Deformation dependence of the form factor of a crosslinked chain in a rubber: Entanglement and orientational effect

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The deformation dependence of the neutron scattering form factor of a labelled chain in a crosslinked melt network can be given, if one takes into account interactions between the chains. In order to do this we have used the already existing models for which the free energy has been calculated and compared with the mechanical experimental measurements. We have calculated the form factor for the standard Flory–Erman model, the sliplink model (Ball–Edwards), and the primitive path model. We have also discussed the effect of the form factor, for one model of local interactions, on the orientational (nematic field) effect between monomers.

(Keywords: neutron scattering; rubbers; crosslink fluctuations; entanglements; sliplinks; primitive path; finite extensibility; nematic effect)

INTRODUCTION

The difficult problem of a detailed understanding of rubber elasticity has been made somewhat easier by the measurement of the form factor $S(\vec{k})$ of the chains inside the polymer network (usually by small-angle neutron scattering (SANS)). Each step of improvement in the technique has brought new information to light. The classical models of rubber elasticity, which consider crosslinked Gaussian chains with no interaction, are those of Kuhn[1], James and Guth[2], Flory[3], Deam and Edwards[4]. These models allow the calculation of the form factor (see next section). Comparison with SANS results produces some important discrepancies[5,6], which can be added to the many unexplained results for former mechanical and orientation studies. One unexplained result in the mechanical studies is the deformation dependence of the reduced stress,

$$f^*(\lambda)=f/(\lambda^2-1/\lambda) \tag{1}$$

(for the uniaxial case; λ is the deformation ratio). A constant f^* is predicted

$$f^*=kT/M_{\text{mesh}} \tag{2}$$

(where M_{mesh} is the molecular weight of the mesh) in the classical models[1-4], but there is a softening around $\lambda=1$ up to $\lambda=3$ and a more rapid increase for larger λ. We will consider here several proposals concerning these two features, and simply give the modifications of the form factor one should expect, in the expectation that comparison with SANS measurements could be made.

The decrease around $\lambda=1$ is often characterized by a 'second Mooney coefficient' as f^* behaves close to

$$f^*=C_1+C_2/\lambda \tag{3}$$

Two models relate this to the presence of entanglements, and the fact that these entanglements have more freedom in space when the network is deformed. In subsequent sections we will consider the Flory–Erman model where the entanglements are assumed to reduce the freedom of the real crosslinks only; consider a model where entanglements are assumed to act as sliding crosslinks (sliplinks); consider an alternative model, related to an orientational effect on the monomers of the chain. Also discussed is the increase at larger λ which is attributed to the finite extensibility of the chain; we observe its effect on the form factor, in particular at the entangled limit.

FORM FACTOR FOR THE CLASSICAL MODELS

Two different types of labelling have been explored in SANS experiments, and we must consider both. Both start from a mixture of deuterated chains and ordinary chains. We wish to measure the form factor of a single labelled object, however, the fraction of deuterated species is low for a rubber containing solvent, but it is possible (and gives a higher signal) to make the fraction of deuterated species large in a dry rubber. In the first type, the chains after mixing are end-linked, and one measures the form factor of a single mesh, $S_m(k)$. In the second case, the chains are crosslinked (e.g. by radiation) at many points for each chain, and one measures the form factor of a single labelled path, walking in the network via numerous meshes, $S_p(k)$.[5]

We first consider $S_m(k)$, calculated as follows. One first calculates the scattering for a couple of points (i,j) inside a

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Gaussian chain of fixed end-to-end distance R,

$$S_{ij}(\underset{\sim}{k};\underset{\sim}{R}) = \frac{\int d\underset{\sim}{R}_i d\underset{\sim}{R}_j G(\underset{\sim}{R}_0,\underset{\sim}{R}_i,0,s_i)G(\underset{\sim}{R}_i,\underset{\sim}{R}_j,s_i,s_j)G(\underset{\sim}{R}_j,\underset{\sim}{R}_L,s_j,L)e^{i\underset{\sim}{k}(\underset{\sim}{R}_i-\underset{\sim}{R}_j)}}{\int d\underset{\sim}{R}_i d\underset{\sim}{R}_j G(\underset{\sim}{R}_0,\underset{\sim}{R}_i,0,s_i)G(\underset{\sim}{R}_i,\underset{\sim}{R}_j,s_i,s_j)G(\underset{\sim}{R}_j,\underset{\sim}{R}_L,s_j,L)} \tag{4}$$

where

$$G(R_x,R_y,s_x,s_y) = (3/2\pi|s_x-s_y|l)^{3/2} \times \exp\{-((3/2|s_x-s_y|l)(\underset{\sim}{R}_x-\underset{\sim}{R}_y)^2)\} \tag{5}$$

is the Green function for a random walk of length $|s_x-s_y|$ from R_x to R_y. Using the Fourier transform

$$S_{ij}(\underset{\sim}{k};\underset{\sim}{R}) = \frac{\int dq_1 \int dq_2 \int dq_3 \int dR_i dR_j e^{i\underset{\sim}{k}(\underset{\sim}{R}_j-\underset{\sim}{R}_i)} e^{i\underset{\sim}{q}_1(\underset{\sim}{R}_i-\underset{\sim}{R}_0)} e^{i\underset{\sim}{q}_2(\underset{\sim}{R}_j-\underset{\sim}{R}_i)} e^{i\underset{\sim}{q}_3(\underset{\sim}{R}_0+\underset{\sim}{R}-\underset{\sim}{R}_j)}}{(3/2\pi Ll)^{3/2}\exp\{-(3R^2/2Ll)\}}$$

$$\times \exp\{-l/6[q_1^2 s_i + q_2^2(s_i-s_j) + q_3^2(L-s_j)\} \tag{6}$$

Integration over $\underset{\sim}{R}_i,\underset{\sim}{R}_j$ produces some δ-functions $\delta(-\underset{\sim}{k}+\underset{\sim}{q}_1-\underset{\sim}{q}_2)$, $\delta(+\underset{\sim}{k}+\underset{\sim}{q}_2-\underset{\sim}{q}_3)$ and final integration over one remaining q gives

$$S_{ij}(k;R) = \exp\{-k^2 Ll\tfrac{1}{6}((|s_i-s_j|/L)-(|s_i-s_j|/L)^2)\} e^{i\underset{\sim}{k}(|s_i-s_j|/L)\underset{\sim}{R}} \tag{7}$$

