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Elastic Scattering of Polymer Networks

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ABSTRACT: Theoretical aspects of the scattering of cross-linked polymers were investigated with emphasis on the fact that the number of spatial neighbors for any given network is finite. A random-phase approximation scheme was used; however, the number of interactions among spatial neighbors was truncated to account for this finiteness. The result indicates that the expression based on infinite neighbors holds true in all the cases.

Introduction

Neutron scattering has been used extensively to determine the chain conformation of thermoplastics in bulk and in solution. Deuterium-labeled chains are blended with the protonated ones to provide the scattering contrast. Various schemes have been developed to extract the single-chain structure or conformation from the scattering data. For thermosets the application of neutron scattering to determine the conformation of an average network is not a straightforward matter. One cannot implant a few deuterium-labeled networks amidst protonated ones without encountering the segregation problem commonly observed in the field of interpenetrated networks. If one blends some deuterium-labeled monomers into the starting materials, the neutron-scattering result of such samples contains no information about the network conformation. This is due to the fact that the spatial distribution of the dueterium-labeled monomers stays unchanged throughout the entire course of curing. The term network conformation merits further clarification; it is the spatial correlation between any given subchain and its chemical or topological neighbors. A subchain is defined as the chain connecting two junctions. The concept of topological neighbors versus spatial neighbors is essential to this work, and the definitions of these terms follow directly those of Flory.[1] It is reasonable to argue that the whole sample of a highly cross-linked polymer consists of just one gigantic molecule; there are no spatial, or physical, neighbors for any given subchain, and every subchain belongs to its topological neighbors. However, the notion of physical and topological neighbors is rather useful, albeit somewhat ambiguous. This point will be illustrated by the following example. Starting with any subchain chosen at random, one can find the spatial correlation of its immediate topological neighbors, its second generation, and so on. If one works hard enough, every subchain within a macroscopic sample will be counted eventually, but this is a nearly impossible task. On the other hand, one can stop the above process at a generation whose spatial correlation to the starting subchain vanishes or goes below a certain value. All the generations or those subchains covered in the above tracing process are called the topological neighbors to that starting subchain, and all those subchains comprise a subnetwork. The farthest distance reached during the above tracing process is defined as R. Within a volume of R^3 all the uncounted subchains constitute the physical neighbors that can be regrouped, in turn, into a number of subnetworks. Let us define f as the volume fraction occupied by one subnetwork within R^3; thus, the sample can be considered as an ensemble of $1/f$ subnetworks. Any pair of subnetworks, even if they are topologically interlocked, is still considered as a physical neighbor to each other. In this work all the topological aspects are completely ignored in both the intranetwork and the internetwork correlations. Hereafter, the term sub will be omitted and a network will simply mean the ensemble of a subchain and all its topological neighbors. For any given network there are $f^{-1} - 1$, hereafter denoted as n, physically neighboring networks to fill up the space with the exact value of n depending upon the functionality of the junction and the molecular weight of the subchain as described by Bastide et al.[3] For thermosets the value of n is usually less than 10 due to the low molecular weight of the subchains. The purpose of this work is to derive an expression for the elastic scattering of the polymer network in terms of the intranetwork spatial correlation functions.

The first successful experiment using neutron scattering to investigate the network conformation in cross-linked polymers, more specifically thermosets, was made by Wu and Bauer.[2] The basic approach of their work was to have all of the monomers partially deuterated. The material after cure resembles, in a linear chain analogue, a multiple block copolymer of $(H–D)_N$ where H and D denote the protonated and deuterated portions of the monomer, respectively. Each subchain of the network is thus a monomer comprising at least one D and one H block.

In this work the theoretical development is confined to an incompressible system within which the density fluctuations are completely suppressed. Under this constraint a scattering expression for a system with an infinite number of physical neighbors was obtained by using a random-phase approximation (RPA) scheme.[4] The scattering intensity $I(q)$, for polymers in a bulk network composed of H and D components is simply

$$I(q) = \Delta\alpha^2 \frac{X_{hh}X_{dd} - X_{hd}^2}{X_{hh} + X_{dd} + 2X_{hd}} \qquad (1)$$

$\Delta\alpha$ denotes the contrast factor between the components H and D. X_{hh} denotes the intranetwork correlation function in Fourier space among all the H segments. X_{dd} and X_{hd} have similar meanings. q denotes the scattering vector. The combination of these three intranetwork correlation functions, X_{hh}, X_{dd}, and X_{hd}, provides a good description of the conformation of an average network.

