a broader temperature range, in various media and with various types of the spin labels and copolymers. The respective experiments are in progress.

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References and Notes

(1) H. Ringsdorf, *J. Polym. Sci. Polym. Symp.*, **51,** 135 (1975).
(2) J. Drobník, J. Kopeček, J. Labský, P. Rejmanová, J. Exner, V. Saudek, and J. Kálal, *Makromol. Chem.*, **177,** 2833 (1976).
(3) S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, *J. Chem. Phys.*, **56,** 716 (1972).
(4) A. T. Bullock, G. G. Cameron, and P. M. Smith, *J. Phys. Chem.*, **77,** 1635 (1973).
(5) J. Čoupek, J. Labský, J. Kálal, and O. Turková, *Biochim. Biophys. Acta*, in press.
(6) J. Kopeček and H. Bažilová, *Eur. Polym. J.*, **9,** 7 (1973).
(7) C. P. Su and H. Morawetz, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(8) E. G. Rozantsev and M. B. Neiman, *Tetrahedron*, **20,** 131 (1964).
(9) E. G. Rozantsev and Y. V. Kochanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1477 (1966).
(10) T. Kurosaki, K. W. Lee, and M. Okawara, *J. Polym. Sci., Part A-1,* **10,** 3295 (1972).
(11) E. G. Rozantsev and V. I. Suskina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1191 (1969).
(12) A. N. Kuznetsov, A. M. Wasserman, A. U. Volkov, and N. N. Korst, *Chem. Phys. Lett.*, **12,** 103 (1971).
(13) A. N. Kuznetsov, A. Y. Volkov, V. A. Livshits, and A. T. Mirzoian, *Chem. Phys. Lett.*, **26,** 369 (1974).
(14) S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Phys. Chem.*, **76,** 1858 (1972).
(15) P. Rejmanová, J. Labský, and J. Kopeček, *Makromol. Chem.*, **178,** 2159 (1977).

Dynamical Scaling for Polymers in Theta Solvents

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ABSTRACT: We construct scaling laws for the motions of very long flexible chains, at the Flory compensation temperature theta; they are more complex than for the case of good solvents. For instance, a single chain in a good solvent makes but few knots on itself. But in a theta solvent we expect it to be self-knotted. In the present paper we concentrate on the problem of *semidilute* (entangled) solutions, and we derive a scaling law for the sedimentation coefficient vs. concentration. We then discuss spontaneous fluctuations of concentration, which can be studied by photon beat methods. At long wavelengths the restoring force (due to the osmotic pressure in the solution) is weak and we predict a cooperative diffusion coefficient D_c *linear* in concentration. At shorter wavelengths one might think that, the frequencies being higher, the restoring forces become dominated by the rubber elasticity of the transient network. However, a simple model suggests that this second regime is never realized.

I. Introduction and Remarks on the Single-Chain Problem

The dynamics of polymer solutions in *good solvents* have been studied recently from the point of view of scaling laws.[2a] The crucial assumption underlying this discussion was the notion that monomer–solvent friction is dominant when compared either to friction between different chains or to internal barrier effects inside one chain. With this assumption, a comparatively simple set of dynamical scaling laws could be produced. Since then, two series of inelastic light-scattering experiments have been performed on polystyrene solutions well above the theta point.[2b,3]

The first experiment probed the collective (gellike) fluctuations of concentration at long wavelengths[2b] and led to a cooperative diffusion coefficient D_c increasing with the monomer concentration c like $D_c \sim c^{0.68}$.

From ref 2a, the scaling prediction for D_c is

$$D_c \sim c^{\nu/(3\nu-1)} \qquad \text{(good solvent)} \qquad \text{(I.A)}$$

where ν is the exponent giving the size R_F of one coil in a good solvent as a function of the polymerization index N.

$$R_F \sim aN^{\nu} \qquad \text{(good solvent)} \qquad \text{(I.B)}$$

With the Flory value $\nu = 3/5$ the theoretical exponent for D_c is 0.75. In fact the agreement is even better if one uses the value of ν which fits best the viscosity and self-diffusion data in the dilute limit, of order of $\nu = 0.55$.

The second experiment,[3] using chains of very high N (molecular masses M up to 10^7 daltons), probed the inner modes of a single coil and showed a non-Lorentzian spectrum with a half-width $\Delta\omega_{\mathbf{k}}$ increasing like a power of the wave vector $\mathbf{k}$

$$\Delta\omega_k \sim \mathbf{k}^x$$

where $x = 2.8 \pm 0.4$. The theoretical prediction here was $x = 3$.

