broad component relaxation time to the EPR and NMR relaxation times.

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Scattered Intensity by a Polymer Chain in a Sample with External Constraints

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ABSTRACT: The configuration of a deformed polymer coil is described by a general distribution function, depending on three parameters. The scattering law is given as a function of momentum transfer and parameter value. The relation between external constraint and parameter value is discussed and a clear interpretation from the scattering law diagram in the intermediate momentum range is predicted.

The fact that in the amorphous state polymer chains have random "Gaussian" configurations is now well established[2a] when no external constraint is applied. Obviously the observation of polymer configurations from neutron scattering experiments by mixtures of deuterated and protonated chains is feasible as well with external constraints on the sample as without. It is therefore of real interest to determine how the scattering law is modified by the onset of constraint and to find a formulation which is general enough to cover most cases of interest.

In order to do so we consider the following expression[2b] for the distribution function of the distance $\mathbf{r}$ between segments i and j of a chain in the deformed state

$$f_{ij}(\mathbf{r}) = \mathfrak{N}_{ij} \exp\left\{\frac{-3/2}{|i-j|l^2}\left(\frac{(X-X_{ij}^0)^2}{\lambda_X^2} + \frac{(Y-Y_{ij}^0)^2}{\lambda_Y^2} + \frac{(Z-Z_{ij}^0)^2}{\lambda_Z^2}\right)\right\} \quad (1)$$

$$\mathfrak{N}_{ij} = \frac{(\lambda_X\lambda_Y\lambda_Z)^{-1}}{((2\pi/3)|i-j|l^2)^{3/2}}$$

where X, Y, Z are the components of vector $\mathbf{r}$, and l^2 is the mean squared length of the elementary step in the chain without constraint. The principal axes of the deformation are the $\hat{X}$, $\hat{Y}$, $\hat{Z}$ axes. The constraint factors are λ_X, λ_Y, λ_Z. The lengths X_{ij}^0, Y_{ij}^0, Z_{ij}^0 are the coordinates of the average end-to-end distance $|i - j|$. The random "Gaussian" chain corresponds to the case where

$$\lambda_X = \lambda_Y = \lambda_Z = 1$$

and

$$X_{ij}^0 = Y_{ij}^0 = Z_{ij}^0 = 0$$

For the purpose of carrying out the calculations in the next paragraph, we assume that the λ_α ($\alpha = X, Y, Z$) are independent of the pair i,j and that

$$X_{ij}^0 = (i-j)b_X \qquad Y_{ij}^0 = (i-j)b_Y \qquad Z_{ij}^0 = (i-j)b_Z \quad (2)$$

These hypotheses correspond in fact to classical modes of deformation, which are discussed in the last paragraph. In order to obtain simpler results, we consider only the case of uniaxial deformations, i.e.,

$$\lambda_Y = \lambda_X = \lambda_{\perp} \text{ and } \lambda_Z = \lambda_{\parallel}$$
$$b_Y = b_X = 0 \text{ and } b_Z = b \qquad (3)$$

The generalization from our results to the general case will be obvious. However, (1) is restricted to deformations of small amplitudes, and our discussion will be concerned with types of deformation rather than effects of greater or lesser amplitude.

The Scattering Law

The classical theory for the scattering by N atoms yields a scattering law $S(q)$, normalized at unity for $q = 0$, with a momentum transfer $q = (4\pi/\lambda) \sin (\theta/2)$ where λ is the wavelength of the neutron beam and θ the scattering angle

$$S(q) = \frac{1}{N^2} \sum_{i,j}^{N} \int \mathrm{d}^3r f_{ij}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} = \frac{1}{N^2} \sum_{ij} \langle e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \rangle \qquad (4)$$

Using cylindrical coordinates ρ, Z, σ (Figure 1)

$$\rho^2 = X^2 + Y^2$$
$$\mathrm{d}^3\mathbf{r} = \rho \mathrm{d}\rho \mathrm{d}Z \mathrm{d}\sigma \qquad (5)$$
$$\mathbf{q}\cdot\mathbf{r} = q_{\parallel} Z + \mathbf{q}_{\perp}\cdot\boldsymbol{\rho}$$

One has

$$\langle e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \rangle = \mathfrak{N}_{ij} \int \exp[qZ + \mathbf{q}\cdot\boldsymbol{\rho}] \left[\exp\frac{-\tfrac{3}{2}\lambda_{\perp}^{-2}\rho^2}{|i-j|\,l^2} \times \frac{\tfrac{3}{2}\lambda_{\parallel}^{-2}}{|i-j|\,l^2} \{Z - (i-j)b\}^2 \right] \rho \mathrm{d}\rho \mathrm{d}\sigma \mathrm{d}Z \qquad (6)$$

or

$$\langle e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \rangle = e^{iq_{\parallel}(i-j)Z_0} \exp\left[-q_{\parallel}^2 \frac{l^2|i-j|}{6\lambda_{\parallel}^{-2}} - q_{\parallel}^2 \frac{l^2|i-j|}{6\lambda_{\perp}^{-2}}\right] \qquad (7)$$

We consider successively the cases where the scattering vector $\mathbf{q}$ is perpendicular and parallel to the axis of deformation OZ.

