Rubber Elasticity and Inhomogeneities in Cross-Link Density

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ABSTRACT: This paper discusses the effects of network defects, such as weak inhomogeneities in the cross-link density. The appearance of inhomogeneities of the cross-link density in space during rubber fabrication is an obvious problem. We ask the question what is the effect of such inhomogeneities on the free energy of the sample, i.e. the mechanical stress–strain relation (this contains macroscopic information), and on the neutron scattering form factor, i.e. the microscopic information. We show there is only a marginal effect on the free energy of the sample. Essentially there is no change in the deformation dependence and in the modulus of the free energy. We predict a strong effect on the neutron scattering of a given inhomogeneous sample.

1. Introduction

The effect of network defects, such as inhomogeneities in cross-link density of a given sample, is of general interest in the theory of rubber elasticity.[1] This has not been considered very deeply and the effect of inhomogeneities of the cross-link density of the sample on the stress–strain behavior and the neutron scattering form factor is not known yet. The problems of inhomogeneities of the cross-link density arise in the cross-linking process of the network. This can be seen in the following example. Imagine a chain crosslinked to another one. The dynamics of the cross-linked chain is now slower compared to the un-cross-linked case. Thus it is more probable that these chains are cross-linked once more; i.e. a cross-link will appear near another one. Therefore one can expect clustering of cross-links; i.e. there are regions of more cross-linked chains and regions with less cross-links, which behave differently upon deformation.

The other possibility where inhomogeneous rubber samples appear is given by the percolation problem. It is believed that the cross-linking process is linked to the percolation problem.[2,3] Many aspects of the simple bond percolation problem can be found in the cross-linking process of rubber and simulations have been carried out to demonstrate this. Imagine a percolation process right at the percolation threshold. The resulting cluster is a very inhomogeneous object. There are regions in space of densely cross-linked (the blobs) and regions of weakly cross-linked material. At later stages of the cross-linking process the material becomes more homogeneous but the general features of the cluster remain the same. Only at full conversion of the cross-linker will all the inhomogeneities become smeared out. But this is very unlikely since there is a tendency of adding cross-links to already higher cross-linked regions. Thus we expect inhomogeneous samples, and we have to investigate the behavior of such materials.

A basic attempt to treat inhomogeneities theoretically in swollen (diluted) samples is due to Bastide, Leibler, and Prost[4] who consider the cross-linking process a percolation phenomenon and impose frozen blobs of cross-linked material. They predict the so-called "butterfly patterns" in neutron scattering.[5] These are butterfly-shaped isointensity lines which one obtains from small angle neutron scattering (SANS) in uniaxially deformed rubber. These authors discuss the behavior of swollen networks, whereas we aim for the bulk behavior of the network in this paper. We do not provide a full explanation of the butterfly effect, but we are interested in the general features of the free energy and the neutron scattering form factor by the presence of inhomogeneities in the cross-link density in the bulk network.

Our idea of treating the inhomogeneities in the bulk state of the rubber goes back to the treatment of networks of Deam and Edwards.[6] In this reference the classical work by James and Guth[7,8] is extended. The general idea is the following. Take a huge Gaussian chain and cross-link it with itself, whenever two chain segments are close to each other. This will produce a piece of rubber. The cross-links act as a constraint in the partition function function. After several mathematical steps, this constraint can be written in a way that it looks like an attractive potential. Then the free energy of the rubber is calculated with a variational method;[6] i.e. the attractive potential of the cross-links is replaced by a repulsive harmonic potential, and the prefactor is adjusted to fit best the real cross-link constraint. The prefactor of the harmonic potential has a physical meaning: It is the strength of the localization of the cross-link and the chain. It turns out that the inverse of the localization parameter has the dimensions of length squared, i.e. the mean square distance of the space available to the cross-link on diffusion, or the volume in which it is localized. Obviously the localization strength depends on the environment, i.e. on the structure of the network. The precise value of the localization parameter is determined by making the free energy stationary.

