purposes, however, we can expect that when a solute/solvent pair have

$$\hat{f}_{21} \gg \hat{f}_{23} = \hat{f}_{13}$$

only a minimum shift in concentration will arise.

An effectively nonseparable solute could then be "added" to the solvent and the mixture in its fixed proportion treated as the new "solvent". Such a step is thermodynamically permissible and meaningful.

If the mixture is even more complex, but all the solutes obey the no separation rule, this step is still permissible and the single "solvent" would in that case be even richer. Note, however, that it is the matrix 3 and its interaction with the mixture which decides whether in equilibrium or in flow the mixture is "one component" or more.

If impermeant species are added to the "solvent" in the phase outside the matrix, again no departure from the simple solvent/matrix case discussed in the first part will arise. Should, however, a solute be added which will only partially be separated from the "solvent" in the matrix, the three-component case discussed in the second part above will be recovered. Here too, however, a set of components 2 may be added which, with respect to their interaction with the "solvent" and the matrix, are identical. Such a situation is less likely to arise in practice than in the case of a mixed "solvent", but in principle at least the "solute" too could be complex and so indeed can the network, provided all its components are immobilized and relatively uniformly distributed.

With these generalizations, but bearing these and earlier assumptions in mind, more complex practical cases, which arise in biology or technology, can sometimes be discussed with success.[3,6,7,11]

Conclusions and Summary

We have expressed the phenomenological forces X_V and X_D in terms of the three (not two) gradients $(-\nabla p)$, $(-\nabla \Pi_2)$, and $(-\nabla \Pi_3)$, which are important. We have shown that $(-\nabla p)$ is related to the gradient in network component extra stress $(-\nabla s)$ and that the pressure level in the network, with respect to some external reference solution, with which its surface is in equilibrium, will depend upon the stress s and the need to balance chemical potentials. The network component itself will have a gradient in chemical potential $(-\nabla \mu_3/\bar{V}_3)$ per unit volume which can be finite whether the network is rigid or not. $(-\nabla \mu_3/\bar{V}_3)$ is in fact a direct measure of X_V.

The equations derived are local equations for the gradients. It is assumed that thermodynamic equilibrium exists locally, i.e., in infinitesimally thin sections normal to the gradient.

Fluxes other than J_V and J_D can easily be derived from the equations given. In particular, the flux $J_{13} = c_1\bar{V}_1v_1$ and the flux $J_{23} = c_2\bar{V}_2v_2$ have been given in eq 50 and 49, respectively.

The nonnegative character of the coefficients $\hat{f}_{21}$, $\hat{f}_{13}$, and $\hat{f}_{23}$[2,3] helps in the analysis. This fact also establishes the phenomenological coefficients L_p and η as nonnegative. For given gradients the sign and value of the fluxes can thus be established.

Only the highly simplified, one-dimensional stress case has been discussed.

References and Notes

(1) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(2) K. S. Spiegler, *Trans. Faraday Soc.*, **54**, 1409 (1958).
(3) O. Kedem and A. Katchalsky, *J. Gen. Physiol.*, **45**, 143 (1961).
(4) R. J. Bearman, *J. Phys. Chem.*, **65**, 1961–1968 (1961).
(5) N. Weiss and A. Silberberg, *Am. Chem. Soc., Symp. Ser.*,**No. 31** 69 (1976).
(6) B. W. Zweifach and A. Silberberg in "International Review of Physiology, Cardiovascular Physiology III", Vol. 18. A. C. Guyton and D. B. Young, Eds., University Park Press, Baltimore, 1979, p 215.
(7) A. G. Ogston and C. C. Michel, *Prog. Biophys. Mol. Biol.*, **34**, 197–217 (1978).
(8) D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 289–296 (1973).
(9) A. Peterlin and H. Yasuda, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1215–1220 (1974).
(10) D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1221–1230 (1974).
(11) A. Silberberg in "Tissue Fluid Pressure and Composition", A. R. Hargens, Ed., Waverly Press Inc., Williams and Wilkins, Baltimore, 1980, in press.

Elasticity and Stability of a Dense Gel

R. C. Ball* and S. F. Edwards

Cavendish Laboratory, Madingley Road, Cambridge, England.

Received December 8, 1979

ABSTRACT: An extension of the normal Gibbs formulation of statistical mechanics is applied to gels with permenent cross-links. The formalism permits an evaluation of the free energy in the case where the gel is dense, taking full account of excluded volume. This theory yields the changes in osmotic pressure upon cross-linkage and allows fully for syneresis; it enables the full elasticity of the network to be calculated, including the bulk modulus. Corrections to the simple addition of the free energy terms from network and solution theories are obtained, and for the case of a network in equilibrium with pure solvent a particularly simple formula is found.

I. Introduction

The study of the elasticity of gels comprises both the problems of rubbers and those of polymer solutions. Whereas rubbers are normally thought of as cross-linked melts whose compressibility is not interesting, once the chains are well separated by a solvent the osmotic pressure becomes a problem of great interest. Roughly speaking it is given by the difference of the positive solution pressure and the negative pressure of the network, but to explore any interactions between these two effects a joint calculation is essential. A complete stress–strain relationship for the material is then to be derived.

---

*The authors consider it an honor to be invited to contribute to a celebration dedicated to Paul Flory, both on account of scientific inspiration and personal friendship.

All the ingredients of this problem have been separately studied by Paul Flory,[2] and answers given to them. What then remains to be done? We seek here to formulate the joint problem in precise mathematical terms and thence to develop techniques for its solution. These latter will apply to various ranges of the specifying parameters and should be extendable to any order of accuracy required.

Let us give an immediate illustration of the problem. Consider the configurational statistics of the chain segments in a polymer network. Flory pointed out that if there is present a large excess of unlinked chains and little solvent then the network chains will have their statistics screened to Gaussian form. This immediately leads to the classical formula for the network elasticity and at the same time to instability of the network to syneresis—in this case a phase separation of the network from the unlinked polymer excess. Only the repulsions of the network chains themselves can prevent total syneresis, but can the interaction of network monomers also generate screened statistics? Though the answer to this question is generally agreed to be yes, it is much more difficult on the basis of simple arguments to say whether the screening is at all perturbed upon elastic deformation. Thus we resort to a complete formulation of the system and a joint calculation of its osmotic and elastic characteristics.

Problems in equilibrium statistical mechanics, in which all states of the system are accessible, are covered in principle by the Gibbs formula

$$e^{-F/k_BT} = \int e^{-\mathcal{H}/k_BT}$$

relating free energy, Hamiltonian, and temperature. In practice this summation over all possible states can seldom be evaluated exactly, recourse being made to such techniques as cluster expansion or Monte-Carlo integration.

The characteristic problem with amorphous materials is that not all states are accessible from each other and their probability distribution is not given by the Gibbs formulation appropriate to the prevailing thermodynamic conditions. Certain degrees of freedom thus have their values frozen with their distribution determined by the former history of the system. It is only recently that the general formulation for amorphous materials, analogous to that of Gibbs, has started to be explored, though there is no doubt about the basic formula that if a series of degrees of freedom x_i are frozen at values X_i then

$$F = \int P(X_i)\, F(X_i)\, \mathrm{d}X_i$$

where

$$e^{-F(X_i)/k_BT} = \int \prod_i \delta(x_i - X_i) e^{-\mathcal{H}/k_BT}$$

and $P(X_i)$ is the probability of the x_i being frozen at a particular set of values X_i. In the case of a polymer network the frozen degrees of freedom are the arc locations of the cross-links whose distribution is often related to thermal equilibrium in the network formation state, and we will be able to present succinct formulas in these cases.

The problem to be studied here will be as follows. A solution of polymer chains is cross-linked in a specified manner—see section II. It will then find its osmotic pressure reduced, or if reduced to beyond zero it will suffer syneresis. Furthermore it will now have a characteristic equilibrium shape, to perturbation about which it will show a solid-type elastic response. We formulate the equation of state generally (i.e., abstractly as above) and then specifically in terms of: the density of polymeric material, ρ; the interaction constant, $w \sim (T - \theta)$ (θ = the Flory temperature); the number density of cross-links, ρ_x; the length of a single chain, L; and the step length of the polymer, l. In terms of the latter the first four parameters can be made dimensionless. Furthermore we will be concerned with the case where the number of cross-links per chain is large and the system is securely gelled; thus L is not an important parameter and we have a three coupling constant problem. The solution developed in this paper will move away from Flory's infinitely high density limit, but remain in the high density regime where clear progress can be made. The main calculation here is an improved version of ref 1, having fewer approximations and full details of computation. There are of course other studies of criticallly low cross-link densities, but these regimes are not considered here.

II. Thermodynamic Formulas

Consider a polymer solution consisting of N chains of length L in a volume V interacting via a pseudopotential U between monomers which, since the properties of the bulk system are determined by the long range correlations, need have no structure and can be replaced by a δ function of strength w where

$$l^2 w = \int \mathrm{d}^3 r\, [1 - e^{-u(r)/k_BT}] \tag{II.1}$$

However the δ function interaction does lead to divergent constant terms in the free energy; in order to handle these as finite terms it is convenient to soften the interaction to a narrow normalized Gaussian:

$$w\delta(\mathbf{r} - \mathbf{r}') \rightarrow w\left(\frac{3}{2\pi a^2}\right)^{3/2} e^{-(3/2a^2)(\mathbf{r}-\mathbf{r}')^2} \tag{II.2}$$

For many purposes the only thing which matters is the total concentration of polymer present, ρ, so that we can neglect chain end effects. Then the system can be regarded as one very long polymer of length $\mathcal{L} = NL$ (where L is the length of one chain) and $\rho = NL/V$. The connectivity of the chain can be handled very simply by using the Wiener integral since it is then possible to consider the averaging in the partition function to be an average over all paths $\mathbf{r}(s)$. The partition function then becomes

$$e^{-F_0/k_BT} = \int (\delta r(s)) \exp\left[-\frac{3}{2l}\int_0^{\mathcal{L}} \mathbf{r}'^2\, \mathrm{d}s - \frac{w}{2}\int_0^{\mathcal{L}}\int_0^{\mathcal{L}} \delta(\mathbf{r}(s) - \mathbf{r}(s'))\, \mathrm{d}s\, \mathrm{d}s'\right] \tag{II.3}$$

Thus we have introduced a pseudo-Hamiltonian which represents the potential energy and entropy of chain configurations (adding the kinetic energy too presents no problem)

$$\mathcal{H}/k_BT = \frac{3}{2l}\int \mathbf{r}'^2\, \mathrm{d}s - \frac{w}{2}\int\int \delta(\mathbf{r}(s) - \mathbf{r}(s'))\, \mathrm{d}s\, \mathrm{d}s' \tag{II.4}$$

and this now yields the conventional formula

$$e^{-F_0/k_BT} = \int e^{-\mathcal{H}/k_BT} \tag{II.5}$$

Now we wish to cross-link the system. This must be done in a completely characterised way; the simpler the way, the simpler the theory. Consider first the introduction of N_c sliding links, at random, onto the chains; this is not strictly possible experimentally but is easy to visualize. These now reach equilibrium with the system attaining a free energy F_1. The constraint of one such link can be expressed as

$$\tfrac{1}{2}\int_0^{\mathcal{L}}\int_0^{\mathcal{L}} \delta(\mathbf{r}(s) - \mathbf{r}(s'))\, \mathrm{d}s\, \mathrm{d}s' \tag{II.6}$$

so that

$$e^{-F_1/k_BT} = \int e^{-\mathcal{H}/k_BT}\left(\tfrac{1}{2}\int_0^{\mathcal{L}}\int_0^{\mathcal{L}}\delta(\mathbf{r}(s) - \mathbf{r}(s'))\ \mathrm{d}s\ \mathrm{d}s'\right)^{N_c} \tag{II.7}$$

The resulting pressure $P_1 = -\partial F_1/\partial V$ will be less than $P_0 = -\partial F_0/\partial V_0 > 0$, and if $P_1 < 0$ the system will contract from volume V to V_1 at which the pressure is restored to zero. Now let the sliding of the links be frozen. There will be no further reduction in pressure (as we shall show) but now there will be an elastic equation of state so we have

$$F_2(\lambda_1,\lambda_2,\lambda_3)$$

as the final free energy with deformation from the state in which the links are frozen.

