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1978 J. Phys. A: Math. Gen. 11 1649

(http://iopscience.iop.org/0305-4470/11/8/024)

J. Phys. A: Math. Gen. Vol. 11, No. 8, 1978. Printed in Great Britain

Neutron scattering from strained polymer networks

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Received 1 March 1978

Abstract. The scattering function $S(\boldsymbol{k})$ for neutrons off a randomly cross-linked phantom network is calculated. Adopting the results of Deam and Edwards in which the mean position of the chain deforms affinely and fluctuations about this mean are random (i.e. non-affine) gives very different results from Benoit and co-workers who assume affine deformation of the chain shape. Some of the results obtained are similar to those of Pearson who calculates $S(\boldsymbol{k})$ using Flory's theory of non-affine fluctuations. However, the predictions for networks more densely cross-linked are different from those of Flory's theory.

1. Introduction

It has been shown that when a network of phantom chains is deformed there is a non-affine component in the deformation of an individual chain (Deam and Edwards 1976, Flory 1976, and James 1947). Deams and Edwards argue that a chain in a rubber is constrained to have a mean position in the network because of the localising effect of cross-links (and further in cases of real chains because of the topological barriers to movement presented by the matrix of other chains). This mean position or trajectory will transform in an affine way, $\bar{\boldsymbol{r}} \rightarrow \boldsymbol{\lambda}\bar{\boldsymbol{r}}$ where $\boldsymbol{\lambda}$ is the deformation tensor given by

$$\boldsymbol{\lambda} \triangleq \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \lambda_3 \end{pmatrix}.$$

However, in the strained state the chains will still fluctuate away from this mean $\bar{\boldsymbol{r}}$ (see figure 1). The precise freedom of the phantom chain to fluctuate will be determined by the degree of cross-linking.

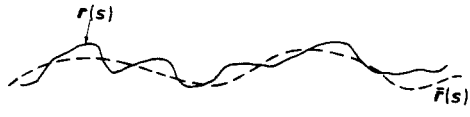

Figure 1. Fluctuation of chain about the mean.

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0305-4770/78/0008-1649$01.00

Deam and Edwards chose an harmonic potential to represent this constraint against fluctuations away from the mean trajectory. A calculation of the free energy of the network was then performed using this trial form for the distribution for the chains. This resulting free energy was then minimised with respect to the choice of trial function. It turned out in their calculation that the harmonic potential governing the fluctuations $\Delta \boldsymbol{r}$ away from the mean depended on the inverse distance between cross-links and not at all on the strain λ. This clearly gives a non-affine contribution to the chain position since

$$\boldsymbol{r}(s) = \boldsymbol{\lambda}\bar{\boldsymbol{r}} + \Delta \boldsymbol{r}$$

and only the $\boldsymbol{\lambda r}$ term is affine.

Thus a calculation of the scattering assuming that the chains deform affinely can only be a first approximation. This has been noticed by Pearson (1977) who extended the work of Benoit *et al* (1975) to allow for non-affine fluctuations. Pearson used the network theory of Flory (1976) which is for junction points equally spaced on chains.

We shall here adopt the model of randomly cross-linked chains forming a network. The chains are phantom, that is they can pass through each other so that the only localising effect is from the cross-links. A real network will most nearly approach this picture if it is cross-linked in as dilute a solution as possible in order to minimise entanglement and other effects most indicative of non-phantom behaviour. The cross-linking junctions in our network will be only tetrafunctional.

Finally a comment on how one can observe the molecular configurations discussed in this paper. When polymer chains are labelled (deuterated) and then formed into part of a mostly unlabelled network they can be observed by neutrons which are sensitive to the contrast thus created. (See Benoit *et al* (1973) for an account of determining the dimensions of single chains when in a dense solution of like chains.) The single chains can then be followed as the sample is stretched and the shape as a function of strain can be determined.

2. Calculation of the scattering function

The scattering function $S(\boldsymbol{k})$ is

$$S(\boldsymbol{k}) = \frac{1}{N^2}\left\langle \sum_{i,j} \exp[i\boldsymbol{k}\cdot(\boldsymbol{r}_i - \boldsymbol{r}_j)] \right\rangle \tag{1}$$

where $\boldsymbol{k}$ is the scattering vector and $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ are the positions of the ith and jth monomers respectively. For the purposes of calculation we picture the network as consisting of one long chain of N monomers cross-linked to itself N_x times.

