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THE THEORY OF RUBBER ELASTICITY

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CONTENTS

This paper attempts to improve several weaknesses in the classical theories of rubber elasticity. It develops a formulation of the statistical thermodynamics of amorphous materials analogous to the Gibbs formalism for conventional statistical mechanics. This then permits the replacement of 'phantom chains', i.e. long polymer molecules with the fictitious property that they experience no forces except at cross link points and are transparent to one another, by realistic molecules which do experience forces and which can become entangled. The crosslinked points are no longer assumed to deform affinely with the gross behaviour of the solid. Under the simplest conditions forms like the classical are recovered but with a different coefficient, and the term representing the degrees of freedom lost by crosslinking, over which the classical theories are in dispute, is found to lie between the previous values in a formula which can reproduce the classical results by making different assumptions. The entanglements give rise to more complicated forms than the classical sum of squares of strain ratios, which under certain circumstances can reproduce the Mooney–Rivlin term which when added empirically to the free energy usually improves the fit with experiment. The general expression is complicated, but is nevertheless an explicit function of the density of crosslinks, the density of the rubber and the interchain forces.

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1. Introduction

This study was prompted by a need to improve the 'phantom chain' models of polymer networks already well known in the literature. Phantom chain models have two major defects. Firstly, phantom chains can pass freely through one another (and themselves); secondly, there are no molecular inter or intra chain forces. These effects have now been put into the model and the theory developed.

The paper is divided into four sections. In the first an abstract exact formula is provided for the free energy for an amorphous system. Just as Gibbs's famous formula provides an abstract formula for the statistical mechanics of systems in which all states are accessible, the new formula extends to systems with frozen-in degrees of freedom. Although the basic ideas here are well known, the formulation is a practical one which proves a basis for calculation. The second section shows how the formalism fits the problem of rubber elasticity. The classical theories all seem to use part of the formalism, but not all of it, and it is believed that by writing down the whole problem albeit in the form of difficult expression a significant advance has been made. The classical theories are rederived in this section. In § 3 the effect of excluded volume, i.e. of short-range forces, is included in the calculation of the free energy of a rubber, while in § 4 the effects of entanglements are included to complete the kinds of force normally encountered. Entanglements produce complex structure into the free energy, but it is interesting that forms like the well known Mooney–Rivlin term appear quite naturally. They do not, however, appear in any unique or clear way as is seen in the formulae (5.46), (5.48), (5.52), (5.53) and (5.54). These last are the principal results of the paper.

2. Statistical mechanics of amorphous materials

The object of this section will be to show that the standard formulae of statistical mechanics as applied to gases, liquids and ordered solids need modification before they can deal effectively with disordered or amorphous solids. Since rubber is an amorphous solid it is well to tackle the statistical mechanics properly before settling on the microscopic model that is going to be used.

The starting point of this treatment will be the need of the statistical formulation to produce a shear modulus for a solid. Solids resist change in shape, therefore any theory of solids must reproduce this property or their essential solidlike nature is lost. Crystalline solids are easily dealt with in this respect. A lattice is given, the problem can then be transformed into 'phonon gas' coordinates and the free energy calculated using the normal formula as applied to gases. The incorporation of shear is done by changing the shape of the lattice and recalculating the free energy. The change in free energy with change in shape is then known and the relevant modulus found. The substance resists change in shape (provided the correct lattice was chosen initially) and therefore is a solid.

The same thing cannot be done for amorphous solids. No lattice is 'given' and thus no transformation to the phonon gas can be made. The structure of an amorphous solid such as a glass or rubber is more liquidlike than solid, yet the normal statistical methods of integrating over all phase space for each particle will not give us any shear property. The shear property of the crystal came from doing two separate calculations on different shapes of the *same* crystal lattice, so that the microscopic topology of the crystal was conserved. This is the clue for the treatment of amorphous solids. Some way of specifying the topology laid down at fabrication must be found, the topology being conserved in strain by the various microscopic constraints in the solid that have been put in when it was made. Thus, in principle, the same calculation could then be made as for the crystal. The free energy is calculated for two different shapes of the solid with the same topology. The shear property has been recovered. There is, however, an additional complication not encountered with the crystal. No *one* topology is 'given'. In fact a very large number of topologies may be possible for any given method of fabrication. So there is now the problem of calculating the free energy strained and unstrained for each topology and doing a weighted average of these at the end. (The 'weights' being determined by the method of fabrication of the solid.) If the number of possible topologies for any given method of fabrication is large enough, then what has been calculated will be the most probable modulus (or whatever property is being calculated) which by the usual statistical argument is equal to the average.

Trouble comes when the number of competing conserved topologies is small each with a substantially different free energy state associated with it; such as might be found at the gel point for polymer systems.

These ideas may be expressed concisely in mathematical form. Consider the Gibbs formula for the partition function Z:

$$Z = \mathrm{e}^{-\beta F} = \int \mathrm{e}^{-\beta H}\,\mathrm{d}\Omega, \tag{2.1}$$

where $\beta = 1/kT$, H is the system Hamiltonian and $\int \mathrm{d}\Omega$ represents integration over all accessible phase space. For a fluid the free energy is independent of the shape of the container but for a crystal all states in phase space are not accessible, the topology of the lattice is conserved if the crystal is strained.

Thus

$$Z_{\mathrm{m}} = \mathrm{e}^{-\beta F_{\mathrm{m}}} = \int \mathrm{e}^{-\beta H}\,\mathrm{d}\Omega_{\mathrm{m}}, \tag{2.2}$$

where the m label restricts phase space to the crystal topology. The dominant contribution to the shear modulus is from the internal energy. In an amorphous solid such as rubber this is not the case, short range forces dominate as far as the bulk properties are concerned and in shear the internal energy contribution is small. There is an entropic shear effect due to the conserved topology of the rubber. How the topology of a rubber is specified will be dealt with when specific microscopic models are considered. If entropic effects only are being considered then Boltzmann's formula can be used:

$$S = k \ln \Omega, \tag{2.3}$$

where S is the entropy of the system and Ω the number of configurations in phase space available to the system. If phase space is restricted by constraints conserving topology then the formula is modified (as for the crystal) to

$$S_{\mathrm{m}} = k \ln \Omega_{\mathrm{m}}, \tag{2.4}$$

where Ω_{m} is now the number of configurations in the restricted phase space with topology 'm'. Let this topology 'm' have a certain probability of being formed in fabrication p_{m}. (Rarely does the fabricator have control over his material, so that he can put in a known topology.) Thus the entropy of such a system, the number of different topologies available being a very large number in a statistical mechanics sense, is

$$S = \sum_{\mathrm{m}} p_{\mathrm{m}} S_{\mathrm{m}} = k \sum_{\mathrm{m}} p_{\mathrm{m}} \ln \Omega_{\mathrm{m}}, \tag{2.5}$$

where

$$p_{\mathrm{m}} = \Omega_{\mathrm{m}}/\Omega, \quad \sum_{\mathrm{m}} p_{\mathrm{m}} = 1. \tag{2.6}$$

A weighted average over all topologies has been taken. However, if the system is strained after fabrication the formula is

$$\tilde{S} = k \sum_{\mathrm{m}} p_{\mathrm{m}} \ln \tilde{\Omega}_{\mathrm{m}} = \sum_{\mathrm{m}} p_{\mathrm{m}} \tilde{S}_{\mathrm{m}}, \tag{2.7}$$

where the tilde denotes the strained system. Note that

$$\tilde{S} \neq k \sum_{\mathrm{m}} \tilde{p}_{\mathrm{m}} \ln \tilde{\Omega}_{\mathrm{m}} \quad \text{and} \quad \Omega_{\mathrm{m}} \neq \tilde{\Omega}_{\mathrm{m}} \tag{2.8}$$

(only for an unstrained system $\tilde{S} = S$).

It is the fact that the p_{m} does not have a tilde over it that means the system is capable of supporting shear.

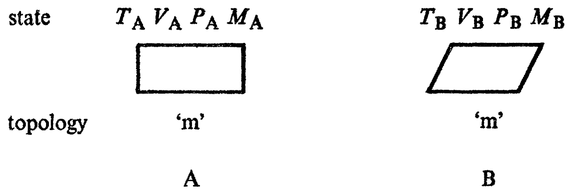
There are then three steps in the calculation of $\tilde{S}$, which is what most of the classical theories of rubber elasticity calculate:

(1) calculate p_{m};
(2) calculate $\tilde{S}_{\mathrm{m}}$;
(3) calculate $\tilde{S} = \sum_{\mathrm{m}} p_{\mathrm{m}} \tilde{S}_{\mathrm{m}}$.

There is an easier way of doing this by combining all three steps (Edwards 1970, 1971).

The method calculates the free energy F from a generalized partition function. Before setting down the method it might be useful to show the thinking behind it. In the calculation of $\tilde{S}$ above there are really two systems in which the statistical mechanics is done. Firstly, the fabrication of the amorphous solid in which the p_{m} are to be calculated; then the altered system (it may be strained or at a different temperature, magnetization, etc.) in which the free energy of that topology is to be found $\tilde{F}_{\mathrm{m}}$.

Pictorially



(2.9)

For system A, p_{m} (the probability of making topology 'm') can be found by allowing *all* topologies at T_A, V_A, etc. and using the Gibbs formula

$$p_{\mathrm{m}} = \mathrm{e}^{-\beta_{\mathrm{A}}(F_{\mathrm{m}} - F)} = Z_{\mathrm{m}}/Z, \tag{2.10}$$

where

$$Z_{\mathrm{m}} = \int \mathrm{e}^{-\beta_{\mathrm{A}} H_{\mathrm{A}}} \,\mathrm{d}\Omega_{\mathrm{m}}; \quad Z = \int \mathrm{e}^{-\beta_{\mathrm{A}} H_{\mathrm{A}}} \,\mathrm{d}\Omega. \tag{2.11}$$

H_{A} is the Hamiltonian of system A. $\int \mathrm{d}\Omega_{\mathrm{m}}$ means integration over all phase space with topologies 'm', alternatively this could have been written as $\int \delta(\mathrm{m} - f(\Omega))\,\mathrm{d}\Omega$; i.e. an integration over all phase space with a delta function constraint picking out the desired topology 'm'. Given this topology $\tilde{F}_{\mathrm{m}}$ has to be found. This is the free energy of topology 'm' in the altered system (B). So using the Gibbs formula again

$$\mathrm{e}^{-\beta_{\mathrm{B}} \tilde{F}_{\mathrm{m}}} = \tilde{Z}_{\mathrm{m}} = \int \mathrm{e}^{-\beta_{\mathrm{B}} H_{\mathrm{B}}} \,\mathrm{d}\tilde{\Omega}_{\mathrm{m}}, \tag{2.12}$$

$$\tilde{Z} = \int \mathrm{e}^{-\beta_{\mathrm{B}} H_{\mathrm{B}}} \,\mathrm{d}\tilde{\Omega}. \tag{2.13}$$

The tilde over the dΩ's represents the change in phase space due to going from system A to system B. If A is different from B only by shearing, then

$$\tilde{Z} = Z, \quad \text{but} \quad \tilde{Z}_{\mathrm{m}} \neq Z_{\mathrm{m}}. \tag{2.14}$$

Now all that remains to be done is to calculate $\tilde{F}$.

$$\tilde{F} = \sum_{\mathrm{m}} p_{\mathrm{m}} \tilde{F}_{\mathrm{m}}. \tag{2.15}$$

Consider the following expression:

$$Z(n) = \sum_{\mathrm{m}} Z_{\mathrm{m}} (\tilde{Z}_{\mathrm{m}})^n = \sum_{\mathrm{m}} \mathrm{e}^{-\beta_{\mathrm{A}} F_{\mathrm{m}}} (\mathrm{e}^{-\beta_{\mathrm{B}} \tilde{F}_{\mathrm{m}}})^n; \tag{2.16}$$

which gives
$$\partial Z(n)/\partial n|_{n=0} = \sum_{\mathrm{m}} -\mathrm{e}^{-\beta_{\mathrm{A}} F_{\mathrm{m}}} \beta_{\mathrm{B}} \tilde{F}_{\mathrm{m}}, \tag{2.17}$$

and
$$\frac{\partial Z(n)/\partial n|_{n=0}}{Z(n=0)} = \sum_{\mathrm{m}} -\beta_{\mathrm{B}} \tilde{F}_{\mathrm{m}} p_{\mathrm{m}} = -\beta_{\mathrm{B}} \tilde{F}, \tag{2.18}$$

whence
$$\tilde{F} = -kT_{\mathrm{B}} \left(\frac{\partial Z/\partial n|_{n=0}}{Z(n=0)} \right). \tag{2.19}$$

If $Z(n)$ can be calculated then $\tilde{F}$ can be found using (2.1). $Z(n)$ can be expressed in terms of a generalized Gibbs formula as follows:

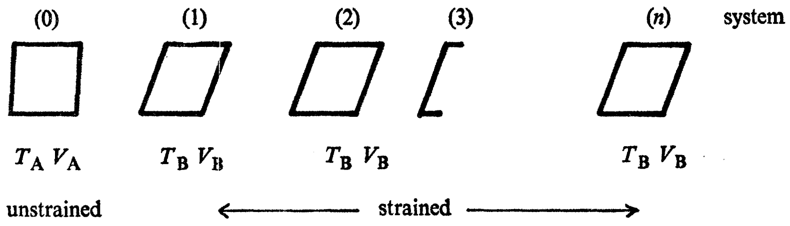
$$Z(n) = \sum_{\mathrm{m}} Z_{\mathrm{m}} (\tilde{Z}_{\mathrm{m}})^n = \sum_{\mathrm{m}} \mathrm{e}^{-\beta_{\mathrm{A}} F_{\mathrm{m}}} (\mathrm{e}^{-\beta_{\mathrm{B}} \tilde{F}_{\mathrm{m}}})^n \tag{2.20}$$

$$= \sum_{\mathrm{m}} \int \mathrm{e}^{-\beta_{\mathrm{A}} H_{\mathrm{A}}} \, \mathrm{d}\Omega_{\mathrm{m}} \left[\int \mathrm{e}^{-\beta_{\mathrm{B}} H_{\mathrm{B}}} \, \mathrm{d}\tilde{\Omega}_{\mathrm{m}} \right]^n. \tag{2.21}$$

Or for integral values of n, $Z(n)$ may be written

$$Z(n) = \sum_{\mathrm{m}} \int \mathrm{e}^{-\beta_{\mathrm{A}} H^{(0)}} \, \mathrm{d}\Omega_{\mathrm{m}}^{(0)} \int \mathrm{e}^{-\beta_{\mathrm{B}} H^{(1)}} \, \mathrm{d}\tilde{\Omega}_{\mathrm{m}}^{(0)} \int \dots \int \mathrm{e}^{-\beta_{\mathrm{B}} H^{(n)}} \, \mathrm{d}\tilde{\Omega}_{\mathrm{m}}^{(n)}. \tag{2.22}$$

Thus there are $n+1$ systems



The formula as written is only valid for n a positive integer, but by analytically continuing the result $Z(n) = \sum_{\mathrm{m}} Z_{\mathrm{m}} (\tilde{Z}_{\mathrm{m}})^n$ would be recovered for all n.

The advantage of the method is that the 'topology conservation' can be put in as a constraint and thus absorbed under the integral sign

$$Z(n) = \iint \dots \int \prod_{\alpha=0}^{n} \mathrm{d}\Omega^{(\alpha)} \exp\left(-\beta_{\mathrm{A}} H^{(0)} - \sum_{\alpha=1}^{n} \beta_{\mathrm{B}} H^{(\alpha)} \right) \prod_{\alpha=1}^{n} \delta(m(0) - m(\alpha)). \tag{2.23}$$

The α labels the system.

Thus $Z(n)$ contains all the information required, $Z(n=0) = Z$, and equation (1.19) gives $\tilde{F}$. A simple way of looking at the properties of $Z(n)$ is to expand $Z(n)/Z$ out in powers of n:

$$\frac{Z(n)}{Z} = 1 + n \sum_{\mathrm{m}} p_{\mathrm{m}}(-\beta_{\mathrm{B}} \tilde{F}_{\mathrm{m}}) + \frac{n^2}{2!} \sum_{\mathrm{m}} p_{\mathrm{m}}(-\beta_{\mathrm{B}} \tilde{F}_{\mathrm{m}})^2 + \dots \tag{2.24}$$

$$= 1 - n\beta_{\mathrm{B}} \tilde{F} + \frac{n^2}{2!} \beta_{\mathrm{B}}^2 \langle \tilde{F}_{\mathrm{m}}^2 \rangle + \dots \tag{2.25}$$

$$= 1 - n\beta_{\mathrm{B}} \tilde{F} + \frac{n^2}{2!} \beta_{\mathrm{B}}^2 \tilde{F}_2^2 + \dots. \tag{2.26}$$

$F = -kT_{\mathrm{A}} \ln Z$ is the free energy of the original system A at fabrication without topology conservation. $\tilde{F}$ is the free energy of the B systems with the topology set by A. $F = \tilde{F}$ only when the B systems are unstrained and at the same thermodynamic point as A. The reason for shear properties being bestowed on the material by topological constraints can now be shown.

Assume $F = \tilde{F}$ (A and B under identical conditions). Then for any change Δ, $\Delta F = \Delta(\sum_{\mathrm{m}} p_{\mathrm{m}} F_{\mathrm{m}})$, whereas

$$\Delta \tilde{F} = \sum_{\mathrm{m}} p_{\mathrm{m}} \Delta F_{\mathrm{m}}. \tag{2.27}$$

If Δ is infinitesimal
$$\sum_{\mathrm{m}} p_{\mathrm{m}} = 1, \quad \Delta \sum_{\mathrm{m}} p_{\mathrm{m}} = 0. \tag{2.28}$$

But
$$p_{\mathrm{m}} = \mathrm{e}^{-\beta(F_{\mathrm{m}}-F)}, \tag{2.29}$$

thus
$$\sum_{\mathrm{m}} \beta \Delta F p_{\mathrm{m}} - \sum_{\mathrm{m}} \beta \Delta F_{\mathrm{m}} p_{\mathrm{m}} = 0, \tag{2.30}$$

$$\Delta F = \Delta \tilde{F} = \sum_{\mathrm{m}} p_{\mathrm{m}} \Delta F_{\mathrm{m}} \quad (\Delta \text{ infinitesimal}). \tag{2.31}$$

Differentiate again
$$\Delta^2 F = \sum_{\mathrm{m}} (\Delta^2 F_{\mathrm{m}} p_{\mathrm{m}} + \Delta F_{\mathrm{m}} \Delta p_{\mathrm{m}}) \tag{2.32}$$

$$= \Delta^2 \tilde{F} + \sum_{\mathrm{m}} \Delta F_{\mathrm{m}}(-\beta \Delta F + \beta \Delta F_{\mathrm{m}}) p_{\mathrm{m}}. \tag{2.33}$$

Thus
$$\Delta^2 F = \Delta^2 \tilde{F} + \beta \sum_{\mathrm{m}} p_{\mathrm{m}}[(\Delta F_{\mathrm{m}})^2 - (\Delta F)^2].$$

Thus second order and higher derivatives at $F = \tilde{F}$ have additional contributions due to the fixing in of the topology in our system and not the other. The part that gives the shear modulus (and additional bulk modulus) is

$$\frac{1}{kT} \sum_{\mathrm{m}} \mathrm{e}^{-\beta(F_{\mathrm{m}}-F)}((\Delta F_{\mathrm{m}}{}^2 - (\Delta F)^2) \neq 0. \tag{2.34}$$

The $\tilde{F}_2$ term in the expansion of $Z(n)/Z$ can be used to give an indication of phase transitions at critical points since $[(\tilde{F})^2 - (\tilde{F}_2)^2]$ is the second moment of the free energy distribution in the solid. $((\tilde{F})^2 - (\tilde{F}_2)^2)/(\tilde{F})^2$ will normally be of order $1/N$ (where N is the number of crosslinks and is large). Thus $((\tilde{F})^2 - (\tilde{F}_2)^2)/(\tilde{F})^2$ is negligible compared to 1, only at the gel point might this be expected to become of order unity, in which case a critical phenomenon will have been encountered.

