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Deformation-Dependent Properties of Polymer Networks Constructed by Addition of Cross-Links under Strain

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ABSTRACT: Final network properties (elasticity and structure factor) are calculated for polymer networks which are constructed by addition of cross-links at a series of deformations. It is shown that the m-network hypothesis (the generalization of the two-network hypothesis first proffered by Andrews, Tobolsky, and Hanson) is valid as an interpretation of the free energy of deformation. A simple modification of this hypothesis allows for a similar interpretation of the structure factor.

Introduction

Both the microscopic and macroscopic (bulk) properties of a polymer network are influenced by the construction history of the network. As a corollary to this a complete knowledge of the cross-linking history of a network is required for any prediction of the final network properties.

A specific case in which this complete knowledge is in principle available is that of a network produced from a basis network, whose structure is known, through a well-defined sequence of addition of cross-links at different strains of this basis network. The history of the network is then characterized by the sequence of these strains and the number of cross-links introduced at each strain. A network constructed in this way for which crosslinks once introduced are always stable (not liable to subsequent breakage) we shall term an addition network.

Experimentally such networks can be constructed through irradiation of basis networks held at a series of deformations, the irradiation acting as a cross-linking agent.

This paper will present a calculation of certain final network properties—the macroscopic elasticity and the microscopic structure factor—of such addition networks for a general history of cross-linking. The results of this calculation for the free energy of deformation $F(\lambda)$ of the final addition network and the structure factor $S(k,L,\lambda)$ for the same are

$$F(\lambda) = \tfrac{1}{2}k_B T \sum_{i=0}^{M} N_i \,\mathrm{Tr}\,(\lambda^T(\lambda_i^T\lambda_i)^{-1}\lambda)$$

and

$$S(k,L,\lambda,p,p') = \exp\Bigg[-k^2 f(\Omega_M,p,p') + \Bigg[\frac{l^2}{6}|p-p'| - f(\Omega_0,p,p')\Bigg]\mathrm{Tr}\,(\mathbf{k}\lambda^T\lambda\mathbf{k}) + \sum_{i=1}^{M}\mathrm{Tr}\,(\mathbf{k}\lambda^T(\lambda_i^T\lambda_i)^{-1}\lambda\mathbf{k})[f(\Omega_{i-1},p,p') - f(\Omega_i,p,p')]\Bigg]$$

where

$$S(k,L,\lambda) = (1/L^2)\int_0^L dp \int_0^L dp'\, S(k,L,\lambda,p,p')$$

λ here denotes the final deformation matrix of a network which is constructed by addition of N_i cross-links at a series of deformations λ_i. The number of such intermediary deformations is M, and the basis network (deformation "1") is constructed by addition of N_0 cross-links to an uncross-linked melt. L is the length of labeled chain, which produces the scattering at wave vector $\mathbf{k}$ while Ω_i is equal to $(6/L_{tot})(N_0 + \ldots + N_i)$ and $f(\Omega_i,p,p')$ is $(1/2\Omega_i)(1 - \exp(-\frac{1}{6}l\Omega_i|p-p'|))$. k_B is Boltzmann's constant, T the absolute temperature, and L_{tot} the total length of chain within the network.

We will also give an interpretation of these results in the light of the independent network hypothesis first proffered by Andrews, Tobolsky, and Hanson.[1]

Formulation of the Problem

The basis of the calculation is the evaluation of the partition function for an amorphous rubber as first performed by Edwards[2] and furthered subsequently by Fricker.[3]

1. The Description of a Network. A network is taken to be fully characterized by its connectivity. This connectivity has two facets. First, the connectivity associated with the initial uncross-linked chains (the linkage of successive monomers to form a polymer) and, second, that due to added cross-links. For a high degree of cross-linking the effect of free ends is minimal and the initial uncross-linked connectivity can be summarized as a single polymer of arc length the same as the total arc length of many polymers. The effect of this is to explicitly eliminate free ends. One can then assign to each monomer segment in the system an arc position along this single chain. The subsequent cross-link constraints are then summarized by specifying the arc coordinates which are tied by each cross-link.

In the calculation, the connectivity of the uncross-linked chain is represented by the conventional Wiener measure form (the continuous limit of a chain of discrete links),

$$P\{R(s)\} = \exp\left(-\frac{3}{2l}\int_0^{L_{tot}} R'^2\, ds\right) \qquad (1)$$

where $\{R(s)\}$ is a configuration of the polymer in which the spatial position R of each arc point s is specified, l is the Kuhn length, and L_{tot} is the total length of polymer, R' denotes $\partial R/\partial s$.

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The connectivity due to the cross-links is then represented by a δ-function for each cross-link,

$$\delta(R(s_i) - R(s_j))$$

where a cross-link ties together arc positions s_i and s_j to the same point $R(s_i)$ in space.

For a given network connectivity, which we will label m, there will be a unique value A_m for any measurable quantity A of the network. However, in general the precise connectivity of a constructed network is not known but rather a probability distribution $p(m)$ for the connectivity is known. The value of a measurable quantity must then be determined by averaging over this probability distribution,

$$\langle A \rangle = \sum_m p(m) A_m \tag{2}$$

A knowledge of the history of the network will determine the probability distribution which fully summarizes the history. It is this distribution we will find for addition networks.

2. Description of an Addition Network. For the addition network,

$$p(m) = p(m_0,m_1,m_2,...,m_{M-1},m_M) \tag{3}$$

where m_i summarizes the cross-link connectivity of the cross-links added at the deformation i in the history, for which there are M stages.

Allowing for the sequence in which the cross-links are introduced we can rewrite this as

$$p(m) = p(m_M|m_0,m_1,...,m_{M-1})p(m_{M-1}|m_0,m_1,...,m_{M-2}) \cdots p(m_2|m_0,m_1)p(m_1|m_0)p(m_0) \tag{4}$$

where $p(A|B)$ denotes the conditional probability of event A occurring given event B occurs.

The conditional probabilities can be calculated on the assumption of thermodynamic equilibrium and using the principle of equal equilibrium probability to give

$$p(m) = \frac{\Omega(m_0,m_1,...,m_{M-1},m_M|\lambda_M)}{\sum_{m_M}\Omega(m_0,m_1,...,m_{M-1},m_M|\lambda_M)} \times \frac{\Omega(m_0,m_1,...,m_{M-1}|\lambda_{M-1})}{\sum_{m_{M-1}}\Omega(m_0,m_1,...,m_{M-1}|\lambda_{M-1})} \cdots \frac{\Omega(m_0,m_1,m_2|\lambda_2)}{\sum_{m_2}\Omega(m_0,m_1,m_2|\lambda_2)} \times \frac{\Omega(m_0,m_1|\lambda_1)}{\sum_{m_1}\Omega(m_0,m_1|\lambda_1)} \frac{\Omega(m_0|1)}{(\sum_{m_0}\Omega(m_0|1))} \tag{5}$$

where $\Omega(m_0,m_1,...,m_I|\lambda_I)$ denotes the total number of configurations available to a network of connectivity $(m_0,m_1,...,m_I)$ at deformation λ_I. The deformation λ_I is the deformation at which the Ith new set of cross-links are introduced and is taken relative to the basis network equilibrium state "1" (or "λ_0"). λ_I is a matrix quantity, though for simplicity of representation will be taken as a scalar in subsequent analysis. Its true tensorial rank will be restored in the final results.

The probability distribution can now be rewritten as

$$p(m) = \Omega(m_0,m_1,...,m_{M-1},m_M|\lambda_M) \times (\Omega(m_0,m_1,...,m_{M-1}|\lambda_M))^{-1}\Omega(m_0,m_1,...,m_{M-1}|\lambda_{M-1}) \times (\Omega(m_0,m_1,...,m_{M-2}|\lambda_{M-1}))^{-1} \cdots \Omega(m_0,m_1,m_2|\lambda_2) \times (\Omega(m_0,m_1|\lambda_2))^{-1}\Omega(m_0,m_1|\lambda_1)(\Omega(m_0|\lambda_1)^{-1})\Omega(m_0|1) \tag{6}$$

where we follow Fricker[3] in using the approximation

$$\sum_{m_J}\Omega(m_0,m_1,...,m_{J-1},m_J|\lambda_J) = K\Omega(m_0,m_1,...,m_{J-1}|\lambda_J) \tag{7}$$

with K a constant.

This approximation is shown to be valid at the level of subsequent approximation (Appendix A). We also here and later remove explicit normalization, although such normalization will always be applied in evaluating an average over a probability distribution function.

$P(m)$ can be further rewritten as

$$p(m) = \lim_{q_1\to-1}\lim_{q_2\to-1}\cdots\lim_{q_M\to-1} B(q_1,q_2,...,q_M) \tag{8}$$

where

$$B(q_1,q_2,...,q_M) = \Omega(m_0,m_1,...,m_{M-1},m_M|\lambda_M) \times (\Omega(m_0,m_1,...,m_{M-1}|\lambda_M))^{q_M}\Omega(m_0,m_1,...,m_{M-1}|\lambda_{M-1}) \times (\Omega(m_0,m_1,...,m_{M-2}|\lambda_{M-1}))^{q_{M-1}} \cdots \Omega(m_0,m_1,m_2|\lambda_2) \times (\Omega(m_0,m_1|\lambda_2))^{q_2}\Omega(m_0,m_1|\lambda_1)(\Omega(m_0|\lambda_1))^{q_1}\Omega(m_0|1) \tag{9}$$

on the assumption that $B(q_1,q_2,...,q_M)$ is analytic.

