Polymer Internal Viscosity: Symmetrization of the Dynamic Equations with Propagating Strain

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In a recent paper[1] the internal viscosity was described as the hindrance to the propagation of intramolecular strain within a macromolecule due to the rotational barriers around skeletal bonds. To that effect, the Brownian motions were separated into two symmetrical and statistically independent subsets, *each propagating along one chain direction only*, and the dynamic equations were obtained for either subset separately. It was shown that whenever the effect of solvent friction is sufficiently small compared with that of internal viscosity, the propagation rate is C/τ_0 bonds s^{-1}, where τ_0 is the effective relaxation time for skeletal bond rotations and C is around unity.[1,2] Otherwise said, C/τ_0 may be regarded as the intrinsic velocity of sound within the macromolecule (provided inertial effects may be disregarded). As was pointed out,[1] this description appears to be intuitive and useful, but the underlying dissymmetry of the physical picture within either subset is obviously artificial. In the present note we will show how symmetrically equivalent equations and results may be obtained.

Let us go straight to eq 15 of I (i.e., ref 1), which we shall rewrite as

$$2\alpha(q)(1-\cos q)x'_1(q,t) + \zeta\dot{x}'_1(q,t) \oplus \tfrac{4}{3}i\alpha(q)\sin q\int_{-\infty}^{t}\dot{x}'_1(q,\tau)e^{-(t-\tau)/\tau_0}\,\mathrm{d}\tau = X'_1(q,t) \tag{1}$$

where q ($-\pi \le q \le \pi$) is the normal-mode angle comprising $2\pi/q$ atoms in its wavelength, $\alpha(q) = 3k_BT/C(q)l^2$ is the elastic constant (with l and $C(q)$ respectively the skeletal bond length and the chain generalized characteristic ratio[3]), ζ is the friction coefficient per chain atom, and x'_1 and X'_1 are defined as

$$x'_1(q,t) = \sum_{k=1}^{N} x_1(k,t)e^{iqk} \tag{2a}$$

$$X'_1(q,t) = \sum_{k=1}^{N} X_1(k,t)e^{iqk} \tag{2b}$$

Here, $x_1(k,t)$ and $X_1(k,t)$ respectively are the x coordinate and the corresponding Brownian force of skeletal atom k at time t ($1 \le k \le N \gg 1$). In eq 1, the circled sign embodies the arbitrary assumption that the chain motion propagates toward increasing k's only; we shall label with a subscript 2 the x and X variables relating to the alternative subset moving along decreasing k's (equation with a circled *minus* instead of the circled *plus* sign). In view of the statistical independence between the Brownian forces of different subsets, we may write[1]

$$\langle X'_1(q,t)\cdot X'_2(q',t')\rangle \boxminus 0 \tag{3}$$

It is easy to see that the effective average coordinates are

$$x_A(k,t) = \frac{1}{2^{1/2}}[x_1(k,t) + x_2(k,t)] \quad \left(\rightarrow x'_A(q,t) = \frac{1}{2^{1/2}}[x'_1(q,t) + x'_2(q,t)]\right) \tag{4}$$

In fact, remembering that the coordinates are linear combinations of the corresponding Brownian forces,[4] from eq 2–4 we get

$$B(k,t) = 3\langle[x_A(k,t) - x_A(0,0)]^2\rangle = 3\{\tfrac{1}{2}\langle[x_1(k,t) - x_1(0,0)]^2\rangle + \tfrac{1}{2}\langle[x_2(k,t) - x_2(0,0)]^2\rangle\} = \tfrac{1}{2}[B_1(k,t) + B_2(k,t)] \tag{5}$$

which corresponds to eq 8 of I. This suggests that we construct two different linear combinations from eq 1 and its symmetrical equation with 1 → 2, $\oplus \rightarrow \ominus$, as their sum and difference after multiplication by $1/2^{1/2}$. Let us omit henceforth specification of the normal-mode angle q, defining for simplicity

$$\begin{gathered} 2\alpha(q)(1-\cos q) \equiv a; \qquad \zeta \equiv b; \\ \tfrac{4}{3}\alpha(q)\sin q \equiv c; \qquad x'_{1(2)}(q,t) \boxminus x_{1(2)}(t); \\ X'_{1(2)}(q,t) \equiv X_{1(2)}(t); \\ x_{A(B)}(t) = \frac{1}{2^{1/2}}[x_1(t) + (-)x_2(t)]; \\ X_{A(B)}(t) = \frac{1}{2^{1/2}}[X_1(t) + (-)X_2(t)] \end{gathered} \tag{6}$$

