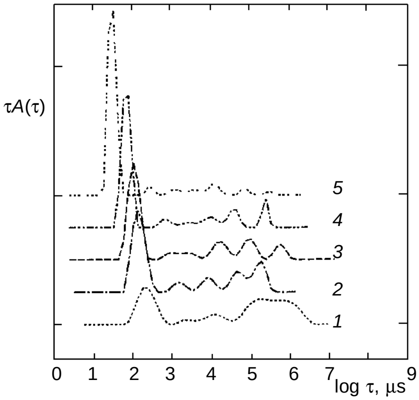

FIG. 3
Distribution function $A(\tau)$ of decay times τ for the polystyrene/cyclohexane solution obtained from the full correlation functions at the angle of 90°. For numbers of curves, see Fig. 2

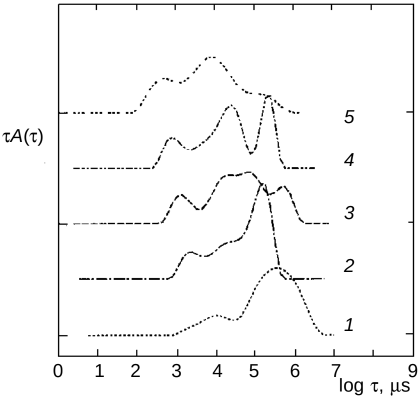

FIG. 4
Distribution function $A(\tau)$ of decay times τ for the polystyrene/cyclohexane solution obtained from the subtracted correlation functions at the angle of 90°. For numbers of curves, see Fig. 2

angles, correlation functions for a solution of polystyrene ($M_w = 3.84 . 10^6$) in THF at 45 °C which indeed appear to contain systematically only one relaxation process. Figure 6 shows the corresponding spectra of decay times. As in the case of the semidilute *theta* solutions discussed above, the sharp dominant component corresponds to the collective diffusion of the entangled polymer structure. We observe, however, that there are always weak contributions present at longer decay times of which no systematic variation can be established. Figure 7 displays the distributions of decay times obtained after subtraction of the cooperative diffusion peak. A clear picture emerges consisting of two peaks whose position can be, within experimental error, considered as independent of angle. By comparison with previously published work, the fast component can be attributed to internal relaxation of the polymer chain. It would be tempting to ascribe again the slower, larger component to the longest viscoelastic relaxation time τ_L. Comparison with data in Fig. 4, however, immediately shows that τ_R is at least 100 times larger than the relaxation time observed in Fig. 7. Let us note that the concentrations of the two solutions corresponding to Figs 4 and 7 are very similar, 6.4% and 8.0%, respectively, so that values of τ_R for these two solutions are comparable; the quality of the solvent has little effect on the longest viscoelastic relaxation time. Figure 8 compares the spectra of relaxation times after subtraction of the cooperative diffusion component, where the horizontal, decay time axis was scaled by the product T/η to remove dependence on the solvent properties. The interesting thing is that the slow peak of the polystyrene/THF spectrum almost exactly corresponds to the fastest peak of the complex structure observed in the polystyrene/cyclohexane spectrum. The internal mode is

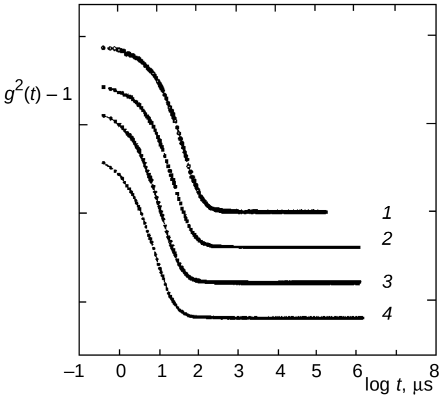

FIG. 5
Intensity correlation functions obtained for the polystyrene/THF solution at 45 °C at the angles: *1* 45, *2* 60, *3* 90, *4* 120°

