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Damping of Acoustic Waves in Dilute Polymer Solutions

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1. Introduction. The shear viscosity of dilute polymer solutions $\eta_S(\omega)$ has been studied in the past in experiments and models and analyzed in a classic book by Ferry.[1] The standard view is that each polymer coil has a sequence of modes discussed by Zimm[2] which are due to hydrodynamic interactions between the monomers; the viscosity η_S then appears as a weighted sum of Lorentzian responses from these modes. For qualitative purposes, at frequencies which are not too high, the first mode dominates, as noticed very early by Peterlin, and η_S can be reduced to a simple form:

$$\eta_S(\omega) = \alpha_s \nu k_B T \frac{\tau_z}{1 + \omega^2 \tau_z{}^2} \qquad (1)$$

Here α_s is a coefficient of order unity, ν is the number of polymer coils per unit volume, $k_B T$ is the thermal energy, ω is the angular frequency, and τ_z is the Zimm relaxation time, with the scaling structure[3]

$$\tau_z \simeq \frac{\eta R_F{}^3}{k_B T} \qquad (2)$$

Here η is the solvent shear viscosity, and R_F is the coil size, which we will estimate for good solvents following Flory's approach[3,4]

$$R_F{}^5 = a^5 (1 - 2\chi) N^3 \qquad (3)$$

where a is the monomer size, N is the number of monomers in a chain, and χ is the Flory interaction parameter.[4]

Our aim in the present note is to discuss the longitudinal viscosity $\eta_L(\omega)$ which may be measured via attenuation of ultrasound—this implies that we now consider the solution as a (weakly) compressible fluid. For incompressible fluids, symmetry imposes that $\eta_L = {}^4\!/_3 \eta_S$. But here we must write

$$\eta_L = \frac{4}{3} \eta_s + \eta_p \qquad (4)$$

where η_p includes specific effects of density changes or (equivalently) of the applied pressure p (see section 3).

Our basic idea is that p modifies the χ parameter, and thus modifies R_F, as indicated in eq 3. We construct a crude model for the resulting dynamics, assuming an analogue of Peterlin's approach, with a single mode relaxation time τ_z.

The equilibrium results are presented in section 2, and the dynamics is schematized in section 3. The surprising conclusion is that η_p is at least comparable to η_S, even in liquids which are not very compressible; this is discussed in section 4. All the exploration is made only at the level of scaling laws.

2. Basic Couplings between Coil Size and Pressure. We start from a coil in good solvent, with a size described by the Flory expression, eq 3. We then raise the pressure by an amount p; the equilibrium size shifts by a certain amount δR. We can think of (at least) two contributions to δR.

The first contribution, δR_K, is due to a change in Kuhn length, which may be written in the form

$$\frac{\delta R_K}{R_K} = \alpha_K \frac{p}{K} \qquad (5)$$

where $K \simeq 10^3$ MPa is the elastic modulus of the solvent, p/K measures the solvent contraction, and α_K is a number which is expected to be of order unity (and which may be positive or negative).

The second contribution, δR_χ, is the consequence of a change $\delta \chi$ in the Flory parameter χ

$$\delta \chi = \alpha_\chi \frac{p}{K} \qquad (6)$$

Again we expect $|\alpha_\chi|$ to be of order unity.[5,6] The resulting shift in size is obtained by differentiating eq 3:

$$\frac{\delta R_\chi}{R_F} = -\frac{2}{5} \frac{\delta \chi}{1 - 2\chi} \qquad (7)$$

Equations 3 and 7 hold provided that we are in a strong swelling regime, i.e., that the perturbation parameter ζ describing the excluded volume is small.[7] The scaling structure of ζ is $\zeta = N^{1/2}(1 - 2\chi)$, and thus eq 7 assumes that

$$1 - 2\chi > N^{-1/2} \qquad (8)$$

We arrive now to an interesting point. When the pressure p is applied, the solvent is contracted—all linear dimensions are reduced by a factor $1 - p/3K$. If the relative shift of δR was just equal to $-p/3K$, the whole system would be just modified by an affine deformation, and no relaxation process would be involved. Thus, we must define an effective chain deformation δR_{eff}, where the affine contribution has been taken out. Collecting all these results, we arrive at

$$\frac{\delta R_{\text{eff}}}{R_F} = \alpha \frac{p}{K} \qquad (9)$$

$$\alpha = \alpha_K - \frac{2}{5} \frac{\alpha_\chi}{1 - 2\chi} - \frac{1}{3} \qquad (10)$$

However, we immediately note that the α_χ term will dominate if

$$1 \gg 1 - 2\chi \gg N^{-1/2} \qquad (11)$$

3. The Longitudinal Viscosity. For a compression wave in a liquid, individual molecules can move parallel or perpendicular to the direction of wave propagation. The existence of these two modes means that energy dissipation depends on two independent quantities; hence there are two fundamental viscosities. The longitudinal compression mode brings about a term **div·v**

in the Navier−Stokes equation, a term which is absent in the more usual case of an incompressible liquid. In the linear theory employed here, it is sufficient to consider only monochromatic waves; the superposition of many modes is trivial. For such a longitudinal wave in the *x*-direction, the velocity of molecules is given by

$$v = v_x = v_0 \cos(kx + \omega t) \tag{12}$$

where ω is the frequency, $c = \omega/k \approx 1500$ m/s is the wave velocity ($c \gg v_0$), and *k* is the wavevector. For frequencies up to megahertz, the sound wavelength is much larger than the coil size. Each chain then feels a time-varying pressure $p = p_0 e^{i\omega t}$, with $v_0/c = p_0/K$. It can be shown[8] that the energy dissipation per unit volume is given by

$$T\dot{S} = \frac{1}{2}v_0^2 k^2 \left(\frac{4}{3}\eta_S + \eta_P\right) \tag{13}$$

$$= \frac{1}{2}\left(\frac{\omega p_0}{K}\right)^2 \eta_L(\omega) \tag{14}$$

where we have defined $\eta_L(\omega) \equiv \frac{4}{3}\eta_S(\omega) + \eta_P(\omega)$. η_P is comparable to η_S and always present in a longitudinal wave. However, in the presence of internal slow relaxation processes (e.g., slow chemical reactions) it is enhanced. In the following, our aim is to find the expression for η_L relevant to polymer solutions.

