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Mesoscopic physics of swollen polymer networks: Statics and dynamics

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We investigate in this paper the origin of the "butterfly" patterns that were discovered during small-angle-neutron-scattering studies of uniaxially stretched gels and rubbers and of polymer blends in extensional flow. We present a general formalism for both gels and liquids which shows that when material parameters such as shear modulus or viscosity are allowed to depend on the internal degrees of freedom (e.g., the monomer concentration), then butterfly patterns are naturally encountered in the isointensity contours of the structure factor. We also show that for higher strains (or strain rates for liquids), one encounters strain-induced decomposition. The dynamics of strain and of flow-induced decomposition are shown to be closely similar. To test the theoretical description, we compute the inelastic-light-scattering spectrum and the time evolution of the small-angle neutron-scattering cross section.

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I. INTRODUCTION

A. Classical theory

A gel or rubber is a complex network consisting of a mesh of randomly cross-linked polymer chains. The connecting sections of the network are polymer coils which, due to their great extensibility, allow the network to have a very low rigidity (i.e., low shear and low Young's moduli [1]). The first description of the physical properties of such networks was provided by the classical theory of rubber elasticity, which dates back to the 1940s [2–4]. For the classical theory, strain is the only macroscopic collective variable because the monomer concentration of a connected network is assumed to be locked to the strain. For networks swollen by a solvent (gels), the classical theory assumes that the free energy is the sum of a purely liquidlike part and a purely elastic part. The equilibrium state is, consequently, characterized by a balance between the "liquid" pressure—which tends to expand the network—and the isotropic elastic stress in the network which tends to contract it.

At the microscopic level, a gel is believed to behave as an elastic solid only beyond a certain characteristic length scale. At shorter length scales, it is better described as a liquid [5]. An elegant, intuitive picture which captures this microscopic regime has been provided by the so-called "c^* theorem" [6]. This principle states that at the microscopic level, an equilibrium gel resembles a *semidilute polymer solution* at the overlap concentration c^*. In the language of solid-state physics we might interpret this c^* theorem as saying that a gel is to be considered as a random mesh with every unit of the mesh (the "basis") containing a liquid polymer coil (or "blob") whose size is the same as that of the mesh [see Fig. 1(a)]. The blobs are connected by the cross links of the mesh. If, following the c^* theorem, we set the blob size equal to the usual Flory radius $R_f \propto N^{3/5}$ of a polymer coil—with N the number of monomers per blob (and thus, roughly, per cross link)—then the monomer concentration c_0 is N/R_f^3 so $c_0 \propto N^{-4/5} v^{-3/5} a^{-6/5}$ (here v is the excluded-volume parameter and a is the monomer length).

The earlier mentioned crossover from liquidlike to solidlike behavior thus occurs at length scales of order R_f. Since in this description there is only one relevant length scale (the Flory radius) and only one relevant energy scale (the entropic energy scale $k_B T$) it follows from dimensional analysis that the gel elastic moduli are of order $k_B T/R_F^3$ [6]. As a consequence, the elastic moduli are strongly dependent on monomer concentration (as $c_0^{9/4}$)—a fact which will play an important role later. Using the same argument, let Π be the osmotic pressure ("swelling pressure") inside the gel. This swelling pressure is, as noted, the sum of two terms: (i) the osmotic pressure of the equivalent semidilute solution (Π_{liq}), and (ii) the negative elastic contribution (Π_{net}), so $\Pi = \Pi_{\text{liq}} - \Pi_{\text{net}}$. From dimensional arguments, both Π_{liq} and Π_{net} again must be of order $k_B T/R_F^3 \propto c_0^{9/4}$. Notice, incidentally, that since at the microscopic level a gel behaves like a liquid, strain and monomer concentration are, at this level, *not* locked together because liquids can support concentration gradients but not elastic strains.

For polymer networks close to equilibrium swelling, i.e., $\Pi = 0$, the above description is well confirmed by osmotic and mechanical measurements [7–9]. However, a series of recent small-angle neutron (SANS) and small-angle x-ray (SAXS) studies of *strained* gels [10–12] have produced results in great disagreement with the classical theory. The aim of this paper is to address the origin of this discrepancy. Small-angle scattering is usually the most direct way to test the hydrodynamic response of a system. Since the hydrodynamic response of a system in general only depends on the symmetry of the basic collective variables and on the conservation laws, a serious discrepancy between theory and experiment is a fundamental challenge to the validity of a theory. Gels far from swelling equilibrium in excess solvent are much less

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well described by the classical theories [13–15], even with no applied strain. We will restrict ourselves in this paper to gels close to swelling equilibrium.

B. Elastic moduli and small-angle scattering

If we probe a system by small-angle elastic scattering, we are in effect measuring the (static) structure factor $S(\mathbf{k})$, the Fourier transform of the density-density correlation function, for small wave vectors $\mathbf{k}$. In the case of a gel there are two contributions to the static structure factor: one associated with thermally driven, dynamic concentration fluctuations and one associated with the static heterogeneous structure of a randomly cross-linked network. In light-scattering experiments the two components can be conveniently separated by time-resolved measurements, e.g., by measuring the decay of the two-time intensity-intensity correlation function. In analyzing SANS experiments the separation is done empirically, by assuming a given functional form (usually Gaussian) of the $\mathbf{k}$ dependence of the scattering intensity from frozen-in inhomogeneities [16]. In this work we concentrate on the thermal diffuse-scattering contribution due to monomer concentration fluctuations which is given (for $k \ll 1/R_F$) by a Lorentzian structure factor:

$$S_0(\mathbf{k})=(c_0^2 k_B T/E)/(1+k^2\xi^2) \tag{1.1}$$

with E an as yet unspecified modulus and with ξ the correlation length for concentration fluctuations. As we will show in the following, the physical interpretation of the modulus in Eq. (1.1) is intimately related to the question of whether, *on length scales probed by scattering experiments,* gels behave as liquids or as solids.

Both light [17]- and neutron [18]-scattering studies reveal that the small-angle-scattering intensity of gels is considerably stronger than that of an equivalent but uncross-linked semidilute solution. Although this enhancement is usually attributed to scattering from static inhomogeneities, recent experiments suggest that, at least in the vicinity of the volume-phase-transition point of the gel, the thermal fluctuation contribution to the scattering is much larger than that of a corresponding semidilute solution [19]. It is believed that there is a strong correlation between the observation of enhanced scattering in *unstrained* gels and the appearance of scattering anomalies in *strained* gels. For this reason we will examine in this section the interpretation of small-angle scattering from unstrained gels.