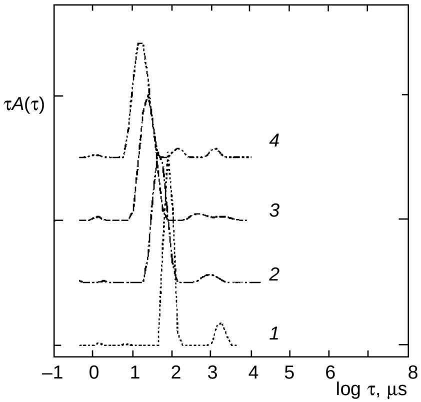

FIG. 6
Distribution function $A(\tau)$ of decay times τ for the polystyrene/THF solution obtained from the correlation functions in Fig. 5 at 45 °C. For numbers of curves, see Fig. 5

not observed in the latter since the data were accumulated several years ago with an old, insufficiently fast photon detection system.

For the polystyrene/THF solution, correlation functions have been measured in a wide temperature range, between –100 and 70 °C. Figures 9 and 10 represent the spectra of decay times obtained at several temperatures from the full correlation curve (Fig. 9) and after subtraction of the cooperative diffusion peak (Fig. 10). A correlation length ξ of the entangled polymer structure can be calculated from the measured cooperative diffusion coefficient D_c using an equation similar to the Stokes–Einstein relation,

$$D_c = \frac{kT}{6\pi\eta\xi} \; , \tag{3}$$

where k is the Boltzmann constant, T absolute temperature and η the viscosity of the solvent.

Figures 11 and 12 show the temperature dependence of the correlation length ξ and of the amplitude A_c of the corresponding cooperative diffusion process. To a good approximation, the amplitude has a constant value of about 0.9 in the whole temperature range, indicating that, from the thermodynamic point of view, this system behaves as an athermal system. We observe a slight temperature dependence of the correlation length, in

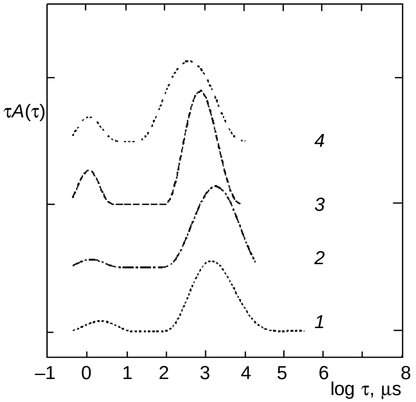

FIG. 7
Distribution function $A(\tau)$ of decay times τ for the polystyrene/THF solution obtained from the subtracted correlation functions at 45 °C. For numbers of curves, see Fig. 5

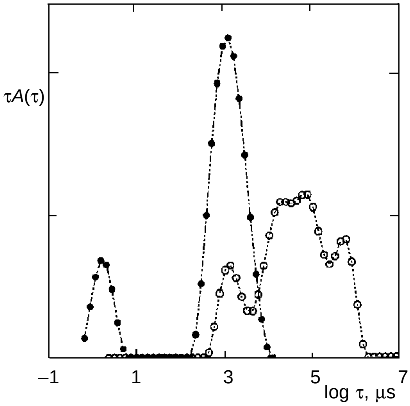

FIG. 8
Distribution function $A(\tau)$ of decay times τ obtained from subtracted correlation functions for the polystyrene/cyclohexane solution at 35 °C (❍), and for the polystyrene/THF solution at 40 °C (●). (The distribution function for the latter was shifted along the τ axis by a factor $T_{\mathrm{THF}}\eta_{\mathrm{cyclohexane}}/T_{\mathrm{cyclohexane}}\eta_{\mathrm{THF}}$ so as to take into account the different temperatures and viscosities of the two solvents.)

particular for temperatures higher than 25 °C which we may tentatively attribute to temperature changes in the statistical segment length. Let us recall that in *theta* and marginal solvents, the correlation length increases with decreasing temperature. This effect, which has been documented previously[10], merely reproduces changes in the osmotic compressibility of the solution in the vicinity of the phase separation tempera-

