QUASI-ELASTIC SCATTERING BY DILUTE, IDEAL, POLYMER SOLUTIONS: II. EFFECTS OF HYDRODYNAMIC INTERACTIONS

E. DUBOIS-VIOLETTE and P.-G. de GENNES

*Laboratoire de Physique des Solides**
Faculté des Sciences d'Orsay, 91 − ORSAY, France

Abstract

Each moving unit of a long, flexible, molecule induces in the surrounding solvent a velocity field which reacts on the motion of other segments. This long-range hydrodynamic interaction modifies strongly the dynamical form factor $S(\mathbf{q}\omega)$ at low frequencies ω and small scattering vectors $\mathbf{q}$. For neutron scattering ($qR_G \gg 1$, where R_G is the radius of gyration of the polymer), the frequency width $\Delta\omega_q$ of $S(q\omega)$ at fixed q becomes proportional to q^3(for an ideal coil). Also the effect of stretching the molecule becomes more dramatic, since stretching greatly reduces the hydrodynamic interactions.

1. Introduction

IN A preceding paper [1] we have discussed the slow, quasi macroscopic motions of a flexible polymer chain in the so-called "Rouse limit": namely when the velocity of each monomer depends only on the forces applied on it. This led to comparatively simple laws for the inelastic scattering of neutrons by a long chain. In particular the frequency width $\Delta\omega_q$ of the scattered beam (for a monochromatic incident beam and a fixed momentum transfer $\hbar q$) was found to be proportional to q^4.

We now turn to the more realistic case where the motion of the solvent is taken into account. Then a number of new effects come into play:

(a) the motion of the solvent can be of interest in itself: typically one could measure the inelastic incoherent scattering of neutrons by hydrogen − containing solvent molecules moving in a macromolecular mesh of low scattering power: this experiment gives a diffusion coefficient, and should supplement in an interesting way the nuclear resonance data. However, in the present paper, we shall not be concerned with this class of problems : if we discuss incoherent scattering, for instance, we assume that the only scattering centers of importance are nuclei of the polymer chain. For coherent scattering, we assume that our solution can be treated as essentially incompressible [2]. Then we can again consider that the solute alone participated in the scattering, the specific scattering amplitude α (per cm^3) being the difference $\alpha_{solute} - \alpha_{solvent}$.

---

* Laboratoire associe au C.N.R.S.

(b) the presence of the solvent leads to long-range interactions between monomers. Let us for instance idealise each monomer as a small sphere of radius b. Then if a force φ_m acts on the m-th monomer, it takes a velocity $\mathbf{w}_m$ relative to the solvent

$$\mathbf{w}_m = \frac{1}{6\pi\eta b}\,\varphi_m = B\,\varphi_m \tag{1}$$

where η is the viscosity of the solvent. This induces a velocity field around the moving sphere, of the form*

$$\delta\,\mathbf{v}_m(\mathbf{r}) = \frac{3b}{4|\mathbf{r} - \mathbf{r}_m|}\,[\mathbf{w}_m + (\mathbf{u}\cdot\mathbf{w}_m)\mathbf{u}] + \frac{b^3}{4|\mathbf{r} - \mathbf{r}_m|^3}\,[\mathbf{w}_m - 3(\mathbf{u}\cdot\mathbf{w}_m)\mathbf{u}] \tag{2}$$

where $\mathbf{u}$ is a unit vector in the direction $\mathbf{r} - \mathbf{r}_m$.

Each monomer drifts in the velocity field δv. The total velocity of the n-th unit is thus

$$\frac{d\mathbf{r}_n}{dt} = B\,\varphi_n + \sum_m \delta\mathbf{v}_m(\mathbf{r}_n) + \mathbf{v}^\circ(\mathbf{r}_n) \tag{3}$$

where $\mathbf{v}^0(\mathbf{r}_n)$ is the velocity field of the solvent in the absence of any polymer molecule (for our scattering problems we always have $\mathbf{v}^0 \equiv 0$).

Equations (1-3) show that $d\mathbf{r}_n/dt$ depends not only on the force φ_n applied on the n-th unit, but also on all other forces φ_m. We assume that the φ's are small, and compute effects only to first order in φ : then we can average equation (2) over all polymer configurations in a state of 0 forces. The terms in $|\mathbf{r}_n - \mathbf{r}_m|^{-3}$ disappear when we perform the angular average, and assuming an ideal coil we are left with :

$$\delta\mathbf{v}_m[\mathbf{r}_n] = \mathbf{w}_m b < \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} > = \xi\,\mathbf{w}_m|n - m|^{-1/2} \tag{4}$$

where

$$\xi = \left[\frac{6}{\pi}\right]^{1/2}\frac{b}{\sigma} \tag{5}$$

and σ^2 is the mean square end-to-end dimension of one sub-unit, as defined in (I). The consequence of this long-range hydrodynamic interaction for the viscosity and other macroscopic properties of the solution have been worked out by Kirkwood and Risemann [3] and more accurately by Zimm [4]. The present paper represents essentially an extension of ref. [4] to cover some problems of inelastic scattering.

