Interpretation of Anomalous Momentum Transfer Dependences of Local Chain Motion of Polymers Observed by Quasielastic Incoherent Neutron Scattering Experiments

K. L. Ngai,[†] **J. Colmenero,*** **A. Alegría, and A. Arbe**

Departamento de Física de Materiales, Facultad de Química, Universidad del País Vasco, Apartado 1072, 20080 San Sebastián, Spain

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Incoherent quasielastic neutron scattering (QENS) experiments[1–4] on motions in polymers with high momentum transfer, Q, explore times that extend from 10^{-10} to 10^{-7} s and length scales shorter than about 5 Å down to about 0.1 Å. This spatial range limits observation to local motions like the local segmental motion which is often referred to as the α-relaxation. The Rouse model[5] is irrelevant in the high Q regime because it is inapplicable when $Q\sigma \gg 1$ where σ, the distance between beads, is found to be larger than 10 Å for several polymers.[6,7] At such high Q, calculations[8,9] for melts indicate a Brownian type of motion of single beads (or monomers) and a Lorentzian scattering law $S(Q,\omega)$ with its full width at half-maximum, $\Delta\omega$, that has a Q^2 dependence corresponding to a correlation time which varies as Q^{-2}.

However, in the first incoherent quasielastic neutron scattering results for several polymer melts[1] including poly(dimethylsiloxane) (PDMS), poly(tetrahydrofuran) (PTHF), poly(propylene oxide) (PPO), and polyisobutylene (PIB), a Q^{κ} dependence of $\Delta\omega$ was observed with $\kappa \approx 4$ even down to $Q = 1$ Å^{-1}. The Q^{κ} dependence with $\kappa = 2$ is never observed and the form for $S_{\rm inc}(Q,\omega)$ from these melts is distinctively non-Lorentzian corresponding well to a correlation function, $\exp[-(\Gamma t)^{1/2}]$, for the Rouse model, even though the experiments were carried out at such high Q that the Rouse model is inapplicable and local monomer diffusion is expected to take over. A recent investigation of QENS in polymers[2–4,10] with higher glass transition temperatures including poly(vinyl chloride) (PVC), poly(vinyl methyl ether) (PVME), and poly(hydroxy ether of bisphenol A) (PH) has found κ as high as 9.5 for PVC, $\kappa = 4.6$ for PH, and $\kappa = 3.8$ for PVME. A κ value much larger than 4 found for the Q^{κ} dependence of $\Delta\omega$ of the observed local motion in PVC dispels any connection to the Rouse model. Colmenero et al.[10] found also that the non-Lorentzian scattering law can be represented by the Havriliak–Negami relaxation function[11] in the frequency domain as $S_{\rm inc}(Q,\omega) \propto -\omega^{-1}\,{\rm Im}\{1 + [i\omega\tau_{\rm HN}(T,Q)]^{\alpha}\}^{-\gamma}$. In that paper, they also show that the Havriliak–Negami scattering law is consistent with an intermediate scattering function for incoherent scattering given by a stretched exponential function $S_{\rm inc}(Q,t) \propto \exp\{-[t/\tau^*(Q,T)]^{\beta}\}$. The values of the fractional β parameter can be deduced from the α and γ values.[12] The correlation time $\tau_{\rm HN}(Q,T)$, like the inverse half-width, varies as $Q^{-\kappa}$. The temperature dependence and the absolute value at a certain Q of $\tau_{\rm HN}(T,Q)$ within the experimental range as well as the dispersion parameters α and γ (or β) obtained from QENS are similar to the corresponding quantities of the local segmental motion (α-relaxation) obtained from dielectric, mechanical, and nuclear magnetic resonance measurements.[2–4,10] These facts leave little doubt that in polymer melts QENS is probing a Brownian diffusion type of segmental motion. The question that remains is why the Q^{-2} dependence of $\tau_{\rm HN}(T,Q)$ expected for diffusion of a bead segment is never observed, but instead the $Q^{-\kappa}$ dependence with larger κ ranging from the lowest value of 2.9 for PIB to the highest value of 9.5 for PVC. Colmenero et al.[10] have also reported an experimentally observed correlation between the non-Debye behavior and the Q behavior. They found $\beta\kappa = 2$ within the experimental errors for the three polymers investigated. In this paper we point out that an explanation of this anomalous $Q^{-\kappa}$ dependence is already contained in the prediction of the coupling model[13,14] for local segmental motion of polymers. The coupling model can explain quantitatively the deviation of the exponent κ from 2 and the large variation of the value of κ from PIB to PVC. Moreover, it predicts also that this variation of κ is correlated with the variation of the steepness index, S, that characterizes the different dependences on the normalized temperature[15] variable, T_g/T, that $\tau_{\rm NH}$ or τ^* can have for different polymers. These predictions are in accord with experimental data.