The distribution completely summarizes the history of an addition network and it is this distribution we will now use to express the final network properties.

3. Measurable Quantities of an Addition Network. The value of a measurable quantity has been shown to be given by

$$\langle A \rangle_\lambda = \sum_m p(m) A_{m,\lambda} \tag{10}$$

where $A_{m,\lambda}$ is the value of A for a network of connectivity m at deformation λ. (We have here explicitly shown the dependence of the measurable quantity A on the deformation λ by use of A_λ.)

We will take two measurable quantities F, the free energy, and $S(k)$, the structure factor. $F_{m,\lambda}$ is given by

$$-kT \ln \Omega(m_0,m_1,...,m_M|\lambda) \tag{11}$$

and $S_{m,\lambda}$ is given by

$$\frac{1}{L^2}\int_0^L dp \int_0^L dp' \frac{\langle \exp[i\mathbf{k}\cdot(\mathbf{R}(p) - \mathbf{R}(p'))]\rangle_{m,\lambda}}{\langle 1\rangle_{m,\lambda}} \tag{12}$$

where $\langle\ \rangle_{m,\lambda}$ denotes an average over all configurations $R(s)$ for a given connectivity m and deformation λ. The parameter L is the length of labeled chain.

The expression for $F_{m,\lambda}$ can be rewritten as

$$-kT \lim_{n\to0}\frac{d}{dn}[\Omega(m_0,m_1,...,m_M|\lambda)^n] = -kT \lim_{n\to0}\frac{d}{dn}\exp\left[-\frac{1}{kT}\bar{F}_{m,\lambda}(n)\right] \tag{13}$$

where

$$\bar{F}_{m,\lambda}(n) = -kT \ln (\Omega(m_0,m_1,...,m_M|\lambda)^n) \tag{14}$$

The expression for $S_{m,\lambda}$ can be rewritten as

$$\frac{1}{L^2}\int_0^L dp \int_0^L dp' \times \lim_{n\to0}\langle \exp[i\mathbf{k}\cdot(\mathbf{R}(p) - \mathbf{R}(p'))]\rangle_{m,\lambda}\langle 1\rangle_{m,\lambda}^{(n-1)} = \frac{1}{L^2}\int_0^L dp \int_0^L dp' \lim_{n\to0}\bar{S}_{m,\lambda}(k,p,p',n) \tag{15}$$

where

$$\bar{S}_{m,\lambda}(k,p,p',n) = \langle \exp[i\mathbf{k}\cdot(\mathbf{R}(p) - \mathbf{R}(p'))]\rangle_{m,\lambda}\langle 1\rangle_{m,\lambda}^{(n-1)} \tag{16}$$

We will determine $\langle \exp(-(1/kT)\bar{F}(n))\rangle_\lambda$ and $\langle \bar{S}(k,p,p',n)\rangle_\lambda$, deriving the free energy from the former quantity and the structure factor from the latter.

4. Introduction of Replica Coordinates. We now determine the averages by introducing replica coordinates and performing the summation over cross-link connectivity. The introduction of the parameters $q_1,q_2,...,q_M$ and n—the replica parameters—and their corresponding co-

ordinates allows this summation to be evaluated before the final approximation scheme is applied.

The number of configurations Ω for a particular connectivity M and deformation Λ can be calculated by performing the functional integration:

$$\Omega(M|\Lambda) = \int_{(\Lambda)} \delta R(s) \exp\left[-\frac{3}{2l}\int_0^{L_{tot}} R'^2\, ds\right] \prod_{i=1}^{N_M} \delta(R(s_i) - R(s'_i)) \quad (17)$$

where N_M is the total number of cross-links for connectivity M and s_i, s'_i are the particular arc points tied by the ith cross-links. The label (Λ) on the integration denotes the integration is to be evaluated for the network of connectivity M under the constraint of being at deformation Λ. Using this form we can write for the various terms of $\langle A\rangle_\lambda$: For $\sum_m$,

$$\sum_m \equiv \prod_{i=1}^{N_0}\int_0^L ds_{0,i} \int_0^L ds'_{0,i} \prod_{i=1}^{N_1}\int_0^L ds_{1,i} \int_0^L ds'_{1,i} \cdots \prod_{i=1}^{N_M}\int_0^L ds_{M,i} \int_0^L ds'_{M,i} \quad (18)$$

where each cross-linked arc point s (and s') is now labeled by the deformation stage at which it is formed, s_K. For $p(m)$,

$$\Omega(m_0,m_1,\ldots,m_J|\lambda_J)(\Omega(m_0,m_1,\ldots,m_{J-1}|\lambda_J))^{q_J} \equiv \int_{(\Lambda_J)} \delta R_{J,0} \int_{(\Lambda_J)} \delta R_{J,1} \cdots \int_{(\Lambda_J)} \delta R_{J,q_J} \times \exp\left[\frac{-3}{2l}\int_0^L (R'^2_{J,0} + R'^2_{J,1} + \cdots + R'^2_{J,q_J})\, ds\right] \times \left[\prod_{i=1}^{N_0} \delta(R_{J,0}(s_{0,i},s'_{0,i}))\delta(R_{J,1}(s_{0,i},s'_{0,i})) \cdots \delta(R_{J,q_J}(s_{0,i},s'_{0,i}))\right] \cdots \left[\prod_{i=1}^{N_{J-1}} \delta(R_{J,0}(s_{J-1,i},s'_{J-1,i})) \cdots \delta(R_{J,q_J}(s_{J-1,i},s'_{J-1,i}))\right] \times \left[\prod_{i=1}^{N_J} \delta(R_{J,0}(s_{J,i},s'_{J,i}))\right] \quad (19)$$

where for each deformation Λ_J at which N_J cross-links are added we introduce replica coordinates $R_{J,p}$, with p running from 0 to q_J. We also here abbreviate $\delta R(s)$ to δR and $\delta(R(s_i) - R(s'_i))$ to $\delta(R(s_i,s'_i))$. Later we shall further abbreviate $\delta(R(s_i) - R(s'_i))$ to $\delta(R)$. And for $A_{m,\lambda}$ when $A_{m,\lambda} = \langle A\{R(s)\}\rangle_{m,\lambda}/\langle 1\rangle_{m,\lambda}$:

$$A_{m,\lambda} = \lim_{n\to 0} \int_{(\lambda)} \delta R_1 \int_{(\lambda)} \delta R_2 \cdots \int_{(\lambda)} \delta R_n A\{R_1(s)\} \times \exp\left[\frac{-3}{2l}\int_0^L (R'^2_1 + R'^2_2 + \cdots + R'^2_n)\, ds\right] \times \left[\prod_{i=1}^{N_0} \delta(R_1(s_{0,i},s'_{0,i}))\delta(R_2(s_{0,i},s'_{0,i})) \cdots \delta(R_n(s_{0,i},s'_{0,i}))\right] \cdots \left[\prod_{i=1}^{N_{M-1}} \delta(R_1(s_{M-1,i},s'_{M-1,i})) \cdots \delta(R_n(s_{M-1,i},s'_{M-1,i}))\right]\left[\prod_{i=1}^{N_M} \delta(R_1(s_{M,i},s'_{M,i})) \cdots \delta(R_n(s_{M,i},s'_{M,i}))\right] \quad (20)$$

Substituting in these forms and actually performing the summation for each of our averaged quantities $\langle \exp(-(1/kT)\bar{F}(n))\rangle_\lambda$ and $\langle \bar{S}(k,p,p',n)\rangle_\lambda$, we find

$$\left\langle \exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda = \int_{(\lambda_0)} \delta R_0 \left[\int_{(\lambda_1)} \delta R_{1,0} \cdots \int_{(\lambda_1)} \delta R_{1,q_1}\right] \cdots \left[\int_{(\lambda_M)} \delta R_{M,0} \cdots \int_{(\lambda_M)} \delta R_{M,q_M}\right]\left[\int_{(\lambda)} \delta R_1 \cdots \int_{(\lambda)} \delta R_n\right]\Delta(\{R^T(s)\}) = \int_{(\lambda^T)} \delta R^T(s)\Delta(\{R^T(s)\}) \quad (21)$$

and

$$\langle \bar{S}(k,p,p',n)\rangle_\lambda = \int_{(\lambda_0)} \delta R_0 \left[\int_{(\lambda_1)} \delta R_{1,0} \cdots \int_{(\lambda_1)} \delta R_{1,q_1}\right] \cdots \left[\int_{(\lambda_M)} \delta R_{M,0} \cdots \int_{(\lambda_M)} \delta R_{M,q_M}\right]\left[\int_{(\lambda)} \delta R_1 \cdots \int_{(\lambda)} \delta R_n\right]\Delta(\{R^T(s)\}) \exp(i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))) = \int_{(\lambda^T)} \delta R^T(s)\Delta(\{R^T(s)\}) \exp(i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))) \quad (22)$$