The c^* theorem indicates that for length scales less than the Flory radius R_F, we should treat the gel as a liquid. For liquids, the compressibility sum rule [6], $S(\mathbf{k}\Longrightarrow 0)=c_0 k_B T \partial c/\partial \Pi$, must be strictly obeyed, which would suggest that the modulus in Eq. (1.1) should be identified with the osmotic modulus $E_o=c_0\partial\Pi/\partial c$. Before discussing the applicability of the compressibility sum rule to gels, we first compute the osmotic modulus E_o using the classical theory. According to the additivity assumption underlying the classical theories of gels [2–4], the free energy (per "site" a^3) for isotropic expansion or contraction of a gel is given as a sum of a "liquid" and an elastic contribution:

$$F(\Phi)\approx(k_B T/a^3)\{(1-\Phi)\ln(1-\Phi)+\chi(T)\Phi(1-\Phi) + \tfrac{3}{2}Q\Phi^{1/3}/N^{4/3}\} \tag{1.2}$$

where $\Phi=ca^3$ the monomer volume fraction. The first two terms constitute the "liquid" contribution to the free energy given by the usual Flory-Huggins free-energy mixing between monomers and solvent (but excluding the chain translational entropy as chains are now connected to an infinite network), with $\chi(T)$ the Flory parameter for the monomer-solvent interaction. It is important to emphasize that the usual assumption of *strict additivity* implies that the χ parameter of a gel is *the same* as that of an equivalent polymer solution. The third term is the (entropic) elastic free energy $k_B T\, R_F^2/Na^2$ of a polymer coil, multiplied by the blob density $1/R_F^3$ (Q is a constant).

It is important to note here that $F(\Phi)$ is a (mean-field) estimate of the free energy assuming mechanical equilibrium. If, for a given Φ, we would apply a pure shear stress which does not alter the mean concentration or blob radius, then the associated free-energy increase is clearly not included in $F(\Phi)$. However, we can use $F(\Phi)$ to compute the osmotic pressure and osmotic modulus assuming that homogeneous osmotic swelling or deswelling is not accompanied by shear stress.

For low monomer concentrations, the gel osmotic pressure $\Pi=\Phi^2\partial(F/\Phi)/\partial\Phi$ is now

$$\Pi/(k_B T/a^3)\approx\tfrac{1}{2}[1-2\chi(T)]\Phi^2-Q\Phi^{1/3}/N^{4/3}\,, \tag{1.3a}$$

where the first term is the osmotic pressure Π_{liq} of the equivalent semidilute solution and the second term is the negative network pressure $-\Pi_{\text{ne}}$ ($\Pi=0$, in swelling equilibrium). The gel osmotic modulus $E_o=\Phi\partial\Pi/\partial\Phi$ is now

$$E_o/(k_B T/a^3)\approx[1-2\chi(T)]\Phi^2-\tfrac{1}{3}Q\Phi^{1/3}/N^{4/3}\,. \tag{1.3b}$$

The first term in the above equation is the osmotic modulus of a polymer solution, so it is clear from Eq. (1.3b) that classical theory predicts that the *osmotic modulus of a gel should always be smaller than that of the equivalent semidilute solution.* This means that if we reduce solvent quality then a gel must decompose before the equivalent semidilute polymer solution.

We now return to the question of the applicability of the compressibility sum rule to gels, to see whether we can understand the enhanced scattering of gels. If we consider concentration fluctuations in gels from the viewpoint of macroscopic elasticity theory of solids, then the fluctuation free-energy must have the form [1]

$$\Delta F=\int d^3r\tfrac{1}{2}\{\lambda\epsilon_{ii}^2+2\mu\epsilon_{ij}^2\} \tag{1.4}$$

with μ the shear modulus and $K=\lambda+\frac{2}{3}\mu$ the bulk modulus. Mechanical stability requires both moduli to be positive [1]. The strain tensor ϵ is, for small displacements, given by

$$\epsilon_{ij}=\frac{1}{2}\left[\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right] \tag{1.5}$$

with $\mathbf{u}(\mathbf{x})$ the displacement field. The long-wavelength fluctuation spectrum is found by decomposing the displacement field into orthogonal longitudinal and transverse parts and inserting the result in ΔF:

$$\Delta F = \sum_{k(\neq 0)} \tfrac{1}{2}k^2\{E_l|u_l(\mathbf{k})|^2+\mu|\mathbf{u}_t(\mathbf{k})|^2\} \tag{1.6}$$

with $u_l(\mathbf{k})=\mathbf{k}\cdot\mathbf{u}(\mathbf{k})/k$, $\mathbf{u}_t(\mathbf{k})_i=(\delta_{i,j}-k_ik_j/k^2)u_j(\mathbf{k})$, and with $E_l=K+\frac{4}{3}\mu$ the so-called "longitudinal" modulus. As we noted, in the classical theory of rubber elasticity—and in elasticity theory in general [1]—a concentration fluctuation $\delta c(\mathbf{x})$ is locked to the displacement field $\mathbf{u}(\mathbf{x})$. Using mass conservation, it follows that the required relation is $\delta c(\mathbf{r})/c_0 \approx -\nabla\cdot\mathbf{u}$. This means that the longitudinal part of the spectrum must also represent concentration fluctuations. If we now apply the equipartition theorem to Eq. (1.6), we can compute the thermal average $\langle |(u_l(\mathbf{k})|^2\rangle$ of the longitudinal fluctuations and then, using the relation between concentration and longitudinal fluctuations, the structure factor $\langle |(\delta c(\mathbf{k})|^2\rangle$ for long-wavelength thermal diffuse scattering. This leads to the well-known result [20] that $S(\mathbf{k} \Longrightarrow \mathbf{0}) \propto k_BT/E_l$.

To estimate K and μ, we return to our calculation of the osmotic modulus E_o. Since it did not involve any shear deformation, we must identify $E_o=K$. A recent model calculation by Onuki [21] confirms this identification. As a consequence we have the relation

$$E_l=E_o+\tfrac{4}{3}\mu \tag{1.7}$$

so we cannot apply the compressibility sum rule to gels, assuming we restrict ourselves to scattering wave vectors $k \ll 1/R_F$ so we are in the regime of "solidlike" behavior.

We now return to the question of the enhanced scattering of gels. Flory theory predicts that the osmotic modulus of gels is reduced as compared to semidilute solutions but we must include the factor $\frac{4}{3}\mu$ to decide whether or not the longitudinal modulus is reduced. Onuki's calculation [21] produces $E_l=E_o(\mathrm{sol})+\mu$, so the cross-linking would enhance the longitudinal modulus and thus reduce scattering in gels. This would provide an argument in favor of enhanced scattering due to inhomogeneities, but as both dynamic light scattering [22] and SANS [19] experiments suggest that even the thermal diffuse-scattering component from gels is stronger than from the equivalent solution, one must reexamine the additivity assumption of classical theories which leads to Onuki's result. A recent calculation which goes beyond the Flory-Huggins scheme suggests that solubility is reduced by the introduction of cross links [23], a prediction which appears to be supported by the analysis of differential-swelling experiments [15,24]. In this case, the resulting gel longitudinal modulus may be reduced below that of a solution, in agreement with the experimental observations [19]. In the following we will assume that $E_l(\mathrm{gel})<E_l(\mathrm{sol})$.