Thus we say the assumptions and the scaling analysis of ref 2a are not too far from reality. At this stage it appeared natural to extend the analysis toward the case of theta solvents, where the static conformations of the chains become nearly ideal. We decided to do this and found, to our great surprise, that theta solvents are considerably more difficult than good solvents!

This can be qualitatively understood from Figure 1, where we consider a single chain in a good, and in a poor, solvent. In a good solvent, the chain is very much swollen and makes no knots on itself. In a poor solvent, it is more compact and makes *many self-knots.* We have found two justifications for this statement.

(1) Let us assume that the number of entanglement points in a coil (K) is proportional to the number of nearest neighbor contacts (P)

$$K = fP \qquad \text{(I.1)}$$

where f is a numerical coefficient. Comparison with mechanical data on strongly entangled systems (molten polymers) suggests that f might possibly be as small as 10^{-2}. We assume that f is a geometrical constant and is independent of the polymerization index N.

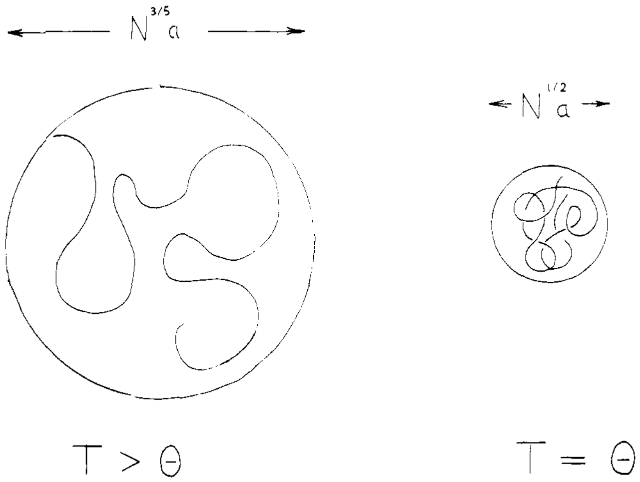

Figure 1. Qualitative aspect of a single chain in a good solvent ($T > \Theta$) and in a poor solvent ($T = \Theta$). In the latter case the chain makes many knots on itself.

The number P can be derived (apart from numerical factors) from appropriate scaling laws:

(a) For a theta solvent we can consider the coil as ideal,[4,5] with a radius $R = N^{1/2}a$ and a concentration of monomers inside the coil

$$c^* = N/R^3 \sim N^{-1/2}a^{-3} \tag{I.2}$$

(where a is a monomer size).

Since the effective monomer–monomer interactions are very weak, for $T = \Theta$ the probability of a binary encounter at any point is proportional to c^{*2}. This gives

$$P_{T=\Theta} \sim c^{*2}a^3R^3 \sim Nc^*a^3 \sim N^{1/2} \tag{I.3}$$

(b) For a good solvent ($T \gg \Theta$), the monomers repel each other, and scaling arguments[6] show that the probability of binary encounters between two monomers at positions (n) and (m) along the chemical sequence is of the form

$$W_{mn} = (\text{constant})|n - m|^{-\psi}$$

where $\psi = 1.97 \sim 2$ for the three-dimensional problem. The total number of direct contacts is then

$$P_{T\gg\Theta} = \sum_{n=1}^{N} \sum_{n=1}^{m} W_{mn} = (\text{constant})\ (\ln N) \tag{I.4}$$

We see that $P_{T=\Theta}$ is much larger than $P_{T\gg\Theta}$.

(2) Recent computer experiments by a Russian group[7] have been directed at the self-knots of a closed random walk. They show that self-avoiding walks on a lattice make very few knots, while "infinity thin" chains (i.e., with no excluded volume) are strongly self-knotted, in agreement with our prediction.

To conclude: (a) In a good solvent, a single chain makes only few knots on itself. Then the standard Zimm analysis[8] (augmented for the inclusion of excluded volume effects in the elastic energy[2a]) is probably nearly correct. (b) In a theta solvent, there are many self-knots, and the Zimm analysis may require some revision whenever the number of self-entanglement points K becomes much larger than unity.