The localization parameter is determined by the number of cross-links, N_c, and the radius of gyration of the total chain present; i.e. it is given by $6N_c/lL$, where l is the Kuhn step length of the polymer and L is the total contour length of the network. Here it was assumed that the cross-links are distributed randomly. In this paper we treat the number N_c as a given realization of the cross-link position; i.e. it is a function of a configurational variable and written as $N_c(\mathbf{r})$ for the cross-link number, which depends on a coarse space variable. This means that we have a given realization of the rubber, i.e. a configuration r, which take the spatial fluctuations in the cross-link density into account. We assume the following form $N_c(\mathbf{r}) = N_c^\circ + n(\mathbf{r})$, where N_c° is the mean density of the cross-links and $n(\mathbf{r})$ accounts for the fluctuation of the cross-link density in space in the sample. The total number of cross-links is given by the integral over the cross-link density; i.e. the mean number corresponds to N_c°, which is the total number of cross-links. The free energy and the neutron scattering form factor are, under this assumption, a

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functional of $N_c(\mathbf{r})$. Since the rubber is an amorphous solid which contains quenched disorder,[6,9,10] we have to calculate the free energy and the neutron scattering form factor for a given realization $N_c(\mathbf{r})$ and average afterward over all possible realizations, i.e. over the distribution for $\{N_c(\mathbf{r})\}$.

We show by averaging of the free energy upon the fluctuations in the cross-link density that such fluctuations lead to a very surprising result. We will have effectively no serious change of the deformation dependence of free energy, except that there is a slight increase of the free energy by the disorder. The modulus is still given by the total number of cross-links, but this comes from the fact that we had used a weak disorder model. For more realistic models, we would predict an effect of the disorder on the modulus which can be 2-fold. Firstly the modulus decreases, since the effective number of cross-links decreases. Secondly there might be an increase due to the filler effect; i.e. if large aggregation of crosslinks are present in the sample, these act as a more or less strong filler and increase the modulus. Such effects cannot be discussed in our weak disorder limit. Nevertheless we predict that the characteristic deformation dependence of the free energy is not altered, i.e. $F \sim N_c{}^{\circ} kT\sum\lambda_i{}^2$ + deformation-independent terms. kT is the thermal energy and the λ_i values are the stretching ratios in the three Cartesian directions.

We predict further that in the case of neutron scattering we can expect a dramatic influence of the fluctuations of the cross-link density. The averaging process leads to a new dependence on the wave vector and introduces a new deformation dependence in the classical form factors. Thus we expect effects in the neutron scattering but not in the free energy.

Note that this disorder model contains more facts about a given rubber sample. We expect sample fluctuations for different realizations. We will not discuss these points further within our oversimplified model and leave the discussion for a more rigorous approach.

The remainder of the paper is organized as follows. In the next section we recall the main ideas of the phantom type theories. This will include the affine model by Kuhn,[11] the phantom model by James and Guth,[7,8] and the Deam–Edwards theory which will lead to the model with spatially varying cross-link densities, which will be discussed in the fourth section. We calculate then the effect of variations in the cross-link density in the free energy and in the neutron scattering form factor.

2. Free Energies for Phantom Type Models

2.1. The Kuhn Model. The simplest approach to rubber elasticity is the classical model by Kuhn[11,12] which contains crude assumptions, such as that the chains are almost independent of each other and that there are no further interactions apart from the cross-links which connect the chains. The deformation is assumed to be affine; i.e. the macroscopic deformation is essentially the same as the microscopic deformation down to length scales to the distance between two cross-links. This is the basic assumption, and in consequence, the cross-links are supposed to be fixed in space; i.e. they do not fluctuate around a mean position. The free energy of deformation is found for four functional cross-links to be

$$F = N_c kT\sum_{i=1}^{3}\lambda_i{}^2 \tag{2.1}$$

where T is the absolute temperature, k is Boltzmann's constant, and the λ_i values are the deformation ratios in Cartesian directions, $i = 1, 2, 3$. For arbitrary cross-link functionality, ϕ, the equation is

$$F = \frac{1}{4}\phi N_c kT\sum_{i=1}^{3}\lambda_i{}^2 \tag{2.1a}$$

2.2. The James and Guth Model. James and Guth[7,8] relaxed the assumption of affine deformation and allowed free motion for the cross-links in the rubber. In their theory the cross-links are not fixed in space and can move freely in space. The only effect on the free energy is a factor 1/2 in the modulus for four functional cross-links, i.e.

$$F = \frac{1}{2}N_c kT\sum_{i=1}^{3}\lambda_i{}^2 \tag{2.2}$$

or more generally for arbitrary functionality ϕ

$$F = \frac{1}{2}\left(\frac{\phi}{2} - 1\right)N_c kT\sum_{i=1}^{3}\lambda_i{}^2 \tag{2.3}$$

It is believed that these two theories are two marginal cases, and it has been claimed that the real value of the free energy is situated between these limiting free energies. This claim has mainly experimental and historical reasons and cannot be rigorously proven very simply.