Notice that classical theory predicts that if the quality of solvent is reduced while maintaining swelling equilibrium, the gel simply readjusts to a new state of swelling equilibrium, up to the point at which the osmotic gel modulus vanishes [this can be seen by applying the swelling equilibrium condition $\Pi=0$ to Eqs. 1.3(a) and 1.3(b)]. Under a fast temperature quench ("T" jump), according to Eq. (1.3b), the osmotic gel modulus can change sign *before* we reach this point, leading to a pure $\mathbf{k}=\mathbf{0}$ mechanical instability. Since at this point the longitudinal modulus is still positive, no unusual growth of concentration fluctuations takes place and therefore a continuous phase transition with a diverging correlation length takes place only upon further reduction of solvent quality, when the longitudinal gel modulus vanishes. If, as we have argued, gels are inherently less soluble than the corresponding solutions, this gel decomposition point ($E_l=0$) can be reached even for nominally good solvents [$E_o(\mathrm{sol})>0$]. Such gel demixing phenomena were reported by Tanaka [17,20].

Let us now discuss the prediction of classical theory concerning the effect of applied strain on the structure factor. Classical theory asserts that under strain, the monomer concentration "follows" the applied strain. More precisely, if $\mathbf{r}$ is the position vector of a monomer in the network, then under an applied strain $\boldsymbol{\epsilon}$, $\mathbf{r}$ is assumed to be displaced to (roughly) $(\mathbf{1}+\boldsymbol{\epsilon})\mathbf{r}$. We will denote this as the "strong" self-affinity assumption. Under conditions of strong self-affinity, the density fluctuations deform conformally to the macroscopic strain deformation of the sample. Thus, if $g(\mathbf{r})=\langle |c(\mathbf{0})c(\mathbf{r})|\rangle$ is the density correlation function in the absence of applied strain then strain should act like a mathematical operation which performs on $g(\mathbf{r})$ the affine transformation

$$g(\mathbf{r}) \Longrightarrow g([\mathbf{1}+\boldsymbol{\epsilon}]^{-1}\mathbf{r}) \tag{1.8}$$

because the joint probability to encounter monomers at $\mathbf{0}$ and $\mathbf{r}$ in the unstrained gel and at $\mathbf{0}$ and $(\mathbf{1}+\boldsymbol{\epsilon})\mathbf{r}$ in the strained gel must be the same. As an example, assume that for the unstrained gel, we have a correlation function whose Fourier transform agrees with Eq. (1.1), i.e., $g(\mathbf{r}) \propto (1/r)\exp(-r/\xi)$, with ξ the correlation length for concentration fluctuations. Under an extensional, volume conserving strain $\epsilon_{zz}=-2\epsilon_{xx}=-2\epsilon_{yy}=2\epsilon$, the correlation length along the strain direction is, according to Eq. (1.8), increased while perpendicular to the strain direction it is reduced:

$$\xi_{\parallel}=(1+2\epsilon)\xi\ , \tag{1.9a}$$

$$\xi_{\perp}=(1-\epsilon)\xi\ . \tag{1.9b}$$

The static structure factor itself transforms as

$$S_{\mathrm{affine}}(\mathbf{k})=S_0([\mathbf{1}+\boldsymbol{\epsilon}]\mathbf{k}) \tag{1.10}$$

since it is the Fourier transform of $g(\mathbf{r})$. The resulting isointensity contours are concentric spheres for the unstrained case and oblate spheroids, contracted along the strain direction for the strained case. Physically, this is a very reasonable result. Elongation of the polymer springs along the strain direction should reduce their elasticity, and thus increase the spring constants. Note that the longitudinal modulus now should be dependent on the direction of $\mathbf{k}$, with $E_l(\mathbf{k})$ larger along the strain direction. Since the structure factor in the long-wavelength limit equals $c_0^2 k_B T / E_l(\mathbf{k})$, we must expect a reduction of the structure factor along the strain direction [25].

For liquids, the analog of the strong self-affinity assumption is known as the "Maxwell construction" [26]. If the shear-rate tensor of a liquid is $\mathbf{A} \equiv \partial \epsilon / \partial t$ and if τ is the lifetime of a density fluctuation, then density fluctuations typically should undergo a shear of order $\mathbf{A}\tau$ before they expire. The Maxwell construction thus asserts that

$$S_{\text{flow}}(\mathbf{k}) = S_{\text{no flow}}([1 + \mathbf{A}\tau]\mathbf{k}) \tag{1.11}$$

in perfect analogy with Eq. (1.10). If γ is a typical shear rate then the dimensionless parameter controlling the amount of deformation of the structure factor is the well-known Deborah number $\mathrm{De} \equiv \gamma\tau$.

SANS and SAXS experiments [10–12] on elongationally strained gels and on blends in extensional flow revealed that the structure factor $S(\mathbf{k})$—and thus the density correlation function—grossly deviates from the predictions of Eqs. (1.9) and (1.10). In one particularly revealing case [12], $S(\mathbf{k})$ actually *did* initially show oblate ellipsoidal isointensity contours immediately after the uniaxial stress was imposed but after a period of waiting—or upon heating—the contours rearranged themselves dramatically, assuming a butterflylike shape directed along the applied strain (obviously suggesting that a slow, internal degree of freedom is responsible for the transformation). The correlation length along the strain direction had decreased and in the perpendicular direction it had (weakly) increased, in complete disagreement with Eq. (1.9).

Previously, Wu *et al.* [27] had found that, for polymer solutions under pure shear flow, the analogous Maxwell construction is invalid, at least near the phase boundary for phase separation. The explanation of this latter effect, as given by Helfand and Frederickson and others [28], is that it is due to flow enhancement of concentration fluctuations originating from the dependence of the viscosity on concentration. It was recently found that semidilute solutions in extensional [29] and in shear [30] flows, under conditions of reduced solvent quality, show butterfly patterns which are quite similar to those of strained gels. As we have argued, gels are intrinsically disposed to decomposition phenomena and they also have concentration-dependent moduli. It would thus seem to be at least suggestive that the breakdown of classical theory in strained gels originates in strain enhancement of fluctuations triggered by concentration dependence of material parameters.

C. Mesoscopic physics of gels

In this paper, we will base our discussion of concentration fluctuations in strained gels, as well as the appearance of the butterfly patterns, on the idea that there is a large *mesoscopic* range of length scales which is probed by the small-angle-scattering experiments and which is neither well described by a purely macroscopic classical elasticity theory of solids, with its condition of slaved concentration fluctuations, nor yet by a "liquid" microscopic model where concentration is the only collective variable.

