Small-Angle Neutron Scattering from Elastomeric Networks. 1. Calculated Scattering from a Path Containing Several Junctions in the James–Guth Model

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ABSTRACT: The form factor for small-angle neutron scattering from a labeled path in a phantom network is evaluated. Calculations are based on the exact form of the James–Guth model. Kratky plots for scattering from isotropic and uniaxially stretched networks are obtained numerically. Effects of the length of the labeled path and of the state of deformation on the Kratky plots are investigated. The extent of contributions from correlations among different chains along the path is estimated.

Introduction

Recent developments in small-angle neutron scattering (SANS) techniques and their application to elastomeric networks[1] have renewed significant interest on the state of deformation at the molecular level and its relation to molecular constitution. The power and versatility of the experimental technique allows for critical assessment of the various molecular theories of rubber elasticity. Specifically, the distortion of the shape of a network chain under external deformation may accurately be measured and compared with predictions based on molecular models. Experiments are conveniently performed on networks containing deuterated chains either end-linked or randomly cross-linked into the network structure. In the first case, a small number of deuterated chains are end-linked into the network. Scattering from such networks reflects the behavior of the single network chain upon macroscopic deformation. The first calculation of SANS from such a system is by Benoit et al.,[2] where the end-linked deuterated chain is assumed to deform affinely at all points along its contour. Scattering from end-linked deuterated chains in a phantom network has subsequently been calculated by Pearson[3] and Ullman.[4] The problem of scattering from a deuterated chain randomly cross-linked into the network structure is more complicated. Cross-correlations of fluctuations of scattering centers along the path of the chain are required for the formulation of the form factor. The first evaluation of the form factor for a deuterated path in a phantom network has been given by Warner and Edwards[5] for the special case of a tetrafunctional network by using the replica model. Formulation for a phantom network of any functionality is given by Ullman.[6] The more general treatment of Ullman rests on the well-known James and Guth model[7,8] of the phantom network, which constitutes a sound statistical model for elastomeric networks. Ullman's formulation of the form factor contains a simplifying assumption according to which different chain vectors along the path are uncorrelated. A recent treatment[9,10] of the James and Guth model indicates, however, that different chains along a path in the network are not uncorrelated. A similar result has been obtained independently by Higgs and Ball[11] using the resistor network method. These authors studied also the problem of polydispersity of network chains and performed calculations of small-angle neutron scattering, but only for affine models, the replica model, and the polydisperse phantom network with replica approximation.

The specific aim of the present paper is to generalize the calculations of Ullman by removing the simplifying assumption mentioned above and adopting the exact form of the James–Guth model.

Model and Calculations

A long deuterated path cross-linked into the phantom network is depicted by the heavy line in Figure 1. The filled circles represent cross-links with which the deuterated path is connected to the network. The light lines denote the undeuterated chains leading to other cross-links of the network. We assume that the deuterated path consists of n chains ($n = 6$ in the figure) of equal path length. There are $n - 1$ ϕ-functional junctions ($\phi > 2$) along the path. We assume that there are N scattering centers along the full path, with N_0 scattering centers in each chain such that $N = nN_0$. For simplicity we assume that there are no dangling chains at the ends of the path. Corrections for the dangling chains may easily be introduced as in Ullman's treatment.

Two scattering centers i and j are shown in Figure 1. The positions of centers i and j relative to the nearest cross-link to the left of each is shown by the fractional distances ζ and θ ($0 \le \zeta, \theta < 1$), respectively. The number of ϕ-functional cross-links between i and j is denoted by d.

The distribution function $\Omega_0(\mathbf{r}_{ij})$ of the vector $\mathbf{r}_{ij}$ between two scattering centers i and j in the undeformed state is assumed to be Gaussian

$$\Omega_0(\mathbf{r}_{ij}) = (3/2\pi\langle r_{ij}^2\rangle_0)^{3/2} \exp(-3r_{ij}^2/2\langle r_{ij}^2\rangle_0) \quad (1)$$

where $\langle r_{ij}^2\rangle_0$ is the mean-square distance between points i and j in the undeformed state, identified by the subscript zero.

