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Quasielastic Light Scattering from Large Macromolecules*

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There is considerable interest in assessing the potential of quasielastic coherent light scattering as a probe for studying internal motions of polymers in dilute solutions. The limiting cases of interest are when $qR \ll 1$ and $qR \gg 1$ where q is the scattering wave vector and R is a characteristic end-to-end distance of the polymer. The former case has been studied extensively by Pecora[1]; the latter case by de Gennes and co-workers.[2,3] In this note we extend the treatment of Dubois-Violette and de Gennes[2] to include the entire range of distributions (assumed Gaussian) for the relative positions $(\mathbf{r}_n - \mathbf{r}_{n+p})$ of monomer units. This generalization for the frequency spectrum is suggested by the earlier treatment for the angular distribution of intensity of scattered light by Ptitsyn[4] and Benoit and co-workers.[5]

The spectrum of scattered light is given by

$$I(\mathbf{q}, \omega) = \mathrm{Re} N^{-2} \sum_{n,p}^{N} \int_0^\infty dt e^{-i\omega t} \times \langle \exp[i\mathbf{q}\cdot\mathbf{r}_n(t)] \exp(-i\mathbf{q}\cdot\mathbf{r}_{n+p}{}^{(0)}) \rangle \quad (1)$$

for a polymer composed of N monomer units of equal polarizability. The dynamics of the polymer are determined according to the Rouse–Zimm[6] model with inertial effects neglected. The motion of the monomer units is a Gaussian Markov process so that only the second moment $\langle [\mathbf{r}_n(t) - \mathbf{r}_{n+p}(0)]^2 \rangle$ must be evaluated.[2] This correlation function may be found from the equations of motion:

$$d\mathbf{r}_n(t)/dt = -\sum_{m,p} \zeta^{-1}[\delta_{np}t + b\langle |\mathbf{r}_n - \mathbf{r}_p|^{-1} \rangle] \mathsf{A}_{pm} \cdot \mathbf{r}_m(t), \quad (2)$$

where $[\mathsf{A}]_{pm}$ is the matrix of force constant between polymer units, ζ is the friction constant, b is the average distance between adjacent polymer units and the term in brackets arises from hydrodynamic effects of the solvent. The equilibrium average indicated by the angular brackets in Eqs. (1) and (2) is with respect to a canonical distribution of the harmonic potential for the polymer.

We obtain the spectrum by transforming to normal coordinates and assert cyclic boundary conditions, an acceptable approximation for the limit $(qR) \gg 1$. The result for the spectrum is

$$I(\mathbf{q}, \omega) = \mathrm{Re} N^{-1} \int_0^\infty dt \int_0^N dr \exp\left(-i\omega t - \frac{q^2}{6\pi} \times \int_0^{2\pi} dk \frac{3k_BT}{A(k)} \{1 - \cos kr \exp[-t/\tau(k)]\} \right), \quad (3)$$

where $A(k)$ is the eigenvalue of the force constant matrix and the relaxation time is

$$\tau(k)^{-1} = A(k) \left(1 + \int_1^\infty dp \cos kpb \langle |\mathbf{r}_n - \mathbf{r}_{n+p}|^{-1} \rangle \right). \quad (4)$$

In order to compute this quantity we assume[4,5] that $(\mathbf{r}_n - \mathbf{r}_{n+p})$ has a Gaussian distribution characterized by a variance $\langle (\mathbf{r}_n - \mathbf{r}_{n+p})^2 \rangle$ which is assumed to be equal to $b^2 |p|^\nu$. The exponent ν may be expected to be between $\nu = 1$ (random coil) and $\nu = 2$ (rigid rod). For small k and $\nu < 2$, the second term in Eq. (4) dominates, $A(k) \sim k^2$, so that $\tau(k)^{-1} = k^{\nu/2+1} W$ where W is a constant independent of k. The integrations in Eq. (3) were accomplished approximately by noting that the dominant contribution is from small k. After a change of variable, the $\cos kr$ term was expanded to terms of order k^2, and the resulting integrals were done analytically. The resulting spectrum was fit to a Gaussian around $\omega = 0$ in order to estimate the width. At half height the result is

$$\Delta\omega = (\text{constant}) q^{\nu+2}. \quad (5)$$

The random coil limit $\nu = 1$ agrees with Dubois-Violette and de Gennes.[3] The case $\nu \to 2$ predicts $\Delta\omega \sim q^4$ which agrees with the case[2] $\tau(k)^{-1} \sim k^2$. However, this is not an accurate limit for the rigid rod with hydrodynamic interaction, for in this case for $\nu = 2$, $\tau(k)^{-1} \sim [-k^2 \ln k]$ in the small k limit. The best analytic estimate of the value of ν is due to Edwards[7] who has taken excluded volume effects into account. He finds $\nu = 6/5$. For this case we find $\Delta\omega \sim q^{16/5}$ which differs from the value $q^{8/3}$ found by Dubois-Violette and de Gennes. We note that the q dependence of the width arises entirely from the small k behavior of the inverse relaxation times, and thus our analysis is restricted to the low frequency part of the spectrum.