To give a formula for F_2 we note that the probability of a set of cross-links being at $\{s_i,s_i'\}$ is

$$P(\{s_i,s_i'\}) = \int \delta\mathbf{r}(s)e^{(F_1-\mathcal{H})/k_BT}\prod_i\delta(\mathbf{r}(s_i) - \mathbf{r}(s_i')) \tag{II.8}$$

i.e., as in eq II.7 but without the $\{s_i,s_i'\}$ being integrated and normalized by $e^{-F_1/kT}$. If the $\{s_i,s_i'\}$ are now chosen (according to the above distribution) and fixed, the free energy of the network is obtained by integrating over all other degrees of freedom

$$e^{-F(\{s_i,s_i'\})/k_BT} = \int e^{-\mathcal{H}/k_BT}\prod_i\delta(\mathbf{r}(s_i) - \mathbf{r}(s_i')) \tag{II.9}$$

and finally averaging the free energy with respect to the probability distribution

$$F_2 = \int F(\{s_i,s_i'\})\ P(\{s_i,s_i'\})\prod_i\tfrac{1}{2}\ \mathrm{d}s_i\ \mathrm{d}s_i' \tag{II.10}$$

Thus

$$F_2 = -k_BT\int P(\{s_i,s_i'\})\log\left[\int \delta r e^{-\mathcal{H}/k_BT}\prod_i\delta(\mathbf{r}(s_i) - \mathbf{r}(s_i'))\right]\prod_i\tfrac{1}{2}\ \mathrm{d}s_i\ \mathrm{d}s_i' \tag{II.11}$$

A neat reformulation when P is given by (II.8) is to note that the logarithm can be expressed as the coefficient of n in $A^n = 1 + n\log A +$ order n^2. Rather than just write $(\int e^{-\mathcal{H}/k_BT}\prod\delta)^n$ one can, for a whole number n, think of n systems or "replicas" and use instead

$$\int e^{-\sum_{\alpha=1}^{n}\mathcal{H}^{(\alpha)}/k_BT}\prod_{\alpha=1}^{n}\prod_i\delta(\mathbf{r}^\alpha(s_i) - \mathbf{r}^\alpha(s_i'))(\delta r^\alpha(s)) \tag{II.12}$$

Thus if we take $\tilde{\int}$ to denote functional integration through a box whose sides have been deformed to $\lambda_1,\lambda_2,\lambda_3$ of their original values, then the free energy F_2 is the coefficient of n in $F(n)$ where

$$e^{-F(n)/k_BT} = \int \delta r^0\prod_{\alpha=1}^{n}\tilde{\int}\delta r^\alpha e^{-\sum_{\alpha=0}^{n}\mathcal{H}^\alpha/k_BT}\prod_i\tfrac{1}{2}\int\int\prod_{\alpha=0}^{n}\delta(\mathbf{r}^\alpha(s_i) - \mathbf{r}^\alpha(s_i'))\ \mathrm{d}s_i\ \mathrm{d}s_i' \tag{II.13}$$

The quantity given by eq II.13 can be visualized as the partition function of a replicated system. This consists of $n + 1$ physical polymer systems of which the first (labeled 0) has undeformed boundary conditions but the others (labeled 1 to n) are in the elastically deformed state. The chain segments in all the replicas explore configurations independently of each other, but the arc locations of the cross-links—the degrees of freedom frozen in the original problem—are common to all the replicas. Only with this total correlation of their locations between all the replicas are the links allowed to slide. Although this discussion has been of one long chain to ease the notation, there is no difficulty in writing the formulae in terms of the N chains with $\delta(\mathbf{r}(s_i) - \mathbf{r}(s_i'))$ being replaced by $\delta(\mathbf{r}_a(s_i) - \mathbf{r}_a(s_i'))$ and $\int_0^{\mathcal{L}}\mathrm{d}s_i$ by $\sum_a\int_0^{L}\mathrm{d}s_i$, where the index a labels different chains.

A more realistic physical situation which is identical mathematically when no collapse occurs is to cross-link the solution by irradiation or any other instantaneous method, or a method giving the same distribution as an instantaneous cross-linkage. Suppose that such a method produces N_c cross-links and that we can take N_c as known. Then the probability distribution of the cross-link locations is that of finding the chains touching at those same N_c pairs of points in the original solution. This probability is again the P of eq II.8 and the same final form results. Another more physical case is that of thermal cross-linking where the links are free to be made and broken. In equilibrium the fractional fluctuation in the number of links will be negligible and the statistics will then be identical with those of the case of sliding links. Furthermore, the notion of freezing the sliding links is equivalent to, in this case, performing subsequent experiments on a faster time scale than that of the link making and breaking processes.

The problem of the cross-linked gel is now reduced to the problem of a generalization of solution theory by using a chemical potential for linking, μ, either as such (thermal links) or by direct derivation by using

$$B^m = \frac{M!}{2\pi i}\oint_C e^{B\mu-(M+1)\log\mu}\ \mathrm{d}\mu \tag{II.14}$$

(where the closed contour C encloses the origin once in the complex μ plane).

This allows the N_c cross-links which give rise to

$$\left[\int\int\prod_{\alpha=0}^{n}\delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))\ \frac{\mathrm{d}s\ \mathrm{d}s'}{2}\right]^{N_c} \tag{II.15}$$

to be written as

$$\oint\mathrm{d}\mu\ \exp\left[\mu\int\int\prod_\mu\delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))\ \frac{\mathrm{d}s\ \mathrm{d}s'}{2} - (N_c + 1)\log\mu + \log\left(\frac{N_c!}{2\pi i}\right)\right] \tag{II.16}$$

This finally leads to

$$e^{-F(n)/k_BT} = \tilde{\int}\int - \tilde{\int}\delta r\oint\mathrm{d}\mu\ e^{-\mathcal{H}/k_BT-N_c\log\mu} \tag{II.17}$$

where

$$\begin{aligned}\mathcal{H}/k_BT = {}& \sum_{\alpha=0}^{n}\frac{3}{2l}\int\mathbf{r}^{\alpha\prime 2}\ \mathrm{d}s \\ &+ w\int\int\sum_{\alpha=0}^{n}\delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))\ \frac{\mathrm{d}s\ \mathrm{d}s'}{2} \\ &- \mu\int\int\sum_{\alpha=0}^{n}\delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))\ \frac{\mathrm{d}s\ \mathrm{d}s'}{2}\end{aligned} \tag{II.18}$$

and terms which cannot contribute in the thermodynamic limit have been dropped. In that limit it can also be shown that,[3] for a gelled state, the integration over μ is dominated by the steepest descent point thus, giving

$$\frac{F(n)}{k_BT} = \operatorname*{Min}_\mu\left[\frac{F(n,\mu)}{k_BT} + N_c\log\mu\right] \tag{II.19}$$

where

$$e^{-F(n,\mu)/k_BT} = \int\cdots\tilde{\int}e^{-\mathcal{H}/k_BT} \tag{II.20}$$

The essential difference between the free interaction of the solution and the permanent constraint of the cross-links lies in the difference between the summation $\sum_\alpha$ of the excluded volume terms and the product $\prod_\alpha$ of the cross-links, as shown in eq II.18.

The formalism can be easily generalized to the creation of the cross-links at one temperature, and the study of the network at another. The temperature enters in $w(T)$ and we can therefore simply incorporate this in (II.18) by changing the excluded volume contribution to

$$\int\int \sum_{\alpha=0}^{n} w(T^\alpha)\delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s')) \ \frac{\mathrm{d}s\ \mathrm{d}s'}{2} \qquad \text{(II.21)}$$

where T^0 is the initial temperature and for $\alpha = 1, \ldots, n$, T^α is the final temperature. The value of w can be obtained empirically from the thermodynamic functions of the solution; at $T = \theta$, w is zero.

This formalism is a complete representation of the problem as formulated and is a minimum representation of the physical problem. Any further simplification would destroy the physics of the problem; by the same token it should be possible to treat any trivial departure from the current model by a low (e.g., first) order cumulant expansion about formula II.17.

Formula II.17 thus represents the simplest complete description of a gel. From it we must try to make an evaluation of the free energy, and it is already a substantial problem in the simplest limit of a dense system. The device of using the replica formalism circumvents the logarithm appearing in eq II.11 and recasts the problem as the Gibbs formula (eq II.13). Thus at the cost of introducing an extra parameter n we revert to a problem in equilibrium statistical mechanics. To obtain F_2 we require the identification of the coefficient of n in $F(n)$: with an analytic calculation for an arbitrary whole number n this can be done by inspection, but formally we must continue analytically the expression for $F(n)$ to all positive real n and evaluate $F_2 = (\partial F(n)/\partial n)_{n=0^+}$.

If the reader worries about the taking of n as an integer while subsequently taking the limit $n \to 0$, he can be reassured in three ways.

First, it is not strictly necessary: one can always go back to the original logarithm and with much greater trouble get the answers below.

Second, such limits occur in many other places in theoretical physics (Regge trajectories,[14] the "$n = 0$ trick" in field theory,[15] etc.) and Carlson's Lemma[16] provides a rigorous mathematical background.

Third, polymer problems are dominated by the Gaussian integral, and this lends itself with unique ease to this kind of manipulation (it is much easier than in the spin–glass problem where the $n \to 0$ limit is much trickier but still seems possible). However it must be made clear that it is still a difficult calculation to carry out and is substantially more complex than the equivalent calculation for the incompressible case by Deam and Edwards.[3] Thus a great deal of algebra is relegated to appendices.

III. Some Special Cases

The problem is to evaluate $\exp[-w\int\int\sum\delta + \mu\int\int\prod\delta]$ against the random chain distribution $\exp[-(3/2l)\int\sum r'^2]$. There are three subproblems valuable for orientation, the first being the case $\mu = 0$ which is polymer solution theory and does not require the replica technique. In general this is difficult but for strongly overlapping chains[4] the introduction of collective variables, the fourier coefficients of the density,

$$\rho_k = \sum_a \int_0^L \mathrm{d}s\ e^{ik\cdot\mathbf{r}_a(s)} \qquad \text{(III.1)}$$

allows the evaluation of partition function as a joint Gaussian integral in the ρ_k:

$$e^{-F/k_\mathrm{B}T} = \int \prod_{k\neq 0} (\mathrm{d}\rho_k) \left[-\tfrac{1}{2}\frac{w}{v}\sum_k \rho_k\rho_k{}^* - \tfrac{1}{2}\sum_k \frac{lk^2}{12\mathcal{L}}\rho_k\rho_k{}^* \right] \exp\left[-\tfrac{1}{2}\sum_k \ln\left(\frac{12\pi\mathcal{L}}{lk^2}\right)\right] \qquad \text{(III.2)}$$

This uses the fact that the Jacobian of the transformation between $\mathbf{r}(s)$ and ρ_k (apart from $k = 0$ for which $\rho = L$) is in the first approximation

$$\exp\left\{-\tfrac{1}{2}\sum_k \left[\frac{lk^2}{12\mathcal{L}}\rho_k\rho_k{}^* + \ln\left|\frac{12\pi\mathcal{L}}{lk^2}\right| \right]\right\} \qquad \text{(III.3)}$$

the resulting free energy being

$$F/k_\mathrm{B}T = \mathcal{L}\left[\frac{w\mathcal{L}}{2v} - \frac{2}{\pi}\frac{w}{l}\left(\frac{3w\mathcal{L}}{lV}\right)^{1/2} + \frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\frac{w}{al} \right] \qquad \text{(III.4)}$$

(see Appendix I). The physical result here is that the repulsive potential between monomers

$$U/k_\mathrm{B}Tl^2 \simeq w\delta(\mathbf{r})$$

is screened into

$$w\left[\delta(\mathbf{r}) - \frac{e^{-r(w/l\rho)^{1/2}}}{4\pi r}\frac{w}{l\rho} \right] \qquad \text{(III.5)}$$

which being a potential with a mean value of zero does not give excluded volume effects. As predicted by Flory, it gives only a small change in step length.

The second limit is $w = 0$ which leaves a ghost network. Such a network left to itself will collapse into a non-uniform ball of material whose size is not proportional to the amount of material, so we make a respectable problem of it by imposing a uniform density on the system at a fixed volume. (This contrivance will not be necessary when we incorporate excluded volume, which is the main aim of this paper.) With this in mind, the replica integral II.17 can be evaluated by simulating

$$\mu\int\int \frac{\mathrm{d}s\ \mathrm{d}s'}{2} \prod_{\alpha=0}^{n} \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))$$

by an harmonic localization which restricts the chains to be near to their affine deformation positions.