We now have to integrate over the distribution of the end-to-end distance R, $W^\lambda(\underset{\sim}{R})$ and this again depends on the model used. All the classical models consider Gaussian non-interacting chains, so that equation (7) always holds. The Kuhn–Flory model assumes

$$W^\lambda(\underset{\sim}{R}) = W^1(\underset{\approx}{\lambda}^{-1}\underset{\sim}{R}) \tag{8}$$

where W^1 is the isotropic probability of the end-to-end distances, and $\underset{\approx}{\lambda}^{-1}$ the inverse of the deformation tensor, $\underset{\approx}{\lambda}$ being the deformation matrix (e.g. $\begin{pmatrix}\lambda_1 & & \\ & \lambda_2 & \\ & & \lambda_3\end{pmatrix}$). Then

$$S_{ij}^\lambda(\underset{\sim}{k}) = \int S_{ij}(\underset{\sim}{k};\underset{\sim}{R})W^\lambda(\underset{\sim}{R})d^3R \tag{9}$$

$$= \int S_{ij}(\underset{\sim}{k};\underset{\sim}{R})W^1(\underset{\approx}{\lambda}^{-1}\underset{\sim}{R})d^3R \tag{9a}$$

or

$$S_{ij}^\lambda(\underset{\sim}{k}) = \int S_{ij}(\underset{\sim}{k};\underset{\approx}{\lambda}\underset{\sim}{R})W^1(\underset{\sim}{R})d^3R \tag{9b}$$

with $$W^1(\underset{\sim}{R}) = (3/2\pi Ll)^{3/2}\exp\{-(3R^2/2Ll)\} \tag{10a}$$

$$W^\lambda(\underset{\sim}{R}) = (3/2\pi Ll)^{3/2}\Pi_\alpha(1/\lambda_\alpha)^{1/2}\exp-((3/2Ll)\textstyle\sum_\alpha R_\alpha^2/\lambda_\alpha^2) \tag{10b}$$

equation (7) combined with equation (9) gives

$$S^\lambda(k) = \textstyle\sum_i\sum_j S_{ij}^\lambda(k) = \sum_i\sum_j \exp\{-k^2 Ll/6[(|s_i-s_j|/L) - (|s_i-s_j|/L)^2(\lambda_k^2-1)]\} \tag{11}$$

where

$$\lambda_k = \underset{\sim}{k}\underset{\approx}{\lambda}\underset{\sim}{k}/k^2$$

The Σ_i and Σ_j terms can be evaluated, or replaced by $\int ds_i$ and $\int ds_j$ respectively which gives analytical functions, the details of which are not given here. A typical shape is given in *Figure 1*, as a Kratky representation.

The James and Guth/Deam and Edwards[2,4] model assumes isotropic fluctuations of the crosslinks (of given functionality ϕ) around the affinely deformed position (α is the cartesian coordinate along a principle axis)

$$\underset{\sim}{R}_\alpha = \underset{\sim}{R}_\alpha + \Delta\underset{\sim}{R}_\alpha \tag{12}$$

so that

$$W^\lambda(\underset{\sim}{R}) = w^\lambda(\underset{\sim}{R})w'^\lambda(\Delta\underset{\sim}{R}) \tag{13}$$

with an affine dependence for

$$w^\lambda(\underset{\sim}{R}) = (3(1-2/\phi)/2\pi Ll)^{3/2}\Pi_\alpha(1/\lambda_\alpha)^{1/2} \times \exp\{-((3/2Ll)(1-2/\phi)\textstyle\sum_\alpha R_\alpha^2/\lambda_\alpha^2)\} \tag{13a}$$

but no deformation dependence for

$$w'^\lambda(\Delta R) = (3(2/\phi)/2\pi Ll)^{3/2}\exp\{-((3/2Ll)(2/\phi)\textstyle\sum_\alpha \Delta R_\alpha^2)\} \tag{13b}$$

Equation (7) becomes

$$S_{ij}^\lambda(k) = \exp\{-\textstyle\sum_\alpha k_\alpha^2(Ll/6)((|s_i-s_j|/L)-(|s_i-s_j|/L)^2)\} \times \exp\{i\textstyle\sum_\alpha k_\alpha(|s_i-s_j|/L)R_\alpha\}\exp\{i\sum_\alpha k_\alpha(|s_i-s_j|/L)\Delta R_\alpha \tag{14}$$

and we integrate as in equation (9b) but with the two variables R and ΔR. Because the two distributions are Gaussian, both give a k^2 term, and we obtain an expression equivalent to equation (11) with λ^2 replaced by

$$\lambda^{*2} = \lambda^2(1-2/\phi)+2/\phi$$

as given in ref. 16.

The form factor of a labelled path, $S_p(k)$, involves couples of monomers (i,j) belonging to different meshes along the path

$$\underset{\sim}{r}_i - \underset{\sim}{r}_j = \underset{\sim}{r}_i - \underset{\sim}{R}_a + \underset{\sim}{R}_a - \underset{\sim}{R}_b + \underset{\sim}{R}_b - \underset{\sim}{r}_j \tag{15}$$

where R_a,R_b are the positions of the crosslinks. In the Kuhn–Flory model, the segments joining two consecutive crosslinks behave as the steplength of a random walk. The calculation, then simple, is given in ref. 5. If now, as in James and Guth, the crosslinks are fluctuating, two such segments are no longer independent, and a proper calculation is not available. Warner and Edwards[7] have worked out the form factor of a simple chain crosslinked on itself, which is the Deam and Edwards model[4]. Here any monomer is likely to be one of the N_x crosslinks, and one averages over the all possible configurations. The effect of such a crosslink constraint is modeled, in the variational way of Feynman, by an harmonic potential acting on each monomer around a mean value, affine to the macroscopic deformation. The variational principle gives an expression for the size of the well, $(\omega l)^{-1}$, such as

$\omega = N_x/Ll$. Warner and Edwards calculated the form factor of such a chain. Here we can make two remarks: firstly, their calculation is only approximate, an exact expression being available (see Note 1 before References section). Secondly, the usual labelled path is not as crosslinked on itself as the Deam–Edwards chain. The difference becomes clear for a small number of meshes; e.g., for $N_x = 2$, a chain twice crosslinked on itself is different from an endlinked chain. The expression of Warner and Edwards for $N_x = 2$ is the same as equation (11) combined with equation (15) at small $(i-j)/L$, i.e. at large k only, in spite of the affirmations of the authors. The nonapproximate mathematical expression gives, in particular, a λ-dependence of the radius of gyration drastically reduced compared with the James and Guth value.

Typical results for $S_p(k)$ are given in *Figure 1*. For $S_m(k)$ the behaviour at large k is the same. A modification on $S_m(k)$ will have a corresponding effect on $S_p(k)$. Simply, at small k, the large size of the labelled path allows us to connect the completely affine behaviour at large distances[5,6] ($S^{\lambda}(k) = S^{1}(\lambda k)$). In this paper we will only detail the behaviour of $S_m(k)$.

THE FLORY–ERMAN MODEL

Inasmuch as the calculations are developed here, they can be extended to this more recent model, which takes into account the interactions between chains via the entanglement concept. The Flory method of handling this latter concept in rubber is to ascribe to the interactions only the role of reducing the freedom of the actual crosslinks, not to act as new crosslinks. If one starts from the James and Guth model; for λ close to 1, the freedom of fluctuations is much decreased by the entanglements, so that the rubber behaves closely to the affine function model. When λ increases, one may remark that there is more freedom for the entanglements, and the real network behaves more closely to the James and Guth model (see also ref. 16).