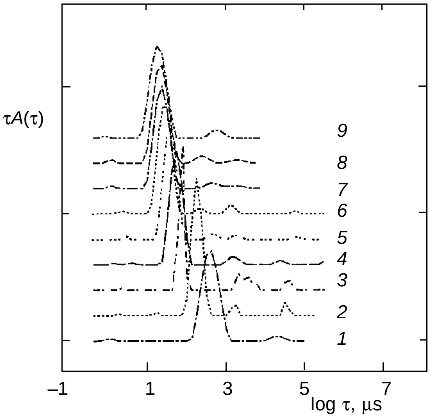

FIG. 9
Distribution function $A(\tau)$ of decay times τ obtained for the solution of polystyrene/THF at the scattering angle of 90° at temperatures: *1* –100, *2* –75, *3* –50, *4* –25, *5* 0, *6* 25, *7* 45, *8* 60, *9* 70 °C

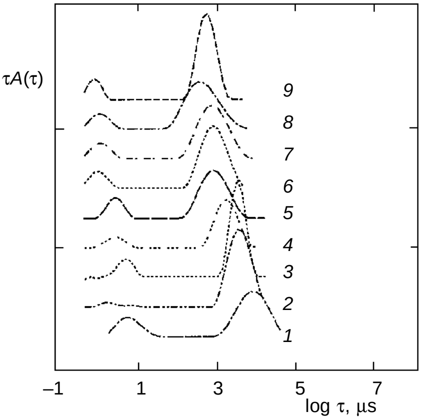

FIG. 10
Distribution function $A(\tau)$ of decay times τ obtained for the solution of polystyrene/THF from the subtracted correlation functions, as explained in the text. For numbers of curves, see Fig. 9

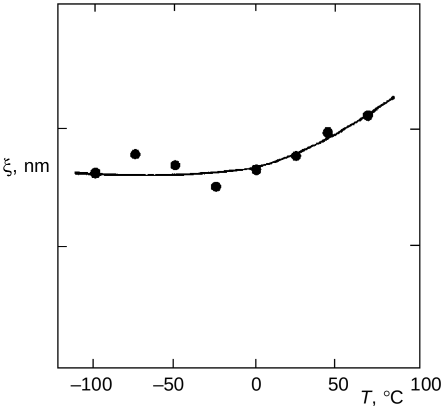

FIG. 11
Temperature dependence of the correlation length ξ for the polystyrene/THF solution

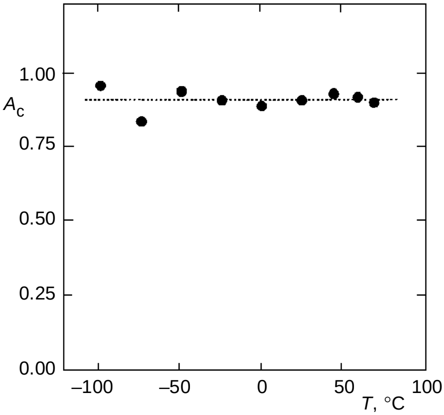

FIG. 12
Temperature dependence of the amplitude A_c of the cooperative diffusion process

ture. For comparison, Fig. 13 displays the temperature dependence of the correlation length for the system polystyrene/cyclohexane, obtained in a similar way from data in Fig. 2.

Both angle-independent components in Fig. 10 slow down with decreasing temperature. Figure 14 presents the data for the first internal mode τ_1, normalized by the ratio T/η to remove the effect of changing solvent properties. The data for temperatures above 40 °C are scattered since they are close to the edge of the correlator window. Interestingly, Fig. 14 indicates that, as temperature is increased, the relaxation time of

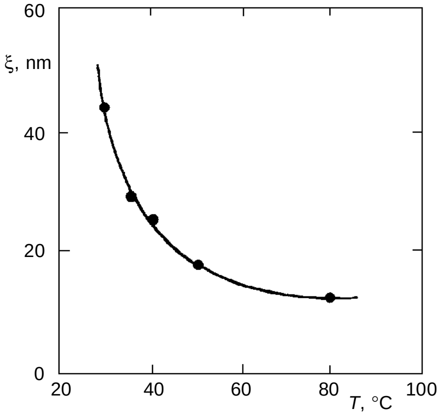

FIG. 13

Temperature dependence of the correlation length ξ for the polystyrene/cyclohexane solution

