Polymer Gels: Frozen Inhomogeneities and Density Fluctuations

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ABSTRACT: We present a phenomenological theory of randomly cross-linked polymer networks based on the separation of solid-like and liquid-like degrees of freedom and taking into account the frozen inhomogeneity of network structure. The complete solution of the statistical mechanics of this model is given, and the monomer density correlation functions are calculated for neutral gels in good and Θ solvents. The theoretical scattering curves are compared to the results of small angle neutron scattering and light scattering experiments, and new experimental tests of our theory are proposed.

1. Introduction

Recently, we presented a comprehensive statistical mechanical analysis of the Edwards model of gels, formed by instantaneous cross-linking of semidilute polymer solutions.[1] The model takes into account both excluded volume interactions between the monomers and the random character of the process of cross-linking but neglects permanent entanglements.[2]

We showed that the thermodynamic conditions (quality of solvent, degree of cross-linking, and monomer concentration) under which the network was prepared determine the statistical properties of its disordered structure. The inhomogeneous distribution of cross-links has a characteristic length scale which depends on the conditions of preparation and can vary from microscopic to macroscopic dimensions, depending on whether the gel was prepared away from or close to the "cross-link saturation threshold".[1] We found that for each choice of thermodynamic conditions, a given network has a unique state of microscopic equilibrium in which the average position of each cross-link and of each monomer is uniquely determined by the thermodynamic parameters. When these parameters (temperature, quality of solvent, degree of swelling, forces applied to the boundary of the gel) change, the new balance of elastic and excluded volume forces produces a new state of equilibrium.

We calculated the monomer density correlation functions (correlators) which can be directly measured in scattering experiments. The total structure factor can be represented as the sum of two terms: the correlator of static inhomogeneities which characterizes the statistical properties of the inhomogeneous equilibrium density profile of the gel, and the correlator of thermal fluctuations about this equilibrium. The presence of static inhomogeneities gives rise to the observed stationary speckle patterns in light scattering from gels.[3] When the gel is stretched, the anisotropy of the inhomogeneous equilibrium density profile leads to enhanced scattering in the stretching direction and to the appearance of butterfly patterns in isointensity plots.[4] The conclusion that the butterfly effect arises due to the effect of stretching on static inhomogeneities and cannot be attributed to the distortion of thermal fluctuations agrees with that of previous investigators.[5,6]

Although the above theory provides a complete solution of the statistical mechanics of polymer gels, it has several drawbacks, the most important of which is its mathematical complexity. The theory uses replica field theory methods which are unfamiliar to the majority of people in the polymer community. It is desirable to develop a more intuitive approach which would capture all the main physical ingredients of the complete theory and yet would not require the use of advanced methods of mathematical physics. Furthermore, although we have presented the complete formal solution for the density correlators, explicit analytic results were obtained only in the long and the short wavelength limits. Thus, we were unable to provide a quantitative description of the interesting phenomena associated with the transition from liquid-like to solid-like behavior, which takes place on length scales of the order of the monomer fluctuation radius R (the typical length scale over which a monomer fluctuates about its mean position in the network). A more complete, even if approximate, description is clearly necessary in order to understand the physics of this intermediate regime and to compare our predictions to the results of neutron and light scattering experiments across the entire range of wavelengths, from several angstroms to microns. Finally, since our earlier work[1] was based on a particular model of polymer gels, it was difficult to distinguish between universal results which apply to all types of polymer networks and those which are specific to instantaneously cross-linked gels. The goal of the present work is to construct a phenomenological theory of density fluctuations and static inhomogeneities in randomly cross-linked polymer gels. In doing so, we are guided by the insights provided by our exact replica field theoretical results, which were not available to previous investigators who attempted to cope with this problem.[5−7]

In section 2 we introduce the mean field free energy which governs small deviations from an arbitrarily swollen and stretched reference state of a polymer gel. The excluded volume (osmotic) part of the free energy is given by the standard quadratic expression in the monomer density ρ. The entropic part is written as the sum of solid-like and liquid-like contributions.[8] The solid-like contribution to the entropy is a functional of the displacement field $\mathbf{u}$ and depends on the anisotropic modulus of the deformed network and on the random force in the network (both the modulus and the correlator of the random force are calculated in the Appendix). The liquid-like entropy depends on the contribution to the density, ρ^{liq}, which comes from the

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small-scale liquid-like degrees of freedom. The introduction of $\rho^{\rm liq}$ is made necessary by the fact that while the monomer density is a truly microscopic variable which remains well-defined down to length scales of the order of the monomer size a, there is no corresponding microscopic definition of the displacement field since the latter is a physically meaningful concept only on length scales larger than the monomer fluctuation radius R. For Gaussian chains, R coincides with the size of an average network chain and is of the order of the mesh size, but unlike the mesh size which stretches affinely with the network, R is unaffected by the stretching.[1]

We generalize the relation between the density and the displacement fields, known from continuum theories of elasticity,[9] to arbitrary wave vectors. This is accomplished by specifying a microscopic reference state of density $\rho^{\rm ref}$ with respect to which the displacement field is defined, as well as by introducing a cutoff function β which ensures that the physically meaningless short wavelength Fourier components of the displacement field do not affect the corresponding components of the density field. The response function α of the liquid-like degrees of freedom is introduced, and its functional form is chosen to ensure that the contribution of these degrees of freedom to the free energy vanishes in the continuum limit, in which the displacement field uniquely defines the density field.

Having obtained the free energy functional $F[\mathbf{u},\rho]$, in section 3 we proceed to study thermal averages of the density field. The Gaussian integration over the displacement field leads to an effective free energy functional that depends on the monomer density field ρ and on another field n which is a function of the density in the reference state $\rho^{\rm ref}$ and of the random force due to the internal stresses in the network, $\mathbf{f}$. Since the latter is a fluctuating local quantity which varies from point to point in the gel, we can only obtain statistical information about it, by calculating its second moment with respect to those realizations of network topology that are consistent with the thermodynamic conditions in the state of preparation (see the Appendix). This information is used to construct an analytic expression for the distribution function of the random field n which characterizes the amplitude of static inhomogeneities in the gel. For the small degrees of frozen disorder considered in this work (it is assumed that the network is prepared sufficiently far away from the cross-link saturation threshold), the distribution function is a Gaussian functional of the field n. Using the effective free energy functional as well as the above distribution function, one can perform the thermal and the structure averages and obtain the fully-averaged monomer density correlation function (structure factor).

In section 4 we present our analytic mean field results for the structure factors of deformed networks. The total monomer density correlation function $S_{\mathbf{q}}$ can be written as the sum of the contributions of the correlator of static inhomogeneities $C_{\mathbf{q}}$ and that of thermal density fluctuations, $G_{\mathbf{q}}$. All the statistical information about the structure of the network is contained in the function $C_{\mathbf{q}}$ which is linearly proportional to the structure factor of the gel in the state of preparation $S_{\mathbf{q}}^{(0)}$. The latter depends only on the quality of solvent, the degree of cross-linking, and the density of monomers in the state of preparation and is nonuniversal in the sense that the functional form of this dependence will itself depend on the details of the cross-linking process (e.g., on whether the gel was formed by irradiation, vulcanization, polycondensation, end-linking of polymers, etc.). Our previous mean field results for the case of instantaneous cross-linking from solution show that $S_{\mathbf{q}}^{(0)}$ is given by a simple Lorentzian expression[1] (its form may be more complicated in other cross-linking scenarios). Comparing our approximate expression for the structure factor in the state of preparation to the exact result for the case of instantaneous cross-linking discussed in ref 1, we determine the hitherto arbitrary constants which appear in the expressions for the phenomenological functions α and β.

The results discussed in the first three sections were derived in the mean field approximation for both the static variations of the equilibrium concentration profile and for the thermal fluctuations about this profile. While the assumption of small stationary inhomogeneities holds as long as the gel is prepared away from the cross-link saturation threshold (the domain of applicability of this approximation is discussed in ref 1), thermal fluctuations on length scales smaller than the thermal correlation length are known to be strong in semidilute polymer solutions[10] and, since on these length scales monomers do not feel the effect of cross-links, these fluctuations should be strong in gels as well. In section 5, the effects of strong thermal fluctuations are treated by renormalization group methods, similar to those used in the description of semidilute polymer solutions in good solvents.[10,11] The only difference from the latter case is that in gels, one has to account for these effects separately in the state of preparation and in the final observed state. Small-scale thermal fluctuations lead to the renormalization of the monomer sizes and the second virial coefficients in both states and to the rescaling of the deformation ratios. The renormalization results in a new expression for the free energy in which the coefficient of the elastic free energy becomes concentration dependent, in violation of the classical additivity assumption.[12,13]

The renormalization of our mean field expressions for the density correlators is carried out in section 6. We show that the fluctuations change the functional form of the thermal density correlation function and that, for wavelengths smaller than the thermal correlation length ξ, it reduces to the well-known expression of the theory of semidilute polymer solutions. On larger length scales, density fluctuations are small and can be accounted for by replacing the mean field parameters with their renormalized values, in all the mean field correlators (note that the correlation length of density fluctuations ξ is smaller than the monomer fluctuation radius R, due to Edwards screening in good solvents[10]). Using a simple interpolation formula, we combine our short- and long-wavelength results and obtain an expression for the structure factor of a deformed gel in a good solvent, which is valid throughout the entire range of wave vectors, $0 \le q \ll a^{-1}$. We proceed to study the dependence of the density correlators on the thermodynamic parameters of the state of preparation (monomer concentration and degree of cross-linking) and on those of the final state of the gel (degree of swelling and stretching ratios). Throughout this analysis we compare the qualitative features of our predictions for the scattering curves with available experimental data.

We find that the structure factor of gels studied at the concentration of preparation decreases with this concentration at wavelengths larger than the monomer fluctuation radius R (since at lower volume fractions, $\phi_{\rm prep}$, one approaches the cross-link saturation threshold at which the correlation length of static inhomogeneities diverges) and increases with it at shorter wavelengths.

A similar short-wavelength behavior is observed for gels studied at saturation swelling in excess solvent, but in this case the long-wavelength ($q \ll R^{-1}$) structure factor varies nonmonotonically with ϕ_{prep}, due to competition between the above-mentioned effect of the cross-link saturation threshold and the increase in the swelling degree with increasing concentration of preparation. We observe that as ϕ_{prep} increases, the structure factor develops a "shoulder" at wave vectors in the range $R^{-1} < q < \xi^{-1}$. The presence of this shoulder in small angle neutron scattering spectra was reported by many investigators.[14] Further analysis reveals that the shoulder is the characteristic signature of the presence of a broad maximum at $q \simeq R^{-1}$ in the thermal correlator $G_{\mathbf{q}}$, followed by subsequent decay at $q > \xi^{-1}$. This means that density fluctuations are enhanced on the characteristic length scale of monomer fluctuations, a result anticipated in our earlier work.[1]

We find that the scattered intensity increases with the degree of cross-linking for gels studied at the concentration of preparation but that the variation of $S_{\mathbf{q}\to 0}$ is nonmonotonic under conditions of equilibrium swelling (for reasons similar to those discussed in the context of the dependence of the structure factor on ϕ_{prep}). In the range $q < R^{-1}$, the structure factor increases monotonically with the degree of swelling, since swelling enhances the contrast between regions of high and low cross-link density and reveals the presence of static inhomogeneities. When gels are submitted to uniaxial stretching, the scattered intensity in the $q < R^{-1}$ range is enhanced along the stretching axis and suppressed normal to it, giving rise to butterfly-shaped patterns in isointensity plots.[14] This angular dependence of the long-wavelength structure factor becomes increasingly more pronounced at higher degrees of swelling. The anisotropy decreases with q and finally disappears in the liquid-like regime ($q > \xi^{-1}$).

We also consider gels prepared in a good solvent and studied under Θ solvent conditions. Although at $q \to 0$ the results are quite similar to the good solvent case, a different behavior takes place at intermediate wave vectors. In this range, no "shoulders" are observed in the scattering profiles, indicating that the correlator of static inhomogeneities and the thermal correlator decay at the same characteristic wave vectors. Indeed, the absence of both swelling and screening in Θ solvents indicates that the monomer fluctuation radius and the thermal correlation length coincide as Θ conditions are approached. The study of uniaxially stretched networks in Θ solvents reveals that the scattering intensity is enhanced normal to the stretching axis, leading to isointensity plots in which the central butterfly features are surrounded by elliptical contours oriented normal to the stretching direction.

In section 7 we discuss the main conclusions of this work. We analyze the various approximations and model assumptions and estimate the domain of applicability of our results. Finally, directions for future research are outlined.

In the Appendix, we present the connection between our theory and the usual continuum theory of elasticity of solids. We show that the elastic free energy of the network is linear in the strain tensor (due to the presence of osmotic pressure and random network stresses) but that the latter is a nonlinear functional of the displacement field. We derive an explicit expression for the moduli of the deformed networks and show that the moduli depend on both the magnitude and the direction of the deformation. We calculate the correlators of the random forces which arise due to the cross-link pressure (proportional to the local concentration gradients in an inhomogeneous gel) and due to the frozen-in fluctuations of the tension in network chains.

2. Mean Field Theory

The free energy of an arbitrarily deformed (i.e., swollen in a good solvent and stretched) gel is given by the sum of osmotic energy and entropic contributions:

$$F = F_{\text{osm}} + F_{\text{ent}} \tag{2.1}$$

where F_{osm} is a functional of the monomer density ρ only. It can be shown[1] that this additivity assumption is exact on a mean field level and that accounting for fluctuations results in the renormalization of the mean field coefficients in the expressions for F_{osm} and F_{ent}. In the mean field (Flory) approximation the osmotic contribution to the free energy is given by

$$F_{\text{osm}}[\rho] = \frac{wT}{2}\int \mathrm{d}\mathbf{x}\, \rho^2(\mathbf{x}) \tag{2.2}$$

where T is the temperature and w is the second virial coefficient.