For example, if there were only two terms in the replica formulation, say R_0 and R_1, and the R_1 system has been deformed by the usual λ_i, one can (for each Cartesian) introduce new coordinates

$$X_0 = \frac{R_0 + \lambda R_1}{(1 + \lambda^2)^{1/2}} \qquad X_1 = \frac{\lambda R_0 - R_1}{(1 + \lambda^2)^{1/2}} \qquad \text{(III.6)}$$

whereupon $R_1'^2 + R_2'^2 = X_0'^2 + X_1'^2$ and

$$\int\int \delta(R_0(s) - R_0(s'))\ \delta(R_1(s) - R_1(s'))\ \frac{\mathrm{d}s\ \mathrm{d}s'}{2}$$

is first transformed rigorously to

$$\int\int \delta(X_0(s) - X_0(s'))\ \delta(X_1(s) - X_1(s'))\ \frac{\mathrm{d}s\ \mathrm{d}s'}{2}$$

and then simulated by

$$Q = \frac{q^2}{6l}\int X_1{}^2\ \mathrm{d}s \qquad \text{(III.7)}$$

One may then write

$$\int \delta r \exp\left\{-\frac{3}{2l}\int (X_0'^2 + X_1'^2)\,\mathrm{d}s - \frac{q^2}{6l}\int X_1^2\,\mathrm{d}s + \left[\frac{q^2}{6l}\int X_1^2\,\mathrm{d}s + \mu\int\int \delta(X_0)\,\delta(X_1)\right]\right\} \simeq \int \delta r \exp\left\{-\frac{3}{2l}\int (X_0'^2 + X_1'^2)\,\mathrm{d}s - \frac{q^2}{6l}\int X_1^2\,\mathrm{d}s + \left\langle \frac{q^2}{6l}\int X_1^2\,\mathrm{d}s + \mu\int\int \delta(X_0)\,\delta(X_1)\right\rangle\right\} \quad \text{(III.8)}$$

where the average $\langle\ \rangle$ is with respect to the rest of the partition integral, i.e., a Wiener distribution for X_0 and a harmonically localized random walk distribution for X_1. In fact there is a variational principle here:

$$\langle e^{A}\rangle \geq e^{\langle A\rangle} \quad \text{(III.9)}$$

so we can optimise the choice of q by imposing $\partial F/\partial q = 0$. In the full replica system $R_0, R_1, \ldots, R_n$ one can generalize to

$$X_0 = \frac{R_0 + \lambda R_1 + \cdots \lambda R_n}{(1 + n\lambda^2)^{1/2}} \quad \text{etc.} \quad \text{(III.10)}$$

which gives the results (Appendix II)

$$q = 3\mu\mathcal{L}/lV \quad \text{(III.11)}$$

$$F(n) = \frac{2N_cV}{\mathcal{L}^2(1+\gamma)}\left\{\frac{3}{4}\,\frac{n\mathcal{L}^2}{V} - \frac{\mathcal{L}^2}{2V\prod_i(1+n\lambda_i^2)^{1/2}}\left(\frac{3}{\pi}\,\frac{N_c}{l\mathcal{L}(1+\gamma)}\right)^{3n/2} - \frac{3\mathcal{L}}{l\pi(1+3n)}\left(\frac{3}{2\pi a^2}\right)^{(3n+1)/2}\right\} + N_c \log\left|\frac{2N_cV}{\mathcal{L}^2(1+\gamma)}\right| \quad \text{(III.12)}$$

$$\tilde{F} = \frac{1}{2}\,\frac{N_c}{1+\gamma}k_BT\sum_i\lambda_i^2 + \text{(terms independent of deformation)} \quad \text{(III.13)}$$

Here the wasted loop correction is

$$\gamma = \frac{6}{\pi}\frac{V}{\mathcal{L}l}\left(\frac{3}{2\pi a^2}\right)^{1/2}$$

whose form is unfamiliar only because short loops have been restricted by softening the contact interaction II.2 rather than by imposing a minimum loop size l_c. These are essentially equivalent given

$$ll_c \sim a^2$$

The final helpful calculation is to consider the two effects characterized by w and μ but for equilibrium sliding links only to begin with. In such a system there is no shear modulus and we have no need of replication, but we still find an interesting extension of the previous work.

Referring to (II.18) the reader will see that with only one replica ($n = 0$) the potentials for cross-linking and excluded volume take identical form and it follows that if $F_s(w)$ denotes the polymer solution free energy of eq III.4 we must now have

$$F/k_BT = \frac{1}{k_BT}F_s(w - \mu) + N_c \log \mu \quad \text{(III.14)}$$

The chemical potential μ is given in terms of N and V by $(\partial F/\partial\mu)_{VN} = 0$, i.e.,

$$\frac{N_c}{\mu} = -\frac{\partial}{\partial\mu}(F_s(w-\mu)/k_BT)_V \quad \text{(III.15)}$$

This enables us to define

$$F_1(N_c,V) = F(N_c,V,\mu(N_c,V)) \quad \text{(III.16)}$$

Now the osmotic pressure π is given by

$$-\pi = \left(\frac{\partial F_1}{\partial V}\right)_{N_c} = \left(\frac{\partial F}{\partial V}\right)_{\mu,N_c} + \left(\frac{\partial F}{\partial\mu}\right)_{V,N_c}\left(\frac{\partial\mu}{\partial V}\right)_{N_c} = \left(\frac{\partial F}{\partial V}\right)_{\mu,N_c} \quad \text{(III.17)}$$

since by the definition of μ the second term is zero. $F(\mu,N,V)$ can itself be expanded as

$$F/k_BT = N_c \log \mu + \frac{\mathcal{L}^2}{2V}(w-\mu)\left[1 + \gamma + \text{order}\left(\frac{V}{\mathcal{L}}(w-\mu)\right)^{1/2}\right] \quad \text{(III.18)}$$

where the wasted loop correction γ is given by eq III.13, so that π becomes

$$\pi/k_BT = \frac{\mathcal{L}^2}{2V^2}(w-\mu)\left[1 + \text{order}\left[\frac{V}{\mathcal{L}}(w-\mu)\right]^{1/2}\right] \quad \text{(III.19)}$$

Thus π is reduced by the links and if the system is allowed to swell or shrink to its equilibrium free size, given by $\pi = 0$, it will end up with $w = \mu$. This is a rather remarkable condition since it results in the polymer chains having Gaussian statistics, the effects of the excluded volume and cross-linking theorem canceling exactly. We can easily calculate μ in terms of N and V from (III.15) and (III.14) since

$$\frac{N_c}{\mu} = -\frac{\partial}{\partial\mu}(F_s/k_BT)_V = \frac{\mathcal{L}^2}{2V}(1 + \gamma + \text{order }(w-\mu)^{1/2}) \quad \text{(III.20)}$$

Thus

$$\mu = \frac{2NV}{\mathcal{L}^2(1+\gamma)} \quad \text{at} \quad w = \mu \quad \text{(III.21)}$$

and the final size of the network is given by

$$V_f = \frac{w\mathcal{L}^2}{2N}(1+\gamma) \quad \text{(III.22)}$$

Note that for the network initially at some larger size the osmotic pressure given by eq III.19 with eq III.21 is negative, and so collapse toward V_f will occur spontaneously.

It will be shown later that if at $V = V_f$ the links are frozen the computations of section IV become much simpler and the astonishingly simple form results

$$F = k_BT\,\frac{N_c}{1+\gamma}\left[\frac{1}{2}\sum_i\lambda_i^2 + \prod_i\frac{1}{\lambda_i}\right] \quad \text{(III.23)}$$

where $N_c/(1 + \gamma)$ is the number of elastically active cross-links. Now in practice the links in a collapsing or swelling network are not free to slide, and one immediate consequence is that the wasted loop factor γ will be fixed at its value at formation conditions, γ_0. This does somewhat disrupt the above analysis, but the description of the equilibrium state by $\mu = w$ and $\gamma = \gamma_0$ is so appealing that we pursue it in this paper.

IV. Full Calculation

We now return to the evaluation of (II.20) which we may rewrite as

$$e^{-F(\mu)/k_BT} = \int \cdots \tilde{\int} e^{-W-wE+\mu X} \tag{IV.1}$$

where

$$W = \sum_\alpha \frac{3}{2l}\int_0^{\mathcal{L}} \mathbf{r}^{\alpha\prime 2}\, ds \tag{IV.2}$$

$$E = \int_0^{\mathcal{L}}\int_0^{\mathcal{L}} \frac{ds\, ds'}{2} \sum_\alpha \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s')) \tag{IV.3}$$

$$X = \int_0^{\mathcal{L}}\int_0^{\mathcal{L}} \frac{ds\, ds'}{2} \prod_\alpha \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s')) \tag{IV.4}$$

The variational principle enables us to model this, just as for the ghost network in section III, by

$$e^{-F(\mu)/k_BT} \geq e^{-F(\mu,q)/k_BT} = \int \cdots \tilde{\int} e^{-W-(w-\mu)E-Q+\langle \mu(X-E)+Q\rangle} \tag{IV.5}$$

where Q is simply the n-replica generalization of (III.7). Note however that we are incorporating here the close similarity between cross-linking X and excluded volume E, taking the localization Q to model only their difference. Thus in the case of only one replica this formulation reverts to that of the end of section III. Another important consequence is that the inequality in (IV.5) is an equality at $n = 0$, so that the inequality itself holds for the terms of order n alone upon which, finally, our attention will be focused. The computation now remaining is slightly eased by noting that

$$F(\mu,q) = \mathcal{F}(w - \mu,q,0) - \frac{q}{2}\frac{\partial}{\partial q}\mathcal{F}(w - \mu,q,0) + \mu\left[\left(\frac{\partial}{\partial \mu'} + \frac{\partial}{\partial w'}\right)\mathcal{F}(w',q,\mu')\right]_{\mu'=0,w'=w-\mu} \tag{IV.6}$$

where

$$e^{-\mathcal{F}(\nu,q,\mu)/k_BT} = \int \cdots \tilde{\int} e^{-W-\nu E-Q+\mu X} \tag{IV.7}$$

and $\mathcal{F}$ is required only to first order in μ.

The problem is to combine the collective density coordinates which solve the polymer solution, together with the linear transformation of position coordinates which solves the ghost network. This we do by introducing collective density coordinates in the whole replica space:

$$\Gamma_{\mathbf{K}} = \int_0^{\mathcal{L}} e^{i\mathbf{K}\cdot r(s)}\, ds \tag{IV.8}$$

where the reciprocal vector $\mathbf{K}$ has both replica and Cartesian indices, α and i, respectively, and $\mathbf{K}\cdot r(s)$ means

$$\sum_{\substack{\text{Cartesians}\\ i}} \sum_{\substack{\text{replicas}\\ \alpha=0,\cdots n}} K_i^\alpha r_i^\alpha(s)$$

Now X and E are readily expressed as quadratic forms in Γ as follows. First

$$X = \frac{1}{2}\left\{\frac{\mathcal{L}^2}{\mathcal{V}} + \frac{1}{\mathcal{V}}\sum_{\mathbf{K}}{}' \Gamma_\kappa\Gamma_\kappa{}^*\right\} \tag{IV.9}$$

where the prime excludes from the summation $\mathbf{K} = 0$ whose contribution is given explicitly by the preceding term, and $\mathcal{V}$ is the hypervolume of the replicated system:

$$\mathcal{V} = \prod_\alpha V^\alpha = V(\tilde{V})^n \tag{IV.10}$$

the tilda denoting the deformed state. The points of summation over $\mathbf{K}$ are the reciprocal lattice vectors of the replicated space. Second

$$E = \frac{1}{2}\left\{\sum_\alpha \frac{\mathcal{L}^2}{V^\alpha} + \sum_{\mathbf{K}}{}'\Gamma_\kappa \sum_\alpha\left[\frac{1}{V^\alpha}\prod_{\beta\neq\alpha}\delta^\kappa(K^\beta)\right]\Gamma_\kappa{}^*\right\} \tag{IV.11}$$

where δ^κ is a Kronecker delta and the second term is conveniently represented as

$$\frac{1}{2\nu}\sum_\kappa{}'\Gamma_\kappa p^2(\kappa)\Gamma_\kappa{}^* \tag{IV.12}$$

where

$$p(\kappa) = \sum_\alpha \left(\frac{\nu}{V^\alpha}\right)^{1/2} \prod_{\beta\neq\alpha}\delta^\kappa(\kappa^\beta) \tag{IV.13}$$

Note that p is just a weighted sum of operators which project out from the Γ_κ the individual replica density coordinates $\rho^\alpha(\kappa^\alpha)$. The two terms $\nu E - \mu X$ may be expressed as

$$\nu E - \mu X = \frac{1}{2}\left\{\sum_\alpha \frac{\nu\mathcal{L}^2}{V^\alpha} - \frac{\mu\mathcal{L}^2}{\mathcal{V}} + \sum_\kappa{}' \Gamma_\kappa G_\kappa \Gamma_\kappa{}^*\right\} \tag{IV.14}$$

where

$$G_\kappa = p^2(\kappa) - \frac{\mu}{\mathcal{V}} \tag{IV.15}$$

is a diagonal matric acting on the vector space of the Γ_κ.