3. MATHEMATICAL MODELS OF RUBBERS

The three models now about to be discussed will be reviewed only with reference to the assumptions inherent in each. The statistical mechanics will be done the same way for each using the theory as developed in the first section. The mathematical framework will be the same for each as well, that is using functional integrals to set up the models. In fact one model will be set up and the assumptions of each theory put into the final integrals, thus it is hoped it will be easier to compare the theories on an equivalent basis. Before setting up the mathematics it is worth emphasizing that the 'peculiar' properties of rubber it is hoped to gain an understanding of, come from the polymeric nature of the material, that is from the long range correlations of atoms in the rubber (greater than 2 nm say). A full understanding of the bulk properties (compressibility, etc.) will come from an understanding of liquid theory which is almost entirely due to short range effects. Generally short range effects are completely unimportant but the motivation for this study was brought about by a desire to understand why a rubber or gel (a dilute rubbery network) does not collapse into a very dense little ball and to understand this it is found that the short range forces between molecules are very necessary to prevent this collapse. Another point worth bearing in mind is that any chain model of a polymer, and indeed the real polymer itself under the Flory θ conditions, will if the chain is long enough (and flexible) tend to obey Gaussian statistics for distances along the chain further than a certain length say l. This l can be thought of as being a measurable constant for experimental systems or theoretically derivable for any particular chain model used, e.g. freely hinged rods or bond rotation models (Flory 1969). The important point being that provided the chain is flexible to allow changes in conformation the details of the bonds will be unimportant for large correlation distances. It is these large distances which are important in rubber elasticity.

With these ideas in mind the mathematics will now be set out in detail and the assumptions of the theories due to (*a*) Flory & Wall (1951), (*b*) James & Guth (1943), (*c*) the present model, will be put into the model and their answers rederived and compared.

(*a*) *Mathematical preliminaries*

A phantom chain will be taken to be the definition as introduced by Flory, namely an infinitely thin chain that can pass through itself and other chains. Let $\boldsymbol{R}$ be a position vector in space and s be an arc length, $0 < s < L$, along a phantom chain of length L. The function $\boldsymbol{R}(s)$ is then a 'phantom chain'. $\boldsymbol{R}(s)$ can now be used to set up the statistics of a chain. Let the probability of finding a particular $\boldsymbol{R}(s)$ be denoted by $P[\boldsymbol{R}(s)]$. If $\boldsymbol{R}(s)$ is to be a Gaussian chain then it is true that

$$P[\boldsymbol{R}(s)] = \mathcal{N} \exp\left(-\frac{3}{2l}\int_0^L |\dot{\boldsymbol{R}}(s)|^2\,\mathrm{d}s\right). \tag{3.1}$$

P is a functional of $\boldsymbol{R}(s)$, $\dot{\boldsymbol{R}}(s) = \partial\boldsymbol{R}(s)/\partial s$. This is because

$$\mathcal{N}\int P[\boldsymbol{R}(s)]\,\delta(\boldsymbol{r}_1-\boldsymbol{R}(s_1))\,\delta(\boldsymbol{r}_2-\boldsymbol{R}(s_2))\,\delta\boldsymbol{R}(s) = \left(\frac{3}{2\pi l|s_1-s_2|}\right)^{\frac{3}{2}} \exp\{-(3/2l)\,[(r_1-r_2)^2/|s_1-s_2|]\} \tag{3.2}$$

where $\int\delta\boldsymbol{R}(s)$ stands for the functional integral over all functions $\boldsymbol{R}(s)$ (Feynman & Hibbs 1965).

This is the desired form of the two body distribution function. Thus, for example, a partition function may be set up for a chain with an interaction potential between points on the chain $\boldsymbol{R}(s_1)$ and $\boldsymbol{R}(s_2)$ of $V(\boldsymbol{R}(s_1)-\boldsymbol{R}(s_2))$. If Z is the partition function then

$$\begin{aligned} Z &= \int \delta\boldsymbol{R}(s) P[\boldsymbol{R}(s)] \exp\left(-\frac{1}{2}\int_0^L\int_0^L V(\boldsymbol{R}(s_1)-\boldsymbol{R}(s_2))\,\mathrm{d}s_1\,\mathrm{d}s_2\right) \\ &= \int \delta\boldsymbol{R}(s) \exp\left(-\frac{3}{2l}\int_0^L \dot{\boldsymbol{R}}^2\,\mathrm{d}s - \frac{1}{2}\int_0^L\int_0^L V(\boldsymbol{R}(s_1)-\boldsymbol{R}(s_2))\,\mathrm{d}s_1\,\mathrm{d}s_2\right). \end{aligned} \tag{3.3}$$

For a single chain in a box of volume V we can define the two body Green function

$$G(\boldsymbol{r}_1, \boldsymbol{r}_2; s_1, s_2) = \mathcal{N} \int_{V_{\text{box}}} \delta \boldsymbol{R}(s) \exp\left(-\frac{3}{2l}\int_0^L \dot{\boldsymbol{R}}^2 \, \mathrm{d}s\right) \delta(\boldsymbol{R}(s_1) - \boldsymbol{r}_1)\, \delta(\boldsymbol{R}(s_2) - \boldsymbol{r}_2), \tag{3.4}$$

where the functional integral can be solved by writing down the equivalent 'Hamiltonian' and thus Schrödinger equation in the spirit of Feynman. $G(\boldsymbol{r}_1, \boldsymbol{r}_2; s_1, s_2)$ therefore satisfies Fick's equation in a box

$$(\partial/\partial s - \tfrac{1}{6}l\nabla^2)\, G(\boldsymbol{r}_1, \boldsymbol{r}_2; s_1, s_2) = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)\, \delta(s_1 - s_2). \tag{3.5}$$

The general development of the formulation for polymers is given by Edwards & Freed (1969, 1970).

The diffusion equation in a box permits two classes of solution depending on the boundary conditions: (1) cyclic boundary conditions; (2) density of polymer zero outside the box. The solutions are

$$(1) \quad G_1 = \frac{1}{V} + (2/V^{\frac{1}{3}})^3 \sum_{\boldsymbol{k}} (\mathrm{Re}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}(s_1)})\, (\mathrm{Re}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}(s_2)}) \exp(-\tfrac{1}{6}l\,|\boldsymbol{k}|^2\,|s_1 - s_2|), \tag{3.6}$$

$$(2) \quad G_2 = (2/V^{\frac{1}{3}})^2 \sum_{\boldsymbol{k}} (\mathrm{Im}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}(s_1)})\, (\mathrm{Im}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}(s_2)}) \exp(-\tfrac{1}{6}l\,|\boldsymbol{k}|^2\,|s_1 - s_2|), \tag{3.7}$$

where $\boldsymbol{k} = (2\pi/V^{\frac{1}{3}})\,(l\boldsymbol{i} + m\boldsymbol{j} + n\boldsymbol{k})$ (note, at large $s - s'$ the small $\boldsymbol{k}$ eigenfunctions dominate the expansion, i.e. when $\pi^2 l|s_1 - s_2|/V^{\frac{2}{3}} \gg 1$). Pictorially

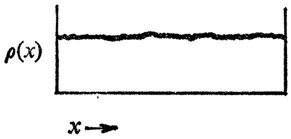


FIGURE 1

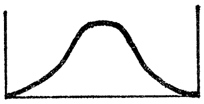


FIGURE 2

The two body correlation function $C(\boldsymbol{r}, \boldsymbol{r}')$ can be calculated from G_1:

$$C(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{L}\int_0^L G_1(\boldsymbol{r}, \boldsymbol{r}'; s, s')\, \mathrm{d}s\, \mathrm{d}s', \tag{3.8}$$

thus

$$C(\boldsymbol{r}, \boldsymbol{r}') \simeq \frac{L}{lV} + \frac{3}{2\pi l^2}\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{3.9}$$

where the first term comes from 'other chains' (cyclic condition) and the second is due to the extra correlation from monomers along the same chain. It is of interest to note that the $Ll/V^{\frac{2}{3}} \ll 1$ condition corresponds to a polymer 'gas' of molecules which have internal degrees of freedom. So the perfect gas law would be obeyed at very low densities independent of the boundary conditions.

However, if $Ll/V^{\frac{2}{3}} \gg 1$ then the 'internal' degrees of freedom have become 'external', the volume of the box is now a limiting factor on the number of configurations the chain can take up.

Thus if it is desired to describe a long 'phantom chain' in a box ($Ll/V^{\frac{2}{3}} > 1$), a choice between G_1 (cyclic boundary conditions) and G_2 (zero density outside the walls) must be made. If a phantom chain really did exist in nature then confining it to a box would produce a density distribution as described by G_2 (i.e. bunched in the centre). Phantom chains are not realistic, intra and inter chain forces for instance favour an even density distribution. These can be put in for solutions of intermediate density quite easily, the main condition on the system being that the $1/r$ correlation effects are small compared with the effects of the mean density of the solutions, (that is fluctuations in polymer density must be small). So for realistic chain models with $lL/V^{\frac{2}{3}} \gg 1$ as in network problems, we are driven back to taking the G_1 solution with the additional caution that the density fluctuations must be small compared with the mean density. Problems involving the choice of G_2 (polymer density zero outside the wall) have been studied. This class of problems arise in the situation where one end of a chain is fixed to a wall so the density at the wall is fixed (Dolan & Edwards 1974, 1975), i.e.

FIGURE 3

The solution to this problem (and for other boundary shapes) is obtained by introducing a small length δ in which the polymer is given 'extra room' in order to build up to its starting density at the wall

FIGURE 4

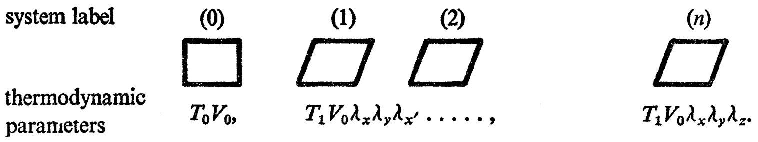
The reason for this is that the chain once it starts away from the wall can never cross it again so configurations that cross the wall are not counted. This forces the maximum density of polymer to be away from the wall, also the mathematics insists that the density at the wall is zero, but the model must not be taken seriously at distances less than one step length (besides in nature the wall is not a sharp infinite potential). A finite density ρ_0 at the wall can be obtained by starting the polymer off at a fictitious wall δ further back (where $\delta \approx l$). This might be thought of as the effective infinite potential for the wall. Thus problems of this type have solutions of the type G_2, there is no even density part as in the G_1 case (or in Fourier transform terms there is no $k = 0$ mode for G_2, there is for G_1).

The mathematics of phantom chains in a box will now be used in setting up the general partition function $Z(n)f$ or a crosslinked phantom chain network.

(b) *The phantom chain network*

The model for the phantom chain network will be set up by considering a very long chain of length L crosslinked at N points in a box of volume V. (Four chain segments eminate from one crosslink point.) The difference between a very long chain crosslinked in this manner and $2N$ separate chains linked together by N crosslinks to form a network is only in construction. It is the topology of the network which is important for the thermodynamic properties of the rubber not the method of construction. The topology of the network is specified for the phantom chain case by the position of the crosslinks along the arc length, e.g. $\delta(\boldsymbol{R}(S_1)-\boldsymbol{R}(S_2))\,\delta(\boldsymbol{R}(S_3)-\boldsymbol{R}(S_4))$ specifies one crosslink at S_1 and S_2 another at S_3 and S_4.

Now the general partition function may be set up. First the $n+1$ systems must be defined:



where systems (1)–(n) have been strained by the extension ratio. λ_x in the x direction ($\lambda_x = X_1/X_0$), where $X_0 Y_0 Z_0 = V_0$, similarly for λ_y and λ_z. Put one chain of length L in each box, the chains will take the system labels, so that $\boldsymbol{R}^{(\alpha)}(s)$ is the chain in the αth box. Each system will have the same crosslinking topology. For one crosslink at s_1 and s_2 this would be put in by the constraint

$$\prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) \tag{3.10}$$

so that for a phantom chain $Z(n)$ for one crosslink is

$$Z(n) = \mathcal{N}\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \int_V \delta\boldsymbol{R}^{(0)}(s) \int_{V\lambda_x\lambda_y\lambda_z} \delta\boldsymbol{R}^{(\alpha)}(s) \int\ldots\int_{V\lambda_x\lambda_y\lambda_z} \delta\boldsymbol{R}^{(n)}(s) \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2))$$
$$\times \exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\int_0^L \dot{\boldsymbol{R}}^{(\alpha)2}\,\mathrm{d}s\right). \tag{3.11}$$

The advantage of introducing $n+1$ systems is now seen because the $\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2$ can be done first. Changing the order of integration we have

$$Z(n) = \mathcal{N}\int_V \int_V \lambda_x\lambda_y\lambda_z \ldots \int \prod_{\alpha=0}^{n} \delta\boldsymbol{R}^{(\alpha)}(s) \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2))$$
$$\times \exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\int_0^L \dot{\boldsymbol{R}}^{(\alpha)2}\,\mathrm{d}s\right). \tag{3.12}$$

Thus for N crosslinks $Z(n)$ becomes

$$Z(n) = \mathcal{N}\int_V \int_V \lambda_x\lambda_y\lambda_z \ldots \int \prod_{\alpha=0}^{n} \delta\boldsymbol{R}^{(\alpha)}(s) \left[\prod_{\alpha=0}^{n} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2))\right]^N$$
$$\times \exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\int_0^L \dot{\boldsymbol{R}}^{(\alpha)2}\,\mathrm{d}s\right). \tag{3.13}$$

This is the general partition function (namely equation 2.22) for a phantom chain network. This formulation of the problem will now be solved with the James & Guth, Flory & Wall and also the present assumptions. Before starting it is more convenient to rewrite the crosslinking constraint by a pole integration

$$Z(n) = \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \mathcal{N}\int_V \int_V \lambda_x\lambda_y\lambda_z \ldots \int \prod_{\alpha=0}^{n} \delta\boldsymbol{R}^{(\alpha)}(s)$$
$$\times \exp\left(\mu \int_0^L \int_0^L \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2))\,\mathrm{d}s_1\,\mathrm{d}s_2 - \sum_{\alpha=0}^{n} \frac{3}{2l}\int_0^L \dot{\boldsymbol{R}}^{(\alpha)2}\,\mathrm{d}s\right). \tag{3.14}$$

A lower bound will now be found for $Z(n)$. (Therefore an upper bound on F.)

Consider $\qquad \mathrm{e}^{x-\langle x\rangle} \geqslant 1 + x - \langle x\rangle,$

therefore $\qquad \langle \mathrm{e}^{x}\rangle\, \mathrm{e}^{-\langle x\rangle} \geqslant \langle 1\rangle,$

thus $\qquad \langle \mathrm{e}^{x}\rangle \geqslant \mathrm{e}^{\langle x\rangle}. \qquad (3.15)$

So in this approximation we may write

$$Z(n) \geqslant \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(\mu \left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) \right\rangle\right)$$

$$= \left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) \right\rangle^N. \tag{3.16}$$

Therefore only $\left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) \right\rangle$ has to be evaluated, although a direct evaluation of

$$\left\langle \left[\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) \right]^N \right\rangle \tag{3.17}$$

is in principle possible. Now what is meant by the averaging $\langle\ \ \rangle$ must be decided, and this is where the difference between the James & Guth and the Flory theory comes.

The Green function for the system is easily solved, since the $n+1$ systems transform into a problem of a random walk in $3(n+1)$ dimensions

$$G(\{\boldsymbol{R}^{(\alpha)}(s_1)\}, \{\boldsymbol{R}^{(\alpha)}(s_2)\}; s_1, s_2) = \mathcal{N} \int \prod_{\alpha=0}^{n} \delta \boldsymbol{R}^{(\alpha)} \exp\left(-\frac{3}{2l} \sum_{\alpha=0}^{n} \dot{\boldsymbol{R}}^{(\alpha)2}\, \mathrm{d}s \right)$$

$$\times \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{r}_1^{\alpha})\, \delta(\boldsymbol{R}^{(\alpha)}(s_2) - \boldsymbol{r}_2), \tag{3.18}$$

where $\{\boldsymbol{R}^{(\alpha)}(s_1)\}$ is a vector in $3(n+1)$ dimensions.

This is the solution of Fick's equation in a box of volume $V^{n+1}(\lambda_x \lambda_y \lambda_z)^n$ in $3(n+1)$ dimensions. As discussed previously, there are two types of solution appropriate, an even density (cyclic boundary conditions) and polymers with a fixed end at a wall.

(c) *The Flory assumption*

Flory assumed that the crosslinks are fixed in space and are randomly distributed over the volume of the rubber. This is an even density assumption appropriate to cyclic boundary conditions with solutions of type G_1.