In the deformed state the distribution function $\Omega(\mathbf{r}_{ij})$ becomes

$$\Omega(\mathbf{r}_{ij}) = [(2\pi)^3\langle x_{ij}^2\rangle\langle y_{ij}^2\rangle\langle z_{ij}^2\rangle]^{-1/2} \times \exp(-x_{ij}^2/2\langle x_{ij}^2\rangle - y_{ij}^2/2\langle y_{ij}^2\rangle - z_{ij}^2/2\langle z_{ij}^2\rangle) \quad (2)$$

where $\langle x_{ij}^2\rangle$, $\langle y_{ij}^2\rangle$, and $\langle z_{ij}^2\rangle$ are the mean-square components of the vector $\mathbf{r}_{ij}$ in the deformed state.

The scattering form factor $S(\mathbf{q})$ from the labeled path in the network is given by the Fourier transform of the distribution function $\Omega(\mathbf{r}_{ij})$ averaged over all pairs of scattering centers along the path as

$$S(\mathbf{q}) = N^{-2}\sum_{i,j=1}^{N}\int e^{i\mathbf{q}\cdot\mathbf{r}_{ij}}\,\Omega(\mathbf{r}_{ij})\,d\mathbf{r}_{ij} \quad (3)$$

Here, $\mathbf{q}$ is the scattering vector representing the difference between the incident and scattered wave vectors, $\mathbf{k}_0$ and

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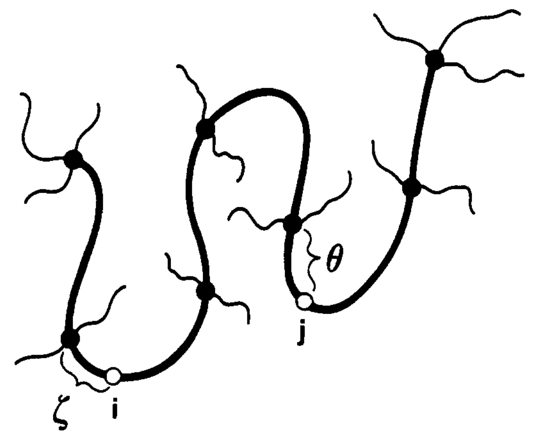

Figure 1. Labeled path (heavy full line) in a cross-linked network. It is assumed that there are no dangling chains at the end of the path. The fractional distances ζ and θ of 2 points i and j along the path with respect to their nearest left cross-links are shown. There are d junctions (cross-links) separating points i and j.

k, respectively, and $q = (4\pi/\lambda)\sin\theta/2$, with θ being the scattering angle and λ the wavelength of radiation.

Substituting the expression for $\Omega(\mathbf{r}_{ij})$ from eq 2 into eq 3 leads to

$$S(\mathbf{q}) = N^{-2}\sum_{i,j=1}^{N}\exp(-q_x^2\langle x_{ij}^2\rangle/2 - q_y^2\langle y_{ij}^2\rangle/2 - q_z^2\langle z_{ij}^2\rangle/2) \quad (4)$$

where q_x, q_y, and q_z are the components of $\mathbf{q}$.

The vector $\mathbf{r}_{ij}$ may be written as

$$\mathbf{r}_{ij} = \mathbf{r}_{ij} + \Delta\mathbf{r}_{ij} \quad (5)$$

where $\mathbf{r}_{ij}$ is the time average of $\mathbf{r}_{ij}$ and $\Delta\mathbf{r}_{ij}$ is the instantaneous fluctuation of $\mathbf{r}_{ij}$ from its time-averaged value. Squaring both sides of eq 5 and taking the ensemble average leads to

$$\langle r_{ij}^2\rangle = \langle \bar{r}_{ij}^2\rangle + \langle(\Delta r_{ij})^2\rangle \quad (6)$$