The evaluation of $\mathcal{F}$ now requires

$$e^{-\mathcal{F}/k_BT} = \int \cdots \times \tilde{\int} \exp\left[-W - Q - \frac{1}{2}\sum{}'\Gamma_\kappa G_\kappa \Gamma_\kappa{}^* - \frac{1}{2}\left[\sum_\alpha \frac{\nu\mathcal{L}^2}{V^\alpha} - \frac{\mu\mathcal{L}^2}{\mathcal{V}}\right]\right]$$

$$= e^{-(1/2)[\sum_\alpha(\nu\mathcal{L}^2/V^\alpha)-(\mu\mathcal{L}^2/\mathcal{V})]-(\mathcal{D}/k_BT)}\langle e^{-(1/2)\sum'\Gamma_\kappa G_\kappa\Gamma_\kappa{}^*}\rangle \tag{IV.16}$$

where

$$e^{-\mathcal{D}/k_BT} = \int \cdots \tilde{\int} e^{-W-Q} = e^{-nl\mathcal{L}q/2} \tag{IV.17}$$

and the average is with respect to the distribution e^{-W-Q}. At this point we can apply the same method as in the polymer solution calculation, changing variables from $\mathbf{r}^\alpha(s)$ to the Γ_κ and replacing the Jacobian by its cumulant expansion truncated at second order. This Gaussian approximation to the distribution is

$$e^{-(1/2)[\text{trace}\ \ln(\pi\mathbf{C})+(\Gamma-\bar{\Gamma})\cdot\mathbf{C}^{-1}\cdot(\Gamma-\bar{\Gamma})^*]} \tag{IV.18}$$

where the $\bar{\Gamma}$ are the first moments,

$$\bar{\Gamma}_\kappa = \langle\Gamma_\kappa\rangle \tag{IV.19}$$

and $\mathbf{C}$ is the variance matrix

$$\mathbf{C}_{K,K'} = \langle(\Gamma_K - \bar{\Gamma}_K)(\Gamma_{K'} - \bar{\Gamma}_{K'})^*\rangle \tag{IV.20}$$

the averages being with respect to e^{-W-Q}. It is important to note that with Q present, $\mathbf{C}_{K,K'}$ is no longer a diagonal matrix in contrast to the simple solution case. Integrating over the Γ_κ then gives (Appendix III)

$$\langle e^{-(1/2)\Gamma\cdot G\cdot\Gamma^*}\rangle = e^{-\mathcal{G}} \tag{IV.21}$$

where

$$\mathcal{G} = \tfrac{1}{2}\ \text{trace}\ \ln\,(1 + \mathbf{C}\cdot G) + \tfrac{1}{2}\bar{\Gamma}\cdot G\cdot(1 + \mathbf{C}\cdot G)^{-1}\cdot\bar{\Gamma}^* \tag{IV.22}$$

and substituting $G = p^2 - (\mu/\mathcal{V})$ gives to order μ

$$\mathcal{G} = \tfrac{1}{2} \text{ trace } \ln (1 + \mathbf{C}p^2) + \tfrac{1}{2}\bar{\Gamma}\cdot p^2(1 + \mathbf{C}p^2)^{-1}\cdot\bar{\Gamma}^* - \frac{\mu}{2\mathcal{V}} \text{ trace } (1 + \mathbf{C}p^2)^{-1}\cdot(\bar{\Gamma}\bar{\Gamma}^* + \mathbf{C}) \quad \text{(IV.23)}$$

Note that $\mathbf{C} + \bar{\Gamma}\bar{\Gamma}^*$ is just the direct second moment matrix,

$$\mathbf{M}_{K,K'} = \langle \Gamma_K \Gamma_{K'}^* \rangle \quad \text{(IV.24)}$$

Furthermore, it is shown (Appendix IV) that in the subspace projected out by p all the first moments are zero, so that

$$\mathbf{C}\cdot p = \mathbf{M}\cdot p \quad \text{(IV.25)}$$

The quantity $\mathcal{G}$ then simplifies to

$$\mathcal{G} = \tfrac{1}{2} \text{ trace } \ln (1 + \mathbf{M}p^2) - \frac{\mu}{2\mathcal{V}} \text{ trace } (1 + \mathbf{M}p^2)^{-1}\cdot\mathbf{M} \quad \text{(IV.26)}$$

and using the cyclicity of a trace with the expansion of both $\ln (1 + \mathbf{M}p^2)$ and $(1 + \mathbf{M}p^2)^{-1}$ this can be rearranged to give

$$\mathcal{G} = \tfrac{1}{2} \text{ trace } \ln (1 + p\mathbf{M}p) - \frac{\mu}{2\mathcal{V}}(\text{trace } \mathbf{M} - \text{trace } p\mathbf{M}^2p(1 + p\mathbf{M}p)^{-1}) \quad \text{(IV.27)}$$

The term $(\mu/2\mathcal{V})$ trace $\mathbf{M}$ is simply the average of μX in the absence of excluded volume, yielding

$$\frac{\mu}{2\mathcal{V}_0}\mathcal{L}^2\left(\frac{q}{2\pi}\right)^{3n/2} + \frac{\mu\mathcal{L}}{l}\,\frac{3}{\pi(3n + 1)}\left(\frac{3}{2\pi a^2}\right)^{(3n+1)/2} + \text{order } q^{1/2} \quad \text{(IV.28)}$$

when the $K = 0$ contribution is included (Appendix Va). The excluded volume correction to this gives

$$-\frac{\mu}{2\mathcal{V}} \text{ trace } p\mathbf{M}^2p(1 + p\mathbf{M}p)^{-1} = -\frac{\mu}{2}\sum_{\alpha}\frac{V^{\alpha}}{V_0}\left(\frac{q}{2\pi}\right)^{3n/2}\frac{6\mathcal{L}}{\pi l}\left(\frac{3\mathcal{L}\nu}{lV^{\alpha}}\right)^{1/2} \quad \text{(IV.29)}$$

(Appendix Vb) where in both of the above expressions V_0 denotes the volume of the X_0 replica,

$$V_0 = V\prod_i(1 + n\lambda_i^2)^{1/2} \quad \text{(IV.30)}$$

The term $^1/_2$ trace ln $(1 + p\mathbf{M}p)$ simply gives the sum of the separate polymer solution contributions together with the following correction due to the harmonic localization

$$\frac{nq}{\pi}\left[\left(\frac{3\nu\mathcal{L}V}{l}\right)^{1/2}I + \left(\frac{3\nu\mathcal{L}\tilde{V}}{l}\right)^{1/2}(3 - I)\right] \quad \text{(IV.31)}$$

(Appendix VI) where

$$I = \sum_i\lambda_i^2 \quad \text{(IV.32)}$$

From this we can reconstruct the generating function $\mathcal{F}$ and hence by eq IV.6 $F(\mu,q)$ (Appendix VIII). The mechanics of making this stationary with respect to both μ and q are also dealt with in that appendix in the limit $\mu/w \ll 1$. For this case of a slightly linked system the free energy of deformation is found to be

$$\tilde{F}/k_{\mathrm{B}}T = \frac{w\mathcal{L}^2}{2V}\left(\frac{1}{B} - \tfrac{2}{3}\phi\,\frac{1}{B^{1/2}}\right) + \frac{N_{\mathrm{c}}}{1 + \gamma}\left[\tfrac{1}{2}\sum_i\lambda_i^2 + \frac{\phi}{1 - \phi}B^{1/2}\right] + \tfrac{3}{2} \ln \left|1 + \frac{\phi}{6}\left[B^{1/2} + \frac{1 - B^{1/2}}{3}\sum_i\lambda_i^2\right]\right| \quad \text{(IV.33)}$$

where the parameter ϕ is given by

$$\phi = \frac{6}{\pi}\left(\frac{3wV}{l^3\mathcal{L}}\right)^{1/2} \quad \text{(IV.34)}$$

and the wasted loop correction is

$$\gamma = \frac{\frac{1}{2}\left(\frac{6}{\pi}\right)^{3/2}\frac{wV}{\mathcal{L}al}}{1 - \phi} \quad \text{(IV.35)}$$

B is the bulk deformation

$$B = \frac{\tilde{V}}{V} = \prod_i\lambda_i \quad \text{(IV.36)}$$

It will be seen that $\phi = 0$ and $N_{\mathrm{c}} = 0$ each return us to the appropriate limits. Note also that the above result is restricted to the regime $\mu/w < 1$ and that the Gaussian approximation to the Jacobian used in (IV.18) is exact only to first order in ϕ. The opposite extreme of cross-linking is the regime $\mu/w = 1$, the collapsed (or swelled) network state discussed at the end of section III. For μ comparable to w, ϕ becomes

$$\phi = \frac{6}{\pi}\left(\frac{3(w - \mu)V}{l^3\mathcal{L}}\right)^{1/2} = 0 \quad \text{for} \quad w = \mu \quad \text{(IV.37)}$$

Also we have

$$\frac{w\mathcal{L}^2}{2V} = \frac{N_{\mathrm{c}}}{1 + \gamma_0} \quad \text{(III.23a)}$$

so that the above formula reduces to

$$\tilde{F} = \frac{N_{\mathrm{c}}}{1 + \gamma_0}\left[\frac{1}{2}\sum_i\lambda_i^2 + \prod_i\frac{1}{\lambda_i}\right] \quad \text{(III.23)}$$

This has a ghost network response to shear deformation and a well-defined positive bulk modulus,

$$K = \frac{N_{\mathrm{c}}}{1 + \gamma_0}[2B^{-3} - \tfrac{1}{3}B^{-1/3}] \quad \text{(IV.38)}$$

Poisson's ratio for this material is $^1/_4$.

V. Discussion

It is interesting to discuss our results in terms of a phase diagram with w and ρ as the variables. This is given in Figure 1. As shown in section III, a network with $w < \mu$ will collapse and, at the end point, $\mu \sim N_{\mathrm{c}}V/\mathcal{L}^2 = \nu/\rho$, where ν is the fraction of cross-links to monomers. Thus the region $w < \nu/\rho$ is unstable. The departure from Gaussian chain statistics is governed by the parameter

$$\phi = \frac{6}{\pi}\left(3\,\frac{w - \mu}{\rho l^3}\right)^{1/2}$$

so that for $w < \mu + \rho l^3$ we are in a screening regime. The main calculation we have presented is valid in the heart of the screened regime, i.e., region II of the diagram. Second we have presented a calculation for the state of zero osmotic pressure ($w = \mu$), i.e., line I of the diagram. The intermediate regime has not been calculated but presents no difficulty in principal, in contrast to region III. Here all the difficulties of a semidilute polymer solution apply and in the absence of a direct analytic approach to that alone, we cannot attempt a replica calculation.

Entanglements have not been considered at all in the present work. Although we would not expect them to be important for dilute gels, it remains to be checked whether neglecting them is consistent with regime II, i.e., screening and light linking ($\mu < w$). Certainly they should not be

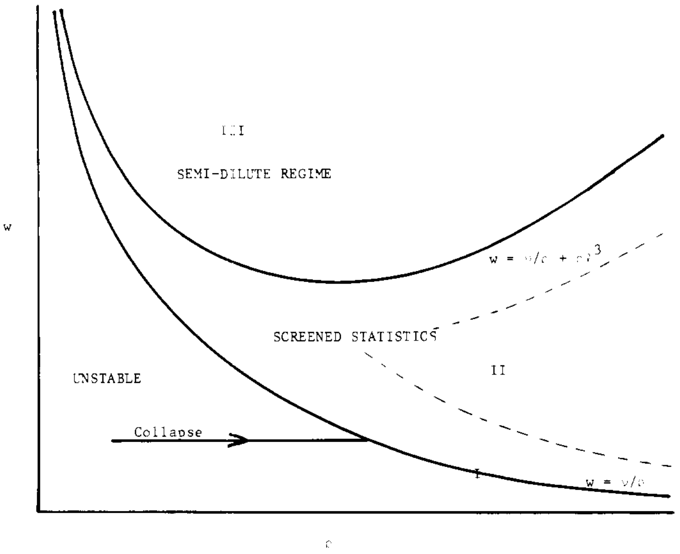

Figure 1.

important for regime I, the free network.

The free energy of deformation, eq IV.33, which applies to regime II reduces to the polymer solution theory of ref 6 in the absence of cross-links. More interesting is the limit of high density ($\phi \to 0$) in which the screening becomes perfect and we obtain exactly the phantom network result for the shear modes together with a positive osmotic pressure. (Interaction between the phantom network and polymer solution responses—a contravention of the so-called "additivity assumption"—appears at first order in ϕ.) The cross-links force increased contact between the chains locally and collectively they impede long range density fluctuation by their elasticity. Wasted loops are increased by the excluded volume since this suppresses interchain contacts more effectively than it does short loops—this is in contrast to the authors' earlier conclusion in ref 1 where the effect on interchain contacts was suppressed by the approximations made there. While the additivity assumption has hitherto been the only tractable basis for the development of network theories, the existence of departures from it—which the present calculation supports—has long been discussed in view of network swelling experiments.[11-13] As to whether the effects calculated here correspond to the experimental observations[13] or not is however a matter left open.

VI. Conclusion

The theory presented has been the simplest which is not just adding together the free energies of network and solution independently. The high-density limit was chosen because of the ease with which that limit can be calculated. In semidilute conditions the problem becomes much more difficult since although solution theory on its own takes on attributes of the mathematics of critical phenomena, it is not at all clear what happens when both network and solution behaviors are present. A more serious fault than this is the neglect of entanglements, which is rigorously justified in the thermodynamics of the solutions but not in network theory and hence not here. Although it is not done here, it is clear that the ideas in the dynamics of dense polymers, their diffusion,[5,6] and viscoelasticity[7-10] suggest that it will not be too difficult to include them under dense conditions. The semidilute region however again presents difficulty.

The inclusion of polymer interactions breaks the symmetry which exists for rotations within the whole replica space. This rotational symmetry is broken by the choice of trial functions with the property that the replicas are on average affinely deformed relative to the initial condition, but without the polymer interaction this choice appears arbitrary even though it is clearly correct on physical grounds.