where

$$\Delta(\{R^T(s)\}) = \Delta(\{R_0(s),R_{1,0}(s),\ldots,R_{1,q_1}(s),R_{M,0}(s),\ldots,R_{M,q_M}(s),R_1(s),\ldots,R_n(s)\}) \quad (23)$$

and is given by

$$\Delta(\{R^T(s)\}) = \exp\left[\frac{-3}{2l}\left[\sum_{J=1}^{M}\sum_{i=0}^{q_J}\int_0^L ds\, R'^2_{J,i} + \sum_{i=0}^{n}\int_0^L ds\, R'^2_i\right]\right] \times \left[\int_0^L dt \int_0^L dt' [\delta(R_0(t,t'))\delta(R_{1,0}(t,t')) \cdots \delta(R_{1,q_1}(t,t'))] \cdots [\delta(R_{M,0}(t,t')) \cdots \delta(R_{M,q_M}(t,t'))] \times [\delta(R_1(t,t')) \cdots \delta(R_n(t,t'))]\right]^{N_0} \times \left[\int_0^L dt \int_0^L dt' [\delta(R_{1,0}(t,t'))\delta(R_{2,0}(t,t')) \cdots \delta(R_{2,q_2}(t,t'))] \cdots [\delta(R_{M,0}(t,t')) \cdots \delta(R_{M,q_M}(t,t'))][\delta(R_1(t,t')) \cdots \delta(R_n(t,t'))]\right]^{N_1} \cdots \left[\int_0^L dt \int_0^L dt' [\delta(R_{M,0}(t,t'))\delta(R_1(t,t')) \cdots \delta(R_n(t,t'))]\right]^{N_M} \quad (24)$$

The expressions for $\langle \bar{S}(k,p,p',n)\rangle_\lambda$ and $\langle \exp(-(1/kT) \times \bar{F}(n))\rangle_\lambda$ are of similar form. Both are averages over the probability distribution function $\Delta(\{R^T(s)\})$. For the structure factor term, the averaged quantity is $\exp(i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))$, and for the free energy term it is 1.

It is the probability distribution function $\Delta(\{R^T(s)\})$ which now summarizes the full history of the network and has replaced $p(m)$ in this capacity. The two aspects of the connectivity of the network—the initial chain and the subsequent cross-links—are readily apparent in $\Delta(\{R^T(s)\})$ and will be further brought out in the next section.

5. Introduction of Chemical Potentials. This section is not vital to the structure of the formulation or to subsequent calculation but is of use in specifically isolating the various contributions to the total network connectivity. It will also be shown (Appendix B) that within the context of the variational theorem applied to the calculation, a closer bound on the averaged quantities is found when the ideas of this section are used.

We introduce by means of the identity

$$[f(x)]^{N_J} = \frac{1}{2\pi i} \oint d\mu_J \frac{N_J!}{(\mu_J)^{M_J+1}} \exp(\mu_J f(x)) \quad (25)$$

a chemical potential μ_J at each stage of cross-linking into the expression for $\Delta(\{R^T(s)\})$. We then obtain

$$\Delta(\{R^T(s)\}) = \frac{1}{(2\pi i)^N} \oint d\mu_0 \frac{N_0!}{(\mu_0)^{N_0+1}} \oint d\mu_1 \frac{N_1!}{(\mu_1)^{N_1+1}} \cdots \oint d\mu_M \frac{N_M!}{(\mu_M)^{N_M+1}} \exp(-A + D_0 + D_1 + \cdots + D_M) \quad (26)$$

where

$$A = \exp\left[\frac{-3}{2l}\left[\sum_{J=1}^{M}\sum_{i=0}^{q_J}\int_0^L ds\, R'^2_{J,i} + \sum_{i=0}^{n}\int_0^L ds\, R'^2_i\right]\right] \quad (27)$$

and

$$D_J = \mu_J\Big[\int_0^L dt \int_0^L dt' [\delta(R_{J,0})\delta(R_{J+1,0}) \dots \delta(R_{J+1,q_{J+1}}) \dots \delta(R_{M,0}) \dots \delta(R_{M,q_M})\delta(R_1) \dots \delta(R_n)]\Big] \quad \text{for } J = 0, (M-1) \tag{28a}$$

$$D_J = \mu_J\Big[\int_0^L dt \int_0^L dt' [\delta(R_{J,0})\delta(R_1) \dots \delta(R_n)]\Big] \quad \text{for } J = M \tag{28b}$$

The term $\exp(-A + D_0 + D_1 + \dots + D_M)$ we now write as $D(\{R^T(s)\})$. All averages over $\Delta(\{R^T(s)\})$ can therefore, using eq 28, be expressed as averages over $D(\{R^T(s)\})$ followed by integration over the μ-contours. It is this second scheme we will adopt in all later sections for evaluating the structure factor and free energy.

This new probability distribution function, $D(\{R^T(s)\})$, explicitly factors out the various connectivities of the network.

The term A summarizes the initial connectivity of the uncross-linked polymer chain—it contains the Wiener measure connectivity alone. The D terms summarizes the connectivity of the cross-links—they contain the δ-function connectivity alone. Further each term D_J contains the full effect on the connectivity of the cross-links introduced at stage J (deformation λ_J).

We will exploit this factorization in the following sections in constructing a suitable approximant to $D(\{R^T(s)\})$ with which to evaluate the averages.

Evaluation Procedure for the Problem

As with the formulation, the evaluation scheme is based on the calculation of Edwards.[2] As there, we proceed in three stages. We first set up an approximate trial probability distribution function (pdf) which contains the essential physics of the true pdf. In the second stage we use a variational theorem to optimize this trial pdf and provide a lower bound for the average from which the free energy is calculated. In the third and final stage we evaluate this lower bound for the free energy term and use it to determine the free energy. At this stage also we determine the structure factor after evaluation of $\langle \bar{S}(k,p,p',n)\rangle_\lambda$ using the optimized pdf.

1. Construction of a Trial pdf. The full pdf is $D(\{R(s)\})$, where

$$D(\{R(s)\}) = \exp(-A + D_0 + \dots + D_M) \tag{29}$$

We shall replace this by a trial pdf of the form, in which $W_0, W_1, \dots, W_M$ are themselves trial functions,

$$W(\{R(s)\}) = \exp(-A + W_0 + \dots + W_M) \tag{30}$$

The motivation for modeling the true pdf in this way comes from the factorization of $D(\{R(s)\})$ into terms $D_0, D_1, \dots, D_M$, each of which characterizes the effects of a particular stage of cross-linking. We thus expect in any model function a similar separation $W_0, W_1, \dots, W_M$ in which W_J models the effects of cross-links added at stage J (deformation λ_J). The effect of the initial chain connectivity, the term A, is retained in the trial pdf.

The particular choice of trial function W to be taken comes from physical considerations.

The term

$$D_J = \mu_J\Big[\int_0^L dt \int_0^L dt' [\delta(R_{J,0})\delta(R_{J+1,0}) \dots \delta(R_{J+1,q_{J+1}}) \dots \delta(R_{M,0}) \dots \delta(R_{M,q_M})\delta(R_1) \dots \delta(R_n)]\Big] \tag{31}$$

involves an integral of a constraint on two specific arc points t,t' over all possible pairs of these arc points.

This integral of a correlated constraint we replace, in a mean-field treatment, by an integral over one arc position of a constraint on that single arc position.

The mean field is constructed on physical grounds to correspond to a simple affine transformation with fluctuations. The affine component of the mean field arises naturally from the mean-field approximation. For, in replacing the double arc point correlated constraints, D_J, by a mean-field single arc point constraint, we must constrain the single arc point absolutely in some way (i.e., without reference to other arc points). This absolute constraint is provided by affineness in the deformation. Fluctuations about this simplest of mean fields allow for microscopic nonaffineness in the deformation and are an important element in any trial mean field.

The affine component of the mean field is readily introduced by constructing an affine coordinate for each D_J,

$$X_{J,0} = \beta_J^{-1}(\lambda_J R_{J,0} + \lambda_{J+1}\sum_{i=0}^{q_{J+1}} R_{J+1,i} \dots + \lambda_M \sum_{i=0}^{q_M} R_{M,i} + \lambda \sum_{i=1}^{n} R_i) \tag{32}$$

where

$$\beta_J^2 = [\lambda_J^2 + (q_{J+1}+1)\lambda_{J+1}^2 + \dots + (q_M+1)\lambda_M^2 + n\lambda^2] \tag{33}$$

Coordinates orthogonal to this affine coordinate are then constructed from the initial $[1 + (q_{J+1} + 1) + \dots + (q_M + 1) + n]$ coordinates constrained by D_J. These new coordinates we term the fluctuation coordinates, of which there are $[(q_{J+1} + 1) + \dots + (q_M + 1) + n]$ for the term D_J.