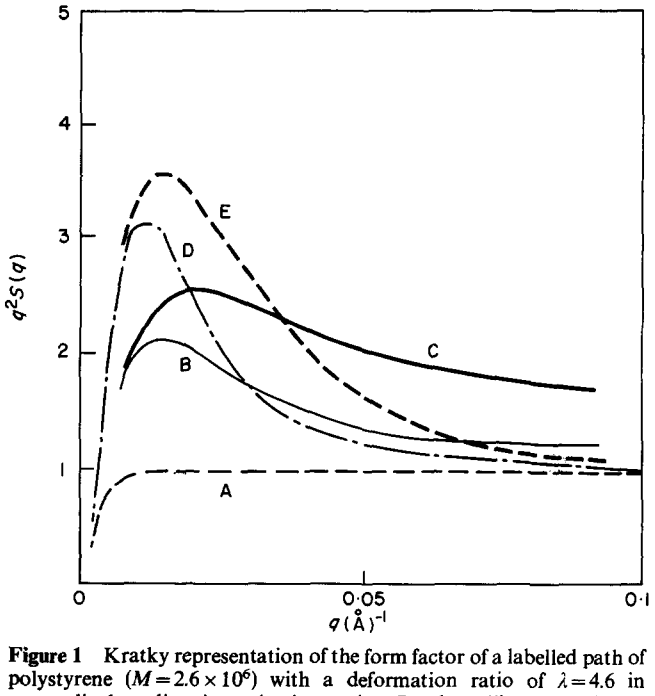

Figure 1 Kratky representation of the form factor of a labelled path of polystyrene ($M = 2.6 \times 10^6$) with a deformation ratio of $\lambda = 4.6$ in perpendicular direction. A, isotropic; B, deswelling experiment $M_{mesh} = 35\,000$ (ref. 5); C, uniaxial stretching experiment $M_{mesh} = 30\,000$–$50\,000$ (ref. 6); D, James and Guth theory ($M_{mesh} = 50\,000$); E, Kuhn and Flory theory ($M_{mesh} = 35\,000$)

The end-to-end distance of a given chain position of a given junction i must, at rest, obey both:

(i) the phantom constraint

$$R_i(t) = \bar{R}_{ph\,i} + \Delta R_{ph\,i}(t) \qquad (R + \Delta R \text{ in ref. 8}) \tag{16}$$

(ii) an entanglement constraint, which is to fluctuate around an entanglement centre of actual R

$$R_i(t) = \bar{R}_{ent\,i} + \Delta R_{ent\,i}(t)$$

$$(\bar{R}_{ent\,i} = \bar{R} + \bar{s},\ \Delta R_{ent\,i} = \Delta s \text{ in ref. 8}) \tag{17}$$

The distribution over time of $\Delta R_{ph\,i}(t)$ is explained by James and Guth, i.e. Gaussian of inverse variance ρ; Flory assumes the distribution, over time, of $\Delta R_{ent\,i}(t)$ to be Gaussian as well, of inverse variance σ_0. There is also a probability distribution for $R_{ent\,i} - R_i$, over all i; for the combination of fluctuations for $R_{ent\,i} - R_i$ and $\Delta R_{ent\,i}$ to agree with the $\Delta R_{ph\,i}$ distribution, it must be Gaussian, of variance η_0, with

$$1/\eta_0 = 1/\rho + 1/\sigma_0 \tag{18}$$

The set of the three can also be represented by a real centre (entanglement plus phantom) $R_{real\,i}$

$$\bar{R}_{real\,i} - \bar{R}_i = \sigma_0/(\rho + \sigma_0)(\bar{R}_{ent\,i} - \bar{R}_i) \tag{19}$$

$$(R_{real\,i} = R + \Delta R,\ \Delta R_{real\,i} = \Delta R \text{ in ref. 8})$$

with a Gaussian fluctuation of inverse variance θ obeying

$$1/\theta = \sigma_0/(\rho + \sigma_0)1/\eta_0 \tag{20}$$

plus a time fluctuation, $\Delta R_{real\,i}$, of inverse variance $\rho + \sigma_0$. If one now deforms the system, η_0 and σ_0 are assumed to be affinely affected. With cartesian coordinates α along the principal axis, $1/\eta_\alpha = 1/\eta_0\lambda_\alpha^2$, $1/\sigma_\alpha = 1/\sigma_0\lambda_\alpha^2$. Equations (19) and (20) still apply with σ_0, η_0 being replaced by $\sigma_\alpha, \eta_\alpha$. With $R_i(\lambda)$ being replaced by equation (17), and by handling the different Gaussian distributions, it is again possible to write

$$R_i^{\lambda} = R_{ph\,i}^{\lambda} + \Delta R_{Flory\text{–}Erman\,i}^{\lambda} \tag{21}$$

where the distribution over i of $R_{ph\,i}$ is the same as suggested by James and Guth, and the distribution over i and t of $\Delta R_{Flory\text{–}Erman\,i}^{\lambda}$ is also Gaussian with variance

$$1/\rho_{*\alpha}^{*} = 1/\theta_\alpha + 1/(\rho + \sigma_\alpha)$$

which depends on ρ and σ. Introducing the parameter $\kappa = \sigma/\rho$, one finally gets

$$1/\rho_{*\alpha}^{*} = 1/\rho[\kappa^2(\lambda_\alpha^2 - 1)/(\lambda_\alpha^2 + \kappa)^2]$$

Inasmuch as all the distributions are Gaussian, we can use the treatment given in equations (12), (13) and (14). This again gives a formula of the type in equation (11) with λ^2 now replaced by a third value λ^{**2}, such that the form

factor is now:

$$S^{\lambda}(k)=\sum_{i,j}\exp\left\{-\frac{l}{6}\sum_{\alpha}k_{\alpha}^{2}\left[|s_i-s_j|+\frac{|s_i-s_j|}{L}\times\left(1-\frac{2}{\phi}\right)\lambda_{\alpha}^{2}+\frac{2}{\phi}\left(\frac{\kappa^2(\lambda_{\alpha}^{2}-1)}{(\lambda_{\alpha}^{2}+\kappa)^2}-1\right)\right]\right\} \quad (22)$$

The Flory–Erman model gives, as expected, a form factor intermediate between the Kuhn–Flory $\kappa=\infty$ (affine junction) and the James and Guth ($\kappa=0$) models, which is closer to the latter inasmuch as the deformation increases.