In a previous paper (hereafter referred to as I) [31], the authors constructed a Landau theory of homogeneous, soft, two-component solids which was meant to describe this range. The condition of strong self-affinity was replaced by a "soft" linkage of concentration fluctuations to strain, i.e., both concentration and strain were included as separate—albeit coupled—collective variables. If the elastic moduli were assumed to be concentration dependent, then butterfly-shaped isointensity contours were encountered, provided the preexisting elastic anharmonicity is weak. The butterfly pattern was, in this case, a precursor of strain-induced spinodal decomposition, a well-known effect in the theory of stressed alloys [32]. Physically, the decomposition is due to the fact that alternation of layers of large and small elastic modulus reduces the work done in stretching a solid, thereby lowering the free energy.

There is no fundamental basis for the validity of the strong self-affinity assumption on all length scales since the degrees of freedom describing the structure of gels at length scales shorter than the Flory length do not obey it. Neutron scattering from labeled network chains in swollen gels [33] indeed clearly reveals that the internal deformation of individual polymer chains is not slaved to the strain. There is however a weaker constraint which must be satisfied for a fully connected gel, namely, that a *macroscopic* deformation $\mathbf{u}(\mathbf{x})$ necessarily produces, by mass conservation, a change in monomer concentration given by the "slaving" relation $\delta c(\mathbf{r})/c_0 \approx -\nabla \cdot \mathbf{u}$. We will call this the "weak" self-affinity condition and it must be obeyed by *any* theory of fully connected gels. Weak self-affinity was not obeyed in I, since it only aimed to provide a description of fluctuations at the mesoscopic range. We thus still need a theory which in the limit of macroscopic length scales (millimeters to centimeters) obeys self-affinity and which for short length scales incorporates liquidlike behavior with no self-affinity. Also, reference I did not address the striking similarity in the diffraction patterns of stressed gels and of polymer liquids in extensional and shear flow. In the polymer liquid case, strain is at best a transient variable so the treatment of I cannot possibly apply. Finally, any theory of the butterfly pattern in gels must go beyond a purely phenomenological Landau description and be consistent with those key ideas of the classical theory which have been well verified. The aim of the present paper is to present such a unified approach to the appearance of butterfly patterns in both gels and polymer liquids.

Finally, we would like to comment on other approaches to the problem. Our whole discussion has focused on the contribution of thermal-diffuse concentration fluctuations to the small-angle scattering but, as mentioned, it is known from the observation of (quasistatic) laser speckle patterns that there is a static heterogeneous contribution as well. It would, naively, seem that far from the percolation threshold of gels, heterogeneous scattering should not be important at small wave vectors but Bastide, Leibler, and Prost [34]—and other authors [35]—showed that static heterogeneous scattering from a stretched gel can also produce butterfly contours, independent of any thermal concentration fluctuations. Similarly, they attribute the enhanced long-wavelength scattering of (unstrained) gels not to thermal-diffuse scattering from concentration fluctuations but to the increase in static heterogeneous scattering in going from a homogeneous liquid to a randomly connected gel. We would like to stress that the observation of laser speckle patterns is by itself not proof that quenched disorder controls the small-angle scattering. Any system which is on the border of spinodal decomposition—such as swollen gels—would be highly sensitive to static disorder since this could produce locally regions of decomposition, the further growth of which could well be arrested by development of elastic stresses during the decomposition process. Such "heterogeneous nucleation" in the presence of modest quenched disorder could produce quasistatic speckle patterns which would evolve slowly in time. This appears to be supported by the observation of very slow relaxation dynamics (on time scales of order of minutes or hours [22]) of the so-called "static" speckle patterns.

There is another argument in favor of the thermal-fluctuation explanation of the butterfly effect in gels. Because polymer blends and semidilute solutions under extensional and shear flow (presumably) are homogeneous, yet still show the butterfly effect, the static heterogeneities argument would require a separate explanation for the case of fluids. At any rate, it will be difficult to decide between these two different approaches on the basis of a measurement of the *static* structure factor alone. However, scattering from quenched inhomogeneities ought to be a truly static effect and should not show up at finite frequencies while, as we shall see, if thermal-diffuse scattering dominates, then the appearance of the butterfly pattern should have important, and testable, consequences for the *dynamics*.

II. STATICS

Landau theory

In this section, we will introduce our model for the mesoscopic physics of gels. In a purely hydrodynamic (i.e., purely macroscopic) theory, the only degrees of freedom would be the gapless hydrodynamic variables. As for any solid, these are the strain tensor ϵ, the concentration c, and the temperature. The strain tensor

$$\epsilon_{ij}(\mathbf{r})=\frac{1}{2}\left[\frac{\partial u_i}{\partial r_j}+\frac{\partial u_j}{\partial r_{ia}}\right] \tag{2.1}$$

is expressed in terms of the vector field $\mathbf{u}(\mathbf{r})$ which we will take to be the continuum limit of the displacements of the position vectors $\mathbf{R}_j$ of the cross links. Since at hydrodynamic length scales, concentration and strain are related through the weak self-affinity condition, it follows that concentration is not a separate hydrodynamic variable. We will assume isothermal conditions, leaving us only with the strain as a hydrodynamic variable.

Next, since we are also interested in the behavior at intermediate length scales, we must include long-lived but nonhydrodynamic modes which describe the liquid internal degrees of freedom of the polymer blobs. Assume we deform a given polymer blob and expand the blob shape in spherical harmonics, without changing the mesh of cross links. The $l=0$ spherical harmonic of the shape deformation describes isotropic changes in the blob radius. We will define the scalar field $\psi(\mathbf{r})$ to be the relative change in the radius of blobs located around $\mathbf{r}$. For polymer coils in solution, this $l=0$ mode is known as the Zimm mode. It has a spring constant of order k_BT/R_F^2 and is believed to be the mode of free polymer coils in solution with the lowest energy gap. It is easy to show that if we place an ideal coil in a mesh fixing its ends, then this mode still survives and with a similar spring constant. The polymer coils of a gel also may have side chains of, presumably, comparable length as the links of the mesh. Changes in the mean radius of these side chains will also be described as a Zimm mode.