Evaluation of $\left\langle \mu \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) \right\rangle$ is simply

$$\mu \int \mathrm{d}^{3(n+1)}R_0\, \mathrm{d}^{3(n+1)}R_1\, \mathrm{d}^{3(n+1)}R_2\, \mathrm{d}^{3(n+1)}R_L\, G_1[0,1]\, G_1[1,2]\, G_1[2,L]\, \delta(12), \tag{3.19}$$

or diagrammatically

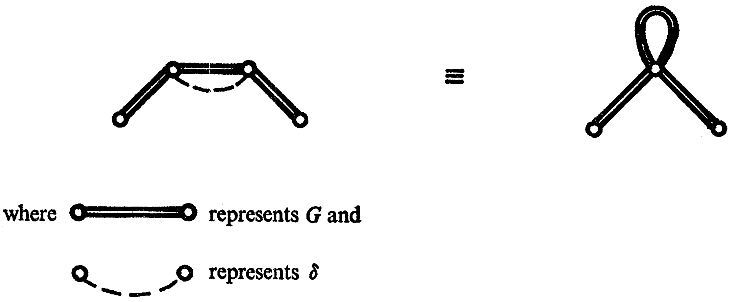


FIGURE 5

G is given by

$$G_1[\{\boldsymbol{R}^{(\alpha)}(s_1)\}, \{\boldsymbol{R}^{(\alpha)}(s_2)\}; s_1, s_2] = \frac{1}{V^{n+1}(\lambda_x\lambda_y\lambda_z)} + \left(\frac{3}{2\pi l\,|s_1-s_2|}\right)^{\frac{3}{2}(n+1)} \times \exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\frac{|\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2)|^2}{|s_1-s_2|}\right), \tag{3.20}$$

where

$$\left(\frac{2}{V^{\frac{1}{3}}}\right)^3 \sum_{\boldsymbol{k}} (\operatorname{Re} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}(s_1)})\,(\operatorname{Re} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}(s_2)})\,\mathrm{e}^{-\frac{1}{6}l|\boldsymbol{k}|^2|s_1-s_2|} \tag{3.21}$$

has been replaced by the approximation

$$\left(\frac{3}{2\pi l|s_1-s_2|}\right)^{\frac{3}{2}} \exp\left(-\frac{3}{2l}\frac{|\boldsymbol{R}(s_1)-\boldsymbol{R}(s_2)|^2}{|s_1-s_2|}\right). \tag{3.22}$$

$$\begin{aligned}&\left\langle \mu\int_0^L \mathrm{d}s_1\int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n}\delta(\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2))\right\rangle\\ &= \mu\int_0^L \mathrm{d}s_1\int_0^L \mathrm{d}s_2 \iiint \mathrm{d}^{3(n+1)}R_0\,\mathrm{d}^{3(n+1)}R_1\,\mathrm{d}^{3(n+1)}R_L \left[\frac{1}{V^{n+1}(\lambda_x\lambda_y\lambda_z)^n} + \left(\frac{3}{2\pi l|s_1-s_2|}\right)^{\frac{3}{2}(n+1)}\right]\\ &\times \frac{1}{V^{n+1}(\lambda_x\lambda_y\lambda_z)^n}\left[\frac{1}{V^{n+1}(\lambda_x\lambda_y\lambda_z)^n} + \left(\frac{3}{2\pi l s_1}\right)^{\frac{3}{2}(n+1)} \exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\frac{|\boldsymbol{R}^{(\alpha)}(s_0)-\boldsymbol{R}^{(\alpha)}(s_1)|^2}{s_1}\right)\right]\\ &\times\left[\frac{1}{V^{n+1}(\lambda_x\lambda_y\lambda_z)^n} + \left(\frac{3}{2\pi l|L-s_2|}\right)^{\frac{3}{2}(n+1)} \exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\frac{|\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2)|^2}{|L-s_2|}\right)\right].\end{aligned} \tag{3.23}$$

In order to evaluate these integrals the following transformation must be made

$$R_i^{(\alpha)}(s) = \lambda_i R_i^{(0)}(s) + \eta_i^{(\alpha)}(s) \quad (\alpha \neq 0,\ i = x, y, z), \tag{3.24}$$

where $\boldsymbol{R}^{(\alpha)}(S)$ is split up into the affine deformation plus the fluctuations about this deformation (the $\eta(s)$'s). Thus

$$\begin{aligned}&\left\langle \mu\int_0^L \mathrm{d}s_1\int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n}\delta(\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2))\right\rangle\\ &= \mu\int_0^L \mathrm{d}s_1\int_0^L \mathrm{d}s_1\left(\frac{1}{V^{n+1}(\lambda_x\lambda_y\lambda_z)^n} + \left(\frac{3}{2\pi l|s_1-s_2|}\right)^{\frac{3}{2}(n+1)}\right)(1+\prod_i(1+n\lambda_i^2)^{-\frac{1}{2}})^2.\end{aligned} \tag{3.25}$$

A minimum loop size is introduced, l_c.

Therefore

$$\left\langle \mu\int_0^L\int_0^L \mathrm{d}s_1\,\mathrm{d}s_2 \prod_{\alpha=0}^{n}\delta(\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2))\right\rangle = \mu\left[\frac{L^2}{V^{n+1}(\lambda_x\lambda_y\lambda_z)^n} + C_n\right][1+\prod_i(1+n\lambda_i^2)^{-\frac{1}{2}}]^2, \tag{3.26}$$

where

$$C_n = \left(\frac{3n}{2}+\frac{1}{2}\right)\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}(n+1)}\frac{L}{l_c^{(\frac{3}{2}n+\frac{1}{2})}}. \tag{3.27}$$

The resulting $\exp(\mathscr{N}\langle\int\int\pi\delta(R_1^\alpha-R_2^\alpha)\rangle)$ in the partition function should now be renormalized by $\exp(-\mu L^2/V^{n+1}(\lambda_x\lambda_y\lambda_z)^n)$ since this alone would give the perfect gas answer.

Thus the general partition function is

$$Z(n) \geqslant \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}}\exp(\mu\{[L^2/V^{n+1}(\lambda_x\lambda_y\lambda_z)^n + C_n][1+\prod_i(1+n\lambda_i^2)^{-\frac{1}{2}}]^2 - L^2/V^{n+1}(\lambda_x\lambda_y\lambda_z)^n\}) \tag{3.28}$$

$$= \exp(N\ln[(1+C_nV^{n+1}(\lambda_x\lambda_y\lambda_z)^n/L^2)\,(1+\prod_i(1+n\lambda_i^2)^{-\frac{1}{2}})^2-1] + N\ln(L^2/V^{n+1}(\lambda_x\lambda_y\lambda_z)^n)), \tag{3.29}$$

which by formula (2.1) gives

$$\tilde{F} \lesssim NkT[\sum_i \lambda_i^2 - \ln\lambda_i]. \tag{3.30}$$

(*d*) *The James & Guth assumption*

James & Guth assume that there are two types of crosslink, one type fixed at the edges of the rubber the other free to move inside the rubber. The appropriate solution here is a G_2 type because polymer is fixed at the wall of the box. The calculation is the same as before except without the $1/V^{n+1}(\lambda_x\lambda_y\lambda_z)^n$ terms from the mean density term. Thus

$$\mu\left\langle\int_0^L\int_0^L\prod_{\alpha=0}^{n}\delta(\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2))\,\mathrm{d}s_1\,\mathrm{d}s_2\right\rangle=\mu LC_n\prod_i(1+n\lambda_i^2)^{-1}. \tag{3.31}$$

In Fourier terms Flory includes a $k=0$ mode whereas James & Guth do not. Thus the James & Guth result is

$$\tilde{F}\leqslant NkT\sum_i\lambda_i^2. \tag{3.32}$$

The logarithmic term is no longer present because the even density assumption does not apply. James & Guth assume the system is held in equilibrium at $\lambda_x=\lambda_y=\lambda_z=1$, by 'internal pressure', that is short range repulsive forces. This was unnecessary in Flory's result.

In both the above treatments it is interesting to calculate $\langle\eta_{(s)}^{(\alpha)^2}\rangle$ and $\langle(\boldsymbol{R}^{(0)}(S)-\overline{\boldsymbol{R}^{(0)}}(S))^2\rangle$. If this is done (see appendix 1) it is found:

$$\langle\eta_i^{(\alpha)^2}\rangle=lL/6N\quad\text{in both cases,} \tag{3.33}$$

$$\langle(\boldsymbol{R}_i^{(0)}-\overline{\boldsymbol{R}_i^{(0)}})^2\rangle=lL/6N\quad\text{for James \& Guth} \tag{3.34}$$

and

$$\langle(\boldsymbol{R}^{(0)}-\overline{\boldsymbol{R}^{(0)}})^2\rangle=\tfrac{1}{4}V^{\frac{2}{3}}+lL/6N\quad\text{for Flory} \tag{3.35}$$

(where the $\frac{1}{4}V^{\frac{2}{3}}$ dominates so that the density is uniform).

Thus the crosslinks fluctuate about a mean position (given by the affine deformation) by a standard deviation of $lL/6N$. This contradicts Flory's assumption of crosslinks *fixed* in space. James & Guth's idea is to fix some crosslinks at the edges and to allow the rest to fluctuate and unless a constraint of constant density is used, this will give rise to a density distribution with the polymer all piled up at the centre of the box.

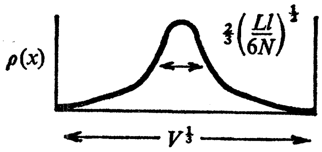


FIGURE 6

(*e*) *The present model*

This model incorporates the uniform density assumption but allows the crosslinks to fluctuate about their affinely deformed positions. The starting point is again (3.14)

$$Z(n)=\oint\frac{\mathrm{d}\mu N!}{\mu^{N+1}}\exp\left(\mu\int_0^L\int_0^L\mathrm{d}s_1\,\mathrm{d}s_2\prod_{\alpha=0}^{n}\delta(\boldsymbol{R}_1^{(\alpha)}-\boldsymbol{R}_2^{(\alpha)})-\frac{3}{2l}\sum_{\alpha=0}^{n}\int_0^L\dot{\boldsymbol{R}}^{(\alpha)^2}\,\mathrm{d}s\right) \tag{3.36}$$

as in the previous analysis $Z(n)$ is going to be approximated by

$$Z(n)\geqslant\oint\frac{\mathrm{d}\mu N!}{\mu^{N+1}}\exp\left(\mu\left\langle\int_0^L\int_0^L\mathrm{d}s_1\,\mathrm{d}s_2\prod_{\alpha=0}^{n}\delta(\boldsymbol{R}_1^{(\alpha)}-\boldsymbol{R}_2^{(\alpha)})\right\rangle\right). \tag{3.37}$$

But this time a more realistic Green function will be used to do the averaging.

The idea can be outlined as follows. It is required to calculate

$$Z = \int \exp\left(V[\boldsymbol{R}] - \int_0^L \dot{\boldsymbol{R}}^2\,\mathrm{d}s\right)\delta\boldsymbol{R}(s), \tag{3.38}$$

i.e. $Z = \langle \mathrm{e}^{V[R]}\rangle_{G_0}$ where $G_0 = \int \exp\left(-\frac{3}{2l}\int_0^L \dot{\boldsymbol{R}}^2\,\mathrm{d}s\right)\delta(\boldsymbol{R}_1-\boldsymbol{r}_1)\,\delta(\boldsymbol{R}_2-\boldsymbol{r}_2)\,\delta\boldsymbol{R}(s)$. (3.39)

This has been approximated by

$$Z \geqslant \mathrm{e}^{\langle V\rangle_{G_0}}\int G_0. \tag{3.40}$$

Now define

$$G_u = \int \exp\left(U(R) - \frac{3}{2l}\int_0^L \dot{\boldsymbol{R}}^2\,\mathrm{d}s\right)\delta(\boldsymbol{R}_1-\boldsymbol{r}_1)\,\delta(\boldsymbol{R}_2-\boldsymbol{r}_2)\,\delta\boldsymbol{R}(s), \tag{3.41}$$

i.e.

$$Z = \int \exp\left(U(R) + V[R] - U[R] - \frac{3}{2l}\int_0^L \dot{\boldsymbol{R}}^2\,\mathrm{d}s\right), \tag{3.42}$$

thus

$$Z = \langle \mathrm{e}^{(V-U)}\rangle_{G_u} \geqslant \left(\textstyle\int G_u\right)\mathrm{e}^{\langle V-U\rangle_{G_u}}, \tag{3.43}$$

where an upper bound is obtained for the free energy $\tilde{F}$, as before. If, however, G_u is a better approximation to reality an upper bound closer to the free energy will result. Also G_u can be varied so as to give the lowest free energy, thus a variational procedure will yield a closer upper bound on the free energy. $U(R)$ may be thought of as a trial potential for which a best fit to $V(R)$ is found. $V[R]$ for the case considered is

$$\mu\int_0^L\int_0^L \mathrm{d}s_1\,\mathrm{d}s_2 \prod_{\alpha=0}^{n}\delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)); \tag{3.44}$$

a good choice for U in this case is

$$U[R] = \tfrac{1}{6}l\sum_i\sum_{\alpha=1}^{n}\omega_i^2\int_0^L \eta_i^{(\alpha)2}(s)\,\mathrm{d}s \quad (i = x, y, z), \tag{3.45}$$

where

$$R_i^{(\alpha)}(s) = \lambda_i R_i^{(0)}(s) + \eta_i^{(\alpha)}(s); \quad \alpha \neq 0 \quad \text{as before.} \tag{3.46}$$

The reason for this is that crosslinks must be localized about their affinely deformed position. An harmonic well will do this, ω_i will be a variational parameter. The Green function is then the solution to

$$\mathscr{G} = \int\ldots\int\prod_{\alpha=0}^{n}\delta\boldsymbol{R}^{(\alpha)}(s)\exp\left(-\frac{l}{6}\sum_i\omega_i^2\sum_{\alpha=1}^{n}\int_0^L\eta_i^{(\alpha)2}(s) - \sum_{\alpha=0}^{n}\frac{3}{2l}\int_0^L\dot{\boldsymbol{R}}^{(\alpha)2}\,\mathrm{d}s\right). \tag{3.47}$$

$\mathscr{G}$ is now the product of $n+1$ Green functions, for turning the problem into the differential equation form, $n+1$ separable differential equations are obtained

$$\{\partial/\partial s - \tfrac{1}{6}l\nabla^2_{\eta^{(\alpha)}} - \tfrac{1}{6}l\sum_i\omega_i^2\eta_i^{(\alpha)2}\}\,G^{(\alpha)} = \delta(\eta_1^{(\alpha)} - \eta_2^{(\alpha)})\,\delta(s_1 - s_2) \tag{3.48}$$

with Fick's equation for the $R^{(0)}$ system.

However, before proceeding it is useful to introduce a transformation $T^{\beta}_{\alpha i}$ that has the following properties

$$\sum_{\alpha=0}^{n} T^{\beta}_{\alpha i}R_i^{(\alpha)}(s) = X_i^{(\beta)}(s) \quad (i = x, y, z), \tag{3.49}$$

the $X^{(\beta)}(s)$'s being such that

$$\sum_{\beta=1}^{n} X_i^{(\beta)}(s) = \sum_{\alpha=1}^{n} C_{\alpha i}\eta_i^{(\alpha)}(s) \tag{3.50}$$

(a linear combination of $\eta^{(\alpha)}(s)$'s only); also

so that

$$\left.\begin{aligned}\sum_{\beta=0}^{n} X_i^{(\beta)2}(s) &= \sum_{\alpha=0}^{n} R_i^{(\alpha)2}(s),\\ \sum_{\beta=0}^{n} \dot{X}_i^{(\beta)2}(s) &= \sum_{\alpha=0}^{n} \dot{R}_i^{(\alpha)2}(s),\\ \sum_{\beta=1}^{n} X_i^{(\beta)2}(s) &= \sum_{\alpha=1}^{n} C\eta_i^{(\alpha)2}(s)\end{aligned}\right\} \tag{3.51}$$

and

$$\prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) = \prod_{\beta=0}^{n} \delta(\boldsymbol{X}^{(\beta)}(s_1) - \boldsymbol{X}^{(\beta)}(s_2)). \tag{3.52}$$

T is therefore merely a rotation in the $n+1$ system space. T has the properties of a rotation matrix, $\det\mathsf{T} = 1$ and $T_\beta^\alpha = [T_\alpha^\beta]^{-1}$. See appendix 2 for an example of T. Special significance is associated with the 'centre of mass' coordinate, which will be $X_i^{(0)}(S)$:

$$X_i^{(0)}(s) = \frac{R_i^{(0)}(s)}{(1+n\lambda_i^2)^{\frac{1}{2}}} + \sum_{\alpha=1}^{n} \frac{\lambda_i R_i^{(\alpha)}(s)}{(1+n\lambda_i^2)^{\frac{1}{2}}}. \tag{3.53}$$

$\left(\text{The } \dfrac{1}{(1+n\lambda_i^2)^{\frac{1}{2}}} \text{ will ensure } \det\mathsf{T} = 1.\right)$

The other $X_i^{(\beta)}(s)$ may be chosen quite arbitrarily provided the rotation condition on T is met and it is found then that $X_i^\beta(s)$ for $\beta \neq 0$ is just a linear combination of the $\eta^{(\alpha)}$'s. Thus

$$\mathscr{G} = \int \prod_{\beta=0}^{n} \delta\boldsymbol{X}^{(\beta)}(s) \exp\left(-\frac{l}{6}\sum_i \omega_i^2 \sum_{\beta=1}^{n} \int_0^L X_i^{(\beta)}(s)\,\mathrm{d}s + \frac{3}{2l}\sum_{\beta=0}^{n} \int_0^L \dot{\boldsymbol{X}}^{(\beta)2}\,\mathrm{d}s\right) \tag{3.54}$$

so that

$$\mathscr{G} = \prod_{\beta=0}^{n} G^{(\beta)}, \tag{3.55}$$

where

$$\{\partial/\partial s - \tfrac{1}{6}l\nabla^2_{X^{(0)}}\}\, G^{(0)} = \delta(\boldsymbol{X}_1^{(0)} - \boldsymbol{X}_2^{(0)})\,\delta(s_1 - s_2). \tag{3.56}$$

The system is in a box of volume $V\prod_i (1+n\lambda_i^2)^{\frac{1}{2}}$ and

$$\{\partial/\partial s - \tfrac{1}{6}l\nabla^2_{x^{(\beta)}} - \sum_i \tfrac{1}{6}l\omega_i^2 X_i^{(\beta)}\}\, G^{(\beta)} = \delta(\boldsymbol{X}_1^{(\beta)} - \boldsymbol{X}_2^{(\beta)})\,\delta(s_1 - s_2) \tag{3.57}$$

for $\beta \neq 0$. Therefore

$$G^{(0)} = \frac{1}{V\prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} + \left(\frac{3}{2\pi l\,|s_1 - s_2|}\right)^{\frac{3}{2}} \exp\left(-\frac{3}{2l}\frac{|\boldsymbol{X}_1^{(0)} - \boldsymbol{X}_2^{(0)}|^2}{|s_1 - s_2|}\right) \tag{3.58}$$

$$G^{(\beta)} = \prod_i \left(\frac{\omega_i}{2\pi \sinh\frac{1}{3}l\omega_i[s_1 - s_2]}\right)^{\frac{1}{2}} \exp\left(-\tfrac{1}{2}\omega_i\left[\frac{(X_{i1}^{(\beta)2} + X_{i2}^{(\beta)2})\cosh\frac{1}{3}l\omega_i(s_1 - s_2) - 2X_{i1}^{(\beta)}X_{i2}^{(\beta)}}{\sinh\frac{1}{3}l\omega_i\,|s_1 - s_2|}\right]\right), \tag{3.59}$$

which, when $l\omega_i|s_1 - s_2|$ is large, is dominated by the lowest eigenfunction

$$G^{(\beta)} \cong \prod_i (\omega_i/\pi)^{\frac{1}{2}} \exp\left(-\tfrac{1}{2}\omega_i(X_i^{(\beta)2}(s_1) + X_i^{(\beta)2}(s_2)) - \tfrac{1}{6}l\omega_i|s_1 - s_2|\right). \tag{3.60}$$

Thus

$$\int \mathscr{G}\,\Pi\,\mathrm{d}x = V\prod_i (1+n\lambda_i^2)^{\frac{1}{2}} \left(\frac{\pi}{\omega_i}\right)^{\frac{1}{2}n} \exp\left(-\tfrac{1}{6}nl\omega_i L\right). \tag{3.61}$$

From this Green function we obtain $\langle V - U\rangle$

$$\langle V - U\rangle = \left\langle \mu\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) - \tfrac{1}{6}l\sum_i \omega_i^2 \sum_{\alpha=1}^{n} \int_0^L \eta_i^{(\alpha)2}(s)\,\mathrm{d}s \right\rangle, \tag{3.62}$$

which was transformed to

$$\langle V-U\rangle = \left\langle \mu \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\beta=0}^{n} \delta(\boldsymbol{X}^{(\beta)}(s_1) - \boldsymbol{X}^{(\beta)}(s_2)) - \tfrac{1}{6} l \sum_i \omega_i^2 \sum_{\beta=1}^{n} \int_0^L X_i^{(\beta)2}(s)\,\mathrm{d}s \right\rangle. \tag{3.63}$$