We shall not discuss this one-chain problem in detail here, for two reasons: (i) The values of N which are required to reach the entanglement limit may become prohibitively large; from eq I.1 and I.2 we have a number of entanglements

$$K \sim fN^{1/2} \tag{I.5}$$

and if $f \sim 10^{-2}$ we would require $N = 10^6$ to make ten entanglements on the chain. With typical flexible polymers this would correspond to molecular weights of order 10^8, which are difficult to synthetize and mechanically very weak. (ii) The single-chain analysis in the entangled regime is a most delicate exercise in dynamical scaling and requires very long explanations.

Thus, after a long reflexion, we decided to restrict the present discussion to the *many-chain* problem (semidilute solutions) at the theta point; this remains comparatively simple, because the fluctuation modes are plane waves. In section II we recall first the main results on static correlations for these theta solutions, which are due to the Saclay group,[8,9] and we introduce the dynamical behavior in the hydrodynamic limit (very long wavelengths). In section III we consider the behavior at slightly shorter wavelengths, where the relaxation rates become higher and comparable to the disentanglement rates. Our model for disentanglement is very primitive and based on a single relaxation time, but it does lead to some unexpected features.

II. Semidilute Solutions: Long-Wavelength Limit

(1) Characteristic Lengths and Elastic Moduli. We now discuss the properties of solutions with concentrations $c > c^*$ where different coils overlap. The behavior of the static correlations near the theta temperature have been analyzed in recent experiments by the Saclay group.[9] A scaling theory due to Daoud and Jannink[10] accounts rather well for these data. Considering only the regime where $T = \Theta$ exactly, we shall first give a summary of the main static properties.

(a) The total density–density correlation function has the screened form

$$\langle c(0)c(r)\rangle - c^2$$

$$\equiv \langle \delta c(0)\delta c(r)\rangle = (\text{constant})\ c^2\frac{a}{r}e^{-r/\xi} \tag{II.1}$$

where ξ is a (concentration dependent) correlation length.

$$\xi \sim 1/ca^2 \qquad (c > c^*) \tag{II.2}$$

For $c \rightarrow c^*$ the length ξ becomes comparable to R_0. For concentrated solutions ($ca^3 \sim 1$) ξ decreases down to the monomer size a.

(b) The osmotic pressure $\pi(c)$ and the isothermal osmotic rigidity $E_0 = c\partial\pi/\partial c$ scale like

$$\pi \sim E_0 \sim Ta^6c^3 \tag{II.3}$$

(c) The concentration of entanglement points is of order c^2a^3 (since the chains overlap freely). The elastic modulus, measured at frequencies such that the entanglements do not relax, E_{gel}, has been discussed extensively in the literature. One of us has given arguments[11] leading to the simple (and rather commonly accepted) form

$$E_{\text{gel}} = f_sTc^2a^3 \tag{II.4}$$

where f_s is a numerical coefficient, similar to the f of eq I.1.

The main question to be discussed here is the following: when we probe a local fluctuation of concentration, at a wave vector $\mathbf{q}$, will the restoring forces involve the *isothermal* rigidity E_0 or the entangled rigidity E_{gel}? The ratio of the two is

$$\rho = \frac{E_{\text{gel}}}{E_0} \sim f_s/ca^3 \tag{II.5}$$

and if f_s is not too small, ρ may be large. Recalling that the minimum concentration for overlapping chains is $c = c^* \sim N^{-1/2}$ we see that $\rho \lesssim \rho(c^*) \sim K \equiv fN^{1/2}$ (where we have put $f_s = f$). In the following we shall assume K large and ρ large; although these conditions may be difficult to realize in practice (as explained in section I) they represent the simplest conceptual limit ($N \rightarrow \infty$) for our problem.

(2) The Slow Limit. Let us consider now a fluctuation of concentration

$$c \rightarrow c + \delta c(x)$$

$$\delta c(x,t) = \delta c \cos \mathbf{q} x e^{-t/\tau_{\mathbf{q}}} \qquad \text{(II.6)}$$

where the wave vector $\mathbf{q}$ is very small and the relaxation rate $1/\tau_{\mathbf{q}}$ very slow. We want

$$\tau_{\mathbf{q}} > T_{\mathrm{r}}$$

where T_{r} is the characteristic time for the relaxation of entanglements (the "terminal time" determined by mechanical measurements[12]). We expect $1/\tau_{\mathbf{q}}$ to have the diffusion form

$$\left.\frac{1}{\tau_{\mathbf{q}}}\right|_{\mathbf{q}\rightarrow 0} = D_{\mathrm{c}}\mathbf{q}^2 \qquad \text{(II.7)}$$

where the cooperative diffusion coefficient D_{c} will be a function of concentration. We shall mention here two approaches to the calculation of D_{c}.

