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"Lozenge" Contour Plots in Scattering from Polymer Networks

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We present a consistent explanation for the appearance of "lozenge" shapes in contour plots of the two dimensional scattering intensity from stretched polymer networks. By explicitly averaging over quenched variables in a tube model, we show that lozenge patterns arise as a result of chain material that is not directly deformed by the stretch. We obtain excellent agreement with experimental data. [S0031-9007(97)03453-4]

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Recently there have been a number of neutron scattering experiments on selectively-labeled and uniaxially deformed polymer networks and melts. A common observation in these experiments is that contour plots of the two dimensional scattering intensity take on a diamond or "lozenge" shape. The experiments fall mainly into two categories; for pure networks with dilute labeled chains [1] the lozenge pattern is permanent and does not relax, but if the labeled species is mobile the lozenge pattern relaxes and is a precursor to "butterfly" contour patterns [2,3]. In this Letter we demonstrate that the lozenge shape can largely be explained by taking into account those chain sections in the system which are not directly deformed by the stretch. We concentrate mainly on the case of pure networks containing labeled chains, and discuss briefly how the concept may be transferred to systems with a mobile species.

In a polymer network, the effect of crosslinks and topological entanglements is to localize the network chains in space. Each monomer is confined to a region around its mean position and deviations from this result in an elastic energy penalty due to the deformation of the surrounding network. To model this effect, Edwards and co-workers [4] introduced the concept of a "tube" by placing each monomer on the chain in an isotropic harmonic localizing potential. The total free energy functional for the chain (in units of k_BT) for a fixed configuration of potentials is then

$$F_{\mathbf{R}}\{\mathbf{r}_l\} = \frac{1}{2}\sum_l \left\{\frac{3}{b^2}\left(\frac{\partial \mathbf{r}_l}{\partial l}\right)^2 + \frac{2b^2}{d^4}(\mathbf{r}_l - \mathbf{R}_l)^2\right\}, \quad (1)$$

where $\mathbf{r}_l$ is the position of monomer l. The first term represents the Gaussian chain statistics (b is the step length) and the second term represents the localizing potentials, centered on $\mathbf{R}_l$ (d is the tube diameter). The tube configuration given by the $\mathbf{R}_l$ is "quenched" in the sense that it is fixed at the time of formation of the network. A stretch may be imposed by affine transformation of the $\mathbf{R}_l$.

This model was used by Warner and Edwards [5] to predict the neutron scattering function for a stretched network in which a fraction of the chains is entirely deuterated. They used the "replica trick" to perform the average over the quenched variables $\mathbf{R}_l$. In terms of the stretch ratio λ_μ in the three main axes ($\mu = x, y, z$) they found a scattering function;

$$S(\mathbf{q}) = \int_0^1 dx \int_0^1 dx' \exp\Bigg\{-\sum_\mu Q_\mu^2 \lambda_\mu^2 |x - x'| + Q_\mu^2(1 - \lambda_\mu^2)\frac{d^2}{2\sqrt{6}R_g^2} \times \left[1 - \exp\left(-\frac{2\sqrt{6}R_g^2|x - x'|}{d^2}\right)\right]\Bigg\}, \quad (2)$$

where R_g is the radius of gyration of the undeformed chain, $Q_\mu = q_\mu R_g$ is the normalized wave vector, and $x = l/N$ and $x' = l'/N$ are chain contour length coordinates. Physically the first term in the exponential is that obtained by affine deformation of a Gaussian chain. The second term allows for local fluctuations about the mean path of the chain.

A modified form of the Warner-Edwards result has been used recently by Straube *et al.* [1,6,7] to interpret a series of experiments on stretched, labeled networks. One experiment [1] involved scattering from networks formed by randomly crosslinking melts which contained a small fraction of deuterated chains, providing a crucial test for the Warner-Edwards result. It was found that the original Warner-Edwards expression did not consistently fit the neutron scattering patterns obtained. Specifically, the expression does not yield the experimentally observed lozenges.

Straube *et al.* [1] presented modifications, empirically introduced at the level of the final result of Warner and Edwards, which fitted the data well and were intended to describe a deformation of the localizing tube-potential [8]. However, we have found [9] that if the assumptions of Straube *et al.* are implemented at the fundamental level of the model, it is impossible to derive their suggested formula. Harmonic localizing potentials can give only a result which is separable in the three main axes, yet their suggested formula does not have axis separability. We find that their assumptions cannot account for the lozenge pattern.