Now

$$\left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\beta=0}^{n} \delta(\boldsymbol{X}^{(\beta)}(s_1) - \boldsymbol{X}^{(\beta)}(s_2)) \right\rangle = \prod_i \left(\frac{\omega_i}{2\pi}\right)^{\frac{1}{2}n} \left\langle \int_0^L \mathrm{d}s_1\,\mathrm{d}s_2\,\delta(\boldsymbol{X}^{(0)}(s_1) - \boldsymbol{X}^{(0)}(s_2)) \right\rangle, \tag{3.64}$$

the lowest eigenfunction contribution being completely dominant for the $\beta \neq 0$ systems, leads to

$$\left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\,\delta(\boldsymbol{X}^{(0)}(s_1) - \boldsymbol{X}^{(0)}(s_2)) \right\rangle = \frac{L^2}{V \prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} + L\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}} \int_{l_c}^{L} \frac{1}{|s|^{\frac{3}{2}}}\,\mathrm{d}s, \tag{3.65}$$

where a minimum loop size has been introduced to mimic chain stiffness over short arc lengths. Then

$$\left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\beta=0}^{n} \delta(\boldsymbol{X}^{(\beta)}(s_1) - \boldsymbol{X}^{(0)}(s_2)) \right\rangle = \prod_i \left(\frac{\omega_i}{2\pi}\right)^{\frac{1}{2}n} \left[\frac{L^2}{V \prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} + \frac{L}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}} \frac{1}{l_c^{\frac{1}{2}}}\right] \tag{3.66}$$

(because $1/L^{\frac{1}{2}} \leqslant 1/l_c^{\frac{1}{2}}$, $1/L^{\frac{1}{2}}$ has been neglected), and

$$\left\langle \sum_l \sum_{\beta=1}^{n} \int_0^L \tfrac{1}{6} l \omega_i^2 X_i^{(\beta)2}(s)\,\mathrm{d}s \right\rangle = n \int_0^L \mathrm{d}s\,\tfrac{1}{6} l \sum_i \omega_i^2 \int X_i^2\,\mathrm{e}^{-\omega_i X_i^2} (\pi/\omega_i)^{\frac{1}{2}} = \sum_i \tfrac{1}{12} n l L \omega_i. \tag{3.67}$$

Thus the general partition function is given by (3.4):

$$Z(n) \geqslant \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(\mu \left[\prod_i \left(\frac{\omega_i}{2\pi}\right)^{\frac{1}{2}n}\right] \left[\frac{L^2}{V \prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} + \frac{1}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}} \frac{L}{l_c^{\frac{1}{2}}}\right] - n \sum_i \frac{lL\omega_i}{12}\right) \tag{3.68}$$

$$= \left[\left(\prod_i \frac{\omega_i}{2\pi}\right)^{\frac{1}{2}n} \left[\frac{L^2}{V \prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} + \frac{L}{2 l_c^{\frac{1}{2}}}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}}\right]\right]^N \exp\left(-n \sum_i \frac{lL}{12} \omega_i\right). \tag{3.69}$$

Now applying (2.1) to find $\tilde{F}$ gives

$$\tilde{F} \leqslant kT\left[\frac{1}{2}\frac{N}{[1+c/\rho]} \sum_i \lambda_i^2 - \frac{N}{2} \sum_i \ln \frac{\omega_i}{2\pi} + \sum_i \frac{lL}{12}\omega_i\right], \tag{3.70}$$

where

$$c = \frac{1}{2 l_c^{\frac{1}{2}}}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}}, \quad \rho = \frac{L}{V}. \tag{3.71}$$

Since ω appears in Z only in as much as it appears in F we can find its value by making F stationary,

$$\frac{\partial \tilde{F}}{\partial \omega_i} = 0 = kT\left[-\frac{N}{2}\frac{1}{\omega_i} + \frac{lL}{12}\right], \tag{3.72}$$

we find

$$\omega_i = 6N/lL. \tag{3.73}$$

Thus the λ_i dependent terms are

$$\tilde{F} \leqslant kT \frac{N}{2} \frac{1}{[1+c/\rho]} \sum_i \lambda_i^2. \tag{3.74}$$

The $1/(1+c/\rho)$ is the wasted loops correction factor, also the answer is a factor of $\frac{1}{2}$ smaller than the classical theories. The short range forces are expected to give the required free energy correction to keep the network from collapsing; thus $\lambda_x \lambda_y \lambda_z = 1$, the incompressibility condition, should be used with this formula. The fact that ω_i is independent of the strain condition means that the $-\sum_i \frac{1}{2}N \ln(\omega_i/2\pi)$ term does *not* contribute to the elastic free energy. The important difference between this and the Flory model is that the localization of the crosslinks has been allowed (standard deviation in their position is $(\sum_i \omega_i)^{-\frac{1}{2}}$) without fixing them to their affine deformation position. It is this localization as measured by ω which decides whether the network is a rubber or not. Obviously if $\omega \sim V^{-\frac{2}{3}}$ then the localization due to crosslinking is the same as that of confinement to the volume of the rubber and the process of gelling would have to be dealt with which is too complicated for a 'mean field theory' such as this.

It is easy to demonstrate how vital the short range repulsive forces are to the equilibrium of the system in the following way. So far the calculations done have been for $Z(n) \geqslant \mathrm{e}^{\langle U-V\rangle}$. An attempt can be made to calculate $\langle \mathrm{e}^{U-V}\rangle_{G_u}$ over the $X^{(0)}$ system. To do this first introduce collective variables in the $X^{(0)}$ system:

$$\rho_k = \int_0^L \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot \boldsymbol{X}^{(0)}(s)}\,\mathrm{d}s, \tag{3.75}$$

thus

$$G^{(0)} \simeq \mathscr{N}\,\mathrm{e}^{-(\rho_k\rho_{-k}/\langle\rho_k\rho_{-k}\rangle)} \quad \text{for} \quad k \neq 0 \tag{3.76}$$

where

$$\langle\rho_k\rho_{-k}\rangle \simeq \frac{1}{V\prod_i (1+n\lambda_i^2)}\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \iint \exp\left(\mathrm{i}\boldsymbol{k}.(\boldsymbol{X}^{(0)}(s_1)-\boldsymbol{X}^{(0)}(s_2))\right)$$
$$\times\left(\frac{3}{2\pi l|s_1-s_2|}\right)^{\frac{3}{2}} \exp\left(-\frac{3}{2l}\frac{|\boldsymbol{X}_1^{(0)}-\boldsymbol{X}_2^{(0)}|^2}{|s_1-s_2|}\right)\mathrm{d}\boldsymbol{X}_1^{(0)}\,\mathrm{d}\boldsymbol{X}_2^{(0)}, \tag{3.77}$$

so that

$$\langle\rho_k\rho_{-k}\rangle = \int_2^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \frac{\exp\left(\frac{1}{6}l|\boldsymbol{k}|^2|s_1-s_2|\right)}{V\pi(1+n\lambda_i^2)^{\frac{1}{2}}} \simeq \frac{6L}{l|\boldsymbol{k}|^2\,V\prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} \tag{3.78}$$

and

$$G^{(0)} = \delta_k \frac{L^2}{V\prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} \quad \text{for} \quad k = 0, \tag{3.79}$$

and

$$Z(n) = \left\langle \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(\mu \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\beta=0}^{n} \delta(\boldsymbol{X}_1^{(\beta)}-\boldsymbol{X}_2^{(\beta)}) + \tfrac{1}{6}l\sum_i \omega_i^2 \sum_{\beta=1}^{n}\int_0^L X^{(\beta)2}\,\mathrm{d}s\right)\right\rangle_{G_u}. \tag{3.80}$$

Doing the average over the $X^{(\beta)}$ systems for $\beta \neq 0$ as before (that is, $\langle V-U\rangle_{\mathrm{all}\,\beta\neq 0}$), leaves

$$Z(n) \geqslant \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}}\left\langle \exp\left(\mu \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{X}_1^{(0)}-\boldsymbol{X}_2^{(0)})\,A(\omega) - n\sum_i \tfrac{1}{12}lL\omega_i\right)\right\rangle, \tag{3.81}$$

where

$$A(\omega) = \prod_i \left(\frac{\omega_i}{2\pi}\right)^{\frac{1}{2}n}. \tag{3.82}$$

On writing this out in collective variables

$$Z(n) \gtrsim \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(\mu A(\omega)\langle\rho_0\rho_0\rangle\right)\mathscr{N}\iint \prod_k \mathrm{d}\rho_k\,\mathrm{d}\rho_{-k} \exp\left(\mu A(\omega)\,\rho_k\rho_{-k} - \rho_k\rho_{-k}/\langle\rho_k\rho_{-k}\rangle\right. . \tag{3.83}$$

$$= \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(\mu A(\omega)\left[\langle\rho_0\rho_0\rangle + \sum_k \langle\rho_k\rho_{-k}\rangle\right]\right)\mathscr{N}\iint \prod_k \mathrm{d}\rho_k\,\mathrm{d}\rho_{-k}$$
$$\times \exp\left(\mu A(\omega)\,\rho_k\rho_{-k} - \rho_k\rho_{-k}/\langle\rho_k\rho_{-k}\rangle - \mu A(\omega)\langle\rho_k\rho_{-k}\rangle\right). \tag{3.84}$$

The first term outside the functional integral is just the result previously calculated. The $\sum_k \langle \rho_k \rho_{-k} \rangle A(\omega)$ term corresponds to the closed loop correction (i.e. wasted crosslinks). The elasticity in the problem has in this theory come entirely from the $k = 0$ term! So the factor

$$\exp\left(-\sum_k \mu A(\omega) \langle \rho_k \rho_{-k} \rangle\right) \mathcal{N} \iint \prod_k \mathrm{d}\rho_k \, \mathrm{d}\rho_{-k} \exp\left[\left(\mu A(\omega) - 1/\langle \rho_k \rho_{-k} \rangle\right) \rho_k \rho_{-k}\right] \tag{3.85}$$

should improve this calculation still further. The same is true for the Flory and James & Guth models. The term in the exponent is *positive* for small k which is where the physics of the problem lies. The exponent is

$$\left\{\mu A(\omega) - \frac{lk^2}{6L} V \prod_i (1 + n\lambda_i^2)^{\frac{1}{2}}\right\}. \tag{3.86}$$

This is only an apparent singularity because on doing the pole integration one finds the functional integral becomes

$$\exp\left(-n \sum_i \tfrac{1}{12} lL\omega_i\right) \mathcal{N} \iint \prod_k \mathrm{d}\rho_k \, \mathrm{d}\rho_{-k} [A(\omega)]^N \left[\sum_k \rho_k \rho_{-k}\right] \exp\left(-\rho_k \rho_{-k}/\langle \rho_k \rho_{-k} \rangle\right). \tag{3.87}$$

This is in fact equal to $Z(n)$ because the boundary conditions should be applied properly (i.e. there are no short range forces in the problem, thus a non uniform density distribution will arise so that $\langle \rho_0 \rho_0 \rangle$ drops out because there is no longer the cyclic boundary condition). This will give a $\rho(x)$ like that of figures 2 and 6. This is due entirely to the 'phantom' nature of the chains. It would then be unnecessary to use the incompressibility condition, $(\lambda_x \lambda_y \lambda_z) = 1$. The system will find its own equilibrium.

However, since short range forces do exist in a rubber and give rise to the uniform density of polymer, these can be put into this formalism giving rise to the $k = 0$ mode and also making the exponent in the functional integral negative. Roughly speaking an excluded volume potential will add a term $-\sum_k V_k \rho_k \rho_{-k}$ to the exponential so the functional integral now becomes

$$Z(n) \geqslant \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(-\eta \sum_i \tfrac{1}{12} lL\omega_i\right) \mathcal{N} \iint \prod_k \mathrm{d}\rho_k \, \mathrm{d}\rho_{-k} \exp\left[\left(\mu A(\omega) - V_k - 1/\langle \rho_k \rho_{-k} \rangle\right) \rho_k \rho_{-k}\right]. \tag{3.88}$$

As long as $\mu A(\omega) \ll V_k$ the fluctuation terms (i.e. $k \neq 0$) are damped away and the cyclic boundary condition comes back (i.e. $k = 0$ term) giving the free energy $\tilde{F}$ as before with the liquid like free energy just tacked on the end. (This corresponds to the $\lambda_x \lambda_y \lambda_z = 1$ condition assumed before.)

As $\mu A(\omega) - V$ goes through zero to become positive apparently some sort of transition occurs quite catastrophically. When $\mu A(\omega) - V = 0$ the system is delicately balanced on the edge of the transition. The transition can be drawn as in figure 1 for $A - V$ negative and figure 2 for $A - V$ positive.

The polymer goes from an even density to a clump of size $\approx (lL/6N)^{\frac{3}{2}}$ in volume. This clearly cannot be the case for a polymer melt, so some way of insuring a maximum density of polymer must be put into the problem, only then will the answer be realistic.

This transition is like the syneresis point for moderately densely crosslinked rubbers in good solvents. Adding more crosslinks increases μ (which can be thought of as a chemical potential) until $\mu A - V$ is positive. Thus the transition is really between two uniform density states. For more lightly crosslinked systems it may be a question of gelation, but this really depends on the localization of the chains. For large excluded volume forces (i.e. good solvents) and moderate densities of polymer the formalism should provide a reasonable approximation to reality because the fluctuations in the system will be small, e.g. if $\mu A(\omega) - V$ is negative, such as must be the case in swelling experiments. It is this case that will now be solved.

4. Excluded volume in rubber

The excluded volume will now be put into the model rigorously and then solved in the spirit of the last section. The inclusion of the intra-chain forces through some potential $V(\boldsymbol{R}(S_1) - \boldsymbol{R}(S_2))$ will be modified by a solvent in the rubber and also by 'screening' of other parts of the polymer chains in the network. In short a theory of liquids is needed to solve this problem. However, polymer solutions at intermediate densities (that is not so low that there are large fluctuations in density and not so high that the second virial coefficient is no longer adequate) can become tractable when a simple form of 'pseudo-potential' is used. The basic idea is that the polymer density is comparable to that of a gas whereas the liquid it is dissolved in just serves to modify the interactions between chains. The excluded volume v of any system is defined by

$$v = \int \mathrm{d}\Omega \sum_{a,b} [\exp(-U(r_a - r_b)/kT) - 1], \tag{4.1}$$

which is just the second virial coefficient. If the system is at sufficiently low density then the free energy may be expressed in terms of this parameter quite adequately. The 'excluded volume' parameter can then be put into the partition function as an effective potential

$$v\delta(\boldsymbol{R}(s_1) - \boldsymbol{R}(s_2)). \tag{4.2}$$

For a polymer solution this leads to a free energy dependence on v given by

$$F = -kT[\mathrm{m} \ln V + \mathrm{m}\epsilon - \tfrac{1}{2}\rho v \mathrm{m} L + (V/24\pi)(v 12\rho/l)^{\frac{3}{2}}], \tag{4.3}$$

where m is the number of polymer chains, V the volume, mL the total chain length in solution and ρ the density of polymer (see Edwards 1966).

The term which is linear in the polymer density is just that which would be expected from a gas. The term which has the three halves power is specific to the chainlike nature of the polymer. It is due to interactions which may be drawn like this:

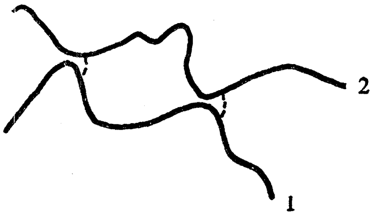


Figure 7

In a network this type of interaction will be modified by the presence of crosslinks, again the same sort of interaction will be present but this would be expected to be enhanced by interactions like:

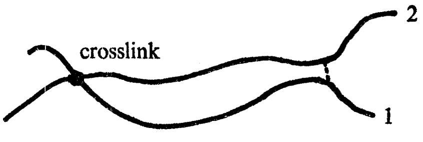


Figure 8

Not only then will there be excluded volume forces holding the networks apart which do *not* depend on crosslinking (as in the Flory–Huggins theory; see, for example, Yamakawa 1971; Flory 1942) but also terms depending on the crosslinking. In other words the free energy of the system is not obtained just by adding the free energy of the network to the free energy of a solution at the same concentration; there is also a cross term

$$F_{\text{gel}} \neq F_{\text{network}} + F_{\text{solution}}. \tag{4.4}$$

The way these 'mixing' interactions add to the free energy could modify both *shear* and bulk properties.

With these thoughts in mind the general partition function will now be written down. It is the same as equation (3.2) modified by the excluded volume in each of the $(n+1)$ systems

$$Z(n) = \oint \frac{N!\,\mathrm{d}\mu}{\mu^{N+1}} \int \prod_{\alpha=0}^{n} \delta \boldsymbol{R}^{(\alpha)}(s) \exp\left(\mu \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) - \sum_k \beta_\alpha H^{(\alpha)}[\boldsymbol{R}^\alpha]\right), \tag{4.5}$$

where $H^{(\alpha)}$ is the Hamiltonian of the αth system. Whereas before $\beta_\alpha H^{(\alpha)}$ was given by

$$\frac{3}{2l} \int_0^L \dot{\boldsymbol{R}}^{(\alpha)^2}(s)\,\mathrm{d}s, \tag{4.6}$$

now the αth system has excluded volume

$$\beta_\alpha H^{(\alpha)} = \frac{3}{2l} \int_0^L \dot{\boldsymbol{R}}^{(\alpha)^2}\,\mathrm{d}s + \tfrac{1}{2} v^{(\alpha)} \int_2^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)). \tag{4.7}$$

Note, $v^{(0)}$ is the excluded volume of the system at fabrication, all the other $v^{(\alpha)}$ are equal and are the excluded volume of the strained rubber.