Note that these models are too simple for our purpose, since they do not take into account the environment. The next model we discuss is doing that, and we can account for heterogeneities in cross-link density in a very simple and naive way.

2.3. The Result of the Deam–Edwards Theory. The model is an extension of the classical model by James and Guth. For the modulus it recovers the same prefactor, i.e. $^1/_2N_c$ for four functional cross-links. We will assume only four functional cross-links from now on. The actual calculation is complex and we do not have the space to go into any details, and we refer the reader to the original paper.[6] It has been used as a harmonic trial potential in the chain variables to model the cross-link constraint, i.e.

$$V = \frac{l}{6}q_0{}^2\int_0^L ds\,\mathbf{R}^2(s) \tag{2.4}$$

The free energy can be evaluated and after a long calculation and is a function of the localization parameter. One finds

$$F = \frac{1}{2}N_c kT\left(\sum_i \lambda_i{}^2 - \log q_0 + \frac{lL}{12}\frac{q_0}{N_c}\right) \tag{2.5}$$

The value of q_0 which fits the cross-link constraint best is found by making the free energy stationary

$$q_0 = 6N_c/lL \tag{2.6}$$

This result provides the physical interpretation of the localization parameter. Its inverse defines the mean distance in which the cross-links are localized; i.e. it is proportional to the mean square radius of gyration of a chain segment between two cross-links, i.e. the mesh size of the system. $q_0{}^{-3/2}$ describes the volume which is explored by the cross-link upon diffusion. Thus it depends on the realization of the environment of a given cross-link or chain.

If we put this best fit value back into the free energy, we find

$$F = \frac{1}{2}N_c kT\left(\sum_i \lambda_i^2 - \log\left\{\frac{6N_c}{lL}\right\} + 1\right) \qquad (2.7)$$

Thus the free energy is a function of the deformation and the number of cross-links, i.e. the realization of the cross-links. This equation is important because it allows us to generalize the free energy to a free energy functional which contains the realization of the cross-links $N_c(\mathbf{r}) = N_c^\circ + n(\mathbf{r})$; i.e. it is a functional of the fluctuations in the cross-link density. Before we turn to that, let us recall the neutron scattering form factor for the different network models.

3. Neutron Scattering Form Factors (SANS) for Phantom Type Models

3.1. General Relations. In the previous sections we discussed the free energy of rubber, which is a fully averaged quantity not too sensitive to molecular details of the chain behavior during deformation. Neutron scattering of deuterated chains between cross-links provides a more useful tool for microscopic investigations. The scattered intensity of a deuterated chain in a network is proportional to form factor, which contains the microscopic details of the chain in the network, i.e. the chain or the labeled path between two or several cross-links. In general the form factor is defined as

$$S(\mathbf{k}) = 1/N^2 \sum_{n,m} \langle \exp(-i\mathbf{k}(\mathbf{r}_n - \mathbf{r}_m)) \rangle \qquad (3.1)$$

where N is the number of scattering elements, $\mathbf{r}_n$ and $\mathbf{r}_m$ are the positions of scattering atoms on the chain, and $\mathbf{k}$ is the wave vector. The average $\langle\ \rangle$ has to be carried out with all conformations accessible to the segments. The procedure $\langle\ \rangle$ requires all information discussed in the case of the free energy, i.e. the positions of the cross-links and the location of the chains. The general result will be the structure factor of the Deam–Edwards model, i.e. the harmonic localization model. This resulting structure factor contains the affine model (Kuhn) and the phantom model (James and Guth) as limiting cases, so we do not discuss them separately.

3.2. Neutron Scattering Form Factor. The calculation of the SANS form factor for the Deam–Edwards model was originally carried out by Warner and Edwards.[13] The general expression for the form factor can be rewritten in terms of distribution functions in the same way as the free energy. The form factor is

$$S(\mathbf{k}) = \frac{1}{L^2}\int_0^L \int_0^L ds\, ds' \exp\left[-\frac{l}{6}k_i^2\lambda_i^2|s-s'| - k_i^2(1-\lambda_i^2)\frac{1}{2q_0}(1 - e^{l^2 q_0|s-s'|/3})\right] \qquad (3.2)$$

where k_i is a Cartesian direction of the wave vector and λ_i is the Cartesian stretching ratio. q_0 is the localization parameter as before and enters naturally as the term accounting for fluctuations of the cross-links around some mean position. Note that this fluctuation is governed by the environment, i.e. the cross-link density in the sample. Here it is assumed to be uniform, and q_0 is a single parameter. If q_0 is small, i.e. in the weak cross-linking limit, the exponent in the exponent containing q_0 may be expanded, and the classical expression derived by Pearson[14] for the James and Guth phantom network is recovered

$$S(\mathbf{k}) = \frac{1}{L^2}\int_0^L \int_0^L ds\, ds' \exp\left[-\frac{l}{6}k_i^2|s-s'| - \frac{l}{6}k_i^2(\lambda_i^2 - 1)\frac{1}{2}\frac{6N_c}{lL}|s-s'|^2\right] \qquad (3.3)$$