The entropic contribution F_{ent} is defined as the free energy in the absence of excluded volume interactions. It depends on the displacement field $\mathbf{u}(\mathbf{x})$ which represents the solid-like degrees of freedom, as well as on the density field $\rho^{\text{liq}}(\mathbf{x})$ which describes the liquid-like degrees of freedom. The latter density field is associated with the entropy of chains between cross-link points which is present even in a non-cross-linked polymer liquid.

Note that while the monomer density field can be defined microscopically by counting the instantaneous number of monomers in an arbitrarily small volume, there is no corresponding definition of the displacement field which is a collective variable that describes the deformation of the network with respect to some reference state. We will characterize this reference state by its monomer density $\rho^{\text{ref}}(\mathbf{x})$ and the local force density $\mathbf{f}(\mathbf{x})$, where the latter describes the internal elastic stresses in the reference network. Since the displacement field does not have an independent microscopic definition, there is inherent arbitrariness in the choice of the reference state which leads to an arbitrariness of choosing the functions ρ^{ref} and $\mathbf{f}$. We would like to stress that this arbitrariness is present even in the theory of elasticity of usual solids. Nevertheless, due to translational invariance, in these solids there exists a convenient choice of "gauge", $\rho^{\text{ref}}(\mathbf{x}) = \text{const}$ and $\mathbf{f}(\mathbf{x}) = 0$. In the case of a disordered network, with an arbitrarily inhomogeneous distribution of cross-link density, no such simple choice is possible. In principle, one could choose the state of preparation (characterized by the density $\rho^{(0)}(\mathbf{x})$) as the reference state of the gel, as was done in ref 15. The choice $\rho^{\text{ref}}(\mathbf{x}) = \rho^{(0)}(\mathbf{x})$ is convenient only if one studies small deformations of the gel but is cumbersome if one considers strongly swollen and deformed networks. In the latter case, it is more convenient to measure displacements with respect to an affinely deformed initial state with density

$$\rho^{\text{ref}}(\mathbf{x}) = \frac{\rho^{(0)}(\lambda^{-1} * \mathbf{x})}{\lambda_x \lambda_y \lambda_z} \tag{2.3}$$

where the denominator is determined by the normalization condition $\int \mathrm{d}\mathbf{x}\, \rho^{\text{ref}}(\mathbf{x}) = M$ (M is the total number of monomers in the network) and $\lambda^{-1} * \mathbf{q}$ is a vector with components $\lambda_\alpha{}^{-1} q_\alpha$ (λ_α is the deformation ratio along the principal deformation axis α). Although the true deformation is not affine, this choice guarantees that the residual displacements with respect to the reference state are small. Note that the magnitude of the deformation is limited only by the requirement of linear elasticity, i.e., $\lambda_\alpha \ll \bar{N}^{1/2}$ where $\bar{N}$ is the number of statistical segments ("monomer") of an average network chain.

The elastic free energy $F_{\text{el}}\{\lambda_\alpha\}$ associated with the deformed reference state is given in eq A11 in the Appendix. The elastic contribution to the entropic free energy for small displacements about the deformed state can be expanded to second order in powers of the corresponding displacement field

$$\Delta F_{\text{el}}[\mathbf{u}] = F_{\text{el}}[\mathbf{u}] - F_{\text{el}}\{\lambda_\alpha\} = \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left[-\mathbf{f}_{-\mathbf{q}}\cdot\mathbf{u}_{\mathbf{q}} + \frac{1}{2}\mathbf{u}_{-\mathbf{q}}\cdot\mathbf{G}_{\mathbf{q}}\cdot\mathbf{u}_{\mathbf{q}}\right] \quad (2.4)$$

where, since the reference state is not an equilibrium state, the functional ΔF_{el} contains a term linear in $\mathbf{u}$. The tensor $\mathbf{G}_{\mathbf{q}}$ is a quadratic form in $\mathbf{q}$, the coefficients of which are the elastic moduli of the deformed network (these moduli depend on the extension ratios λ_α). Concrete expressions for the components of this tensor and for the force density $\mathbf{f}_{\mathbf{q}}$ are derived in the Appendix.

Since on macroscopic length scales far exceeding the radius of monomer fluctuations R (or, alternatively, the average mesh size of the undeformed network), the gel can be considered as a usual solid, the relation between density and strain has to coincide with that given by the usual theory of elasticity of solids[9] (where it follows from mass conservation), i.e.,

$$\rho(\mathbf{x}) \simeq \rho^{\text{ref}}(\mathbf{x})(1 - \nabla\cdot\mathbf{u}(\mathbf{x})) \quad (2.5)$$

In the Fourier representation this mass conservation law takes the form

$$\rho_{\mathbf{q}} \simeq \rho_{\mathbf{q}}^{\text{ref}} - i\bar{\rho}\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}} \quad (2.6)$$

where $\bar{\rho} = \rho_{\mathbf{q}=0}^{\text{ref}} = M/V$ is the average monomer density in a network with volume V. These relations hold only to lowest order in q and have to be modified due to the fact that on length scales smaller than the monomer fluctuation radius, the gel can no longer be considered as a continuous solid. On these length scales one has to account for density fluctuations due to local motions of the chain monomers between cross-links which would occur even if one were to fix the positions of all cross-links. Thus, one must introduce an additional contribution to the density field, $\rho^{\text{liq}}(\mathbf{x})$, which describes those independent (liquid-like) degrees of freedom that cannot be defined by (2.6). The generalization of the latter relation to the case of arbitrary wavelengths (length scales) is

$$\rho_{\mathbf{q}} \equiv \beta_{\mathbf{q}}(\rho_{\mathbf{q}}^{\text{ref}} - i\bar{\rho}\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}}) + \rho_{\mathbf{q}}^{\text{liq}} \quad (2.7)$$

where $\rho_{\mathbf{q}}^{\text{liq}}$ is the Fourier transform of $\rho^{\text{liq}}(\mathbf{x})$. Although the functional form of the cutoff function $\beta_{\mathbf{q}}$ is not known in general, its asymptotic behavior can be determined from simple physical arguments. Comparison with eq 2.6 combined with the condition that the liquid-like degrees of freedom do not contribute in the long wavelength limit ($\rho_{\mathbf{q}\to 0}^{\text{liq}} \to 0$) dictates that $\beta_{\mathbf{q}\to 0} = 1$. In the opposite limit of wavelengths much smaller than R, we expect that the Fourier components of the density $\rho_{\mathbf{q}}$ do not depend on those of the displacement field $\mathbf{u}_{\mathbf{q}}$ and on the choice of the reference state ρ^{ref} (since solid elasticity is established only on much larger length scales) and, therefore, $\beta_{\mathbf{q}} \to 0$ for $q \gg 1/R$. A stronger constraint on the form of $\beta_{\mathbf{q}}$ follows from our exact asymptotic results for the structure factor.[1] It can be shown that on wavelengths much smaller than the monomer fluctuation radius, $\beta_{\mathbf{q}} \propto 1/q^2$. Therefore, both limiting behaviors can be modeled by the simple interpolation formula

$$\beta_{\mathbf{q}} = \frac{1}{1 + (Rq)^2} \quad (2.8)$$

The radius of monomer fluctuations R depends on the structure of the network under consideration. In the mean field approximation $R = a\bar{N}^{1/2}$, where a is the monomer size.[1] In the following we will consider the case of a phantom network, i.e., neglect the effect of permanent entanglements. In this case $\bar{N}$ is the average number of chain monomers between neighboring cross-links, so that R coincides with the spatial size of an average network chain. A more general expression for R which applies to the semidilute regime will be given later.

We now consider the entropic contribution F_{liq} of the liquid-like degrees of freedom which is not included in ΔF_{el}, eq 2.4 and which depends only on the density $\rho^{\text{liq}}(\mathbf{x})$. For small $\rho_{\mathbf{q}}^{\text{liq}}$, F_{liq} is given by the quadratic form (there is no linear term in $\rho_{\mathbf{q}}^{\text{liq}}$ since the liquid-like degrees of freedom are always in equilibrium)

$$F_{\text{liq}}[\rho^{\text{liq}}] = \frac{T}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\frac{|\rho_{\mathbf{q}}^{\text{liq}}|^2}{\alpha_{\mathbf{q}}} \quad (2.9)$$

where $\alpha_{\mathbf{q}}$ is the linear susceptibility of the liquid-like subsystem. Although the precise analytic form of $\alpha_{\mathbf{q}}$ is unknown, its limiting behaviors can be determined from simple physical considerations. The long-wavelength ($\mathbf{q} \to 0$) asymptotic behavior of this function can be found from the observation that in this limit the gel is a solid, i.e., $\rho_{\mathbf{q}\to 0}^{\text{liq}} \to 0$. Since for $\mathbf{q} \to 0$ the Boltzmann factor corresponding to the liquid-like degrees of freedom is $\exp(-|\rho_{\mathbf{q}}^{\text{liq}}|^2/2\alpha_{\mathbf{q}} \sim \delta[\rho_{\mathbf{q}}^{\text{liq}}]$, we must have $\alpha_{\mathbf{q}\to 0} = 0$. From dimensional considerations we conclude that in the above limit this function should be of the form $\alpha_{\mathbf{q}} = C_1\bar{N}\bar{\rho}(qR)2$, with a certain dimensionless constant C_1. On small length scales ($q \gg 1/R$) the gel is indistinguishable from a polymer liquid and this function turns into the usual response function of a solution of polymer chains, $\alpha_{\mathbf{q}} = 2\bar{\rho}(aq)^{-2}$. Note that in order to match the two asymptotics for $q \simeq 1/R$, the constant C_1 should be of order unity. We can now construct a simple interpolation formula for the response function $\alpha_{\mathbf{q}}$ which matches both these asymptotic behaviors

$$\frac{1}{\alpha_{\mathbf{q}}} = \frac{1}{\bar{\rho}}\left[\frac{(aq)^2}{2} + \frac{1}{C_1\bar{N}(qR)^2} + C_2\right] \quad (2.10)$$

The first term in the square brackets in (2.10) gives the usual Lifshitz entropy of polymer solutions.[16] The second term, first introduced by de Gennes for heteropolymer networks,[17] describes the suppression of density fluctuations on length scales larger than the monomer fluctuation radius. The constants C_1 and C_2 will be determined later in this work, by fitting our expressions for the density correlation functions to exact results for the structure factor in the state of preparation, obtained in ref 1.

Combining eqs 2.1, 2.2, 2.4, 2.7, and 2.9, we arrive at an expression for the free energy as a functional of the displacement and monomer density fields, $F[\mathbf{u},\rho]$, valid for arbitrary wave vectors

$$
\begin{aligned}
F[\mathbf{u},\rho] &= F_{\mathrm{osm}}[\rho] + \Delta F_{\mathrm{el}}[\mathbf{u}] + F_{\mathrm{liq}}[\rho^{\mathrm{liq}}] \\
&= \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\Bigg[\frac{wT}{2}\left|\rho_{\mathbf{q}}\right|^2 - \mathbf{f}_{-\mathbf{q}}\cdot\mathbf{u}_{\mathbf{q}} + \frac{1}{2}\mathbf{u}_{-\mathbf{q}}\cdot\mathbf{G}_{\mathbf{q}}\cdot\mathbf{u}_{\mathbf{q}} + \\
&\qquad T\frac{|\rho_{\mathbf{q}} - \beta_{\mathbf{q}}(\rho_{\mathbf{q}}^{\mathrm{ref}} - i\bar{\rho}\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}})|^2}{2\alpha_{\mathbf{q}}}\Bigg]
\end{aligned}
\tag{2.11}
$$

3. Thermal and Structure Averages

The statistical description of polymer networks is based on the observation that a network with a given network structure and thermodynamic parameters has a unique microscopic equilibrium state characterized by a density distribution $\rho_{\mathbf{q}}^{\mathrm{eq}}$ (a detailed proof of this statement is given in ref 1). When the network is deformed, a new equilibrium state results which is characterized by a different density distribution. Gels are, of course, nonergodic in the sense that the configurational space available to the cross-linked network is smaller than that of the pre-cross-linked polymer solution. Nevertheless, the existence of a single state of equilibrium under given thermodynamic conditions implies that they possess *restricted ergodicity,* i.e., that if we were able to prepare an ensemble of gels with *identical* structures, averaging over this ensemble with respect to the Gibbs distribution is the same as measuring time averages in a single gel. We therefore conclude that time averaging is equivalent to thermal (annealed) averaging and that the free energy in eq 2.11 can be used to calculate arbitrary statistical averages for a given network, the microscopic structure of which is represented by the two functions $\mathbf{f}(\mathbf{x})$ and $\rho^{\mathrm{ref}}(\mathbf{x})$.

In order to focus on issues which are of direct relevance to neutron and light scattering experiments which probe static density inhomogeneities and thermal density fluctuations in the gel, we will eliminate the displacement field $\mathbf{u}$ and obtain a reduced description in terms of the density field ρ only. The only meaningful information about the density profile one can obtain from our statistical mechanical description involves moments of the density field (e.g., density correlation functions).