We shall discuss first the limit of an infinitely long polymer chain (Section 2), since the calculations are comparatively simple for this case. In practice, this limit will be realised if $qR_G \gg 1$ where R_G is the radius of gyration of the molecule and q is the scattering vector

---

* See for instance Landau-Lifshitz, *Fluid mechanics*, Chap. 2, Pergamon Press, Oxford.

$$q \cong \frac{4\pi}{\lambda} \sin \theta/2 \tag{6}$$

(θ : scattering angle; λ : incident wavelength). For thermal or subthermal neutrons q^{-1} will usually be smaller than 150 Å (corresponding to $\lambda = 6$ Å and $\theta = 2°$) and the condition $qR_G \gg 1$ is satisfied in general. For light scattering, on the other hand, we usually have $qR_G \gtrsim 1$ and a more complicated discussion allowing for the finite size of the molecule must be carried out.

The physical principles of this discussion are given in Section 3. The calculational aspects are described in an appendix.

2. Inelastic Scattering by a Very Long Chain ($qR_G \gg 1$)

(1) Equation of motion and relaxation modes of an ideal coil

The force φ_n acting on the .n-th sub-unit has been rederived in (I) and is given by

$$\varphi_n = \mathbf{F}_n + \frac{3k_BT}{\sigma^2} [\mathbf{a}_n - \mathbf{a}_{n+1}] \tag{7}$$

where $\mathbf{a}_n = \mathbf{r}_{n+1} - \mathbf{r}_n \cong \partial \mathbf{r}/\partial n$. The first term $\mathbf{F}_n$ is the external force. The second term is a force proportional to $\partial^2\mathbf{r}/\partial n^2$, i.e. to the curvature of the chain. We now restrict our attention to a free chain ($\mathbf{F}_n \equiv 0$) in a solvent at rest ($\mathbf{v}_0 \equiv 0$). Using equations (3) and (4) we arrive at an irreversible equation of motion of the form

$$\frac{d\mathbf{r}_n}{dt} = W \left[\mathbf{a}_n - \mathbf{a}_{n-1} + \xi \sum_{m \neq n} |m - n|^{-1/2} [\mathbf{a}_m - \mathbf{a}_{m-1}] \right] \tag{8}$$

where

$$W = \frac{3k_BT}{\sigma^2} B = \frac{1}{2\pi} \frac{k_BT}{\eta_0 b \sigma^2} \tag{9}$$

η_0 being the viscosity of the solvent.

For our infinite chain the eigenmodes of equation (8) are still very simple, namely

$$\mathbf{r}_n = \text{const.} \quad e^{ipn} e^{-t/\tau_p} \tag{10}$$

with relaxation frequencies $1/\tau_p$ given by

$$\frac{1}{W\tau_p} = 2(1 - \cos p) + 4\xi \sum_{s=1}^{\infty} s^{-1/2} \cos(ps)(1 - \cos p). \tag{11}$$

Again we are only interested in the modes of low relaxation frequency ($p \ll 1$) for which

equation (11) can be reduced to:

$$\frac{1}{W \tau_p} = p^2 \left[1 + 2\xi \int_0^\infty ds\ s^{-1/2} \cos ps \right]$$

(12)

$$= p^2 + \sqrt{2\pi}\ \xi\ p^{3/2}\ .$$

We conclude that, as soon as the parameter ξ is non zero, the hydrodynamic interactions dominate the relaxation behavior at low frequencies $(p \to 0)$: in this limit we can drop the p^2 term and write

$$\frac{1}{\tau_p} = \tilde{W}\ p^{3/2}$$

(13)

with

$$\tilde{W} = \sqrt{2\pi}\ \xi\ W$$

(14)

$$= \frac{\sqrt{3}}{\pi}\ \frac{k_B T}{\eta_0 \sigma^3}$$

We can think of $\tilde{W}$ as of the microscopic jump frequency of a single monomer moving in the solvent, and expect for $\tilde{W}$ values in the range $10^{10} - 10^{13}\ \mathrm{sec}^{-1}$.

An important question arises at this stage : the Stokes formula for the velocity field (equation (2)), on which our analysis is based, is valid only for motions at very low frequencies and not too long distances $|\mathbf{r}_n - \mathbf{r}_m|$. Is it in fact correct for our purposes? The answer is yes in the limit $p \to 0$, and the proof proceeds as follows: If the frequency scale in which we are interested is $\Omega \sim 1/\tau_p$, equation (2) applies for distances $|\mathbf{r}_n - \mathbf{r}_m| < L$ where $L^2 = \eta_0/\rho_0 \Omega$ and ρ_0 is the solvent density. This corresponds to $s = |n - m| < L^2/\sigma^2$, and leads to a cut-off in the summation $\sum_s$ of equation (11) at the value

$$s_{\mathrm{max}} \cong \frac{L^2}{\sigma^2} \cong \frac{\eta_0\ \tau_p}{\rho_0\ \sigma^2} \cong \frac{\eta_0^2 \sigma}{\rho_0 k_B T}\ p^{-3/2} = p_0^{1/2}\ p^{-3/2}$$

(15)

where

$$p_0 = \eta_0^4 \left[\frac{\sigma}{\rho_0 k_B T} \right]^2$$

(16)

If p is much smaller than p_0, s_{max} is much larger than $1/p$: then the convergence of the sum $\sum_s$ in equation (11) is controlled by the factor $\cos ps$, and is independent of the existence of the cut-off s_{max}. For all typical solvents at room temperature p_0 is large (of the order 10^3). The values of p in which we are interested are much smaller than 1 : thus $p \ll p_0$ and equation (2) is correct.