Therefore

$$\begin{aligned} Z(n) = \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \int \exp\Bigg\{ & \mu \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \\ & - \sum_{\alpha=0}^{n} \left[(3/2l) \int_0^L \dot{\boldsymbol{R}}^{(\alpha)^2}\,\mathrm{d}s + \tfrac{1}{2} v^{(\alpha)} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \right] \Bigg\} \prod_{\alpha=0}^{n} \delta \boldsymbol{R}^{(\alpha)}(s). \end{aligned} \tag{4.8}$$

Using the same transformation on the $\{\boldsymbol{R}^{(\alpha)}(s)\}$ systems to go to the $\{\boldsymbol{X}^{(\beta)}(s)\}$ coordinates one finds that the $\sum_{\alpha=0}^{n} \frac{1}{2} v^{(\alpha)} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)})$ does not go to anything simple,

$$\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \sum_{\alpha=0}^{n} (\tfrac{1}{2} v^{(\alpha)} \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \xrightarrow{\mathrm{T}} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \sum_{\alpha=0}^{n} \tfrac{1}{2} v^{(\alpha)} \delta\left(\sum_{\alpha=0}^{n} \boldsymbol{T}_\beta^\alpha (\boldsymbol{X}_1^{(\beta)} - \boldsymbol{X}_2^{(\beta)}) \right). \tag{4.9}$$

However, it is still possible to use the same procedure as in the previous section. The harmonic well potential is introduced as before and $(V-U)$ in this case is

$$\begin{aligned} (V-U) = \mu \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\beta=0}^{n} \delta(\boldsymbol{X}_1^{(\beta)} - \boldsymbol{X}_2^{(\beta)}) - \sum_{\alpha=0}^{n} \tfrac{1}{2} v^{(\alpha)} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{T}_\beta^\alpha (\boldsymbol{X}_1^{(\beta)} - \boldsymbol{X}_2^{(\beta)})) \\ - \tfrac{1}{6} l \sum_{\beta=1}^{n} \sum_i \omega_i^2 \int_0^L X_i^{(\beta)2}\,\mathrm{d}s, \end{aligned} \tag{4.10}$$

which is the same as before with excluded volume added in. Averaging this over the $\{X^{(\beta)}(s)\}$ systems except for the $X^{(0)}(s)$ coordinate can be done for all the terms, except the excluded volume term, as before, giving

$$\begin{aligned} \langle V-U \rangle_{\text{except } \beta=0} = \mu \int_0^L \int_0^L \mathrm{d}s_1\, \mathrm{d}s_2\, \mathrm{A}(\omega)\, \delta(\boldsymbol{X}_1^{(0)} - \boldsymbol{X}_2^{(0)}) \\ + \left\langle \sum_{\alpha=0}^{n} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \tfrac{1}{2} v^{(\alpha)} \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \right\rangle - n \sum_i \tfrac{1}{12} l L \omega_i, \end{aligned} \tag{4.11}$$

where
$$\mathrm{A}(\omega) = \prod_i \left(\frac{\omega_i}{2\pi}\right)^{\frac{1}{2}n}. \tag{4.12}$$

The $\left\langle \sum_{\alpha=0}^{n} \tfrac{1}{2}v^{(\alpha)} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \right\rangle$ average can be done by rewriting the delta function as a Fourier transform

$$\begin{aligned}\langle v\rangle_{\beta\neq 0} &= \left\langle \sum_{\alpha=0}^{n} \sum_{k(\alpha)} \tfrac{1}{2}v^{(\alpha)} \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \exp\left(\mathrm{i}\boldsymbol{k}_{(\alpha)}\,.\,(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)})\right) \right\rangle_{\beta=0} \\ &= \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \left\langle \sum_{\alpha} \sum_{k(\alpha)} \tfrac{1}{2}v^{(\alpha)} \exp\left(\mathrm{i}\boldsymbol{k}_{(\alpha)}\,.\,T_0^{\alpha}(\boldsymbol{X}_1^{(0)} - \boldsymbol{X}_2^{(0)}) + \sum_{\beta=1}^{n} \mathrm{i}\boldsymbol{k}_{(\alpha)}\,.\,T_\beta^{\alpha}(\boldsymbol{X}_1^{(\beta)} - \boldsymbol{X}_2^{(\beta)})\right)\right\rangle \end{aligned} \tag{4.13}$$

taking the lowest eigenfunction approximation for the $G^{(\beta)}$ Green function (3.7)

$$\prod_i \left(\frac{\omega_i}{\pi}\right)^{\frac{1}{2}} \exp\{-\tfrac{1}{2}\omega_i(X_i^{(\beta)2}(s_1) + X_i^{(\beta)2}(s_2))(-\tfrac{1}{12}\omega_i l\,|s_1 - s_2|)\} \tag{4.14}$$

and completing the square. This approximation will be valid at large $s_1 - s_2$ (therefore small k).

$$\langle v\rangle_{\beta\neq 0} = \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \sum_{\alpha} \sum_{k(\alpha)} \exp\left(\mathrm{i}\boldsymbol{k}_{(\alpha)}\,.\,T_0^{\alpha}(\boldsymbol{X}_1^{(0)} - \boldsymbol{X}_2^{(0)}) - \sum_{\beta=1}^{n} \sum_i (\boldsymbol{k}_{(\alpha)i}^2\,|T_{\beta i}^{\alpha}|^2)/\omega_i\right). \tag{4.15}$$

Notice that in this approximation the average of the $\beta \neq 0$ systems is independent of $s_1 - s_2$, thus allowing the introduction of collective variables for the $X^{(0)}$ system. It is a property of the transformation that

$$\sum_{\beta=0}^{n} |T_{\beta i}^{\alpha}|^2 = 1, \tag{4.16}$$

$$\sum_{\beta=1}^{n} |T_{\beta i}^{\alpha}|^2 = 1 - |T_{0i}^{\alpha}|^2, \tag{4.17}$$

where
$$|T_{0i}^{0}|^2 = (1 + n\lambda_i^2)^{-1}, \quad |T_{0i}^{\alpha}|^2 = (1 + n\lambda_i^2)^{-1}\lambda_i^2. \tag{4.18}$$

Introducing collective variables for the centre of mass system $X^{(0)}$,

$$\rho_k = \int_0^L \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{X}(0)}\,\mathrm{d}s \tag{4.19}$$

and transforming
$$T_{0i}^{\alpha}\, k_{(\alpha)i} \rightarrow k_{(\alpha)i}, \quad T_{0i}^{\alpha}\, \Delta k_{(\alpha)i} \rightarrow \Delta k_{(\alpha)i}, \tag{4.20}$$

the excluded volume comes in its final form to be

$$\langle v\rangle_{\beta\neq 0} = \sum_{\alpha=0}^{n} \sum_{k(\alpha)} \frac{v^{(\alpha)}}{2} \frac{1}{\prod_i T_{0i}^{\alpha}} \rho_{k_{(\beta)}} \rho_{-k_{(\alpha)}} \exp\left(-\sum_i \frac{k_{(\alpha)i}^2}{\omega_i} \frac{(1 - T_{0i}^{\alpha 2})}{T_{0i}^{\alpha 2}}\right) \tag{4.21}$$

$$\begin{aligned} &= \sum_{\boldsymbol{k}} \tfrac{1}{2}v^{(\alpha)} \prod_i (1 + n\lambda_i^2)^{\frac{1}{2}} \exp\left(-\sum_i \frac{k_i^2}{\omega_i} n\lambda_i^2\right) \rho_{\boldsymbol{k}} \rho_{-\boldsymbol{k}} \\ &\quad + \sum_{\alpha=1}^{n} \sum_{k_\alpha} \tfrac{1}{2}v^{(\alpha)} \prod_i \frac{(1 + n\lambda_i^2)^{\frac{1}{2}}}{\lambda_x \lambda_y \lambda_z} \exp\left(-\sum_i \frac{k_{(\alpha)i}^2}{\omega_i} \frac{(1 + (n-1)\lambda_i^2)}{\lambda_i^2}\right) \rho_{k_{(\alpha)}} \rho_{-k_{(\alpha)}}. \end{aligned} \tag{4.22}$$

Equation (4.22) will be denoted by:

$$\langle v\rangle_{\beta\neq 0} = \sum_{k(\alpha)} v^{(\alpha)}(\boldsymbol{k}_{(\alpha)})\, \rho_{k_{(\alpha)}} \rho_{-k_{(\alpha)}}. \tag{4.23}$$

The calculation as outlined by (3.84) can now be attempted:

$$Z(n) = \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(\left(A\mu - \sum_{\alpha=0}^{n} v^{(\alpha)}(k=0)\right)\langle\rho_0\rho_0\rangle + \sum_k \left(A\mu - \sum_{\alpha=0}^{n} v^{(\alpha)}(k)\right)\langle\rho_k\rho_{-k}\rangle - n\sum_i \tfrac{1}{12} lL\omega_i\right)\mathscr{F}, \tag{4.24}$$

where $\mathscr{F}$ is the functional integral given by

$$\mathscr{F} = \mathscr{N}\iint \prod_{\alpha=0}^{n}\prod_{k} \mathrm{d}\rho_k\,\mathrm{d}\rho_{-k}\exp\left(-\left(v^{(\alpha)}(k)-A\mu\right)\left(\rho_k\rho_{-k}-\langle\rho_k\rho_{-k}\rangle\right)-\rho_k\rho_{-k}/\langle\rho_k\rho_{-k}\rangle\right), \tag{4.25}$$

$$\mathscr{N} = \iint \prod_{\alpha=0}^{n}\prod_{k}\exp\left(-\rho_k\rho_{-k}/\langle\rho_k\rho_{-k}\rangle\right), \quad A = A(\omega) = \prod_{i}\left(\omega_i/\pi\right)^{\frac{1}{2}n}. \tag{4.26}$$

The contribution to $Z(n)$ outside the functional integral is given by the same answer as before plus excluded volume terms:

$$\begin{aligned}&\exp\left(\left(A\mu-\sum_{\alpha=0}^{n}v^{(\alpha)}(0)\right)\langle\rho_0\rho_0\rangle\right)+\sum_{k}\left(A\mu-\sum_{\alpha=0}^{n}v^{(\alpha)}(k)\right)\langle\rho_k\rho_{-k}\rangle\\ &\quad=\exp\left(A\mu\left[\frac{L^2}{V\prod\limits_{i}(1+n\lambda_i^2)^{\frac{1}{2}}}+Lc\right]-\sum_{\alpha=0}^{n}v^{(\alpha)}(0)\frac{L^2}{V\prod\limits_{i}(1+n\lambda_i^2)^{\frac{1}{2}}}-\sum_{\alpha=0}^{n}\sum_{k}v^{(\alpha)}(\boldsymbol{k})\langle\rho_k\rho_{-k}\rangle\right),\end{aligned} \tag{4.27}$$

where

$$c = \frac{1}{2}\left(\frac{1}{2\pi l}\right)\frac{1}{l_c^{\frac{1}{2}}}$$

and l_c = minimum loop size. By using (3.22) for $V^{(\alpha)}(k)$, the $k = 0$ term gives a contribution

$$-\left(\frac{v^{(0)}}{2V}L^2+\frac{nv^{(\alpha)}L^2}{2V\lambda_x\lambda_y\lambda_z}\right), \tag{4.28}$$

(which provides the necessary stability condition). The sum over the $k \neq 0$ modes is the self energy of the chain (mϵ for the single system formula, which is the excluded volume equivalent of closed loops on the same chain). This has to be cut off in a similar way to the closed loop calculation due to chain flexibility, the cut off length being smaller than $(l\omega)^{-1}$, the full harmonic Green function should be used to average the excluded volume term over the $\beta \neq 0$ systems. Therefore, by using (3.59) $\sum\limits_{\alpha=0}^{n}\sum\limits_{k}v^{(\alpha)}(k)\langle\rho_k\rho_{-k}\rangle = \gamma$ say, the self energy is really

$$\begin{aligned}\gamma = \int_0^L \mathrm{d}s_1\int_0^L \mathrm{d}s_2\int \mathrm{d}^3k\prod_{i}\frac{(1+n\lambda_i^2)^{\frac{1}{2}}}{2}&\left[v^{(0)}\exp\left(-\sum_{i}\frac{k_i^2}{\omega_i}n\lambda_i^2\tanh\tfrac{1}{6}l\omega_i|s_1-s_2|\right)\right.\\ &\left.+\frac{nv^{(\alpha)}}{\lambda_x\lambda_y\lambda_z}\exp\left(-\sum_{i}\frac{k_i^2}{\omega_i}\frac{(1+(n-1)\lambda_i^2)}{\lambda_i^2}\tanh\tfrac{1}{6}l\omega_i|s_1-s_2|\right)\right]\exp\left(-\tfrac{1}{6}|k|^2l|s-s|\right).\end{aligned} \quad 4.29)$$

On doing the k integration one obtains

$$\begin{aligned}\gamma \simeq \int_{\substack{0\\|s_1-s_2|}}^{L}\mathrm{d}s_1\int_0^L\mathrm{d}s_2\prod_{i}\frac{(1+n\lambda_i^2)^{\frac{1}{2}}}{2}&\left[v^{(0)}\prod_{i}\left\{\frac{n\lambda_i^2}{\omega_i}\tanh\tfrac{1}{6}l\omega_i|s_1-s_2|+\tfrac{1}{6}l|s_1-s_2|\right\}^{-\frac{1}{2}}\right.\\ &\left.+\frac{nv^{(\alpha)}}{\lambda_x\lambda_y\lambda_z}\prod_{i}\left\{\frac{1+(n-1)\lambda_i^2}{\lambda_i^2\omega_i}\tanh\tfrac{1}{6}l\omega_i|s_1-s_2|+\tfrac{1}{6}l|s_1-s_2|\right\}^{-\frac{1}{2}}\right].\end{aligned} \tag{4.30}$$

The integral is dominated by the behaviour at small $|s_1-s_2|$ if the cut off length is smaller than the localization (which is the case for a rubber). Therefore the self energy becomes

$$\simeq \prod_{i}\frac{(1+n\lambda_i^2)^{\frac{1}{2}}}{2}\left[v^{(0)}\prod_{i}(1+n\lambda_i^2)^{-\frac{1}{2}}c_1+\frac{nv^{(\alpha)}}{\lambda_x\lambda_y\lambda_z}\prod_{i}\left[\frac{1+n\lambda_i^2}{\lambda_i^2}\right]^{-\frac{1}{2}}c_1\right], \tag{4.31}$$

where
$$c_1 = \frac{1}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}}\frac{1}{l_b^{\frac{1}{2}}} \quad (l_b \leqslant l_c) \tag{4.32}$$

$$\tfrac{1}{6}\omega l l_b \ll 1. \tag{4.33}$$

So finally
$$\gamma = \tfrac{1}{2}v^{(0)}LC_1 + \tfrac{1}{2}nv^{(\alpha)}LC_1. \tag{4.34}$$

This is just the form for the self energy that would be expected (i.e. independent of V and λ_i). So for the non-functional part of $Z(n)$ in (4.2) we obtain

$$Z(n) \geqslant \oint \frac{N!\,\mathrm{d}\mu}{\mu^{N+1}} \exp\left(A\mu\left[\frac{L^2}{V\prod_i (1+n\lambda_i^2)^{\frac{1}{2}}} + LC_1\right] - \frac{nlL}{12}\sum_i \omega_i - \frac{v^{(0)}}{2}\frac{L^2}{V} - \frac{nv^{(\alpha)}L^2}{2V\lambda_x\lambda_y\lambda_z} - \frac{C_1 L}{2}(v^{(0)} + nv^{(\alpha)})\right)\mathscr{F}, \tag{4.35}$$

where $\mathscr{F}$ is given by (4.26).

The evaluation of $\mathscr{F}$, the functional integral, will now be made. The existence of $\mathscr{F}$ will determine under what conditions the model is valid. If $\mathscr{F}$ does not exist then syneresis has occurred, as discussed in the previous chapter. Combining equations (4.22) and (4.26) we have

$$\mathscr{F} = \mathscr{N}\iint \prod_k \delta\rho_k\,\mathrm{d}\rho_{-k} \exp\left(-V(k)\,\rho_k\rho_{-k} - (\rho_k\rho_{-k}/\langle\rho_k\rho_{-k}\rangle) + A\mu\rho_k\rho_{-k} + [V(k) - A\mu]\,\langle\rho_k\rho_{-k}\rangle\right), \tag{4.36}$$

and on doing the ρ_k integrals,

$$\mathscr{F} = \exp\left(-\tfrac{1}{2}\sum_k\left[\ln\left(1 + [V(k) - \mathrm{A}\mu]\frac{6L}{lk^2V\prod_i(1+n\lambda_i^2)^{\frac{1}{2}}}\right) - (V(u) - \mathrm{A}\mu)\frac{6L}{lk^2V\prod_i(1+n\lambda_i^2)^{\frac{1}{2}}}\right]\right), \tag{4.37}$$

where

$$V(k) = \frac{v^{(0)}}{2}\prod_i(1+n\lambda_i^2)^{\frac{1}{2}}\exp\left(-\sum_i\frac{k_i^2}{\omega_i}n\lambda_i^2\right) + \frac{nv^{(\alpha)}}{2\lambda_x\lambda_y\lambda_z}\prod_i(1+n\lambda_i^2)^{\frac{1}{2}}\exp\left(-\sum_i\frac{k_i^2}{\omega_i}\left(\frac{1+(n-1)\lambda_i^2}{\lambda_i^2}\right)\right) \tag{4.38}$$

as in (4.22).

The condition for the existence of $\mathscr{F}$ being that $V(k) - \mathrm{A}\mu > 0$ for all k. Thus

$$\frac{v^{(0)}}{2} + \frac{nv^{(\alpha)}}{2\lambda_x\lambda_y\lambda_z} > \frac{\mathrm{A}\mu}{\prod_i(1+n\lambda_i^2)^{\frac{1}{2}}} \tag{4.39}$$

and if the μ integration is done by steepest descents then it is found that

$$\mu_0 \simeq \frac{NV}{AL^2}\prod_i(1+n\lambda_i^2)^{\frac{1}{2}}, \tag{4.40}$$

where μ_0 is the saddle point:

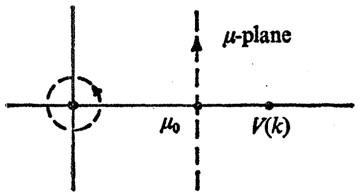


FIGURE 9

Therefore if the μ integration can be done with the contour going through the saddle point such that $V - \mathrm{A}\mu > 0$, then the even density boundary conditions hold. If the contour has to be closed so as not to include μ_0, in order to keep $v - \mathrm{A}\mu$ positive, then the non-even density boundary conditions prevail.

Thus for this model,
$$V(k)-\mathrm{A}\mu_0 > 0; \tag{4.41}$$

therefore
$$\frac{v^{(0)}L}{2V}\exp\left(-\sum_i\frac{k_i^2}{\omega_i}n\lambda_i^2\right)+\frac{nv^{(\alpha)}L}{2V\lambda_x\lambda_y\lambda_z}\exp\left(-\sum_i\frac{k_i^2}{\omega_i}\left(\frac{1+(n-1)\,\lambda_i^2}{\lambda_i^2}\right)\right) > 0, \tag{4.42}$$

i.e.
$$\frac{v^{(0)}L}{2V} > \frac{N}{L} \quad \text{for} \quad n=0, \tag{4.43a}$$

and
$$-v^{(0)}\sum_i\lambda_i^2+\frac{v^{(\alpha)}}{\lambda_x\lambda_y\lambda_z}\left(1-\sum_i\left(\frac{1-\lambda_i^2}{\lambda_i^2}\right)\right) > 0, \tag{4.43b}$$

i.e.
$$\frac{v^{(\alpha)}}{\lambda_x\lambda_y\lambda_z} \gtrsim v^{(0)} \tag{4.44}$$
to order n.

The k integral in (4.5) is only valid up to $k \simeq \omega^{\frac{1}{2}}$ because, as in the self-energy calculation, the lowest eigenfunction approximation is not good enough when $k > \omega^{\frac{1}{2}}$ and a more elaborate theory would be needed. The lowest eigenfunction approximation has the advantage of allowing the problem to be expressed in collective variables for the $X^{(0)}$ system. The integral can now be done by approximating the $\mathrm{e}^{-k^2/\omega}$ terms by 1, since convergence is ensured in any case for large k. The main contribution coming from the physically interesting small k modes. Now
$$\int_0^{\omega^{\frac{1}{2}}}\mathrm{d}^3k\,\{\ln[1+a/k^2]-a/k^2\} \simeq -\alpha\tfrac{1}{2}\pi a^{\frac{3}{2}} \quad (\tfrac{1}{2} < \alpha \leqslant 1) \tag{4.45}$$
provided $\omega/a > 1$.