We begin the calculation of the density correlation functions with the definition of thermal (time) averages (the equivalence between the two types of averages was proven in ref 1). For a given network structure (which enters through the values of $\mathbf{f}(\mathbf{x})$ and $\rho^{\mathrm{ref}}(\mathbf{x})$), such averages are taken with respect to the Gibbs probability distribution

$$
P[\mathbf{u},\rho] \equiv \frac{\exp(-F[\mathbf{u},\rho]/T)}{\int \mathrm{D}\mathbf{u}'\, \mathrm{D}\rho' \exp(-F[\mathbf{u}',\rho']/T)} \tag{3.1}
$$

where $F[\mathbf{u},\rho]$ is defined in eq 2.11. The thermal average of a functional $A[\rho]$ which does not depend on $\mathbf{u}$, can be written as

$$
\langle A[\rho]\rangle \equiv \int \mathrm{D}\mathbf{u}\, \mathrm{D}\rho\, P[\mathbf{u},\rho]A[\rho] = \int \mathrm{D}\rho\, P_n[\rho]A[\rho] \tag{3.2}
$$

where the last integration is taken with the weight

$$
P_n[\rho] \equiv \frac{\exp(-F_n[\rho]/T)}{\int \mathrm{D}\rho' \exp(-F_n[\rho']/T)} \tag{3.3}
$$

and where density functional $F_n[\rho]$ is defined as

$$
F_n[\rho] \equiv -T \ln\left[\int \mathrm{D}\mathbf{u} \exp(-F[\mathbf{u},\rho]/T)\right] \tag{3.4}
$$

Straightforward calculation of the Gaussian integral in eq 3.4 yields the following simple expression for the density functional:

$$
F_n[\rho] = \frac{T}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left(w|\rho_{\mathbf{q}}|^2 + g_{\mathbf{q}}^{-1}|\rho_{\mathbf{q}} - n_{\mathbf{q}}|^2\right) \tag{3.5}
$$

where the function $g_{\mathbf{q}}$ is defined as

$$
g_{\mathbf{q}} = \alpha_{\mathbf{q}} + \frac{2\bar{\rho}\bar{N}\beta_{\mathbf{q}}^{2}\mathbf{q}^2}{(\lambda^*\mathbf{q})^2} \tag{3.6}
$$

The functions $\beta_{\mathbf{q}}$ and $\alpha_{\mathbf{q}}$ are given by expressions 2.8 and 2.10, respectively. The function $n_{\mathbf{q}}$ in eq 3.5 is defined as

$$
n_{\mathbf{q}} \equiv \beta_{\mathbf{q}}\left(\rho_{\mathbf{q}}^{\mathrm{ref}} - i\frac{2\bar{N}}{T}\,\frac{\mathbf{q}\cdot\mathbf{f}_{\mathbf{q}}}{(\lambda^*\mathbf{q})^2}\right) \tag{3.7}
$$

and can be interpreted as the Fourier component of the monomer density $n(\mathbf{x})$ which maximizes the entropy of polymer network. Note that $n_{\mathbf{q}}$ can be obtained from the elastic part of $\rho_{\mathbf{q}}$, eq 2.7 with $\rho_{\mathbf{q}}^{\mathrm{liq}} = 0$, by the substitution $\mathbf{u}_{\mathbf{q}} \rightarrow \mathbf{G}_{\mathbf{q}}^{-1}\cdot\mathbf{f}_{\mathbf{q}}$, which is the standard relation between displacement and force in the continuous theory of elasticity[9] (recall that $\mathbf{G}_{\mathbf{q}\to 0}$ is proportional to the elastic modulus).

The fact that the free energy, eq 3.5, depends only on the variable $n_{\mathbf{q}}$ (i.e., on a particular combination of $\rho_{\mathbf{q}}^{\mathrm{ref}}$ and $\mathbf{f}_{\mathbf{q}}$) is intimately related to the ambiguity in the choice of the reference state. Thus, two different choices of the functions $\rho_{\mathbf{q}}^{\mathrm{ref}}$ and $\mathbf{f}_{\mathbf{q}}$ (i.e., two different reference states) correspond to the same realization of network structure, as long as both satisfy eq 3.7, with the same value of $n_{\mathbf{q}}$. Conversely, the function $n_{\mathbf{q}}$ and its Fourier transform $n(\mathbf{x})$ depend only on network structure $\mathbf{S}$ and on the deformation ratios but are independent of the choice of the reference state, i.e., are invariant under "gauge" transformations which change $\rho_{\mathbf{q}}^{\mathrm{ref}}$ and $\mathbf{f}_{\mathbf{q}}$ without affecting their combination given by eq 3.7. Although, in principle, a given realization of network structure is described by the value of the field $n(\mathbf{x})$ at each point $\mathbf{x}$ in this particular network, if we are only interested in statistical information, all we have to know is the probability $P[n(\mathbf{x})]$ of observing this function in the ensemble of all possible gel structures consistent with given thermodynamic conditions of preparation. This probability is given by

$$
P[n] \equiv \sum_{\mathbf{S}} P(\mathbf{S})\delta[n - n(\mathbf{S})] \tag{3.8}
$$

where $P(\mathbf{S})$ is the probability of realization of a given network structure $\mathbf{S}$.

The method of calculation of the averages in eq 3.2 is based on the observation that static density inhomogeneities in a randomly cross-linked polymer network are uncorrelated over macroscopic distances. We can, therefore, mentally decompose the entire network into small but still macroscopic domains, each one of which is characterized by a different structure. In the thermodynamic limit, the probability to find a region with a given structure $\mathbf{S}$ is the same as that to find a network with this structure, in the ensemble of networks with all possible structures (but prepared under the same conditions, i.e., temperature, average density of cross-links, etc.). Thus, the *structure average* of a quantity over the latter ensemble is equivalent to the *spatial average* of this quantity over the volume of a single network. The averages we calculate are structure averages over the ensemble of different structures, and the above equivalence ensures that our results can be directly applied to scattering experiments which measure averages over the volume of a single gel with a unique structure.

The structure average of a functional $B[n]$ will be denoted by

$$\overline{B[n]} \equiv \int \mathrm{d}\mathbf{S}\; P(\mathbf{S}) B[n(\mathbf{S})] = \int \mathrm{D}n\; P[n] B[n] \equiv \langle B[n]\rangle_n \qquad (3.9)$$

where we used eq 3.8 to replace the averaging over the structure by averaging with respect to the density distribution n. Finally, the complete structure and thermal (spatial and time) average of the functional $C_n[\rho]$ is defined as

$$\overline{\langle C_n[\rho]\rangle} \equiv \int \mathrm{D}n\; P[n] \int \mathrm{D}[\rho]\; P_n[\rho] C_n[\rho] \qquad (3.10)$$

As long as we are interested in observable quantities such as density correlation functions, which can be represented as statistical averages, we do not need the explicit functional form of $n(\mathbf{S})$ and it is sufficient to specify the probability functional $P[n]$ or, alternatively, the correlation function

$$\nu_{\mathbf{q}} = \langle n_{\mathbf{q}} n_{-\mathbf{q}}\rangle_n \qquad (3.11)$$

This function $\nu_{\mathbf{q}}$ depends on the structure of the network and on the deformation but does not depend on the quality of solvent in the final deformed state. In the Gaussian approximation, the distribution function $P[n]$ has the form

$$P[n] = \exp\left\{\frac{1}{2}\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left[\ln(2\pi\nu_{\mathbf{q}}) - \frac{n_{\mathbf{q}} n_{-\mathbf{q}}}{\nu_{\mathbf{q}}}\right]\right\} \qquad (3.12)$$

The validity of the Gaussian (random phase) approximation is based on the assumption of a small amplitude of network inhomogeneities. It can be shown[1] that this assumption holds for moderate degrees of cross-linking (away from the cross-link saturation threshold which will be discussed later in this work).

In order to obtain further insight into the meaning of n, we note that the nonaveraged free energy $F_n[\rho]$ defines (through the Boltzmann factor, eq 3.3) the probability of observing a thermal fluctuation of the monomer density at a wave vector $\mathbf{q}$, where the fluctuation amplitude $\rho^{\mathrm{th}}_{\mathbf{q}} = \rho_{\mathbf{q}} - \rho^{\mathrm{eq}}_{\mathbf{q}}$ is defined with respect to the inhomogeneous *equilibrium* density profile in the final deformed state of the network, $\rho^{\mathrm{eq}}_{\mathbf{q}}$. We refer to the Fourier transform of the deviation from the average monomer density as the "density" distribution, since the latter can be recovered from it by the Fourier transform, $\rho^{\mathrm{eq}}(\mathbf{x}) = \bar{\rho} + \delta\rho^{\mathrm{eq}}(\mathbf{x}) = \bar{\rho} + \int[\mathrm{d}\mathbf{q}/(2\pi)^3]\; \rho^{\mathrm{eq}}_{\mathbf{q}} \exp(i\mathbf{q}\cdot\mathbf{x})$.

The equilibrium monomer density profile can be found by minimizing the free energy $F_n[\rho_{\mathbf{q}}]$ with respect to $\rho_{\mathbf{q}}$. This gives

$$\rho^{\mathrm{eq}}_{\mathbf{q}} = \langle\rho_{\mathbf{q}}\rangle = \frac{n_{\mathbf{q}}}{1 + wg_{\mathbf{q}}} \qquad (3.13)$$

Since, for $w = 0$, this density coincides with $n_{\mathbf{q}}$, we conclude that $n_{\mathbf{q}}$ can be interpreted as the equilibrium density profile of the network in the absence of excluded volume interactions but under the constraint that the macroscopic deformation of the gel is the same as it was in the original state (in the presence of excluded volume forces). Under the above conditions (no excluded volume) only elastic forces act in the bulk of the network and, if no external forces were applied to its surface, the network would collapse to dimensions of the order of the mesh size. In view of the above, we will refer to the state characterized by the static density distribution $n_{\mathbf{q}}$ as the noninteracting reference state (this state was named the "elastic reference state" in ref 1). Note that the density $n_{\mathbf{q}}$ vanishes in the short wavelength limit (since the cutoff function $\beta_{\mathbf{q}}$ vanishes for $q \gg 1/R$; see eqs 3.7 and 2.8), since there can be no spatial inhomogeneities in a network on length scales smaller than the monomer fluctuation radius.

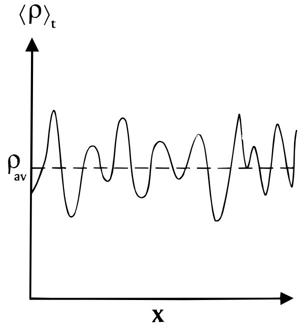

Figure 1. Schematic drawing of the time-averaged monomer concentration $\langle\rho\rangle_t$ as a function of the position x in the polymer solution (broken line) and in the gel (solid line). The mean concentration in both cases is ρ_{av}.

In the general case ($w \neq 0$), the presence of excluded volume interactions results in a new unique equilibrium state which is characterized by the inhomogeneous density distribution $\rho^{\mathrm{eq}}_{\mathbf{q}}$. As can be seen from eq 3.13, the new density profile is more homogeneous than that of the corresponding noninteracting reference state. We conclude that *the presence of excluded volume tends to suppress local density variations due to the frozen disorder of network structure* but that it can eliminate them entirely only in the limit of a dense melt (i.e., rubber).

4. Density Correlation Functions

One of the salient characteristics of gels is the presence of static spatial inhomogeneities of the density. While in liquids the time (and ensemble) average of the density fluctuations vanishes ($\langle\rho_{\mathbf{q}\neq 0}\rangle = 0$), *static spatial density inhomogeneities are always present in swollen polymer gels gue to the statistical nature of the process of cross-linking* which results in a unique equilibrium density distribution, with nonvanishing Fourier components $\rho^{\mathrm{eq}}_{\mathbf{q}}$. Straightforward calculation (by Gaussian integration, using the probability distribution defined in eq 3.3) of the thermally-averaged Fourier component of the density fluctuations, gives the amplitude of this density distribution, eq 3.13. Since every given realization of the network is characterized by a unique equilibrium density profile $\rho^{\mathrm{eq}}(\mathbf{x})$, the time-averaged density $\langle\rho(\mathbf{x})\rangle$ fluctuates in space across the network (Figure 1). This phenomenon leads to the appearance of stationary speckle patterns and to the observation of a time-independent component in measurements of the temporal decay of intensity correlations in light scattering from gels.[3,18] Finally, we note that $\overline{\rho^{\mathrm{eq}}_{\mathbf{q}}} \equiv \overline{\langle\rho_{\mathbf{q}}\rangle} = 0$, as expected for an average deviation from the mean density $\bar{\rho} \equiv M/V$.

Using the above equation we can introduce the amplitude of thermal density fluctuations $\delta\rho^{\text{th}}(\mathbf{x},t)$ as the deviation of the instantaneous density $\rho(\mathbf{x},t)$ from its equilibrium value, eq 3.13,

$$\delta\rho^{\text{th}}(\mathbf{x},t) \equiv \rho(\mathbf{x},t) - \rho^{\text{eq}}(\mathbf{x}) \tag{4.1}$$

which satisfies $\langle\delta\rho^{\text{th}}(\mathbf{x})\rangle = 0$ (we replace time averaging by ensemble averaging). We proceed to calculate the density correlators, by evaluating the appropriate Gaussian integrals.

The correlator of the thermal density fluctuations is obtained by substituting eq 4.1 into the definition (3.2) of the thermal average (taken with respect to the Boltzmann weight defined by eqs 3.5 and 3.3). This yields

$$G_{\mathbf{q}} \equiv \langle\rho_{\mathbf{q}}^{\text{th}}\rho_{-\mathbf{q}}^{\text{th}}\rangle = \frac{g_{\mathbf{q}}}{1 + wg_{\mathbf{q}}} \tag{4.2}$$

The above expression can be rewritten in a form that emphasizes the similarity with the random phase approximation in the theory of polymer liquids,[19] according to which the effective free energy of thermal fluctuations ($G_{\mathbf{q}}^{-1}\rho_{\mathbf{q}}^{\text{th}}\,\rho_{-\mathbf{q}}^{\text{th}}$) can be written as the sum of entropic and excluded volume contributions:

$$G_{\mathbf{q}}^{-1} = g_{\mathbf{q}}^{-1} + w \tag{4.3}$$

Thus, $g_{\mathbf{q}}$ can be interpreted as the thermal structure factor of the gel, in the absence of excluded volume interactions (i.e., in the noninteracting reference state). Note that according to eq 3.6, this function retains its angular dependence (associated with the direction of the wave vector $\mathbf{q}$) on the anisotropic deformation, even in the limit $q \to 0$. The presence of the $q^2/(\lambda^*\mathbf{q})^2$ term is related to the fact that $g_{\mathbf{q}\to 0}$ is a response function which governs thermal fluctuations about the anisotropic equilibrium state of the deformed network (in the absence of excluded volume interactions). This angular dependence follows from the anisotropy of the elastic moduli of the deformed network (see the Appendix).