The cross-term $\langle \mathbf{r}_{ij}\cdot\Delta\mathbf{r}_{ij}\rangle$ in eq 6 is equated to zero inasmuch as the means and instantaneous fluctuations are uncorrelated. The components of the quantities on the right-hand side of eq 6 are related to the corresponding components in the undeformed state by the well-known relations[3,12]

$$\langle \bar{x}_{ij}^2\rangle = \lambda_x^2\langle \bar{x}_{ij}^2\rangle_0 \quad (7)$$

$$\langle(\Delta x_{ij})^2\rangle = \langle(\Delta x_{ij})^2\rangle_0$$

Similar expressions follow for the y and z components. λ_x in eq 7 represents the x-component of the principal deformation gradient tensor λ defined as

$$\lambda = \mathrm{diag}\,(\lambda_x, \lambda_y, \lambda_z) \quad (8)$$

where λ_z, λ_y, and λ_z represent the ratio of the final dimensions of the network to the corresponding dimensions in the state of reference.

Using eq 7 in eq 6, the following expression may be written

$$\langle x_{ij}^2\rangle = \lambda_x^2\langle \bar{x}_{ij}^2\rangle_0 + \langle(\Delta x_{ij})^2\rangle_0 = \left[\lambda_x^2 + (1-\lambda_x^2)\frac{\langle(\Delta x_{ij})^2\rangle_0}{\langle x_{ij}^2\rangle_0}\right]\langle x_{ij}^2\rangle_0 \quad (9)$$

with similar expressions for the y and z components.

In the undeformed state

$$\langle r_{ij}^2\rangle_0 = \eta\langle r^2\rangle_0 \quad (10)$$

where $\langle r^2\rangle_0$ is the mean-square end-to-end distance for a network chain between two cross-links (the path consists of n such chains), and $0 \le \eta \le n$ is the fractional distance between points i and j

$$\eta = |i - j|/N_0 \quad (11)$$

Defined in this way, η represents the ratio of the length of the contour path between points i and j to the length of the single chain.

The fluctuations $\langle(\Delta r_{ij})^2\rangle_0$ in the case when points i and j belong to the same chain (i.e., there are no cross-links between points i and j) have been first given by Pearson[3] for the James–Guth model with the structure of a symmetrically grown tree as

$$\langle(\Delta r_{ij})^2\rangle_0 = [\eta - (1 - 2/\phi)\eta^2]\langle r^2\rangle_0 \quad (12)$$

where ϕ is the junction functionality. Recently, the results of Pearson have been generalized,[9] and the fluctuations $\langle(\Delta r_{ij})^2\rangle_0$ have been calculated for points i and j separated by several ϕ-functional junctions. The result is

$$\langle(\Delta r_{ij})^2\rangle_0 = \left\{\frac{2(\phi-1)}{\phi(\phi-2)}[1 - 1/(\phi-1)^d] + (1-2/\phi)[\zeta(1-\zeta) + \theta(1-\theta) - (\zeta+\theta-2\zeta\theta)/(\phi-1)^d] + (\eta-d)/(\phi-1)^d\right\}\langle r^2\rangle_0 \quad (13)$$

Here, d is the number of ϕ-functional cross-links between points i and j and ζ and θ are as defined previously. The fractional distance η between points i and j may be written as

$$\eta = \begin{cases} d + \theta - \zeta & i \text{ is on the left of } j \\ d + \zeta - \theta & i \text{ is on the right of } j \end{cases} \quad (14)$$

In the special case of $d = 0$ and $\eta = |\zeta - \theta|$, we obtain the expression (eq 12) given by Pearson. However, the important difference between eq 12 and 13 is that the latter expression depends not only on the relative distance between points i and j but also on their specific locations along the path. In the case when $\zeta = 1$ and $\theta = 0$, points i and j become two junctions separated by $d - 2$ other ϕ-functional junctions. The mean-square vector $\langle(\Delta r_{1d})^2\rangle$ is then obtained as

$$\langle(\Delta r_{1d})^2\rangle = \frac{2(\phi-1)}{\phi(\phi-2)}[1 - (\phi-1)^{1-d}]\langle r^2\rangle_0 \quad (15)$$

a result obtained by Ullman[6] by a different method.