We shall evaluate the configurational average $\langle\ \rangle$ by adopting the philosophy of Deam and Edwards (1976). There it is shown that for a system with permanent constraints care must be taken in evaluating partition integrals and the averages of *physical* quantities. A good example is the free energy where one must first evaluate the free energy of a system with a given topology, 'm' say, (corresponding in our case to a given set of cross-links) and then average this over topologies. That is

$$F = \sum_m p_m F_m \tag{2}$$

where p_m is the probability of a topology 'm':

$$p_m = \frac{e^{-F_m\beta}}{\Sigma_m e^{-F_m\beta}}$$

$$F = \frac{\Sigma_m \int d\Omega_m \, e^{-\beta H} \ln \left(\int d\Omega_m \, e^{-\beta' H} \right)}{\Sigma_m \int d\Omega_m \, e^{-\beta H}} \tag{2'}$$

(where $\int d\Omega_m$ denotes the integral over systems restricted to have the topology 'm'). This is a radically different result from the usual evaluation of F which is effectively an average of $Z_m = e^{-F_m\beta}$:

$$F = \sum_m \int d\Omega_m \, e^{-\beta H}. \tag{3}$$

p_m is of course purely a property of the system *at the time of fabrication* and does not alter with strain, whereas F_m will. This is shown by Deam and Edwards to give rise to a modulus. That is, the averaging of the logarithm in (2') gives us a solid rather than the melt implied by (3).

Similarly here it is the physical quantity $S_m(\boldsymbol{k})$, the scattering function due to the system with the topology 'm', which must be averaged. We shall get around the awkward problem of the denominator in the average by introducing an analogous free energy and performing its average by the same replica method that Deam and Edwards employed for the normal free energy. Hence

$$S_m(\boldsymbol{k}) = \frac{1}{N^2} \frac{\Sigma_{i,j} \int_{\sim} d\Omega_m \, e^{-\beta' H} \exp[i\boldsymbol{k}.(\boldsymbol{r}_i - \boldsymbol{r}_j)]}{\int_{\sim} d\Omega_m \, e^{-\beta' H}} \tag{4}$$

where the tilde on the integral indicates that the phase integral is over the strained volume. Let us put

$$\phi_{\boldsymbol{k}} = \frac{1}{N^2} \sum_{i,j} \exp[i\boldsymbol{k}.(\boldsymbol{r}_i - \boldsymbol{r}_j)].$$

Then (4) can be rewritten as

$$S_m(\boldsymbol{k}) = \frac{\partial}{\partial p} \ln \left(\int_{\sim} d\Omega_m \exp(-\beta' H + p\phi_{\boldsymbol{k}}) \right) \Big|_{p=0} \equiv \frac{\partial}{\partial p} F(p, \boldsymbol{k}) \Big|_{p=0} \tag{5}$$

where $F(p, \boldsymbol{k})$ can be thought of as a free energy resulting from a Hamiltonian with sources $p\phi_{\boldsymbol{k}}$ in it. This is akin to the propagator formulation in quantum field theory where source fields are put into the Lagrangian and where the propagator can be written

$$\frac{\delta}{\delta\phi} \frac{\delta}{\delta\phi^*} Z[\phi, \phi^*] \Big|_{\phi=\phi^*=0}$$

and where

$$Z = \int \delta\psi \exp \left(\int \mathcal{L}[\psi, \phi] \right).$$

Hence on averaging $S(\boldsymbol{k})$ becomes

$$S(\boldsymbol{k}) = \frac{\partial}{\partial p}\bigg|_{p=0} \frac{\Sigma_m \int \mathrm{d}\Omega_m \, \mathrm{e}^{-\beta H} F(p, \boldsymbol{k})}{\Sigma_m \int \mathrm{d}\Omega_m \, \mathrm{e}^{-\beta H}}$$

$$= -\frac{\partial}{\partial p}\bigg|_{p=0} \frac{\partial}{\partial n}\bigg|_{n=0} \ln\Big(\sum_m \int \mathrm{d}\Omega_m \exp(-\beta H - nF(p, \boldsymbol{k}))\Big) \tag{6}$$