(2) *Self correlation function and incoherent scattering*

The basic correlation function derived from equation (8) is

$$< \mathbf{a}_n(o) \cdot \mathbf{a}_m(t) > = \sigma^2 \, G_{mn}(t)$$

$$= \sigma^2 \, \frac{1}{2\pi} \, \int_{-\pi}^{\pi} dp \, e^{ip(n-m)} \, e^{-|t|/\tau_p} \; .$$

(17)

This is identical with equation (6) of I : the only new feature is that $1/\tau_p$ is now proportional to $p^{3/2}$ as shown by equation (13) while in the Rouse limit of I ($\xi \to 0$), $1/\tau_p$ was proportional to p^2.

We now apply these results to the self correlation function

$$S(q, \, t) = < e^{-i\mathbf{q} \cdot \mathbf{r}_n(o)} \, e^{-i\mathbf{q} \cdot \mathbf{r}_n(t)} >$$

(18)

$$= \exp \, \left[- \frac{1}{2} \, q^2 < [x_n(o) - x_n(t)]^2 > \right]$$

(the latter form being valid in the small q, large t, limit – as explained in I – and x_n being the projection of $\mathbf{r}_n$ along $\mathbf{q}$). Writing the $\mathbf{r}_n$'s in terms of the $\mathbf{a}_m$'s and using equation (17), we arrive at the formula

$$\frac{1}{2} < [x_n(o) - x_n(t)] > = \frac{\sigma^2}{6\pi} \, \int_{-\alpha}^{\infty} \frac{dp}{p^2} \, [1 - \exp \, [- \widetilde{W} \, |p|^{3/2} \, |t|] \,]$$

(19)

$$= \frac{\sigma^2}{6\pi} \, \Gamma(\tfrac{1}{3}) \, |\widetilde{W}t|^{2/3} \; .$$

Finally we construct the dynamic form factor for incoherent scattering

$$S(q, \, \omega) = \frac{1}{2\pi} \, \int_{-\infty}^{\infty} S(qt) \, e^{i\omega t} \, dt$$

(20)

$$= \frac{1}{\pi \, \widetilde{W} \, \varepsilon^{3/2}} \, \int_{0}^{\infty} d\theta \, \exp \, \left[- \sigma\theta^{2/3} \right] \cos(\omega\theta)$$

where we have introduced the reduced variables

$$\varepsilon' = \frac{q^2 \, \sigma^2}{6}$$

$$\theta = \varepsilon^{3/2} \, \widetilde{W} |t|$$

(21)

$$\bar{\omega} = \frac{\omega}{\widetilde{W} \, \varepsilon^{3/2}}$$

and the constant $\alpha = (2/\pi)\Gamma(1/3)$.

It is useful to compute the dynamic form factor at 0 frequency

$$S(q, \ \omega = 0) = \frac{1}{\pi \ \tilde{W} \ \varepsilon^{3/2}} \int_0^\infty d\theta \ \exp\left[- \ \alpha\theta^{2/3}\right]$$

(22)

$$= \frac{3}{4\sqrt{\pi} \ \alpha^{3/2} \ \tilde{W} \ \varepsilon^{3/2}}$$

and to plot the results in terms of the dimensionless function

$$\frac{S(q, \ \omega)}{S(q, \ 0)} = \frac{4\alpha^{3/2}}{3\sqrt{\pi}} \int_0^\infty d\theta \ \exp\left[- \ \alpha\theta^{2/3}\right] \cos(\tilde{\omega}\theta) = g_i(\tilde{\omega}).$$

(23)

A graph of this function $g_i(\tilde{\omega})$ is given on Fig. 1. The half width at half maximum is $\Delta\tilde{\omega} = 1.1$ corresponding to

$$\Delta\omega_q = 0.075 \ \tilde{W} \ q^3 \ \sigma^3$$
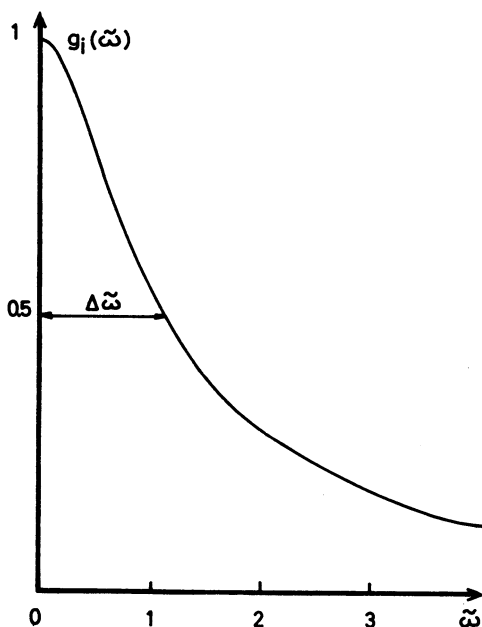
(24)

FIGURE 1

$\Delta\omega$ is now *proportional to q^3* : this is somewhat more favorable, from an experimental point of view, than the q^4 dependence which we had obtained in the Rouse limit : $\Delta\omega$ at a fixed, small q

is now larger.