The same problem was resolved in James and Guth's[10] treatment by fixing chains to the walls of the containing box, but this should not be physically necessary. These difficulties are resolved by the incorporation of solution theory. They would not have been resolved in entanglement theory since entanglements have the nature of cross-links from the point of view of this particular question.

Appendix I

First note that the distribution, eq III.3, is simply the normalized joint Gaussian distribution with the correct second moments

$$\langle \rho_k \rho_{k'}^* \rangle = \frac{12\mathcal{L}}{lk^2}\delta^\kappa(k-k')$$

where here as elsewhere in this paper δ^κ is a Kronecker δ. It is important to take account of the fact that the density in real space is a real number so that $\rho_k^* = \rho_{-k}$; then performing the integral of eq III.2 gives immediately

$$e^{-F/k_BT} = \exp\left[-\frac{1}{2}\sum_k \ln\left|\frac{12\pi\mathcal{L}}{lk^2}\right| - \frac{1}{2}\sum_k \ln\frac{1}{\pi}\left|\frac{lk^2}{12\mathcal{L}} + \frac{w}{V}\right| - \frac{1}{2}\frac{w\mathcal{L}^2}{V}\right]$$

where the last term is simply the contribution of the $k = 0$ mode. Thus

$$F/k_BT = \frac{1}{2}\sum_k \ln\left|1 + \frac{12\mathcal{L}w}{lk^2V}\right| + \frac{1}{2}\frac{w\mathcal{L}^2}{V} =$$
$$\frac{1}{2}\sum_k\left[\ln\left|1 + \frac{12\mathcal{L}w}{lk^2V}\right| - \frac{12\mathcal{L}w}{lk^2V}\right] + \frac{1}{2}\sum_k\frac{12\mathcal{L}w}{lk^2V} + \frac{1}{2}\frac{w\mathcal{L}^2}{V}$$

Now at large k the first summand above has k^{-4} as its leading term and so the first summation clearly exists. The second term we shall see to be independent of volume and hence not contributory to the osmotic pressure, but divergent unless we use the softened interaction given in (II.2). This exactly introduces a cutoff factor $e^{-a^2k^2/6}$ so by using

$$\sum_k \to \frac{V}{(2\pi)^3}\int d^3k$$

we obtain, with $\xi^2 = lV/12\mathcal{L}w$

$$F/k_BT = \frac{1}{2}\frac{V}{(2\pi)^3}\int_0^\infty 4\pi k^2\, dk \times$$
$$\left[\left(\ln\left|1 + \frac{1}{k^2\xi^2}\right| - \frac{1}{k^2\xi^2}\right) + \frac{1}{k^2\xi^2}e^{-a^2k^2/6}\right] + \frac{1}{2}\frac{w\mathcal{L}^2}{V}$$

The first integral gives

$$\frac{4\pi}{2}\frac{V}{(2\pi)^3}\frac{1}{\xi^3}\int_0^\infty dx\, x^2\left[\ln\left|1 + \frac{1}{x^2}\right| - \frac{1}{x^2}\right] =$$
$$-\frac{V}{(2\pi)^2}\frac{1}{\xi^3}\int_0^\infty dx\,\frac{x^3}{3}\frac{2}{x^3}\frac{1}{1+x^2}$$

by parts

$$= -\frac{V}{(2\pi)^2}\frac{\pi}{3}\left(\frac{12\mathcal{L}w}{lV}\right)^{3/2}$$

the second integral gives

$$\frac{V}{(2\pi)^2}\frac{1}{\xi^2}\int_0^\infty \mathrm{d}k\, e^{-a^2k^2/6} = \frac{V}{(2\pi)^2}\frac{12\mathcal{L}w}{lV}\frac{1}{2}\left(\frac{6\pi}{a^2}\right)^{1/2}$$

and reassembling all the terms we obtain

$$F/k_{\mathrm{B}}T = \mathcal{L}\left[\frac{w\mathcal{L}}{2V} - \frac{2}{\pi}\frac{w}{l}\left(\frac{3w\mathcal{L}}{lV}\right)^{1/2} + \frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\frac{w}{al}\right]$$

Appendix II

For full details of this calculation and various extensions of it the reader is referred to the work of Deam and Edwards.

The replica integral we require here is

$$e^{-F(n,\mu)/k_{\mathrm{B}}T} = \int \delta\mathbf{r}^\alpha \exp\left[-\frac{3}{2l}\sum_\alpha\int_0^{\mathcal{L}}\mathbf{r}^{\alpha\prime 2}\,\mathrm{d}s + \mu\int_0^{\mathcal{L}}\int_0^{\mathcal{L}}\frac{\mathrm{d}s\,\mathrm{d}s'}{2}\prod_\alpha\delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s')) - N_{\mathrm{c}}\log\mu\right]$$

Making an orthogonal transformation among the replica indices from $\mathbf{r}^\alpha$ to X_α with X_0 given by eq III.10 we introduce the trial harmonic localization as

$$Q = \sum_{\alpha=1}^{n}\frac{q^2}{6l}\int_0^{\mathcal{L}}X_\alpha^{\ 2}\,\mathrm{d}s$$

The orthogonality of the transformation ensures that

$$\sum_{\alpha=0}^{n}\mathbf{r}^{\alpha\prime 2} = \sum_{\alpha=0}^{n}X_\alpha^{\ \prime 2} \quad\text{and}\quad \prod_{\alpha=0}^{n}\delta(\mathbf{r}^\alpha) = \prod_{\alpha=0}^{n}\delta(X_\alpha)$$

so by using the variational principle (eq III.9) we can write

$$e^{-F(n,\mu)/k_{\mathrm{B}}T} \geq e^{-F(n,\mu,q)/k_{\mathrm{B}}T} =$$

$$\int \delta X_\alpha \exp\left[\frac{-3}{2l}\sum_{\alpha=0}^{n}\int_0^{\mathcal{L}}X_\alpha^{\ \prime 2}\,\mathrm{d}s - \frac{q^2}{6l}\sum_{\alpha=1}^{n}\int_0^{\mathcal{L}}X_\alpha^{\ 2}\,\mathrm{d}s + \left\langle\mu\int_0^{\mathcal{L}}\int_0^{\mathcal{L}}\frac{\mathrm{d}s\,\mathrm{d}s'}{2}\prod_\alpha\delta(X_\alpha(s) - X_\alpha(s')) + \frac{q^2}{6l}\sum_{\alpha=1}^{n}\int_0^{\mathcal{L}}X_\alpha^{\ 2}\,\mathrm{d}s - N_{\mathrm{c}}\log\mu\right\rangle\right]$$

Then

$$F(n,\mu,q)/k_{\mathrm{B}}T = G/k_{\mathrm{B}}T + \left\langle -\mu\int_0^{\mathcal{L}}\int_0^{\mathcal{L}}\frac{\mathrm{d}s\,\mathrm{d}s'}{2}\prod_\alpha\delta(X_\alpha(s) - \mathrm{x}_\alpha(s')) - \frac{q^2}{6l}\sum_{\alpha=1}^{n}\int_0^{\mathcal{L}}X_\alpha^{\ 2}\,\mathrm{d}s + N_{\mathrm{c}}\log\mu\right\rangle$$

where as shown by Deam and Edwards

$$G/k_{\mathrm{B}}T = -\sum_{\alpha=0}^{n}\log\int\delta X_\alpha(s)\exp\left[-\frac{3}{2l}\int_0^{\mathcal{L}}X_\alpha^{\ \prime 2}\mathrm{d}s - \frac{q^2}{6l}\int_0^{\mathcal{L}}X_\alpha^{\ 2}\,\mathrm{d}s\right] = \frac{nl\mathcal{L}q}{2} + \text{(terms which do not contribute physically)}$$

$$\left\langle\int_0^{\mathcal{L}}\int_0^{\mathcal{L}}\frac{\mathrm{d}s\,\mathrm{d}s'}{2}\prod_{\alpha=0}^{n}\delta(X_\alpha(s) - X_\alpha(s'))\right\rangle = \frac{\mathcal{L}^2}{2V\prod_i(\mathrm{u} + n\lambda_i^{\ 2})^{1/2}}\left(\frac{q}{2\pi}\right)^{3n/2} + \frac{3\mathcal{L}}{1\pi(1 + 3n)}\left(\frac{3}{2\pi a^2}\right)^{(1+3n)/2}$$

$$\left\langle\frac{q^2}{6l}\sum_{\alpha=1}^{n}\int_0^{\mathcal{L}}X_\alpha^{\ 2}\,\mathrm{d}s\right\rangle = \frac{nl\mathcal{L}q}{4}$$

Making $F(n,\mu,q)$ stationary with respect to q then gives

$$0 = +\frac{nl\mathcal{L}}{4} - \frac{\mu\mathcal{L}^2}{2V}\frac{3}{2}n\frac{1}{q} + \text{order } n^2$$

so that

$$q = 3\frac{\mu\mathcal{L}}{lV} + \text{order } n$$

Substituting this value of q gives to first order in n

$$F(n,\mu) = \frac{nl\mathcal{L}}{4}\cdot\frac{3\mu\mathcal{L}}{lV} - \frac{\mu\mathcal{L}^2}{2V\prod_i(1 + n\lambda_i^{\ 2})^{1/2}}\left(\frac{3\mu\mathcal{L}}{2\pi lV}\right)^{3n/2} - \frac{3\mu\mathcal{L}}{l\pi(1 + 3n)}\left(\frac{3}{2\pi a^2}\right)^{(3n+1)/2} + N_{\mathrm{c}}\log\mu$$

Now making this stationary with respect to μ gives

$$0 = -\left(\frac{\mathcal{L}^2}{2V} + \frac{3\mathcal{L}}{l\pi}\left(\frac{3}{2\pi a^2}\right)^{1/2}\right) + \frac{N_{\mathrm{c}}}{\mu} + \text{order } n$$

$$\mu = \frac{2N_{\mathrm{c}}V}{\mathcal{L}^2}\left(1 + \frac{6}{\pi}\frac{V}{\mathcal{L}l}\left(\frac{3}{2\pi a^2}\right)^{1/2}\right)^{-1} + \text{order } n$$

which on substitution gives $F(n)$ as per eq III.12. The free energy of deformation is then $[\partial F(n)/\partial n]_{n=0}$ which gives eq III.13.

Appendix III

It must first be noted that Γ_κ is the fourier transform of a real density so that $\Gamma_\kappa^* = \Gamma_{-\kappa}$. Within this space eq IV.21 can be evaluated directly as

$$\int \mathrm{d}\Gamma\, e^{-(1/2)[\text{trace ln }\pi\mathbf{C}+(\Gamma-\bar{\Gamma})\mathbf{C}^{-1}(\Gamma-\bar{\Gamma})^*+\Gamma G\Gamma^*]} \qquad \text{(AIII.1)}$$

where the quadratic form in the exponent can be rewritted as

$$(\Gamma - \bar{\Gamma}\mathbf{C}^{-1}(\mathbf{C}^{-1} + G)^{-1})(\mathbf{C}^{-1} + G) \times (\Gamma^* - (\mathbf{C}^{-1} + G)^{-1}\mathbf{C}^{-1}\bar{\Gamma}^*) + \bar{\Gamma}\mathbf{C}^{-1}\bar{\Gamma}^* - \bar{\Gamma}\mathbf{C}^{-1}(\mathbf{C}^{-1} + G)^{-1}\mathbf{C}^{-1}\bar{\Gamma}^* \qquad \text{(AIII.2)}$$

The integral then gives $e^{-\mathcal{G}}$ where

$$\mathcal{G} = \tfrac{1}{2}\text{ trace ln }\pi\mathbf{C} - \tfrac{1}{2}\text{ trace ln }[\pi(\mathbf{C}^{-1} + G)^{-1}] + \tfrac{1}{2}\bar{\Gamma}\{1 - \mathbf{C}^{-1}(\mathbf{C}^{-1} + G)^{-1}\}\mathbf{C}^{-1}\bar{\Gamma}^* = \tfrac{1}{2}\text{ trace ln }(1 + \mathbf{C}G) + \tfrac{1}{2}\bar{\Gamma}G(1 + \mathbf{C}G)^{-1}\bar{\Gamma}^*$$

as stated in eq IV.22.

