Dynamical Scaling in Polymer Solutions Investigated by the Neutron Spin-Echo Technique

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Applying the recently developed technique of neutron spin-echo spectroscopy, we found it possible to verify unambiguously the scaling predictions of the Zimm model: $\Delta\omega \sim q^3$ for the dynamics of a single chain. At higher polymer concentrations, experimental indications for the predicted crossover to many-chain behavior, which is accompanied by a change in exponent from 3 to 2, were observed. Line-shape analysis rules out a simple exponential decay, indicating the importance of memory effects.

The thermodynamic behavior of polymer solutions shows a close similarity to critical phenomena near second-order phase transitions.[1] Certain static scaling predictions have recently found remarkable experimental proof.[2] As in the general development of the theory of phase transitions, the static scaling laws have been extended to dynamical scaling.[3,4] An experimental proof of this theory can in principle be achieved by quasielastic scattering experiments which probe the relaxation spectrum of the polymer. Neutron-scattering experiments, in particular, reach the required region of momentum and energy transfer q and ω. However, until very recently there was no instrument available which provided high energy resolution at small enough momentum transfers. As a result, apart from some attempts to determine the exponent for the q dependence of quasielastic linewidths in dilute solutions,[5,6] little progress has so far been made. In the present work we have applied the newly developed neutron spin-echo technique,[7,8] and for the first time it has been possible (i) to reach the q region of interest in the dilute case, (ii) to perform a line-shape analysis in the time regime, and (iii) to investigate the influence of concentration. In particular, the scaling prediction of the Zimm model in dilute solutions was confirmed unambiguously; the decay of correlations was found to deviate considerably from a simple exponential law and the crossover from single- to many-chain behavior was observed.

The theoretical description of polymer relaxation in solution on the scale of segmental diffusion (Flory radius $R_F > r >$ segment length l) has so far been based on hydrodynamic equations.[9,10] In these theories, deviations from equilibrium are counterbalanced by entropic restoring forces, and the hydrodynamic interaction between the monomers has to be included (Zimm model[11]) in order to obtain physically realistic predictions. With respect to scaling, the excluded-volume interaction has also been considered.[3,4] The influence of concentration was treated by introducing a correlation length ξ which is roughly the distance between entanglement points of different polymers.[3,4] ξ scales with the concentration as $c^{-3/4}$ (Ref. 2) in good solvents. For spatial dimensions $r < \xi$ one expects to observe essentially the behavior of a single chain, while for large r the many-chain behavior should be dominant.

For the single-chain regime the half-width of the relaxation spectrum is predicted to scale with $(T/\eta)q^3$, independent of excluded-volume effects, where T is the temperature and η the viscosity of the solvent.[4,12] In the many-chain regime, the influence of entanglements becomes important. For short times, this gives rise to a gel-like rigidity modulus $E \propto 1/\xi^3$.[2,3] The half-width of the relaxation spectrum is predicted to scale with q^2.[3,4] The proportionality factor may be taken as the cooperative diffusion coefficient D_c of the gel. From the condition of smooth crossover between single- and many-chain regimes $D_c \sim c^{3/4}$ follows.

Scaling theories do not give proportionality factors, nor do they provide information about the shape of the scattering law. For this purpose direct calculations on model systems are necessary. The first direct attack on this problem was undertaken by Dubois-Violette and de Gennes,[9] who treated the Zimm model under θ conditions. For the half width at half maximum they found $\Delta\omega$ (μeV) = $0.28(T/\eta)q^3$ K/cP Å^3. The calculated line shape exhibits considerable deviations from an exponential decay (see Fig. 1). Employing Kirkwood's generalized diffusion equation together with Mori's projection-operator technique, Akcasu and Gurol[10] have calculated the initial slope $\Omega(q,t)$ in the t regime which (apart from a numerical factor) is identical with the half width $\Delta\omega$.[13] Because this approach uses only equilibrium properties of the polymer, it has the further advantage of yielding results for good solvents, where a 30% increase in $\Delta\omega$ is predicted compared with that for a θ solvent at the same temperature and viscosity.[13] The transition regions towards smaller and larger q may also be treated. The theory has the disadvantage of giving no information on line shape as long as memory effects are not included. Calculations with this method have shown that earlier experiments have been performed mainly in the transition region between segment diffusion and "monomer diffusion."[6]