What are the respective domains of validity of the Rouse limit and of the present approximation? In all cases we have $\Delta\omega_q \sim 1/\tau_p$ and $p \sim q\sigma$. The relaxation frequency $1/\tau_p$ is given by equation (2.6). The contribution of the hydrodynamic effects dominates when $\xi p^{3/2} \gg p^2$ or $p \ll \xi^2$. Thus we arrive at the following set of rules:

$$q\sigma \ll \xi^2 \rightarrow \text{Apply equations (23, (24)}$$

$$1 \gg q\sigma \gg \xi^2 \rightarrow \text{Apply equations (11) and (12) of I}$$

In practice, if ξ is in a suitable range and if the transition between the two domains can be observed, one may derive ξ from the experimental data.

(3) Coherent scattering

Our starting point here is equation (17) of I : the time-dependent correlation function to be studied is

$$S_{coh}(q, t) = |F(q)|^2 \sum_{nm} e^{-\frac{1}{2}q^2 < [x_n(0) - x_m(t)]^2 >}$$

(25)

where $F(q)$ is a form factor for the monomer (and can be replaced by $F(o)$ for most cases of interest). Expressing the $\mathbf{r}_n$'s in terms of the $\mathbf{a}_m$'s and making use of equation (17) we arrive at

$$\frac{q^2}{2} < [x_n(o) - x_{n+s}(t)]^2 > = \frac{q^2\sigma^2}{6\pi} \int_{-\infty}^{\infty} \frac{dp}{p^2} (1 - e^{-t/\tau_p} \cos ps)$$

(26)

$$= \epsilon |s| \left[1 + h(u) \right]$$

where

$$\epsilon = \frac{q^2 \sigma^2}{6}$$

$$|s| h = \frac{2}{\pi} \int_0^\infty \frac{dp}{p^2} (1 - e^{-t/\tau_p}) \cos ps$$

(27)

$$h(u) = \frac{4}{\pi} \int_0^\infty \frac{dy}{y^3} [1 - \exp[-y^3 u^{-3/2}]] \cos y^2$$

$$u = |s| |\widetilde{W}t|^{-2/3}$$

In the small q limit we can replace the sum $\sum_m$ in equation (25) by an integral and write

$$S_{coh}(q, \ t) \ = \ 2N|F(q)|^2 \ \int_0^\infty ds \ e^{-\varepsilon s(1+h)}$$

$$= \ \frac{2}{\varepsilon} \ N|F(q)|^2 \ f(\theta)$$

(28)

where θ is still defined by equation (21) and

$$f(\theta) \ = \ \theta^{2/3} \ \int_0^\infty du \ \exp \left[- \ \theta^{2/3} \ u[1 \ + \ h(u)] \right]$$

(29)

$$f(o) \ = \ 1.$$

Finally, the dynamic form factor per monomer unit is

$$\frac{1}{N} \ S_{coh}(q\omega) \ = \ \frac{1}{2\pi} \ \int_{-\infty}^\infty dt \ S_{coh}(qt) \ e^{i\omega t}$$

(30)

$$= \ \frac{2}{\pi \ \tilde{W} \ \varepsilon^{5/2}} \ |F(q)|^2 \ \int_0^\infty d\theta \ f(\theta) \ \cos(\omega\theta)$$
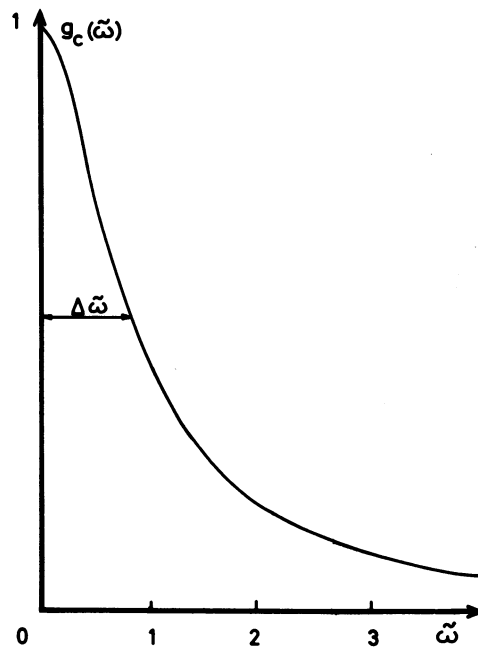

FIGURE 2

The function $f(\theta)$ and the Fourier transform $g_c(\tilde{\omega}) = \int_0^\infty f \cos \tilde{\omega} \theta \, d\theta$ have been computed numerically, and the results for g_c are shown on Fig. 2. The half-width at half maximum of g_c is $\Delta\tilde{\omega} = 0.8$, and this leads to

$$\Delta\omega_{q(coh)} = 0.055 \, \tilde{W} \, q^3 s^3 . \tag{31}$$

Again the width is proportional to q^3 and all the qualitative remarks of the preceding paragraph remain valid.

3. Light Scattering by a Chain of Finite length

(1) Weakness of internal motion effects

As explained in the introduction, the experiments on the inelastic scattering of light correspond to situations where qR_G is of order unity, or smaller: the finite size of the chain must be taken into account.