Thus doing the k integral in (4.5) we find
$$\mathscr{F} = \exp\left(\frac{\alpha}{12\pi}\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}\,V\left[\frac{v^{(0)}}{2V}+\frac{nv^{(\alpha)}}{2V\lambda_x\lambda_y\lambda_z}-\frac{\mathrm{A}\mu_0}{V\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}}\right]^{\frac{3}{2}}\left(\frac{12L}{l}\right)^{\frac{3}{2}}\right) \tag{4.46}$$

provided
$$\frac{l\omega\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}}{6\rho(\frac{1}{2}v(k)-(\mathrm{A}\mu_0/\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}})} > 1, \tag{4.47}$$

i.e.
$$\tfrac{1}{6}l\omega+N/L > \rho\tfrac{1}{2}v^{(0)} \quad \text{at} \quad n=0. \tag{4.48}$$

This term gives the desired mixing of excluded volume and crosslinking. Putting all this back into the formula for $Z(n)$, (4.35), we find
$$Z(n) \geqslant \oint\frac{\mathrm{d}\mu N!}{\mu^{N+1}}\exp\left\{\mathrm{A}\mu\left[\frac{L^2}{V\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}}+cL\right]-\frac{nlL}{12}\sum_i\omega_i-(v^{(0)}+nv^{(\alpha)})c_1L\right. \tag{4.49}$$
$$\left.-\frac{v^{(0)}L^2}{2V}-\frac{nv^{(\alpha)}L^2}{2V\lambda_x\lambda_y\lambda_z}+\frac{\alpha}{12\pi}V\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}\left[\frac{v^{(0)}}{V}+\frac{nv^{(\alpha)}}{V\lambda_x\lambda_y\lambda_z}-\frac{-\mathrm{A}\mu}{V\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}}\right]^{\frac{3}{2}}\left(\frac{12L}{l}\right)^{\frac{3}{2}}\right\} \tag{4.50}$$

and since the model is only valid for
$$\frac{v^{(0)}}{2V}+\frac{nv^{(\alpha)}}{2V\lambda_x\lambda_y\lambda_z} > \frac{\mathrm{A}\mu_0}{V\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}} \tag{4.51}$$

then we may expand the exponent in powers of
$$\frac{\mathrm{A}\mu_0}{V\prod_i\,(1+n\lambda_i^2)^{\frac{1}{2}}}$$

giving
$$Z(n) \gtrsim \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left\{ \mathrm{A}\mu \left[\frac{L^2}{V \prod\limits_i (1+n\lambda_i^2)^{\frac{1}{2}}} + cL \right] - \frac{nlL}{12} \sum_i \omega_i - (v^{(0)} + v^{(\alpha)})\, c_1 L \right.$$
$$- \frac{\alpha A\mu}{12\pi} \left[\frac{v^{(0)}}{V} + \frac{nv^{(\alpha)}}{V\lambda_x\lambda_y\lambda_z} \right]^{\frac{1}{2}} \left(\frac{12L}{l} \right)^{\frac{3}{2}} - \frac{v^{(0)}L^2}{2V} - \frac{nv^{(\alpha)}L^2}{2V} + O(\mu^2)$$
$$\left. + \frac{\alpha}{12\pi} V \prod_i (1+n\lambda_i^2)^{\frac{1}{2}} \left[\frac{v^{(\beta)}L}{V} + \frac{nv^{(\alpha)}}{V\lambda_x\lambda_y\lambda_z} \right]^{\frac{3}{2}} \left(\frac{12L}{l} \right)^{\frac{3}{2}} \right\}. \tag{4.52}$$

Dropping powers of μ greater than the first and then doing the contour integration we find
$$Z(n) \gtrsim A^N \left[\frac{L^2}{V \prod\limits_i (1+n\lambda_i^2)^{\frac{1}{2}}} + CL - \frac{\alpha}{12\pi} \left[\frac{v^{(0)}L}{V} + \frac{nv^{(0)}L}{V\lambda_x\lambda_y\lambda_z} \right]^{\frac{1}{2}} \left(\frac{12}{l} \right)^{\frac{3}{2}} L \right]^N \exp\left(-\frac{nlL}{12} \sum_i \omega_i \right)$$
$$\times \exp\left\{ -\frac{v^{(0)}L^2}{2V} - \frac{nv^{(\alpha)}L^2}{2V\lambda_x\lambda_y\lambda_z} - (v^{(0)} + nv^{(\alpha)})\, LC_1 + \frac{\alpha}{12\pi} V \prod_i (1+n\lambda_i^2)^{\frac{1}{2}} \left[\frac{v^{(0)}L}{V} + \frac{nv^{(\alpha)}L}{V\lambda_x\lambda_y\lambda_z} \right]^{\frac{3}{2}} \left(\frac{12}{l} \right)^{\frac{3}{2}} \right\}, \tag{4.53}$$

where
$$\frac{\alpha}{12\pi} V \prod_i (1+n\lambda_i^2)^{\frac{1}{2}} \left[\frac{v^{(0)}L}{V} + \frac{nv^{(\alpha)}L}{V\lambda_x\lambda_y\lambda_z} \right]^{\frac{3}{2}} \left(\frac{12}{l} \right)^{\frac{3}{2}} \tag{4.54}$$

comes from
$$\int_0^{\omega^{\frac{1}{2}}} \mathrm{d}^3k \left[\ln\left(1 + V(k) \langle \rho_k \rho_{-k} \rangle\right) - V(k) \langle \rho_k \rho_{-k} \rangle \right]. \tag{4.55}$$

Here again a similar argument as for the self-energy calculation should apply. The term is really $\ln \langle \mathrm{e}^v \rangle$ and as such would be expected to give
$$\frac{V}{24\pi} (v^{(0)} 12\rho)^{\frac{3}{2}} + \frac{nV\lambda_x\lambda_y\lambda_z}{24\pi} \left(\frac{v^{(\alpha)} 12\rho}{\lambda_x\lambda_y\lambda_z} \right)^{\frac{3}{2}}, \tag{4.56}$$

i.e. just the same answer as from $n+1$ uncrosslinked systems. Thus
$$Z(n) \gtrsim \mathrm{A}^N \left[\frac{L^2}{V \prod\limits_i (1+n\lambda_i^2)^{\frac{1}{2}}} + CL - \frac{\alpha}{12\pi} \left[\frac{v^{(0)}L}{V} + \frac{nv^{(\alpha)}L}{V\lambda_x\lambda_y\lambda_z} \right]^{\frac{1}{2}} \left(\frac{12}{l} \right)^{\frac{3}{2}} L \right]^N \exp\left(-\frac{nlL}{12} \sum_i \omega_i \right)$$
$$\times \exp\left\{ -\frac{v^{(0)}L}{2V} - \frac{nv^{(\alpha)}L^2}{2V\lambda_x\lambda_y\lambda_z} - (v^{(0)} + nv^{(\alpha)})\, LC_1 + \frac{V}{24\pi} \left(\frac{v^{(0)} 12\rho}{l} \right)^{\frac{3}{2}} + \frac{nV\lambda_x\lambda_y\lambda_z}{24\pi} \left(\frac{v^{(\alpha)} 12\rho}{\lambda_x\lambda_y\lambda_z} \right)^{\frac{3}{2}} \right\}. \tag{4.57}$$

Therefore on looking for terms of order n as in formula (2.19) we find
$$\tilde{F} \lesssim kT \frac{N}{[1 + \{c - \alpha/\pi l (v^{(0)} 12\rho/l)^{\frac{1}{2}}\}\, 1/\rho]} \left[\tfrac{1}{2} \sum_i \lambda_i^2 + \frac{\alpha}{24\pi} \left(\frac{12}{l} \right)^{\frac{3}{2}} \frac{v^{(\alpha)}}{(v^{(0)}\rho)^{\frac{1}{2}}} \frac{1}{\lambda_x\lambda_y\lambda_z} \right]$$
$$+ \frac{lL}{12} \sum_i \omega_i - \frac{N}{2} \sum_i \ln \omega_i + \frac{v^{(\alpha)}\rho L}{V\lambda_x\lambda_y\lambda_z} + v^{(\alpha)} LC_1 - \frac{V\lambda\lambda\lambda}{24\pi} \left(\frac{v^{(\alpha)} 12\rho}{l\lambda_x\lambda_y\lambda_z} \right)^{\frac{3}{2}}. \tag{4.58}$$

The localization has been unaffected by the excluded volume, $\omega_i = 6N/lL$ as before.

The closed loop correction to the crosslinks has been modified by the excluded volume at fabrication so that less closed loops form as would be expected. The other N-dependent term is the 'mixing' term expected and may be thought of as the modification to the heat of mixing by the crosslinks. The other terms are just the contribution from an uncrosslinked solution.

The formalism used (collective variables) with the inherent approximations means that the formula derived is valid only when the density of polymer is low enough so that a second virial coefficient (or excluded volume parameter) provides a good description of the system. The density also must be high enough for gel formation above the syneresis point (i.e. there must be no separation of the gel from the solvent during formation of the network) $(v^{(0)}L/2V > N/L)$.

(The system is homogeneous.) If the excluded volume effect is very large then presumably the localization of chains is effected, the chains becoming locked into position to form a glass. Restriction to the excluded volume as given by (4.48) sees that the localization is not affected by the excluded volume. The correction to the 'heat of mixing' is linear in N (the number of crosslinks) because the expansion in μ was only taken to first order in (4.52). Near the syneresis point higher ordered terms in μ will be more important thus terms of higher order in N could be expected near syneresis.

Thus the excluded volume has contributed both to the shear properties by cutting down the wasted loops at the crosslinking process and the bulk properties by modifying the 'heat of mixing'. The free energy of the network is then

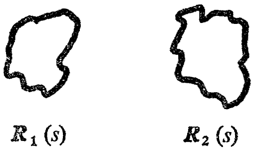
$$\tilde{F} \lesssim kT \frac{N}{[1+\{c-\alpha/\pi l(v^{(0)}12\rho/l)^{\frac{1}{2}}\}\,1/\rho]}\left[\frac{1}{2}\sum_i \lambda_i^2 + \frac{\alpha}{24\pi}\left(\frac{12}{l}\right)^{\frac{3}{2}} \frac{v^{(\alpha)}}{(v^{(0)}\rho)^{\frac{1}{2}}}\frac{1}{\lambda_x\lambda_y\lambda_z}\right] \quad \left(c = \frac{1}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}}\frac{1}{l_c^{\frac{1}{2}}}\right) \tag{4.59}$$

to which the usual solution term is added. The above formula being valid in the lightly crosslinked regime above the syneresis point and at low densities.

5. ENTANGLEMENTS IN RUBBER (Edwards 1967, 1968)

In the models considered so far the phantom nature of the chains has been a major defect. Polymer chains cannot pass through one another. At low densities this will be a small perturbation on the phantom chain system, thus for swollen rubbers or rubbers gelled in a solvent at fairly low polymer densities excluded volume effects could well be more important. At higher and higher densities the chains must become more and more entangled and in crepe rubber it is these entanglements that give rise to the elasticity. At sufficiently high densities it could well be that a regime exists where the topological nature of the chains (i.e. their length and the fact that they are *not* phantom) is far more important than the details of the molecular forces. It is in this spirit that this section will be developed.

In setting up the problem a specification for the topology of the network must now include the entanglements of the chain as well as the crosslinks. The entanglements will be specified by invariants. The basic idea is that a knot is a topological classification. A knot in one class cannot be topologically deformed into a knot of another. However, 'invariants' can be written down that also classify topologies, and although this classification is different from the knot classification (it appears an infinite number of invariants are needed to classify one class of knot) the first class of invariant seems an adequate way to specify the entanglement topology of the network. Consider the two diagrams



and

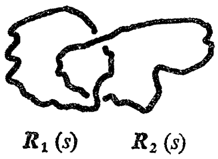


FIGURE 10

FIGURE 11

An invariant I_{12} can be defined that distinguishes between (*a*) and (*b*). Figure 11 is the familiar integral of Gauss

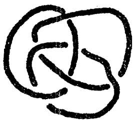
$$I_{12} = \oint \mathrm{d}s_1 \oint \mathrm{d}s_2 \frac{\dot{\boldsymbol{R}}_1(s_1) \times \dot{\boldsymbol{R}}_2(s_2) \,.\, (\boldsymbol{R}_1(s_1) - \boldsymbol{R}_2(s_2))}{|\boldsymbol{R}_1(s_1) - \boldsymbol{R}_2(s_2)|^3}. \tag{5.1}$$

I_{12} is like a solid angle and is analogous to the scalar magnetic potential.

$$I_{12} = 0 \quad \text{for } (a) \text{ and } \quad I_{12} = 4\pi \text{ for } (b).$$

(Note, in order that these Invariants are truly conserved the chains have to be either infinite in length or closed.)

The important point is that when $I_{12} = 4\pi$ the loops cannot be pulled apart. A more complicated invariant I_{123} exists for three loops that can distinguish Borromean Rings (i.e. $I_{12} = I_{23} = I_{13} = 0$ but $I_{123} \neq 0$). Borromean Rings can be pulled apart if any one ring is removed but not if all three are present.



Borromean Rings

FIGURE 12

Similarly there exist self invariants.

$$I_{11} = \int \mathrm{d}s_1 \int \mathrm{d}s_2 \frac{\dot{\boldsymbol{R}}_1(s_1) \times \dot{\boldsymbol{R}}_1(s_2) \,.\, (\boldsymbol{R}_1(s_1) - \boldsymbol{R}_1(s_2))}{|\boldsymbol{R}_1(s_1) - \boldsymbol{R}_1(s_2)|^3} \tag{5.2}$$

and higher invariants I_{1234} for four loops, etc. Thus a simple knot for one chain has to be specified by $(I_{11}, I_{111}, I_{1111} \ldots)$. The most important restriction comes in the first invariant I_{12}. If this is conserved in the network then hopefully the conservation of the other invariants will have a small effect. I_{12} is basically a two-body effect, the rest of the invariants three-body and higher. It should also be noted that in the continuum chain model used knots may exist on any length scale with equal 'measure' or weight (i.e. in lengths very much smaller than l the random flight step length). Thus putting in chain stiffness or cutting of integrals at $S < l$ will exclude the existence of these knots which often lead to divergences in the theory.

The specification of entanglements being settled on, now the general partition function for the $n+1$ systems can be set up. The theory will be for dense rubbers (melts not gels), thus excluded volume effects will be left out since a full theory of liquids would be needed to put molecular forces in as discussed previously, also chain statistics are very little altered in the melt. The starting point will be (3.13)

$$Z(n) = \int \prod_{\alpha=0}^{n} \delta \boldsymbol{R}^{(\alpha)}(s) \exp\left(\sum_{\alpha=0}^{n} -\frac{3}{2l} \int_0^L \dot{\boldsymbol{R}}^{(\alpha)2}(s)\, \mathrm{d}s \right) \left[\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)) \right]^N; \tag{5.3}$$

this specifies the crosslinking. The conservation of the invariant I_{12} can be put in by the constraints $I_{12}[\boldsymbol{R}^{(0)}] = I_{12}[\boldsymbol{R}^{\alpha)}]$ for all $\alpha \neq 0$.

Thus
$$Z(n) = \int \prod_{\alpha=0}^{n} \delta \boldsymbol{R}^{(\alpha)}(s) \exp\left(\sum_{\alpha=0}^{n} -\frac{3}{2l} \int_0^L \dot{\boldsymbol{R}}^{(\alpha)2}\, \mathrm{d}s \right) \left[\int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2\, \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \right]^N$$
$$\times \prod_{\alpha=1}^{n} \delta(I[\boldsymbol{R}^{(0)}] - I[\boldsymbol{R}^{(\alpha)}]). \tag{5.4}$$

Since the invariant I changes by multiples of 4π the delta functions in

$$\prod_{\alpha=0}^{n} \delta(I[\boldsymbol{R}^{(0)}] - I[\boldsymbol{R}^{(\alpha)}]) \tag{5.5}$$

are Kronecker delta functions and not Dirac delta functions.

We shall now use exactly the same approach to solve the functional integral for $Z(n)$ as set out previously. The same transformation of variables T^{α}_{β} and the same Green functions will be used.

The $U-V$ in formula (3.4) now becomes

$$V-U = \mu\int_0^L \mathrm{d}s_1\int_0^L \mathrm{d}s_2 \prod_{\beta=0}^{n} \delta(\boldsymbol{X}_1^{(\beta)}-\boldsymbol{X}_2^{(\beta)}) + \sum_{\alpha=1}^{n} \ln\delta(I[\boldsymbol{R}^{(0)}]-I[\boldsymbol{R}^{(\alpha)}]) - \tfrac{1}{6}l\int_0^L \mathrm{d}s\sum_i\sum_{\beta=1}^{n}\omega_i^2 X_i^{(\beta)2}, \tag{5.6}$$

where the $\prod_{\alpha=1}^{n}(\delta(I[\boldsymbol{R}^{(0)}]-I[\boldsymbol{R}^{(\alpha)}]))$ has been rewritten $\exp\left(\sum_{\alpha=1}^{n}\ln\delta(I[\boldsymbol{R}^{(\alpha)}]-I[\boldsymbol{R}^{(0)}])\right)$. Introducing collective variables $\rho_k = \int_0^L \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{X}^{(0)}}\,\mathrm{d}s$ as before and averaging $(V-U)$ over all systems except $X^{(0)}$, we have

$$\langle V-U\rangle_{\beta\neq 0} = \mu\mathrm{A}(\omega)\,\rho_k\rho_{-k} - \tfrac{1}{12}nlL\sum_i{}'\,\omega_i + \left\langle\sum_{\alpha=1}^{n}\ln\delta(I[\boldsymbol{R}^{(0)}]-I[\boldsymbol{R}^{(\alpha)}])\right\rangle_{\beta\neq 0}. \tag{5.7}$$

The first two terms are unchanged. In fact with excluded volume forces $\langle V-U\rangle_{\beta\neq 0}$ looks like

$$\langle V-U\rangle_{\beta\neq 0} = \mu\mathrm{A}\rho_k\rho_{-k} - \tfrac{1}{12}nlL\sum_i\omega_i - v(k)\,\rho_k\rho_{-k} + \left\langle\sum_{\alpha=1}^{n}\ln\delta(I[\boldsymbol{R}^{(0)}]-I[\boldsymbol{R}^{(\alpha)}])\right\rangle_{\beta\neq 0}. \tag{5.8}$$

So the problem is in the same form as before with the effect of entanglements added into the exponent as $\left\langle\sum_{\alpha=1}^{n}\ln\delta(I[\boldsymbol{R}^{(0)}]-I[\boldsymbol{R}^{(\alpha)}])\right\rangle$ which now will be expressed in terms of the collective variables. Given that I changes by multiples of 4π, the Kronecker function can be written as

$$\delta(\Delta I) = \sin(\tfrac{1}{2}\Delta I)/\tfrac{1}{2}\Delta I \tag{5.9}$$

$(\Delta I = 4\pi n,\ n = 0, \pm 1, \pm 2, \ldots)$. When many entanglements are present each contributing a small effect one can use an expansion for the sine:

$$\delta(\Delta I) \simeq 1 - \frac{(\Delta I)^2}{2^2 . 3!} + \ldots. \tag{5.10}$$

Expansion of the Kronecker delta function to this order should be a good approximation provided that the system is well gelled, the justification becoming clearer as the calculation develops. Thus consider

$$I[\boldsymbol{R}^{(\alpha)}] - I[\boldsymbol{R}^{(0)}] = I[\boldsymbol{\lambda}\boldsymbol{R}^{(0)}+\boldsymbol{\eta}^{(\alpha)}] - I[\boldsymbol{R}^{(0)}]. \tag{5.11}$$

It is a property of the invariants that they are conserved under any topological deformation, e.g. $I[\boldsymbol{R}^{(0)}] = I[\boldsymbol{\lambda}\boldsymbol{R}^{(0)}]$ since the affine deformation does not alter the topology. Therefore if $\boldsymbol{\eta}^{(\alpha)}(S)$ is small, which is true when the system is well gelled, then

$$I[\boldsymbol{R}^{(\alpha)}] \simeq I[\boldsymbol{\lambda}\boldsymbol{R}^{(0)}] = I[\boldsymbol{R}^{(0)}].$$