SLIPLINK TREATMENT OF THE ENTANGLEMENTS

This model also treats the topological interactions between non-phantom chains, also called entanglements, but these act now as additional crosslinks. The modulus is then related to the action of the N_c crosslinks plus the action of the N_s entanglements. Ball *et al.*[9] have included the treatment of entanglements in the frame of the Deam and Edwards formulation of the rubber elasticity ('replica theory'). The entanglements are modelled as sliplinks: a piece of chain ended by two crosslinks can slip inside a small ring, which links two entangled chains. Ball *et al.* worked out the first order approximation in which the Edwards harmonic, which adequately models the crosslinks, does depend only on the crosslinks (see Note 2 before Reference section), but where the free energy depends on both kinds of links

$$F=F_c+F_s=1/2\,k_BT\left\{N_c\sum_{i=1}^{3}\lambda_i^2+N_s\sum_{i=1}^{3}[\lambda_i^2(1+\eta)/(1+\eta\lambda_i^2)+\log(1+\eta\lambda_i^2)]\right\} \quad (23)$$

where η is the average of the slippage and is found theoretically to be $\eta\simeq0.2$ (ref. 9) and experimentally $\eta\simeq0.4$ (ref. 10).

If λ departs from 1 the modulus then decreases as found experimentally. The theoretical reasoning behind equation (23) is that when the material is stretched, there is, after averaging over all the directions, more freedom for the chain to slip inside the sliplinks. The deformation weakens the effect of the entanglements as in the Flory–Erman model.

To derive the form factor, one could then apply the method described in ref. 7 to calculate the form factor $S(k)$ in the case of slip links (see Note 2). Instead of calculating the form factor by the replica theory one can attempt to do it by more elementary methods such as that done for the free energy[11]. The idea is to give a simple distribution function which adequately models the result (equation (23). In ref. 11 it was found that

$$G(\underset{\sim}{R},\underset{\sim}{L})=\int_{-\varepsilon}^{+\varepsilon}\frac{da}{2\varepsilon}\left(\frac{3}{2\pi l(L+a)}\right)^{\frac{3}{2}}\exp\left\{-\frac{3R^2}{2l(L+a)}\right\} \quad (24)$$

fits the replica results (equation 16) quite well in the small deformation regime. a is the slip variable and ε the amount of slips (see *Figure 2*). We recall the outline of the calculation briefly (see Appendix A), in order to make the same approximations for the form factor later. The free energy of the rubber is given by[4]

$$F(\underset{\approx}{\lambda})=\int d^3R\,\log(G(\underset{\approx}{\lambda}\underset{\sim}{R},L))G(\underset{\sim}{R},L) \quad (25)$$

where $\underset{\approx}{\lambda}$ is the deformation tensor. Hence, in this representation the crosslinks are fixed and not allowed to fluctuate. Adding a fluctuation as in the James and Guth model is not the major problem. Using for $G(\underset{\sim}{R},L)$ expression (24) and expanding $G(\underset{\sim}{R},L)$ to the order $(a/L)^2$, averaging on a and on $\underset{\sim}{R}$ we indeed find for the free energy, expression (24) (see appendix A for details).

To obtain the form factor, following equation (4), we have to perform the average on $G(\underset{\sim}{R},L)$, which is now given by equation (24). We now end up with

$$S^{\lambda}(k)=\sum_i\sum_j\int_{-\varepsilon}^{\varepsilon}da/(2\varepsilon)\int_{-\varepsilon}^{\varepsilon}db/(2\varepsilon)\exp\{-(k^2l/6)[|s_i-s_j|-(|s_i-s_j|^2/(L+a))(\lambda_k^2((L+b)/(L+a))-1)]\} \quad (26)$$

where the second integral ($\int db$) comes from the average procedure $<\ >$ (see Appendix B for details). Performing the a and b integrals on the same lines, as was done in the free energy case, we achieve the final result

$$S^{\lambda}(k)=\sum_{i,j}\exp\left\{-\frac{l}{6}k^2|s_i-s_j|-\frac{Q(\lambda^2-1)}{1+\eta\left\{\frac{\frac{1}{2}Q\lambda^4+\frac{1}{2}(2\lambda^2-1)Q-(3\lambda^2-1)}{\lambda^2-1}\right\}}\right.$$

with

$$Q=\frac{l}{6}k^2\frac{|s_i-s_j|^2}{L}$$

If $\eta\rightarrow0$ (so that the slip link acts as a crosslink with the amount of slips being zero) the classical expression is recovered. If $\lambda\rightarrow1$, we are left with the isotropic form factor. We obtain an additional k^2 dependence in the argument of the exponential. We note that equation (22) assumes $\Sigma(\lambda_i^2-1)$ is small, so λ is close to 1. In practice it may be more accurate to compute directly from equation (21).

FINITE EXTENSIBILITY

So far we have only considered the small deformation regime. In this section we calculate the influence of the

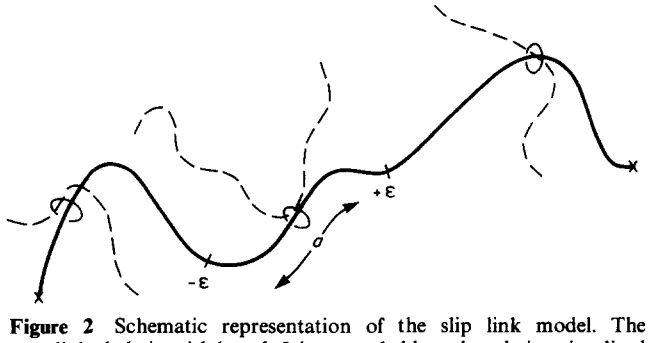

Figure 2 Schematic representation of the slip link model. The crosslinked chain with length L is entangled by other chains visualized by the rings. The ring can slide along the chain up to a maximum value ε

finite extensibility on the neutron scattering data. From considering the force it is known that for deformation ratios greater than 4–5 the extension limit becomes important (see ref. 11) and the distribution function is no longer Gaussian. In principle we have to consider two regimes (a) the case where no entanglements are present, (b) the fully entangled case[12].

As we have shown in ref. 12 the increase of the force is more drastic if the rubber is crosslinked in the melt and a lot of trapped entanglements are present. Therefore, we restrict ourselves to the latter case and we use the concept of the primitive path[13] as in the considerations concerning the free energy[11,12]. If we use the fact that the real free part of the chain is given by the difference between the real contour of the polymer and the primitive path, the distribution function can be approximated by

$$G(\underline{R},L,L_{pp}))=(3/2\pi l(L-L_{pp}))^{3/2}\exp-(3R^2/2l(L-L_{pp})) \tag{28}$$

where L_{pp} is the length of the primitive path. This primitive path itself is a random walk with step length $a>l$ (l is the step length of the polymer) and has the same end-to-end distance as the polymer chain. We find then

$$L/L_{pp}=a/l=1/\alpha \tag{29}$$

If we deform the rubber the primitive path will be deformed so that

$$L_{pp}\rightarrow L_{pp}\left(1/3\sum_{i=1}^{3}\lambda_i^2\right)^{1/2} \tag{30}$$

We can use these relations to calculate the form factor, where we are left by the same formalism as in the section dealing with form factors for classical models, if we replace L by $L-L_{pp}$ and keeping in mind that the primitive path will be deformed according to equation (30). The result of the form factor is then (see Appendix C)

$$S^{\lambda}(k)=\sum_{i,j}\exp\left\{-\frac{l}{6}k^2|s_i-s_j|-\frac{l}{6}k^2\frac{|s_i-s_j|^2}{L(1-\alpha J)}\left(\frac{\lambda^2(1-\alpha)}{1-\alpha J}-1\right)\right\} \tag{31}$$

where $\alpha=l/a$ and $J^2=1/3\Sigma\lambda_i^2$. The limits $\alpha\rightarrow 0$ and $\lambda\rightarrow 1$ again give the classical cases.