We shall first consider the simplest type of scattering, where depolarisation effects can be neglected : we assume that the induced dipole P_n induced on the n-th monomer by the electric field $E(r_n)$ is of the form

$$P_n = \alpha \, E(r_n)$$

α being a scalar. We also assume that the frequency dependence of α on the frequency band of interest (width $\sim \Delta\omega_q$) can be neglected : this is quite correct in general. Then the frequency distribution of the scattered light at a fixed scattering angle θ is still given by the coherent dynamic form factor $S_{coh}(q\omega)$ with q defined by (6). For the present problem we can again reduce $S_{coh}(qt)$ to the gaussian form of equation (25).

(α) *when the molecule is comparatively small* $(qR_G \ll 1)$, it is clear that we cannot study its internal motions by light scattering : we can replace without error the coordinates x_n of each monomer by the coordinate g of the center of gravity, and we have

$$S_{coh}(qt) := |NF|^2 \, e^{-q^2/2 < [g(o) - g(t)]^2 >} \tag{32}$$

If the molecule diffuses in the solvent with a diffusion coefficient D, then in the large time limit of interest we can write:

$$< [g(o) - g(t)]^2 > = 2Dt \tag{33}$$

$$S_{coh}(qt) = |NF|^2 \, e^{-Dq^2 t}$$

and the Fourier transform $S_{coh}(q\omega)$ is a Lorentz curve of width Dq^2. Thus in the small q limit the only parameter which can be derived from this type of experiment is the diffusion coefficient D.

(β) *when* $qR_G \sim 1$, can we extract from the inelastic scattering data a significant information

on the *internal* motions of the molecule? We shall now show that the answer to this question is *no*, unless qR_G reaches really high values (of the order of 2.5) which are not usually realisable in practice.

The discussion is particularly simple in one case : namely when the internal motions are completely decoupled from the motion of the center of gravity : let us write the coordinate x_n of the n-th monomer in the form

$$x_n = g + \rho_n \tag{34}$$

where $\sum\limits_{n} \rho_n \equiv 0$. Then :

$$< [x_n(0) - x_m(t)]^2 > \; = \; < [g(0) - g(t)]^2 > + < [\rho_n(0) - \rho_m(t)]^2 > \tag{35}$$

$$+ \; 2 < [g(0) - g(t)][\rho_n(0) - \rho_m(t)] >$$

We say that the internal motions are decoupled from g when the third term in equation (35) vanishes. Physically, this decoupling property is related to the following question: if we act on each monomer with a constant force $F_n = F$, the center of gravity of the molecule takes a uniform motion : is the internal shape of the molecule distorted? In the Rouse limit there is no distortion; but, with hydrodynamic interactions, there is a (small) distortion : the two ends of the molecule tend to lag backwards*. However, even in this case, the deviations from the uncoupled behavior lead to corrections of order 2 per cent only (see Appendix). Thus, in the following, we shall drop the last term in equation (35). Then, returning to equation (25), we can write:

$$\frac{1}{|NF|^2} \; S_{coh}(qt) = e^{-Dq^2t} \; S_{red}(qt) \tag{36}$$

$$S_{red}(qt) = \frac{1}{N^2} \sum\limits_{nm} \exp\left[-\frac{q^2}{2} < [\rho_n(0) - \rho_m(t)]^2 > \right] \tag{37}$$

For $t = 0$, $S_{red}(q, 0)$ is the familiar Debye function for coherent scattering by a freely orienting chain

$$S_{red}(q, \; t = 0) = \frac{2}{y} \left[1 - \frac{1}{y} [1 - e^{-y}] \right] \tag{38}$$

$$y = q^2 \; R_G{}^2 = \frac{N \; q^2 \; \sigma^2}{6} \; .$$

---

*   This coupling between overall and internal motions is reflected mathematically in the Zimm analysis by the non-orthogonality of the various relaxation modes. It is amusing to note that for a ring-shaped chain (no arms to be left behind) the orthogonality is restored and equation (35) is decoupled.

For $t \to \infty$, $S_{red}(q, t)$ tends towards a finite limit $\bar{S}(q)$: We might call $\bar{S}$ the Debye-Waller factor for the long chain. At large times t, $\rho_n(0)$ and $\rho_m(t)$ are uncorrelated. Thus we may write

$$\bar{S} = \frac{1}{N^2} \sum_{nm} \exp\left[-\frac{q^2}{2} < \rho_n^2 + \rho_m^2 > \right]$$

(39)

$$\bar{S}^{1/2} = \frac{1}{N} \sum_n \exp\left[-\frac{q^2}{2} < \rho_n^2 > \right] .$$

Making use of classic results for a freely orienting chain, we have

$$< \rho_n^2 > = \frac{N\sigma^2}{9} \left| \left[\frac{n}{N} \right]^3 + \left[1 - \frac{n}{N} \right]^3 \right|$$

and replacing the sum $\sum_n$ by an integral we arrive at

$$\bar{S} = e^{-y/6} \left[\int_{-1/2}^{1/2} du \ e^{-yu^2} \right]^2 .$$

(40)

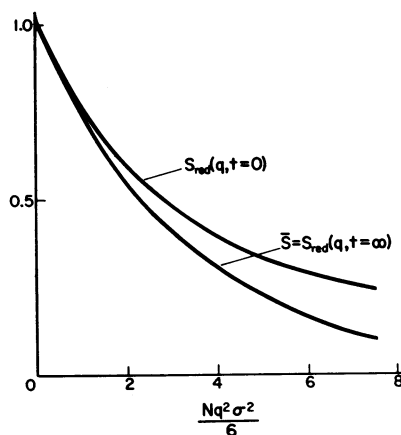The two curves giving $S_{red}(q, 0)$ and $S_{red}(q, \infty) = \bar{S}(q)$ as a function of $y = q^2 R_G^2$ are shown