Thus $I[\boldsymbol{R}^{(\alpha)}]-I[\boldsymbol{R}^{(0)}]$ is a good expansion parameter when the localization is good (i.e. when ω is large). Now we may use the formula for the invariants to write down the values of $(\Delta I)^2$, where

$$\Delta I = I[\boldsymbol{R}^{(\alpha)}] - I[\boldsymbol{R}^{(0)}].$$

Thus

$$(\Delta I)^2 = \int_0^L - \int_0^L \left[\epsilon_{ijk}\frac{\dot{R}_i^{(\alpha)}(s_1)\,\dot{R}_j^{(\alpha)}(s_2)\,(R_k^{(\alpha)}(s_1)-R_k^{(\alpha)}(s_2))}{|\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2)|^3} - \epsilon_{ijk}\frac{\dot{R}_i^{(0)}(s_3)\,\dot{R}_j^{(0)}(s_4)\,(R_k^{(0)}(s_3)-R_k^{(0)}(s_4))}{|\boldsymbol{R}^{(\alpha)}(s_3)-\boldsymbol{R}^{(\alpha)}(s_4)|^3}\right]$$
$$\times\left[\epsilon_{ijk}\frac{\dot{R}_i^{(\alpha)}(s_5)\,\dot{R}_j^{(\alpha)}(s_6)\,(R_k^{(\alpha)}(s_5)-R_k^{(\alpha)}(s_6))}{|\boldsymbol{R}^{(\alpha)}(s_5)-\boldsymbol{R}^{(\alpha)}(s_6)|^3} - \epsilon_{ijk}\frac{\dot{R}_i^{(0)}(s_7)\,\dot{R}_j^{(0)}(s_8)\,(R_k^{(0)}(s_7)-R_k^{(0)}(s_8))}{|\boldsymbol{R}^{(0)}(s_7)-\boldsymbol{R}^{(0)}(s_8)|^3}\right]\mathrm{d}s_1\ldots\mathrm{d}s_8. \tag{5.12}$$

It is shown in appendix 3 that, provided the correlation term $-l^2\omega_i \exp(-\frac{1}{3}l\omega_i(s_1-s_2))$ is neglected,

$$\langle \dot{R}_i^{(\alpha)}(s_1)\, \dot{R}_j^{(\alpha)}(s_2)\rangle \simeq \tfrac{1}{3}l\delta(s_1-s_2)\,\delta_{ij} \quad (\text{all } \alpha) \tag{5.13}$$

and

$$\langle \dot{R}_i^{(\alpha)}(s_1)\, \dot{R}_j^{(0)}(s_2)\rangle \simeq 0 \quad (\alpha \neq 0). \tag{5.14}$$

We may average over all directions of the chain tangents at s_1 and s_2 giving

$$(\Delta I^2) = \iint \left(\frac{1}{|\boldsymbol{R}^{(\alpha)}(s_1) - \boldsymbol{R}^{(\alpha)}(s_2)|^4} + \frac{1}{|\boldsymbol{R}^{(0)}(s_1) - \boldsymbol{R}^{(0)}(s_2)|^4} \right) \mathrm{d}s_1\, \mathrm{d}s_2. \tag{5.15}$$

Thus writing $(\Delta I)^2$ in terms of collective coordinates

$$(\Delta I)^2 = \sum_{\boldsymbol{k}} \int_0^0 \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \,[\mathscr{I}(k)\, \mathrm{e}^{\mathrm{i}k(\boldsymbol{R}^{(\alpha)}(s_1)-\boldsymbol{R}^{(\alpha)}(s_2))} + \mathscr{I}(k)\, \mathrm{e}^{\mathrm{i}k(\boldsymbol{R}^{(0)}(s_1)-\boldsymbol{R}^{(0)}(s_2))}], \tag{5.16}$$

where

$$\mathscr{I}(k) = \int \frac{1}{|\boldsymbol{R}|^4}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}^3R. \tag{5.17}$$

$\mathscr{I}(k)$ is infinite but it must be recalled that the entanglements only have meaning on length scales greater than one step length l. Thus $\mathscr{I}(k)$ may be cut off by taking R^{-4} to be a phenomenological parameter C times the function

$$\int C\delta(\boldsymbol{R})\, \mathrm{d}^3R = C \simeq \mathscr{I}(k) \tag{5.18}$$

C being the order l^{-1}. Thus

$$\begin{aligned}(\Delta I)^2 = \sum_{\boldsymbol{k}} C \iint & \exp\left\{\mathrm{i}\boldsymbol{k}\,.\left[\boldsymbol{T}^{\alpha}_{\beta}(\boldsymbol{X}^{(0)}_1 - \boldsymbol{X}^{(0)}_2) + \sum_{\beta=1}^{n} \boldsymbol{T}^{\alpha}_{\beta}(\boldsymbol{X}^{(\beta)}_1 - \boldsymbol{X}^{(\beta)}_2)\right]\right\} \\ & + \exp\left\{\mathrm{i}\boldsymbol{k}\,.\left[\boldsymbol{T}^{0}_{0}(\boldsymbol{X}^{(0)}_1 - \boldsymbol{X}^{(0)}_2) + \sum_{\beta=1}^{n} \boldsymbol{T}^{0}_{\beta}(\boldsymbol{X}^{(\beta)}_1 - \boldsymbol{X}^{(\beta)}_2)\right]\right\} \mathrm{d}s_1\, \mathrm{d}s_2. \end{aligned} \tag{5.19}$$

Averaging over the $X^{(\beta)}$ systems and introducing $\rho_k = \int_0^L \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{X}^{(0)}}\, \mathrm{d}s$ as before,

$$(\Delta I)^2 = \sum_{\boldsymbol{k}} C[\rho_{T^{(\alpha)}_{(0)}k}\,\rho_{T^{(0)}_{(0)}k} \exp(-\sum_{\boldsymbol{i}} k_i^2(1-T^{(\alpha)2}_{(0)i})/\omega_i) + \rho_{T^{(\alpha)}_{(0)}k}\,\rho_{T^{(\alpha)}_{(0)}k} \exp(-\sum_{\boldsymbol{i}} k_i^2(1-T^{(0)2}_{(0)i})/\omega_i)] \tag{5.20}$$

$$\begin{aligned} &= \sum_{\boldsymbol{k}} C\left[\left\{\sum_i \left(\frac{1}{T^{\alpha 2}_{0i}}\right)\right\} \exp(-\sum_i k_i^2(1-T^{\alpha 2}_{0i})/\omega_i\, T^{\alpha 2}_{0i}) \right. \\ &\qquad \left. + \left\{\sum_i \left(\frac{1}{T^{02}_{0i}}\right)\right\} \exp(-\sum_i k_i^2(1-T^{02}_{0i})/\omega_i\, T^{02}_{0i})\right] \rho_k\rho_{-k} \end{aligned} \tag{5.21}$$

$$= \sum_{\boldsymbol{k}} I_2(k, \omega, n)\, 2^2\,.\,3!\, \rho_k\rho_{-k}, \tag{5.22}$$

by using

$$T^{\alpha}_{0i} = \lambda_i/(1+n\lambda_i^2)^{\frac{1}{2}} \quad \text{and} \quad T^{0}_{0i} = 1/(1+n\lambda_i^2)^{\frac{1}{2}}.$$

This gives

$$\delta(I[\boldsymbol{R}^{(\alpha)}] - I[\boldsymbol{R}^{(0)}]) = (1 - \sum_{\boldsymbol{k}} \rho_k\rho_{-k} I_2(k, \omega, n) + \ldots). \tag{5.23}$$

Now the invariant conserving constraint comes into the expression for the generalized partition function as $\prod_{\alpha=1}^{n} \delta(I[\boldsymbol{R}^{(\alpha)}] - I[\boldsymbol{R}^{(0)}])$.

In collective variables with the Kronecker delta function expanded to first order this looks like

$$\prod_{\alpha=1}^{n} (1 - \sum_i I_2(\boldsymbol{k}, \omega, n)\, \rho_k\rho_{-k}). \tag{5.24}$$

This is a finite product expression for the n systems and excludes terms

$$\sum_{\alpha=1}^{n}\Big(\sum_{k} I_2(\boldsymbol{k},\omega,n)\,\rho_k\rho_{-k}\Big)^2$$

and those of higher order

$$\sum_{\alpha=1}^{n}\Big(\sum_{k} I_2\rho_k\rho_{-k}\Big)^m \quad (m>1), \tag{5.25}$$

i.e.

$$\prod_{\alpha=1}^{n}\Big(1-\sum_{k} I_2(\boldsymbol{k},\omega,n)\,\rho_k\rho_{-k}\Big) = 1+\sum_{\alpha=1}^{n}\Big(\sum_{k} I_2(k,\omega,n)\,\rho_k\rho_{-k}\Big) + \sum_{\substack{\alpha=1\\ \alpha\neq\beta}}^{n}\sum_{\beta=1}^{n}\Big(\sum_{k} I_2(k,\omega,n)\,\rho_k\rho_{-k}\Big)+\dots. \tag{5.26}$$

A better approximation for $\delta(I)$ could be thought to be $\delta(I)\simeq \mathrm{e}^{-\langle I^2\rangle}$, but this is no good because this *includes* $\sum_{\alpha=1}^{n}\big(\sum_{k} I_2\rho_k\rho_{-k}\big)^2$ as may be seen on expansion,

$$\prod_{\alpha=1}^{n}\exp\Big(\sum_{k} I_2\rho_k\rho_{-k}\Big) = 1-\sum_{\alpha=1}^{n}\Big(\sum_{k} I_2\rho_k\rho_{-k}\Big)+\frac{\Big(\sum_{\alpha=1}^{n}\sum_{k} I_2\rho_k\rho_{-k}\Big)^2}{2!}+\dots, \tag{5.27}$$

which is correct to first order in I_2 but includes the terms

$$\sum_{\alpha=1}^{n}\Big(\sum_{k} I_2\rho_k\rho_{-k}\Big)^m\big[(-1)^{m+1}/m!\big] \quad \text{for} \quad m>1.$$

It is important to exclude these terms because they come into the final answer at order n which means they contribute to $\tilde{F}$.

Therefore an improved approximation to $\delta(I[\boldsymbol{R}^{(\alpha)}]-I[\boldsymbol{R}^{(0)}])$ is given by

$$\delta(I[\boldsymbol{R}^{(\alpha)}]-I[\boldsymbol{R}^{(0)}]) \simeq \prod_{k}\big(1-I_2(\boldsymbol{k},\omega,n)\,\rho_k\rho_{-k}\big), \tag{5.28}$$

which in the limit $\Delta k\to 0$ tends to $\exp\big(-\sum_{k} I_2\rho_k\rho_{-k}\big)$, but writing the full expression for the constraints,

$$\prod_{\alpha=1}^{n}\delta(I[\boldsymbol{R}^{(\alpha)}]-I[\boldsymbol{R}^{(0)}]) = \prod_{\alpha}\prod_{k}\big(1-I_2(k,\omega,n)\,\rho_k\rho_{-k}\big), \tag{5.29}$$

which explicitly *excludes* terms $\sum_{\alpha=1}^{n}\big(\sum_{k} I_2\rho_k\rho_{-k}\big)^m$ for $m>1$ because of the finite product nature of the form.

Thus we may write

$$\exp\Big(\sum_{\alpha=1}^{n}\ln\delta(I[\boldsymbol{R}^{(\alpha)}]-I[\boldsymbol{R}^{(0)}])\Big) \simeq \exp\Big(\sum_{\alpha=1}^{n}\sum_{k}\ln\big(1-I_2\rho_k\rho_{-k}\big)\Big). \tag{5.30}$$

This approximation has the correct properties to order n in the exponent.

Now we may write down the full expression for $Z(n)$ including entanglements using (5.5) and (3.4).

$$Z(n) \gtrsim \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}}\mathcal{N}\iint\prod_{k}\mathrm{d}\rho_k\,\mathrm{d}\rho_{-k}\exp\big(A\mu\rho_k\rho_{-k}+n\ln(1-I_2\rho_k\rho_{-k}) - V_k\rho_k\rho_{-k}-\rho_k\rho_{-k}/\langle\rho_k\rho_{-k}\rangle-\tfrac{1}{12}nlL\sum_{i}\omega_i\big). \tag{5.31}$$

In order to do this functional integral the even density assumption *must* be employed, even without excluded volume (the polymerization takes place at the even density of the monomer, thus locking the entanglements in at uniform density). The difference between this and the phantom chain calculation being that once the entanglements are locked in stability is given to the rubber. The rubber cannot 'clump up' into the centre of the box because the entanglements do not allow it. The short range forces $\sum_k V_k \rho_k \rho_{-k}$ damp out large fluctuations in the density as argued in chapter two, thus

$$Z(n) \gtrsim \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(\sum_k \{\mathrm{A}\mu \langle \rho_k \rho_{-k}\rangle + n \ln\left(1 - I_2(k, \omega, n) \langle \rho_k \rho_{-k}\rangle\right)\} - \tfrac{1}{12} nlL \sum_i \omega_i\right) \tag{5.32}$$

(even without crosslinks and short range forces this gives

$$Z(n) \gtrsim \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}} \exp\left(n \sum_k \ln\left(1 - I_2(k, \omega, n) \langle \rho_k \rho_{-k}\rangle\right) - \tfrac{1}{12} nlL \sum_i \omega_i\right) \tag{5.33}$$

for small n). Thus the crosslinks give the same result as before, (3.69),

$$\sum_k \mathrm{A}\mu \langle \rho_k \rho_{-k}\rangle = \mathrm{A}\mu \left[\frac{L^2}{V \prod_i (1 + n\lambda_i^2)^{\frac{1}{2}}} + Lg\right] \tag{5.34}$$

with

$$g = \frac{1}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}} \frac{1}{l_c^{\frac{1}{2}}}, \tag{5.35}$$

where the main contribution to the elasticity for the crosslinks will be from the $k = 0$ mode as before. The entanglements yield

$$n \sum_k \ln\left(1 - I_2(\boldsymbol{k}, \omega, n) \langle \rho_k \rho_{-k}\rangle\right). \tag{5.36}$$

Using (5.21) for $I_2(k, \omega, n)$ and putting $n = 0$ in the $I_2(k, \omega, n)$ because it is only terms linear in the exponent that contribute to $\tilde{F}$, we have

$$I_2(\boldsymbol{k}, \omega, n = 0) = C_2\left[\left(\sum_i \frac{1}{\lambda_i^2}\right) \exp\left(-\sum_i (1/\lambda_i^2 - 1)(k_i^2/\omega_i)\right) + 3\right]. \tag{5.37}$$

Expanding the logarithm out in a series about the $X^{(0)}$ contribution since the fluctuations (i.e. $\boldsymbol{\eta}$'s) will be small, gives

$$n \sum_k \ln\left(1 - C_2\left[\left(\sum_i \frac{1}{\lambda_i^2}\right) + 3\right] \langle \rho_k \rho_{-k}\rangle\right) + \frac{C_2(\sum_i 1/\lambda_i^2)\left(1 - \exp\left(-\sum_i (1/\lambda_i^2 - 1)(k_i^2/\omega_i)\right)\right) \langle \rho_k \rho_{-k}\rangle}{1 - C_2[(\sum_i 1/\lambda_i^2) + 3] \langle \rho_k \rho_{-k}\rangle} + \dots. \tag{5.38}$$

Where the first term is entirely due to the $X^{(0)}$ or 'centre of mass' coordinate and the other terms are due to localization around the $X^{(0)}$ coordinate. Only terms of order $1/\omega_i (1/\omega_i = \langle \boldsymbol{\eta}^{(\alpha)^2}\rangle)$ will be retained in this expansion since the localization is strong (i.e. large ω_i). It is the term in $1/\omega$ which will be variational balanced against the trial potential

$$-\sum_{\beta=1}^{n} \tfrac{1}{6} l \sum_i \omega_i^2 \int_0^L X_i^{(\beta)^2} \mathrm{d}s = -\tfrac{1}{12} nlL \sum_i \omega_i.$$

Thus rewriting (5.38) we have

$$n \sum_k \Bigg\{ -I_2(k) \langle \rho_k \rho_{-k}\rangle + \ln\left(1 - I_2(k) \langle \rho_k \rho_{-k}\rangle\right) + I_2(k) \langle \rho_k \rho_{-k}\rangle \\ + \frac{C_2(\sum_i 1/\lambda_i^2)\left(1 - \exp\left(-\sum_i (1/\lambda_i^2 - 1)(k_i^2/\omega_i)\right)\right) \langle \rho_k \rho_{-k}\rangle}{1 - C_2((\sum_i 1/\lambda_i^2) + 3) \langle \rho_k \rho_{-k}\rangle} + \dots \Bigg\}, \tag{5.39}$$

where
$$I_2(k) = C_2 \sum_i (1/\lambda_i^2+1) = I_2 \quad (k, \omega = 0, n = 0). \tag{5.40}$$

The integrals have to be cut off at some $k = 1/l_e$, where the cut off represents some property of chain stiffness. Thus (5.11) becomes on doing the integrals

$$n\left\{-C_2 \sum_i \left(\frac{1}{\lambda_i^2}+1\right)\left[L\rho+\frac{L}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}}\frac{1}{l_e^{\frac{1}{2}}}\right]+C_2^{\frac{3}{2}}\left[\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\frac{6}{l}\right]^{\frac{3}{2}} L\rho^{\frac{1}{2}} \right.$$
$$\left. +\frac{C_2(\sum_i 1/\lambda_i^2)\,(1-\exp{(-\sum_i (1/\lambda_i^2-1)\,(k_i^2/\omega_i)))}\,\langle\rho_k\rho_{-k}\rangle}{1-C_2\sum_i (1/\lambda_i^2+1)\,\langle\rho_k\rho_{-k}\rangle}\right\} \tag{5.41}$$

(using $\langle\rho_k\rho_{-k}\rangle = 6\rho/lk^2$ for $n = 0$ – see (3.8)). $\rho = L/V$, density at *fabrication*. The $X^{(0)}$ contribution to the entanglements has been to give the well known Mooney–Rivlin (Mooney 1940; Rivlin 1948, 1949) term at the $k = 0$ mode, plus a term of the opposite sign due to the fluctuations in the $X^{(0)}$ system. The fluctuation in the $X^{(\beta)}$ systems may now be calculated and the calculation completed. The $X^{(\beta)}$ systems contribute approximately

$$\sum_k \left[\frac{C_2(\sum_i 1/\lambda_i^2)\,(1-\exp{(-\sum_i (1/\lambda_i^2-1)\,(k_i^2/\omega_i)))}\,\langle\rho_k\rho_{-k}\rangle}{1-C_2(\sum_i (1/\lambda_i^2+1))\,\langle\rho_k\rho_{-k}\rangle}\right]$$
$$\simeq \sum_k \frac{C_2(\sum_i 1/\lambda_i^2)\,(\sum_i (1/\lambda_i^2-1)\,(k_i^2/\omega_i))\,\langle\rho_k\rho_{-k}\rangle}{1-C_2(\sum_i (1/\lambda_i^2+1))\,\langle\rho_k\rho_{-k}\rangle}, \tag{5.42}$$

where the sum is to be cut off at large $k = 1/l_e$.