One may expect that in the limit $qR \gg 1$ the width of the quasielastic peak will vary in angle dependence between q^3 and q^4. This is not likely to be an experimentally dramatic effect and will not be affected by inclusion of explicit separations of the monomer units. The result, Eq. (5), is valid for $0 < \nu < 2$ and thus includes the possibility of negative excluded volume, $\nu < 1$.

Our interest in this problem was stimulated by a lecture of and private conversation with Professor Robert Pecora.

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Molecular Beam Electric Deflection Studies of Water Polymers[*]

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The formation of water polymers in molecular beam sources has been extensively studied using mass spectroscopy.[1–3] Particularly in supersonic nozzle beam sources, large water polymers are formed, giving rise to $(H_2O)_nH^+$ ions in mass spectra. At present there is very little experimental information about the molecular structure of these polymers. Such structural information is pertinent to the theory of liquid water,[4] hydrogen bonding theory, and studies of the earth's atmosphere.[5] Molecular beam electric deflection experiments provide information about the electric dipole moments and, therefore, about the structure of the polymers.[6]

A beam of polar molecules can be refocused around an obstacle which blocks the direct path of molecules from the source to the detector, by using electrostatic quadrupole focusing fields. In the case of normal polar molecules, this refocusing will be a large fraction of the beam intensity observed with the obstacle removed and no voltage applied to the fields.[7] In the case of nonpolar or very slightly polar molecules, the number of molecules reaching the beam detector because of scattering will decrease when voltage is applied to the focusing fields due to induced dipole moments. The intensity of the beam with obstacle removed and no voltage applied to the fields is referred to as the straight-through beam; refocusing or defocusing is the increase or decrease, respectively, in beam intensity with the obstacle in place when voltage is applied to the fields, expressed as a percentage of the straight-through-beam intensity. The molecular beam apparatus used for these studies has been described elsewhere.[8] The beam source was a nozzle, 0.10 mm in diameter in 0.13 mm thick nickel foil. The temperature of the beam source was maintained at 95°C and the pressure of water vapor behind the nozzle (the nozzle stagnation pressure) was determined by adjusting the temperature of a liquid water reservoir. No skimmer was used with the nozzle. The mass spectrometer beam detector was designed for maximum ionization efficiency, has relatively low resolution, and is ill-suited for observing appearance potentials.

Tables I and II give the mass spectral and deflection data for H_2O and D_2O beams produced with moderate nozzle stagnation pressures. Table I lists straight-through-beam intensities in arbitrary units and Table II lists the relative refocused or defocused beam intensity with 20 kV applied to the focusing fields. With stagnation pressures approaching one atmosphere, ions as large as $(H_2O)_{16}H^+$ have been observed. In all cases the ion intensities decrease monotonically with increasing mass and higher pressures favor higher masses. The mass 19 data in Tables I and II have been corrected for the presence of the tail of the much larger 18 peak, the mass 20 data has been corrected for the natural abundance of $H_2{}^{18}O$.

The refocusing of the monomer species is that expected from the polar nature of water. The dimer molecule also refocuses strongly and is therefore quite polar. The remaining polymers either refocus very slightly or defocus and thus indicate very slightly polar or nonpolar character. The difference in re-

TABLE I. Water polymer ion intensities.

Ion	Intensity[a] at		
	149 mm	84 mm	27 mm
$(H_2O)^+$	470	380	212
$(H_2O)H^+$	37.1	25.2	6.4
$(H_2O)_2H^+$	15.2	6.6	···
$(H_2O)_3H^+$	5.8	1.9	···
$(H_2O)_4H^+$	2.5	0.2	···
$(H_2O)_5H^+$	1.0	···	···
	237 mm	165 mm	33 mm
$(D_2O)^+$	360	378	149
$(D_2O)D^+$	29.9	24.9	1.0
$(D_2O)_2D^+$	12.0	7.9	···
$(D_2O)_3D^+$	4.5	2.0	···
$(D_2O)_4D^+$	2.4	0.6	···
$(D_2O)_5D^+$	1.2	0.2	···

[a] Intensities in arbitrary units for the nozzle stagnation pressure given at the head of each column.