Our mean field is then introduced as a harmonic constraint on these fluctuation coordinates. Specifically, if we denote the fluctuation coordinates for D_J as $u_{J,0} \dots u_{J,q_{J+1}}; u_{J+1,0} \dots u_{J+1,q_{J+2}}; \dots; u_{M-1,0} \dots u_{M-1,q_M}; u_{M,1} \dots u_{M,n}$, our trial function is

$$W_J = -\frac{l}{6}\omega_J^2 \int_0^L ds\ (\bar{u}_J^2 + \dots + \bar{u}_M^2) \tag{34}$$

where

$$\bar{u}_I = (u_{I,0}, u_{I,1}, \dots, u_{I,q_{I+1}}) \quad \text{for } 0 \le I \le M-1 \tag{35a}$$

$$\bar{u}_I = (u_{I,1}, \dots, u_{I,n}) \quad \text{for } I = M \tag{35b}$$

The parameter ω_J characterizes the strength of the fluctuations. For $\omega_J \to \infty$, we obtain a pure affine transformation. For ω_J finite, we obtain fluctuations about affineness. The values of the parameters ω_J will be determined in the next section when we find the optimized mean-field fit to our initial correlated constraints.

The u or fluctuation coordinates have here been constructed and labeled in a specific way. First of all we construct the affine coordinate Y_J for the group of δ-function constraints

$$\delta(R_{J,0}),\ \delta(R_{J+1,1}),\ \dots,\ \delta(R_{J+1,q_{J+1}})$$

as

$$Y_J = \alpha_J^{-1}(\lambda_J R_{J,0} + \lambda_{J+1}\sum_{i=1}^{q_{J+1}} R_{J+1,i}) \quad \text{for } 0 \le J \le M-1 \tag{36a}$$

$$Y_J = \alpha_J^{-1}(\lambda_J R_{J,0} + \lambda \sum_{i=1}^{n} R_i) \quad \text{for } J = M \tag{36b}$$

where

$$\alpha_J^2 = (\lambda_J^2 + q_{J+1}\lambda_{J+1}^2) \quad \text{for } 0 \le J \le M-1 \tag{37a}$$

$$\alpha_J^2 = (\lambda_M^2 + n\lambda^2) \quad \text{for } J = M \tag{37b}$$

The q_{J+1} coordinates orthogonal to this affine coordinate Y_J we label $u_{J,1}, ..., u_{J,q_{J+1}}$. It is not necessary to use an explicit transformation to construct these coordinates in terms of our initial coordinates. For it can be seen that these u coordinates appear in the trial function as an invariant of an orthogonal transformation, $u_{J,1}^2 + ... + u_{J,q_{J+1}}^2$. Rather we simply note that these u coordinates can be constructed.

We then note that the affine coordinates for each of the $D_0, ..., D_M$ constraints can be constructed in terms of this set of Y_J,

$$X_{J,0} = \gamma_J^{-1}(\alpha_J Y_J + \alpha_{J+1} Y_{J+1} + ... + \alpha_M Y_M) \quad (38)$$

where $\gamma_J^2 = (\alpha_J^2 + \alpha_{J+1}^2 + ... + \alpha_M^2)$.

The coordinates already constructed to be orthogonal to each of the Y_I provide some of the coordinates orthogonal to $X_{J,0}$. In particular $u_{J,1} ... ... u_{J,q_{J+1}}$; $u_{J+1,1} ... u_{J+1,q_{J+2}}$; ...; $u_{M,1} ... u_{M,n}$ are all orthogonal to $X_{J,0}$.

The further $M - J$ coordinates which must be constructed orthogonal to $X_{J,0}$ can now be explicitly represented in terms of the Y_J by an orthogonal transformation matrix A_{ij} such that

$$u_{i-2,0} = A_{ij} Y_j \qquad \text{for } 2 \le i \le M + 1 \quad (39)$$

where the new coordinates orthogonal to $X_{J,0}$ are $u_{J,0}, ..., u_{M-1,0}$.

A_{ij} is defined by

$$A_{ij} = \frac{\alpha_{j-1}\alpha_{i-2}}{\gamma_{i-1}\gamma_{i-2}} \qquad 2 \le i \le j \quad (40a)$$

$$A_{ij} = -\frac{\gamma_j}{\gamma_{j-1}}\delta_{i,j+1} \qquad i > j \quad (40b)$$

$$A_{ij} = \alpha_{j-1}/\gamma_0 \qquad i = 1 \quad (40c)$$

where $\delta_{i,k} = 1$ if $i = k$ and it is 0 otherwise.

The coordinate $A_{1j}Y_j$ is the affine coordinate for the whole network, $X_{0,0}$.

Using these specially constructed orthogonal coordinates u, we obtain the trial function W_J given in eq 35. The full trial pdf then becomes

$$W(\{u^T(s)\}) = \exp\left[\frac{-3}{2l}\int_0^L (X'_{0,0}{}^2 + \bar{u}'_0{}^2 + ... + \bar{u}'_M{}^2)\, ds\right] \exp\left[-\frac{l}{6}\sum_{J=0}^{M}\Omega_J{}^2 \int_0^L ds\, \bar{u}_J{}^2\right] \quad (41)$$

where

$$\Omega_J{}^2 = \sum_{I=0}^{J} \omega_I{}^2 \quad (42)$$

and

$$\{u^T(s)\} = \{X_{0,0}(s), \bar{u}_0(s), ..., \bar{u}_M(s)\} \quad (43)$$

In the second stage of this evaluation we introduce a variational theorem which allows us to optimize this trial function.

2. The Variational Theorem. For a real pdf $W(\{R^T(s)\})$ and a real functional $f(\{R^T(s)\})$ we have the inequality

$$\langle \exp f(\{R^T(s)\})\rangle_W \ge \langle 1\rangle_W \exp\frac{\langle f(\{R^T(s)\})\rangle_W}{\langle 1\rangle_W} \quad (44)$$

where $\langle\ \rangle_W$ denotes an average over $W(\{R^T(s)\})$.

We shall use this inequality as our variational theorem. We will construct the averages on the right-hand side (rhs) of the equation for our trial pdf $W(\{R^T(s)\})$ and then maximize the resultant rhs with respect to the variational parameters ω_J. The maximized result on the right-hand side we will take as our approximation for the average $\langle \exp f(\{R^T(s)\})\rangle_W$.

To make use of the above inequality for the average $\langle \exp(-(1/kT)\bar{F}(n))\rangle_\lambda$, we first express this average as an average over our trial pdf,

$$\left\langle \exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda = \frac{1}{(2\pi i)^N}\oint d\mu_0 \frac{N_0!}{(\mu_0)^{N_0+1}}\oint d\mu_1 \frac{N_1!}{(\mu_1)^{N_1+1}} ... \oint d\mu_M \frac{N_M!}{(\mu_M)^{N_M+1}} \langle \exp\sum_{I=0}^{M}(D_I - W_I)\rangle_W \quad (45)$$

In the notation introduced above we now have

$$f(\{R^T(s)\}) = \sum_{I=0}^{M}[D_I(\{R^T(s)\}) - W_I(\{R^T(s)\})] \quad (46)$$

Upon use of the inequality and subsequent evaluation of the contour integrals we then have

$$\left\langle \exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda \ge \langle 1\rangle_W \prod_{I=0}^{M}\left[\frac{\langle D_I\rangle_W}{\langle I\rangle_W}\right]^{N_I} \exp\left(-\frac{\langle W_I\rangle_W}{\langle 1\rangle_W}\right) \quad (47)$$

The various averages on the rhs of this equation we determine in the next section where we perform the variational procedure for constructing the optimum trial pdf. This final pdf we use to evaluate the free energy and structure factor.

3. Determination of Free Energy and Structure Factor. We here evaluate the rhs of eq 47 as a prelude to constructing our optimum pdf.

We first write each of the averages there in terms of the affine coordinates $X_{J,0}$ and orthogonal coordinates $\bar{u}_J$ constructed earlier. We have

$$\langle 1\rangle_W = \int \delta u^T(s)\, W(\{u^T(s)\}) \quad (48)$$

$$\langle D_J\rangle_W = \int \delta u^T(s)\, W(\{u^T(s)\}) \times \left[\int_0^L dt \int_0^L dt' [\delta(\bar{u}_J) ... \delta(\bar{u}_M)\delta(X_{J,0})]\right] \quad (49)$$

$$\langle W_J\rangle = \int \delta u^T(s)\, W(\{u^T(s)\})\left[-\frac{l}{6}\omega_J{}^2\int_0^L ds\, (\bar{u}_J{}^2 + ... + \bar{u}_M{}^2)\right] \quad (50)$$

where $W(\{u^T(s)\})$ is defined in eq 41. We further substitute in eq 49

$$X_{J,0} = \gamma_J\left[\frac{X_{0,0}}{\gamma_0} + \sum_{i=0}^{(J-1)}\frac{\alpha_i}{\gamma_{i+1}\gamma_i}u_{i,0}\right] \quad (51)$$

so that

$$\langle D_J\rangle_W = \frac{\gamma_0}{\gamma_J}\int db_0 \int db_1 ... \int db_{J-1} \int \delta u^T(s)\, W(\{u^T(s)\}) \times \left[\int_0^L dt \int_0^L dt' \left[\delta(u_J) ... \delta(u_M)\delta(X_{0,0} - b_0) \times \delta\left(\frac{\gamma_0\alpha_0}{\gamma_1\gamma_0}u_{0,0} - b_1\right) ... \delta\left(\frac{\gamma_0\alpha_{J-2}}{\gamma_{J-1}\gamma_{J-2}}u_{J-2,0} - b_{J-1}\right) \times \delta\left(\frac{\gamma_0\alpha_{J-1}}{\gamma_J\gamma_{J-1}}u_{J-1,0} - \sum_{i=0}^{(J-1)} b_i\right)\right]\right] \quad (52)$$