Relaxation of monomer units involves translational diffusion and reorientations. In a melt where monomer units are densely packed, their relaxations are correlated and intermolecularly cooperative in nature. Not all units can relax in the same manner at the same time. Although units are equivalent, some have to relax earlier before other units will have a chance to relax similarly later. The relaxations of units are thus inherently "heterogeneous",[16] but, in the consideration of the relaxation of a macroscopic variable, an effective description that on the average the relaxation rate of each unit is slowed down by cooperativity is valid. At short times each unit tends to relax with the uncoupled or independent rate, $W_0 \equiv \tau_0^{-1}$, until at a characteristic time, $t_c \equiv \omega_c^{-1}$, after which the effects of correlations set in, making the process cooperative in nature. On the basis of various theoretical considerations,[13,14] we have arrived at the result that beyond t_c the rate W_0 is slowed down by a self-similar function of time, $(\omega_c t)^{-n}$, where n is called the coupling parameter and lies within the range $0 < n < 1$.[17] From this time-dependent rate it follows that the normalized correlation function has the stretched exponential form

$$\phi(t) = \exp[-(t/\tau^*)^{1-n}] \quad (1)$$

where the observed relaxation time τ^* is related to the independent τ_0 by

$$\tau^* = [(1-n)\omega_c^{\,n} W_0^{\,-1}]^{1/(1-n)} \quad (2)$$

These two coupled results are referred to as the coupling model,[13,14] and it has proven itself in explaining several experimental features of polymer viscoelasticity that are most difficult to understand. There were similar successes when it was applied to other correlated relaxing systems such as vitreous ionic conductors in which the ionic motions are correlated by their mutual interactions.[18] We shall show that the two coupled results of the coupling model given by eqs 1 and 2, when applied to local segmental dynamics involved in the α-relaxation of polymer melts, can explain the anomalous $Q^{-\kappa}$ dependence of τ^* which, as we shall show, is related to $\tau_{\rm HN}$ used in the analysis of QENS data.

Actually this coupling approach has been applied in exactly the way described above to local segmental relaxations[13–15] that involve (1) the orientational degrees of freedom as in shear viscoelasticity, dielectric, and NMR relaxations, (2) the longitudinal compliance as in photon correlation spectroscopy, and (3) bulk compliance as in

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[†] Naval Research Laboratory, Washington, D.C. 20375-5000.

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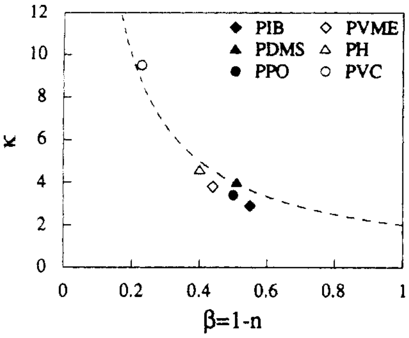

Figure 1. Experimental κ values as a function of the $\beta = 1 - n$ value. The dashed line corresponds to the $2/\beta$ law predicted by the coupling model.