The correlator of the static density inhomogeneities (the Fourier transform of the spatially averaged two-point correlation function $\overline{\delta\rho^{\text{eq}}(\mathbf{x})\delta\rho^{\text{eq}}(\mathbf{x}')}$ can be calculated using the definition (3.13) and eq 3.11:

$$C_{\mathbf{q}} \equiv \overline{\rho_{\mathbf{q}}^{\text{eq}}\rho_{-\mathbf{q}}^{\text{eq}}} = \frac{\nu_{\mathbf{q}}}{(1 + wg_{\mathbf{q}})^2} \tag{4.4}$$

Setting $w = 0$ in the above expression we find that $\nu_{\mathbf{q}}$ can be interpreted as the spatially-averaged (structure-averaged) equilibrium density correlator, in the absence of excluded volume interactions (in the noninteracting reference state). The presence of the w-dependent denominators in eqs 4.2 and 4.4 reflects the homogenization of the density profile due to excluded volume effects. Note that for $wg_{\mathbf{q}} \gg 1$, the suppression of static inhomogeneities is stronger than that of thermal fluctuations (the latter are suppressed due to the usual Edwards screening[19]).

The explicit functional form of $C_{\mathbf{q}}$ can be obtained by substituting eqs A24 and A25 (in the Appendix) for the random force associated with internal network stresses, into the definition of $n_{\mathbf{q}}$, eq 3.7. The averaging is performed using expression A26 for the correlator of random force $\tilde{\mathbf{f}}$ and the definition

$$S_{\mathbf{q}}^{(0)} \equiv \overline{\langle\rho_{\mathbf{q}}^{(0)}\rho_{-\mathbf{q}}^{(0)}\rangle} \tag{4.5}$$

of the correlation function of monomer density fluctuations in the state of preparation of the network. The resulting expression takes the form

$$\nu_{\mathbf{q}} = \beta_{\mathbf{q}}^{2}\left(6\bar{\rho}\bar{N} + \frac{9S_{\lambda^*\mathbf{q}}^{(0)}}{\lambda_x\lambda_y\lambda_z}\right) \tag{4.6}$$

where the first term in the parentheses comes from the correlator of the force density associated with the frozen-in variations of network structure (eq A26). Note that since the $\beta_{\mathbf{q}}^2$ coefficient reproduces all the q dependence (q^{-4}) of the exact short-wavelength limit of $\nu_{\mathbf{q}}$,[1] knowledge of the long-wavelength expressions for the correlator of random force $\tilde{\mathbf{f}}$ (given in the Appendix) suffices to determine $\nu_{\mathbf{q}}$. The second term in the brackets in eq 4.6 is obtained by collecting the different contributions proportional to the correlator of the density in the reference state.

The calculation of the structure factor of a gel in the state of preparation, $S_{\mathbf{q}}^{(0)}$, for instantaneous cross-linking of a semidilute polymer solution, has been reported elsewhere.[1] In the random phase approximation, this correlator is given by the Ornstein–Zernicke expression

$$S_{\mathbf{q}}^{(0)} = \frac{\bar{\rho}^{(0)}}{w^{(0)}\bar{\rho}^{(0)} - 1/\bar{N} + a^2\mathbf{q}^2/2} \tag{4.7}$$

The surprisingly simple form of this correlator, which includes unknown contributions from thermal fluctuations and from static inhomogeneities, follows from the fact that density variations in the gel in the state of preparation are nearly the same as those which arise from purely thermal fluctuations in the pre-cross-linked polymer liquid. The only difference is that since some of the monomers act as cross-links, they do not contribute to excluded volume repulsions and, therefore, the full structure factor of the gel in the state of preparation is given by that of a polymer liquid, with $w^{(0)} \to w^{(0)} - (\bar{\rho}^{(0)}\bar{N})^{-1}$.

The divergence of $S_{\mathbf{q}\to 0}^{(0)}$ at $w^{(0)}\bar{\rho}^{(0)}\bar{N} = 1$ is the signature of the *cross-link saturation threshold* (CST) for gels formed by instantaneous cross-linking from semidilute polymer solutions.[1] The physical origin of the CST is as follows. When the cross-link density approaches the saturation point at which the number of cross-links coincides with the average number of intermonomer contacts in the pre-cross-linked polymer liquid, cross-linking takes place preferentially from instantaneous configurations of the polymer liquid in which there are large domains with (slightly) increased density of contacts and the resulting network becomes increasingly inhomogeneous. The CST corresponds to the point at which the frozen inhomogeneity of network structure is present on all the length scales in the gel. Away from the CST, cross-link density variations take place on length scales of the order of the monomer fluctuation radius R.

An interesting limit of eq 4.6 corresponds to cross-linking in the melt, where $S_{\mathbf{q}}^{(0)} = 0$. The fact that $\nu_{\mathbf{q}}$ does not vanish in this limit tells us that even though there are no density fluctuations in the melt, there are still finite inhomogeneities of cross-link density, which can be revealed upon swelling.

Using eq 4.1, we arrive at the following expression for the total structure factor, which includes the contributions of both static inhomogeneities and thermal fluctuations and which is a measure of the total deviation of the density from its mean value, $\bar{\rho} = M/V$:

$$S_{\mathbf{q}} \equiv \overline{\langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}} \rangle} = G_{\mathbf{q}} + C_{\mathbf{q}} \tag{4.8}$$

The scattered intensity at a wave vector $\mathbf{q}$, measured in static scattering experiments, is proportional to this structure factor. Note that while the above expression is exact, the correlator of thermal fluctuations $G_{\mathbf{q}}$ contains information about the quenched structure of the network (through its dependence on $g_{\mathbf{q}}$) and the correlator of static inhomogeneities is modified by excluded volume interactions (depends on w).

In order to estimate the constants C_1 and C_2 which appear in the expression for the response function $\alpha_{\mathbf{q}}$, eq 2.10, we compare our expressions for $g_{\mathbf{q}}$ and for the structure factor in the state of preparation to the corresponding expressions in ref 1. In this reference, the exact form of $g_{\mathbf{q}}$ was calculated to order $\mathbf{q}^2$ and it was shown that the coefficient of the $\mathbf{q}^2$ term is a small positive number (0.033). Consistent with our simple approximation for the form of $\alpha_{\mathbf{q}}$, eq 2.10, we demand that the coefficient of the $\mathbf{q}^2$ term in the small-q expression of $g_{\mathbf{q}}$, eq 3.6, vanish and obtain $C_1 = 4$. The constant C_2 is determined from the requirement that our expression for the structure factor in the state of preparation gives the best fit to the exact result, eq 4.7, throughout the entire q range. The choice $C_2 = 1$ ensures that the two expressions give numerically identical results in both the small-q and the large-q range and that the discrepancy does not exceed a few percent for $q \approx 1/R$.

The expressions for the correlation functions derived in this section were obtained by assuming that deviations from the mean concentration due to both static inhomogeneities and thermal fluctuations are small. While we can always ensure that the former statement is correct by preparing the network away from the cross-link saturation threshold (the exact criterion is given in ref 1), strong thermal fluctuations on small length scales always exist in semidilute polymer solutions and are expected to occur in gels as well. Thus, in order to make a direct connection with scattering experiments on gels in good solvents, we have to account for the effect of strong thermal fluctuations on the structure factor. This is done in the next section.

5. Gels in Good Solvent

Up to this point we assumed that both static inhomogeneities and thermal fluctuations in the gel are small and expanded the free energy to second order in $\mathbf{u}_{\mathbf{q}}$ and $\rho_{\mathbf{q}}$. This allowed us to carry out the resulting Gaussian integrals and to calculate the mean field density correlation functions. Although our mean field results can be directly applied to some physically relevant situations (e.g., to gels permeated by free polymer chains[1]), here we will only consider polymer networks in good solvents where strong thermal fluctuations lead to the breakdown of the mean field approach. The difficulties with the applicability of the mean field approach to gels in good solvents can be resolved using the well-known de Gennes blob picture of semidilute solutions.[10] We will adapt this method to the present case and obtain a scaling description of gels in good solvents. The application of methods used in the theory of semidilute solutions to cross-linked gels is based on the observation that while static density inhomogeneities exist only on scales comparable to or larger than the monomer fluctuation radius R (i.e., on the length scale which characterizes the fluctuations of monomers about their average positions in the network[1]), thermal density fluctuations are dominated by small-scale (smaller than blob size ξ) phenomena which are quite similar to those in semidilute polymer solutions.

The fundamental distinction between the study of fluctuations in polymer networks and in polymer solutions is that, in the former case, we have to consider monomer density fluctuations in both the initial (where the gel was prepared) and the final (where it is being studied) states. This observation stems from the fact that since the gel is prepared by random cross-linking of chains in a semidilute polymer solution, its inhomogeneous structure is determined by the statistical properties of the fluctuating density profile in this solution.

In the following we consider the case in which both the initial and the final states of the network correspond to the semidilute regime in an *athermal* solvent. Here we will only repeat the main results of the analysis given in ref 1. On length scales smaller than the correlation lengths

$$\xi^{(0)} = a^{-5/4}(\bar{\rho}^{(0)})^{-3/4} \qquad \text{and} \qquad \xi = a^{-5/4}\bar{\rho}^{-3/4} \tag{5.1}$$

density fluctuations are large and the gel behaves as a polymer solution (“liquid-like” regime).

On scales larger than the blob size (i.e., for wave vectors $q^{(0)} \ll 1/\xi^{(0)}$ and $q \ll 1/\xi$), density fluctuations are small and we can use our mean field description, with appropriately renormalized parameters[1]

$$a \rightarrow a_{\mathrm{fp}}^{(0)} \qquad \lambda_\alpha \rightarrow \lambda_\alpha \frac{a_{\mathrm{fp}}^{(0)}}{a_{\mathrm{fp}}} \tag{5.2}$$

where the subscript fp stands for “fixed point” values that differ from the “bare” ones. The renormalized monomer sizes $a_{\mathrm{fp}}^{(0)}$ and a_{fp} in the initial and the final states can be evaluated from the mean field expressions for the corresponding blob sizes, $\xi^{(0)} = a_{\mathrm{fp}}(g^{(0)})^{1/2}$ and $\xi = a_{\mathrm{fp}} g^{1/2}$ ($g^{(0)}$ and g are the numbers of renormalized monomers per blob, in the initial and the final state of the gel, respectively). This yields

$$a_{\mathrm{fp}}^{(0)} = a(\bar{\rho}^{(0)}a^3)^{-1/8} \qquad a_{\mathrm{fp}} = a(\bar{\rho}a^3)^{-1/8} \tag{5.3}$$

The renormalized virial coefficients $w_{\mathrm{fp}}^{(0)}$ and w_{fp} were calculated in ref 1:

$$w^{(0)} \rightarrow w_{\mathrm{fp}}^{(0)} = a^3(\bar{\rho}^{(0)}a^3)^{1/4} \qquad w \rightarrow w_{\mathrm{fp}} = a^3(\bar{\rho}a^3)^{1/4} \tag{5.4}$$

Equations 5.3 and 5.4 complete our discussion of the renormalization of our model. We emphasize again that in order to describe a gel in a good solvent on length scales larger than the thermal correlation length, we only have to replace the bare parameters in the previously derived expressions for the free energy, correlation functions, etc., by their renormalized values.

Renormalizing the mean field energy given by eqs 2.1, 2.2, and A1 (see the Appendix), with the aid of eqs 5.3 and 5.4, we obtain the following scaling expression for the free energy of the deformed gel[20−22]

$$\frac{F\{\lambda_\alpha\}}{VT} = \nu \sum_\alpha \left(\frac{\lambda_\alpha R^{(0)}}{R} \right)^2 + \bar{\rho}^{9/4} a^{15/4} \tag{5.5}$$

where

$$R^{(0)} \equiv a_{\mathrm{fp}}^{(0)}\bar{N}^{1/2} = a(a^3\bar{\rho}^{(0)})^{-1/8}\bar{N}^{1/2} \tag{5.6}$$

and

$$R \equiv a_{\mathrm{fp}}\bar{N}^{1/2} = a(a^3\bar{\rho})^{-1/8}\bar{N}^{1/2} \tag{5.7}$$

are the monomer fluctuation radii which depend on the densities in the initial and the final states, respectively, but are independent of the stretching ratio in the final deformed state. The $\bar{\rho}^{9/4}$ term in eq 5.5 contains the well-known fluctuation correction to the mean field expression ($\bar{\rho}^2$) for the osmotic pressure.[10] The above elastic free energy resembles some modified variants of the classical theories of gel elasticity which also contain a correction factor of the form $(R^{(0)}/R)^2$, but in these theories this ratio is not affected by the swelling-induced change of the monomer fluctuation radius.[23] In our model this ratio is given by

$$\left(\frac{R^{(0)}}{R}\right)^2 = \left(\frac{\bar{\rho}}{\bar{\rho}^{(0)}}\right)^{1/4} \tag{5.8}$$

from which the limit of cross-linking in the melt is obtained by the substitution $\bar{\rho}^{(0)} = a^{-3}$. The thermodynamics of polymer networks based on eq 5.5 was studied in ref 1 and will not be discussed here.