The experiments were performed at the neutron spin-echo spectrometer IN11 at the Institut Laue-Langevin, Grenoble. The neutron spin-echo method has been discussed elsewhere.[7,8] Performing a neutron spin-echo experiment, the final neutron polarization $P(q,H)$ is measured as a function of the applied magnetic field H. In contrast to conventional neutron-scattering techniques—for an ideally defined q—$P(q,H)$ is proportional to the real part of the intermediate scattering law $S(q,t)$, where t is a linear function of H.

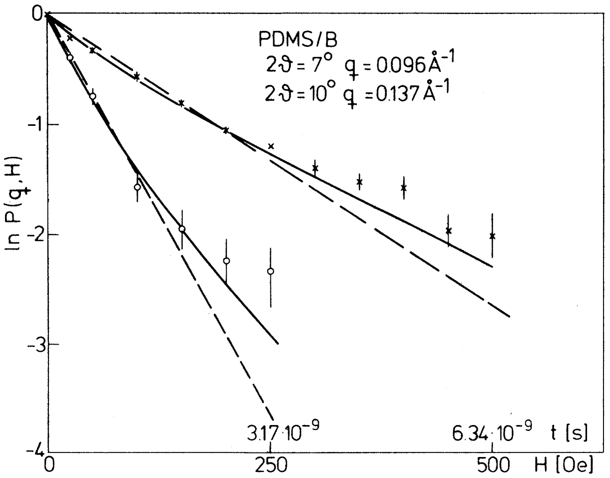

FIG. 1. Polarization $\ln P(q,H)$ as a function of magnetic field H corresponding to time t: solid lines, scattering law as calculated by Dubois-Violette and de Gennes (Ref. 9); dashed lines, exponential decay function.

The scattering experiments were performed using two different protonated polymers: atactic polymethylmethacrylate (PMMA) (mol. weight 7×10^6) and polydimethylsiloxane (PDMS) (mol. weight 3×10^4) dissolved in deuterated benzene. The polymer concentrations were 0.05, 0.15, and 0.30 g/cm^3 in the case of PDMS and 0.05 g/cm^3 for PMMA. The measurements were carried out at 72°C at a mean incident wavelength of 8 Å, with scattering angles 2θ between 2° and 10°, corresponding to q values between 0.027 and 0.137 Å^{-1}. The width of the incident-wavelength distribution was ± 17%; this width is effectively unrelated to instrumental resolution in the spin-echo method. The instrumental resolution was determined using a 9:1 mixture of deuterated and protonated polyethylene, which gives rise to strong elastic coherent scattering in the relevant angular region. The solvent scattering was measured in separate runs. The instrumental background was negligibly small.

The quasielastic intensity $I(q,t)$ scattered by the polymer solutions contains three contributions so that

$$I(q,t) = cK^2 S_{\text{pol}}^{\text{coh}}(q,t) + c\,\frac{\sigma_{\text{inc}}^{\text{pol}}}{4\pi} S_{\text{pol}}^{\text{inc}}(q,t) + (1-c)\frac{\sigma_{\text{tot}}^{\text{sol}}}{4\pi} S_{\text{sol}}(q,t), \qquad (1)$$

where K is the scattering-length contrast between polymer and solvent, the $S(q,t)$ are the intermediate scattering laws and σ the corresponding cross sections. For our samples the coherent cross section of the polymer was always predominant. The data were corrected for the solvent scattering and instrumental resolution, the latter being a simple scale factor in the spin-echo technique. For the incoherent scattering of the polymer, no correction was made. This is justifiable as a very good approximation, since (i) the incoherent scattering was always only a few percent of coherent scattering, (ii) due to the spin-flip scattering the incoherent part enters only with a factor[8] $\frac{1}{3}$, and (iii) the coherent and incoherent contributions are a result of the same dynamical process—the scattering laws differ only slightly.[9]