Appendix IV

We require first the moments

$$\langle\Gamma_{\mathbf{K}}\rangle = \left\langle\int_0^{\mathcal{L}}\mathrm{d}s\, e^{i\mathbf{K}\cdot r(s)}\right\rangle$$

where the average is with respect to e^{-W-Q}. It is most convenient to change from the coordinates $\mathbf{r}^\alpha(s)$ to $X_\alpha(s)$ of which it suffices to know that

$$X_0(s)_i = \sum_\alpha\frac{\lambda_i^{\ \alpha}r_i^{\ \alpha}(s)}{(\sum_\beta(\lambda_i^{\ \beta})^2)^{1/2}}$$

for each Cartesian i and that the others complete an orthogonal transformation. To preserve the scalar produce we also transform the reciprocal vectors $\mathbf{K}$, again requiring only

$$\mathbf{K}_{0i} = \sum_{\alpha} \frac{\lambda_i^{\alpha} K_i^{\alpha}}{(\sum_{\beta}(\lambda_i^{\beta})^2)^{1/2}}$$

Note the use of subscript for the transformed coordinates. Now the distribution factorizes in the X_α so that

$$\langle e^{i\mathbf{K}\cdot r(s)} \rangle = \prod_{\alpha} \langle e^{iK_\alpha X_\alpha(s)} \rangle$$

Since $X_0(s)$ alone is uniformly distributed over a box of volume

$$V_0 = V \prod_i \frac{1 + n\lambda_i^2}{(1 + n\lambda_i^2)^{1/2}} = V \prod_i (1 + n\lambda_i^2)^{1/2}$$

it follows that

$$\langle e^{iK_0 X_0(s)} \rangle = \delta^{\kappa}(K_0)$$

Thus the first moments vanish unless K_0 is zero. The operator $p(K)$ projects out only the single replica density coordinates, i.e., $\Gamma(K)$ for K such the $K^\alpha \neq 0$ for only one α; with $K = 0$ excluded it follows that such K can never have $K_0 = 0$ and hence $p\bar{\Gamma}^* = \bar{\Gamma} p = 0$ as required for eq IV.25.

Appendix V

The Second Moment Matrix. The second moments are

$$\mathbf{M}_{K,K'} = \left\langle \int_0^{\mathcal{L}} \mathrm{d}s \int_0^{\mathcal{L}} \mathrm{d}s' \, e^{i[K\cdot r(s) - K'\cdot r(s')]} \right\rangle$$

Using the transformed coordinates as in Appendix IV this becomes

$$\mathbf{M}_{K,K'} = \int_0^{\mathcal{L}} \mathrm{d}s \int_0^{\mathcal{L}} \mathrm{d}s' \prod_{\alpha} \langle e^{i[K_\alpha \cdot X_\alpha(s) - K_\alpha' X_\alpha(s')]} \rangle$$

The factor from $\alpha = 0$ gives $\delta^{\kappa}(K_0 - K_0')e^{-(l/6)|s-s'|K_0^2}$ and each $\alpha > 0$ gives

$$e^{-(K_\alpha^2/4q) - (K_\alpha'^2/4q) + (K_\alpha \cdot K_\alpha'/2q) e^{-(lq/3)|s-s'|}}$$

so we obtain

$$\mathbf{M}_{K,K'} = \int_0^{\mathcal{L}} \mathrm{d}s \int_0^{\mathcal{L}} \mathrm{d}s' \, \delta^{\kappa}(K_0 - K_0') \exp[-\sum_{\alpha>0} \frac{1}{4q}(K_\alpha - K_\alpha')^2 - \frac{l}{6} K_0^2 |s - s'| - \sum_{\alpha>0} \frac{K_\alpha \cdot K_\alpha'}{2q}(1 - e^{-lq|s-s'|/3})$$

Now it is convenient to introduce the following notation:

$$x = K_0(2q)^{-1/2}; \ \eta_\alpha = K_\alpha(2q)^{-1/2} \qquad \alpha = 1, \cdots, n$$

so that x is the collective zero component of $\mathbf{K}$ and η is the rest of the vector $\mathbf{K}$, both being reduced by $(2q)^{1/2}$.

In this new notation

$$\mathbf{M}_{K,K'} = \int_0^{lq\mathcal{L}/3} \frac{3}{ql} \mathrm{d}u \int_0^{lq\mathcal{L}/3} \times \frac{3}{ql} \mathrm{d}u' \, \delta^{\kappa}(x - x') e^{-1/2(\eta - \eta')2} e^{-x^2|u-u'| - \eta\cdot\eta'(1 - e^{-|u-u'|})} \simeq \frac{6\mathcal{L}}{ql} \int_0^{lq\mathcal{L}/6} \mathrm{d}y \, \delta^{\kappa}(x - x') e^{-(1/2)(\eta-\eta')^2} e^{-x^2 y - \eta\cdot\eta'(1 - e^{-y})} \quad \text{(AV.1)}$$

From this form we can readily derive the approximations used in Appendix VI. First for $q \rightarrow 0$ we have $y \ll 1$ always giving

$$\mathbf{M} = \delta^{\kappa}(K - K') \frac{6\mathcal{L}}{ql(\eta^2 + x^2)} \quad \text{(AV.2)}$$

For small $\eta\cdot\eta'$ we expand

$$e^{-\eta\cdot\eta'(1-e^{-y})} = 1 - \eta\cdot\eta'(1 - e^{-y}) + \text{order } (\eta\cdot\eta')^2$$

which gives

$$\mathbf{M} = \delta^{\kappa}(x - x') e^{-(1/2)(\eta-\eta')^2} \frac{6\mathcal{L}}{lqx^2} \left(1 - \frac{\eta\cdot\eta'}{1 + x^2} + \text{order } (\eta\cdot\eta')^2 \right) \quad \text{(AV.3)}$$

At large x it is convenient to rewrite the integral in eq AV.1 as

$$\int_0^{\infty} \mathrm{d}y \, e^{-x^2 y - \eta\cdot\eta'(1-e^{-y})} = \frac{1}{x^2} \int_0^1 \mathrm{d}z \exp[-\eta\cdot\eta'(1 - z^{1/x^2})]$$

Now

$$1 - z^{1/x^2} = -\frac{1}{x^2} \log z - \frac{1}{2} \frac{1}{x^4} (\log z)^2 + \text{order } x^{-6}$$

giving

$$\frac{1}{x^2} \int_0^1 \mathrm{d}z \, z^{\eta\cdot\eta/x^2} \exp\left[\frac{\eta\cdot\eta'}{2x^4} (\log z)^2 + \text{order } x^{-6}\eta\cdot\eta' \right] = \frac{1}{x^2} \int_0^1 \mathrm{d}z \, z^{\eta\cdot\eta'/x^2} \left(1 + \frac{\eta\cdot\eta'}{2x^4} (\log z)^2 + \text{order } \left[\frac{\eta\cdot\eta'}{x^6}, \left(\frac{\eta\cdot\eta'}{x^4} \right)^2 \right] \right) = \frac{1}{x^2 + \eta\cdot\eta'} \left(1 + \frac{\eta\cdot\eta'}{(x^2 + \eta\cdot\eta')^2} + \text{order } \left[\frac{\eta\cdot\eta'}{x^6}, \left(\frac{\eta\cdot\eta'}{x^4} \right)^2 \right] \right)$$

and putting this approximation back into expression AV.1, $\mathbf{M}$ becomes

$$\mathbf{M} = \delta(x - x') e^{-(1/2)(\eta\cdot\eta')^2} \frac{6\mathcal{L}}{lq(x^2 + \eta\cdot\eta')} \times \left(1 + \frac{\eta\cdot\eta'}{[x^2 + \eta\cdot\eta']^2} + \text{order } x^{-4} \right)$$

In the rest of this appendix we revert to the essentially exact expression AV.1.

(a) $\mathcal{L}^2$ + trace M.

$$\mathcal{L}^2 + \text{trace } \mathbf{M} = \sum_{\text{all } K} \frac{6\mathcal{L}}{ql} \int_0^{lq\mathcal{L}/6} \mathrm{d}y \, e^{-x^2 y - \eta^2(1-e^{-y})}$$

We now procede to replace summation by integration, but in doing so great care must be taken with the subspace $x = 0$ for which the integrand does not vanish as y becomes large. Thus

$$\sum_{\text{all } K} \rightarrow \bar{\nu} \int \mathrm{d}^{3n+3}K + \frac{\bar{\nu}}{\bar{V}_0} \int \mathrm{d}^{3n}K|_{x=0}$$

where the bar denotes reduction by appropriate factors of 2π:

$$\bar{\mathcal{V}} = \mathcal{V}(2\pi)^{-3n-3} \qquad \bar{V}_0 = V_0(2\pi)^{-3}$$

In terms of x,η this becomes

$$\sum_K \rightarrow \bar{\mathcal{V}}(2q)^{(3n+3)/2} \int \mathrm{d}^3x \, \mathrm{d}^{3n}\eta + \frac{\bar{\mathcal{V}}}{\bar{V}_0}(2q)^{3n/2} \int \mathrm{d}^{3n}\eta|_{x=0}$$

One final complication is that without softening the real space Dirac delta function, as discussed in section II, this quantity will not converge. That softening exactly gives a cutoff factor

$$e^{-a^2K^2/6} = e^{-(qa^2/3)(x^2+\eta^2)}$$

Finally

$$\mathcal{L}^2 + \text{trace}\,(\mathbf{M}e^{-a^2\kappa^2/6}) = \left[\bar{\mathcal{V}}(2q)^{(3n+3)/2}\int \mathrm{d}^3x\, \mathrm{d}^{3n}\eta + \frac{\bar{\mathcal{V}}}{\bar{V}_0}(2q)^{3n/2}\int \mathrm{d}^{3n}\eta|_{x=0}\right]\frac{6\mathcal{L}}{ql}\int_0^{lq\mathcal{L}/6}\mathrm{d}y \times \exp\left[-x^2y - \eta^2(1-e^{-y}) - \frac{qa^2}{3}(x^2+\eta^2)\right] =$$

$$\bar{\mathcal{V}}(2q)^{(3n+3)/2}\pi^{(3n+3)/2}\frac{6\mathcal{L}}{lq} \times \int_0^{lq\mathcal{L}/6}\mathrm{d}y\left(y + \frac{qa^2}{3}\right)^{-3/2}\left(1 - e^{-y} + \frac{qa^2}{3}\right)^{-3n/2} + \frac{\bar{\mathcal{V}}}{\bar{V}_0}(2q)^{3n/2}\pi^{3n/2}\frac{6\mathcal{L}}{lq}\int_0^{lq\mathcal{L}/6}\mathrm{d}y\left(1 - e^{-y} + \frac{qa^2}{3}\right)^{-3n/2}$$

The first integral is dominated by small y but the second by large y. Ignoring corrections smaller by an order of $(qa^2)^{1/2}$ we obtain

$$\bar{\mathcal{V}}\left(\frac{3}{2\pi a^2}\right)^{(3n+1)/2}\frac{6\mathcal{L}}{\pi l}\frac{1}{(1+3n)} + \frac{\mathcal{V}}{V_0}\left(\frac{q}{2\pi}\right)^{3n/2}\mathcal{L}^2$$

which is the result required in eq IV.28.

(b) Trace $[p\mathbf{M}^2p(1 + p\mathbf{M}p)^{-1}]$. First let us evaluate directly the matrix

$$\mathbf{M}^2{}_{K,K'} = \sum_{K''}\mathbf{M}_{K,K''}\mathbf{M}_{K'',K'} = \left(\frac{6\mathcal{L}}{ql}\int_0^{lq\mathcal{L}/6}\mathrm{d}u\right) \times \left(\frac{6\mathcal{L}}{ql}\int_0^{lq\mathcal{L}/6}\mathrm{d}\nu\right)\sum_{x''}\delta^{\kappa}(x - x'')\delta^{\kappa}(x'' - x')e^{-x^2u-x'^2\nu}\frac{\bar{\mathcal{V}}}{\bar{V}_0}(2q)^{3n/2}\int \mathrm{d}^{3n}\eta''\, e^{-(1/2)(\eta-\eta'')^2-(1/2)(\eta''-\eta')2-\eta\cdot\eta''(1-e^{-u})-\eta''\cdot\eta'(1-e^{-\nu})}$$

$$= \left(\frac{6\mathcal{L}}{ql}\int_0^{lq\mathcal{L}/6}\mathrm{d}u\right) \times \left(\frac{6\mathcal{L}}{ql}\int_0^{lq\mathcal{L}/6}\mathrm{d}\nu\right)e^{-x^2u-\eta^2(1-e^{-u})-x^2\nu-\eta'^2(1-e^{\nu})}\frac{\bar{\mathcal{V}}}{V_0}\left(\frac{q}{2\pi}\right)^{3n/2}\delta^{\kappa}(x - x')e^{-(1/4)(\eta-\eta')^2}$$

For light linking q, and hence u and ν, are small, x and η are large, and $\eta \sim \eta'$ giving us finally

$$\mathbf{M}_{K,K'}{}^2 \simeq \frac{\bar{\mathcal{V}}}{V_0}\left(\frac{q}{2\pi}\right)^{3n/2}\left[\frac{6\mathcal{L}}{ql(x^2+\eta^2)}\right]^2\delta^{\eta}(x - x')\delta^{\kappa}(\eta - \eta') + \text{corrections smaller by } q^{1/2}$$