The resulting linear combinations are

$$ax_{A(B)}(t) + b\dot{x}_{A(B)}(t) \oplus ic\int_{-\infty}^{t}\dot{x}_{B(A)}(\tau)e^{-(t-\tau)/\tau_0}\,\mathrm{d}\tau = X_{A(B)}(t) \tag{7}$$

and the fluctuation-dissipation theorem[5] reads in this case (see eq 3 and 6 above and eq II-2 and 3 of I)

$$\langle X_{A(B)}(t)X^*_{A(B)}(0)\rangle = \tfrac{1}{2}[\langle X_1(t)X^*_1(0)\rangle + \langle X_2(t)X^*_2(0)\rangle] = 2Nk_BT\zeta\cdot\delta(t) \tag{8a}$$

$$\langle X_{A(B)}(t)X^*_{B(A)}(0)\rangle = \tfrac{1}{2}[\langle X_1(t)X^*_1(0)\rangle - \langle X_2(t)X^*_2(0)\rangle] = \oplus iNk_BTce^{-t/\tau_0} \quad \text{(if } t \ge 0\text{, zero otherwise)} \tag{8b}$$

Multiplying both sides of one of eq 7 by e^{t/τ_0}, differentiating with time, and dividing again by e^{t/τ_0} gives

$$b\ddot{x}_A(t) + (a + b/\tau_0)\dot{x}_A(t) + (a/\tau_0)x_A(t) \oplus ic\dot{x}_B(t) = \dot{X}_A(t) + X_A(t)/\tau_0 \tag{9}$$

which allows us to get $\dot{x}_B$ as a function of x_A, X_A, and their time derivatives. Two further differentiations analogously give $\ddot{x}_B$ and $\dddot{x}_B$. Also, differentiating the equation symmetrical to (9) (A ⇄ B), we have on the left-hand side terms with $\dddot{x}_B$, $\ddot{x}_B$, $\dot{x}_B$, and $\ddot{x}_A$; substitution of the first three terms as functions of x_A etc.... gives at last

$$\begin{aligned} &b^2x_A^{(\mathrm{iv})}(t) + 2b(a + b/\tau_0)\dddot{x}_A(t) + (a^2 + c^2 + 4ab/\tau_0 + b^2/\tau_0^2)\ddot{x}_A(t) + 2a/\tau_0(a + b/\tau_0)\dot{x}_A(t) + (a^2/\tau_0^2)x_A(t) = \\ &[b\dddot{X}_A(t) + (a + 2b/\tau_0)\ddot{X}_A(t) + (2a/\tau_0 + b/\tau_0^2)\dot{X}_A(t) + (a/\tau_0^2)X_A(t)] \ominus ic[\ddot{X}_B(t) + \dot{X}_B(t)/\tau_0] \end{aligned} \tag{10}$$

The only solution of eq 10 that does not vanish in the long-time limit is the particular integral

$$x_A(t) = \int_{-\infty}^{t}\{\sum_{j=1}^{4}[A_jX_A(\tau) \ominus iB_jX_B(\tau)]e^{\Omega_j(t-\tau)}\}\,\mathrm{d}\tau \tag{11}$$

where $\{\Omega_j\}$ are the roots of the characteristic equation

$$\sum_{r=0}^{4}\alpha_r\Omega^r = 0 \tag{12}$$

Here α_r is the coefficient of $x_A^{(r)}(t)$ in eq 10, while $\{A_j,B_j\}$ may be obtained by substituting (11) in (10). In view of all the constants $\{A_j,B_j,\Omega_j\}$ occurring in pairs of complex conjugate numbers, it is easy to check that the functions multiplying $X_A(\tau)$ and $X_B(\tau)$ within the integral of eq 11 are purely real and purely imaginary, respectively. As a

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particular, simplified example, let us consider the important case that the time scale of interest is large compared with τ_0, so that the integral in eq 1 may be replaced by $\tau_0\dot{x}'_1(q,t)$ and the final differential equation equivalent to (10) is of the second order only. The solution is

$$x_A(t) = \frac{1}{(b^2 + c^2\tau_0^2)^{1/2}} \int_{-\infty}^{t} \left\{ X_A(\tau) \cos\left[\frac{t-\tau}{T_1} - \gamma_1\right] \oplus iX_B(\tau) \sin\left[\frac{t-\tau}{T_1} - \gamma_1\right] \right\} e^{-(t-\tau)/\tau_1}\, d\tau \quad (13)$$

where

$$\tau_1 = (b^2 + c^2\tau_0^2)/ab; \qquad T_1 = (b^2 + c^2\tau_0^2)/ac\tau_0; \qquad \gamma_1 = \arctan\,(c\tau_0/b) \quad (14)$$

Needless to say, all the above results are fully equivalent to a superposition of the normal modes propagating along opposite directions, as obtained in I. It should be pointed out that the arbitrary (circled) signs left in eq 8 and 11 (or (13)) do not entail any ambiguity; in fact, a typical quantity relevant to physical measurement is the average $\langle x_A(t) \cdot x^*_A(t') \rangle$, which is given by the same expression whether the circled signs are as given above or they are *both* changed, as they could be. In analogy with the previous picture,[1,2] eq 11 and 13 imply a relaxation mechanism through damped oscillations, which in turn is strictly associated with the strain propagation along the chain.