Substituting $\lambda_\alpha = (\bar{\rho}^{(0)}/\bar{\rho})^{1/3}$ and $V = M/\bar{\rho}$ into the free energy, eq 5.5, and minimizing the resulting expression yield the maximal (saturation) swelling degree at osmotic equilibrium with excess solvent (defined with respect to the volume of the dry network),

$$Q^{\max} = (a^3\bar{\rho}^{(0)})^{-1/4}(a^3c^*)^{-3/4} = (a^3\bar{\rho}^{(0)})^{-1/4}\bar{N}^{3/5} \tag{5.9}$$

where $c^* = a^{-3}\bar{N}^{-4/5}$ is the overlap concentration of network subchains. We have shown in ref 1 that the smallest concentration at which a gel can be prepared by cross-linking from a semidilute solution is $\bar{\rho}_{\min}^{(0)} = c^*$ and that the c^* theorem ($\bar{\rho}_{\min} = c^*$) does not hold under most preparation conditions. The condition $\bar{\rho}_{\min}^{(0)} \geq c^*$ defines the maximal degree of cross-linking $R_{\mathrm{c}}^{\max} = 1/(2\bar{N})$ that can be obtained by instantaneous cross-linking of a polymer solution of concentration $\bar{\rho}^{(0)}$ and may be interpreted as the good solvent analog of the mean field cross-link saturation threshold.[1] At this threshold, the frozen inhomogeneity of network structure diverges and our mean field (random phase approximation) approach for the static density inhomogeneities breaks down. In all the subsequent calculations we verify that the condition $R_{\mathrm{c}} < R_{\mathrm{c}}^{\max}$ is always obeyed.

6. Static Scattering Profiles

We now turn to the analysis of the density correlation function $S_{\mathbf{q}}$ which can be measured in static neutron and light scattering experiments through the detection of the scattered intensity at a wave vector $\mathbf{q}$. In order to avoid dealing with the effect of segregation on the process of cross-linking in a poor solvent, we will restrict our consideration to networks synthesized in good solvents. However, since the quality of solvent may be changed at will following the synthesis of the network (e.g., by changing the temperature), we will calculate the structure factors of gels studied at Θ as well as at good solvent conditions.

We first present the general expressions for the scattering functions, for gels prepared and studied in a good solvent. In order to consider the effect of swelling and uniaxial extension on the magnitude and the angular dependence of the scattered intensity, our general expressions will contain both swelling and deformation parameters.

Consider a gel which is uniaxially stretched along the z axis, with stretching ratios $\lambda_z = \lambda\alpha$ and $\lambda_x = \lambda_y = \lambda^{-1/2}\alpha$ along the z direction and perpendicular to it, respectively, where $\alpha = (\bar{\rho}^{(0)}/\bar{\rho})^{1/3}$ is the swelling ratio defined with respect to preparation conditions. In the following, we will express all monomer concentrations through the dimensionless volume fractions, $\phi \equiv a^3\bar{\rho}$ and $\phi_{\mathrm{prep}} \equiv a^3\bar{\rho}^{(0)}$.

For wave vectors exceeding the inverse correlation length (short-wavelength limit), the only contribution to the total structure factor comes from the correlation function of thermal fluctuations, which is identical to that for a semidilute solution of un-cross-linked chains[10]

$$G_{\mathbf{q}}^{\mathrm{SW}} \simeq \frac{\phi}{a^3(aq)^{5/3}} \qquad q\xi \gg 1 \tag{6.1}$$

Note that in this range the structure factor is unaffected by the stretching of the network.

In the range $q\xi \ll 1$, $q\xi^{(0)} \ll 1$, thermal fluctuations are small and affect the correlators only through their effect on the thermodynamic parameters (i.e., they lead to the renormalization of the monomer sizes and the second virial coefficients in the initial and the final state of the gel). The renormalized correlators can be obtained from the corresponding mean field expressions by changing $a^2\bar{N}\mathbf{q}^2 \rightarrow R^2\mathbf{q}^2 \equiv Q^2$, replacing the bare second virial coefficients by their renormalized values given in (5.4) and substituting $\lambda_\alpha \rightarrow (R^{(0)}/R)\lambda_\alpha$ in the mean field results for the correlators $g_{\mathbf{q}}$, $\nu_{\mathbf{q}}$, $G_{\mathbf{q}}$, and $C_{\mathbf{q}}$ discussed in the previous section.[1] This yields the following expression for the long-wavelength structure factor, valid for wave vectors $q\xi \ll 1$

$$S_{\mathbf{q}}^{\mathrm{LW}} = G_{\mathbf{q}}^{\mathrm{LW}} + C_{\mathbf{q}}^{\mathrm{LW}} \tag{6.2}$$

The contribution of thermal fluctuations is given by

$$G_{\mathbf{q}}^{\mathrm{LW}} = \frac{a^{-3}\phi\bar{N}\hat{g}_{\mathbf{q}}}{1 + \hat{w}\hat{g}_{\mathbf{q}}} \tag{6.3}$$

and that of static density inhomogeneities is

$$C_{\mathbf{q}}^{\mathrm{LW}} = \frac{a^{-3}\phi\bar{N}}{(1 + \hat{w}\hat{g}_{\mathbf{q}})^2(1 + Q^2)^2} \times \left[6 + \frac{9}{\hat{w}^{(0)} - 1 + ({Q_{\|}}^2\lambda^2 + {Q_{\perp}}^2/\lambda)(\phi_{\mathrm{prep}}/\phi)^{5/12}/2}\right] \tag{6.4}$$

where we defined ${Q_{\|}}^2 \equiv R^2{q_z}^2$ and ${Q_{\perp}}^2 \equiv R^2({q_x}^2 + {q_y}^2)$ ($Q^2 = {Q_{\|}}^2 + {Q_{\perp}}^2$). $R = a\phi^{-1/8}\bar{N}$ is the monomer fluctuation radius (see eq 5.7). The dimensionless function $\hat{g}_{\mathbf{q}}$ is defined as

$$\hat{g}_{\mathbf{q}} \equiv \frac{g_{\mathbf{q}}^{\mathrm{LW}}}{\bar{\rho}\bar{N}} = \frac{1}{Q^2/2 + (4Q^2)^{-1} + 1} + \frac{2Q^2(\phi/\phi_{\mathrm{prep}})^{5/12}}{(1 + Q^2)^2({Q_{\|}}^2\lambda^2 + {Q_{\perp}}^2/\lambda)} \tag{6.5}$$

The quantities $\hat{w}^{(0)}$ and $\hat{w}$ which appear in eqs 6.3 and 6.4 are the effective dimensionless virial coefficients in the state of preparation and in the deformed state,

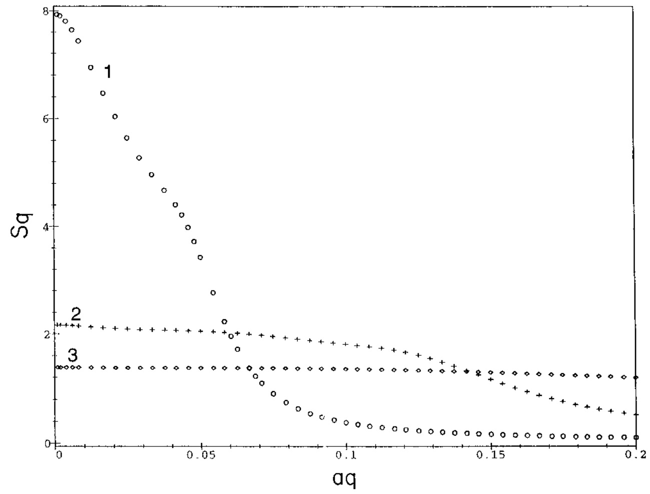

Figure 2. Total structure factor $S_{\mathbf{q}}$ of a gel studied at the concentration of preparation is plotted vs the wave vector q (in units of a^{-1}). The degree of cross-linking is 0.0025, and the volume fractions at preparation are $\phi_{\rm prep} = 0.02$ (1), 0.077 (2), and 0.3 (3).

respectively. In the case of athermal solvent conditions in both states, they are given by

$$\hat{w}^{(0)} \equiv w_{\rm fp}^{(0)}\bar{\rho}^{(0)}\bar{N} = {\phi_{\rm prep}}^{5/4}\bar{N} \tag{6.6}$$

and

$$\hat{w} \equiv w_{\rm fp}\bar{\rho}\bar{N} = \phi^{5/4}\bar{N} \tag{6.7}$$

in the initial and in the final state, respectively.

The short-wavelength limit, $q\xi \gg 1$, of the thermal correlator $G_{\mathbf{q}}^{\rm SW}$ is given by eq 6.1 (note that since $\xi/R \lesssim 1$, the correlator of static inhomogeneities $C_{\mathbf{q}}$ vanishes in the above limit). A general expression for the structure factor which is valid for the entire range of wavelengths can be obtained by smooth interpolation between our short- and long-wavelength expressions:

$$S_{\mathbf{q}} = S_{\mathbf{q}}^{\rm LW}\tanh[(q\xi)^{-4}] + G_{\mathbf{q}}^{\rm SW}\{1 - \tanh[(q\xi)^{-4}]\} \tag{6.8}$$

This interpolation formula reproduces the correct asymptotics of the structure factor (up to exponentially small corrections).

6.1. Good Solvent. In line with the convention used in the experimental literature (in which absolute units are used for the wave vectors), we will scale all wave vectors with the constant monomer size a, rather than with the concentration and chain length dependent R.

We first consider unstretched gels $\{\lambda_\alpha = 1\}$ and study the dependence of the structure factor on conditions of preparation, i.e., on the monomer density in the state of preparation $\phi_{\rm prep}$ and on the degree of cross-linking, $R_{\rm c} \equiv 1/(2\bar{N})$ (the latter can be replaced by the experimentally observable maximal swelling degree, $Q^{\rm max}$; see eq 5.9). Note that the cross-link saturation threshold condition which defines the maximal attainable degree of cross-linking (for a given density in the state of preparation) in our model, can be written as $R_{\rm c}^{\rm max} = {\phi_{\rm prep}}^{5/4}/2$. In the following we will always choose the parameters such that $R_{\rm c} < R_{\rm c}^{\rm max}$.

In Figure 2 we present the dependence of $S_{\mathbf{q}}$ on the initial volume fraction $\phi_{\rm prep}$, for lightly cross-linked gels with $R_{\rm c} = 0.0025$, studied at the concentration of preparation ($\phi = \phi_{\rm prep}$). The intensity decreases monotonically with $\phi_{\rm prep}$ for $qR \ll 1$ and increases with it for $qR \gg 1$. The small-q behavior is dominated by scattering from static inhomogeneities and the scattering increases as the cross-link saturation threshold is approached at smaller initial concentrations. The large-q behavior is dominated by thermal scattering and coincides with that of a semidilute polymer solution.

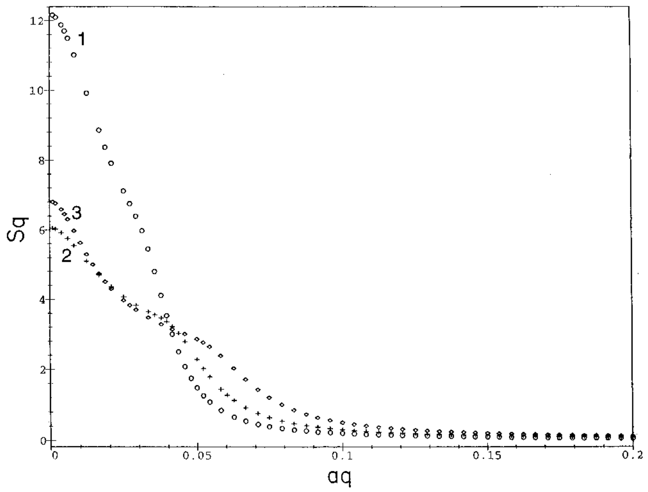

Figure 3. Saturation swelling: dependence of the total structure factor $S_{\mathbf{q}}$ on concentration of preparation. The parameters correspond to the same preparation conditions as in Figure 2.

Figure 3 shows the variation of the structure factor at saturation swelling, with the initial volume fraction $\phi_{\rm prep}$ (all parameters are the same as in Figure 2). Note that the small-q intensity is higher than in Figure 2. A new feature clearly observed in Figure 3 is that the scattered intensity at $q \to 0$ varies nonmonotonically with $\phi_{\rm prep}$, i.e., it first decreases with increasing $\phi_{\rm prep}$ and then increases with it (in the high-q range the intensity increases monotonically with the concentration of preparation, similarly to Figure 2). Since the small-q scattering is dominated by the contribution of static inhomogeneities ($C_{\mathbf{q}\to 0}$), the initial decrease with increasing $\phi_{\rm prep}$ is associated with increasing distance from the cross-link saturation threshold (CST). Away from the CST, the increase of intensity with $\phi_{\rm prep}$ is the result of the increase of the degree of equilibrium swelling with concentration of preparation, at a fixed degree of cross-linking (static inhomogeneities are enhanced by swelling). Analysis of eqs 6.2–6.4 shows that $S_{\mathbf{q}\to 0}$ is a nonmonotonic function of $\phi_{\rm prep}$ and that, for $R_{\rm c} = 0.0025$, it goes through a minimum at $\phi_{\rm prep} \simeq 0.08$. Further inspection of Figure 3 suggests that the variation of the structure factor with the concentration of preparation is strongly q-dependent and that different behaviors may be observed in small angle neutron scattering and in light scattering experiments (the latter probe significantly smaller values of q).

Another prominent feature in Figure 3 is the presence of a "shoulder" at intermediate values of q ($q \approx R^{-1}$), which becomes more prominent with increasing $\phi_{\rm prep}$. "Shoulders" of varying shapes were often reported by the experimentalists and were even classified according to type.[14] As can be seen in Figure 4 where we plot the thermal correlator $G_{\mathbf{q}}$, the correlator of static inhomogeneities $C_{\mathbf{q}}$, and the total structure factor $S_{\mathbf{q}}$, this shoulder arises because of enhanced thermal fluctuations on wavelengths of the order of the monomer fluctuation radius, i.e., on the characteristic length scale of the inhomogeneous equilibrium density profile (the presence of a broad peak in $G_{\mathbf{q}}$, at $q \approx R^{-1}$, was discussed in ref 1). The form of the shoulder varies with preparation conditions and degree of swelling. Note

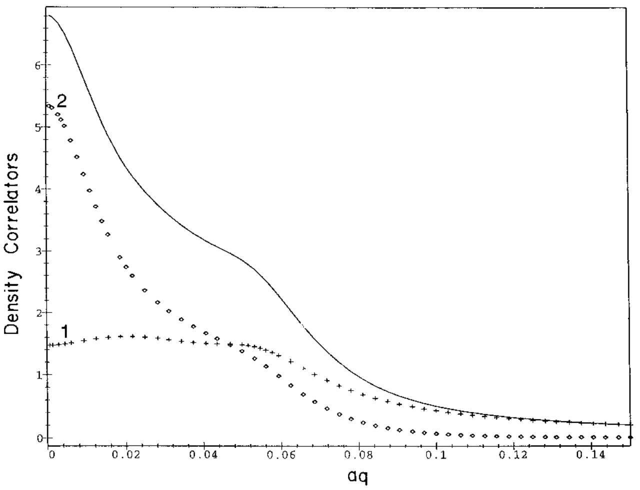

Figure 4. Saturation swelling: plots of the total structure factor $S_{\mathbf{q}}$ (line) and the correlators of thermal fluctuations $G_{\mathbf{q}}$ (1) and of static inhomogeneities $C_{\mathbf{q}}$ (2). The parameters are $R_c = 0.0025$ and $\phi_{\text{prep}} = 0.3$.