volume recovery. QENS is different from these techniques in giving explicit spatial information. In the experimental Q range, incoherent quasielastic neutron scattering in protonated samples is caused by the translational diffusion of protons of the monomers participating in local segmental dynamics, i.e., is related to the short-line part of the α-relaxation. The microscopic relaxation rate here is Q-dependent and is given by $W_0 = D_0Q^2$ where D_0 is the microscopic diffusion coefficient. We assume $D_0 = a^2/\tau_0$ where a is the actual length scale and τ_0 is the corresponding microscopic relaxation time of the diffusion process. The intermediate scattering function $S_{\mathrm{inc}}(\mathbf{Q},t)$, related via Fourier transformation to the scattering law $S_{\mathrm{inc}}(\mathbf{Q},\omega) = \int_{-\infty}^{\infty} S_{\mathrm{inc}}(\mathbf{Q},t) \exp(-i\omega t)\,\mathrm{d}t$, is the time correlation function obtained from solving the rate equation with the time-dependent rate $D_0Q^2(\omega_c t)^{-n}$ where n is the coupling parameter for local segmental motion. It follows that $S_{\mathrm{inc}}(\mathbf{Q},t)$ is proportional to the stretched exponential

$$S_{\mathrm{inc}}(Q,t) \propto \exp\{-[t/\tau^*(Q,T)]^{1-n}\} \qquad (3)$$

similar to eq 1 except now τ^* is both Q and T dependent. As it has been mentioned, a stretched exponential representation of $S_{\mathrm{inc}}(Q,t)$ is consistent with the Havriliak–Negami representation of the product $\omega S_{\mathrm{inc}}(Q,\omega)$ used in the analysis of QENS data.[2-4,10] In fact, as was shown for PVME, PH, and PVC, the HN parameters used are equivalent, with a good approximation, to a stretched exponential with stretched exponent, $\beta \equiv 1 - n$, equal to 0.44, 0.40, and 0.23 respectively.

Like eq 2, $\tau^*(Q,T)$ in eq 3 is related to the microscopic relaxation rate, $W_0 = a^2Q^2/\tau_0(T)$. The relation reads

$$\tau^*(Q,T) = [(1 - n)\omega_c^{\,n}\tau_0(T)/a^2Q^2]^{1/(1-n)} \qquad (4)$$

which gives rise to the anomalous Q dependence of

$$\tau^*(Q,T) \propto Q^{-\kappa} \qquad (5)$$

where

$$\kappa = 2/(1 - n) \qquad (6)$$

The exponent κ is always larger than 2, and its value depends on n as was experimentally found by Colmenero et al.[10] The coupling parameter for local segmental motion obtained from fitting $S_{\mathrm{inc}}(Q,\omega)$ is approximately the same as that determined from other measurements.[2-4,10] Hence, we may substitute the known values of the coupling parameter previously determined from shear viscoelastic or dielectric measurements into eqs 4–6. The predicted values of κ for several polymers agree quite well with that determined directly from their QENS data, if consideration is taken of the errors involved in the experimental measurements. This is shown in Figure 1 as well as displayed in Table I. It is remarkable that among polymers studied by quasielastic neutron scattering so far PIB has both the smallest n and the smallest κ, while PVC has both the largest n and the largest κ. Of course, this remarkable correlation between n and κ follows as a consequence of eq 6. Considering the fact that the values of n and κ for a polymer are quantities that are determined independently from very different kinds of experimental data, this correlation provides strong support for the coupling model.

An additional prediction simultaneous with the $Q^{-\kappa}$ dependence, eqs 5 and 6, is the dependence of the temperature variation of τ^* on the coupling parameter n. In a first approximation we can assume that the shift factors, $a_T{}^\circ$, of the relaxation times, τ_0, for all polymers have the same temperature dependence given by the Vogel–Fulcher–Tamann–Hesse equation[15]

$$\log a_T{}^\circ = -c_1 + B_0T_\infty/(T - T_\infty) \qquad (7)$$

where $B_0 = c_1c_2/(1 - c_2)$, $T_\infty = (1 - c_2)T_g$, and c_1 and c_2 are constants for all polymers. The reference temperature is T_g defined as the temperature at which $\tau^*(T_g)$ from eq 2 reaches 10^2 s. This definition of T_g is used for all polymers. As a consequence of eq 2, the shift factor a_T of $\tau^*(T)$, again with T_g as the reference temperature, will have the form

$$\log a_T = -\left[\frac{c_1(T - T_g)}{c_2T_g + T - T_g}\right]/(1 - n) \qquad (8)$$