This scalar field $\psi(\mathbf{r})$ will describe the effect of local "liquidlike" fluctuations of the internal structure of the blobs at larger length scales. Higher-order blob modes, with nonzero l, are neglected here as they would produce internal order parameters of a more general tensorial character, associated with more exotic phase transitions such as the appearance of liquid-crystalline order [36]. In Fig. 1, we illustrate the difference in the definitions of $\epsilon_{ij}(\mathbf{r})$ and $\psi(\mathbf{r})$. If we keep the blob radius fixed, but swell the cross-link network, then this must be a "pure" ϵ_{ij} strain deformation [Fig. 1(b)]. If, on the other hand, we fix the cross links but swell the blobs, we have a pure ψ deformation [Fig. 1(c)]. Clearly, in both cases we produce variations in the monomer concentration on length scales of order the mesh size (Flory radius), so the fluctuation free-energy cost must be high for each of these

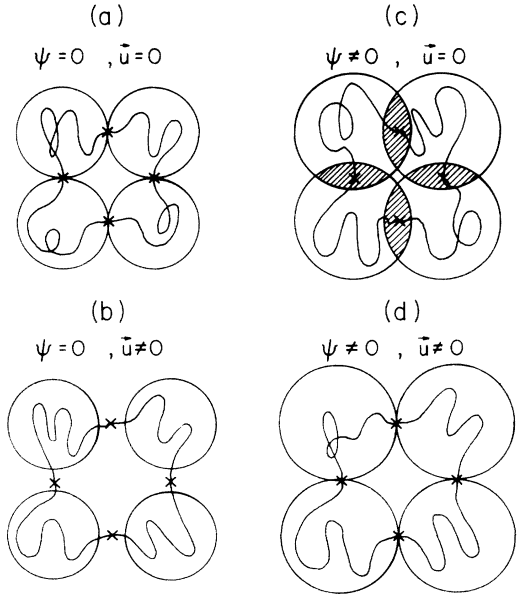

FIG. 1. Possible deformations of polymer gels: (a) swelling equilibrium (undeformed gel), (b) expanded cross-link network, equilibrium blobs, (c) expanded blobs, cross-link network at equilibrium, and (d) both blobs and cross-link network are expanded. Note that while cases (a) and (d) correspond to uniform monomer density, there are large variations in the local monomer density in cases (b) and (c).

"pure" modes. A low free-energy fluctuation $\psi^0(\mathbf{x})$ with no large local concentration variations clearly requires a combination of $\epsilon_{ij}(\mathbf{r})$ and $\psi(\mathbf{r})$ [see Fig. 1(d)]. Since ψ is the relative change in blob radius, it follows from Fig. 1(d) that $\psi^0(\mathbf{x})\approx\epsilon_{ii}$ for a low-energy fluctuation.

The fluctuation free energy of our coupled degrees of freedom is, to lowest order in the amplitudes,

$$\Delta F=\int d^3r\tfrac{1}{2}\{\lambda(\psi)\epsilon_{ii}^2+2\mu(\psi)\epsilon_{ij}^2+L(\nabla\epsilon_{ii})^2+2C_c\epsilon_{ii}\psi+M(\nabla\psi)^2+B\psi^2\}\ . \qquad (2.2)$$

This free energy is the general Landau free energy of any scalar order parameter coupled to the strain energy of an isotropic solid. A related free energy (but with coupling term quadratic rather than linear in ψ) is encountered in the case of deformable magnets [37], as well in the study of structural transformations of solids with a nontrivial unit cell [38]—a problem which has obvious analogies with the present case.

We now must identify the various phenomenological parameters entering the Landau free energy. The first two terms of Eq. (2.2) produce the conventional elastic free energy Eq. (1.4) of an isotropic gel with Lame constants $\lambda(\psi)$ and $\mu(\psi)$, with both constants of order k_BT/R_F^3. Note however that these are the elastic constants for fixed ψ so they are not the measured elastic constants. They must in general be considerably larger than the measured elastic constants because, as we saw, the "unit cells" of the mesh suffer from concentration inhomogeneities if we fix ψ. The third term is also conventional [6] with L of order k_BT/R_F (it controls the correlation length ξ).

The last two terms give the free-energy cost of fluctuations of ψ at fixed strain. To estimate the restoring modulus B, recall that the spring constant per coil is of order k_BT/R_F^2 and since there is one spring per volume R_F^3, B must be of order k_BT/R_F^3. The constant M measures the degree of coherence of the internal order parameter: if we expand or contract the radius of a given blob we will induce a change in radius in nearby blobs. The equilibrium "healing" length of such a perturbation in blob radii, $\xi_\psi=(M/B)^{1/2}$, must again be the Flory radius so $M\propto L\propto k_BT/R_F$. Finally, the $\epsilon_{ii}\psi$ term couples between the liquid and the solid degrees of freedom and introduces a free-energy penalty for creating local concentration inhomogeneities (Fig. 1). To find the coupling constant C_c between strain and blob radius degrees of freedom, we minimize the free energy with respect to ψ for long wavelengths at fixed finite strain. The result is that $\psi^0(\mathbf{x})\approx-(C_c/B)\epsilon_{ii}$. This must represent the low-energy mode, for which we saw that $\psi^0(\mathbf{x})\approx\epsilon_{ii}$, so we conclude that $(C_c/B)\approx-1$.

The key difference with classical elasticity theory is not only the introduction of the internal order parameter, but also the fact that we will allow the elastic constants to locally depend on the internal order parameter. Expanding to lowest order

$$\lambda(\psi)\approx\lambda_g+\left[\frac{\partial\lambda}{\partial\psi}\right]_g\psi\ , \qquad (2.3a)$$

$$\mu(\psi)\approx\mu_g+\left[\frac{\partial\mu}{\partial\psi}\right]_g\psi \qquad (2.3b)$$

with both $(\partial\lambda/\partial\psi)_g$ and $(\partial\mu/\partial\psi)_g$ negative. As we saw, the c^* theorem demands that for a uniform system the elastic moduli are dependent on the global monomer concentration through a power law. To estimate the parameters $(\partial\lambda/\partial\psi)_g$ and $(\partial\mu/\partial\psi)_g$, recall that $\psi^0(\mathbf{x})\approx\epsilon_{ii}$ for low-energy fluctuations and that $\delta c(\mathbf{r})/c_0$ is of order $-\epsilon_{ii}$. Assuming that the elastic moduli also locally have a power-law dependence on concentration, it follows that $(\partial\lambda/\partial\psi)_g\propto(\partial\mu/\partial\psi)_g\propto k_BT/R_F^3$.

It is important to be somewhat more precise about the relation between our scalar field $\psi(\mathbf{r})$ and the monomer concentration. Although for long-wavelength, low-energy fluctuations $\psi(\mathbf{r})$ is proportional to ϵ_{ii}, and thus to the concentration, it is, unlike the concentration, not a conserved variable. Blobs can increase (or decrease) their radius over a large volume without requiring transport across the boundary of that volume. However, it is shown in the Appendix that for long wavelengths, the monomer concentration $\delta c(\mathbf{r})$ must be related to the internal order parameter and to the strain by

$$\delta c(\mathbf{r})/c_0\approx-\epsilon_{ii}+\Gamma R_F^2\nabla^2\psi+O(\nabla^4\psi) \qquad (2.4)$$

with Γ a numerical constant. The first term is the usual self-affine contribution and the second term is the correction due to the internal order parameter. For a low-energy mode with $\psi^0(\mathbf{x})\approx\epsilon_{ii}$, the self-affine contribution dominates at long wavelengths so Eq. (2.4) obeys the condition of weak self-affinity.