(a) $q = q_{\perp}$. Summation over the indices (i,j) gives

$$S(q_{\perp}) = \frac{2}{X_{\perp}^2}(e^{-X_{\perp}} - 1 + X_{\perp}) + \frac{1}{N} \qquad (8)$$

with

$$X_{\perp} = q_{\perp}^2(\langle R^2 \rangle / 6\lambda_{\perp}^{-2})$$

where $\langle R^2 \rangle$ is the mean squared end-to-end distance of the polymer chain without constraint.

For small angle scattering ($X_{\perp} \ll 1$)

$$S(q_{\perp}) = 1 - q_{\perp}^2 \frac{\langle R^2 \rangle}{18\lambda_{\perp}^{-2}} \qquad (9)$$

In the submolecular (or asymptotic, or intermediate) range ($X_{\perp} \gg 1$)

$$S(q_{\perp}) = \frac{2}{q_{\perp}^2(Nl^2/6\lambda_{\perp}^{-2}) + 1} \qquad (10)$$

(b) $q = q_{\parallel}$.

$$S(q_{\parallel}) = \frac{1}{N} + \frac{1}{N^2} 2Re \sum_{i<j}^{N-1} \exp\left\{-|i-j|\left(q_{\parallel}^2 \frac{l^2}{6\lambda_{\parallel}^2} + iq_{\parallel}b\right)\right\} \qquad (11)$$

Summation over (i,j) in (10) yields a result similar to (8), with the substitution of $X_{\perp}$ to $X_{\parallel}$, where

$$X_{\parallel} = \frac{q^2\langle R^2 \rangle}{6\lambda_{\parallel}^{-2}} + iNbq_{\parallel} \qquad (12)$$

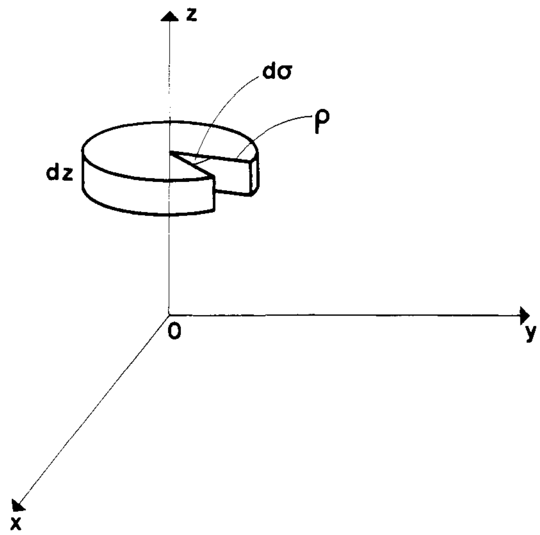

Figure 1. Cylindrical coordinate system used in the integration of (4).

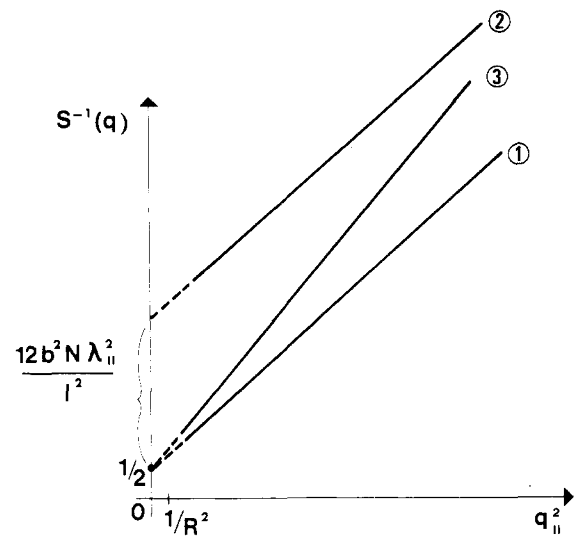

Figure 2. Representation of the inverse scattering law $S^{-1}(q)$ as a function of $q_{\parallel}^2$, i.e., in a direction parallel to the deformation axis. This representation is valid in the intermediate momentum range $\langle R^2 \rangle^{-1/2} < q < 1/l$: 1, random polymer coil with no external constraint; 2, deformed random coil $b > 0$, $\lambda_{\perp} = \lambda_{\parallel} = 1$; 3, deformed random coil $b = 0$, $\lambda_{\perp}$ and $\lambda_{\parallel} \neq 1$.