For the other extreme, namely, the case in which the whole space is filled by just one network, i.e., the number of spatial neighbors is zero, the corresponding expression for scattering is simply

$$I(q) = \Delta\alpha^2 X_{hh} = \Delta\alpha^2 X_{dd} = -\Delta\alpha^2 X_{hd} \qquad (2)$$

It is noteworthy that all the $X_{ij}(q)$s in both eq 1 and 2 are the bare intranetwork correlation functions, and the above *equation holds true if and only if $n = 0$.* At n equals zero, by definition the bare intranetwork correlation function and the total correlation function are identical; hence, the relation given as eq 2 follows. There are many examples where the above expression holds true; e.g., in a diamond all the carbon atoms can be regarded as the H component and the empty space between these atoms is the D component.

For polymer networks made of flexible subchains of a given molecular weight, the $n = 0$ limit implies a completely collapsed network; as n increases the individual network must become more open and the $X_{ij}(q)$s will change accordingly. In other words, for one given polymer network with its chemical structure and every topological structural parameter fixed, the appropriate form of $X_{ij}(q)$s for $n = 0$ (eq 2) is different from the case where $n > 0$ (eq 1). This difference can be illustrated by using the following example of linear polymers. For linear flexible chains of large molecular weight, it is well-known that the Debye function is a good approximation for $X_{ij}(q)$s. However, at the $n = 0$ limit the Debye function can no longer be the appropriate choice; instead of a puffy Gaussian coil, the $n = 0$ limit dictates a completely collapsed polymer coil. The density within such a coil shall approach the bulk limit, and the function form for $X_{ij}(q)$s has to be very different from the Debye function. For the same reason, in a polymer network with a fixed topological structure its bare intranetwork correlation functions $X_{ij}(q)$s must depend on the value of n. In other words, the $X_{ij}(q)$s one should put into eq 1 or eq 2 are different even for the same polymer network. Besides the well-established case of linear chains in bulk with n approaching infinity as mentioned above, very little is known about the $X_{ij}(q)$s for all other cases. It is not the objective of this work to determine the appropriate function form for $X_{ij}(q)$s, but rather our purpose is to establish a relationship between the scattering intensity $I(q)$ and $X_{ij}(q)$s. Since $I(q)$ can be determined experimentally, one can use the result of this work to deduce $X_{ij}(q)$s. In fact, for both the RPA[4] and the RISM[6] (reference interaction site model) approaches, the focal point is the interparticle interaction where the shape, or $X_{ij}(q)$s, of individual particles (it can be long chains, networks, or diatomic or single-atom molecules) is given as an input. There is no feedback loop to adjust the shape of an individual particle.

At the $n = 0$ extreme, both the numerator and the denominator of the RPA expression (eq 1) are zero based on the relation for the $X_{ij}(q)$s given in eq 2. Hence, the RPA expression is indeterminate at the $n = 0$ extreme; it does not convert itself into eq 2. The RPA result was derived originally by using a linear density response function approach.[4] This equation was rederived with a diagrammatical approach,[7] where n was included implicitly in the derivation and its value is allowed to be infinity. In this work the diagrammatical approach was adopted, with n being treated explicitly. It will be demonstrated in the latter part of this work that eq 1 holds true for all positive integers. In the following section a system with one physical neighbor will be treated first followed by a system with a finite number of physical neighbors.