(a) Qualitative approach. We may think of each chain as a sequence of "blobs" each occupying a volume ξ^3 and each having a number of monomers

$$g = \left(\frac{\xi}{a}\right)^2 = c\xi^3 = \frac{1}{(ca^3)^2}$$

Let us assume that blobs act as independent units; then the Stokes friction factor for one blob is $6\pi\eta_{\mathrm{s}}\xi$ (η_{s} being the viscosity of the solvent). Also the number of blobs per cm^3 is

$$c/g = 1/\xi^3$$

Thus, following the two-fluid model of ref 2a we may write the balance between viscous and elastic forces in the form:

$$(c/g)6\pi\eta_{\mathrm{s}}\xi(\dot{\mathbf{r}} - \mathbf{u}) = E_0\nabla^2\mathbf{r} \qquad \text{(II.8)}$$

The left-hand side of eq II.8 represents the analogue of Darcy's law: $\dot{\mathbf{r}}$ is the local velocity of the chains and $\mathbf{u}$ is the solvent velocity. It may be of interest to discuss the corresponding permeability coefficient λ defined by

$$\lambda = \frac{g}{6\pi c\xi} \sim \xi^2 \qquad \text{(II.9a)}$$

Equation II.9 applies both for good solvents or theta solvents, the only changes being in the structure of $\xi(c)$.

Permeabilities of this type have been derived from sedimentation experiments.[13,14] The predictions from scaling are

$$\lambda \sim \begin{matrix} c^{-3/2} & \text{(good solvent)} \\ c^{-2} & \text{(theta solvent)} \end{matrix}$$

It is not quite feasible to extract exponents from the data of ref 14, but one qualitative point is of interest; at a fixed concentration c in the semidilute regime, ξ (and thus λ) is expected to be bigger for theta conditions than in a good solvent. This is precisely what has been observed.[18]

Equation II.8 leads to a diffusion law (u being negligible in semidilute solutions) with

$$D_{\mathrm{c}} = T/6\pi\eta_{\mathrm{s}}\xi \qquad \text{(linear in } c\text{)} \qquad \text{(II.9b)}$$

(b) Quantitative Approach. A good starting point for the calculation of the cooperative diffusion coefficient is a Kubo formula[15]

$$D_{\mathrm{c}} = \frac{\int_0^\infty \mathrm{d}t \int \mathrm{d}\mathbf{r}\, \langle j_x(00) j_x(\mathbf{r}t)\rangle}{\int \mathrm{d}r\, \langle \delta c(0)\delta c(\mathbf{r})\rangle} \qquad \text{(II.10)}$$

where j represents the local current of monomers and $\langle \delta c \delta c\rangle$ is a correlation function for the fluctuations of concentration. One may also think in terms of the pair correlation function $g(\mathbf{r})$ given the excess probability of finding a monomer at $\mathbf{r}$ when another monomer is known to be at the origin

$$g(\mathbf{r}) = (1/c)\langle \delta c(0)\delta c(\mathbf{r})\rangle \qquad \text{(II.11)}$$

In eq II.10 we write the current as

$$j = \delta c \mathbf{v}$$

(where $\mathbf{v}$ is a local hydrodynamic velocity) and factorize

$$\langle jj\rangle = \langle \delta c \delta c\rangle \langle vv\rangle$$

Furthermore we ignore the time delay in the $\langle \delta c \delta c\rangle$ part (all these operations are standard in the theory of critical binary mixtures; see for instance ref 15). Finally the integration upon time of the $\langle vv\rangle$ correlation function gives simply the Oseen hydrodynamic tensor

$$\int \mathrm{d}t\, \langle v_\alpha(00) v_\beta(\mathbf{r}t)\rangle = \frac{T}{8\pi\eta_{\mathrm{s}} r}\left[\delta_{\alpha\beta} + \frac{r_\alpha r_\beta}{r^2}\right]$$

Averaging over angles we get

$$D_{\mathrm{c}} = \frac{\int g(\mathbf{r}) \dfrac{T}{6\pi\eta_{\mathrm{s}} r}\,\mathrm{d}\mathbf{r}}{\int g(\mathbf{r})\mathrm{d}\mathbf{r}} \qquad \text{(II.12)}$$

and inserting the (II.1) for the correlations we obtain eq II.9b exactly. The main approximations in this approach are: the factorization of the $\langle jj\rangle$ correlations; the assumption that the viscosity η_{s} to be used in the Oseen tensor is not renormalized.