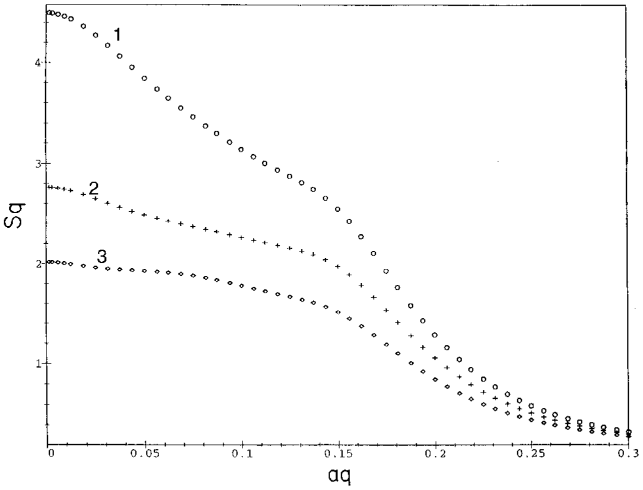

Figure 5. Total structure factor $S_{\mathbf{q}}$ of a gel studied at the concentration of preparation, $\phi_{\text{prep}} = 0.1$, for various degrees of cross-linking: $R_c = 0.017$ (1), 0.01 (2), and 0.0033 (3).

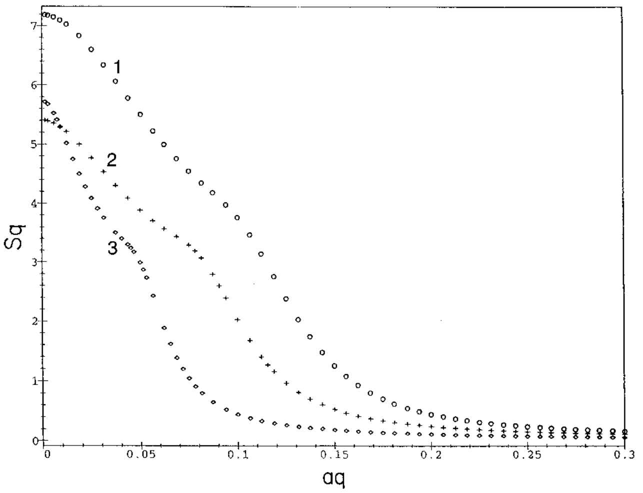

Figure 6. Total structure factor $S_{\mathbf{q}}$ of a gel studied at saturation swelling. The parameters correspond to the same preparation conditions as in Figure 5.

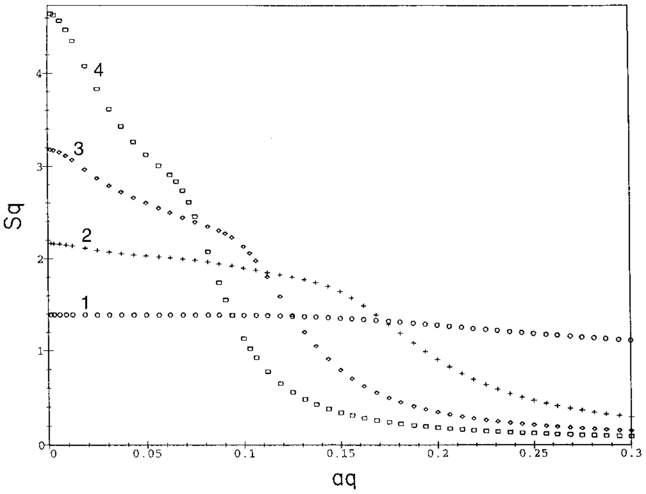

Figure 7. Variation of $S_{\mathbf{q}}$ with the degree of swelling $a \equiv (\phi_{\text{prep}}/\phi)^{1/3} = 0.7$ (1), 1 (2), 1.2 (3), and 1.41 (4). The parameters are $R_c = 0.005$ and $\phi_{\text{prep}} = 0.1$.

that although scattering from static inhomogeneities dominates the thermal scattering at small q ($q \ll R^{-1}$), the situation is reversed at larger wave vectors because the correlator of static inhomogeneities decays on wavelengths of the order of the monomer fluctuation radius R, while that of thermal fluctuations decays only on much smaller wavelengths, of the order of the correlation length ξ.

In Figure 5 we present $S_{\mathbf{q}}$ for different degrees of cross-linking R_c, for gels studied at the concentration of preparation ($\phi_{\text{prep}} = 0.1$). The scattered intensity increases with R_c as expected from scattering off static inhomogeneities ($C_{\mathbf{q}\to 0}$ diverges at the cross-link saturation threshold). All the scattering curves coalesce in the large-q limit since they correspond to the same density and thus have the same correlation length ξ. Both behaviors were observed in small angle neutron scattering experiments.[24] The form of the "shoulders" in the scattering curves changes with varying degrees of cross-linking, in agreement with experimental observations.[25]

Figure 6 gives $S_{\mathbf{q}}$ for different degrees of cross-linking R_c, for gels studied at saturation swelling in excess solvent (all parameters are the same as in Figure 5). Observe that the scattered intensity at saturation swelling is much higher than in the state of preparation. While for large q the intensity increases with the degree of cross-linking, the behavior is nonmonotonic at small q. Analysis of eqs 6.2–6.4 shows that for $\phi_{\text{prep}} = 0.1$, $S_{\mathbf{q}\to 0}$ goes through a minimum at $R_c \simeq 0.006$. Since the nonmonotonic variation of the scattered intensity with degree of cross-linking is limited to very small q values, it may be inaccessible to small angle neutron scattering experiments but can be probed by light scattering.

In Figure 7 we study the dependence of $S_{\mathbf{q}}$ on the degree of swelling, for $\phi_{\text{prep}} = 0.1$ and $R_c = 0.005$ (away from the CST). At small q, the scattering increases monotonically with the degree of swelling (swelling enhances density contrasts, thus revealing the presence of static inhomogeneities), and the behavior is reversed at large q where thermal fluctuations dominate the scattered signal. The resulting crossing of the scattering curves has been observed in small angle neutron scattering experiments.[14,26] Note that the presence of a "shoulder" is most pronounced at intermediate degrees of swelling. This is a consequence of the fact that although the ratio $G_{\mathbf{q}}/C_{\mathbf{q}}$ increases with increasing concentration, the peak in $G_{\mathbf{q}}$ disappears as the concentration of preparation is approached.

In Figure 8 we plot the structure factor of a uniaxially stretched gel studied at saturation swelling, for $\phi_{\text{prep}} = 0.1$, $R_c = 0.005$, and stretching ratio $\lambda = 1.4$. The small-q ($\ll R$) scattered intensity parallel to the stretching axis is larger than that for an undeformed gel, and

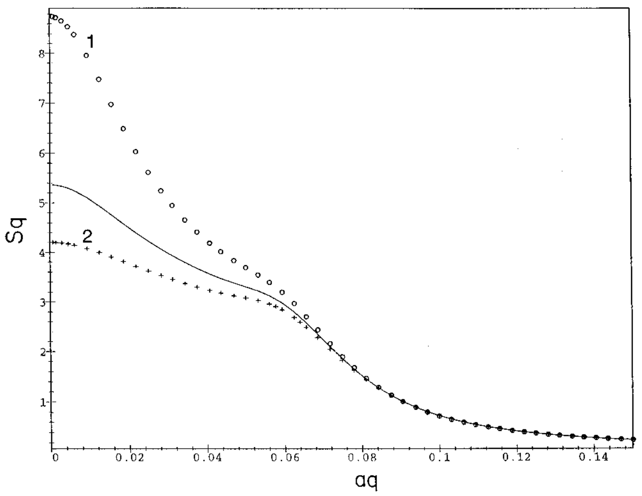

Figure 8. Angular-dependent structure factor of a uniaxially deformed gel, studied at saturation swelling, for wave vectors along (1) and normal to (2) the stretching axis. The deformation ratio is 1.4, and the parameters of preparation are $R_c = 0.005$ and $\phi_{\text{prep}} = 0.1$. The structure factor of an unstretched gel (line) is shown for comparison.

the situation is reversed in the direction normal to this axis (the enhancement in the parallel direction is much stronger than the suppression in the normal one). All the curves coincide in the large-q limit (actually, in this limit the scattering in the direction normal to the stretching axis becomes larger than that in the parallel direction but the effect is nearly unobservable for gels in good solvents). The observed anisotropy of the small-q scattering gives rise to the appearance of "butterfly"-shaped patterns oriented along the stretching direction, in contour plots of the isointensity lines. The angular anisotropy is present only for wave vectors smaller than the inverse monomer fluctuation radius, and the scattering becomes nearly isotropic in the large-q limit (see Figure 8). These effects have been the subject of numerous neutron and light scattering studies (for a review, see ref 14).

6.2. Θ Solvent. We now turn to the case of gels prepared in a good solvent and studied under Θ conditions. The general expressions for the correlators, eqs 6.2–6.4, are the same as for gels in good solvents, but since in Θ solvents mean field analysis works for all the length scales in the gel, the above long-wavelength expressions apply throughout the entire q range. As there is no renormalization of monomer size in Θ solvents, the monomer fluctuation radius is given by the Gaussian chain result, $R = a\bar{N}^{1/2}$. Since we assume that the gel is synthesized in a good solvent, the effective second virial coefficient $\hat{w}^{(0)}$ is the same as in eq 6.6. The second virial coefficient w in the final state of the gel should be replaced by the product of the density and of the third virial coefficient, $\bar{\rho}a^6$. This leads to the following modification of eq 6.7 for $\hat{w}$:

$$\hat{w} = \phi^2\bar{N} \tag{6.9}$$

In the Θ solvent case, the dimensionless function $\hat{g}_{\mathbf{q}}$ is given by

$$\hat{g}_{\mathbf{q}} \equiv \frac{g_{\mathbf{q}}}{\bar{\rho}\bar{N}} = \frac{1}{Q^2/2 + (4Q^2)^{-1} + 1} + \frac{2Q^2\phi^{2/3}\phi_{\text{prep}}{}^{-5/12}}{(1+Q^2)^2(Q_{\parallel}{}^2\lambda^2 + Q_{\perp}{}^2/\lambda)} \tag{6.10}$$

The degree of swelling in a Θ solvent can be calculated by balancing the elastic and osmotic forces (note that the osmotic pressure scales as ϕ^3). This gives the equilibrium volume swelling ratio $\alpha_{\text{eq}}{}^3 \equiv \phi_{\text{prep}}/\phi = (\phi_{\text{prep}}{}^{9/4}\bar{N})^{3/8}$, and we conclude that for gels prepared in a good solvent and reswollen in a Θ solvent, the volume fraction at equilibrium ("saturation") swelling may be either larger or smaller than that in the state of preparation, depending whether $\phi_{\text{prep}}{}^{9/4}/(2R_c)$ is larger than unity (both cases are possible since $\phi_{\text{prep}} \le 1$ and the CST condition imposes the constraint $\phi_{\text{prep}}{}^{5/4}/(2R_c) \ge 1$).

The general features of the scattering profiles of unstretched gels studied in Θ solvents are quite similar to those of gels in good solvents, except that the presence of "shoulders" is much less pronounced than in the latter. The explanation of this apparently trivial difference involves some unexpectedly profound physics. In the absence of excluded volume interactions (and forgetting for the moment the small effect of the nonvanishing third virial coefficient) both the monomer fluctuation radius and the thermal correlation length coincide with the radius of the Gaussian chain

$$R \simeq \xi \simeq a\bar{N}^{1/2} \qquad \Theta \text{ solvent} \tag{6.11}$$

Since R^{-1} determines the q range which the correlator of static inhomogeneities decays and ξ^{-1} determines the corresponding range for the decay of the thermal correlator, we conclude that in Θ solvents both correlators are characterized by the same correlation length, $a\bar{N}^{1/2}$, and their sum (the structure factor) will decay smoothly on this wavelength. In good solvents, the presence of excluded volume interactions results in splitting of the two length scales. These repulsive interactions swell the network chains and therefore increase the monomer fluctuation radius R above its unperturbed value ($a\bar{N}^{1/2}$), but at the same time, they decrease the thermal correlation length from the chain radius to the size of a thermal blob

$$R > a\bar{N}^{1/2} > \xi \qquad \text{good solvent} \tag{6.12}$$

Because of this splitting the correlator of static inhomogeneities decays faster than that of thermal fluctuations, resulting in the appearance of a shoulder in the scattering profiles.