where we have written $\delta(X_{J,0})$ as a product of δ-functions using

$$\delta(x-y) = \int dz\ \delta(x-z)\delta(z-y) \tag{53}$$

It will be seen that each of eq 48, 50, and 52 factor out as products of integrals over each component of $u^T(s)$. Each of these integrals has been evaluated elsewhere[2] and the results are merely summarized here:

$$\int \delta X_{0,0} \exp\left(\frac{-3}{2l}\int_0^L ds\ X'^2_{0,0}\right) = \gamma_0 \tag{54}$$

$$\int \delta u_J \exp\left[\frac{-3}{2l}\int_0^L ds\ \bar{u}'^2_J - \frac{l}{6}\Omega_J^2\int_0^L ds\ \bar{u}_J^2\right] = \frac{1}{\Omega_J^{1/2}}\exp\left(-\frac{l}{6}L\Omega_J\right) \tag{55}$$

$$\int \delta u_J \delta(\bar{u}_J - b) \exp\left[\frac{-3}{2l}\int_0^L ds\ \bar{u}'^2_J - \frac{l}{6}\Omega_J^2\int_0^L ds\ \bar{u}_J^2\right] = \exp\left(-\frac{l}{6}L\Omega_J + \frac{b^2\Omega_J}{2}\right) \tag{56}$$

$$\int \delta X_{0,0}\delta(X_{0,0} - b) \exp\left(\frac{-3}{2l}\int_0^L ds\ X'^2_{0,0}\right) = \gamma_0^{-1} \tag{57}$$

$$\int \delta u_J\left(-\frac{l}{6}\Omega_J^2\int_0^L ds\ \bar{u}_J^2\right)\exp\left[\frac{-3}{2l}\int_0^L ds\ \bar{u}'^2_J - \frac{l}{6}\Omega_J^2\int_0^L ds\ \bar{u}_J^2\right] = \frac{l}{12}L\Omega_J\Omega_J^{1/2}\exp\left(\frac{l}{6}L\Omega_J\right) \tag{58}$$

On substitution of the results of these integrals into eq 48, 50, and 53 and evaluation of the rhs of eq 47 we find

$$\left\langle \exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda \geq \gamma_0\left(\frac{\gamma_0}{\gamma_M}\right)^{N_M}\exp[(\tfrac{1}{2}n)\times [(\sum_{K=0}^{M} N_K - 1)\ln\Omega_M - (l/6)L\Omega_M]]\prod_{I=0}^{M-1}\left(\frac{\gamma_0}{\gamma_I}\right)^{N_I}\times \exp\left[\tfrac{1}{2}(q_{I+1}+1)\left[(\sum_{K=0}^{I} N_K - 1)\ln\Omega_I - \frac{l}{6}L\Omega_I\right]\right] \tag{59}$$

The rhs of this inequality we now maximize with respect to the parameters Ω_J (or ω_J). At $n = 0$ and $q_i = -1$ for $i = 1$ to M this gives

$$\Omega_J = \frac{6}{lL_{tot}}\sum_{K=0}^{J} N_K, \qquad \omega_J = \frac{6}{lL_{tot}}(N_J^2 + N_J\sum_{K=0}^{(J-1)} N_K) \tag{60}$$

Such a result is in accord with the adoption of the trial function form of eq 30 in so far as $W_i \to 0$ for $N_i \to 0$. In the spirit of the variational calculation one might enlarge the variational parameter space for W to allow for replica[4] or stage[3,9] symmetry breaking. When such allowance is made the optimized form reduces to the replica and stage symmetric form of eq 30 and 60. Any symmetries or simple physical forms found for quantities averaged over the trial function are not artifacts of a trial potential restricted to exhibit symmetry. Such symmetry actually exists.

It has been shown[4] that for the initial rubber elasticity calculation, the trial pdf need only be evaluated at $n = 0$. For this problem it need only be evaluated at $q_i = -1$ for $i = 1$ to M and $n = 0$. Thus we have for our optimum trial pdf:

$$\bar{W}(\{u^T(s)\}) = \exp\left[\frac{-3}{2l}\int_0^L (X'^2_{0,0} + \bar{u}'^2_0 + \ldots \bar{u}'^2_M)\ ds\right]\exp\left[-\frac{6}{lL_{tot}^2}\sum_{J=0}^{M}(\sum_{K=0}^{J} N_K^2)\int_0^L ds\ \bar{u}_J^2\right] \tag{61}$$

To determine the free energy we now take the best estimate of the lhs of the inequality, eq 47, to be the maximum value of the rhs of the same equation. Specifically, we evaluate the rhs for $W = \bar{W}$, that is we use eq 59 and 60. Differentiation of this result with respect to n, in line with eq 13, gives the free energy of deformation to be

$$F(\lambda) = \tfrac{1}{2}k_BT\sum_{J=0}^{M} N_J\left[\frac{\lambda}{\lambda_J}\right]^2 \tag{62}$$

or restoring the true matrix nature of λ,

$$F(\lambda) = \tfrac{1}{2}k_BT\sum_{i=0}^{M} N_i\ \mathrm{Tr}\ (\lambda^T(\lambda_i^T\lambda_i)^{-1}\lambda) \tag{62a}$$

To determine the structure factor we again use the optimized pdf $\bar{W}$. We first note

$$\langle\bar{S}(k,p,p',n)\rangle_\lambda = \frac{1}{(2\pi i)^N}\oint d\mu_0\frac{N_0!}{(\mu_0)^{N_0+1}}\oint d\mu_1\frac{N_1!}{(\mu_1)^{N_1+1}}\ldots \oint d\mu_M\frac{N_M!}{(\mu_M)^{N_M+1}}\langle\exp\sum_{I=0}^{M}(D_I - W_I)\times \exp[i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))]\rangle_W \tag{63}$$

We now use a preaveraging approximation in writing

$$\langle\exp\sum_{I=0}^{M}(D_I - W_I)\exp[i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))]\rangle_{\bar{W}}$$

as

$$\langle\exp\sum_{I=0}^{M}(D_I - W_I)\rangle_{\bar{W}}\langle\exp[i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))]\rangle_{\bar{W}} \tag{64}$$

Such an approximation is essentially a restatement of the arc position invariance adopted in the trial function[5]—the effect of inhomogeneity has recently been considered by Ball and Higgs.[10] On substitution of this approximate form in eq 63 and subsequent performance of the contour integrations we find

$$\langle\bar{S}(k,p,p',n)\rangle_\lambda = \langle\exp[i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))]\rangle_{\bar{W}}\left\langle\exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda \tag{65}$$

We also note that at $k = 0$,

$$\langle\bar{S}(k,p,p',n)\rangle_\lambda = 1 \tag{66}$$

This we use as our normalization condition, leaving

$$\langle\bar{S}(k,p,p',n)\rangle_\lambda = \langle\exp[i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))]\rangle_{\bar{W}} \tag{67}$$

This expression for $\langle\bar{S}(k,p,p',n)\rangle_\lambda$ is the same as used by Warner and Ewards.[5]

As earlier with the free energy evaluation we first express the terms involved in eq 65 as functions of $u^T(s)$. The only new term to be so expressed is $\exp[i\mathbf{k}\cdot(\mathbf{R}_1(p) - \mathbf{R}_1(p'))]$. We note that

$$X_1 = \frac{\lambda Y_M}{\alpha_M} + \sum_{i=1}^{n} a_i u_{M,i} \tag{68}$$

where

$$\sum_{i=1}^{M} a_i^2 = 1 - \frac{\lambda^2}{\alpha_M^2} \tag{69}$$

(Note the full transformation, that is the particular values of a_i, need not be specified.) We have further that

$$Y_M = [A_{1,M+1}X_{0,0} + \sum_{i=0}^{(M-1)} A_{i+2,M+1}u_{i,0}] \tag{70}$$

so that

$$X_1 = \frac{\lambda}{\alpha_M}[A_{1,M+1}X_{0,0} + \sum_{i=0}^{(M-1)} A_{i+2,M+1}u_{i,0}] + \sum_{i=1}^{n} a_i u_{M,i} \quad (71)$$

$$X_1 = \frac{\lambda}{\gamma_0}X_{0,0} + \sum_{i=0}^{(M-1)} \frac{\alpha_i}{\gamma_i\gamma_{i+1}}u_{i,0} + \sum_{i=1}^{n} a_i u_{M,i} \quad (72)$$