(using a similar trick to get rid of the second denominator). We then rewrite the F term:

$$\exp(-nF(p, \boldsymbol{k}))$$

$$= \Big(\int_{\sim} \mathrm{d}\Omega_m \exp(-\beta H - p\phi_{\boldsymbol{k}})\Big)^n$$

$$= \int_{\sim} \prod_{\alpha=1}^{n} \mathrm{d}\Omega_m^{(\alpha)} \exp\Big(-\beta \sum_{\alpha=1}^{n} H^{(\alpha)} - p \sum_{\alpha=1}^{n} \phi_{\boldsymbol{k}}^{(\alpha)}\Big) \tag{7}$$

by converting to an n-fold multiple integral where each integrand now has a label α. Hence the problem remains of evaluating

$$\ln\Big[\sum_m \int \mathrm{d}\Omega_m^{(0)} \int_{\sim} \prod_{\alpha=1}^{n} \mathrm{d}\Omega_m^{(\alpha)} \exp\Big(-\beta' H^{(0)} - \sum_{\alpha=1}^{n} \beta H^{(\alpha)} - p \sum_{\alpha} \phi^{(\alpha)}\Big)\Big] \tag{8}$$

where effectively we have one unstrained system ($\alpha = 0$) and n strained systems ($\alpha = 1, \ldots, n$) which Deam and Edwards (1976) call replication.

The constraint in this case ('m') is

$$\sum_m \int \prod_\alpha \mathrm{d}\Omega_m^{(\alpha)} \to \int \prod_\alpha \delta \boldsymbol{r}^{(\alpha)} \Big(\int \mathrm{d}s_1 \, \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{r}^{(\alpha)}(s_1) - \boldsymbol{r}^{(\alpha)}(s_2))\Big)^{N_x}$$

Where N_x points have $\boldsymbol{r}_\alpha(s) = \boldsymbol{r}_\alpha(s')$ expressed by the δ function. (In this paper we interchange freely between the discrete ($\boldsymbol{r}_i$) and continuous representations for a chain.) Pictorially one has the situation shown in figure 2, and the phase integral $\int \delta \boldsymbol{r}_\alpha$ is over configurations where this is fixed.

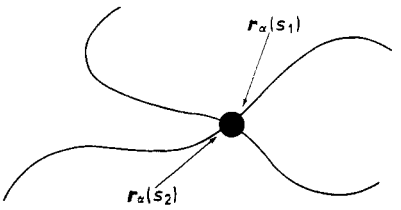

Figure 2.

In the argument of the logarithm the propagator used for averaging $e^{-p\phi}$ is

$$\int \prod_\alpha \delta \boldsymbol{r}_\alpha(s) \Big(\int \mathrm{d}s_1 \, \mathrm{d}s_2 \prod_\alpha \delta(r_\alpha(s_1) - r_\alpha(s_2))\Big)^{N_x} \exp\Big(-\frac{3}{2l} \sum_\alpha \int_0^L \mathrm{d}s \, \dot{r}_\alpha^2(s)\Big).$$

This is what Deam and Edwards evaluated when finding the free energy. The δ constraint is modelled by an harmonic well acting against fluctuations away from the chain's affinely-deformed mean path. It is found that the variation of this potential

can give a minimum for the free energy on straining. Hence this value for the potential will give an optimised model form for the propagator G:

$$G\{\boldsymbol{X}^{(\beta)}\} = \int \prod_{\beta} \delta X^{(\beta)} \exp\Big(- \sum_{\beta=0}^{n} \int \hat{X}^{(\beta)}(s) - \sum_{\beta=1}^{n} \int \tfrac{1}{6} w^2 l X^{(\beta)2}(s)\, \mathrm{d}s \Big) \tag{9}$$

where the well parameter w is given by

$$w = 6N_x / lL$$

We have taken a new coordinate system for convenience. $\boldsymbol{X}^{(\beta)}$ is related to the old $\{\boldsymbol{r}_{(\alpha)}\}$ by a 'rotation' $\mathbf{T}$:

$$\boldsymbol{r}_{(\alpha)} = T^{\alpha\beta} \boldsymbol{X}^{(\beta)}$$

($\|\mathbf{T}\| = 1$ and hence any Jacobian will be 1). The new coordinates have the following characteristics:

$$X_{(i)}^{(0)} = (\boldsymbol{r}_{(i)}^{(0)} + \lambda_i \textstyle\sum_{\alpha=1}^{n} \boldsymbol{r}_{(i)}^{\alpha}) / A_i \tag{10a}$$

is a free 'centre of mass-like coordinate' corresponding to a chain $\boldsymbol{X}^{(0)}$ in a volume $V \prod_i A_i$ (i here is a Cartesian coordinate x, y, z). $\boldsymbol{X}^{(n)}$ is a relative coordinate

$$X_i^{(n)} = \frac{1}{A_i} \Big(\lambda_i n^{1/2} r_i^{(0)} - \frac{1}{n^{1/2}} \sum_{\alpha=1}^{n} r_i^{(\alpha)} \Big) \tag{10b}$$

and there are $n-1$ rotated coordinates ($\beta = 1, \ldots, n-1$):

$$X_i^{(\beta)} = \frac{1}{n^{1/2}} \sum_{\alpha=1}^{n} r_i^{(\alpha)} \exp(2\pi \mathrm{i} \beta\alpha / n). \tag{10c}$$

