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LETTER TO THE EDITOR

The effects of finite velocity correlation in a polymer chain

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Abstract. The existence of a finite velocity correlation between points in a polymer chain is shown to be observable by means of the second moments of the scattering law for the dynamical system. Differences between the coherent and incoherent second moments are considered explicitly. Finally some experimental evidence is given which supports the calculation for the incoherent second moment.

This letter is concerned with several points which arose from some previous work on the dynamics of polymer chains (Edwards and Goodyear 1972a, b). The latter of these papers worked out the detailed consequences of the fact that polymerization removed one of the translational degrees of freedom from each point in the chain. The missing N degrees of freedom become those of vibration along the chain, and as far as neutron scattering is concerned they will show up in the inelastic spectrum. Here we shall assume that these vibrations appear at a high energy and that it is possible to separate these vibrations clearly from the quasi-elastic peak†. This point will be returned to at a later stage. It is already well established that the second order moments of the scattering law $S(Q, \omega)$ are a direct measure of the number of degrees of translational freedom. This letter will illustrate the calculation of these moments and also give some experimental evidence to illustrate the results. Similar calculations were presented by de Gennes (1959) for the second moments of a diatomic molecule.

The expression for the incoherent second moment may be written as

$$\int_{-\infty}^{\infty} \omega^2 S_s(Q, \omega) d\omega = \frac{Q^2}{\hbar N} \sum_j \langle \dot{R}_j^2 \rangle = \frac{Q^2}{\hbar} \langle \dot{R}^2 \rangle. \tag{1}$$

The $\langle \dots \rangle$ represents an average with respect to the Maxwell-Boltzmann distribution for the particular scattering system. For the case of a classical monatomic liquid, the result is found to be

$$\int_{-\infty}^{\infty} \omega^2 S_s(Q, \omega) d\omega = \frac{Q^2}{\hbar M} k_B T. \tag{2}$$

It was shown by Edwards and Goodyear (1972b) that the distribution governing the polymer chain was different by a numerical constant. This has the effect of reducing the moment to

$$\int_{-\infty}^{\infty} \omega^2 S_s(Q, \omega) d\omega = \frac{Q^2}{\hbar M} \frac{2k_B T}{3}. \tag{3}$$

† For polydimethyl siloxane the quasi-elastic and inelastic peaks are 165 cm^{-1} apart and the separation of the two peaks is straightforward at low momentum transfers.

A consideration of the coherent second moment is more involved. The equivalent calculation for a simple monatomic liquid relies on there being no velocity correlation between different atoms. For the case of a polymer chain this is not longer true. There appears to be a finite range over which velocity correlations exist. This in turn effects the coherent second moment. Previously it was shown that

$$\langle \dot{\mathbf{R}}_i \cdot \dot{\mathbf{R}}_j \rangle = A \exp(-c \cdot |i-j|). \quad (4)$$

A gives the energy per particle and c gives a measure of the length over which velocities are correlated; i and j refer to different atoms. The coherent second moment is

$$\int_{-\infty}^{\infty} \omega^2 S(Q, \omega) d\omega = \frac{Q^2}{\hbar N} \sum_{i,j} \langle \dot{\mathbf{R}}_i \cdot \dot{\mathbf{R}}_j \exp\{iQ \cdot (\mathbf{R}_i - \mathbf{R}_j)\} \rangle. \quad (5)$$

It was shown in Edwards and Goodyear (1972b) that this expression can be broken down as follows:

$$\langle \dot{\mathbf{R}}_i \cdot \dot{\mathbf{R}}_j \exp\{iQ \cdot (\mathbf{R}_i - \mathbf{R}_j)\} \rangle = \langle \dot{\mathbf{R}}_i \cdot \dot{\mathbf{R}}_j \rangle \langle \exp\{iQ \cdot (\mathbf{R}_i - \mathbf{R}_j)\} \rangle. \quad (6)$$

Evaluation of the latter term gives

$$\langle \exp\{iQ \cdot (\mathbf{R}_i - \mathbf{R}_j)\} \rangle = \exp\left(-\frac{Q^2 l^2}{6|i-j|}\right), \quad (7)$$

where l is the length of a monomer link in the chain. The second moment is rewritten as

$$\int_{-\infty}^{\infty} \omega^2 S(Q, \omega) d\omega = \frac{Q^2}{\hbar N} A \sum_{i,j} \exp(-c|i-j|) \exp\left(-\frac{Q^2 l^2}{6|i-j|}\right). \quad (8)$$