It is easy to show that the affine model (Kuhn model), where the cross-links are supposed to be fixed, gives a factor of 2 more in the second term in the exponential.[15] The SANS form factor depends now also on the realization of the cross-links N_c and we can generalize this to any realization of cross-links, i.e. to the fluctuation of the cross-link density $N_c(\mathbf{r}) = N_c^\circ + n(\mathbf{r})$.

We have recalled the classical expressions and relations for the free energy and the neutron scattering in order to write such expression for an arbitrary spatial varying cross-link density and average over all possible realizations.

4. Extension to Gaussian Fluctuations in the Cross-Link Density—Simple Weak Inhomogeneous Networks

4.1. Free Energy of the Generalized Deam–Edwards Model. The idea is very simple. We use now the Deam–Edwards model, since this is the only model which takes the environment—in a mean field way—into account. The localization parameter q_0 depends on the environment of a cross-link, since the cross-link density around a given cross-link determined the strength of the localization. That means if around a given cross-link the cross-link density is high, the localization will be strong, whereas if it is weak, the localization will be also weak. In order to make a simple model we assume now that the localization depends on a given distribution of cross-links. Thus we give the localization parameter a label, i.e. the spatial coordinate $\mathbf{r}$. Thus we write $q_0(\mathbf{r})$. This is equivalent to say that we have a spatial variation, i.e. a fluctuation in the cross-link density $N_c(\mathbf{r})$.

Now we have to do the same calculation as Deam and Edwards did, but keep in mind that the cross-link density is not uniform. Thus we find a free energy which depends on the spatially varying cross-link density; i.e. we get a free energy functional. In a self-consistent way we have then to assume that the localization parameter is also a function of the configurational space coordinate, i.e. $q_0(\mathbf{r})$. We can then employ the same variational principle for the function $q_0(\mathbf{r})$ and we will find a similar value for the localization parameter as given earlier, i.e.

$$q_0(\mathbf{r}) = 6N_c(\mathbf{r})/(lL) \qquad (4.1)$$

In this simple ansatz we have neglected all effects coming from excluded volume interactions and also packing effects for a very dense sample. These are the same limitations as in the theory by Deam and Edwards. On the other hand it has been argued by the same authors that the localization is not altered by taking into account excluded volume interactions.

The free energy is now a functional of $N_c(\mathbf{r})$, i.e. it has the same functional dependence as before but the cross-link density is now a function of the spatial coordinate

$$F(\{N_c(\mathbf{r})\}) = \frac{1}{2}N_c(\mathbf{r})kT\left(\sum_i \lambda_i^2 - \log\left\{\frac{6N_c(\mathbf{r})}{lL}\right\} + 1\right) \qquad (4.2)$$

Now we have to average over all possible realizations of $N_c(\mathbf{r})$ since they are random variables, i.e. we have to

calculate the experimental measurable free energy F, which is defined as a functional integral

$$F = \int \mathcal{D}N_c(\mathbf{r}) F(\{N_c(\mathbf{r})\}) P(\{N_c(\mathbf{r})\}) \tag{4.3}$$

where $P(\{N_c(\mathbf{r})\})$ is the normalized distribution of all realizations of the cross-link density. Note that this is precisely a quenched average of the free energy functional, and one can formulate this in a more rigorous theoretical way, which will be postponed to a later paper.