We can once more decompose our new free energy into orthogonal modes by going to longitudinal and transverse Fourier components. Including only harmonic terms we find

$$\Delta F=\sum_{k(\neq0)}\{\tfrac{1}{2}[Lk^2+E_g]k^2|u_l(\mathbf{k})|^2+\tfrac{1}{2}\mu_gk^2|\mathbf{u}_t(\mathbf{k})|^2+\tfrac{1}{2}[Mk^2+B]|\psi(\mathbf{k})|^2+\tfrac{1}{2}ikC_c[\psi(\mathbf{k})^*u_l(\mathbf{k})-\mathrm{c.c.}]\} \qquad (2.5)$$

with $E_g=\lambda_g+2\mu_g$. This parameter E_g is however no longer the longitudinal modulus. To find the true longitudinal modulus, we diagonalize ΔF and use the equipartition theorem with the result

$$\langle|\psi(\mathbf{k})|^2\rangle=k_BT/[B+Mk^2-C_c^2/(E_g+Lk^2)]\approx k_BT/(B'+M'k^2)\ , \qquad (2.6a)$$

$$k^2\langle|u_l(\mathbf{k})|^2\rangle=k_BT/[E_g+Lk^2-C_c^2/(B+Mk^2)]\approx k_BT/(E'+L'k^2)\ , \qquad (2.6b)$$

$$-ik\langle\psi(\mathbf{k})^*u_l(\mathbf{k})\rangle=[C_c/(E_g+Lk^2)]\langle|\psi(\mathbf{k})|^2\rangle\ , \qquad (2.6c)$$

where

$$E'=E_g-C_c^2/B\ , \qquad (2.7a)$$

$$B'=(B/E_g)E'\ , \qquad (2.7b)$$

$$M'=M+L(C_c/E_g)^2\ , \qquad (2.8a)$$

$$L'=L+M(C_c/B)^2 \ . \tag{2.8b}$$

If we use Eq. (2.4) for the concentration fluctuations we find, from Eq. (2.6), for the structure factor $S_0(\mathbf{k})\equiv\langle|c(\mathbf{k})|^2\rangle$ of unstrained gels a conventional Lorentzian line shape:

$$S_0(\mathbf{k})\approx k_B T c_0^2/(E'+L_s k^2) \tag{2.9}$$

with $L_s \approx L'+2\Gamma R_F^2 C_c E'/B$. The compressibility sum rule then informs us that the parameter E' is the true, experimentally accessible longitudinal modulus. The correlation length ξ for concentration fluctuations is now of order $(L_s/E')^{1/2}$. In the following, we will always use primed quantities, e.g., E', to indicate "relaxed" moduli while unrelaxed moduli are indicated with the subscript g (e.g., E_g).

The spinodal boundary $E'=0$, where concentration fluctuations become large, is now located at $E_g=C_c^2/B$. Note that there is a *second* instability: fluctuations in the order parameter ψ diverge when $B'=0$, indicating the approach of a phase transition to a state where $\langle\psi(\mathbf{r})\rangle$ is finite. This second instability is however also at $E_g=C_c^2/B$, so at the spinodal boundary both concentration fluctuations and order-parameter fluctuations become gapless highlighting the importance of including the nonhydrodynamic degree of freedom as we reduce solvent quality. In fact, it would be perfectly consistent to treat $\psi(\mathbf{r})$ as the primary order parameter driving the onset of strong fluctuations near the spinodal boundary, and to treat the strain as the "slaved" variable. Notice finally that Eq. (2.9) is again an illustration of weak self-affinity: in the long-wavelength limit, $S(\mathbf{k}=\mathbf{0}) =c_0^2\langle|\epsilon_{ii}(\mathbf{k}=0)|^2\rangle$ as required by self-affinity, but since L_s differs from L', $S(\mathbf{k})$ is *not* proportional to $\langle|\epsilon_{ii}(\mathbf{k})|^2\rangle$ for finite wave vectors.

For a gel with no applied strain, we recovered the standard gel concentration fluctuation spectrum, except that the longitudinal modulus was renormalized. We would like to emphasize that the reduction of the longitudinal modulus which controls concentration fluctuations at arbitrarily large (but finite) wavelengths, compared to its "bare" value, is a consequence of coupling solid elasticity to "liquid" degrees of freedom and reflects the intermediate nature (in between solid and liquid) of the mesoscopic physics of gels. We now turn to the behavior under applied external strain—in essence the key question of gel elasticity—on which the internal order parameter will have a major effect. Assume the gel is subjected to a volume preserving external extensional strain along the z direction. The strain tensor ϵ_0 is

$$\epsilon_0=\begin{vmatrix} -\epsilon & 0 & 0 \\ 0 & -\epsilon & 0 \\ 0 & 0 & 2\epsilon \end{vmatrix}$$

with ϵ less then 1 (this requires a force per unit area on the end surfaces of the sample equal to $4\mu\epsilon$, and a force per unit area of $-2\mu\epsilon$ on the side surfaces).

Decomposing the free energy into longitudinal and transverse modes and expanding to second order in the mode amplitudes gives

$$\Delta F=\sum_{k(\neq 0)}\left\{\tfrac{1}{2}[Lk^2+E_g]k^2|u_l(\mathbf{k})|^2+\tfrac{1}{2}\mu_g k^2|\mathbf{u}_t(\mathbf{k})|^2+\tfrac{1}{2}[Mk^2+B]|\psi(\mathbf{k})|^2+\tfrac{1}{2}ikC_c[\psi(\mathbf{k})^* u_l(\mathbf{k})-\text{c.c.}]\right.$$
$$\left.+i\epsilon k\left[\frac{\partial\mu}{\partial\psi}\right]_g[\psi(\mathbf{k})^* u_l(\mathbf{k})(3k_z^2/k^2-1)-\text{c.c.}]+3i\epsilon k_z\left[\frac{\partial\mu}{\partial\psi}\right]_g[\psi(\mathbf{k})^*\mathbf{z}\cdot\mathbf{u}_t(\mathbf{k})-\text{c.c.}]\right\} . \tag{2.10}$$

Unlike the strain-free case [Eq. (2.5)], the concentration dependence of the elastic moduli now explicitly enters the second-order fluctuation energy.