The expression given by eq 13 for $\langle(\Delta r_{ij})^2\rangle$ is exact within the assumptions of the original James–Guth model and generalizes the previous results of Ullman.[4,6] According to Ullman[6] the mean-square distance between points i and j separated by d ϕ-functional junctions is

$$\langle r_{ij}^2\rangle = \langle r_{i1}^2\rangle + \langle r_{1d}^2\rangle + \langle r_{dj}^2\rangle \quad (16)$$

where

$$\langle r_{i1}^2\rangle = \zeta(1-\zeta)\langle r^2\rangle_0 + \zeta^2\langle r^2\rangle \quad (17)$$

and

$$\langle r_{dj}^2\rangle = \theta(1-\theta)\langle r^2\rangle_0 + \theta^2\langle r^2\rangle \quad (18)$$

are mean-square distances between point i and the nearest (first) ϕ-functional junction on the right and between point j and the nearest ϕ-functional junction (dth junction) on the left, respectively. Here $\langle r^2\rangle$ is the mean-square end-to-end distance for a network chain between two cross-links in the deformed state, with the x-component equal to

$$\langle x^2 \rangle = \left[\lambda_x^2 + (1 - \lambda_x^2)\frac{2}{\phi}\right]\langle r^2 \rangle_0/3 \tag{19}$$

The x-component of the mean-square distance $\langle r_{1d}^2 \rangle$ between d ϕ-functional junctions is:

$$\langle x_{1d}^2 \rangle = \left\{\lambda_x^2(d-1) + (1-\lambda_x^2)\frac{2(\phi-1)}{\phi(\phi-2)}[1-(\phi-1)^{1-d}]\right\}\frac{\langle r^2 \rangle_0}{3} \tag{20}$$

In the case when points i and j belong to the same chain (they are not separated by ϕ-functional junctions)

$$\langle r_{ij}^2 \rangle = \eta(1-\eta)\langle r^2 \rangle_0 + \eta^2 \langle r^2 \rangle \tag{21}$$

with $\eta = |\zeta - \theta|$. Equation 16 is based on the assumption that correlations $\langle \mathbf{r}_{i1}\cdot\mathbf{r}_{1d} \rangle$, $\langle \mathbf{r}_{i1}\cdot\mathbf{r}_{dj} \rangle$, and $\langle \mathbf{r}_{1d}\cdot\mathbf{r}_{dj} \rangle$ are negligible, since different subchains are randomly oriented. This assumption might be true for chains separated by many ($d \gg 1$) junctions but seems unjustified for chains that are neighbors. Since the main contribution to the scattering form factor $S(q)$ results from the neighboring, correlated points, it is important to calculate the extent of contributions from correlations among different chains to the scattering form factor.

The state of macroscopic deformation for uniaxial tension is expressed as

$$\lambda = \begin{bmatrix} \lambda_\parallel & & \\ & \lambda_\perp & \\ & & \lambda_\perp \end{bmatrix} = (v_{20}/v_2)^{1/3} \begin{bmatrix} \alpha_\parallel & & \\ & \alpha_\perp^{-1/2} & \\ & & \alpha_\perp^{-1/2} \end{bmatrix} \tag{22}$$

where $\parallel$ and $\perp$ represent the directions parallel and perpendicular to the direction of stretch, respectively, and α is the ratio of final length to initial, swollen but undistroted length. Here v_{20} and v_2 are polymer volume fractions in the network in the reference state and during the experiment, respectively, and $\alpha_\parallel \alpha_\perp^2 = 1$ according to definition.

Substituting the x-component of eq 13 (identified with the component along the direction of stretch) into eq 9 and using the resulting expression in eq 4, with $q_x = q_\parallel$, $q_y = q_z = 0$, leads to

$$S_\parallel(q) = \frac{1}{n^2}\sum_{n_i=1}^{n}\sum_{n_j=1}^{n}\int_0^1 d\theta \int_0^1 d\zeta \exp\left\{-\nu_\parallel\left[\lambda_\parallel^2|n_j + \theta - n_i - \zeta| + (1-\lambda_\parallel^2)\left[\frac{2(\phi-1)}{\phi(\phi-2)}(1 - 1/(\phi-1)^{|n_j-n_i|}) + (1-2/\phi)[\zeta(1-\zeta) + \theta(1-\theta) - (\zeta + \theta - 2\zeta\theta)/(\phi-1)^{|n_j-n_i|}] + (|n_j + \theta - n_i - \zeta| - |n_j - n_i|)/(\phi-1)^{|n_j-n_i|}\right]\right]\right\} \tag{23}$$