Another important difference between the scattering profiles of gels in good and in Θ solvents becomes apparent when one studies the structure factors of uniaxially stretched gels. While the $q \to 0$ scattering along the stretching axis is enhanced in both solvents, in Θ solvents the scattered intensity in the direction normal to this axis becomes larger than in the parallel direction, for larger values of q. This leads to butterfly patterns along the stretching axis in the small-q range, which are enveloped by elliptical patterns oriented normal to this axis, for larger values of q (see Figure 9). These elliptical patterns originate from the correlator of static inhomogeneities, eq 4.6, which contains the term $S^{(0)}_{\lambda^*\mathbf{q}}$ that "remembers" the affinely deformed structure of the network. Only this angular dependence contributes in the intermediate q range, provided that the condition $wg_{\mathbf{q}} \ll 1$ is obeyed (regardless of the magnitude of $wg_{\mathbf{q}}$, the angular singularity of $g_{\mathbf{q}}$ will always dominate the scattering at sufficiently small values of q, giving rise to a butterfly pattern). Note that for yet higher values of q ($q > \xi^{-1}$, R^{-1}), the scattering probes the "liquid-like" degrees of freedom which are unaffected by the deformation. In this range, the

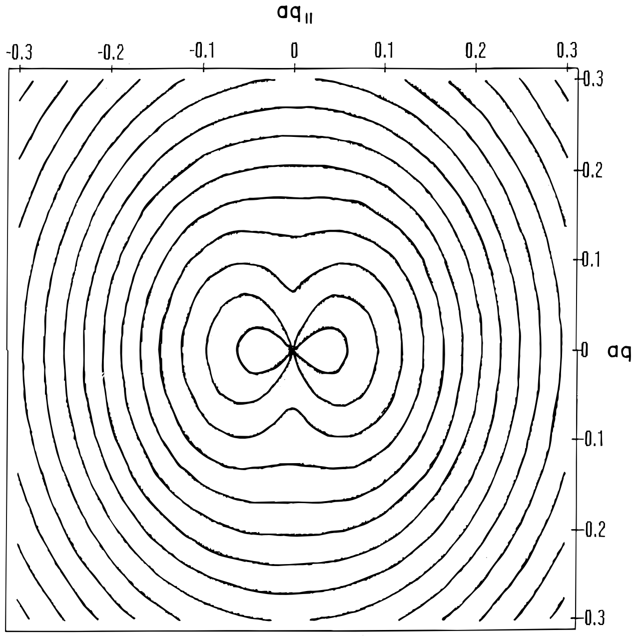

Figure 9. Uniaxially stretched gel in a Θ solvent, at the concentration of preparation. Contour plot of the structure factor, in the $(q_{\parallel}/q_{\perp})$ plane of wave vectors along and normal to the stretching axis. The gel is prepared in a good solvent with parameters $R_c = 0.005$ and $\phi_{\text{prep}} = 0.03$. The deformation ratio is 1.4.

structure factor becomes isotropic and circular contours appear in the isointensity plots.

7. Discussion

In this work we studied the statistical mechanics of randomly cross-linked polymer networks. Instead of beginning with a microscopic description based on the Edwards Hamiltonian and using the machinery of replica field theory to obtain an exact solution of the statistical mechanical problem (as we did in ref 1), we took a simpler phenomenological approach based on the separation of length scales and expressed the total free energy as the sum of long-wavelength ("solid-like") and short-wavelength ("liquid-like") contributions. Averaging over the ensemble of all the network structures consistent with conditions of preparation as well as over thermal fluctuations about these structures, we obtained explicit analytic expressions for the density correlators, valid for the entire range of wavelengths, from microscopic ($q \gg \xi^{-1}$) to continuum ($q \to 0$) length scales.

We analyzed the scattering spectra and studied their dependence on the thermodynamic parameters of the gel, both in the state of preparation and in the final state. The predicted dependence on the concentration of preparation, degree of cross-linking, degree of swelling, and the deformation ratios agrees with the results of small angle neutron scattering experiments. However, some of the results depend sensitively on the wavelength and the dependence on the parameters of the state of preparation undergoes a qualitative change, i.e., becomes nonmonotonic with ϕ_{prep} and R_c, at wavelengths much larger than the mesh size. These wavelengths lie outside of the present small angle neutron scattering range, and light scattering experiments which probe much longer wavelengths may be necessary in order to test our predictions.

Unlike static experiments which only measure the total scattering intensity and must involve some phenomenological assumptions to distinguish between the contributions of the truly static concentration inhomogeneities and of thermal fluctuations, the present analysis allows us to calculate the two ($C_{\mathbf{q}}$ and $G_{\mathbf{q}}$) separately and to put to rest all controversies regarding the relative role of these phenomena. We showed that under most conditions, static inhomogeneities dominate the scattering from the gel at wavelengths much larger than the monomer fluctuation radius R but that the situation is reversed in the opposite limit, since there are no frozen inhomogeneities of network structure at wavelengths much smaller than R. While the correlator of static inhomogeneities is always observed to be a monotonically decreasing function of the wave vector, with a characteristic decay range of $q \simeq R^{-1}$, we found that, under most conditions, the thermal correlator has a broad maximum at wavelengths on the order of the monomer fluctuation radius, followed by a decay at wavelengths smaller than the thermal correlation length ξ (the latter is the same as in semidilute polymer solutions of identical concentration). The presence of this maximum leads to the appearance of a "shoulder" in the scattering profile which becomes more pronounced when the parameters are chosen to maximize the difference between R and ξ.

How general and reliable are our results for the scattering spectra? Our fundamental results for the correlators, eqs 4.2 and 4.4, are completely general and apply to all polymer gels formed sufficiently far away from the gel point. The explicit forms of the functions $g_{\mathbf{q}}$ and $\nu_{\mathbf{q}}$, eqs 3.6 and 4.6, are model-dependent. Here, we calculated $g_{\mathbf{q}}$ for networks made of cross-linked Gaussian chains, assuming that permanent entanglements do not contribute to the elastic properties. This assumption may break down for chains that are longer than the entanglement length but, since the latter increases with the degree of swelling, permanent entanglements are expected to have an important effect only in the limit of dense gels (e.g., cross-linked melts), not considered in this work. Furthermore, although we matched our results to the exact asymptotic expressions for $g_{\mathbf{q}}$ (with 3% accuracy for the coefficient of the $\mathbf{q}^2$ term in the small-q expansion of $g_{\mathbf{q}}$), there is some freedom in the choice of the functional form of the functions, $\alpha_{\mathbf{q}}$ and $\beta_{\mathbf{q}}$, and the particular choice made in this work was dictated by simplicity considerations and by physical intuition.

The function $\nu_{\mathbf{q}}$ and the structure factor in the state of preparation $S_{\mathbf{q}}^{(0)}$ which appears in it were calculated for the case of instantaneous cross-linking from solution and are, therefore, nonuniversal. However, the most important features of these functions, such as the existence of a point at which the correlation length of static inhomogeneities diverges (the cross-link saturation threshold, in our model) and the existence of a characteristic length scale (the monomer fluctuation radius) on which the transition from liquid-like to solid-like behavior takes place, are quite general and apply to other methods of gel synthesis such as end-linking and polycondensation reactions (in the latter case, this point corresponds to the spinodal of the monomer–solvent mixture). Thus, although for quantitative comparisons it would be best to test our predictions on gels formed by instantaneous cross-linking from semidilute polymer solutions in a good solvent, we believe that the qualitative features of our results apply to all polymer gels, regardless of the method of their preparation. This sweeping claim is supported by our inspection of the recent review of the scattering data obtained from various gels.[14] As far as we can tell, all the observed qualitative features of the scattering spectra can be recovered from our theory, by an appropriate choice of thermodynamic parameters. In view of the above, it would be interesting to attempt a quantitative comparison of our predictions with experiment, throughout the entire range of wave vectors. If successful, our theory could then be used in combination with experiments, to obtain all the structural information about the network directly from the scattering spectra.

We would like to end this discussion with a comment on a new and important generalization of our work. Since we now have a theory of polymer networks which covers the entire range of wavelengths, we can address small-scale phenomena such as microphase separation in poor solvents. Such effects can be studied in the transient regime for neutral networks (before the shrinking of the entire gel sample has taken place), or even in equilibrium for charged networks in poor solvents in which counterion pressure counterbalances the tendency toward macroscopic segregation. Our preliminary results[27] show that in this case the correlator of static inhomogeneities develops a maximum at a finite q, indicating that the network reorganizes into a new state, which is ordered on a length scale on the order of the monomer fluctuation radius. For some choices of the parameters, one approaches the weak crystallization line at which the correlator of static inhomogeneities diverges, indicating that the gel forms a periodically modulated structure. The period of the modulation can be changed by tuning the parameters, and one can reach the Lifshitz point[28] at which the wavelength of the pattern diverges and the gel becomes opaque.

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Appendix A. Elasticity of Deformed Networks

Anisotropic Moduli of Homogeneous Networks. We begin with the elastic contribution to the mean field free energy of a *homogeneous* gel, with a constant density of cross-links $\nu = \bar{\rho}/(2\bar{N})$. Following the classical theories of gel elasticity,[12,13] the free energy associated with the deformation along the principal axes can be written as

$$F_{\mathrm{el}}\{\lambda_\alpha\} = T\frac{\nu}{2}V\sum_\alpha({\lambda_\alpha}^2 - 1) \tag{A1}$$

We would like to extend this expression to a general class of deformations characterized by an arbitrary displacement field $\mathbf{u}^{(0)}(\mathbf{x}^{(0)}) \equiv \mathbf{x} - \mathbf{x}^{(0)}$ which describes the displacement of a point $\mathbf{x}^{(0)} \rightarrow \mathbf{x}$ in a solid under a given deformation. We can follow the path of the usual continuum theory of elasticity of isotropic solids[9] by expanding the free energy in the gradients of this displacement field. However, since we are interested in large deformations (strains on the order of or larger than unity), we must retain the nonlinear terms in the definition of the strain tensor (the importance of introducing second-order strains in the present context was emphasized by Alexander[29])

$$u^{(0)}_{\alpha\beta}(\mathbf{x}^{(0)}) \equiv \frac{1}{2}\left[\frac{\partial u^{(0)}_\alpha}{\partial x^{(0)}_\beta} + \frac{\partial u^{(0)}_\beta}{\partial x^{(0)}_\alpha} + \sum_\gamma \frac{\partial u^{(0)}_\gamma}{\partial x^{(0)}_\alpha}\frac{\partial u^{(0)}_\gamma}{\partial x^{(0)}_\beta}\right] \tag{A2}$$

Although, in principle, one must keep all higher (than second) orders in the strain tensor in the expansion of the free energy, it can be shown that only the linear term in the strain tensor contributes to the free energy.[1] The expansion coefficients will be determined by the requirement that, for deformations given by $\mathbf{u}^{(0)}(\mathbf{x}^{(0)}) = \lambda^*\mathbf{x}^{(0)} - \mathbf{x}^{(0)}$, the free energy is given by eq A1. Thus,

$$F^{(0)}_{\mathrm{el}}[\mathbf{u}^{(0)}] = T\int \mathrm{d}\mathbf{x}^{(0)}\, [\nu^{(0)}\sum_\alpha u^{(0)}_{\alpha\alpha}(\mathbf{x}^{(0)}) + \theta\sum_{\alpha,\beta}[u^{(0)}_{\alpha\beta}(\mathbf{x}^{(0)})]^2 + \kappa\sum_\alpha[u^{(0)}_{\alpha\alpha}(\mathbf{x}^{(0)})]^2 + ...] \tag{A3}$$

where the scalar form of the expansion coefficients is dictated by the isotropy of the undeformed solid (the assumption of local isotropy has to be modified in the presence of static heterogeneities which will be considered later).

Substituting the displacement $\mathbf{u}^{(0)}(\mathbf{x}^{(0)}) = \lambda^*\mathbf{x}^{(0)} - \mathbf{x}^{(0)}$ into the definition of the strain tensor, eq A2, gives

$$u^{(0)}_{\alpha\beta} = \frac{1}{2}({\lambda_\alpha}^2 - 1)\delta_{\alpha\beta} \tag{A4}$$

Inserting this expression into eq A3 and comparing with eq A1, we conclude that the term linear in $u_{\alpha\alpha}$ reproduces our mean field elastic free energy and, therefore, that the coefficients of all higher order terms must vanish identically. Furthermore, since the integration in eq A3 is over the volume of the undeformed gel, $V^{(0)} = V/(\lambda_x\lambda_y\lambda_z)$, the coefficient $\nu^{(0)}$ is given by $\nu^{(0)} = \nu\lambda_x\lambda_y\lambda_z$ and can be interpreted as the density of cross-links in the initial state. We conclude that the generalization of our elastic entropy for arbitrary deformations (because of the contribution of second-order strains this diagonal form describes shear deformations as well as volume changes) is given by

$$F^{(0)}_{\mathrm{el}}[\mathbf{u}^{(0)}] = T^{(0)}\int \mathrm{d}\mathbf{x}^{(0)}\, \nu^{(0)}\sum_\alpha u^{(0)}_{\alpha\alpha}(\mathbf{x}^{(0)}) \tag{A5}$$

Note that the term in the free energy functional, eq A3, which describes the elasticity of polymer networks is neglected in ordinary continuum theories of elasticity of solids.[9] The reason for omitting this term is that the theory of elasticity is an expansion about the equilibrium state of the solid and it is usually assumed that there are no internal stresses in this state. A different situation exists in a polymer gel which is a solid permeated by a liquid. The equilibrium state of a gel is achieved by balancing the entropic tension in the chains against the osmotic pressure (which appears in the full free energy of the gel, eq 2.1), and therefore, nonvanishing elastic stresses exist in the network even in the absence of externally applied deformation.[29]

We proceed to calculate the elastic modulus which governs the response to small fluctuations in the final deformed state of the homogeneous gel, and to this end, we consider a small displacement with respect to the deformed state. Referred to the initial undeformed state, the displacement can be written as

$$\mathbf{u}^{(0)}(\mathbf{x}^{(0)}) = \lambda^*\mathbf{x}^{(0)} - \mathbf{x}^{(0)} + \mathbf{u}(\lambda^*\mathbf{x}^{(0)}) \tag{A6}$$

where $\mathbf{u}(\lambda^*\mathbf{x}^{(0)}) = \mathbf{u}(\mathbf{x})$ is a small displacement of the point $\mathbf{x} = \lambda^*\mathbf{x}^{(0)}$ in the affinely stretched state of the network.