If we minimize ΔF with respect to ψ to find the low-energy hybridized mode, we find a more complex relationship:

$$\psi^0(\mathbf{k})=-i[Mk^2+B]^{-1}$$
$$\times\left\{[C_c+2\epsilon\left[\frac{\partial\mu}{\partial\psi}\right]_g(3k_z^2/k^2-1)]ku_l(\mathbf{k})\right.$$
$$\left.+6\epsilon k_z\left[\frac{\partial\mu}{\partial\psi}\right]_g\mathbf{z}\cdot\mathbf{u}_t(\mathbf{k})\right\} . \tag{2.11}$$

For long wavelengths and $\epsilon=0$, Eq. (2.11) reduces to our old relation $\psi^0(\mathbf{x})\approx-(C_c/B)\epsilon_{ii}$, but for finite strain, our internal order parameter is no longer proportional to the trace of the strain tensor. The two anisotropic correction factors are both controlled by the dependence of the elastic moduli on ψ (which played no role for the unstrained case). We can now compute the structure factor by expanding $\psi(\mathbf{k})$ around $\psi^0(\mathbf{k})$ and inserting the result into ΔF. We find

$$S(\mathbf{k})\approx k_B T c_0^2/(E'_{\text{eff}}(\mathbf{k})+L_s k^2) \tag{2.12}$$

with

$$E_{\text{eff}}(\mathbf{k})\approx E'-2\epsilon(C_c/B)\left[\frac{\partial\mu}{\partial\psi}\right]_g[3(k_z/k)^2-1] \ . \tag{2.13}$$

The structure factor in the presence of strain, Eq. (2.12), is no longer a simple Lorentzian because the effective longitudinal modulus of a strained gel, $E_{\text{eff}}(\mathbf{k})$, depends on the direction of the wave vector. As discussed in the Introduction, it is not surprising that the longitudinal modulus of a strained material is direction dependent—it should be expected from any system whose rotational symmetry is broken. What is surprising is that along the strain direction $k_z = k$, the modulus $E_{\text{eff}}(\mathbf{k})$ is *less* then E', since $C_c(\partial\mu/\partial\psi)_g$ is positive, whereas classical theory predicts an increased modulus. The analogy of strained gels with flow induced decomposition discussed in the Introduction is thus meaningful: strain enhances concentration fluctuations.

The new isointensity contours $S(\mathbf{k}) = \text{const}$ are shown in Fig. 2. We indeed find a butterfly shape oriented along the direction of imposed strain. The appearance of butterfly contours is thus the by-product of the existence of a "hidden variable," our internal order parameter. The macroscopic consequences of this effect will become dramatic when E' is less then $\epsilon(\partial\mu/\partial\psi)_g$. In that case, our effective modulus $E_{\text{eff}}(\mathbf{k})$ becomes negative along the strain direction, predicting an anisotropic decomposition of the gel. This requires a strain bias ϵ of order $E'/[k_B T/R_F^3]$. For a gel in *good* solvent, E' is of order $k_B T/R_F^3$ and the required bias would be rather considerable (strains of order 1). The present theory is not really valid for such large strains—even though butterfly effects ought to be expected. However, if we begin to reduce solvent quality to the point that E' becomes significantly smaller than $k_B T/R_F^3$, then the threshold strain can be written as $(R_F/\xi)^3$. This critical strain is now quite small, even though the concentration correlation length ξ exceeds R_F by only a modest amount. The intensity of the butterfly pattern in a strained gel should thus be directly correlated with the reduction of E', i.e., with the degree small-angle scattering is enhanced in the unstrained gel.

Our conclusions must however be qualified. At the purely macroscopic level, our hidden parameter effectively produces *third*-order anharmonic elastic terms in the elastic free energy of the unstrained gel [see Eq. (2.2)] which become *second*-order harmonic terms in strained gels. Consistency requires us to include third-order anharmonic elastic terms from the start, describing the stiffening of polymer chains on extension. As discussed in the Introduction, stiffening of chains is expected to produce results more in agreement with classical theory and in opposition to the butterfly effect. Indeed, if this type of elastic anharmonicity is included, we find for the effective osmotic modulus [31]

$$E_{\text{eff}}(\mathbf{k}) \approx E' - 2\epsilon(C_c/B)\left[\left(\frac{\partial\mu}{\partial\psi}\right)_g - C_c A/E_g\right] \times [3(k_z/k)^2 - 1] \qquad (2.14)$$

with $A > 0$ an anharmonic elastic modulus which is related to chain stiffening. The butterfly effect should only be observable if $(\partial\mu/\partial\psi)_g$ exceeds $C_c A/E_g$.

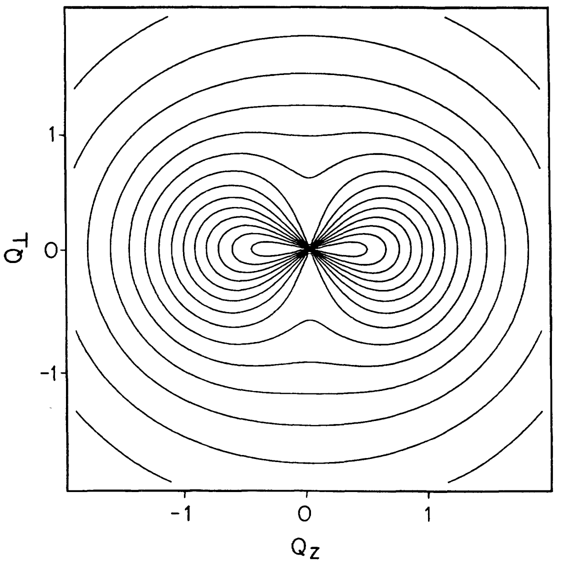

FIG. 2. A contour plot of the structure factor in the $(Q_z, Q_\perp)$ plane where $Q = k\xi$ is the dimensionless wave vector measured in units of inverse correlation length ($Q_\perp^2 = Q_x^2 + Q_y^2$). The coupling constant which determines the asymmetry of the profile, $\delta = 2\epsilon C_c(\partial\mu/\partial\psi)_g/BE'$, is taken as 0.4.

III. DYNAMICS: TWO-FLUID MODEL

A. Semidilute solutions

We discussed in the Introduction that butterfly-type effects are encountered not only in uniaxially strained gels but also in polymer liquids in extensional flow, in particular if the monomer solubility has been reduced. The equilibrium treatment of Sec. II cannot apply to liquids. In this section we will give a purely dynamical interpretation of butterfly patterns, both for gels and for polymer liquids. Such a dynamical interpretation is most straightforward for the second case, so in this subsection we discuss first the dynamics of semidilute solutions in extensional flow.

For incompressible semidilute solutions, the only gapless collective mode is collective diffusion. At higher relaxation rates, we encounter internal relaxation modes of polymer blobs. For good solvents, these blob modes relax rapidly and play no important role in the hydrodynamics. For theta solvents longitudinal transient strain relaxation by chain reptation is so slow however, due to entanglement effects, that the blob mode hybridizes with the collective diffusion mode [39]. This hybridization occurs at unexpectedly large wavelengths and at unexpectedly low frequencies (i.e., at wavelengths much larger than the blob radius and at relaxation rates much slower than the reptation rate) and it strongly affects the mode spectrum in the optical range (and for shorter wavelengths).