Our experience with (i) critical mixtures and (ii) polymers in good solvents suggests that these assumptions are reasonable for a first approximation, although they will have to be refined in future work.

III. Dynamical Behavior at Higher Wave Vectors

If we compare the two above approaches to eq II.9 we see that the first approach had one merit: it shows clearly the role of the elastic modulus E_0. If we want now to extend eq II.9 to higher $\mathbf{q}$ values, we might expect that at some point the relaxation rate $1/\tau_{\mathbf{q}}$ becomes fast and that the network then behaves like a rubber, with a larger modulus E_{gel}. Thus we would be tempted to replace eq II.7 and II.8 by

$$1/\tau_{\mathbf{q}} \rightarrow E_{\mathrm{gel}}\lambda\mathbf{q}^2 \qquad (\tau_{\mathbf{q}} < T_{\mathrm{r}})$$

and to expect a much larger diffusion coefficient

$$\tilde{D}_{\mathrm{c}} = \rho D_{\mathrm{c}} = f_{\mathrm{s}}\frac{T}{6\pi\eta_{\mathrm{s}} a} \qquad (\tau_{\mathbf{q}} < T_{\mathrm{r}})$$

We shall now show that the coefficient $\tilde{D}_{\mathrm{c}}$ is *not* observable. In fact, when we increase $\mathbf{q}$ the rate $1/\tau_{\mathbf{q}}$ becomes comparable to $1/T_{\mathrm{r}}$ and then sticks to this value.

The argument is based on a dynamic equation of the form

$$\lambda^{-1}(\dot{r} - u) = \frac{\partial}{\partial x}(\sigma_0 + \sigma_1) - \frac{\partial W}{\partial x} \qquad \text{(III.1)}$$

where $\dot{r}$ is the displacement of the chains (measured here along the direction x parallel to $\mathbf{q}$) and σ_0 is the isothermal stress

$$\sigma_0 = E_0\,(\partial r/\partial x) \qquad \text{(III.2)}$$

and σ_1 is the stress contribution due to the entanglements. We write for σ_1 an equation corresponding to a dashpot and a spring in series

$$E_{\rm gel}^{-1}\dot{\sigma}_1 + \frac{\sigma_1}{\eta} = \frac{\partial f}{\partial x} \tag{III.3}$$

where $\eta = E_{\rm gel}T_{\rm r}$ is a bulk viscosity of the entangled system. Equation III.3 corresponds to the simplest Maxwell model with correct limiting behaviors at low and high frequencies.

Finally the energy $W(x,t)$ in eq III.1 represents an external perturbing potential. The introduction of W is essentially a convenient device to calculate the power spectrum of inelasticity scattered light $S(\mathbf{q}\omega)$. Namely from eq II.1–3 we compute first the displacement r induced by a weak perturbation $W = W_0 \exp i(\mathbf{q}x - \omega t)$ and write it as

$$r = -\chi(\mathbf{q}\omega)\frac{\partial W}{\partial x} = -i\mathbf{q}\chi W \tag{III.4}$$

Then a general theorem tells us that the power spectrum of interest is[16]

$$S(\mathbf{q}\omega) \equiv \frac{1}{2\pi}\int \langle \delta c(0)\delta c(rt)\rangle e^{i(\mathbf{qr}-\omega t)}\,\mathrm{d}\mathbf{r}\,\mathrm{d}t$$
$$= -\frac{Tc\,\mathbf{q}^2}{\pi\omega}\,\mathrm{Im}\,\{\chi(\mathbf{q}\omega)\} \tag{III.5}$$

In the present case eq III.1–4 give

$$\chi^{-1}(\mathbf{q}\omega) = i\omega\lambda^{-1} + E_0\mathbf{q}^2 + E_{\rm gel}\mathbf{q}^2\frac{i\omega T_{\rm r}}{1 + i\omega T_{\rm r}} \tag{III.6}$$

Our aim is to consider $S(\mathbf{q}\omega)$ at one fixed $\mathbf{q}$ and to estimate the half-width at half-maximum $\Delta\omega_{\mathbf{q}}$. The algebraic discussion of eq III.5 and III.6 is heavy, and we shall simplify it by assuming that $E_{\rm gel}/E_0 = \rho$ is much larger than unity.