In order to produce a simple model to see the main consequences of such assumptions, we define for $N_c(\mathbf{r})$

$$N_c(\mathbf{r}) = N_c^\circ + n(\mathbf{r}) \tag{4.4}$$

where N_c° is the mean value of the cross-link number and $n(\mathbf{r})$ is the fluctuation, which is a random variable. We approximate its distribution by

$$P(\{N_c(\mathbf{r})\}) = \mathcal{N} \exp\left\{-\frac{1}{2\Delta\Omega}\int d\mathbf{r}\,\{N_c(\mathbf{r}) - N_c^\circ\}^2\right\} \tag{4.5}$$

where Ω is the volume of the sample. Thus we assume that the fluctuation of the cross-link number $n(\mathbf{r})$ is a Gaussian variable, i.e. the mean value vanishes, $\langle n(\mathbf{r})\rangle = 0$, and for the quadratic fluctuation we have

$$\langle n(\mathbf{r}) n(\mathbf{r}')\rangle = \Delta\delta(\mathbf{r} - \mathbf{r}') \tag{4.6}$$

where Δ is a measure of the strength of the network disorder. This is clearly far too simple to account for real situations, but here we restrict ourselves to the principal results, rather than to compare our formulas to experiments.

Therefore the average of the free energy is very simple and the result is

$$F = \frac{1}{2}N_c^\circ kT\left(\sum_i \lambda_i^2 - \log\left\{\frac{6N_c^\circ}{lL}\right\} + 1 + \frac{3}{2}\frac{\Delta}{N_c^\circ}\right) \tag{4.7}$$

where we have expanded the logarithm in powers of $n(\mathbf{r})/N_c$ and truncated the series after the first term.

This is a very interesting result. The free energy is only marginally changed. There is an additive term proportional to the fluctuation of the cross-link density which increases the free energy, but it does not affect the modulus or the deformation dependence. The modulus (given by the mean number N_c°) and the deformation dependence of the free energy are not altered. Thus we may conclude that the deformation dependence and the free energy are not sensitive to weak inhomogeneities in the sample. This is in accordance with the physical intuition: The free energy is a macroscopic quantity and this is less sensitive to microscopic details. This is not the case in small angle neutron scattering, where all the microscopic details matter, as we will see in the next section.

4.2. Inhomogeneities in Neutron Scattering. Here we employ the same ideas. We take a given realization of the network, formulate the same theory as that described above, and calculate the structure factor and then we average over all possible realizations of the cross-link densities. Thus we write for the SANS form factor

$$S(\mathbf{k},\{n(\mathbf{r})\}) = \frac{1}{L^2}\int_0^L\int_0^L ds\,ds' \exp\left[-\frac{l}{6}k_i^2|s-s'| - \frac{l}{6}k_i^2(\lambda_i^2-1)\frac{1}{2}\frac{6N_c(\mathbf{r})}{lL}|s-s'|^2\right] = \frac{1}{L^2}\int_0^L\int_0^L ds\,ds' \exp\left[-\frac{l}{6}k_i^2|s-s'| - \frac{l}{6}k_i^2(\lambda_i^2-1)\frac{1}{2}\frac{6N_c}{lL}|s-s'|^2 - \frac{l}{6}k_i^2(\lambda_i^2-1)\frac{1}{2}\frac{n(\mathbf{r})}{lL}|s-s'|^2\right] \tag{4.8}$$

Now we perform the average over the Gaussian distribution of $\{n(\mathbf{r})\}$, i.e.

$$P(\{n(\mathbf{r})\}) = \mathcal{N} \exp\left\{-\frac{1}{2\Delta}\int d\mathbf{r}\, n^2(\mathbf{r})\right\} \tag{4.9}$$

where $\mathcal{N}$ is a constant of normalization. The functional integral is very simple; it is a standard Gaussian integral and we find for the averaged neutron scattering form factor

$$S(\mathbf{k}) = \int \mathcal{D}n(\mathbf{r}) S(\mathbf{k},\{n(\mathbf{r})\}) P(\{n(\mathbf{r})\}) \tag{4.10}$$

the expression

$$S(\mathbf{k}) = \frac{1}{L^2}\int_0^L\int_0^L ds\,ds' \exp\left[-\frac{l}{6}k_i^2|s-s'| - \frac{l}{6}k_i^2(\lambda_i^2-1)\frac{1}{2}\frac{6N_c}{lL}|s-s'|^2 + \frac{\Delta}{L^2}\frac{1}{36}k_i^4(\lambda_i^2-1)^2|s-s'|^4\right] \tag{4.11}$$

This can be rearranged into a more compact notation

$$S(\mathbf{k}) = \frac{1}{L^2}\int_0^L\int_0^L ds\,ds' \exp\left[-\frac{l}{6}k_i^2|s-s'|\left\{1 + \frac{6N_c}{L}(\lambda_i^2-1)|s-s'|\left\{1 - \frac{\Delta}{N_c L}\frac{1}{6}k_i^2(\lambda_i^2-1)^2|s-s'|^2\right\}\right\}\right] \tag{4.12}$$

Thus we find a correction in the exponent of the neutron scattering form factor. The fluctuation of the cross-link density introduces a new wave vector and a new deformation dependence.