The corrected data were fitted with the scattering law $S_{\text{DV}}(q,t)$ calculated by Dubois-Violette and de Gennes,[9] and also by an exponential decay function. The fit parameter in both cases was $T/\eta z$, where z allows for deviations in the prefactor (nominally 0.28). Two typical results are shown in Fig. 1 together with the experimental spectra. In addition, a fit of all spectra obtained from one sample was performed with common variation of the parameter. If the q^3 power law is valid, the $T/\eta z$ values for one sample should coincide at all q values. In Fig. 2, $\Delta\omega/q^3 \propto T/\eta z$ is plotted versus q for PMMA and PDMS at $c = 0.05$ g/cm^3. The solid lines give the values obtained by the common fit. There is excellent agreement between the predicted q^3 power law and the experimental results. A fit of the exponent x by common variation of parameters for all spectra of one sample yields $x = 3.02 \pm 0.03$ for PDMS and $x = 2.93 \pm 0.03$ for PMMA. The proportionality factors $T/\eta z$ for $x = 3$ are 515 ± 12 and 878 ± 14 K/cP for PMMA and PDMS, respectively. For $z = 1$, the expected value[9] is 960 K/cP.

The results at higher concentration are shown in Fig. 3. Here $(T/\eta z)q$ (corresponding to $\Delta\omega/q^2$) is plotted versus q. While the results at 0.05 g/cm^3 follow a straight line indicating the q^3 law, the data obtained at 0.30 g/cm^3 PDMS show up strong deviations from this behavior at small q. Indications for increased linewidth at small q are also found at 0.15 g/cm^3. After detecting this behavior using the above-mentioned fit procedure, the data points below 0.1 Å^{-1} for the 0.3 g/cm^3 and below 0.07 Å^{-1} for the 0.15-g/cm^3 samples were refined by fitting to an exponential decay function, which turned out to be a reasonable description in this region. The $1/e$ decay was taken as $\Gamma = D_c q^2$, yielding $D_c(0.15) = (3.06 \pm 0.15) \times 10^{-6}$ cm^2 s^{-1}, and $D_c(0.30) = (4.70 \pm 0.17) \times 10^{-6}$ cm^2 s^{-1}.

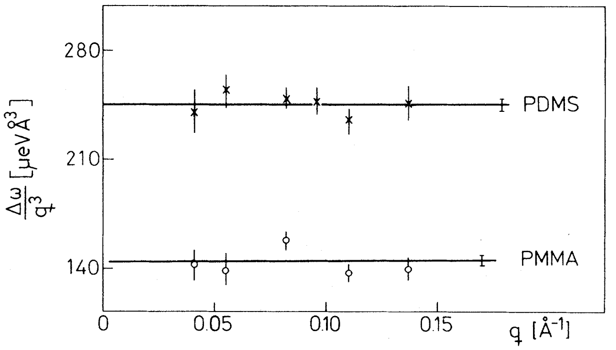

FIG. 2. Linewidth $\Delta\omega$ divided q^3 as a function of q: solid lines, result of a fit with common variation of parameters.

The experiments on dilute solutions and good solvents verify clearly the scaling prediction of the Zimm model. However, the prefactors $(T/\eta z)$ obtained from the fits require some discussion. The model of Dubois-Violette and de Gennes,[9] for example, derives $z = 1$ in the reference case of a θ solvent. For PDMS we have $z = 1.1$, whereas PMMA yields $z = 1.9$. Akcasu[12] predicts an increase of linewidth of about 30% due to the excluded-volume interaction passing over from a θ to a good solvent. In this case the deviations would be even larger. As a consequence, the proportionality factor between $\Delta\omega$ and q^3 has no universal nature, but it seems to differ from polymer to polymer (see also Ref. 6).

Concerning the line shape, the shape functions $S_{\rm DV}(q,t)$ of Dubois-Violette and de Gennes shows clearly a better agreement with the experimental spectra than the exponential decay (Fig. 1). However, as already evident from the figure, at longer times still systematic deviations from this shape function appear in all data sets.