Here

$$\nu_\parallel = q_\parallel^2 \langle r^2 \rangle_0/6 \tag{24}$$

The double sum over all scattering centers along the path has been replaced by sums over chains and sums over scattering centers within a given chain, and the latter have then been replaced by integrals according to

$$\frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} = \frac{1}{n^2 N_0^2}\sum_{n_i=1}^{n}\sum_{n_j=1}^{n}\sum_{\nu_i=1}^{N_0}\sum_{\nu_j=1}^{N_0} = \frac{1}{n^2}\sum_{n_i=1}^{n}\sum_{n_j=1}^{n}\int_0^1 d\zeta \int_0^1 d\theta \tag{25}$$

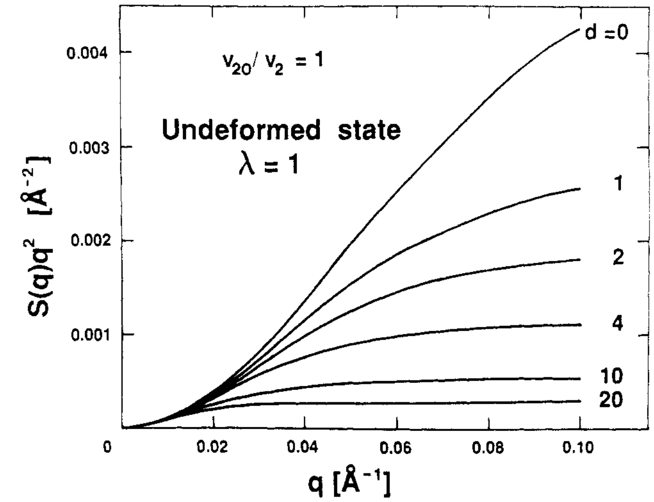

Figure 2. Kratky plot for the unswollen ($v_{20}/v_2 = 1$), undeformed ($\lambda = 1$) network. The length of the labeled path changes from one chain ($d = 0$ cross-links along the path) up to 21 chains ($d = 20$ cross-links along the path).

For scattering in the lateral direction, the form factor $S(q)$ is obtained by replacing $\parallel$ by $\perp$ in eq 23 and 24.

The expression for the form factor can only be evaluated numerically. Below, we report results of representative calculations. These are conveniently presented in the form of Kratky plots, where the ordinate is $q^2 S(q)$ and the abscissa is q.

Results of Calculations

Calculations have been performed for three different cases: (a) the unswollen, uniaxially stretched network, (b) the isotropic deswollen network, and (c) the deswollen, uniaxially stretched network. The term deswollen refers to the case where the network is formed in solution after which part or all of the solvent is removed or replaced by a smaller amount of another solvent. In this case the term v_{20}/v_2 in eq 22 is less than unity. Recent experimental work[13-15] by Bastide and collaborators has indicated that, for networks with labeled paths and deswollen in this manner, there is a strong maximum in the Kratky plots in the direction perpendicular to that of the stretching.

The numerical calculations have been performed for tetrafunctional networks ($\phi = 4$). It has been assumed that the unperturbed mean-square end-to-end vector for a chain between two cross-links is $\langle r^2 \rangle_0 = 2000$ Å^2. Figure 2 shows the Kratky plot for the undeformed ($\lambda = 1$), unswollen ($v_{20}/v_2 = 1$) networks with varying length of the path from $d = 0$ cross-links along the path (single chain) up to $d = 20$ cross-links (21 chains). Results of calculations show that $q^2 S(q)$ decreases with increase of the path, due to the fact that correlations between points on different chains decrease rapidly as the number of cross-links separating them increases. The main contribution to the scattering form factor is by points belonging to the same chain. Since $S(q)$ is given by the double sum $n^{-2}\sum_{n_i=1}^{n}\sum_{n_j=1}^{n}$ and there are only n terms in the sum when $n_i = n_j$, $S(q)$ behaves approximately as n^{-1} for large n. Figure 2 shows that, for large q ($q \simeq 0.1$ Å) when the Kratky plots reach their plateau, the $n^{-1}[=1/(d+1)]$ dependence of $S(q)$ is well satisfied. It is to be noted that the Kratky plots for undeformed, unswollen networks show no maxima with respect to the scattering wave vector q.