In conclusion, the $2N$ normal-mode equations of the previous description, represented by the N equations (1) plus the N associated ones with $1 \rightarrow 2$, $\oplus \rightarrow \ominus$, are now replaced by the N equations (10). The classical physical picture with N normal modes for N chain atoms is thus recovered. In view of eq 5, $x_A(t)$ is the authentic normal-mode amplitude and may be conveniently labeled as $x'(q,t)$. The new equations are symmetrical and no sign ambiguity is left.

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References and Notes

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Communications to the Editor

Self-Diffusion of Polymers in Concentrated Ternary Solutions by Dynamic Light Scattering

The mechanism of molecular transport in entangled polymer systems is a problem of fundamental interest. The concept of reptation and the related process of tube renewal lead to specific predictions for the molecular weight and concentration dependence of the self-diffusion coefficient D_S for polymers in the melt and in solutions of sufficiently high concentration.[1-5] Several experimental techniques have been used to investigate these predictions, including IR microdensitometry,[6,7] pulsed field gradient nuclear magnetic resonance (PFGNMR),[8-11] forced Rayleigh scattering (FRS),[12,13] and dynamic light scattering.[14,15] It is the purpose of this communication to present preliminary data which indicate that self-diffusion behavior in entangled solutions may also be investigated by dynamic light scattering from ternary systems.

The ternary system selected for this study was polystyrene/poly(vinyl methyl ether)/*o*-fluorotoluene. Under suitable conditions polystyrene (PS) and poly(vinyl methyl ether) (PVME) form a compatible pair,[16,17] and thus it is possible that small amounts of PS dissolved in concentrated PVME solutions will display dynamical behavior equivalent to that for PS in concentrated binary solutions. The solvent, *o*-fluorotoluene (*o*-FT), was chosen to match the refractive index of PVME very closely ($\partial n/\partial c$ for PVME/*o*-FT is 0.0016 at 25 °C[22]); thus the observed dynamic scattering may be attributed solely to the PS component. Static and dynamic scattering results from the ternary system PS/PVME/toluene have been reported elsewhere.[18] However, the refractive indices for toluene (1.495) and PVME (1.467)[19] are sufficiently different that it may not be feasible to extract the PS contribution directly when the PVME concentration greatly exceeds that of PS. Dynamic scattering has also been investigated from the PS/PMMA/toluene system.[20]

Table I
Composition of Solutions

concn, g/cm^3		concn, g/cm^3	
PS	total	PS	total
	PS705		
0.0140	0.0380	0.0114	0.167
0.0128	0.0610	0.0117	0.292
0.0128	0.116	0.0125	0.389
	PS1479		
0.0034	0.0202	0.0048	0.171
0.0048	0.0312	0.0044	0.300
0.0048	0.0507	0.0043	0.403
0.0034	0.0936		

Experimental Section. Two monodisperse PS samples were used, with molecular weights 179 000 (NBS 705) and 1 050 000 (NBS 1479). The PVME was obtained from Polysciences, Inc.; it is polydisperse and has a molecular weight of 5×10^4, as determined by light scattering measurements in methyl ethyl ketone. The *o*-FT was obtained from Aldrich and used without further purification. The ternary solutions were prepared gravimetrically by combining appropriate quantities of binary PS/*o*-FT and PVME/*o*-FT solutions. Concentrations were converted to g/cm^3 assuming additivity of volumes and densities of 1.05, 1.02, and 1.00 for PS, PVME, and o-FT respectively. The ternary solutions were allowed to mix thoroughly over the course of 2 weeks, assisted by gentle agitation. Prior to use, the solutions were filtered directly into clean scattering cells through Millipore filters (0.22 μm for PS705 solutions and 0.45 μm for PS1479), and the cells were subsequently sealed. The compositions of the solutions are listed in Table I. The PS concentrations were designed to provide ample scattered intensity, while remaining below the overlap concentration (i.e., $c_{PS} \leq c^*_{PS}$). In the future, it will be appropriate to vary the PS con-

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