Usage of this substitution for X_1 finally leads to

$$\langle \bar{S}(k,p,p',n)\rangle_\lambda = A\int \delta X_{0,0} \times \exp\left[\frac{-3}{2l}\int_0^L ds\, X'_{0,0}{}^2 + \frac{\lambda}{\gamma_0} i\mathbf{k}\cdot(\mathbf{X}_{0,0}(p) - \mathbf{X}_{0,0}(p'))\right] \times \prod_{i=0}^{M-1}\int \delta u_{i,0} \exp\left[\frac{-3}{2l}\int_0^L ds\, u'_{i,0}{}^2 - \frac{l}{6}\Omega_i^2 \times \int_0^L ds\, u_{i,0}{}^2 + \frac{\lambda\alpha_i}{\gamma_i\gamma_{i+1}} i\mathbf{k}\cdot(\mathbf{u}_{i,0}(p) - \mathbf{u}_{i,0}(p'))\right] \times \prod_{i=1}^{n}\int \delta u_{M,i} \exp\left[\frac{-3}{2l}\int_0^L ds\, u'_{M,i}{}^2 - \frac{l}{6}\Omega_M{}^2\int_0^L ds\, u_{M,i}{}^2 + a_i[i\mathbf{k}\cdot(\mathbf{u}_{M,i}(p) - \mathbf{u}_{M,i}(p'))]\right] \quad (73)$$

where A is independent of $\mathbf{k}$. The initial term, A, in eq 73 we need not evaluate—again it can be removed by normalization so that $\langle \bar{S}(0,p,p',n)\rangle_\lambda = 1$. The evaluation of the other terms has been done elsewhere[5] and as before we merely summarize the results:

$$\int \delta X_{0,0} \exp\left[\frac{-3}{2l}\int_0^L ds\, X'_{0,0}{}^2 + \frac{\lambda}{\gamma_0} i\mathbf{k}\cdot(\mathbf{X}_{0,0}(p) - \mathbf{X}_{0,0}(p'))\right] = \exp\left[-\frac{k^2\lambda^2}{\gamma_0{}^2}\frac{l}{6}|p - p'|\right] \quad (74)$$

$$\int \delta u \exp\left[\frac{-3}{2l}\int_0^L ds\, u'^2 - \frac{l}{6}\Omega^2\int_0^L ds\, u^2 + Ui\mathbf{k}\cdot(\mathbf{u}(p) - \mathbf{u}(p'))\right] = \exp[-k^2U^2 f(\Omega,p,p')] \quad (75)$$

where

$$f(\Omega,p,p') = \frac{1}{2\Omega}\left(1 - \exp\left(-\frac{1}{3}l\Omega|p - p'|\right)\right) \quad (76)$$

Substitution of these results finally leaves

$$\langle \bar{S}(k,p,p',n)\rangle_\lambda = \exp\left[-\frac{k^2\lambda^2}{\gamma_0{}^2}\frac{l}{6}|p - p'|\right] \exp\left[-k^2\sum_{i=0}^{M}\frac{\alpha_i{}^2\lambda^2}{\gamma_i{}^2\gamma_{i+1}{}^2} f(\Omega_i,p,p')\right] \quad (77)$$

The structure factor is now directly reconstructed from eq 77 by using eq 15:

$$S(\lambda) = \frac{1}{L^2}\int_0^L dp \int_0^L dp' \lim_{n\to 0}\langle \bar{S}(k,p,p',n)\rangle_\lambda \quad (78)$$

This gives

$$S(\lambda) = \frac{1}{L^2}\int_0^L dp \int_0^L dp'\, S(\lambda,p,p') \quad (79)$$

where

$$S(\lambda,p,p') = \exp\left[-k^2\lambda^2\frac{l}{6}|p - p'|\right] \times \exp\left[-k^2\sum_{i=0}^{(M-1)}\frac{(\lambda_i{}^2 - \lambda_{i+1}{}^2)\lambda^2}{\lambda_i{}^2\lambda_{i+1}} f(\Omega_i,p,p')\right] \times \exp\left[-k^2\frac{(\lambda_M{}^2 - \lambda^2)\lambda^2}{\lambda_M{}^2\lambda^2} f(\Omega_M,p,p')\right] \quad (80)$$

As with eq 60a we now restore the true matrix nature of λ to give

$$S(\lambda,p,p') = \exp\left[-\left[k^2 f(\Omega_M,p,p') + \left[\frac{l}{6}|p - p'| - f(\Omega_0,p,p')\right] \mathrm{Tr}\,(\mathbf{k}\lambda^{\mathrm{T}}\lambda\mathbf{k}) + \sum_{i=1}^{M} \mathrm{Tr}\,(\mathbf{k}\lambda^{\mathrm{T}}(\lambda_i{}^{\mathrm{T}}\lambda_i)^{-1}\lambda\mathbf{k})[f(\Omega_{i-1},p,p') - f(\Omega_i,p,p')]\right]\right] \quad (80a)$$

Equations 62 and 80 give the results for the deformation dependence of the free energy and structure factor for an addition network and are the basic results of this paper. In the next section we will discuss the implications of these results.

Discussion and Conclusions

We note first that when the number of stages of cross-linking is just 1 (that is, simply the construction of the basis network) the expressions for $F(\lambda)$ and $S(\lambda)$ reduce to those of Edwards[2] and Warner and Edwards,[5] respectively. We further note that the free energy and the structure factor have the correct limits as $N_i \to 0$; that is, the terms in $\lambda^2/\lambda_i{}^2$ disappear in this limit. These limits provide a ready check on the results.

The deformation free energy $F(\lambda)$, eq 62, shows a simple additive structure,

$$F(\lambda) = \sum_{i=0}^{M} B_i\frac{\lambda^2}{\lambda_i{}^2}, \qquad B_i = kTN_i/2 \quad (81)$$

in which the ith term is the same as the deformation free energy of a basis network constructed at λ_i (relative to "1") with N_i cross-links. This result substantiates the generalization of Andrews and Tobolsky's two-network hypothesis, that an addition network with $1 + M$ stages of cross-linking should behave as $1 + M$ independent networks (Figure 1). This hypothesis has previously been shown[6,7] to hold for the "classical" model of elasticity in which cross-links are viewed as localizing polymer segments in space rather than to other segments of polymer.

The deformation structure factor $S(\lambda,p,p')$, eq 80, is of the form

$$\exp\left[-k^2\left(A + \sum_{i=0}^{M} B_i\frac{\lambda^2}{\lambda_i{}^2}\right)\right] \quad (82)$$

for which $A = f(\Omega_M,p,p')$, $B_0 = (l|p - p'|/6 - f(\Omega_0,p,p')$, and $B_i = f(\Omega_{i-1},p,p') - f(\Omega_i,p,p')$ for $i \geq 1$.

Since $f(\Omega,p,p')$ is a positive definite function which is monotonically decreasing with Ω and has maximum value $(l/6)|p - p'|$, each of the terms A, B_i is positive as required. The sum of these terms $A + \sum B_i$ gives $(l/6)|p - p'|$, the free-chain Debye term, again as required.

The form of the exponent of eq 82 does not exhibit the simple additive structure of eq 81 in which B_i is the (normalized) value found for a network constructed at deformation λ_i with N_i cross-links. For such to be the case

$$B_i = \frac{N_i}{N_{\mathrm{tot}}}\left[\frac{l}{6}|p - p'| - f(\omega_i',p,p')\right] \quad (83)$$

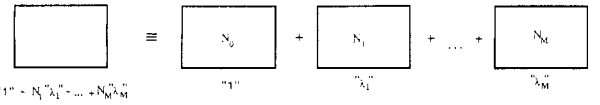

Figure 1. Additive independent network hypothesis. A network constructed in $M + 1$ stages (label i) by addition of N_i cross-links at deformation "λ_i" behaves as $M + 1$ independent basis networks. Each stage i provides one such network constructed from N_i cross-links at equilibrium deformation λ_i. The contribution from each stage and network is simply additive.

with $A = f(\Omega_M,p,p')$ and where $\omega_i' = 6N_i/L_i l = \Omega_M$ and L_i is the (average) length in the ith independent network, $L_i = N_i L_{tot}/N_{tot}$. N_{tot} is the total number of cross-links added, $N_{tot} = (N_0 + N_1 + ... + N_M)$. The normalization factor $N_i/N_{tot} = L_i/L_{tot}$ weights the contribution of the ith network by the amount of such network and ensures the "1-network" result for $\lambda_i = 1\ \forall\ i$.

The correctness of the form for B_i, eq 82, over the simple (additive) independent network result of eq 83 shows up most clearly in the Guinier regime, $k \to 0$ for which $S(k,L) = 1 - k^2R_g^2(L)/3$ where R_g is the radius of gyration of the section of chain of length L. For such a limit,

$$6R_g^2 = G(\Omega_M) + [Ll - G(\Omega_0)]\lambda^2 + \sum_{i=1}^{M}[G(\Omega_{i-1}) - G(\Omega_i)]\frac{\lambda^2}{\lambda_i^2} \tag{84}$$

for eq 82 and

$$6R_g^2 = G(\Omega_M) + [Ll - G(\Omega_M)]\sum_{i=0}^{M}\frac{N_i}{N_{tot}}\frac{\lambda^2}{\lambda_i^2} \tag{85}$$

for the additive independent network result where

$$G(\Omega_j) = \frac{9}{\Omega_j}\left[1 - \frac{6}{Ll\Omega_j} + \frac{18}{(Ll\Omega_j)^2}\left(1 - \exp\left(-\frac{Ll\Omega_j}{3}\right)\right)\right] \tag{86}$$

For $Ll\Omega_M \ll 1$, that is $L \ll L_{xl} = L_{tot}/N_{tot}$, where L_{xl} is the average intercross-link arc length, $G(\Omega_j) = Ll(1 - Ll\Omega_j/12)$, and eq 84 and 85 both give

$$6R_g^2/Ll = \left[(1 - \tfrac{1}{2}L/L_{xl}) + \tfrac{1}{2}L/L_{xl}\sum_{i=0}^{M}\frac{\lambda^2}{\lambda_i^2}\frac{N_i}{N_{tot}}\right] \tag{87}$$