FIGURE 3

on Fig. 3. The contribution to the scattering function of the internal motions is measured by the difference $S_{red}(q, 0) - S_{red}(q, \infty)$. To observe clearly the internal motions we require

$$\frac{S_{red}(q, 0) - S_{red}(q, \infty)}{S_{red}(q, 0)} \stackrel{\sim}{>} \frac{1}{2} .$$

This will be realised only for $qR_G \stackrel{>}{\sim} 2.5$. Typical values for R_G in flexible chains are of order

500 $\overset{o}{A}$. The maximum q for a given wavelength λ is $4\pi/\lambda$ (corresponding to $\theta = \pi$). Thus, to get an interesting signal, one would probably have to work with $\lambda < 3000 \overset{o}{A}$. Such experiments with ultraviolet laser sources may become feasible in the future. General formulae, applicable for all values of qR_G, are given in the appendix.

4. Conclusions

(1) Experiments using neutrons or light

The existence of long-range hydrodynamic interactions between monomers modifies profoundly the frequency spectrum of the internal motions in an ideal coil. This change is rather favorable from the point of view of inelastic neutron scattering experiments, since the frequency width $\Delta\omega_q$ vanishes now less rapidly (like q^3) in the small q limit of interest : thus $\Delta\omega_q$ becomes slightly less difficult to detect.

As regards the inelastic scattering of photons, we have seen that the experiments with un-polarised light can bring in information on the internal motions only for very short wavelengths or very large molecules ($R_G \overset{\sim}{>} 1300 \overset{o}{A}$ for $\lambda = 6000 \overset{o}{A}$). Such large values of R_G occur only in semi-rigid molecules such as DNA : in such a case the subunits are large, the frequency scale is reduced, and also the analysis must be modified. An important parameter for semi-rigid molecules is the ratio of the persistence length L [6] to q^{-1}. For $qL \gg 1$, we are essentially dealing with a rigid rod, and expect a rather well defined phonon spectrum : $S(q\omega)$ should give some information on this spectrum (rather blurred, however, because of the orientational dis-order). For $qL \ll 1$, we expect a central peak of the type described here. What happens for $qL \sim 1$ is not known.

Can the frequency distribution of the *depolarised* light scattered by the polymer give us any interesting information? What is measured here is a quadrupole correlation function. It is certainly sensitive to internal motions even when $qR_G \ll 1$. But it is much more difficult to compute than the vector-vector correlation functions (17). The calculation can be done within the model used by Zimm [4] in his study of flow birefringence. But the validity of this model is dubious : each monomer is described as a deformable object with a gaussian probability dis-tribution. Of course, we can always define larger subunits which are gaussian; but then the average quadrupole of the subunit is not the quantity which dominates the depolarisation effect. Thus, at the present stage, we cannot make any clear-cut prediction on the depolarised light.

Another type of problems is related to what happens when the chain is extended — in practice by associating the chains in a loose, but connected, network on which mechanical stresses can be applied. In the Rouse limit, as explained in (I), this reacts on $\Delta\omega_q$ only for coherent scattering. With hydrodynamic interactions on the other hand, the effects are more drastic: on extension, the coupling terms of the equation of motion (8) go progressively from an $|n - m|^{-\frac{1}{2}}$ dependence to a $|n - m|^{-1}$ dependence*. Thus the relaxation times $1/\tau_p$ are modified : as a result we expect $\Delta\omega_q$ (for fixed q) to be changed by the extension, even in the case of incoherent scattering.

---

* This is one of the main causes for the non - Newtonian viscous behvaior observed in dilute polymer solutions. Another complication brought in by stretching, and to be mentioned, is that, in this case, the static Stokes formula (2) cannot be used.

(2) Excluded volume effects

All the analysis of the present paper was restricted to the case of an ideal coil : the power laws derived here (such as $\Delta\omega_q \sim q^3$ in Section 2) can at best apply only in poor solvents where an attraction between neighboring monomers compensates the large repulsion for overlapping monomers : that is to say, very close to the compensation temperature θ, where the first virial coefficient vanishes.

But, in general, excluded volume effects may be important, and they will react on the relaxation time spectrum in two different ways:

(1) The distribution of relative distances $r_n - r_m$ is strongly modified: according to the self-consistent calculation of Edwards [7] the average in equation (4) now becomes:

$$< \frac{1}{\left| r_n - r_m \right|} > = \text{const.} \ s^{-3/5} , \qquad s = \left| n - m \right| .$$

(2) During the motion, each chain portion cannot be crossed by another chain portion (this occurs even at the θ temperature) : no serious predictions concerning this effect are available at the present time.

If we boldly assumed that (1) is the only important effect, we would again be led to rather simple power laws, namely

$$\frac{1}{\tau_p} = \hat{W} \ p^{8/5}$$

$$\Delta\omega_q \sim \hat{W} \ q^{8/3}$$

where $\hat{W}$ is a characteristic rotational frequency of the monomer. It is very much to be hoped that the future high-resolution, high-flux neutron spectrometers will allow for a detailed comparison between these proposed power laws and the experimental data.