A_i is $(1 + n\lambda_i^2)^{1/2}$ which retains the orthonormality of the transformation. This transformation is given by Deam and Edwards but their $\mathbf{T}$ is the transpose of ours and their $\boldsymbol{X}^{(1)}$ our $\boldsymbol{X}^{(n)}$, their $\boldsymbol{X}^{(2)}$ our $\boldsymbol{X}^{(1)}$ and so on up to $\boldsymbol{X}^{(n)}$.

We evaluate the argument of the logarithm in (8) by expanding the exponential for small p:

$$\int \delta \boldsymbol{X}^{(0)} \int \prod_{p=1}^{n} \delta \boldsymbol{X}^{(\beta)} \exp\Big(- \sum_{\beta=0}^{n} \int \mathrm{d}s\, \hat{\boldsymbol{X}}^{(\beta)2}(s) - \sum_{\beta=1}^{n} \int \tfrac{1}{6} \omega^2 l \boldsymbol{X}^{(\beta)2}(s)\, \mathrm{d}s \Big)$$

$$\times (1 - p \sum_{\alpha} \phi^{(\alpha)}(\{\boldsymbol{X}^{(\beta)}\}) + \mathrm{O}(p^2)). \tag{11}$$

The function $\phi^{(\alpha)}$ transforms (using the relations (10)) to

$$\phi_{\boldsymbol{k}}^{(\alpha)} = \frac{1}{N^2} \sum_{p,q} \exp\Big(\mathrm{i}\boldsymbol{k} \frac{1}{n^{1/2}} \sum_{\beta=1}^{n-1} \exp(-2\pi \mathrm{i} \alpha\beta / n)(\boldsymbol{X}_p^{(\beta)} - \boldsymbol{X}_q^{(\beta)})$$

$$+ \frac{\mathrm{i}k_i \lambda_i}{A_i} (X_{ip}^{(0)} - X_{iq}^{(0)}) - \frac{\mathrm{i}k_i}{A_i n^{1/2}} (X_{ip}^{(n)} - X_{iq}^{(n)}) \Big).$$

The first term in (11) is simply $Z(n)$, the partition function for the replicated system.

In the second term we do the integrations one by one to give

$$\int \delta \boldsymbol{X}^{(0)} \to \exp\left(-\frac{k_i^2 \lambda_i^2}{A_i^2} \frac{l^2|p-q|}{6}\right)$$

$$\int \delta \boldsymbol{X}^{(n)} \to \exp\left(-\frac{k_i^2}{nA_i^2} \frac{1}{2\omega_i}[1-\exp(-l^2\omega_i/3|p-q|)]\right)$$

$$\int \prod_{\beta=1}^{n-1} \delta \boldsymbol{X}^{(\beta)} \to \exp\left(-k_i^2 \frac{n-1}{n} \frac{1}{2\omega_i}[1-\exp(-l^2 w_i/3|p-q|)]\right).$$

Hence we get in (8)

$$\ln\left(1-\frac{pn}{N^2}\sum_{p,q}\exp\left[-\frac{k_i^2\lambda_i^2}{A_i^2}\frac{l^2|p-q|}{6}-k_i^2\left(1-\frac{\lambda_i^2}{A_i^2}\right)\frac{1}{2w_i}[1-\exp(-l^2 w_i|p-q|/3)]\right]\right)$$

(having taken out a factor of $Z(n)$ which also has the effect of normalising the second term correctly; it is a p-independent term). The $(\partial/\partial n)|_{n=0}$ has the effect of only acting on the n factor. This is because the n appearing in the A_i give harmless contributions on differentiation. Thus $\partial \ln(\ldots)/\partial n|_{n=0}$ has the result (also doing $(\partial/\partial p)|_{p=0}$)

$$S(\boldsymbol{k}) = \frac{1}{N^2}\sum_{p,q}\exp\left(-k_i^2\lambda_i^2 l^2|p-q|/6 - k_i^2(1-\lambda_i^2)\frac{1}{2w_i}[1-\exp(-\tfrac{1}{3}l^2 w_i|p-q|)]\right). \tag{13}$$

Equation (13) is the principal result of this paper. The first term would be the only one present if the chain shape deformed affinely (Benoit *et al* 1975). The second term represents the non-affine fluctuations that the chain executes. It depends on the well parameter w, that is, the extent of the additional fluctuations depends upon how constrained the chain is by cross-links.

