

TRANSVERSE ACOUSTIC WAVES IN SEMI DILUTE POLYMER SOLUTIONS

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SOMMAIRE

Dans un certain domaine de fréquence, une solution de polymères enchevêtrés doit pouvoir propager des ondes lentes de cisaillement avec un amortissement faible. En bon solvant, la vitesse de propagation varierait comme $c^{2/3}$ (où c est la concentration).

SUMMARY

In a certain low frequency range, semi dilute polymer solutions should propagate shear waves with relatively low damping. In good solvents, the corresponding velocity is expected to vary like $c^{2/3}$ where c is the concentration.

The relaxation of longitudinal modes (concentration fluctuations) in an entangled polymer solution has been analysed by scaling methods (1). Some of the resulting power laws have been checked recently by Adam and Delsanti, using photon beat methods (2). In the present note, we extend the discussion of ref. (1) to transverse modes: for these modes, as we shall see, solvent and solute move with nearly equal velocities and the friction is very much reduced: we expect to find oscillating waves.

At frequencies ω much larger than the terminal relaxation rate $1/T_r$, the polymer behaves like an elastic network with a shear modulus E_t . Scaling predicts $E_t \sim T/\xi^3(c)$ where $\xi(c)$ is the correlation length (3) ($\xi \sim c^{-3/4}$), and T is the temperature. Introducing a displacement field r for the network, and a velocity field u for the solvent, we have a force balance on the polymer of the form

$$c\bar{B}^{-1}(u - \dot{r}) + E_t \nabla^2 r = 0 \quad (1)$$

where $\dot{r} \equiv \frac{\partial r}{\partial t}$ and \bar{B}^{-1} is a friction coefficient defined in ref. (1). The force on the solvent is the sum of a viscous term (solvent viscosity η) and a mutual friction term

$$\rho \dot{u} = \eta \nabla^2 u + c\bar{B}^{-1}(\dot{r} - u) \quad (2)$$

Eqs (1, 2) are specialised for transverse waves, in

semi dilute solutions (for instance all the inertia is attributed to the solvent, with density ρ). Writing $\frac{\partial}{\partial t} = i\omega$ and $\nabla = ik$ we get a dispersion relation of the form

$$\omega^2 - i\omega(D + \nu)k^2 + (A + \nu k^2)Dk^2 = 0 \quad (3)$$

where $D = E_t \bar{B} c^{-1}$, $\nu = \eta \rho^{-1}$ and $A = c\bar{B}^{-1} \rho^{-1}$. Noting that $\nu k^2 \ll A$ and $D \ll \nu$ for all practical situations, and solving for k , we get

$$k = \frac{\omega}{V_t} \left[1 + \frac{i\omega}{\Delta} \right]^{-1/2} \quad (4)$$

where

$$V_t = (E_t/\rho)^{1/2} \quad (5)$$

is the sound velocity, and

$$\Delta = \frac{V_t^2}{\nu} \approx \frac{T}{\eta \xi^2} \sim c^{2/3} \quad (6)$$

is a characteristic frequency introduced in ref. (1). Eq. (4) shows that the waves are weakly damped when $\omega \ll \Delta$. In this regime the two velocities v and \dot{r} are nearly equal, and the damping is due mainly to the solvent viscosity. Typical values would be $\xi \approx 100 \text{ \AA}$, $\nu = 10^{-2}$ (for water) $\Delta = 5 \cdot 10^6 \text{ sec}^{-1}$ and $V_t \sim 2$ meters/sec. Consider now the damping, ruled by the imaginary part k'' of k . From eq (4)

$$2k'' = \frac{\omega^2}{V_t \Delta} = \frac{\omega^2 \nu}{V_t^2} \quad (\omega \ll \Delta) \quad (7)$$

Taking $\omega = 10^4$ this corresponds to an extinction length $(2k'')^{-1} \sim 10 \text{ cm}$ while the wavelength $2\pi k^{-1}$ is of order 1 mm. Thus the waves should propagate.

Our analysis assumed $\omega \gg \frac{1}{T_r}$. Formally, this is always obtained by choosing large molecular masses, since T_r increases fast with M . In practice, for finite T_r , one may incorporate disentanglement damping by making E_t complex

$$E_t \rightarrow E_t \frac{i\omega T_r}{1 + i\omega T_r}$$

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Then (for ω/Δ small) eq (4) becomes

$$k = \frac{\omega}{v_t} \left[1 - i \left(\frac{\omega}{\Delta} + \frac{1}{\omega T_r} \right) \right] \quad (4')$$

Eq (4') is based on a primitive Maxwell model for E_r but it does display both the high and low frequency limits for shear waves.

The present results are rather different from those of Edwards and Miller (4). However, the existence of transverse waves is not a surprise: many viscoelastic data on polymer solutions have been taken on shear waves (5). But we wish to emphasize the interest of systematic studies on sound velocity (V_t) and sound attenuation (k'') as a function of concentration. The most universal regime is the semi dilute one, where the coils are entangled, but monomer/monomer friction is still not dominant. Ideally, one would like to measure V_t and k'' for monodisperse fractions of increasing molecular

masses, and to extrapolate the data towards infinite mass, thus disposing of the complications associated with T_r .

Our analysis has been restricted to good solvents. In Θ solvents we expect $E_r \sim c^2$ and $V_t \sim c$, a very slight change in exponent.

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