$$\text{Sum} \simeq \int_0^{1/l_e} Vk^2\,\mathrm{d}k\,C_2(\sum_i (1/\lambda_i^2))\,(\sum_i (1/\lambda_i^2-1)\,(k_i^2/\omega_i))\,\langle\rho_k\rho_{-k}\rangle(1+C_2(\sum_i (1/\lambda_i^2+1))\,\langle\rho_k\rho_{-k}\rangle+\ldots$$
$$= VC_2\left(\sum_i \frac{1}{\lambda_i^2}\right)\left[\sum_i \frac{(1/\lambda_i^2-1)}{\omega_i}\right]\frac{6\rho}{l}\left(\frac{1}{3l_e^3}+\frac{C_2}{3l_e}\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\frac{6\rho}{l}\right)$$
$$= C_2\frac{6L}{l}\left(\sum_i \frac{1}{\lambda_i^2}\right)\left[\sum_i \frac{(1/\lambda_i^2-1)}{\omega_i}\right]\left(\frac{1}{3l_e^3}+\frac{C_2}{3l_e}\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\frac{6\rho}{l}\right); \tag{5.43}$$

l_e is like a self-entanglement length. Putting all this in the formula for $Z(n)$, (5.32), we have

$$Z(n) \geqslant \oint \frac{\mathrm{d}\mu N!}{\mu^{N+1}}\exp\left\{A\mu\left[\frac{L^2}{V\prod_i (1+n\lambda_i^2)^{\frac{1}{2}}}+LC\right]-nC_2\left[\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right]\left[L\rho+\frac{L}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}}\frac{1}{l_e^{\frac{1}{2}}}\right]\right.$$
$$+nC_2^{\frac{3}{2}}\left[\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\frac{6}{l}\right]^{\frac{3}{2}}L\rho^{\frac{1}{2}}+nC_2\frac{6L}{l}\left(\sum_i\frac{1}{\lambda_i^2}\right)\left[\sum_i\frac{(1/\lambda_i^2-1)}{\omega_i}\right]$$
$$\left.\times\left(\frac{1}{3l_e^3}+\frac{C_2}{3l_e}\left(\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\frac{6\rho}{l}\right)\right)-\frac{nlL}{12}\sum_i \omega_i\right\}, \tag{5.44}$$

where
$$A = \prod_i \left(\frac{2\pi}{\omega_i}\right)^{\frac{1}{2}n}, \quad C = \frac{1}{2}\left(\frac{3}{2\pi l}\right)\frac{1}{l_c^{\frac{1}{2}}}. \tag{5.45}$$

Thus applying (2.19) to find the first order in n

$$\bar{F} \lesssim kT\left[\frac{N}{2}\frac{1}{(1+C/\rho)}\sum_i \lambda_i^2-C_2\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\left[L\rho+\frac{L}{2}\left(\frac{3}{2\pi l}\right)^{\frac{3}{2}}\frac{1}{l_e^{\frac{1}{2}}}\right]\right.$$
$$+\left(\frac{6C_2}{l}\right)^{\frac{3}{2}}\left[\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right]^{\frac{3}{2}}L\rho^{\frac{1}{2}}-\frac{N}{2}\sum_i \ln\omega_i+\frac{lL}{12}\sum_i\omega_i$$
$$\left.+C_2\frac{6L}{l}\left(\sum_i\frac{1}{\lambda_i^2}\right)\left[\sum_i\left(\frac{1-1/\lambda_i^2}{\omega_i}\right)\right]\left(\frac{1}{3l_e^3}+\frac{C_2}{3l_e}\left(\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right)\frac{6\rho}{l}\right)\right]. \tag{5.46}$$

As before, ω_i is found by the variational principle

$$\frac{\partial}{\partial \omega_i}\tilde{F}(\omega) = 0,$$

$$\frac{N}{2}\frac{1}{\omega_i}-\frac{C_2 6L}{\omega_i^2 l}\left(\sum_i \frac{1}{\lambda_i^2}\right)\left(\frac{1}{3l_e^3}+\frac{C_2}{3l_e}\left(\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right)\frac{6\rho}{l}\right)\left[1-\frac{1}{\lambda_i^2}\right] = \frac{lL}{12}. \tag{5.47}$$

Therefore

$$\omega_i = \frac{3N}{Ll}+\left\{\left(\frac{3N}{Ll}\right)^2+12\frac{C_2 6}{l^2}\left(\sum_i \frac{1}{\lambda_i^2}\right)\left(\frac{1}{3l_e^3}+\frac{C_2}{3l_e}\left(\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right)\frac{6\rho}{l}\right)\left[1-\frac{1}{\lambda_i^2}\right]\right\}^{\frac{1}{2}}. \tag{5.48}$$

When crosslinks dominate the localization:

$$\omega_i = \frac{6N}{Ll} \quad \text{(independent of } \lambda_i \text{ as before)}$$

and when entanglements dominate:

$$\omega_i \leqslant \frac{6N}{Ll}+24\left(\frac{L}{N}\right)\left(\frac{C_2}{l}\right)^2\frac{\rho}{l_e}\left(\sum_i \frac{1}{\lambda_i^2}\right)\left(\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right)\left[1-\frac{1}{\lambda_i^2}\right] \tag{5.49}$$

self-entanglements *not* dominant:

$$(1/6l_e)^2 \ll C_2\rho/l, \tag{5.50}$$

which for small strains ϵ_i, $(\lambda_i = 1+\epsilon_i)$ and taking terms linear in ϵ's only gives

$$\omega_i = \frac{6N}{Ll}+24\left(\frac{C_2}{l}\right)^2\left(\frac{N}{L}\right)\frac{\rho}{l_e}36\epsilon_i. \tag{5.51}$$

Therefore the free energy is given by (5.46) with ω_i given by (5.48). Since the model is valid at high densities (when entanglements will dominate over molecular forces in shear) (5.46) can be simplified

$$\tilde{F} \lesssim kT\left[\frac{N}{2}\sum_i \lambda_i^2 - C_2 L\rho\sum_i\left(\frac{1}{\lambda_i^2}+1\right)+\left(\frac{6C_2}{l}\right)^{\frac{3}{2}}L\rho^{\frac{1}{2}}\left[\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right]^{\frac{3}{2}}+f(\omega)\right], \tag{5.52}$$

where $f(\omega)$ is given by the ω dependent terms in (5.46) but has two limiting cases:

(1) Highly crosslinked rubber $\left(\dfrac{N}{L} \gg 4C_2\left(\dfrac{\rho}{ll_e}\right)^{\frac{1}{2}}\right)$:

$$\begin{aligned} f(\omega) &= \sum_i \frac{C_2^2}{3l_e l}L\rho\left(\frac{L}{N}\right)\left(\sum_i \frac{1}{\lambda_i^2}\right)\left(\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right)\left(1-\frac{1}{\lambda_i^2}\right) \\ &= \frac{C_2^2}{3l_e l}L\rho\left(\frac{L}{N}\right)\left(\sum_i \frac{1}{\lambda_i^2}\right)\left(1-\left(\sum_i \frac{1}{\lambda_i^2}\right)^2\right). \end{aligned} \tag{5.53}$$

(2) Lightly crosslinked rubber $\left(\dfrac{N}{L} \ll 4C_2\left(\dfrac{\rho}{ll_e}\right)^{\frac{1}{2}}\right)$:

$$\begin{aligned} f(\omega) &= -\frac{N}{2}\sum_i \ln\left(1+4\left(\frac{C_2}{l}\right)^2\rho\frac{l}{l_e}\left(\sum_i \frac{1}{\lambda_i^2}\right)\left(\sum_i\left(\frac{1}{\lambda_i^2}+1\right)\right)\left[1-\frac{1}{\lambda_i^2}\right]\right) \\ &= -\frac{N}{2}\sum_i \ln\left(1+\left(\frac{12C_2}{l}\right)^2\rho\frac{l}{l_e}\epsilon_i\right) \end{aligned} \tag{5.54}$$

for small strains.

Summarizing equation (5.52) we have the normal crosslink contribution plus a term due to the affine deformation on the entanglements plus another term due to the non-affine part of the deformation on the entanglements. The $f(\omega)$ is due to the fluctuations about the mean deformed position of the chain. As can be seen from (5.52) an equilibrium is assured by the entanglements and excluded volume is no longer needed to provide the equilibrium. It should be noted that the density, ρ, in all these equations is the density at fabrication (i.e. independent of the λ's).

Various special problems could now be studied, for example the problem of polymer ring molecules formed at high density so that they are entangled. The only change in the mathematics being that $\langle \rho_k \rho_{-k} \rangle$ is now given

$$\langle \rho_k \rho_{-k} \rangle = \rho \exp\left(-lk^2 L/6\right), \tag{5.55}$$

where L now is the length of circumference of the ring. This solid would exhibit the Mooney–Rivlin term but the non-affine term and the fluctuation term would be different.

6. Conclusions

The defects of the phantom chain model of a rubber have the consequence of not allowing an even density state for the rubber, unless the even density state is artificially imposed on it through cyclic boundary conditions. If this is done the rubber is not in equilibrium. Modification of the model to include entanglements and excluded volume forces give rise to the equilibrium even density state. At low polymer densities excluded volume effects dominate in providing this even density, at high densities entanglements alone are sufficient. The localization of the polymer chains which is so necessary in gel formation, for if the chains did not localize then the network would remain a liquid, has been found by a self-consistent field approach.

The simple physical argument used by Flory to justify the $-N\ln\lambda_x\lambda_y\lambda_z$ term in the free energy can only be used for solutions not gels. The argument is that each crosslink takes away one degree of freedom and the chains are in a volume $V\lambda_x\lambda_y\lambda_z$. Therefore the free energy must have a term like $-N\ln\lambda_x\lambda_y\lambda_z$ in it. This is right provided the system has not gelled (and therefore is not a solid) having the whole volume $V\lambda_x\lambda_y\lambda_z$ available to it. In a gel, however, each monomer of the chain is localized in a volume of $(\omega_x\omega_y\omega_z)^{-\frac{1}{2}}$, thus $N\ln(\omega_x\omega_y\omega_z)^{-\frac{1}{2}}$ is the term that comes into the free energy. For a crosslink dominated gel ω is independent of λ, therefore there is no $-N\ln\lambda_x\lambda_y\lambda_z$. However, for an entanglement dominated rubber ω is a subtle function of λ, thus a term $-\frac{1}{2}N\ln\omega(\lambda)$ comes in.

The excluded volume calculation finds that less closed loops (i.e. wasted crosslinks) are formed in the crosslinking process and a modification to the heat of mixing not in Flory–Huggins type theories which is due to an enhancement of the excluded volume by the crosslinking. The entanglement calculation derives the empirical Mooney–Rivlin term plus another term which is due to the non-affine deformation of the polymer chains and comes in with the opposite sign of the Mooney–Rivlin term.

Appendix 1

It is required to calculate $\langle \eta_x^{(\alpha)2} \rangle$.

Now
$$Z(n) \gtrsim \left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \right\rangle^N \quad (\text{all } R^{(\alpha)}(s));$$

therefore

$$Z(n, \eta_x^{(\alpha)}) \gtrsim \left\langle \int_0^L \mathrm{d}s_1 \int_0^L \mathrm{d}s_2 \prod_{\alpha=0}^{n} \delta(\boldsymbol{R}_1^{(\alpha)} - \boldsymbol{R}_2^{(\alpha)}) \right\rangle^N \quad (\text{all coordinates except } \eta_x^{(\alpha)}),$$

$$= \text{constant} \times \exp\left(-\frac{3N\eta_x^{(\alpha)2}}{2l\,s_1} - \frac{3N}{2l}\frac{\eta_x^{(\alpha)2}}{L-s_2} \right),$$

where the integration is over all coordinates except $\boldsymbol{\eta}_x^{(\alpha)}$. Now the average may be calculated

$$\langle \boldsymbol{\eta}_x^{(\alpha)2} \rangle = \int \frac{Z(n, \eta_x^{(\alpha)})}{Z(n)} \eta_x^{(\alpha)2} \, \mathrm{d}\boldsymbol{\eta}_x^{(\alpha)}$$

$$= \mathcal{N} \int \boldsymbol{\eta}_x^{(\alpha)2} \exp\left(- \frac{3NL}{2l(L-s_2)\,s_1} \boldsymbol{\eta}_x^{(\alpha)2} \right) \mathrm{d}\boldsymbol{\eta}_x^{(\alpha)},$$

where $\mathcal{N}$ is the normalization.

$$\langle \boldsymbol{\eta}_{xi}^{(\alpha)2} \rangle = \frac{1}{2} \frac{2ls_1(L-s_2)}{3NL},$$

which averaging over all s_1 and s_2 given $0 \leqslant s_1 \leqslant s_2 \leqslant L$ yields

$$\langle \eta_{xi}^{(\alpha)2} \rangle = \frac{lL}{6N}.$$

APPENDIX 2

An example of the transformation $T_{\alpha i}^{\beta}$, where $X_i^{\beta}(s) = T_{\alpha i}^{\beta} R_i^{(\alpha)}(s)$

$$\begin{array}{ccccccc}
 & \alpha & (0) & (1) & . & . & R_i \\
\beta & . & . & . & . & . & . \\
(0) & . & (1+n\lambda_i^2)^{-\frac{1}{2}} & \lambda_i(1+n\lambda_i^2)^{-\frac{1}{2}} & . & . & . \\
. & . & \sqrt{(n)}\,\lambda_i(1+n\lambda_i^2)^{-\frac{1}{2}} & \frac{1}{\sqrt{n}}(1+n\lambda_i^2)^{-\frac{1}{2}} & . & . & . \\
. & . & 0 & \frac{1}{\sqrt{n}}\mathrm{e}^{2\pi\mathrm{i}\alpha\beta/n} & . & . & . \\
. & . & 0 & . & . & . & . \\
X_i & . & . & . & . & . & . \\
T_{\beta i}^{\alpha} & . & . & . & . & . & . \\
. & \beta & (0) & . & . & . & X_i \\
\alpha & . & . & . & . & . & . \\
(0) & . & (1+n\lambda_i^2)^{-\frac{1}{2}} & \lambda_i\sqrt{(n)}\,(1+n\lambda_i^2)^{-\frac{1}{2}} & 0 & 0 & . \\
(1) & & \lambda_i(1+n\lambda_i^2)^{-\frac{1}{2}} & -\frac{1}{\sqrt{(n)}}(1+n\lambda_i^2)^{-\frac{1}{2}} & 0 & 0 & . \\
. & . & \frac{1}{\sqrt{(n)}}\mathrm{e}^{-2\pi\mathrm{i}\alpha\beta/n} & . & . & . & . \\
. & . & . & . & . & . & . \\
. & . & . & . & . & . & . \\
. & . & . & . & . & . & . \\
R_i & . & . & . & . & . & .
\end{array}$$

APPENDIX 3

To calculate $\langle \dot{R}_i^{(\alpha)}(s_1)\, \dot{R}_j^{(\alpha)}(s_2) \rangle$. Introduce the variables

$$X_q^{(\beta)} = \int_0^L \mathrm{d}s\, \mathrm{e}^{\mathrm{i}qs} X^{(\beta)}(s). \qquad \text{(A 3.1)}$$

So that
$$G^{(0)} = \mathscr{N}\int \delta X^{(0)}(s)\exp\left(-\frac{3}{2l}\int_0^L \dot{X}^{(0)2}\,\mathrm{d}s\right) = \mathscr{N}\int \prod_q \mathrm{d}X_q \exp\left(-\frac{3}{2l}q^2 X_q X_{-q}\right), \tag{A 3.2}$$

$$\begin{aligned} G^{(\beta)} &= \mathscr{N}\int \delta X^{(\beta)}(s)\exp\left(-\frac{3}{2l}\int_0^L \dot{X}^{(0)2}\,\mathrm{d}s - \frac{l}{6}\omega^2\int_0^L X^2\,\mathrm{d}s\right) \\ &= \mathscr{N}\int \prod_q \mathrm{d}X_q \exp\left(-\left(\frac{3}{2l}q^2 + \frac{l}{6}\omega^2\right)X_q X_{-q}\right). \end{aligned} \tag{A 3.3}$$

Thus
$$\begin{aligned} \langle \dot{X}^{(0)}(s_1)\,\dot{X}^{(0)}(s_2)\rangle &= \mathscr{N}\int \prod_q \mathrm{d}X_q\Big(\sum_q qX_q\,\mathrm{e}^{\mathrm{i}qs_1}\sum_{q'} q'X_{q'}\,\mathrm{e}^{\mathrm{i}q's_2}\Big)\exp\left(-\frac{3}{2l}q^2X_qX_{-q}\right) \\ &= \sum_q\sum_{q'}\delta qq'\,\frac{1}{2}\,\frac{qq'\,\mathrm{e}^{\mathrm{i}qs_1-\mathrm{i}q's_2}}{(3/2l)\,q^2} = \tfrac{1}{3}l\,\delta(s_1-s_2), \end{aligned} \tag{A 3.4}$$

$$\begin{aligned} \langle \dot{X}^{(\beta)}(s_1)\,\dot{X}^{(\beta)}(s_2)\rangle &= \mathscr{N}\int \prod_q \mathrm{d}X_q\Big(\sum_{q'} X_q\,\mathrm{e}^{\mathrm{i}qs_1}\sum_{q'} q'X_{q'}\,\mathrm{e}^{\mathrm{i}q's_2}\Big)\exp\left(-\left[\frac{3}{2l}q^2+\frac{l}{6}\omega^2\right]X_qX_{-q}\right) \\ &= \sum_q\sum_{q'} qq'\,\frac{1}{2}\,\frac{qq'\,\mathrm{e}^{\mathrm{i}qs_1-\mathrm{i}q's_2}}{(3/2l)\,q^2+\frac{1}{6}l\omega^2} \\ &= \tfrac{1}{3}l\,\delta(s_1-s_2) - \frac{1}{2}\sum_q \frac{\frac{1}{6}l\omega^2\,\mathrm{e}^{\mathrm{i}q|s_1-s_2|}}{(3/2l)\,q^2+\frac{1}{6}l\omega^2} \\ &= \tfrac{1}{3}l\,\delta(s_1-s_2) - \tfrac{1}{3}l\tfrac{1}{3}l\omega\,\mathrm{e}^{-(l\omega/3)\,|s_1-s_2|}. \end{aligned} \tag{A 3.5}$$

Also
$$\langle \dot{X}^{(\beta)}(s_1)\,\dot{X}^{(\beta')}(s_2)\rangle = 0 \quad (\beta \neq \beta'), \tag{A 3.6}$$

since
$$R_i^{(\alpha)}(s) = \sum_{\beta=0}^{n} T^{\alpha}_{\beta i}X_i^{(\beta)}(s). \tag{A 3.7}$$

Then
$$\langle \dot{R}_i^{(\alpha)}(s_1)\,\dot{R}_i^{(\alpha)}(s_2)\rangle = \sum_{\beta=0}^{n}|T^{\alpha}_{\beta i}|^2\,\tfrac{1}{3}l\,\delta(s_1-s_2) - \sum_{\beta=1}^{n}|T^{\alpha}_{\beta i}|^2\,\tfrac{1}{3}l\tfrac{1}{3}l\omega\,\mathrm{e}^{-(l\omega/3)\,|s_1-s_2|}, \tag{A 3.8}$$

$$\langle \dot{R}_i^{(\alpha)}(s_1)\,\dot{R}_i^{(\alpha')}(s_2)\rangle = \sum_{\beta=0}^{n} T^{\alpha}_{\beta i}\,T^{\alpha'}_{\beta i}\,\tfrac{1}{3}l\,\delta(s_1-s_2) - \sum_{\beta=1}^{n} T^{\alpha}_{\beta i}\,T^{\alpha'}_{\beta i}\,\tfrac{1}{3}l\,\tfrac{1}{3}l\omega\,\mathrm{e}^{-(l\omega/3)\,|s_1-s_2|}. \tag{A 3.9}$$

But
$$\sum_{\beta=0}^{n}|T^{\alpha}_{\beta i}|^2 = 1 \quad \text{and} \quad \sum_{\beta=1}^{n} T^{\alpha}_{\beta i}\,T^{\alpha'}_{\beta i} = 0 \quad (\alpha \neq \alpha'),$$

therefore neglecting the $\mathrm{e}^{-(l\omega/3)\,|s_1-s_2|}$ terms we have the desired form.

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