It is important to realize that, for an acoustic wave, the coefficient α is renormalized by a thermal effect. The wave is adiabatic with temperature modulation

$$\delta T = qp \tag{15}$$

where $q = (T/C_p V)(\partial V/\partial T)_p$ and *V* is the volume.

For instance, the Kuhn length term α_K is renormalized to a new value

$$\tilde{\alpha}_K = \alpha_K + \frac{q}{R_K}\frac{dR_K}{dT} \tag{16}$$

We expect a similar renormalization for α_χ. This renormalization should not affect the scaling law which we postulated in section 2.

As we saw in the previous section, the equilibrium size of the coil is modified from its Flory radius R_F by an amount $\alpha p R_F/K$ proportional to the external pressure. The polymer, characterized by a "response time" τ_z, does not follow this size instantaneously, but rather with a certain time lag. This time lag leads to dissipation. Thus, we may denote δR as the instantaneous deviation of the coil size from the Flory size and write

$$\delta\dot{R} = \frac{1}{\tau_z}\left(\alpha\frac{p}{K}R_F - \delta R\right) \tag{17}$$

The solution is straightforward: $\delta R = \delta R_0 e^{i\omega t}$ and

$$\delta R_0 = \frac{\alpha}{K}\frac{p_0}{1 + i\omega\tau_z}R_F \tag{18}$$

An equivalent formulation is to imagine an oscillating spring in a viscous media characterized by a friction constant ξ

$$\xi\delta\dot{R} = \frac{k_B T}{R_0^2}\left(\alpha\frac{p}{K}R_F - \delta R\right) \tag{19}$$

Here the spring constant is $k_B T/R_0^2$. Hence, we identify the friction constant as $\xi = \tau_z k_B T/R_0^2$, and the total dissipation per unit volume is then

$$T\dot{S} = \frac{1}{2}\nu\xi|\delta\dot{R}|^2$$

$$= \frac{1}{2}\nu\tau_z\frac{k_B T}{R_0^2}\left(\frac{\alpha p_0}{K}\right)^2 R_F^2 \frac{\omega^2}{1 + \omega^2\tau_z^2}$$

$$\simeq \frac{1}{2}\nu\tau_z k_B T\left(\frac{\omega p_0}{K}\right)^2 \frac{1}{(1 - 2\chi)^2}\frac{1}{1 + \omega^2\tau_z^2} \tag{20}$$

In the last line we assumed that α is dominated by the α_χ term (eq 10) and that α_χ is of order unity.

Comparison with eq 14 leads to the identification of η_L as

$$\eta_L(\omega) = \nu\tau_z k_B T\frac{1}{(1 - 2\chi)^2}\frac{1}{1 + \omega^2\tau_z^2} \tag{21}$$

This expression is identical in form to the one-mode expression for the shear viscosity η_S in polymer solutions (eq 1), *except* for the $(1 - 2\chi)^{-2}$ prefactor, which can be large in the vicinity of the Θ point.

How is the wave damped? In the above we have assumed that the wavevector *k* is purely real. In fact, damping is described by an imaginary part of *k* given in

$$k = \frac{\omega}{c} + i\frac{1}{2\rho c^3}\eta_L\omega^2 \tag{22}$$

with the imaginary part much smaller than the real one.

4. Conclusions. (1) We expect a specific (pressure induced) longitudinal viscosity $\eta_L(\omega)$ in polymer solutions. The pressure contribution should be most visible near the Θ point, with an enhancement factor

$$f = \left(\frac{1}{1 - 2\chi}\right)^2 \sim \left(\frac{\Theta}{T - \Theta}\right)^2 \tag{23}$$

(provided that *f* remains smaller than *N*). If we go below the Θ point, the pressure wave modulates a phase separation—there is another dynamics to consider (this was pointed out to us by a referee). (2) We discussed the frequency dependence of η_P in a "one-mode approximation". For the shear viscosity, the restriction to one mode is acceptable when $\omega\tau_z < 1$. But the one-mode approximation could be worse for our case. We can look at the related problem of chain collapse under a temperature jump (from above Θ to below it). The early stages of collapse involve "local clumps" along the chain—this is rather different from the standard deformation in shear. (3) Our main conclusion is that $\eta_P(\omega)$ may be observable in certain dilute polymer solutions. Can we expect this idea to hold for polymer melts? In a melt, the coils are ideal (as first understood by Flory[4]) and the χ parameter becomes irrelevant. But we may still have a small effect of the pressure on the Kuhn length. (4) The pressure dependence of χ may also be of interest in block copolymer melts. Consider, for instance, a lamellar phase; a change in χ leads to a change in the

interfacial area per chain and to chain extension. However, in the strong segregation limit the lamellar period scales as $\sim N^{2/3}\chi^{1/6}$ and depends only weakly on the χ parameter.

References and Notes

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