Acknowledgements

APPENDIX

Correlation Functions for Finite Chains

(1) Introduction of response functions

Our aim is to compute averages such as

$$< [x_n(0) - x_m(t)]^2 >$$

in an ideal coil of N segments. In the gaussian approximation of equation (18) and equation (25), such averages suffice to compute all dynamic form factors.

Our starting-point is to introduce a set of response functions $\beta_{nm}(t)$ defined as follows: assume that a system of small external forces $F_m(t)$ (all parallel to the x axis) is applied on the chain. The average velocity of the n-th unit is then of the form

$$\overline{\overset{o}{x}_n(t)} = \sum_m \int_{-\infty}^{t} dt' \; \beta_{nm}(t - t') \; F_m(t') \; .$$

The β_{nm}'s will be obtained from the equations of motion (3). When they are known, we can derive correlation functions from them by the Kubo formula [8]: for a classical system, this takes the form

$$< \overset{o}{x}_n(t_1) \; \overset{o}{x}_m(t_2) > = k_B T \; \beta_{nm}(|t_1 - t_2|) \; . \qquad (A.1)$$

We can write

$$< [x_n(t_1) - x_m(t_2)]^2 > = g_{nm}(t_2 - t_1)$$

$$2 < \overset{o}{x}_n(t_1) [x_n(t_1) - x_m(t_2)] > = + \frac{\partial}{\partial t_1} g_{nm}(t_2 - t_1)$$

$$2 < \overset{o}{x}_n(t_1) \; \overset{o}{x}_m(t_2) > = \frac{-\partial^2}{\partial t_1 \, \partial t_2} g_{nm}(t_2 - t_1) = + \frac{\partial^2}{\partial t_2^2} g_{nm}(t_2 - t_1) \; .$$

Thus we can go from the response functions (A.1) to the correlation functions g by two successive integrations. As regards the integration constants, we note that for a classical system (with 0 magnetic field) $g_{nm}(t)$ is real and even in t; thus $\partial g_{nm}/\partial t|_{t=0} = 0$. Finally we obtain

$$g_{nm}(t) = |n - m| \frac{\sigma^2}{3} + 2k_B T \int_0^t dt_1 \int_0^{t_1} dt_2 \; \beta_{nm}(t_1 - t_2) \; . \qquad (A.2)$$

(2) Response functions in the Zimm model

The equation of motion, derived from (3) for a solvent at rest ($v_0 \equiv 0$), is:

$$\frac{dx_n}{dt} = \sum_m B_{nm} \; \varphi_m \qquad (A.3)$$

$$B_{nn} = W/\rho$$

$$B_{nm} = W/\rho \; \xi |n - m|^{-1/2} \qquad (n \neq m) \tag{A.4}$$

$$\rho = \frac{3k_B T}{\sigma^2}$$

The force φ_m has been written down in equation (7)

$$\varphi_m = F_m - \rho \sum_{m'} A_{mm'} \; x_{m'} \tag{A.5}$$

where $\hat{A}$ is the symmetric matrix introduced by Zimm [4]

$$A_{mm} = 2 \qquad A_{m+1, m} = -1 \qquad \text{for } 1 < m < N \qquad \text{etc.}$$

In an operator notation we rewrite equations (A.3) and (A.5) as :

$$\frac{d|x)}{dt} = \hat{B}|\varphi) = \hat{B} \left[|F) - \hat{A}|x) \right] \; . \tag{A.6}$$

We then introduce the eigenvectors $|p)$ and eigenvalues $1/\rho \; \tau_p$ of the matrix $\hat{B}\hat{A}$

$$\hat{B}\hat{A} \; |p) = \frac{1}{\rho \tau_p} |p) \; .$$

As explained in ref. [4], the matrix $\hat{B}\hat{A}$ is not hermitian, and the vectors $|p)$ do not form an orthogonal set (except for the Rouse limit). But we have the property

$$(p|\hat{A}|q) = 0 \qquad \text{for} \qquad p \neq q \; .$$

We also introduce a normalised vector $|0)$, for which all components are equal to $N^{-1/2}$, and a vector $|\beta_0) = \hat{B}^{-1}|0) \; [(0|\hat{B}^{-1}|0)]^{-1}$. This is such that

$$(\beta_0 |0) = 1$$

$$(\beta_0 |p) = 0 \qquad (p \neq 0) \; .$$

We can analyse $|x)$ in the eigenmodes $|p)$ now :

$$|x) = \sum_p c_p(t) \; |p) \; .$$

Taking the scalar product with $(p|\hat{A}$ (for $p \neq 0$), we get

$$\frac{dc_p}{dt} + \frac{c_p}{\tau_p} = \frac{[p|F(t)]}{\rho \ \tau_p (p|A|p)}$$

(A. 7a)

$$\frac{dc_p}{dt} = \frac{1}{\rho \ \tau_p (p|\hat{A}|p)} \left[[p|F(t)] - \frac{1}{\tau_p} \int_{-\infty}^{t} dt' \ e^{(t'-t)/\tau_p} \ [p|F(t')] \right]$$

For $p = 0$ we take the scalar product with $(\beta_0|$ and get

$$\frac{dc_0}{dt} = \frac{[0|F(t)]}{(0|\hat{B}^{-1}|0)} \ ,$$

(A. 7b)