For $Ll\Omega_0 \gg 1$, that is $L \gg L_{tot}/N_0 > L_{xl}$, $G(\Omega_j) = 9/\Omega_j$ and eq 84 give

$$6R_g^2/Ll = \left[3L_{xl}/2L + (1 - 3L_{xl}N_{tot}/2LN_0)\lambda^2 + \frac{3L_{xl}}{2L}\sum_{i=1}^{M}\frac{\lambda^2}{\lambda_i^2}\left[\frac{1}{N_{tot}^{i-1}} - \frac{1}{N_{tot}^{i}}\right]\right] \tag{88}$$

where $N_{tot}^{i} = (N_0 + N_1 + ... + N_i)$. The additive independent network gives

$$6R_g^2/Ll = \left[3L_{xl}/2L + (1 - 3L_{xl}/2L)\sum_{i=0}^{M}\frac{\lambda^2}{\lambda_i^2}\frac{N_i}{N_{tot}}\right] \tag{89}$$

We note that for $L < L_{xl}$ the additive independent network result gives the same form as the actual result. This is to be expected since we know that for a Gaussian network,

$$F(\lambda) \propto \sum\langle R_{g,seg}^2\rangle/lL_{seg} \sim N_{tot}\langle R_{g,xl}^2\rangle/lL_{xl} \tag{90}$$

which with the form of eq 87 reproduces eq 81.

For $L \gg L_{xl}N_{tot}/N_0$ the additive independent network suggests $6R_g^2/Ll = \sum_{i=0}^{M}(\lambda^2/\lambda_i^2)(N_i/N_{tot})$, an averaged affine result over the independent networks, while eq 88

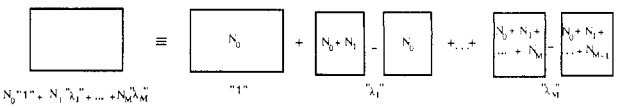

Figure 2. Generalized independent network hypothesis. A network constructed in $M + 1$ stages (label i) by addition of N_i cross-links at deformation "λ_i" behaves as $2M + 1$ independent basis networks. Each stage i (except the zeroth, which provides one) provides two such networks each constructed at equilibrium deformation λ_i, the first with $N_{tot}^{i} = N_0 + N_1 + ... + N_i$ cross-links, the second with $N_{tot}^{i} + N_i$ cross-links. The contribution from each stage i is the difference between the former and latter of these two networks.

gives $6R_g^2/Ll = \lambda^2$, an affine result for the original network. That this latter result is not an artifact of the trial pdf, eq 41, or any other elements of the calculational procedure may be verified by its agreement with a "classical" calculation which does not rely on such a trial. Consider (Appendix C) the radius of gyration of a chain of length L with N_0 classical cross-links, separated along the arc by $L/(N_0 - 1)$, added at strain "1" and N_1 cross-links, separated by $L/(N_0 + N_1 - 1)$, added at strain "λ_1", the latter added according to eq 4. The method of calculation for R_g^2 straightforwardly follows that of Ullman[8] (for f, the functionality, $\to\infty$) with the results from Scanlan[6] and gives

$$6R_g^2/Ll = [1/(N_0 + N_1 - 1) - 1/(N_0 + N_1 - 1)^2] + [1 - 1/(N_0 - 1) + (1/2)/(N_0 - 1)^2]\lambda^2 + [1/(N_0 - 1) - (1/2)/(N_0 - 1)^2 - 1/(N_0 + N_1 - 1) + 1/(N_0 + N_1 - 1)^2]\lambda^2/\lambda_1^2 \tag{91}$$

As N_0 increases so that $L \gg L_{tot}/N_0$, the condition for eq 88, the chain behaves affinely with respect to the original equilibrium deformation "1". In fact the whole functional form of eq 91 is the same as that of eq 81 (or eq 88) with the coefficient of λ^2 dependent on N_0, the coefficient of "1" dependent on $(N_0 + N_1)$, and the coefficient of λ^2/λ_1^2 the difference of these two.

As a conclusion we may state that the simple additive structure of the free energy does not apply for the structure factor in general but does for $L \ll L_{x1}$. Such a conclusion suggests a more general independent network result, different from the simple additive one, might apply. With this is mind we note that we may rewrite B_i of eq 82 as

$$B_i = \left[\frac{l}{6}|p - p'| - f(\Omega_i,p,p')\right] - \left[\frac{l}{6}|p - p'| - f(\Omega_{i-1},p,p')\right] \tag{92}$$

and A as $f(\Omega_0) + \sum_{i=1}^{M}(f(\Omega_i) - f(\Omega_{i-1}))$ so that the exponent of eq 82 has the form

$$S_0^{N_0} + (S_1^{N_0+N_1} - S_1^{N_0}) + ... + (S_M^{N_0+N_1+...+N_M} - S_M^{N_0+N_1+...+N_{M-1}})$$

where S_i^N is the value for a simple network of length L constructed at deformation λ_i with N cross-links,

$$S_i^N = f(\Omega) + \left[\frac{l}{6}|p - p'| - f(\Omega,p,p')\right]\lambda^2/\lambda_i^2, \qquad \Omega = 6N/lL_{tot} \tag{93}$$

The form (92) suggests the contribution from the ith "independent" network is a term

$$B_i = B_i^{N_0+N_1+...+N_i} - B_i^{N_0+N_1+...+N_{i-1}} \tag{94}$$

where B_i^N is the contribution from a simple network of length L_{tot} constructed at equilibrium deformation λ_i with N cross-links. The simple additive form of Figure 1 should be replaced by Figure 2 where each additional term has the form of eq 94. Such a generalization of the inde-

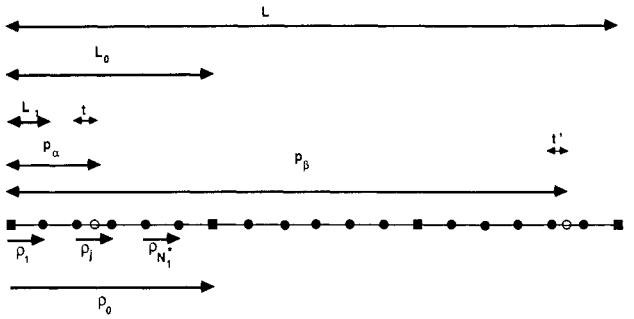

Figure 3. Classical two-stage network. A chain of length L with N_0 zeroth (■) and N_1 first-stage cross-links (●) evenly distributed. Each section of chain length $L_0 = L/(N_0 - 1)$ between zeroth-stage cross-links is divided into $N_1^* + 1$ segments, $N_1^* = N_1/(N_0 - 1)$, each of length $L_1 = L/(N_0 + N_1 - 1)$. The arc points p_α and $p_{\beta'}$ are located in the αth and βth zeroth-stage segments, $1 \le \alpha, \beta \le (N_0 - 1)$; $\alpha = 1$, $\beta = 3$ above. ρ_j denote spatial separation of segments; ρ_0 for the zeroth-stage segment, ρ_j, $j = 1, N_1^*$ for N_1^* first stage segments.

pendent network result from Figure 1 to Figure 2 clearly includes the simpler result, eq 81, for the free energy since $B_i^N = {}^1/_2kTN$ so that B_i from eq 94 $= {}^1/_2kTN_i$.

The final conclusion upon the results for the free energy, eq 81 or 62, and the structure factor, eq 82 or 80a, is therefore to suggest that both may be interpreted in terms of a generalized independent network hypothesis (summarized in Figure 2), perhaps applicable to all (averaged) deformation-dependent properties. Equation 87 suggests that the additive independent network hypothesis is sufficient on length scales less than the average cross-link spacing but on larger scales, eq 88 and 89, correlation effects between intercross-link segments cause it to break down.

A particular feature new to the generalized network hypothesis is its prediction of a dependence on the sequence or order of construction deformations, a dependence absent in the original hypothesis under which the order of cross-linking deformations is unimportant.

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Appendix A

It has been stated in the text that the approximation used in eq 7 is valid at the level of approximation used in the calculation. By this we mean that the approximations subsequently used lead to the same result regardless of whether or not this approximation is explicitly used.

If we use the exact probability distribution function without this approximation we find the probability distribution Δ is now given by

$$\Delta(\{R^T(s)\}) = \Delta_0(\{R^T(s)\})\left[\int_0^L dt \int_0^L dt' \delta(R_{M,1}(t,t'))\right] \cdots \left[\int_0^L dt \int_0^L dt' \delta(R_{M,q_M}(t,t'))\right]^{N_M} \times \left[\int_0^L dt \int_0^L dt' \delta(R_{M-1,1}(t,t'))\right]^{N_{M-1}} \cdots \left[\int_0^L dt \int_0^L dt' \delta(R_{M-1,q_{M-1}}(t,t'))\right]^{N_{M-1}} \cdots \left[\int_0^L dt \int_0^L dt' \delta(R_{1,1}(t,t'))\right]^{N_1} \cdots \left[\int_0^L dt \int_0^L dt' \delta(R_{1,q_1}(t,t'))\right]^{N_1} \quad (A.1)$$

where Δ_0 is given by eq 24 and is the pdf when the approximation (7) is made.