The double sum is easily evaluated and the final result is

$$\int_{-\infty}^{\infty} \omega^2 S(Q, \omega) d\omega = \frac{Q^2}{\hbar N} \frac{2k_B T}{3m} (2f(Q^2 l^2) + N); \quad (9)$$

$$f(Q^2 l^2) = \frac{\exp\{-(Q^2 l^2/6+c)\}}{1-\exp\{-(Q^2 l^2/6+c)\}} \left(1 + \frac{\exp\{-(Q^2 l^2/6+c)\}}{1-\exp\{-(Q^2 l^2/6+c)\}}\right) - \frac{\exp(-NQ^2 l^2/6)}{1-\exp(-Q^2 l^2/6)}$$

$$\times \left(N + \frac{\exp(-Q^2 l^2/6)}{1-\exp(-Q^2 l^2/6)}\right). \quad (10)$$

In the limit of $Q = 0$ the coherent second moment reduces to the incoherent second moment:

$$\int_{-\infty}^{\infty} \omega^2 S(Q, \omega) d\omega = \frac{Q^2}{\hbar} \frac{2k_B T}{3m} = \int_{-\infty}^{\infty} \omega^2 S_g(Q, \omega) d\omega. \quad (11)$$

Expanding (10) in the small Q limit, it can be seen that two natural limits arise:

(i) $Q^2 l^2/6 \ll c$

$$\omega^2(Q)_{\text{coherent}} = \frac{\int_{-\infty}^{\infty} \omega^2 S_g(Q, \omega) d\omega}{\int_{-\infty}^{\infty} S_g(Q, \omega) d\omega} = \frac{Q^2}{S(Q)} \frac{2k_B T}{3m} \left(1 + \frac{2}{c}\right) \quad (12)$$

(ii) $Q^2 l^2/6 \gg c$

$$\omega^2(Q)_{\text{coherent}} = \frac{Q^2}{S(Q)} \frac{2k_B T}{3m} \left(1 + \frac{12}{Q^2 l^2}\right). \quad (13)$$

Thus an intimate knowledge of the parameter c is required before it might be possible to estimate which of these limits apply.

It can be shown that the magnitude of c is related to the zero energy eigenvalues of a gaussian potential well and it has proved possible to calculate these states numerically. A nuclear physics program was modified to calculate the minimum depth of the well required to just bind a state. Preliminary results indicated that c was about 0.5. Thus the velocity correlation is seen to extend over about two monomers. Thus it might seem that limit (ii) might be observable.

The only experimental evidence available to date involves a measurement of the incoherent second moment. The results are at a preliminary stage but the agreement is reasonable. Using results obtained at UKAEA (Harwell) by scattering thermal neutrons from samples of polydimethyl siloxanes of varying length; it has proved possible to compare the incoherent second moments of a very 'small' molecule with a very 'large' molecule. The small molecule was a dimer of the dimethyl siloxane chain ($T = 25^\circ\text{C}$), whereas the large molecule was a polymer of 2 200 units ($T = 100^\circ\text{C}$). A more complete description of these experiments is found in Allen *et al* (1972). The results of the calculations on the second moment are given in figure 1.

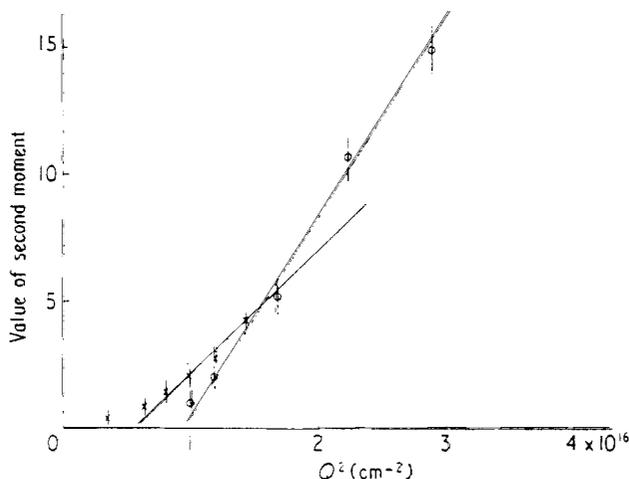


Figure 1. Comparison of incoherent second moments of dimer chain (\odot) and polymer chain of 2 200 units (\times).

Two major experimental problems place severe limitations on the accuracy of the evaluation. Firstly because the nature of the scattering law is unknown, it is difficult to remove the effects of the instrumental profile (deconvolution procedures proved unstable).

To counter this effect the experiments were carried out at the highest resolution possible. In both cases considered the instrumental effects were of the order of 10% of the observed quasi-elastic width. Secondly the inelastic background which lies underneath the quasi-elastic peak is not yet fully explained. In order to obtain finite second moments a consistent flat background was subtracted. The error that this procedure introduces becomes progressively worse as Q becomes large.

After the temperature correction the ratio of the two slopes was found to be 0.60 ± 0.2 whereas the theoretical result should be 0.80. If a monatomic liquid had been used then the result would have been 0.67.

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