Other calculations making the approximations of phantom networks [10] or uniform density fields [11] have

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given lozenge scattering patterns, but have not been able to identify their physical origin.

Instead, we propose a physical mechanism for the appearance of lozenges in neutron scattering patterns from deformed networks. We suggest that in all the experiments which give lozenges, there exists chain material which is not directly deformed by the strain. It is the combination of deformed and undeformed material and the interactions between them which gives rise to the lozenges. We illustrate this argument by taking a simple model for a pure network in which some of the chain paths are labeled. Each labeled chain is constrained by crosslinks and entanglements, modeled by a harmonic tube potential. The crucial aspect of the model is that the free ends of the chain can relax their orientation. These "dangling ends" extend as far down the chain as the first crosslink, since entanglement constraints on this part of the chain may be relaxed by starlike breathing modes [12]. For this reason, the length of the dangling end may in fact be several tube diameters.

In our model the dangling end fraction is preaveraged, assuming that each chain in the system has two dangling ends of identical length, each a fraction f of the total length of the chain. Since all the averages involving the chain variables are Gaussian, the single chain scattering function is of the form

$$S(\mathbf{q}) = \frac{1}{N^2} \sum_{l,l'} \exp[-G_{\mathbf{q}}(l,l')], \tag{3}$$

where

$$G_{\mathbf{q}}(l,l') = \frac{1}{2} \overline{\langle [\mathbf{q} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})]^2 \rangle} \tag{4}$$

and $\overline{\langle \cdots \rangle}$ represents an average over all quenched (i.e., tube) and annealed (i.e., chain) variables.

For the central chain segment confined to the tube, we take the original Warner-Edwards model (with isotropic tube potentials). We find that for any two monomers in the central tube section,

$$\begin{aligned} G_{\mathbf{q}}(x,x') &= \eta_{\mathbf{q}}(x,x'), \\ \eta_{\mathbf{q}}(x,x') &= \sum_\mu Q_\mu^2 \lambda_\mu^2 |x - x'| + Q_\mu^2 (1 - \lambda_\mu^2) \frac{d^2}{2\sqrt{6} R_g^2} \\ &\quad \times \left[1 - \exp\left(-\frac{2\sqrt{6} R_g^2 |x - x'|}{d^2} \right) \right], \end{aligned} \tag{5}$$

where we have used the contour length variables $x = l/N$ and $x' = l'/N$. Note that $\eta_{\mathbf{q}}(x,x')$ is identical to the exponent in the Warner-Edwards expression (2), although the calculation was done without recourse to the replica trick, but by diagonalizing the free energy functional (1) using normal modes $\mathbf{r}_p$ and $\mathbf{R}_p$, where

$$\begin{aligned} \mathbf{r}_l &= \sum_p \mathbf{r}_p \exp(ilp), \\ \mathbf{R}_l &= \sum_p \mathbf{R}_p \exp(ilp). \end{aligned} \tag{6}$$

The weights for the $\mathbf{R}_p$ are chosen so as to yield the standard Gaussian chain result for the scattering in the limit $\lambda_\mu = 1$.

$$\overline{R_{\mu,p} R_{\mu,-p}} = \frac{\lambda_\mu^2 b^2}{3p^2} \left(1 + \frac{3p^2 d^4}{2b^4} \right). \tag{7}$$

Note that the $\mathbf{R}_p$ depart from the behavior of a Gaussian walk at short length scales (high p). The quenched and annealed averages can then be performed explicitly using Gaussian integrals.

For the isotropic dangling ends, we take standard Gaussian chain statistics. For any two monomers in the same dangling end,

$$\begin{aligned} G_{\mathbf{q}}(x,x') &= \kappa_{\mathbf{q}}(x,x'), \\ \text{where } \kappa_{\mathbf{q}}(x,x') &= \sum_\mu Q_\mu^2 |x - x'|. \end{aligned} \tag{8}$$