In Figure 3, Kratky plots for deformed ($\alpha_\parallel = 4$), unswollen ($v_{20}/v_2 = 1$) networks are shown for the scattering wave vector parallel to the direction of stretch. The ordinate values are less than those corresponding to the

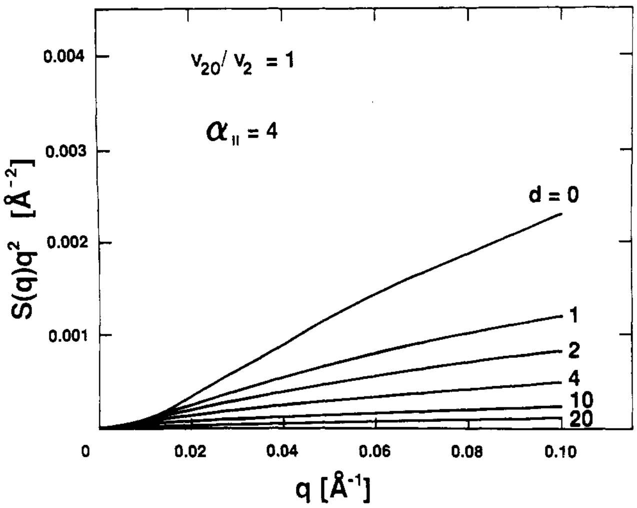

Figure 3. Kratky plot for the unswollen ($v_{20}/v_2 = 1$), deformed network ($\alpha_\parallel = 4$) for the scattering parallel to the principal axis of deformation as a function of the number d of cross-links along the path.

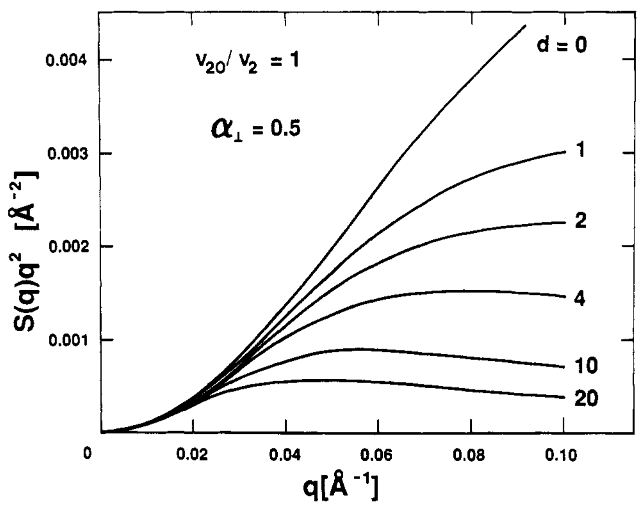

Figure 4. Kratky plot for the unswollen deformed network ($\alpha_\perp = 0.5$) for the scattering perpendicular to the principal axis of deformation as a function of the number d of cross-links along the path.

undeformed network of Figure 2. In Figure 4, Kratky plots for scattering perpendicular to the direction of stretch are presented for $\alpha_\perp = 0.5$ and $v_{20}/v_2 = 1$. The ordinate values are larger than those corresponding to the undeformed case. For sufficiently long paths, a maximum is observed in the Kratky plots. As the length of the labeled path increases, i.e., the number of cross-links along the path increases, the maxima of the Kratky plots shift toward smaller q or toward the long-wave region of the spectrum. For scattering parallel to the deformation, no maximum exists even for very large values of q.