ORIENTATIONAL EFFECT

Some measurements of the orientation (e.g. quantity $\langle P_2(\theta)\rangle=\langle 3\cos^2\theta-1/2)\rangle$,$\theta$ being the angle between the monomer and the axis of the uniaxial deformation), have shown evidence of orientational interaction between the chains. In some polarization fluorescence experiments[14] P_2 is twice as large in the dry rubber than in fully swollen rubber for the same deformation. The same technique has been applied to a melt of small labelled chains solved in a matrix of large chains. During deformation, if the typical time of the deformation for these large chains is smaller than the terminal time of the mixture but greater than that for the short chains, which should remain isotropic, these latter chains, however, show a deformation[15a]. The situation is the same for dangling chains in a deformed rubber[15b]. For free chains in a network under static deformation, deuterium magnetic resonance shows that P_2 is of the same order as for the end-linked chains[17]. These interactions can be simulated in a mean field way by an orientational field as in nematic materials (see ref. 12 and refs. therein). An interesting point is that it gives a decrease in the elastic force around $\lambda=1$ in a way that is close to the published data[12,14]. Following ref. 12 we propose here to derive the form factor of a chain, in which the monomers are submitted to an orientational field, meanwhile it has still a fixed end-to-end distance. Thus we consider an anisotropic random walk of step $\mu_\alpha l$ in the direction α, joining two points distant from R. The Green function is

$$G_{\mu}^{ij}(R)=\Pi_{\alpha}(3/2\pi|i-j|\mu_\alpha^2a^2)\exp\{-(3/2Ll\textstyle\sum_\alpha R_\alpha^2/\mu_\alpha^2)\} \tag{32}$$

For such a random walk, the mean square of $\cos\theta$ would be:

$$\langle\cos^2\theta\rangle=\mu_x^2/(\mu_x^2+2\mu_y^2) \tag{33}$$

and we assume[12,14]

$$\langle(3\cos^2\theta-1)/2\rangle(=[\mu_x^2+\mu_y^2]/[\mu_x^2+2\mu_y^2])=\lambda^2-1/\lambda \tag{34}$$

where λ is the macroscopic deformation.

If we now look at an endlinked chain we can use the classical expression of $W^{\lambda}(R)$ for the distribution of the crosslinks and it can be verified that the result is obtained only by replacing k_α^2 by $k_\alpha^2\mu_\alpha^2$, which gives

$$S^{\lambda}(k)=\textstyle\sum_i\sum_j\exp\{-\sum_\alpha k_\alpha^2\mu_\alpha^2(Ll/6)((|s_i-s_j|/L)-(|s_i-s_j|/L)^2(\lambda_\alpha^2-1))\} \tag{35}$$

At small k both μ and λ will combine in a multiplicative way for the anisotropy. At large k, $S(k)$ will return to unity for the uncrosslinked chain, but it will be monomer oriented, i.e. $S(k/\text{direction }\alpha)\sim 1/k_\alpha^2\mu_\alpha^2$. In a Kratky plot, $k^2S(k)$ will appear as a plateau of ordinate $1/\mu_\alpha^2$ and in the perpendicular direction for example, the plateau will be higher. The question now is what will be the expected value of μ_α: if we refer to the experimental values from quoted experiments, P_2 is rather weak, $\sim 10^{-2}(\lambda^2-1/\lambda)$. For $\lambda\sim 1.4$ this would give $1/\mu^2\sim 1+10^{-2}$. For $\lambda=4.5$, $1/\mu^2\sim 1.1$. Thus, except for strong deformations, the effect would be very hard to see by SANS, for which the uncertainty is of order of 5% for an already reasonably accurate experiment. For example, an experiment[17a] has been done parallel to the d.m.r. measurement[17b]; $S(k)$ is measured for a small PDMS free chain solved in a deformed network: anisotropy is not apparent, the largest value of λ being 1.35. Meanwhile, d.m.r. displays a neat orientation. One would then extrapolate a similar effect for the case of an end-linked chain, i.e. μ very close to unity. In that case, for the small k regime, the relevant quantity is $\lambda_\alpha\mu_\alpha$, quite close to λ_α and it is slightly more anisotropic. This is not in agreement with the SANS results, for which the form factor is less strongly anisotropic than predicted. If λ is relatively large, the effect would be sufficiently strong to explain the large anisotropy observed at high k values. However, in this case the limited extensibility must also be considered.

QUALITATIVE BEHAVIOUR AND EXPERIMENTAL SITUATION

The experimental situation is shown in *Figure 1* for two representative cases: (a) deformation by deswelling a network crosslinked in semidilute theta solution; (b) by stretching a network crosslinked in a very concentrated solution (80%). The form factors are from labelled paths, while the calculations are for a labelled mesh, but keeping that in mind, some comparison is possible. Two important features appear: at low k (large distances) the deformation is lower than from both classical models (Kuhn–Flory and Deam and Edwards); at large k, the anisotropy is larger. The deformation ratios are large ($1.2<\lambda<5$) because SANS has been up until now not very sensitive to very small deformations.

First, the Flory–Erman model is shown to be unable to cope with this type of behaviour; with expression (21) clearly falling between the results for both classical models ($\kappa=0, \kappa\rightarrow\infty$). The Flory–Erman model will then have the same discrepancies, more deformed than the data at low k, less at large k. The conclusion is valid also for the form that a labelled path would give, as this one would still lie between those for the two classical models.

Secondly, the sliplink model could be closer to experiments for entangled systems. To allow a comparison with theoretical classical form factors, the average mesh molecular weight is evaluated from the modulus at $\lambda=1$ ($G\sim N_s+N_c$), which accounts for the entanglements. For the large deformations used in the experiments, the sliplink model reduces significantly their effect on the deformation of the chain. Then the anisotropy at small k will be reduced compared with the classical expressions. As k becomes larger and larger, the couples of monomers (i,j) producing scattering correspond to smaller and smaller (s_i-s_j) values. In equation (27), Q is then smaller, so large k behaviour would be less sensitive to the reduction of the anisotropy.

If large deformations are used, it is useful to understand the role of the limited extensibility. Equation (31) shows that the contribution of the term $|s_i-s_j|^2/L$ is increased not only through an apparent λ and this will result in a larger anisotropy at large k. For a labelled path, this will not be important for large distances: above the scale of one mesh, no effect is predicted by the model, the small k behaviour will then not differ from classical models.

Finally, the orientational effect has been estimated at the end of the previous section from experimental data and we have seen that it would be apparent only for $\lambda>3$.