In the small angle range ($q^2\langle R^2 \rangle \ll 1$)

$$S(q_{\parallel}) = 1 - q_{\parallel}^2 \left(\frac{\langle R^2 \rangle}{18\lambda_{\parallel}^{-2}} + \frac{N^2b^2}{12}\right) \qquad (13)$$

In the intermediate range ($q^2\langle R^2 \rangle \gg 1$)

$$S(q_{\parallel}) = 2Re \frac{1}{X_{\parallel} + 1} = \frac{2}{q_{\parallel}^2 \frac{Nl^2}{6\lambda_{\parallel}^{-2}} + \frac{6b^2N\lambda_{\parallel}^2}{l^2} + 1} \qquad (14)$$

We note that (11) can be interpreted as the Fourier transform of an exponential function

$$S(q_{\parallel}) = \int_0^{\infty} \mathrm{d}\alpha(\cos \alpha b) \exp\left(-\alpha q_{\parallel}^2 \frac{l^2}{6}\right) \qquad (11a)$$

which gives the Lorentzian shape of (14). The $S^{-1}(q)$ representation vs. q^2 (Figure 2) in the intermediate range more clearly expresses the result in (14) and indicates the purpose of our calculation. For the undeformed coil ($b = 0$, $\lambda_{\parallel} = \lambda_{\perp} = 1$), the $S^{-1}(q)$ function is line 1, which has a slope $\langle R^2\rangle/12$. The presence of $b > 0$ with $\lambda_\perp = \lambda_\parallel = 1$ introduces a Lorentzian[3] broadening of the $1/q^2$ function 14, i.e., an upward parallel shift of line 1 (line 2). On the contrary, a modification of $\lambda_\parallel$ with $b = 0$ modifies the slope of line 1 (line 3) without upward shift.

Discussion

Expression 1 in its simplified version of (3) depends on three parameters $\lambda_\perp$, $\lambda_\parallel$, and b. We discuss here some known relations between external constraints and these parameters and show that in the intermediate range one can unambiguously determine the value of the parameters.

(a) We shall first try to find examples in which b differs from zero and $\lambda_\perp = \lambda_\parallel = 1$. The simplest example is the case where both ends of the chain are fixed at known distance L along the Z direction. In this case

$$b = L/Nl = l\langle\cos\omega\rangle$$

It has been shown by Levy[4] that at least in a first approximation for $L \ll Nl$ the parameters $\lambda_\parallel$ and $\lambda_\perp$ remain constant as b increases.

For another example, let us assume that we have a chain of dipoles μ, all of them with the same orientation along the chain. In an electric field E each of them has the energy $-\mu E\cos\omega$. If we assume that μE is small compared to kT then $b = l\langle\cos\omega\rangle = l(\mu E/3kT)$ and the $(\lambda - 1)$ are of the order $(\mu E/3kT)^2$, i.e., negligible.

(b) We next consider examples for which $b = 0$, but $\lambda_\parallel$ and $\lambda_\perp \neq 1$. In the statistics[5] of rubber elasticity it has always been assumed that the theory of affine deformation is valid for the ends of the elastic chain. This means that for $|i - j| = N$, the λ's are proportional to the deformations and that due to the incompressibility $\lambda_\parallel\lambda_\perp^2 = 1$. If we assume that these relations are valid for any pair of segments (i,j) with the same values for λ, we can use eq 10 and 14 with $b = 0$.

Another possibility to obtain a similar result would be to consider the orientation due to the action of an electric field on *induced*[6] dipoles having two polarizabilities, one α in the direction of the segments, the other β perpendicular to that direction. In this case each segment has an orientational energy $(\alpha - \beta)E^2\cos^2\omega$. It is easy to show that this implies that $b = 0$ and for low electric fields that

$$\langle\cos^2\omega\rangle = \frac{1}{3} + \frac{4}{45}(\alpha - \beta)\frac{E^2}{kT}$$

This gives for the λ's the values

$$\lambda_\parallel = 1 + \frac{4}{15}(\alpha - \beta)\frac{E^2}{kT}$$

$$\lambda_\perp = 1 - \frac{2}{15}(\alpha - \beta)\frac{E^2}{kT}$$

These examples are not restrictive and one can find many types of deformations in shear flows, for instance, where in a first approximation deformations of this kind have been introduced to describe the behavior of the macromolecule with external constraints.

We have shown that deformations of *small amplitude*, belonging to either of the two mechanisms described in this paper, can be unambiguously identified by a scattering experiment in the "intermediate" range of momentum transfer.

Of course, a real deformation may result from the combined action of the two mechanisms.

Also, the models may be refined. For instance, one finds in the literature that the *average* distance between segments (i,j) is often not a uniform function of $|i - j|$, as in (2). In ref 7 the electric charge is concentrated at the two ends of the chain. Other theories consider on the contrary the validity of (2) for small chemical distances $|i - j|$. Such refinements are very important and can be included in our calculation. They will however not modify the classification discussed in this section.

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