For a network with two components H and D, the correlation function S between H and D can be written as

$$\mathbf{S} = \mathbf{X} + \mathbf{X}\mathbf{V}^{(1)}\mathbf{X} + \mathbf{X}\mathbf{V}^{(1)}\mathbf{X}\mathbf{V}^{(2)} + \ldots + \mathbf{X}\mathbf{V}^{(1)}\mathbf{X}\mathbf{V}\ldots\mathbf{V}^{(n)}\mathbf{X} \quad (3)$$

$\mathbf{X}$ is a 2×2 symmetric matrix with components X_{11}, X_{12}, and so on. Hereafter, the subscripts 1 and 2 denote H and D, respectively, for simplicity. $\mathbf{V}$ is another 2×2 matrix; its element V_{ij} denotes the direct intermolecular correlation function[5] between elements i and j. n is the number of spatial neighbors. Matrices ${}^{(1)}\mathbf{X}$, ${}^{(2)}\mathbf{X}$, ..., ${}^{(n)}\mathbf{X}$ are also 2×2 symmetric ones, and their elements are identical to those of $\mathbf{X}$ in terms of their q dependence. They are only different from each other by a scalar factor, and this factor is introduced to account for the fact that each network occupies a finite fraction of the whole space. To be more precise, the physical meaning of X_{ij} at $q = 0$ will be examined first. Following an earlier publication,[2] we have $X_{11}(q=0) = \phi_1 m_1$, $X_{22}(q=0) = \phi_2 m_2$, and $X_{12}(q=0) = X_{21}(q=0) = \phi_1 m_2 = \phi_2 m_1$.

ϕ_1 and ϕ_2 denote the volume fraction occupied by elements 1 and 2, respectively. m_1 and m_2 are the molecular weights of the respective elements or blocks. Let us consider the physical meaning of the second term $\mathbf{X}\mathbf{V}^{(1)}\mathbf{X}$ of the right side of eq 3; this term $\mathbf{X}\mathbf{V}^{(1)}\mathbf{X}$ accounts for the pair interaction between *two different networks* or among two spatial neighbors. The probability of two elements of type 1 situated next to each other is simply ϕ_1^2. However, if these two elements must belong to two different networks, the probability will change to $(1 - 1/(n+1))\phi_1^2$. As defined earlier, n is the number of spatial neighbors; therefore, $n + 1$ is the total number of networks, and the factor $1 - 1/(n + 1)$ is the probability that the second element belongs to another network. Following the same reasoning, the probability for a three-body interaction is $(1 - 1/(n + 1))(1 - 2/(n + 1))\phi_1^3$ and so on. Accordingly we arrive at the following relations for ${}^{(1)}\mathbf{X}$, ..., ${}^{(n)}\mathbf{X}$.

$${}^{(1)}\mathbf{X} = \left(1 + \frac{1}{n+1}\right)\mathbf{X}$$

$$\vdots$$

$$\text{and} \quad {}^{(n)}\mathbf{X} = \left(1 - \frac{n}{n+1}\right)\mathbf{X}$$

The $n + 1$ term or ${}^{(n+1)}\mathbf{X}$ is zero, and that is why eq 3 is truncated instead of being an infinite series. As n approaches infinity, all the ${}^{(1)}\mathbf{X}$, ${}^{(2)}\mathbf{X}$, ..., ${}^{(t)}\mathbf{X}$ are identical as long as t stays finite.

Equation 3 is just a viral expansion of the total correlation except one minor difference in its notation; these quantities n, $n(n-1)$, $n(n-1)(n-2)$, etc., are missing from the first, second, third, etc., terms compared to the conventional expression of this kind. This is because the quantity $n - t$ is already included in ${}^{(t)}\mathbf{X}$.

The scattering intensity, $I(q)$, is related to S through

$$I(q) = \alpha^{\mathrm{T}}\mathbf{S}\alpha \quad (4)$$

where α is a scattering contrast vector $|\alpha_1, \alpha_2|$ and the superscript T denotes transpose.