It is convenient to introduce dimensionless parameters

$$\omega T_{\rm r} = \alpha$$
$$\Delta\omega_{\mathbf{q}}T_{\rm r} = \alpha_{\rm c}$$
$$D_{\rm c}T_{\rm r}\mathbf{q}^2 = \mu \tag{III.7}$$

and to study

$$\tilde{S}(\mu,\alpha) \equiv S(\mathbf{q}\omega)\frac{\pi E_0}{cTT_{\rm r}} \tag{III.8}$$

Let us first investigate the poles of the response function S; as usual these poles will describe the spontaneous modes of the system. To display the modes, we write

$$\tilde{S} = -\alpha^{-1}\,\mathrm{Im}\left\{\frac{1 + i\alpha}{D(\alpha)}\right\} \tag{III.9}$$

where

$$D(\alpha) \equiv 1 + i\alpha(1 + \rho + \mu^{-1}) - \mu^{-1}\alpha^2$$
$$= -\mu^{-1}(\alpha - is_1)(\alpha - is_2)$$

Here s_1 and s_2 are the two relaxation rates of interest (for a given wave vector, fixed μ). There is one slow mode with relaxation rate

$$s_1 \sim (1 + \rho + \mu^{-1})^{-1} \sim (\rho + \mu^{-1})^{-1} \qquad (\ll 1) \tag{III.10}$$

and one fast mode with rate

$$s_2 = \mu s_1^{-1} \sim 1 + \rho\mu \qquad (\gg 1) \tag{III.11}$$

(The reader may check that these approximate formulas for the two roots are correct for all μ values, provided that $\rho \gg 1$.) The aspect of these relaxation modes is shown on Figure 2. Transforming $D^{-1}(\alpha)$ into a sum of single pole contributions

$$D^{-1}(\alpha) = \frac{i\mu}{s_2 - s_1}\left[\frac{1}{\alpha - is_2} - \frac{1}{\alpha - is_1}\right]$$

and using the inequality $s_2 \gg s_1$ we can rewrite eq III.9 in the explicit form

$$\tilde{S}(\mu\alpha) = \frac{\pi\mu}{s_2}\left[L_2(\alpha) + s_1^{-1}L_1(\alpha)\right] \tag{III.12}$$

where $L_i(\alpha)$ is a short hand for a Lorentzian curve of unit area

$$L_i(\alpha) = \frac{1}{\pi}\frac{s_i}{s_i^2 + \alpha^2} \qquad \left(\int L_i(\alpha)\,\mathrm{d}\alpha = 1\right) \tag{III.13}$$

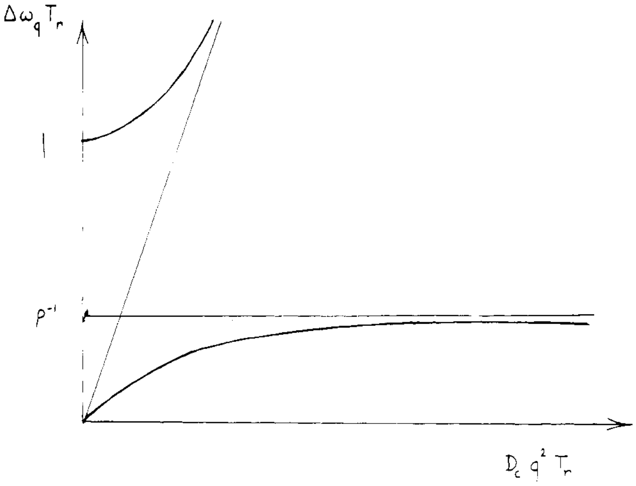

Figure 2. Width $\Delta\omega_{\mathbf{q}}$ of the signals expected in inelastic light scattering by semidilute solutions at the theta point. There are two modes with very different widths. When the rubber elasticity modulus $E_{\rm gel}$ is much larger than the osmotic modulus E_0 ($E_{\rm gel}/E_0 = \rho \gg 1$), the intensity for the slow mode dominates. Notice the formal analogy between these curves and the dispersion relation $\omega(\mathbf{q})$ for transverse waves in polar crystals.