In evaluating excluded volume corrections we will anticipate $\mu \sim q$ and focus upon the lightly linked limit in which terms of higher order than one in μ can be neglected. Thus we can almost neglect q in a term which carries an explicit factor of μ, save for logarithmic corrections, i.e., terms of the form $\mu q^n = \mu(1 + n \log q + \text{order } n^2)$. It will be seen that the above expression for $\mathbf{M}^2$ is, apart from the correction $(\mathcal{V}/V_0)(q/2\pi)^{3n/2}$, the value obtaining at $q = 0$,

$$[\mathbf{M}^2]_{q=0} = [\mathbf{M}]_{q=0}{}^2 = \left(\frac{12\mathcal{L}}{lK^2}\right)^2\delta^{\mathrm{K}}(K - K')$$

For $\mathbf{M}$ we can use the $q = 0$ value directly:

$$[\mathbf{M}]_{q=0} = \frac{12\mathcal{L}}{lK^2}\delta^{\mathrm{K}}(K - K')$$

The operator p premultiplies every term in the trace which we are calculating so that only those values of K for which $p(K)$ is nonzero can contribute. Thus the implied summation

$$\text{trace} \equiv \sum_{\text{all } K}$$

can be replaced by $\sum_\alpha\sum_{K^\alpha}$ where we understand $\sum_{K^\alpha}$ to mean the summation over K^α with $K^\beta = 0$ for $\beta \neq \alpha$. Since both $\mathbf{M}$ and $\mathbf{M}^2$, hence $p\mathbf{M}p$ and $p\mathbf{M}^2p$, have been reduced to diagonal approximations above, the matrix multiplications are trivial and the whole trace now becomes:

$$\sum_\alpha\sum_{K^\alpha}\frac{\nu}{V^\alpha}\left(\frac{12\mathcal{L}}{lK^{\alpha 2}}\right)^2\left(1 + \frac{\nu}{V^\alpha}\frac{12\mathcal{L}}{lK^{\alpha 2}}\right)^{-1}\frac{\bar{\mathcal{V}}}{V_0}\left(\frac{q}{2\pi}\right)^{3n/2}$$

Replacing $\sum_{K^\alpha}$ by $\bar{V}^\alpha\int \mathrm{d}^3K^\alpha$ and substituting $K^\alpha(lV^\alpha/12\mathcal{L}\nu)^{1/2} = k$ brings this to

$$\sum_\alpha\bar{\mathcal{V}}\frac{6\mathcal{L}V^\alpha}{\pi l V_0}\left(\frac{3\mathcal{L}\nu}{lV^\alpha}\right)^{1/2}\left(\frac{q}{2\pi}\right)^{3n/2}$$

as used on eq IV.28.

Appendix VI

We set out here to calculate trace ln $(1 + p\mathbf{M}p)$ up to first order in q. Just as in Appendix Vb we can exploit the projective nature of p to reduce the trace to

$$\text{trace} \equiv \sum_\alpha\sum_{K^\alpha}$$

We cannot however take a $q = 0$ approximation to $\mathbf{M}$, which would be diagonal, but we can exploit the fact that $\mathbf{M}$ is at least diagonal in K_0. Thus for each α we express K^α in terms of K_0 writing

$$\text{trace} \equiv \sum_{K_0}\sum_\alpha$$

and for each K_0 we can treat ln $(1 + p\mathbf{M}p)$ as a matrix problem in the replica indices α only.

The sum over K_0 is then trivial once we have evaluated

$$\underset{\alpha}{\text{trace}}\ln(1 + p\mathbf{M}p) \text{ at each } K_0$$

For given K_0 there are only five different elements of the matrix $(p\mathbf{M}p)_{\alpha\beta}$ coming from the following cases: a, $\alpha = \beta = 0$; b, $\beta > \alpha = 0$; c, $\alpha > \beta = 0$; d, $\alpha = \beta > 0$; e, $0 < \alpha \neq \beta > 0$. So the matrix has the form

$$p\mathbf{M}p = \begin{vmatrix} a & b & b & b\ldots \\ c & d & e & e\ldots \\ c & e & d & e\ldots \\ c & e & e & d\ldots \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix} \qquad \text{(AVI.1)}$$

for which explicit evaluation gives (Appendix VII)

$$\underset{\alpha}{\text{trace}}\ln(1 + p\mathbf{M}p) = \ln(1 + a) + n\ln(1 + d - e) + n\left(\frac{e - \dfrac{bc}{a+1}}{1 + d - e}\right) + \text{order } n^2 \qquad \text{(AVI.2)}$$

It will be seen that for $q = 0$ (when $\mathbf{M}$ itself is diagonal), b, c, and e are all zero so that

$$\underset{\alpha}{\mathrm{trace}} \ln (1 + p\mathbf{M}p) = [\underset{\alpha}{\mathrm{trace}} \ln (1 + p\mathbf{M}p)]_{q=0} + \ln \left|\frac{1 + a}{1 + a_0}\right| + n \ln \left|\frac{1 + d}{1 + d_0}\right| + n \left(\frac{e - \dfrac{bc}{a + 1}}{1 + d - e} \right) + n \ln \left|1 - \frac{e}{1 + d}\right| + \text{order } n^2$$

The value at $q = 0$ will just give the unlinked polymer solution contributions, for which the calculation has been given in section III and Appendix I, so we confine our attention here to the q dependent corrections. The final summation over K_0 we will express as

$$\sum_{K_0} \boxminus \bar{V}_0(2q)^{3/2} \int \mathrm{d}^3x$$

so that with the terms of eq AVI.3 expressed in terms of x we seek, to final order q, only those terms whose integral diverges like $q^{-1/2}$ as $q \to 0$. Thus only the forms of the terms of AVI.3 at large x will be required; to this end the expansions of the matrix elements of **M** given in Appendix V will be used.

(i) $\sum_{K_0} \ln |(1 + a)/(1 + a_0)|$. Here $a = (\nu/V)\mathbf{M}(K^0,K^0)$ so that in the notation of Appendix V we have $K = K'$ and

$$\varkappa^2 = \frac{K^2}{2q} - x^2 = \frac{K^{0\,2}}{2q} - x^2 = x(1 + n\Lambda^2)x - x^2 = nx\cdot\Lambda^2\cdot x$$

Thus we need only first order expansion in η^2, which gives

$$a = \frac{\nu}{V} \frac{6\mathcal{L}}{lqx^2}\left(1 - \frac{\eta^2}{1 + x^2} \right) + \text{order } \eta^4 \text{ (by (AV.3))} = \frac{\nu}{V} \frac{6\mathcal{L}}{lqx^2}\left(1 - n \frac{x\cdot\Lambda^2\cdot x}{1 + x^2} \right) + \text{order } n^2$$

Also

$$a_0 = \frac{\nu}{V} \frac{6\mathcal{L}}{lqx^2}\left(1 - n \frac{x\cdot\Lambda^2\cdot x}{x^2} \right) + \text{order } n^2 \text{ (by (AV.2))}$$

so that

$$a - a_0 = \frac{\nu}{V} \frac{6\mathcal{L}}{lqx^2}\, n \frac{x\cdot\Lambda^2\cdot x}{x^2(1 + x^2)}$$

Then

$$\ln \left(\frac{1 + a}{1 + a_0} \right) = \ln \left(1 + \frac{a - a_0}{1 + a_0} \right) = \frac{a - a_0}{1 + a_0} + \text{order } n^2 = \frac{nx\cdot\Lambda^2\cdot x}{x^2(1 + x^2)(1 + \zeta^2x^2)}$$

$$\zeta^2 = lqV/6\mathcal{L}\nu$$

Summing this over K_0 gives

$$\bar{V}_0(2q)^{3/2} \int \mathrm{d}^3x\, n \frac{x\cdot\Lambda^2\cdot x}{x^2(1 + x^2)(1 + \zeta^2x^2)} = n\bar{V}_0(2q)^{3/2}\left(\frac{1}{3}\sum_i \lambda_i^2 \right) 4\pi\frac{\pi}{2\zeta}(1 + \text{order } \zeta)$$

Note that ζ is order $q^{1/2}$ so that the leading term is of order q.

(ii) $n\sum_{K_0} \ln |(1 + d)/(1 + d_0)|$. Since this term carries an explicit factor of n the rest of its evaluation can be made at $n = 0$. It is most convenient here to express the reciprocal vectors in terms of $k = K^\alpha(2q)^{-1/2}$ so that

$$K^2 = 2qk^2 \qquad \eta^2 = k^2 - x^2 = k\cdot(1 - \Lambda^2)\cdot k$$

To examine the large k behavior we use

$$d = \frac{\nu}{\tilde{V}}\mathbf{M} = \frac{\nu}{\tilde{V}} \frac{6\mathcal{L}}{lqk^2}\left(1 + \frac{\eta^2}{k^4} + \text{order } k^4 \right) \text{ (by (AV.4))}$$

$$d_0 = \frac{\nu}{\tilde{V}} \frac{6\mathcal{L}}{lqk^2} \text{(by (AV.2))}$$

This gives

$$\ln \left|\frac{1 + d}{1 + d_0}\right| = \ln \left|1 + \frac{d - d_0}{1 + d_0}\right| = \ln \left|1 + \frac{\dfrac{1}{\tilde{\zeta}^2k^2}[1 + \eta^2/k^4 + \cdots]}{1 + \dfrac{1}{\tilde{\zeta}^2k^2}}\right| = \frac{\eta^2}{k^4(1 + \tilde{\zeta}^2k^2)} + \text{order } k^{-4}$$

where $\tilde{\zeta}^2 = lq\tilde{\mathrm{V}}/6\mathcal{L}\nu$. Summing over K_0 is equivalent to summing over k which gives

$$\sum_{K_0} n \ln \left(\frac{1 + d}{1 + d_0} \right) = n(2q)^{3/2}\, \tilde{\mathrm{V}} \int \mathrm{d}^3k\, \frac{k(1 - \Lambda^2)k}{k^4(1 + \tilde{\zeta}^2k^2)} = n(2q)^{3/2}\, \frac{\tilde{V}}{8\pi^3} 4\pi \frac{\pi}{2\tilde{\zeta}}\left[1 - \frac{1}{3}\sum_i \lambda_i^2 \right]$$

(iii) For the terms $(e - bc)/(1 + a)/(1 + d - e)$ and $\ln (1 - \mathrm{e}/(1 + d))$ we first note that a and d fall off like K^{-2} at large K. By contrast the off diagonal elements e, b, and c fall off like $e^{-(\eta-\eta')^2/2}$, using eq AV.4, where $(\eta - \eta')^2 \sim 2x^2$. As a result

$$\sum_{K_0} \left\{ \frac{e - \dfrac{bc}{1 + a}}{1 + d - e} + \ln \left(1 - \frac{e}{1 + d} \right) \right\}$$

has its leading term simply of order $q^{3/2}$ and the corrections to this are higher powers of q.

Then only the diagonal elements of **M** contribute to order q in trace ln $(1 + p\mathbf{M}p)$, and contributions (i) and (ii) above give expression IV.3.

Appendix VII

We require trace ln $(1 + p\mathbf{M}p)$ = ln det$(1 + p\mathbf{M}p)$ where

$$(1 + p\mathbf{M}p) = \left| \begin{array}{llllll} 1 + a & b & b & b & b & b \ldots \\ c & 1 + d & e & e & e & e \ldots \\ c & e & 1 + d & e & e & e \ldots \\ c & e & e & 1 + d & e & e \ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{array} \right|$$

Making an orthogonal transformation by a matrix **T** of the form

$$\mathrm{T} = \left| \begin{array}{lllllll} 1 & 0 & 0 & 0 & 0 & 0 & \ldots \\ 0 & n^{-1/2} & n^{-1/2} & n^{-1/2} & n^{-1/2} & n^{-1/2} & \ldots \\ 0 & n^{-1/2} & & & & & \\ 0 & n^{-1/2} & & & & & \\ \cdot & \cdot & & & & & \\ \cdot & \cdot & & & & & \\ \cdot & \cdot & & & & & \end{array} \right|$$

(where the unspecified elements are only restricted to keep **T** orthogonal) the matrix becomes

$\mathrm{T}(1 + p\mathrm{M}p)\mathrm{T}^{-1} =$

$$\begin{vmatrix} 1+a & b\sqrt{n} & 0 & 0 & \cdots \\ c\sqrt{n} & 1+d-e+ne & 0 & 0 & \cdots \\ 0 & 0 & 1+d-e & 0 & \cdots \\ 0 & 0 & 0 & 1+d-e & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{vmatrix}$$

whence $\det(1 + p\mathbf{M}p) = \det[\mathbf{T}(1 + p\mathbf{M}p)\mathbf{T}^{-1}] = [(1 + a)(1 + d - e - ne) - nbc](1 + d - e)^{n-1}$, from which eq AVI.2 follows immediately.