Equation 3 is applicable to systems of more than two components. The only adjustments needed to apply eq 3 to an N-component system are to change both $\mathbf{X}$ and $\mathbf{V}$ to $N \times N$ square matrices. The component X_{ij} of matrix $\mathbf{X}$ is the pair correlation function in Fourier space between components i and j if these two components are topological neighbors. Otherwise, X_{ij} equals zero. The element v_{ij} of matrix $\mathbf{V}$ denotes the direct internetwork correlation expressed in Fourier space. The value of v_{ij} depends on the chemical composition of components i and j and other factors as delineated by Schweizer and Curro[5] in their applications of the RISM theory of Chandler and coworkers[6] to various polymer problems. The ramification of eq 3 is rather straightforward; a diagrammatical presentation of individual terms in eq 3 can be found in the work by Benoit and Benmouna[7] for linear chains and in the work of Benmouna, Benoit, and Wu[8] for block copolymers. For the case of n approaching infinity, the sum of all the internetwork terms of eq 3 is denoted as $\mathbf{H}(q)$ or

$$\mathbf{H}(q) = \mathbf{XVX} + ... + \mathbf{X}(\mathbf{VX})^t + ... \tag{3'}$$

The element H_{ij}, according to the above relation, is the sum of all the products of $x_{il}V_{lm}X_{mn}V_n...X_{oj}$. The indices l, m, n, ..., o, etc., embrace all the possible combinations between 1 and N, which is the number of elements in the system. As the value of n, the number of spatial neighbors, approaches infinity, eq 3′ can be written as

$$\mathbf{H} = \frac{\mathbf{XVX}}{\mathbf{I} - \mathbf{VX}} \tag{3''}$$

or alternatively as

$$\mathbf{H} = \mathbf{XVX} + \mathbf{HVX} \tag{3'''}$$

I denotes an identity matrix. The above equation is the classical Ornstein–Zernicke[9] self-consistent theorem.

For the case of n approaching infinity, eq 3 is simply

$$\frac{1}{\mathbf{S}} = \frac{1}{\mathbf{X}} - \mathbf{V} \tag{5}$$

This is a generalized Zimm formula of scattering for multicomponent systems.

Hereafter, the scope of our work will be confined to the case of $N = 2$, i.e., a two-component system. In addition, all the elements of the direct correlation matrix **V** are assumed to be identical, or the Flory–Huggins interaction parameter between these two components is zero. The above simplification of the zero interaction parameter is a reasonable one in light of the fact that the molecular weight of the subchain or the starting prepolymer is small; no segregation is expected for a polymer network composed of block prepolymers of small molecular weight.

For the case of $n = 1$, i.e., two networks occupy the whole space, the correlation function **S** is

$$\mathbf{S} = \mathbf{X} + \frac{1}{2}\mathbf{XVX} \tag{6}$$

In an expanded form eq 6 is

$$\mathbf{S} = \begin{pmatrix} X_{11} + \frac{\upsilon}{2}(X_{11} + X_{12})^2 & X_{12} + \frac{\upsilon}{2}(X_{11} + X_{12})(X_{12} + X_{22}) \\ X_{12} + \frac{\upsilon}{2}(X_{11} + X_{12})(X_{12} + X_{22}) & X_{22} + \frac{\upsilon}{2}(X_{12} + X_{22})^2 \end{pmatrix} \tag{6'}$$

The quantity υ is the element of matrix **V**.

The incompressibility constraint leads to the following relation for **S**:

$$S_{11} = S_{22} = -S_{12} = -S_{21} \tag{7}$$

The above relation holds true for every incompressible two-component system. With combination of eqs 6 and 7 the direct correlation parameter υ is found to have the following relation:

$$\upsilon = \frac{-2}{X_{11} + X_{22} + 2X_{12}} \tag{8}$$

It is noteworthy that the direct internetwork correlation V is q dependent. With combination of eqs 6 and 8, the resultant expression for the scattering intensity is exactly as given in eq 1.

At this point, we have demonstrated that the correlation function **S** for $n = 1$ is identical with that for $n = \infty$. In other words there is a sharp transition from eq 1 to eq 2 at n equals unity. Alternatively, eq 8 can be regarded as an incompressibility criterion.