Clearly, the comparisons must be advanced further, in particular by using graphic comparison of the plots for different models, and calculating the labelled path form factor, for information over a much wider range. This is also linked to the progress of systematic experiments on model rubbers.

SUMMARY

We have given the expression of the form factor of a labelled mesh in a network, starting from the classical models of Kuhn–Flory, James–Guth, and adding some interactions between chains. For that we have used theories developed in the literature in order to explain the mechanical static properties, mainly the λ dependence of the modulus. The interactions are either entanglements or local alignment; the excluded volume is not studied, thus the theories discussed here do not apply to rubbers swollen in a good solvent. We also give indications of the behaviour of the form factor of a labelled path of many meshes through the network. We comment, qualitatively, on how the different theories would transform the form factor of the classical models bringing them closer into line with the current neutron scattering data on deformed rubbers. In all cases we still retain the classical hypothesis of affine deformation of the mean positions of the crosslinks. The Flory–Erman model, because it lies between the two classical models and assumes Gaussian fluctuations, allows simple calculation. The hypothesis of an orientational field at the level of the monomer leads to a simple expression, namely where k is replaced by $\mu.k$ (μ being the orientational matrix). The influence of the entanglements, in a dense medium, on the extensibility can also be calculated in a simplistic fashion. The sliplink model is derived through the replica calculation for the free energy: the first order approximation has no corresponding effect on the form factor and any higher orders are too complex. Thus we returned to the genuine expression and considered a chain with the two ends attached to slipping crosslinks. An approximate expression may be used for λ close to 1, with the results being better computed.

Comparing with current data, one may first aim to explain the high deformation observed at large k. The Flory–Erman model does not give any clue, inasmuch as only the ends of the chain, the crosslinks, are affected by the entanglements. The orientational hypothesis does exhibit effects; however, using available data from the orientation measurements, these effects would be visible only at large k. In that case, the limited extensibility also gives a higher anisotropy.

If one is more interested by the small k behaviour, in the range of universal laws for most of the polymer physics, the orientational and limited extensibility seem weakly relevant. The Flory–Erman model, because it interpolates between the two classical models which both predict too high an anisotropy at small k, does not produce a possible explanation. The sliplink model is relevant because all the soft crosslinks due to entanglements are weakened at large λ. This could be effective for highly entangled systems. It would be of interest to observe by SANS both very entangled and weakly entangled rubbers, depending on the preparation. It is still valuable to question the hypothesis of affine deformation of the mean positions of the crosslinks, if it seems sensible for phantom chains with a connectivity are likely to be accounted by a mean field theory, and clearly it could be modified by the 'nonphantomness', and also for some special connectivities which appear in the gelation theories[18].

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NOTES

Note 1

Warner and Edwards[7] have calculated

$$\int \delta \underset{\sim}{X}(s) \exp\left\{ -\int ds\{[\partial X(s)/\partial s]^2 + l\omega^2 (X(s))^2\} \times \exp[i\gamma k(X(s_i) - X(s_j))] \right. \quad \text{(N1a)}$$

for which they give

$$\exp\{-\gamma^2 k^2 [1/2\omega(1 - \exp(\omega l|s_i - s_j|/3)]\} \quad \text{(N1b)}$$

For $(\omega l|s_i - s_j|/3) \ll 1$, and $N_x = 2$ $(\omega = N_x/Ll = 2/Ll)$ the expansion of $\exp -(\omega l|s_i - s_j|/3)$ leads to

$$\exp -k^2(\lambda^2 - 1)1/2(s_i - s_j)^2/L \quad \text{(N1c)}$$

which corresponds to the $(s_i - s_j)^2/L$ term in the exponent of equation (11) with $\lambda^2 \rightarrow \lambda^{*2} = (\lambda^2 + 1)/2$ (equation (24) with $\phi = 4$), i.e. Pearson's result for a single endlinked chain.

$$\exp -\gamma^2 k^2 \tfrac{1}{2} 3[(\coth(\omega l|s_i - s_j|/3) - 1/(\omega l|s_i - s_j|/3)) \quad \text{(N1d)}$$

It follows then that the expression for the radius of gyration is found, $1/4\ \lambda^2 + 3/4$ in the James and Guth model for $\phi = 4$, i.e. a weak λ dependence.

Note 2

Technical difficulties in use of replica theory for the form factor. Ball *et al.* have modelled the effect of both crosslinks and sliplinks as in the work by Deam and Edwards, by an harmonic well of inverse width ωl. The free energy is calculated as a function of $\omega, l, \varepsilon, L$ and then minimized with respect to ω. This gives for $x = \varepsilon\omega l/3$ the implicit equation

$$x_\alpha = 2\varepsilon(N_s + N_c)/L\{1 - (N_s/(N_s + N_c))\lambda_\alpha^2 (d\eta(x_\alpha)/dx_\alpha[2 - \lambda_\alpha^2 + \lambda_\alpha^2 \eta(x_\alpha)]/(1 + \lambda_\alpha^2 \eta(x_\alpha)^2\} \quad \text{(N2a)}$$

with $\eta(x) = x^{-2}(x - x^2 + 2/3x^3 - e^{-x}\sinh x)$. The authors just take $x = 2\varepsilon(N_s + N_c)/L$, thus $\omega^B = 6(N_s + N_c)/Ll$. If ε is estimated as the freedom of an average number $N_s/2N_c$ of entanglements confined on each mesh between the end crosslinks, $x = 1$, thus $\eta = 0.2$. Reporting ω^B in the free energy one finds expression (23), which contains extra terms depending on λ, from the first order perturbation expansion. However, for the form factor, Warner and Edwards just represent the system with the harmonic well ω which here does not depend on λ. We have solved graphically equation (N2a) and found a variation $\omega(\lambda)$, insignificant for $N_s \ll N_c$, and within a factor of 2.5 for $N_s \gg N_c$. x departs from its value at $\lambda = 1$ (e.g. $x = 1$) to saturate at $\lambda > 5$ (e.g. $x = 2.5$). This development now complicates the free energy, and η, and may be outside the boundaries for the validity of the replica method as applied in that case.