Appendix VIII

First we must reconstruct the generating function $\mathcal{F}$. From eq IV.16, IV.17, and IV.21

$$\mathcal{F}/k_{\mathrm{B}}T = -\frac{1}{2}\mu\frac{\mathcal{L}^2}{\mathcal{V}} + \frac{1}{2}\sum_\alpha \frac{\nu\mathcal{L}^2}{V^\alpha} + \frac{nl\mathcal{L}q}{2} + \mathcal{G}$$

and $\mathcal{G}$ is given by eq IV.27. Incorporating the polymer solution terms (of the form of expression 3.4), there correction, eq IV.31, and the cross-link contributions, eq IV.28 and IV.29, then gives

$$\mathcal{F}(\nu,q,\mu)/k_{\mathrm{B}}T = \sum_\alpha\left[\frac{1}{2}\frac{\mathcal{L}^2\nu}{V^\alpha} - \frac{2\mathcal{L}\nu}{\pi l}\left(\frac{3\nu\mathcal{L}}{lV^\alpha}\right)^{1/2} + \frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\frac{\nu\mathcal{L}}{al}\right] + nq\frac{l\mathcal{L}}{2}\left[1 + \frac{2}{\pi l\mathcal{L}}\left(\frac{3\nu\mathcal{L}V}{l}\right)^{1/2}I + \frac{2}{\pi l\mathcal{L}}\left(\frac{3\nu\mathcal{L}\tilde{V}}{l}\right)^{1/2}(3 - I)\right] - \mu\left[\frac{\mathcal{L}^2}{2V_0}\left(\frac{q}{2\pi}\right)^{3n/2} + \frac{3\mathcal{L}}{l\pi(1 + 3n)}\left(\frac{3}{2\pi a^2}\right)^{(3n+1)/2} - \frac{1}{2}\sum_\alpha\frac{V^\alpha}{V_0}\left(\frac{q}{2\pi}\right)^{3n/2}\frac{6\mathcal{L}}{\pi l}\left(\frac{3\mathcal{L}\nu}{lV^\alpha}\right)^{1/2}\right] \quad \text{(AVIII.1)}$$

Now we must use eq IV.6 to generate $F(\mu,q)$ which gives

$$F(\mu,q)/k_{\mathrm{B}}T = \sum_\alpha\left[\frac{1}{2}\frac{\mathcal{L}^2w}{V^\alpha} - \frac{2\mathcal{L}w}{\pi l}\left(\frac{3w\mathcal{L}}{lV^\alpha}\right)^{1/2} + \frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\frac{w\mathcal{L}}{al}\right] + \frac{nql\mathcal{L}}{4}\left[1 + \frac{2}{\pi}\left(\frac{3wV}{\mathcal{L}l^3}\right)^{1/2}I + \frac{2}{\pi}\left(\frac{3w\tilde{V}}{\mathcal{L}l^3}\right)^{1/2}(3 - I)\right] - \mu\left[\frac{\mathcal{L}^2}{2V_0}\left(\frac{q}{2\pi}\right)^{3n/2} + \frac{3\mathcal{L}}{l\pi(1 + 3n)}\left(\frac{3}{2\pi a^2}\right)^{(3n+1)/2} - \frac{1}{2}\sum_\alpha\frac{V^\alpha}{V_0}\left(\frac{q}{2\pi}\right)^{3n/2}\frac{6\mathcal{L}}{\pi l}\left(\frac{3\mathcal{L}w}{lV^\alpha}\right)^{1/2}\right] + \text{order }\frac{\mu^2}{w} \quad \text{(AVIII.2)}$$

To order n, the terms containing q are

$$\frac{nql\mathcal{L}}{4}\left[1 + \frac{1}{3}\phi I + \frac{1}{3}\phi B^{1/2}(3 - I)\right] - \frac{3n}{2}\log q\left[\frac{\mu\mathcal{L}^2}{2V}(1 - \phi)\right] \quad \text{(AVIII.3)}$$

where $\phi = 6/\pi(3wV/\mathcal{L}l^3)^{1/2}$ and $B = \tilde{V}/V$. These are made stationary with

$$q = \frac{3\mu\mathcal{L}}{lV}\,\frac{(1 - \phi)}{(1 + 3\phi[I + B^{1/2}(3 - I)])}$$

the stationary value being

$$\frac{3n}{4}\mu\frac{\mathcal{L}^2}{V}(1 - \phi)\left(1 - \log\left|\frac{3\mu\mathcal{L}}{lV}(1 - \phi)\right| + \log\left|1 + 3\phi[I + B^{1/2}(3 - I)]\right|\right)$$

Now we must determine μ to give $F(n)$ in accordance with eq II.19. It was shown in ref 1 that it is sufficient to take the value of μ which makes $F(n)$ stationary at $n = 0$, for which the μ dependence of $F(n = 0,\mu)/k_{\mathrm{B}}T + N_{\mathrm{c}}\log\mu$ is

$$N_{\mathrm{c}}\log\mu - \mu\left[\frac{\mathcal{L}^2}{2V}(1 - \phi) + \frac{\mathcal{L}}{l}\,\frac{3}{\pi}\left(\frac{3}{2\pi a^2}\right)^{1/2}\right]$$

This is made stationary with respect to μ for

$$\mu = \frac{2VN_{\mathrm{c}}}{\mathcal{L}^2\left(1 + \frac{6V}{\pi l\mathcal{L}}\left(\frac{3}{2\pi a^2}\right)^{1/2} - \phi\right)}$$

but in this case the stationary value is not of interest since we are interested in the free energy of deformation, this being the coefficient of n in $F(n)$. This comes solely from the n dependence of $F(\mu,q)$, wherein the coefficient of n is, from eq AVIII.2,

$$\tilde{F}/k_{\mathrm{B}}T = \frac{1}{2}\,\frac{\mathcal{L}^2w}{\tilde{V}}\left(1 - \frac{1}{3}\phi B^{1/2}\right) + \frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\frac{w\mathcal{L}}{al} + \frac{3}{4}\mu\frac{\mathcal{L}^2}{V}(1 - \phi)\left(1 - \log\left|\frac{3\mu\mathcal{L}}{lV}(1 - \phi)\right| + \log|1 + 3\phi[I + B^{1/2}(3 - I)]|\right) - \mu\left[\frac{\mathcal{L}^2}{2V}\left(-\frac{1}{2}I(1 - \phi) - B^{1/2}\phi\right) + \frac{3\mathcal{L}}{\pi l}\left(\frac{3}{2\pi a^2}\right)^{1/2}\left(-3 + \frac{3}{2}\log\left|\frac{3}{2\pi a^2}\right|\right)\right]$$

Dropping terms independent of deformation gives

$$\tilde{F}/k_{\mathrm{B}}T = \frac{1}{2}\frac{w\mathcal{L}^2}{V}\left(\frac{1}{\mathrm{B}} - \frac{2}{3}\phi\frac{1}{\mathrm{B}^{1/2}}\right) + N_{\mathrm{c}}\frac{2}{\left(1 + \frac{6V}{\pi l\mathcal{L}}\left(\frac{3}{2\pi a^2}\right)^{1/2} - \phi\right)} \times \left\{\frac{3}{4}(1 - \phi)\log(1 + 3\phi[I + (3 - I)B^{1/2}]) + \frac{1}{4}(1 - \phi)I + \frac{1}{2}\phi B^{1/2}\right\} = \frac{1}{2}\frac{w\mathcal{L}^2}{V}\left(\frac{1}{\mathrm{B}} - \frac{2}{3}\phi\frac{1}{B^{1/2}}\right) + \frac{N_{\mathrm{c}}}{1 + \gamma}\left(\frac{1}{2}I + \frac{\phi}{1 - \phi}B^{1/2} + \frac{3}{2}\log\left|1 + 3\phi[I + (3 - I)B^{1/2}]\right|\right)$$

where the wasted loop correction γ is

$$\gamma = \frac{1}{1 - \phi}\,\frac{6V}{\pi l\mathcal{L}}\left(\frac{3}{2\pi a^2}\right)^{1/2}$$

References and Notes

(1) Ball, R. C.; Edwards, S. F. *Polymer* **1979**, *20*, 1357.

(2) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.

(3) Deam, R. T.; Edwards, S. F. *Philos. Trans. R. Soc., London* **1976**, *11*, 317.

(4) Edwards, S. F. *Proc. Phys. Soc., London* **1966**, *88*, 265.

(5) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.

(6) Klein, J. *Nature (London)* **1978**, *271*, 143.

(7) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978,** *74,* 1789.

(8) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978,** *74,* 1802, 1818.

(9) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1979,** *75,* 38.

(10) James, H. M.; Guth, E. *J. Chem. Phys.* **1943,** *11,* 455.

(11) Gee, Herbert; Roberts *Polymer* **1969,** *6,* 541.

(12) Yen; Eichinger *J. Polym. Sci., Polym. Phys. Ed.* **1978,** *16,* 121.

(13) Flory, P. J. *Macromolecules* **1979,** *12,* 119.

(14) Collins, P. D. B. "Regge Theory and High Energy Physics"; CUP 1977, p 64.

(15) de Gennes, P.-G. *Phys. Lett. A* **1972,** *38,* 339.

(16) Titchmarsh, E. C. "Theory of Functions", CUP 1939, 186.

Graph-Like State of Matter. 14. Statistical Thermodynamics of Semidilute Polymer Solution

P. Irvine and M. Gordon*

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, England.

Received December 31, 1979

ABSTRACT: The phase equilibrium behavior of solutions of polystyrene in cyclohexane, covering broad neighborhoods of their critical points, is well-described by a pseudo-two-phase "bridging" theory. This theory retains the essential contribution of athermal Poisson statistics of the original version by Koningsveld, Stockmayer, Kennedy, and Kleintjens. However, the theory has been substantially simplified and amends the Flory–Huggins model along the lines suggested by its originators. Neither the mean-field character nor the implicit status of a nonlocalized model is abandoned. Indeed, the *translational* partition function of the original model is the only part amended, in order to differentiate the behavior of polymer chains in the "dilute" and "concentrated" pseudophases. Although the differential effect between the two phases is minute, of order kT per polymer chain, it reproduces well the expected transitional behavior around the concentration ϕ^* (entanglement point). The correction, reinforced by the Huggins second-nearest-neighbor correction, drastically changes the theoretical virial series and produces the shapes of spinodal and cloud point curves which are indeed observed. The model is fitted to extensive spinodal data by pulse-induced critical scattering (PICS), to cloud points, and to critical points. The effects of polydispersity are nicely reproduced by the theory. The strategy of validating models through successive refinements is briefly discussed. Further refinement of the statistical mechanical mean-field theory of nonpolar polymer solutions around their critical points now hinges on the production of test samples more accurately characterized than at present with respect to molecular weight.

The problem of refining statistical-thermodynamic models of the free energy ΔG of mixing of a polymer solution, the basic function from which all its thermodynamic properties flow, exemplifies the kind of vicious circle which frequently challenges physical science. It is not that we lack experimental techniques of sufficient sensitivity: simple experiments contain an enormous wealth of information. But unfortunately we need to be in possession of an excellent free energy function already if we are to be able to extract that information unambiguously. To exploit highly sensitive thermodynamic measurements requires exceedingly well-characterized polymer samples, but such characterization requires prior knowledge of the thermodynamics. For an example at a low level: ΔG depends on $\bar{M}_n$, the number-average molecular weight, but the search for precision in $\bar{M}_n$ founders on the effects of higher virial coefficients on the requisite extrapolation if pressed too far.

The strategy to be adopted for breaking such a vicious circle has been well formulated by Bachelard[1] in a passage which may be translated: "As the application (i.e., of theory) is submitted to successive approximations, one may say that the scientific concept corresponding to a particular phenomenon is the *pattern* of well-ordered successive approximations. Scientific conceptualization needs a series of concepts progressing toward perfection in order to realize the dynamism we aim at, to serve as a fulcrum for inventive ideas." In the present case, the pattern of orderly progression is clear. Refinement of ΔG and the characterization of polymers must work in close harmony, as near as possible between the unknown domain and what is firmly established. The next experiment to develop is dictated by the next most sensitive physical quantity measurable which the current state of the statistical-mechanical theory can just embrace. It would be counterproductive to tackle the highly sensitive properties straight away. If we did, we would be forced to fit several unknown parameters all at once. Even if we guessed their relative importance correctly, the set of parameters obtained by optimization will be vitiated by statistical coupling within the set. Only at the interface between the known and the unknown can we hope to introduce one parameter at a time. This is the correct procedure, which allows the circle to be broken by constant feedback between characterization and refinement.

Successive Refinements of ΔG

It will emerge that the pattern of well-ordered successive approximations coincides neither with the historical order in which they have been proposed nor with the sequence based on decreasing absolute magnitudes of changes induced in ΔG itself. A small change in ΔG may be reflected in a large change of a derived quantity like a spinodal.

The correct sequence, in the absence of adjustable parameters, is in decreasing fractional changes in the variance σ^2 of the relevant optimization in fitting data. The absence of adjustable parameters is an ideal not fully attainable; one adjustable parameter is present in the original Flory–Huggins model, and a second was introduced soon after (β_0 and β_1 below). Thereafter, three more parameters are associated with four of the succeeding refinements selected for testing in this work, but all three have molecular significance which suggests restrictions to their adjustments within narrow ranges.

0024-9297/80/2213-0761$01.00/0