A plot of $\log a_T$ vs $(T - T_g)/T_g$ will distinguish polymers with different coupling parameters.[15] Polymers with larger coupling parameters will have steeper variations, because of the appearance of the factor $(1 - n)$ in the denominator in eq 8. We can rank the steepness of the variation by a single parameter, the steepness index, S, defined as $\mathrm{d}(\log a_T)/\mathrm{d}(T_g/T)$ evaluated at $T = T_g$. From eq 8 it follows that

$$S = (c_1/c_2)/(1 - n) \qquad (9)$$

demonstrating explicitly that larger S is associated with larger n. In Table I we listed also the available values of S determined from dielectric and viscoelastic data for some of the polymers studied by QENS. By inspection it is clear that both κ and S increase with n as expected from eqs 6 and 9 of the coupling model. Figure 2 shows the empirical correlation between the experimental values of κ and S shown in Table I. Taking into account the experimental errors involved in the determination of these quantities, we can fit the data of Figure 2 by a linear

Table I
Characterizing Parameters

polymer	n	$\beta = 1 - n$	$\kappa = 2/(1 - n)$ from coupling model	κ from experiment	S	ref
PIB	0.45 ± 0.05	0.55	3.6	2.9	46	1, 15
PDMS	0.49 ± 0.02	0.51	3.9	4.0	*a*	1, 19
PPO	0.50 ± 0.02	0.50	4.0	3.4	75	1, 15, 20
PVME	0.56 ± 0.02	0.44	4.5	3.8 ± 0.4	92	3, 4, 10
PH	0.60 ± 0.02	0.40	5.0	4.6 ± 0.4	118	10, 21
PVC	0.77 ± 0.03	0.23	8.7	9.5 ± 1.0	220	10, 15, 22, 23

[a] Not available.

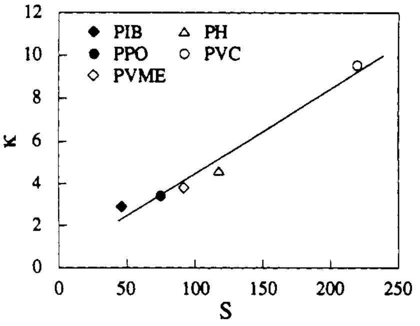

Figure 2. Correlation between κ and S values. The solid line is a linear regression fit of the data.

correlation between κ and S as should be expected from eqs 6 and 9. Deviations from this linear behavior are probably due not only to the experimental errors involved but also to the assumption that c_1/c_2 takes a constant value for all polymers not being strictly valid. This assumption implies that the temperature dependence of τ_0 is the same for all the polymers. It is probable that c_1/c_2, although similar for different polymers, may depend on the particular macromolecular structure.

In summary we have shown that the anomalous Q^κ dependence of $\Delta\omega$, the full width at half-maximum, and the non-Lorentzian line shape of $S_{\text{inc}}(Q,\omega)$ follow as natural consequences of the coupling model. The model predicts correctly the variation of κ from polymer to polymer. It also draws attention to a strong correlation between the value of κ and the steepness of the variation of the local segmental relaxation time with normalized temperature variables $(T - T_g)/T_g$ or T_g/T. For any polymer, from the degree of nonexponentially of the local segmental relaxation (i.e., the stretch exponent β) or from its steepness index, S, of the variation of the relaxation time with normalized temperature, we can predict the Q dependence of the scattering law, $S_{\text{inc}}(Q,\omega)$, i.e., the Q^κ variation of the full width at half-maximum before making the QENS measurements.

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