Figure 5 shows the Kratky plots for isotropically deswollen networks with $v_{20}/v_2 = 0.1$, $\alpha = 1$. The plots exhibit maxima in agreement with the experiments of Bastide.[13-15]

Figures 6 and 7 show the Kratky plots for swollen ($v_{20}/v_2 = 0.2$), deformed networks. For scattering parallel to the direction of stretch, no maxima is observed (Figure 6), whereas pronounced maxima are present in the case of scattering perpendicular to the direction of stretch (Figure 7).

The dependence of the form factor or the Kratky plots on the length, $\langle r^2\rangle_0^{1/2}$, of the network chain is only through the parameter ν as seen from eq 17 and 18. Changing $\langle r^2\rangle_0$ therefore changes only the q scale of the plots presented in Figures 2–7.

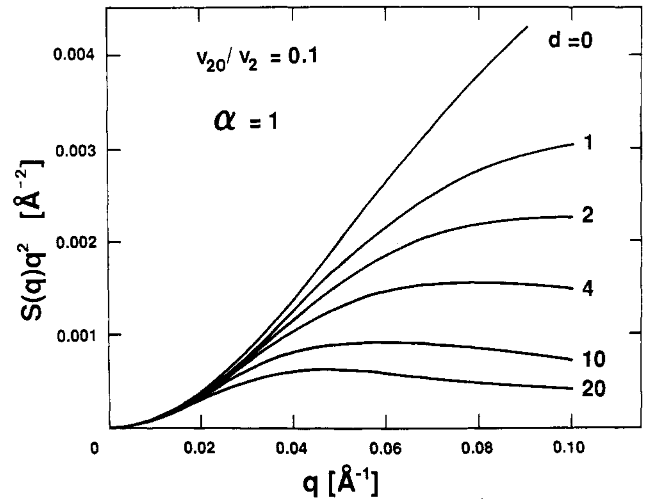

Figure 5. Kratky plot for the isotropically deswollen network ($v_{20}/v_2 = 0.1$, $\alpha = 1$) as a function of the number d of cross-links along the path.

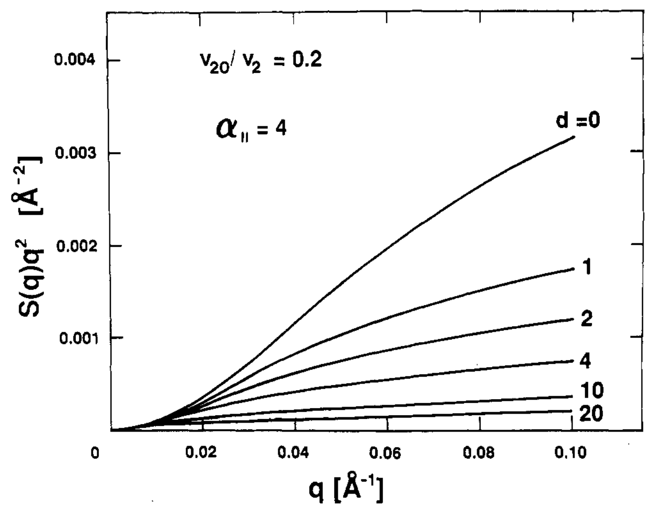

Figure 6. Kratky plot for the swollen ($v_{20}/v_2 = 0.2$) uniaxially deformed network ($\alpha_\parallel = 4$) for the scattering parallel to the principal axis of deformation as a function of the number d of cross-links along the path.