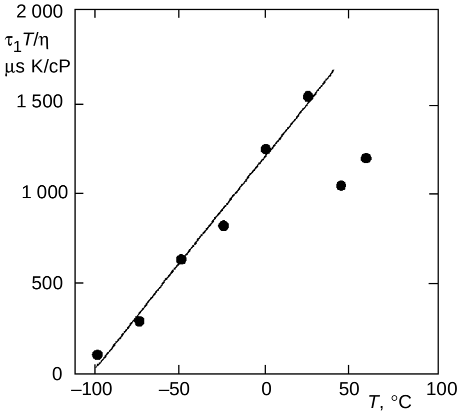

FIG. 14

Temperature dependence of the decay time τ_1 of the internal mode for the polystyrene/THF solution. (The values of decay times have been normalized by T/η to remove the dependence on solvent properties.)

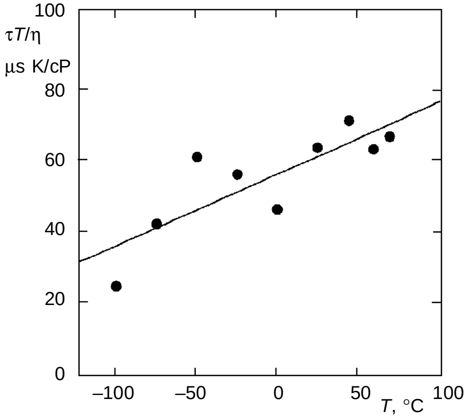

FIG. 15

Temperature dependence of the decay time τ_1 of the slow mode for the polystyrene/THF solution. (The values of decay times have been normalized by T/η to remove the dependence on solvent properties.)

the first internal mode of the chain increases, at least at low temperatures, which could again be attributed to changes in the statistical segment length.

The temperature dependence of the relaxation time of the other, as yet unidentified mode, is presented in Fig. 15, after correction for solvent viscosity and temperature. This temperature dependence is less pronounced than that in the previous case. Further work is under way on other polymer–solvent pairs and using a global technique of mathematical analysis of correlation functions[11] to establish the nature of this second angle-independent relaxation process.

CONCLUSION

We have shown that the subtraction technique enables a meaningful analysis of correlation functions containing a dominant narrow component mixed with additional relaxational structure. We have applied this approach to dynamic light scattering from semidilute solutions both in *theta* and good solvents, where several weak relaxations are obscured by the presence of a strong cooperative diffusion process. On the basis of the results of this contribution, we may conclude that the slow mode present in semidilute *theta* solutions consists of at least three components: (i) the longest viscoelastic relaxation time τ_L, (ii) an angle-independent relaxation observed also in good solvent solutions and located on the fast side of the slow mode, and (iii) the remaining, intermediate part of the spectrum.

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REFERENCES

1. Brown W., Stepanek P. in: *Physical Gels* (S. Ross-Murphy, Ed.), Chap. 9. Elsevier, Amsterdam-New York 1990.
2. Jakes J.: Czech. J. Phys., B *38*, 1305 (1988).
3. Provencher S. W. in: *Laser Light Scattering in Biochemistry* (S. E. Harding, D. B. Satelle and V. A. Bloomfield, Eds). Roy. Soc. Chem., London 1992.
4. Stepanek P. in: *Dynamic Light Scattering: The Method and Some Applications* (W. Brown, Ed.). Clarendon Press, Oxford 1993.
5. Provencher S. W.: Makromol. Chem. *180*, 201 (1979).
6. Brown W., Johnsen R. M., Stepanek P., Jakes J.: Macromolecules *21*, 2859 (1988).
7. Nicolai T., Brown W., Hvidt S., Heller K.: Macromolecules *23*, 5088 (1990).
8. Brown W., Nicolai T., Hvidt S., Stepanek P.: Macromolecules *23*, 357 (1990).
9. Adam M., Delsanti M.: Macromolecules *10*, 1229 (1977).
10. Stepanek P., Perzynski R., Delsanti M., Adam M.: Macromolecules *17*, 2340 (1984).
11. Provencher S. W., Stepanek P. in: *Proceedings of the 6th European Symposium on Particle Characterization* (K. Leschonski, Ed.), p. 193. Nurnberg Messe GmbH, Nurnberg 1995.