It is interesting to note that the radius of gyration upon deformation, R_g, which can be related to the form factor as

$$R_g^2 = -\frac{\partial}{\partial \mathbf{k}^2} S(\mathbf{k})|_{\mathbf{k}=0} \tag{4.13}$$

does not alter with the disorder parameter Δ, since the Gaussian disorder produces only terms of order k^4 in the exponent. This is in accord with the result that we did not obtain a change in the deformation dependence in the free energy. The limit $k = 0$, which has to be taken in the calculation of the radius of gyration, corresponds to the macroscopic limit, i.e. a quantity similar to the free energy.

Clearly, such disorder models are far too simple to be realistic and we do not compare it to experimental data. Nevertheless we believe that the general features are predicted quite well, i.e. no significant alteration in the macroscopic quantities, but severe changes in the microscopic quantities, such as the neutron scattering form factor.

5. Discussion

We have discussed the effect of simple network imperfections such as "weak Gaussian inhomogeneities" on the free energy and the neutron scattering form factor of a given sample. We have shown that such inhomogeneities do not change the deformation dependence of the

free energy, i.e. the stress–strain relation, which is a measurable quantity. This is in accordance with recent considerations by Schimmel and Heinrich,[16] where correlations between the cross-link positions have been considered. There it was predicted that the modulus becomes reduced but the deformation dependence remains the same. A more extended study on their model and the approach in this paper is under preparation.[17]

In the case of neutron scattering we have predicted an effect in the small angle neutron scattering form factor. We have shown that the effects of such inhomogeneities may produce a new wave vector and deformation dependence in the neutron scattering form factor. Looking at the final formula for the form factor, we see that new contributions at large wave vectors become significant. This is in qualitative agreement with experiments, which predict a larger scattering at larger wave vectors compared to the classical models of James and Guth.

An interesting question, which has to be solved in the future, is: How do such inhomogeneities and entanglements change the dynamics of a chain in the network, or more generally, how do they affect the dynamics of the network? That we can expect some effect can be seen immediately if one follows ref 18. The dynamical equations to study the Brownian motion in rubber localized chains can be written down as the modified Rouse equation. The model is a chain in a harmonic potential. Let us suppose that the localization parameter is a constant; i.e. we have no inhomogeneities. The segments of the chain obey the equation of motion

$$\nu \frac{\partial \mathbf{R}(s,t)}{\partial t} - \frac{3kT}{l^2}\frac{\partial^2 \mathbf{R}(s,t)}{\partial s^2} - \frac{lkT}{3} q_0^2 \mathbf{R}(s) = \mathbf{f}(s,t) \quad (5.1)$$

which reduces to the classical Rouse equation for $q_0 = 0$. ν is the segmental friction coefficient. We see that the localization parameter enters the equation of motion. $\mathbf{f}(s,t)$ is a Gaussian random force. In terms of the Fourier transform in time and contour length s, this equation can be solved for $\mathbf{R}(q,\omega)$, i.e. the Rouse modes of the system. Thus we find

$$\mathbf{R}(q,\omega) = \frac{\mathbf{f}(q,\omega)}{i\nu\omega + \epsilon(q^2 + q_0^2)} \quad (7.2)$$

where we have defined $\epsilon = 3kT/l^2$. The mean square distance of two points along the chain is then given by

$$\langle\{\mathbf{R}(s,t) - \mathbf{R}(s',t')\}^2\rangle = \frac{h}{4\pi^2}\int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} d\omega \frac{1}{(\nu\omega)^2 + \{\epsilon(q^2 + q_0^2)\}^2}(1 - e^{i[q(s-s')+\omega(t-t')]}) \quad (7.3)$$

where h is determined to $h = 4l^2\epsilon\nu$ by the fluctuation dissipation theorem.

The corresponding neutron scattering form factor is then given by

$$S(\mathbf{k},t) = \frac{1}{L^2}\int_0^L \int_0^L ds\, ds' \exp\left(-\frac{1}{6}k^2\langle\{\mathbf{R}(s,t) - \mathbf{R}(s',0)\}^2\rangle\right) \quad (7.4)$$

which is also a function of the localization parameter q_0.

If this localization parameter contains some randomness, we have to average the Green functions of the equations of motion and recalculate the scattering. This will be the subject of a separate paper.

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