There is no correlation between the distributions of the dangling ends and the central tube segment. This means that for monomer pairs in different chain sections we can always split $G_{\mathbf{q}}(x,x')$ into separate contributions from each chain section between the two monomers. Writing the sum over monomers in (3) as an integral, we find that the scattering function is

$$S(\mathbf{q}) = 2 \int_0^1 dx \int_0^x dx' \exp[-G_{\mathbf{q}}(x,x')], \tag{9}$$

where

$$G_{\mathbf{q}}(x,x') = \begin{cases} \kappa_{\mathbf{q}}(x,x'), & \text{for } \{x,x'\} < f. \\ \kappa_{\mathbf{q}}(f,x') + \eta_{\mathbf{q}}(x,f), & \text{for } f < x \le 1 - f,\ x' \le f. \\ \kappa_{\mathbf{q}}(f,x') + \eta_{\mathbf{q}}(1-f,f) + \kappa_{\mathbf{q}}(x,1-f), & \text{for } 1 - f < x,\ x' \le f. \\ \eta_{\mathbf{q}}(x,x'), & \text{for } f < \{x,x'\} \le 1 - f. \\ \eta_{\mathbf{q}}(1-f,x') + \kappa_{\mathbf{q}}(x,1-f), & \text{for } 1 - f < x,\ f < x' \le 1 - f. \\ \kappa_{\mathbf{q}}(x,x'), & \text{for } 1 - f < \{x,x'\}. \end{cases} \tag{10}$$

To illustrate that our model does indeed produce lozenges, we present in Fig. 1 a fit to the data of Straube *et al.* [1], obtained at a stretch of $\lambda = 2.9$. The lozenge shape is reproduced extremely well. The pattern can qualitatively be considered as a superposition of the isotropic scattering from the undeformed material and the elliptic scattering from the stretched chains, with cross correlations. The dangling end fraction $f = 0.23$ required

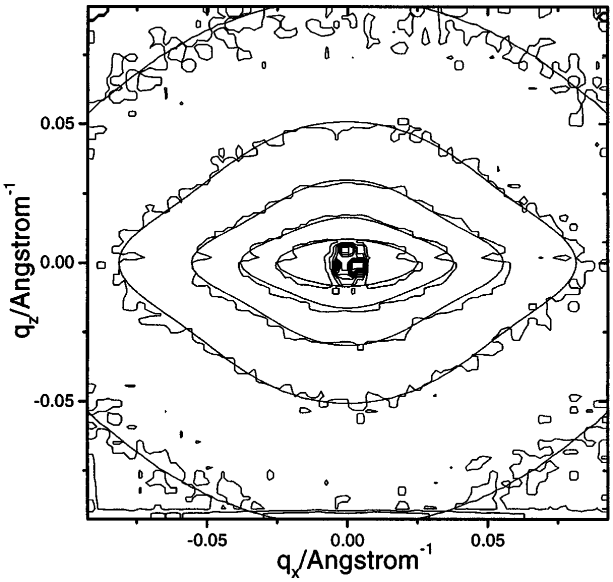

FIG. 1. Contour plot of a fit to the data of Straube *et al.* for $\lambda_z = 2.9$, $\lambda_x = \lambda_y = 0.587$, and $R_g = 142$ Å. Fitting parameters were $f = 0.23$ and $d = 24$ Å. Contours are at intensities of (from the outside) 1.6, 3.3, 6.9, 14, and 30 in arbitrary units.

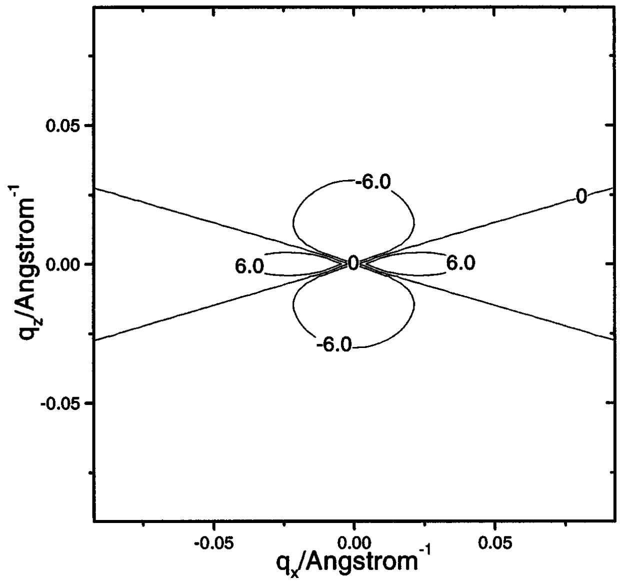

FIG. 2. Contour plot of the difference $S - S_0$ between the stretched and undeformed scattering functions for the same system as Fig. 1.

to fit that data is a little higher than expected from measurements of chain mass between crosslinks. This is to be expected because of the additional effect of chain scission and interactions with unlabeled chains, both of which are present in the Straube system.