Returning now to the physical problem, we conclude that the light-scattering signal (for a fixed $\mathbf{q}$, as a function of frequency ω) is the sum of two Lorentzians: a narrow Lorentzian of half-width

$$\Delta\omega_{\mathbf{q}}|_{\rm slow} = s_1T_{\rm r}^{-1} = \frac{D_{\rm c}\mathbf{q}^2}{1 + \rho T_{\rm r}D_{\rm c}\mathbf{q}^2} \tag{III.14}$$

and a broad Lorentzian of width

$$\Delta\omega_{\mathbf{q}}|_{\rm fast} = s_2T_{\rm r}^{-1} = \frac{1}{T_{\rm r}} + \rho D_{\rm c}\mathbf{q}^2 = \frac{1}{T_{\rm r}} + \tilde{D}_{\rm c}\mathbf{q}^2 \tag{III.15}$$

(a) Consider first the "hydrodynamic" limit of very small wave vectors ($\rho\mu \ll 1$). Then one Lorentzian has a width $\Delta\omega_{\mathbf{q}}|_{\rm slow} = D_{\rm c}\mathbf{q}^2$ as predicted in section II. The other Lorentzian is of width $\sim 1/T_{\rm r}$ but eq III.12 shows that the weight of the fast mode is smaller than the weight of the slow mode by a factor $s_1 \sim \mu \ll 1$; only the slow mode will be seen.

(b) Let us now turn to the opposite regime ($\rho\mu \gg 1$). Then the slow mode has a constant width $\Delta\omega_{\mathbf{q}}|_{\rm slow} \to 1/\rho T_{\rm r}$, and the fast mode shows a rapid diffusion $\Delta\omega_{\mathbf{q}}|_{\rm fast} \to \tilde{D}_{\rm c}\,\mathbf{q}^2$. But again the weights make the fast mode unobservable; the ratio of the weights is $s_1 \sim 1/\rho \ll 1$.

These results have an analogue in a simpler system; if we consider the scattering of light by a simple fluid, we find, at fixed $\mathbf{q}$, a central Rayleigh peak of intensity $I_{\rm R}$ and two lateral Brillouin peaks, of total intensity $I_{\rm B}$. The latter component corresponds to adiabatic sound waves, and the intensity ratio is related to the corresponding compressibilities.

$$\frac{I_{\rm B}}{I_{\rm B} + I_{\rm R}} = \left(\frac{\partial\rho}{\partial p}\right)\bigg|_{\rm adia}\bigg/\left(\frac{\partial\rho}{\partial p}\right)_{\rm iso}$$

In our case the analogue of "adiabatic" is "fixed entanglements" and the two modes are diffusive. But we have the same general features; when the restoring force for the fast mode becomes very large, the relative intensity of the fast mode becomes small.

IV. Conclusions

The first, and more important, prediction of this paper concerns the sedimentation coefficient, or the related permeation coefficient λ of eq II.9a. More systematic studies on the concentration dependence of λ would be most helpful.

The second result concerns the cooperative diffusion coefficient D_c, which should be a linear function of concentration; D_c can be measured by macroscopic means or by photon beat methods.

The third point is negative; it does not seem possible to probe the rubber-like behavior of an entangled solution by inelastic scattering of light. Equation III.12 suggests that when the scattering wave vector **q** is increased, the line width $\Delta\omega_{\mathbf{q}}$ never becomes of order $\lambda E_{\mathrm{gel}}\mathbf{q}^2$ but saturates at a value $\rho^{-1}T_r^{-1}$. This lack of a rubbery regime appears to be confirmed by preliminary experiments of Adam and Delsanti (unpublished); it was, in fact, their observations which induced us to perform the analysis of section III.

Of course there are some limitations to the model and to our discussion. (a) Our analysis in section III assumes a single relaxation time T_r for the entanglements (eq III.3) and this is an over simplification. (b) We constantly assumed that $\mathbf{q}\xi \ll 1$. The regimes at larger **q**'s could be interesting, since they could probe the distance between entanglement points. However, the **q** values of interest are too large for photon beat studies, and the corresponding $\Delta\omega_{\mathbf{q}}$ are too small for neutron inelastic scattering experiments; this part of the problem belongs to a rather distant future.

(c) We have not discussed the disentanglement time T_r. An estimate of T_r can in fact be constructed from the reptation model[17] and is of the form

$$T_r = (\text{constant})\,\frac{\eta_s a^3}{T}\,N^3(f_s c a^3)^{3/2}$$

However, this suffers from the usual defect of being proportional to N^3 rather than $N^{3.3}$ as suggested by the mechanical data. It is of interest to note that at the lower concentration limit ($c = c^*$) T_r is still comparatively large (proportional to $N^{9/4}$). This means that the self-knots of a single coil do not disentangle easily.