We now express the free energy, eq A5, in terms of the displacement field, referred to the final deformed (and, depending on the deformation, possibly anisotropic) state. For this we need to substitute eq A6 into eq A2, insert the expression for $u_{\alpha\alpha}$ into (A5) and introduce the change of variables $\mathbf{x}^{(0)} \to \mathbf{x}$. Under this transformation, the gradient operators in the two states are related by

$$\frac{\partial}{\partial x^{(0)}_{\alpha}} = \lambda_{\alpha}\frac{\partial}{\partial x_{\alpha}} \qquad \text{(A7)}$$

and the volume element transforms as

$$\mathrm{d}\mathbf{x}^{(0)} = \frac{\mathrm{d}\mathbf{x}}{\lambda_x\lambda_y\lambda_z} \qquad \text{(A8)}$$

Substituting these replacements into eq A3 and noticing that, upon integration, the terms linear in $\partial u_{\alpha}(\mathbf{x})/\partial x_{\alpha}$ contribute a surface term which balances the externally applied force (this term is omitted in the following), we obtain the elastic free energy functional (we allow for the possibility that the temperature T in the final state may differ from that in the initial state, $T^{(0)}$)

$$\mathcal{F}_{\mathrm{el}}[\mathbf{u}] = \mathcal{F}_{\mathrm{el}}\{\lambda_{\alpha}\} + \frac{T}{2}\int \mathrm{d}\mathbf{x}\ \nu\sum_{\alpha\beta}\left(\lambda_{\alpha}\frac{\partial u_{\beta}(\mathbf{x})}{\partial x_{\alpha}}\right)^2 \qquad \text{(A9)}$$

where $\mathcal{F}_{\mathrm{el}}\{\lambda_{\alpha}\}$ is given by our mean field expression, eq A1, and defines the reference free energy of the deformed homogeneous state.

In the Fourier representation, the free energy associated with deformations (not necessarily small!) and fluctuations about the affinely deformed state can be written as

$$\Delta\mathcal{F}_{\mathrm{el}}[\mathbf{u}] \equiv \mathcal{F}_{\mathrm{el}}[\mathbf{u}] - \mathcal{F}_{\mathrm{el}}\{\lambda_{\alpha}\} = \frac{T}{2}\int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\ \nu(\lambda^*\mathbf{q})^2(\mathbf{u}_{\mathbf{q}}\cdot\mathbf{u}_{-\mathbf{q}}) \qquad \text{(A10)}$$

We conclude that the modulus of an anisotropically deformed network (for which some of the $\{\lambda_{\alpha}\}$ differ from each other) depends on the externally imposed deformation and is, in general, anisotropic. Comparing expression A10 to the quadratic in $\mathbf{u}$ part of the elastic free energy, eq 2.4, we find that the components of the tensor $\mathbf{G}_{\mathbf{q}}$ are given by the expression[1]

$$\mathbf{G}_{\mathbf{q}\alpha\beta} = \nu T(\lambda^*\mathbf{q})^2\delta_{\alpha\beta} \qquad \text{(A11)}$$

The tensor of the elastic moduli is obtained by dividing the tensor $\mathbf{G}_{\mathbf{q}}$ by q^2.

Random Stresses in Inhomogeneous Networks. We proceed to generalize the elastic free energy, eq A5, for the case of inhomogeneous gels. In section 2 we showed that in the case of inhomogeneous gels there is an ambiguity in the choice of the reference state with respect to which the displacement field is defined and therefore we demand that the elastic free energy is invariant under gauge transformations which do not affect the physically observable monomer density $\rho(\mathbf{x})$ (see eq 2.6):

$$\rho^{\mathrm{ref}}_{\mathbf{q}} \to \rho^{\mathrm{ref}}_{\mathbf{q}} + \epsilon_{\mathbf{q}} \qquad \text{(A12)}$$

$$\mathbf{u}_{\mathbf{q}} \to \mathbf{u}_{\mathbf{q}} - i\mathbf{q}\epsilon_{\mathbf{q}}/(\bar{\rho}q^2) \qquad \text{(A13)}$$

where $\epsilon_{\mathbf{q}}$ is an arbitrary (infinitesimal) function of $\mathbf{q}$. The condition of gauge invariance demands that the free energy depends only on the gauge invariant displacement vector $\hat{\mathbf{u}}_{\mathbf{q}}$

$$\mathcal{F}_{\mathrm{el}}[\mathbf{u}] \equiv \hat{\mathcal{F}}_{\mathrm{el}}[\hat{\mathbf{u}}] \qquad \hat{\mathbf{u}}_{\mathbf{q}} \equiv \mathbf{u}_{\mathbf{q}} - \mathbf{u}^{\mathrm{ref}}_{\mathbf{q}} \qquad \text{(A14)}$$

where the vector $\mathbf{u}^{\mathrm{ref}}_{\mathbf{q}}$ depends on the choice of the reference state and changes as

$$\mathbf{u}^{\mathrm{ref}}_{\mathbf{q}} \to \mathbf{u}^{\mathrm{ref}}_{\mathbf{q}} - i\mathbf{q}\epsilon_{\mathbf{q}}/(\bar{\rho}q^2) \qquad \text{(A15)}$$

under the gauge transformation (A13).

We first consider the undeformed reference state which will be denoted by the superscript (0). For small deviations from this state, the free energy functional can be expanded in powers of the gauge invariant strain tensor $\hat{u}^{(0)}_{\alpha\beta}$ defined by eq A2, where we have to substitute the function $\hat{\mathbf{u}}^{(0)}$, eq A14, instead of the displacement vector $\mathbf{u}^{(0)}$. This expansion has the form of eq A3, where the expansion coefficients are now gauge invariant. In the case of a Gaussian network one can keep only the linear term in $\hat{u}^{(0)}_{\alpha\beta}$ (all the higher order contributions vanish identically) and the free energy functional takes the form

$$\mathcal{F}^{(0)}_{\mathrm{el}}[\mathbf{u}^{(0)}] = T^{(0)}\int \mathrm{d}\mathbf{x}^{(0)}\ \nu^{(0)}\sum_{\alpha}\hat{u}^{(0)}_{\alpha\alpha}(\mathbf{x}^{(0)}) \qquad \text{(A16)}$$

We first find the vector $\mathbf{u}^{\mathrm{ref}} = \mathbf{u}^{(0)\mathrm{ref}}$ for the undeformed reference state with the density $\rho^{\mathrm{ref}}(\mathbf{x}^{(0)}) = \rho^{(0)}(\mathbf{x}^{(0)})$ (see eq 2.3 for the case of $\lambda_{\alpha} = 1$). Equation A16 shows that the "gauge field" $\mathbf{u}^{(0)\mathrm{ref}}$ can be considered as the equilibrium displacement vector in such an elastic reference state. Under the gauge transformation the vector $\mathbf{u}^{\mathrm{ref}}$ changes linearly with the change of the density of the reference state (see eqs A12 and A15), and therefore it should depend linearly on this density:

$$\mathbf{u}^{(0)\mathrm{ref}}_{\mathbf{q}} = ia\mathbf{q}\rho^{(0)}_{\mathbf{q}}/(\bar{\rho}^{(0)}q^2) + \tilde{\mathbf{u}}^{(0)}_{\mathbf{q}} \qquad \text{(A17)}$$

Here, the vector $\tilde{\mathbf{u}}^{(0)}$ does not depend on the density of the initial state. It distinguishes between different network structures which have the same density distribution in the initial state, $\rho^{(0)}(\mathbf{x}^{(0)})$. Following the analogy between such statistical fluctuations and thermal fluctuations of shear displacements and using the equipartition theorem, we can write the correlator of the displacement vector $\tilde{\mathbf{u}}^{(0)}$ in the form

$$\overline{\tilde{u}^{(0)}_{\alpha\ \mathbf{q}}\tilde{u}^{(0)}_{\beta\ -\mathbf{q}}} = b\delta_{\alpha\beta}/(\nu^{(0)}q^2) \qquad \text{(A18)}$$

The presence of the Kronecker δ function expresses the fact that different components of the vector $\tilde{\mathbf{u}}^{(0)}$ are uncorrelated.

The dimensionless coefficients a and b in eqs A17 and A18 depend on the method of preparation of the network. In the case of gels prepared by instantaneous cross-linking they can be found by comparing the continuous limit of the density correlation function $S_{\mathbf{q}\to 0}$ (which follows from our expression for the free energy) with the exact result given in eq 4.7. This procedure was used in the derivation of the expressions 6.2−6.4 for the correlation functions, and it yields $a = 2$ and $b = 3$ (the direct replica theory calculation of these coefficients was performed in ref 30).

Comparing the resulting free energy with expression 2.4, we observe that the condition of gauge invariance leads to the following expression for the Fourier components of the force density

$$\mathbf{f}^{(0)}_{\mathbf{q}} \equiv \mathbf{G}^{(0)}_{\mathbf{q}}\cdot\mathbf{u}^{(0)\mathrm{ref}}_{\mathbf{q}} = \mathbf{f}^{(0)}_{\mathrm{pres}\ \mathbf{q}} + \tilde{\mathbf{f}}^{(0)}_{\mathbf{q}} \qquad \text{(A19)}$$

where the two contributions to the displacement vector $\mathbf{u}^{\mathrm{ref}}$, eq A17, give rise to corresponding force densities.

The cross-link pressure contribution to the force density is given by

$$\mathbf{f}^{(0)}_{\mathrm{pres}\ \mathbf{q}} = iaT^{(0)}(2\bar{N})^{-1}i\mathbf{q}\rho^{(0)}_{\mathbf{q}} \qquad \text{(A20)}$$

and its statistical properties are completely defined by those of the density of cross-links in the state of preparation of the network. The correlator of the components of the random force $\tilde{\mathbf{f}}^{(0)}$ is given by

$$\overline{\tilde{f}^{(0)}_{\mathbf{q}\alpha}\tilde{f}^{(0)}_{-\mathbf{q}\beta}} = b(T^{(0)})^2\frac{\bar{\rho}^{(0)}}{2\bar{N}}q^2\delta_{\alpha\beta} \qquad \text{(A21)}$$

The fact that the above correlator vanishes at $q \to 0$ is consistent with the condition of mechanical equilibrium according to which the integrated force due to internal stresses in the entire sample must vanish, $\int \mathrm{d}\mathbf{x}^{(0)}\ \tilde{\mathbf{f}}(\mathbf{x}^{(0)}) = \tilde{\mathbf{f}}_{\mathbf{q}=0} = 0$.

We now derive the elastic part of the network free energy for an anisotropically stretched network. Let us define the gauge invariant strain tensor for displacements about the affinely deformed state $\hat{u}_{\alpha\beta}(\mathbf{x})$ by eq A2 in which one has to omit the superscript (0) and substitute the function $\hat{\mathbf{u}} = \mathbf{u} - \mathbf{u}^{\mathrm{ref}}$, eq A14, instead of the displacement vector $\mathbf{u}^{(0)}$. Using eqs A6 and A7, one can show that

$$\hat{u}^{(0)}_{\alpha\beta}(\mathbf{x}^{(0)}) = \frac{1}{2}({\lambda_\alpha}^2 - 1)\delta_{\alpha\beta} + \lambda_\alpha\lambda_\beta\hat{u}_{\alpha\beta}(\lambda^*\mathbf{x}^{(0)}) \qquad \text{(A22)}$$

Substituting this expression in $F^{(0)}_{\mathrm{el}}$ (A16) and changing variables from $\mathbf{x}^{(0)}$ to the coordinates of the deformed state $\mathbf{x} = \lambda^*\mathbf{x}^{(0)}$ in the last integration, we find the elastic part of the free energy which describes arbitrary displacements about the final deformed state of the network,

$$\Delta F_{\mathrm{el}}[\mathbf{u}] = \int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left[\frac{T\bar{\rho}}{4\bar{N}}(\lambda^*\mathbf{q})^2\mathbf{u}_{-\mathbf{q}}\cdot\mathbf{u}_{\mathbf{q}} - \mathbf{f}_{-\mathbf{q}}\cdot\mathbf{u}_{\mathbf{q}}\right] \qquad \text{(A23)}$$

Note that the temperature T as well as the average density $\bar{\rho} = \bar{\rho}^{(0)}/\lambda_x\lambda_y\lambda_z$ can differ from their values $T^{(0)}$ and $\bar{\rho}^{(0)}$ in the state of preparation of the network.

The force density can be written as a sum of two contributions:

$$\mathbf{f}_{\mathbf{q}} \equiv \mathbf{G}_{\mathbf{q}}\cdot\mathbf{u}^{\mathrm{ref}}_{\mathbf{q}} = \mathbf{f}_{\mathrm{pres}\ \mathbf{q}} + \tilde{\mathbf{f}}_{\mathbf{q}} \qquad \text{(A24)}$$

where the components of the force density associated with the cross-link pressure in the final deformed state are given by

$$(\mathbf{f}_{\mathrm{pres}\ \mathbf{q}})_\alpha = ia{\lambda_\alpha}^2T(2\bar{N})^{-1}q_\alpha\rho^{\mathrm{ref}}_{\mathbf{q}} \qquad \text{(A25)}$$

Here ρ^{ref} is the monomer density in the affinely deformed initial state, eq 2.3. The correlator of the components of the force density associated with the frozen-in fluctuations of network structure in the final state can be obtained from eq A21,

$$\overline{\tilde{f}_{\mathbf{q}\alpha}\tilde{f}_{-\mathbf{q}\beta}} = b{\lambda_\alpha}^2T^2\frac{\bar{\rho}}{2\bar{N}}(\lambda^*\mathbf{q})^2\delta_{\alpha\beta} \qquad \text{(A26)}$$

The above expressions, eqs A25 and A26, are identical to the more general expressions obtained by rigorous replica field theoretical methods.[30]

References and Notes

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