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APPENDIX A

The free energy of the slip link

Here we demonstrate that the free energy given by the replica calculation

$$F = \tfrac{1}{2}kT\sum_i \left\{ \frac{\lambda_i^2(1+\eta)}{1+\eta\lambda_i^2} + \log(1+\eta\lambda_i^2) \right\} \quad \text{(A1)}$$

can be modelled by the expression

$$G(\underset{\sim}{R}, L) = \int_{-\varepsilon}^{\varepsilon} \frac{da}{2\varepsilon} \frac{\exp\left\{ -\dfrac{3R^2}{2l(L+a)} \right\}}{\left(\dfrac{2\pi}{3} l(L+a) \right)^{3/2}} \quad \text{(A2)}$$

where a is the slip variable and ε is the amplitude of the slippage. The free energy in the deformed network is given by

$$-\frac{F}{k_B T} = \int d^3R \log G(\underset{\sim}{\lambda} \cdot \underset{\sim}{R}, L) G(\underset{\sim}{R}, L) \quad \text{(A3)}$$

we then write

$$G(\underset{\sim}{\lambda} \cdot \underset{\sim}{R}) = \int_{-\varepsilon}^{\varepsilon} \frac{da}{2\varepsilon} \left(\frac{3}{2\pi l(L+a)} \right)^{3/2} \exp\left\{ \frac{3\sum_{i=1}^{3} \lambda_i^2 R_i^2}{2l(L+a)} \right\} \quad \text{(A4)}$$

where the i are the cartesian indices. We rewrite this expression as

$$G(\underset{\sim}{\lambda} \cdot \underset{\sim}{R}) = \left(\frac{3}{2\pi l L} \right)^{3/2} \int_{-\varepsilon}^{\varepsilon} \frac{da}{2\varepsilon} \exp\left[-\frac{3\Sigma\lambda_i^2 R_i^2}{2lL(1+a/L)} - \frac{3}{2}\log\left(1 + \frac{a}{L}\right) \right] \quad \text{(A5)}$$

and expand in (a/L) to the second order in the exponent.

$$G(\underset{\sim}{\lambda}\cdot\underset{\sim}{R})\simeq\left(\frac{3}{2\pi lL}\right)^{3/2}\int_{-\varepsilon}^{\varepsilon}\frac{da}{2\varepsilon}\exp\left[-\frac{3}{2lL}\sum_i\lambda_i^2R_i^2\times\left(1-\frac{a}{L}+\left(\frac{a}{L}\right)^2\right)-\frac{3}{2}\left(\frac{a}{L}-\frac{1}{2}\left(\frac{a}{L}\right)^2\right)\right] \tag{A6}$$

After collecting terms we expand each of the exponentials again to order $(a/L)^2$ and find

$$G(\underset{\sim}{\lambda}\cdot\underset{\sim}{R})\simeq\left(\frac{3}{2\pi lL}\right)^{3/2}\exp\left(-\frac{3}{2lL}\sum\lambda_i^2R_i^2\right)\int_{-\varepsilon}^{\varepsilon}\frac{da}{2\varepsilon}\left\{1+\frac{3}{2lL}\left(\frac{a}{L}\right)\times\sum_i\lambda_i^2R_i^2+\frac{1}{2}\left(\frac{3}{2lL}\right)^2\left(\sum_i\lambda_i^2R_i^2\right)^2\left(\frac{a}{L}\right)^2-\frac{3}{2lL}\times\left(\sum_i\lambda_i^2R_i^2\right)\left(\frac{a}{L}\right)^2-\frac{3}{2}\left(\frac{a}{L}\right)-\frac{3}{2}\left(\frac{3}{2lL}\right)\sum_i\lambda_i^2R_i^2\left(\frac{a}{L}\right)^2\right. \tag{A7}$$

We then perform the average of the slippage by $\int_{-\varepsilon}^{\varepsilon}\frac{da}{2\varepsilon}$. We find

$$G\simeq\left(\frac{3}{2\pi lL}\right)^{3/2}\exp\left(-\frac{3}{2lL}\sum\lambda_i^2R_i^2\right)\left\{1+\overline{\left(\frac{a}{L}\right)^2}\left[\frac{15}{8}+\frac{1}{2}\left(\frac{3}{2lL}\right)^2\times\left(\sum\lambda_i^2R_i^2\right)^2-\frac{5}{2}\left(\frac{3}{2lL}\right)\sum\lambda_i^2R_i^2\right]\right\} \tag{A8}$$

using the abbreviation

$$\int_{-\varepsilon}^{\varepsilon}\frac{da}{2\varepsilon}\left(\frac{a}{L}\right)^2=\overline{\left(\frac{a}{L}\right)^2}$$

We now use equation (A3); we expand the logarithmic term by the use of

$$\log e^{-A}(1+\alpha B)\approx -A+\alpha B \tag{A9}$$

To calculate the average, we approximate the weight distribution $G(R,L)$ to its value for $\varepsilon=0$. This is valid since we work to order $\overline{(a/L)^2}$ only. It gives for the free energy:

$$\frac{F}{k_BT}\simeq\frac{1}{2}\sum_i\lambda_i^2-\frac{1}{2}\overline{\left(\frac{a}{L}\right)^2}\frac{1}{4}\left\{15-10\sum\lambda_i^2+3\sum_i\lambda_i^2+2\sum_{i\neq j}\lambda_i^2\lambda_j^2\right\} \tag{A10}$$

The question now is: does this fit the replica expression (A1)? To check this we expand equation (A1) to the order η and find

$$\frac{F}{k_BT}\cong\frac{1}{2}\sum_i\{\lambda_i^2+2\eta\lambda_i^2-\eta\lambda_i^4\} \tag{A11}$$

Rearranging equation (A10) to

$$\frac{F}{k_BT}=\frac{1}{2}\left\{\sum\lambda_i^2-\overline{\left(\frac{a}{L}\right)^2}\left(\sum\lambda_i^2-3\right)^3+\overline{\left(\frac{a}{L}\right)^2}\sum(\lambda_i^2-1)^2\right\} \tag{A12}$$

we see that both equations are equivalent, to the order $(\lambda_i-1)^2$, with $(a/L)^2=\eta$.

APPENDIX B

Calculation of the slip link form factor

If we start from equation (1) to obtain the form factor. We therefore calculate

$$S(k,\lambda,R_{0,L+a})=\sum_{i,j}\frac{\int d\underset{\sim}{R}_i d\underset{\sim}{R}_j G(\underset{\sim}{\lambda}\underset{\sim}{R}_0,\underset{\sim}{R}_i,s_i)G(\underset{\sim}{R}_i,\underset{\sim}{R}_j,s_j-s_i)}{\int d\underset{\sim}{R}_i d\underset{\sim}{R}_j G(\underset{\sim}{\lambda}\cdot\underset{\sim}{R}_0,\underset{\sim}{R}_i,s_i)G(\underset{\sim}{R}_i,\underset{\sim}{R}_j,s_i-s_j)}\times\frac{G(\underset{\sim}{R}_j,\underset{\sim}{\lambda}\underset{\sim}{R}_{L+a},L+a-s_j)\exp[ik(\underset{\sim}{R}_i-\underset{\sim}{R}_j)]}{G(\underset{\sim}{R}_j\underset{\sim}{\lambda}\underset{\sim}{R}_{L+a},L+a-s_i)} \tag{B1}$$

by the use of the distribution functions given in equation (18). We use equation (7), which leads, after some algebra, to

$$S(k,\lambda R_{0,L+a})=\sum_{i,j}\exp\left[-\frac{l}{6}k_\alpha^2|s_i-s_j|\left(1-\frac{|s_i-s_j|}{L+a}\right)\right]\times\exp\left(ik_\alpha\lambda_\alpha R_\alpha\frac{|s_i-s_j|}{L+a}\right) \tag{B2}$$

where α is the cartesian index.