We note that each of the extra terms in the brackets provides a constraint on just one replica coordinate. Introduction of a chemical potential for each of these extra terms and subsequent construction of a trial function, along the lines on which eq 34 is constructed, thus give the trial function to be the same as eq 34. The extra terms do not localize further the fluctuation coordinates. Useage of the variational theorem and performance of the contour integrals finally lead to

$$\left\langle \exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda \ge \langle 1\rangle_W \prod_{I=0}^{M}\left[\frac{\langle D_I\rangle_W}{\langle 1\rangle_W}\right]^{N_I} \times \exp\left[-\frac{\langle W_I\rangle_W}{\langle 1\rangle_W}\right] \cdots \prod_{J=1}^{M}\left[\left\langle \int_0^L dt \int_0^L dt' \delta(R_{J,1}(t,t'))\right\rangle_W\right]^{q_J N_J} \quad (A.2)$$

(note that $\langle \int_0^L dt \int_{L0} dt' \delta(R_{J,i}(t,t'))\rangle_W$ is independent of i). The rhs of this inequality is the rhs of eq 47 multiplied by

$$\prod_{J=1}^{M}\left[\left\langle \int_0^L dt \int_0^L dt' \delta(R_{J,1}(t,t'))\right\rangle_W\right]^{q_J N_J}$$

Each of the terms in this product is given by

$$\left\langle \int_0^L dt \int_0^L dt' \delta(R_{J,1}(t,t'))\right\rangle_W = 1/\lambda_J \quad (A.3)$$

Thus we finally have as the revised version of eq 47 without using eq 7

$$\left\langle \exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda \ge \langle 1\rangle_W \prod_{I=0}^{M}\left[\frac{\langle D_I\rangle_W}{\langle 1\rangle_W}\right]^{N_I} \exp\left[-\frac{\langle W_I\rangle_W}{\langle 1\rangle_W}\right] \cdots \prod_{J=1}^{M}[1/\lambda_J]^{q_J N_J} \quad (A.4)$$

The difference between this and eq 47 is the multiplicative term $\prod_{J=1}^{M}(1/\lambda_J)^{q_J N_J}$. This term depends neither on n nor Ω. As such, it contributes neither to the optimization of Ω nor to the deformation free energy. It merely contributes a multiplicative factor which is removed by renormalization.

Appendix B

Were one to proceed without the introduction of a chemical potential then as with the previous appendix eq 47 would be revised. The procedure for constructing the inequality (47) would involve replacing the average over Δ by an average over W without any subsequent contour integration. This would lead to

$$\left\langle \exp\left(-\frac{1}{kT}\bar{F}(n)\right)\right\rangle_\lambda \ge \langle 1\rangle_W \prod_{I=0}^{M}\left[\exp\frac{\langle \ln D_I\rangle_W}{\langle 1\rangle_W}\right]^{N_I} \exp\left[-\frac{\langle W_I\rangle_W}{\langle 1\rangle_W}\right] \quad (B.1)$$

as the revised form of eq 47.

We note that the only difference between (B.1) and eq 47 is that $\exp[\langle \ln D_I\rangle_W/\langle 1\rangle_W]$ has replaced $\exp[\ln \langle D_I\rangle_W/\ln \langle 1\rangle_W]$ (or $\langle D_I\rangle_W/\langle 1\rangle_W$). We further note that use of eq 44 gives

$$\frac{\ln \langle D_I \rangle_W}{\ln \langle 1 \rangle_W} \geq \frac{\langle \ln D_I \rangle_W}{\langle 1 \rangle_W} \tag{B.2}$$

Use of this inequality shows that the rhs of eq B.1 ≥ the rhs of eq 47 and so the rhs of eq 47 always provides a better upper bound on the true average to be evaluated. Introduction of the chemical potential provides this better bound.

Appendix C

The form of (82) may be reproduced by a "classical" calculation. Consider a network of length L constructed with N_0 cross-links at strain "1" and N_1 at strain "λ_1". Each classical cross-link is taken to bind an arc point of the network to a point in space and be affinely moved under strain. For ease of calculation cross-links are taken to be uniformly distributed (Figure 3), zeroth-stage cross-links separated by $L_0 = L/(N_0 - 1)$ and first stage by $L_1 = L/(N_0 + N_1 - 1)$. The number of first-stage cross-links per zeroth-stage segment (section of chain between consecutive zeroth-stage cross-links) is $N_1^* = N_1/(N_0 - 1)$.

The probability distribution function which summarizes the configuration of the network and is akin to $\Delta(\{R^T(s)\})$, eq 24, is the distribution function for positions of the cross-link points. Using ρ to denote an affine displacement at strain λ ($\rho \rightarrow \rho/\lambda$ for strain "1") we clearly have after the zeroth-stage cross-linking

$$P(\rho_0) = G_0(\rho_0, \lambda^2 L_0) \tag{C.1}$$

and after the first-stage cross-linking

$$P(\rho_1,...,\rho_{N_1}^*|\rho_0) = [G_0(\rho_1,\lambda^2 L_1/\lambda_1^2) \ ... \ G_0(\rho_{N_1}^*,\lambda^2 L_1/\lambda_1^2) G_0(\rho_0 - \rho_1 - ... - \rho_{N_1}^*,\lambda^2)(L_0 - N_1^* L_1)/\lambda_1^2]/[G_0(\rho_0,\lambda^2 L_0/\lambda_1^2)] \tag{C.2}$$

for sections of chain between zeroth-stage cross-links. Sections of chain between different zeroth-stage cross-links are uncorrelated with one another. G_0 here is given by

$$G_0(\rho,s) = (3/(2\pi ls))^{3/2} \exp(-3\rho^2/2ls) = (1/\lambda) G_0(\rho/\lambda, s/\lambda^2) \tag{C.3}$$

Equation C.2 is the equivalent of (5) for $M = 1$ and for "m_i", the topology of cross-links added at stage i, specified by ρ_0 for $i = 0$ and ρ_1, ..., $\rho_{N_1}^*$ for $i = 1$, N_1^*. The number of configurations of a segment, separation $\rho\lambda/\lambda_1$, and arc length s_i are proportional to $G_0(\rho\lambda/\lambda_1, s_i) \propto G_0(\rho, s_i\lambda^2/\lambda_1^2)$.

Averaging $S(k,p,p') = e^{i\mathbf{k}\cdot(\mathbf{R}(p)-\mathbf{R}(p'))}$ over (C.1) and (C.2) with uncorrelated zeroth stage sections gives

$$\langle S(k,p_\alpha,p_\beta') \rangle = G_0(\mathbf{R}(p_\alpha) - \mathbf{R}(p_\beta'), S_{pp'})$$

where

$$S_{pp'} = |p' - p| \left[1 - \frac{|p' - p|}{L_1} \right] + \frac{|p' - p|^2}{L_0} \lambda^2 + \frac{|p' - p|^2}{L_1} \left(1 - \frac{L_1}{L_0} \right) \frac{\lambda^2}{\lambda_1^2};$$
$$\alpha = \beta, \ \text{int}\ (p'/L_1) - \text{int}\ (p/L) = 0$$

$$S_{pp'} = \frac{t_p(L_1 - t_p)}{L_1} + \frac{t_{p'}(L_1 - t_{p'})}{L_1} + \frac{|p' - p|^2}{L_0} \lambda^2 + \left[|p' - p| - \frac{|p' - p|^2}{L_0} - \frac{t_p(L_1 - t_p)}{L_1} - \frac{t_{p'}(L_1 - t_{p'})}{L_1} \right] \frac{\lambda^2}{\lambda_1^2};$$
$$\alpha = \beta, \ \text{int}\ (p'/L_1) - \text{int}\ (p/L) \neq 0$$

$$S_{pp'} = \frac{t_p(L_1 - t_p)}{L_1} + \frac{t_{p'}(L_1 - t_{p'})}{L_1} + \left[\frac{|p' - \beta L_0|^2}{L_0} + \frac{|(1 + \alpha)L_0 - p|^2}{L_0} + (\beta - \alpha)L_0 \right] \lambda^2 + \left[|p' - p| - \frac{t_p(L_1 - t_p)}{L_1} - \frac{t_{p'}(L_1 - t_{p'})}{L_1} - \frac{|p' - \beta L_0|^2}{L_0} - \frac{|(1 + \alpha)L_0 - p|^2}{L_0} - (\beta - \alpha)L_0 \right] \frac{\lambda^2}{\lambda_1^2}; \ \alpha \neq \beta \tag{C.4}$$

Evaluating the structure factor from (79) and expanding to $0(k^2)$ to give R_g^2 (eq 84) leaves eq 91

$$6R_g^2/Ll = [1/(N_0 + N_1 - 1) - 1/(N_0 + N_1 - 1)^2] + [1 - 1/(N_0 - 1) + (1/2)/(N_0 - 1)^2]\lambda^2 + [1/(N_0 - 1) - (1/2)/(N_0 - 1)^2 - 1/(n_0 + N_1 - 1) + 1/(N_0 + N_1 - 1)^2]\lambda^2/\lambda_1^2 \tag{C.5}$$

where $L_0 = (N_1^* + 1)L_1$ with N_1^* a positive integer.

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