For the case in which n is greater than 1 but remains finite, the correlation function **S** is given by eq 3. In order to sum up this series, the following relation is found to be useful:

$$(\mathbf{VX})^n = \upsilon^n(X_{11} + X_{22} + 2X_{12})^{n-1}\begin{pmatrix} X_{11} + X_{12} & X_{12} + X_{22} \\ X_{11} + X_{12} & X_{12} + X_{22} \end{pmatrix} \tag{9}$$

The sum $X_{11} + X_{22} + 2X_{12}$ will be replaced by the X_T and represents the total intranetwork correlation of an average network. The counterpart of X_T for linear Gaussian chains is a Debye function. Through a simple manipulation, one has the following expression for the $\mathbf{X}(\mathbf{VX})^n$:

$$\mathbf{X}(\mathbf{VX})^n = \upsilon^n {X_\mathrm{T}}^{n-1}\begin{pmatrix} (X_{11} + X_{12})^2 & (X_{11} + X_{12})(X_{12} + X_{22}) \\ (X_{11} + X_{12})(X_{12} + X_{22}) & (X_{12} + X_{22})^2 \end{pmatrix} \tag{10}$$

We further define the product $(1 - 1/(n + 1))(1 - 2/(n + 1))...(1 - t/(n + 1))$ as $g(t)$. With substitution of eq 10 into eq 3 the correlation function **S** can be written as eq 11.

$$\mathbf{S} = \mathbf{X} + \upsilon(\sum_{t=0}^{n-1} g(t)\ (\upsilon X_\mathrm{T})^t)\begin{pmatrix} (X_{11} + X_{12})^2 & (X_{11} + X_{12})(X_{12} + X_{22}) \\ (X_{11} + X_{12})(X_{12} + X_{22}) & (X_{12} + X_{22})^2 \end{pmatrix} \tag{11}$$

According to eq 8, the quantity υ is related to $(-X_\mathrm{T})^{-1}$. In order to simplify the series of $(\upsilon X_\mathrm{T})^t$ in the above equation, we have $\upsilon = -\delta/X_\mathrm{T}$ where δ is just some numerical constant. Equation 9 can then be reduced to

$$\mathbf{S} = \mathbf{X} - f(\delta)\frac{1}{X_\mathrm{T}}\begin{pmatrix} (X_{11} + X_{12})^2 & (X_{11} + X_{12})(X_{12} + X_{22}) \\ (X_{11} + X_{12})(X_{12} + X_{22}) & (X_{12} + X_{22})^2 \end{pmatrix} \tag{12}$$

where $f(\delta)$ is a function of δ and can be regarded as a constant. The incompressibility requirement (eq 7) when applied to the above equation results in $f(\delta) = 1$. Consequently, the matrix **S** of eq 12 has the following expression:

$$\mathbf{S} = \begin{pmatrix} \frac{X_{11}X_{22} - {X_{12}}^2}{X_\mathrm{T}} & -\frac{X_{11}X_{22} - {X_{12}}^2}{X_\mathrm{T}} \\ -\frac{X_{11}X_{22} - {X_{12}}^2}{X_\mathrm{T}} & \frac{X_{11}X_{22} - {X_{12}}^2}{X_\mathrm{T}} \end{pmatrix} \tag{13}$$

The exact values of δ and $f(\delta)$ do not enter into the final expression for **S**, and they can then be regarded as fugacities. Insofar, the results obtained can be summed up by noting that eq 1 is valid for all these polymer networks with at least one spatial neighbor. The transition for the scattering expression from $n = 0$ to $n = 1$ is a sharp one.

A few remarks will be given concerning the calculation of $X_{ij}(q)$, the intranetwork correlation function; this function plays the same role as the Debye function for Gaussian coil when the RPA formula is used in linear polymers. An example of formulating the $X_{ij}(q)$ for epoxies has been published.[2] A typical mean-field approximation was used to account for the fact that each network is different from one another in terms of the subchain length and the conformation. Basically we assumed that $\langle \mathbf{XVX} \rangle$ could be approximated by $\langle \mathbf{X} \rangle \langle \mathbf{V} \rangle \langle \mathbf{X} \rangle$ and so on for the other higher order terms. This approximation leads to the use of $\langle \mathbf{X} \rangle$ in place of **X** for all the equations discussed herein. The bracket $\langle\ \rangle$ stands for the ensemble average over the distributions of subchain size and conformation. This approximation scheme is entirely parallel to what has been used for linear chains within RPA theory.

References and Notes

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