For the final form factor we have to average this expression (B2) on the equilibrium distribution function and average on the slippage, so that

$$S(k,\lambda)=\int S(k,\lambda R_{0,L+a})\frac{3}{2\pi l(L+b)}\exp\left(-\frac{3}{2l(L+b)}R_{0,L+a}^2\right) \tag{B3}$$

which gives

$$S(k_\alpha,\lambda)=\sum_{i,j}\exp\left(-\frac{l}{6}k_\alpha^2|s_i-s_j|\right)\int_{-\varepsilon}^{\varepsilon}\frac{da}{2\varepsilon}\int_{-\varepsilon}^{\varepsilon}\frac{db}{2\varepsilon}\exp\left(\frac{l}{6}k_\alpha^2\frac{|s_i-s_j|^2}{L+a}\right)\times\exp\left(-\frac{\lambda_\alpha^2k_\alpha^2|s_i-s_j|^2}{(L+a)^2}\frac{l}{6}(L+b)\right) \tag{B4}$$

or

$$S(k_\alpha,\lambda_\alpha)=\sum_{i,j}\exp\left(-\frac{l}{6}k_\alpha^2|s_i-s_j|\right)\int_{-\varepsilon}^{\varepsilon}\frac{da}{2\varepsilon}\int_{-\varepsilon}^{\varepsilon}\frac{db}{2\varepsilon}\times\exp\left(-\frac{l}{6}\frac{k_\alpha^2|s_i-s_j|^2}{L+a}\left\{\lambda^2\frac{L+b}{L+a}-1\right\}\right) \tag{B5}$$

we see that for $\varepsilon\to0$ this contains the classical expression.

If we now do the same approximations as in the free energy calculation, we should get the equivalent form factor. We consider the integrals

$$I=\int_{-\varepsilon}^{\varepsilon}\frac{da}{2\varepsilon}\int_{-\varepsilon}^{\varepsilon}\frac{db}{2\varepsilon}\exp\left[-\frac{Q}{(1+a/L)}\left\{\lambda^2\frac{(1+b/L)}{(1+a/L)}-1\right\}\right] \tag{B6}$$

with

$$Q=\frac{1}{L}\,\frac{l}{6}k^2|s_i-s_j|^2$$

If we expand the exponent to orders $(a/L)^2$ and $(b/L)^2$ we find for the integrand

$$\exp\left[-Q\left(1-\frac{a}{L}+\left(\frac{a}{L}\right)^2\right)\left\{\lambda^2\left(1-\frac{a}{L}+\left(\frac{a}{L}\right)^2+\frac{b}{L}-\frac{ab}{L}\right)-1\right\}\right]$$

If we drop terms of order (ab), or any higher orders than 2, we find the integrand to be

$$\exp\left[-Q\left\{(\lambda^2-1)-\left(\frac{a}{L}\right)(2\lambda^2-1)+\left(\frac{a}{L}\right)^2(3\lambda^2-1)+\frac{b}{L}\lambda^2\right\}\right]$$

We then expand each of the exponentials to order $(a/L)^2$, $(b/L)^2$ and find

$$e^{-Q(\lambda^2-1)}\left\{1-\frac{b}{L}\lambda^2Q+\frac{1}{2}\left(\frac{b}{L}\right)^2\lambda^4Q^2-\left(\frac{a}{L}\right)^2(3\lambda^2-1)Q\right.$$
$$\left.+Q\left(\frac{a}{L}\right)(2\lambda^2-1)+\tfrac{1}{2}Q^2\left(\frac{a}{L}\right)^2(2\lambda^2-1)^2\right\}$$

if we perform the integrations $\int da\int db$ as given in equation (B6) we see again that the linear terms give no contribution. Defining $\int\frac{b^2}{L^2}\frac{db}{2\varepsilon}=\eta$ we get

$$I\simeq e^{-Q(\lambda^2-1)}\{1+Q\eta(\tfrac{1}{2}Q\lambda^4+\tfrac{1}{2}(2\lambda^2-1)-(3\lambda^2-1))\}\quad(B7)$$

We then approximate I by the exponential

$$I\approx e^{-Q(\lambda^2-1)}\exp\{+Q\eta(\tfrac{1}{2}\lambda^4+\tfrac{1}{2}(2\lambda^2-1)-(3\lambda^2-1))\}\quad(B8)$$

Since the dominant terms in equation (B5) come from $\exp(-Q/(L+a))$ we rearrange equation (B8) to give

$$I\approx\exp\left[-\frac{Q(\lambda^2-1)}{1+\eta\left\{\frac{\frac{1}{2}Q\lambda^4+\frac{1}{2}(2\lambda^2-1)Q-(3\lambda^2-1)}{(\lambda^2-1)}\right\}}\right]\quad(B9)$$

The final result is given by

$$S(k,\lambda)-\sum_{i,j}\exp\left[-\frac{l}{6}k^2|s_i-s_j|\right.$$
$$\left.-\frac{Q(\lambda^2-1)}{1+\eta\{[\frac{1}{2}Q\lambda^4+\frac{1}{2}(2\lambda^2-1)Q-(3\lambda^2-1)]/(\lambda^2-1)\}}\right]\quad(B10)$$

APPENDIX C

Finite extensibility form factor

For this calculation we can directly use the preliminary calculations from the second section of the paper as well as equation (B2) from Appendix B. We recall equation (9):

$$S(k,R_{0L})=\sum_{i,j}\exp\left[-\frac{l}{6}k^2|s_i-s_j|\left(1-\frac{|s_i-s_j|}{L}\right)\right]$$
$$\times\exp\left(ikR_{0L}\frac{|s_i-s_j|}{L}\right)\quad(C1)$$

We use the expression (9b). In $S_{ij}(k;\lambda R)$, L must be replaced by $L-L_{pp}$, with the deformed value for L_{pp}. Equation (C1) then becomes

$$S(k,\lambda,R_{0L})=\sum_{i,j}\exp\left[-\frac{l}{6}k^2|s_i-s_j|\left(1-\frac{|s_i-s_j|}{L(1-\alpha J)}\right)\right]$$
$$\times\exp\left[ik\lambda R\frac{|s_i-s_j|}{L(1-\alpha J)}\right]\quad(C2)$$

where α and J are defined in the section dealing with 'Finite extensibility'. If we perofrm the average

$$S(k,\lambda)=\langle S(k,\lambda R_{0L})\rangle$$

by the use of the distribution function (equation (28)) we get the final result

$$S(k,\lambda)=\sum_{i,j}\exp\left[-\frac{l}{6}k^2|s_i-s_j|-\frac{l}{6}k^2\frac{|s_i-s_j|^2}{L(1-\alpha J)}\right.$$
$$\left.\times\left\{\lambda^2\frac{(1-\alpha)}{(1-\alpha J)}-1\right\}\right]\quad(C4)$$

which reduces for $\alpha\to0$ to the classical limit.