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References and Notes

(1) (a) Faculté des Sciences; (b) Collège de France.

(2) (a) P. G. De Gennes, *Macromolecules*, **9**, 587, 594 (1976); (b) M. Adam, J. Delsanti, G. Jannink, *J. Phys. (Paris), Lett.*, **37L**, 53 (1976); M. Adam and J. Delsanti, *Macromolecules*, to be published.

(3) M. Adam and J. Delsanti, *J. Phys. (Paris), Lett.*, to be published.

(4) P. G. De Gennes, *J. Phys. (Paris), Lett.*, **36L**, 55 (1975).

(5) M. Stephen, *Phys. Lett. A*, **53**, 363 (1975).

(6) J. des Cloiseaux, *Phys. Rev. A*, **10**, 1665 (1974).

(7) A. Vologodski, A. Lakashin, M. F. Kamentskii, and V. Ansaelevich, *Sov. Phys. JETP (Engl. Transl.)*, **39**, 1059 (1975).

(8) (a) B. Zimm, *J. Chem. Phys.*, **24**, 269 (1956); (b) W. H. Stockmayer, "Fluides Moléculaires", Balian and Weill, Ed., Gordon and Breack, New York, N.Y., 1976. p 107.

(9) J. P. Cotton et al., *J. Chem. Phys.*, **65**, 1101 (1976).

(10) M. Daoud, Thèse, Paris, 1977.

(11) P. G. De Gennes, *J. Phys. (Paris) Lett.*, **35L**, 133 (1974).

(12) J. Ferry, ref 8b. p 227.

(13) M. Jacob, R. Varoqui, S. Klenine, and M. Daune, *J. Chim. Phys. Phys.-Chim. Biol.*, 865 (1962).

(14) P. Mijnlieff and W. Jaspers, *Trans. Faraday Soc.*, **67**, 1837 (1971).

(15) See R. Ferrel, *Phys. Rev. Lett.*, **24**, 1169 (1970).

(16) See for instance R. Kubo, *Rep. Prog. Phys.*, **29**, 255 (1966).

(17) P. G. De Gennes, *J. Chem. Phys.*, **55**, 572 (1971).

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Notes

The Sorption of Chemicals by Perfluorocarbon Polymers

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One of the most useful and familiar properties of poly(tetrafluoroethylene) (PTFE) is its resistance to chemical attack.[1-3] Only a few substances such as molten alkali metals, chlorine trifluoride, and gaseous fluorine can attack the polymer, and there are no known solvents below the melting point. This does not mean, however, that there is no penetration by relatively small molecules.

In a general way, Sperati[3] has referred to the sorption of certain solvents. A number of investigators have studied the adsorption of various substrates on the surface of fine powders of nascent PTFE which is very crystalline.[4-7] In a study of the kinetics for the adsorption of carbon tetrachloride on PTFE, Wade[8] concluded that there must be diffusion into the bulk. There have also been a few reports of significant levels of swelling at elevated temperatures, e.g., 3.7% carbon tetrachloride at 200 °C[9] and 2% perchloroethylene and 0.7% methylene chloride at their boiling points.[3]

The sorption of various compounds at room temperature was investigated for two kinds of 2 mil perfluorocarbon film. One sample was a commercial film of PTFE made by casting an aqueous dispersion followed by sintering. This material was then melted and quenched in ice water. The degree of crystallinity estimated from the density[2] was 41%. The other sample had been melt-extruded from a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP resin). It was estimated to be 42% crystalline. Samples of both materials were immersed in the test liquids until the weight no longer increased. They were wiped dry and weighed quickly to minimize evaporation. The weight gains are presented in Table I, together with solubility parameters taken from the literature.[10,11]

The test compounds can readily be divided into two categories, those which contain hydrogen and those which do not. The sorption of the hydrogen-containing compounds is always low, less than 1% in most cases, and does not depend on the solubility parameter over a wide range. While this behavior might reflect an adsorption process, this is considered unlikely in view of the relatively small amount of surface. The perfluorocarbon polymers absorb up to 11% of compounds which do not contain hydrogen. As shown in Figure 1, the weight gain is strongly dependent on the solubility parameter, δ, declining from the maximum amount near $\delta = 6$ to less than 1% at $\delta = 10$. Admittedly, compounds such as chloroform, methylene chloride, the dichloroethanes, and bromoform which contain relatively small amounts of hydrogen and have solubility

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