Writing $F_n = (n \ | \ F)$, etc., we obtain the response functions from equation (A.7)

$$\beta_{nm}(t) = \frac{(n|0)(0|m)}{(0|\hat{B}^{-1}|0)} \ \delta_+(t) + \sum_{p\neq0} \frac{1}{\rho\tau_p} \cdot \frac{(n|p)(p|m)}{(p|\hat{A}|p)} \left[\delta_+(t) - \frac{1}{\tau_p} e^{-t/\tau_p} \right]$$

(A. 8)

The first term is independent of n and m since $(n|0) = (0|m) = N^{-1/2}$. In both terms the symbol δ_+ represents a δ function with a peak immediately after $t = 0$ (such that $\int_0^\infty \delta_+(t)dt = 1$).

(3) Correlation functions

Inserting (A.8) and (A.2) and performing the time integrals, we obtain:

$$< [x_n(0) - x_m(t)]^2 > = |n - m| \ \frac{\sigma^2}{3} + \frac{2k_BT \ t}{N(0|\hat{B}^{-1}|0)} + \frac{2\sigma^2}{3} \sum_{p\neq0} \frac{(n|p)(p|m)}{(p|\hat{A}|p)}(1 - e^{-t/\tau_p}).$$

(A. 9)

Also a similar calculation gives for the motion of the center of gravity (along x)

$$< [g(0) - g(t)]^2 > = 2 \ Dt + \frac{2\sigma^2}{3N} \sum_{p\neq0} \cdot \frac{|(0|p)|^2}{(p|\hat{A}|p)} (1 - e^{-t/\tau_p})$$

(A. 10)

where $D = k_BT \ N^{-1}[(0|\hat{B}^{-1}|0)]^{-1}$ is the diffusion coefficient. The last term in equation (A.10) shows the coupling between the motion of g and the internal deformations. At large times equation (A.10) is dominated by the term $2Dt$: this corresponds to the approximation of equation (33), and is valid when $t \gg \tau_1$, where τ_1^{-1} is the lowest relaxation frequency of the chain $(\tau_1^{-1} \sim D \ R_G^{-2})$. In the opposite limit $(t \ll \tau_1)$, equation (A.10) becomes:

$$< [g(0) - g(t)]^2 > = \frac{2k_B T \; t}{N} \; (0|\hat{B}|0), \quad (t << \tau_1).$$

(4) Expansion of $S_{coh}(q\omega)$ to order $q^2 R_G^2$

Equations (A.9) and (18) can be used to compute numerically the dynamical form factors at all values of qR_G. Here we consider only the corrections of order $q^2 R_G^2$ to the coherent form factor : the result is :

$$S_{coh}(q, \; \omega) = L_0(\omega) \left[1 - \frac{q^2}{3} (R_G^2 + \delta R^2) \right] + \frac{q^2 \sigma^2}{3N} \sum_{p \neq 0} \frac{|(0|p)|^2}{(p|\hat{A}|p)} L_p(\omega) \quad (A.11)$$

with

$$L_p(\omega) = \frac{1}{\pi} \; \frac{Dq + \tau_p^{-1}}{\omega^2 + (Dq^2 + \tau_p^{-1})^2}$$

$$\delta R^2 = \frac{\sigma^2}{N} \sum_{p \neq 0} \frac{|(0|p)|^2}{(p|\hat{A}|p)}$$

(a) *in the Rouse limit* the modes $|p)$ are orthogonal to $|0)$ and we are left with

$$S_{coh}(q, \; \omega) = L_0(\omega) \left[1 - \frac{q^2 R_G^2}{3} \right]$$

Thus, to order $q^2 R_G^2$, there is no effect of the internal motions on the dynamical form factor.

(b) *in the hydrodynamic limit* there is an effect, the relative importance of which is measured by $\delta R^2/R_G^2$. Making use of the numerical calculations of ref. [4] we find that the dominant contribution comes from $p = 2$ (first non-trivial even mode). The corresponding relaxation frequency is

$$\frac{1}{\tau_2} = 12.79 \; \xi W(2/N)^{3/2}.$$

Keeping only this mode we find $\delta R^2/R_G^2 \sim \nu \; 1.7 \; 10^{-2}$: thus there is now an effect of the internal motions, but it represents less than 2 per cent of the signal.

References

1. P.G. de GENNES, *Physics* 3, 37 (1967) – hereafter referred to as (I).

2. The Brillouin doublet occurring at $\omega = \pm sq$ (where s is the sound velocity of the solution) can be extracted rather easily from the interesting signal.

3. J.G. KIRKWOOD and J. RISEMAN, *J. Chem. Phys.* **16**, 565 (1948).

4. B.H. ZIMM, *J. Chem. Phys.* **24**, 269 (1956).

   B.H. ZIMM, G.M. ROE and L.F. EPSTEIN, *J. Chem Phys.* **24**, 279 (1956).

5. See for instance C. TANFORD, *Physical Chemistry of Macromolecules.* Wiley, New York (1961).

6. G. POROD, *Z. Naturf.* **4a**, 401 (1949)

7. S.F. EDWARDS, *Proc. Phys. Soc.* **85**, 613 (1965).

8. R. KUBO, *Rep. Prog. Phys.* **29**, 255 (1966).