If we let $w(=6N_x/lL)$ get very small (i.e. we have a weakly cross-linked network) then we get:

$$S(\boldsymbol{k}) = \frac{1}{N^2}\sum_{p,q}\exp\left[-\frac{k_i^2}{6}\left(l^2|p-q| + l^3|p-q|^2\frac{N_x}{L}(\lambda_i^2-1)\right)\right].$$

Further noting that $L = N$ and that for tetrafunctional cross-links $N_s = 2N_x$(N_s is the number of chain segments) we can re-arrange the result to the form

$$S(\boldsymbol{k}) = \frac{1}{N^2}\sum_{p,q}\exp\left[-\frac{k_i^2}{12}\left(2l^2|p-q| + \frac{l^3|p-q|^2}{L_s}(\lambda_i^2-1)\right)\right] \tag{14}$$

(L_s is the length of the average segment). This result can be considered as being for a single labelled chain in which case N becomes N_s. The result (14) is then precisely the result Pearson (1977) obtained and we refer the reader to his paper for the form of the scattering law this implies in the various limiting cases. These are now merely summarised:

$$S(\boldsymbol{k}) = \begin{cases} \dfrac{2}{\nu}\left(1-\dfrac{\lambda^2}{\nu}\right) & \text{intermediate regime, } \nu \gg 1 \\ 1-\dfrac{\nu}{3}\left(\dfrac{\lambda^2+3}{4}\right) & \text{small-angle regime, } \nu \ll 1 \end{cases}$$

where $\nu = \frac{1}{6}k^2 l^2(N/N_x)$ is the ratio of the mean square distance between cross-links to the square of the scattering 'wavelength' ($\lambda \sim 2\pi/k$).

The other limit of interest is that of the tightly cross-linked network (w large). In that case, returning to (13) we can neglect the exponential term in the non-affine

fluctuations, that is if

$$l^2 w/3 \sim 1 \qquad \text{or} \qquad 2N_x/N \sim 1.$$

This means that every few monomers there is a cross-link. Obviously this will severely reduce the fluctuations away from the mean (affine) position and (13) becomes:

$$\frac{1}{N^2}\sum_{p,q} \exp\left(-\frac{k_i^2\lambda_i^2 l^2|p-q|}{6} - \frac{k_i^2(1-\lambda_i^2)}{2w_i}\right) = \frac{2}{\gamma^2}(e^{-\gamma} - 1 + \gamma)\exp[-\gamma(1-\lambda_i^2)] \tag{15}$$

(where $\gamma = \lambda_i^2 k_i^2 l L_s/6$) and where we consider labelled chains of average length L_s between cross-link points.

The first factor is the Debye term for scattering from a chain which has been deformed in a purely affine manner (it is the result of Benoit *et al* 1975). The second term represents the non-affine part:

$$\exp[\gamma(\lambda^2 - 1)]. \tag{16}$$

For such a rubber $\lambda \sim 1$ since large deformations of such a tightly cross-linked system are hardly possible. To observe the rather small effects implied by (16) λ will have to be as large as possible and $\boldsymbol{k}$ as large as possible, that is in the intermediate regime where

$$S(\boldsymbol{k}) = \frac{2}{\gamma}\left(1 - \frac{1}{\gamma}\right)\exp[\gamma(\lambda^2 - 1)]$$

3. Summary

We have presented the scattering cross sections for both lightly and heavily cross-linked networks. It is suggested that entanglement effects should be minimised by cross-linking in fairly dilute solution. This would maximise the effects of fluctuations and mostly nearly approach our phantom chain model for which the only constraining influence on the fluctuations is that of the cross-links.

It is found for such a system that the non-affine fluctuations of the chains give a considerable contribution to the scattering. The limit of weak cross-linking is the same as that calculated by Pearson using Flory's model of fluctuating networks. However, the limit of dense cross-linking is different, and it is apparent from the general form (13) that the full result requires some investigation of the localising effect of links. In the Flory theory the restricting effect of the links appears only from the finite length of the segments, L_s. Taking the Deam and Edwards view that the localising effect is much more serious and should be determined in some variational way gives a lower estimate for the free energy. Likewise here the averaging over the constraint gives the extra factor in $S(\boldsymbol{k})$.

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