Futhermore, our model reproduces precisely the observation of an "isotropy angle" [13]. It is found that for a specific angle between the scattering vector $\mathbf{q}$ and the stretch direction, the scattering is to a good approximation the same as that of the undeformed system. Experimentally [1], this angle is found to be given by the condition

$$\sum_{\mu} q_{\mu}^2 \lambda_{\mu}^2 = \sum_{\mu} q_{\mu}^2 . \tag{11}$$

Substituting this condition into our expression (10) we find that

$$G_{\mathbf{q}}(x, x') = \sum_{\mu} Q_{\mu}^2 |x - x'| \quad \text{for all } \{x, x'\}, \tag{12}$$

which is the value of $G_{\mathbf{q}}(x, x')$ for an undeformed chain. The reproduction of the isotropy angle is illustrated in Fig. 2, which is a contour plot of the difference between the stretched and undeformed scattering functions. The "zero contour" consists of two straight lines at a fixed angle to the stretch direction. We note that this feature is reproduced only under the assumption that the tube potential does not couple to the strain.

The dangling end model above is appropriate for networks of the type used by Straube *et al.* [1], formed by random crosslinking along the melt chains. Dangling ends may be partially eliminated by tailoring the reaction chemistry to produce specific end linking of chains, though complete elimination is impossible, due to incomplete reaction. We are not presently aware of any relevant scattering experiments on pure networks of this latter type. Such experiments would constitute a strong test of our present theory.

We now briefly discuss the lozenges observed in the recent butterfly scattering experiments [2,3]. The butterfly is the name given to a contour plot where the contours have a characteristic "figure 8" shape, aligned in the stretch direction. Butterflies appear in scattering from stretched networks swollen by labeled mobile chains. It is generally accepted [3,14] that the appearance of the butterflies is related to static inhomogeneities in the density of network crosslinks or entanglements, and requires the forced diffusion of mobile chains towards regions with fewer crosslinks or entanglements.

The butterfly patterns do not appear immediately on stretching the system; there is typically a progression from elliptical contours to lozenges to butterflies. An explanation of the three shapes must take into account the time window in which each pattern is observed. In a recent experiment [3] it was observed that the ellipses appear when the system is first stretched and the entire system deforms affinely. Lozenges appear at times of the order of the orientational relaxation time for the short mobile chains. Butterflies appear at times a good deal greater than this, when the mobile chains have had sufficient time to diffuse several radii of gyration.

Clearly the important time scale is the orientational relaxation time τ_s of the short chains. At times of the order of τ_s the short chains will have relaxed their orientation, but will have had time to diffuse one radius of gyration at most. We propose that the interaction between the relaxed short chains and oriented network chains is sufficient to explain the lozenge shape in the scattering.

The uniform density field approach of Edwards and McLeish [11] provides some mathematical justification for this conjecture. There may also be some additional contribution due to dangling ends in the network.

Finally, we mention an alternative explanation for the lozenge pattern. It has been proposed [3,15] that the lozenges are due to a mechanism similar to the one which gives rise to butterfly scattering patterns. It is possible that the inhomogeneities in crosslink density give rise to nonaffine local deformations which result in anisotropic scattering, even in a pure network. The explanation is that the lozenge is somehow a superposition of elliptic and butterfly scattering patterns. We believe that this idea arose historically because lozenges were often seen in experiments as a precursor to butterflies. It should be noted, however, that in these butterfly patterns the zero wave vector limit of the scattering is multivalued and depends upon the direction of the scattering vector [15,16]. This does not appear to be a characteristic feature of the lozenge pattern. Furthermore, this model will not in general reproduce the isotropy angle observed in deformed pure networks.

In conclusion, we find that models involving a proper combination of isotropic and deformed chains will yield lozenge scattering patterns. This provides a reasonable and consistent explanation for the neutron scattering patterns observed in deformed polymer systems.

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