Both statements are supported by the evaluated normalized χ^2 values. For all but one experiment $S_{\rm DV}(q,t)$ turned out to be a reasonable description of the data ($0.79 < \chi^2 < 1.74$; exponential decay function: PDMS at $2\theta = 10°$, $\chi^2 = 3.04$ vs $\chi^2 = 0.99$; or at $2\theta = 8°$, $\chi^2 = 4.6$ vs 1.11). One experiment was performed with better statistics (measuring time increased by a factor of 5). It showed significant deviations from $S_{\rm DV}(q,t)$ ($\chi^2 = 4.0$; for exponential decay function, $\chi^2 = 11.5$).

The strong deviations from an exponential decay, which occurred in all data taken at the lowest concentration, indicate the importance of the

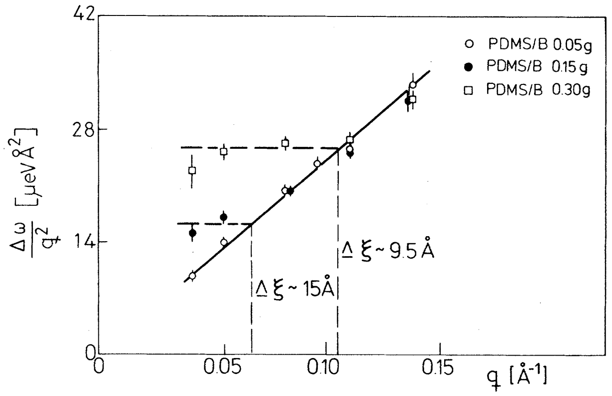

FIG. 3. Linewidth $\Delta\omega$ divided by q^2 as a function of q: solid line, result of a fit with common variation of parameters for the 0.05-g sample. The dashed lines are guides for the eye.

memory terms which have been neglected so far in Akcasu's approach. In view of the simplifications made in the calculations of Dubois-Violette and de Gennes, it is not surprising to also find some discrepancies at long times. While the preaveraging of the Oseen tensor has only a minor influence on the linewidth[12] and probably also on the line shape in the q region considered, the neglect of the excluded-volume interaction seems to be the most severe simplification. An experimental check of this statement will be carried out by future measurements under θ conditions.

At higher concentrations, Fig. 3 clearly shows strong deviations from the q^3 behavior in going to smaller q. This can be taken as an experimental indication for the crossover from a q^3 to a q^2 behavior, as predicted by de Gennes[4] for entangled systems. (This crossover is not to be confused with the expected q^2 behavior at very low q due to the diffusion of the polymer as a whole.) However, the small number of data points prevents an accurate determination of the exponent in the low-q range. For this purpose, more experiments will be necessary. Within the de Gennes theory the position of the crossover point q^* in momentum space allows a dynamical estimate of the screening length ξ, although in order to give a numerical value, one has to know the proportionality factor. The values given on Fig. 3 were obtained assuming $q^*\xi = 1$, and their order of magnitude agrees quite well with those found in static experiments on polystyrene in benzene.[2] Using $q^*\xi = \sqrt{6}$ as given by Akcasu[12] would increase ξ. To prove the predictions concerning the concentration dependence of ξ or D_c again more experiments will be necessary. For the two concentrations we have $D_c(0.3\ \mathrm{g/cm^3})/D_c(0.15\ \mathrm{g/cm^3}) = 1.54 \pm 0.09$ and for the monomer concentrations $(0.26/0.15)^{3/4} = 1.51$, which is in agreement with the proposed behavior.

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Relaxation of Tunneling Systems by Conduction Electrons in a Metallic Glass

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Acoustic experiments on the metallic glass $Pd_{0.775}Si_{0.165}Cu_{0.06}$ are presented which show a tunneling-system decay rate at 0.01 K enhanced by a factor of 10^4 over insulating glass. A theory is presented for decay based upon the coupling of tunneling systems to conduction electrons, and the parameters of the theory are obtained from experiment. Relaxational absorption and dispersion in this amorphous metal are interpreted in terms of a tunneling model with a broad spectrum of decay rates.

In this Letter we show that a strong interaction exists between the conduction electrons and the intrinsic two-level tunneling systems of an amorphous metal. This coupling is inferred by observation in acoustic experiments of a greatly enhanced tunneling-system decay rate T_1^{-1} in the metallic glass $Pd_{0.775}Si_{0.165}Cu_{0.06}$ in comparison with amorphous insulators such as SiO_2. A theory