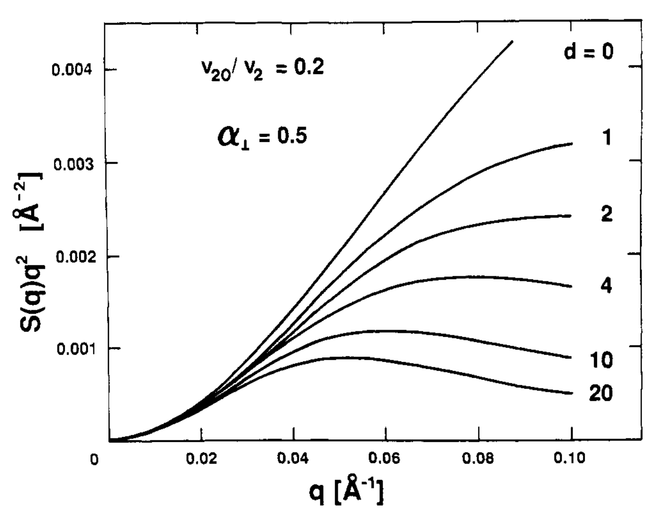

Figure 7. Kratky plot for the swollen ($v_{20}/v_2 = 0.2$) uniaxially deformed network ($\alpha_\perp = 0.5$) for the scattering perpendicular to the principal axis of deformation as a function of the number d of cross-links along the path.

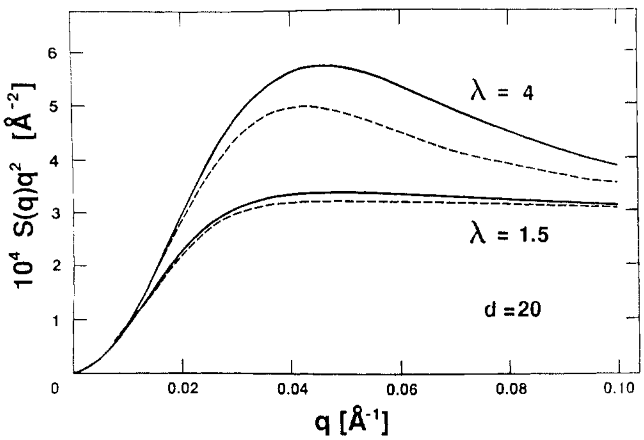

Figure 8. Comparison of the results obtained by using the Ullman approximation (dotted lines) with the exact solution of the James–Guth model (solid lines) for a labeled path with $d = 20$ cross-links along the path, for the scattering perpendicular to the deformation, from the unswollen network for two values of the deformation $\lambda = 4$ ($\alpha_\perp = 0.5$) and $\lambda = 1.5$ [$\alpha_\perp = 1/(1.5)^{1/2}$].

Discussion

Results of calculations of Kratky plots based on the exact James–Guth model of a phantom network, presented in Figures 2–7, show satisfactory agreement with the experimental data of Bastide et al.[13-15] Specifically, the presence of maxima in the plots for scattering in the direction perpendicular to stretch and in deswollen networks indicates that the theory based on the phantom network model reflects the essential features of the phenomenon.

Figure 8 shows the comparison of our results with Ullman's results based on eq 16–21. As previously we assumed $\langle r^2 \rangle_0 = 2000$ Å^2. The calculations were performed for labeled path consisting of 21 chains, i.e., with $d = 20$ cross-links along the path for scattering perpendicular to the deformation, for the unswollen network ($v_{20}/v_2 = 1$), for two values of the deformation $\lambda = 4$ (i.e., $\alpha_\perp = 0.5$) and $\lambda = 1.5$ [$\alpha_\perp = 1/(1.5)^{1/2}$]. We see that by using Ullman's approximation (dotted lines) we also obtain maxima on the Kratky plots although this maxima are less pronounced than for plots obtained using the exact solution of the James–Guth model (solid lines). For the undeformed network ($\lambda = 1$) both Ullman's and our solutions are identical. For increasing values of the deformation λ the difference between the approximate Ullman solution and our exact solution increases. For deformation $\lambda = 1.5$ the maxima on the Kratky plot for scattering perpendicular to the deformation are so flat that Figure 5 from Ullman's paper[6] might be misleading, suggesting that there is no maximum at all. For larger λ the maxima on the Kratky plots for scattering perpendicular to the deformation become more distinctive. Since the difference between Ullman's results and our results is due to the contributions from correlations among different chains on the path, it means that with the increasing deformation the extent of these correlations also increases.

Calculations based on the phantom network model of Warner and Edwards[5] also show maxima in Kratky plots.[13]

Effects on Kratky plots or the form factor of intermolecular correlations, present in real networks but not in the phantom model, are not yet treated in sufficient detail. Preliminary theoretical work in this direction has been given by Vilgis and Boué.[16]

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