If we recall, from the discussion of Sec. II, that we expect butterfly effects when the monomer solubility has been reduced, then we should expect theta solvents in extensional flow to be more likely to exhibit significant butterfly effects than semidilute solutions in good solvent. Following this argument, hybridization should be expected to play an important role in a dynamical interpretation of the butterfly effect. We will adopt the description of mode hybridization in semidilute solutions given by Brochard and de Gennes (BG) [39] which agrees with inelastic light-scattering data [40].

The key idea of the BG theory is that polymer blobs in a semidilute solution act independently on the solvent, with a Stokes friction coefficient $\zeta = 6\pi\eta_s\xi$ (η_s is the solvent viscosity and ξ is the blob size). If $\mathbf{v}(\mathbf{x},t)$ is the velocity field of the blobs and if $\mathbf{u}(\mathbf{x},t)$ is the solvent velocity field, then since $1/\xi^3$ is the blob density, the frictional force density on the blobs is $\zeta(\mathbf{v}-\mathbf{u})/\xi^3$. This counterflow force density must be balanced by some external force density $\mathbf{f}$ on the blobs:

$$\eta_s(\mathbf{v}-\mathbf{u})=\Lambda\mathbf{f} \ . \tag{3.1}$$

Here, $\Lambda\propto\xi^2$ is the "permeability," interpreting Eq. (3.1) as Darcy's law for permeable media. The force density in a semidilute solution is a combination of a purely osmotic pressure Π and a transient elastic stress term (describing unrelaxed entanglements)

$$\mathbf{f}=\nabla\cdot\boldsymbol{\sigma}-\nabla\Pi \tag{3.2}$$

with $\boldsymbol{\sigma}$ the transient stress tensor. The osmotic pressure due to a concentration fluctuation δc is $\delta\Pi=E'\delta c/c_0$ (with $E'\approx k_BT/\xi^3$ the equilibrium osmotic modulus—recall that osmotic and longitudinal moduli are identical for solutions). If we set the transient stress $\boldsymbol{\sigma}$ and the solvent velocity $\mathbf{u}$ equal to zero in Eqs. (3.1) and (3.2), we find a diffusion equation with the well-known collective diffusion constant of semidilute solutions, $D_c=(\Lambda/\eta_s)E'$, which is proportional to the osmotic modulus.

For the residual stress of a polymer solution, BG assume a simple Maxwell model:

$$\frac{\partial\sigma}{\partial t}+\frac{\sigma}{\tau}=\frac{\partial}{\partial t}\left[\frac{\delta F_g}{\delta\epsilon}\right] . \tag{3.3}$$

Here, τ is the entanglement stress-relaxation time (by reptation) while F_g and ϵ are, respectively, the elastic free energy and the strain of that "gel" we would obtain if we had forbidden reptation ("plateau" moduli):

$$F_g=\int d^3r\tfrac{1}{2}\{\lambda_g\epsilon_{ii}^2+2\mu_g\epsilon_{ij}^2\} \ . \tag{3.4}$$

The "gel" elastic moduli are of order k_BT/ξ_e^3 with ξ_e the typical distance between entanglement sites. For theta solvents, these unrelaxed moduli are large compared to the equilibrium osmotic modulus E' ($\lambda_g/E'\approx\xi/a$). For short time scales, the stress σ in Eq. (3.3) is close to the stress $\delta F_g/\delta\epsilon$ of the unrelaxed gel with its relatively large moduli. For long time scales, the solution of Eq. (3.3) assumes the form of a purely viscous stress of a liquid with a viscosity $\eta_{\text{eff}}\propto\tau k_BT/\xi_e^3$ (which is large compared to the solvent viscosity η_s). Note that Eq. (3.3) assumes that the relaxation rate is the same for shear and for longitudinal strain. During the stress-relaxation process, mass conservation demands that the trace of the strain tensor produces a concentration fluctuation:

$$\frac{\partial\epsilon_{ii}}{\partial t}=\nabla\cdot\mathbf{v} \tag{3.5a}$$

and

$$\frac{\partial\epsilon_{ii}}{\partial t}=\frac{-\partial(\delta c/c_0)}{\partial t} \ . \tag{3.5b}$$

The solvent itself must obey the Navier-Stokes equation:

$$\rho_0\frac{\partial\mathbf{u}}{\partial t}=\eta_s\nabla^2\mathbf{u}+\nabla\cdot\boldsymbol{\sigma}-\nabla P \tag{3.6}$$

with ρ_0 the mean solvent density and P the pressure inside the solvent. This pressure can be eliminated if the system of monomers plus solvent together is assumed to be incompressible. Mass conservation then imposes the continuity equation

$$\nabla\cdot\mathbf{u}=(\Omega_mc_0/\Omega_s\rho_0)\frac{\partial c}{\partial t} \tag{3.7}$$

with Ω_s and Ω_m the solvent and monomer atomic volumes. For a dilute gel with $c_0\ll\rho_0$, $\nabla\cdot\mathbf{u}\approx0$ so the solvent flow fluctuations are predominantly transverse. Assuming this, Eq. (3.6) gives $\nabla\nabla:\boldsymbol{\sigma}=\nabla^2P$.

Restricting ourselves to longitudinal modes for which we thus can neglect the solvent flow, the mode spectrum of a concentration wave $e^{i\mathbf{k}\cdot\mathbf{r}-\omega(k)t}$ can be found using Eqs. (3.1)–(3.5) with the result

$$[\omega(k)-(\Lambda/\eta_s)(E'+E_g)k^2][\omega(k)-\tau^{-1}] \\ -k^2E_g\tau^{-1}(\Lambda/\eta_s)=0 \ , \tag{3.8}$$

where $E_g=\lambda_g+2\mu_g$ is the unrelaxed longitudinal "gel" modulus. There are two solution branches to Eq. (3.8):

$$\omega^-(k)\approx D_ck^2/[1+\tau(\Lambda/\eta_s)E_gk^2] \ , \tag{3.9a}$$

$$\omega^+(k)\approx\tau^{-1}+(\Lambda/\eta_s)E_gk^2 \ . \tag{3.9b}$$

The $\omega^-(k)$ branch represents, for small wave vectors, the collective diffusion spectrum. As the wave vector increases, collective diffusion hybridizes with stress relaxation when k is of order $[\tau(\Lambda/\eta_s)E_g]^{-1/2}$ and for larger k this branch saturates at $\tau^{-1}E'/E_g$. For theta solvents, with E' small compared to E_g, $\tau^{-1}E'/E_g$ is small compared to the stress relaxation rate τ^{-1}. The crossover length scale $[\tau(\Lambda/\eta_s)E_g]^{1/2}$—called the "gel length"—is much larger than the Flory radius (it is in the optical range). The upper branch represents (for small wave vectors) pure stress relaxation while for large k it crosses over to the "bare" longitudinal mode spectrum of a gel.

How will this BG formalism be affected if we impose a background flow? In analogy to the extensional strain imposed in Sec. II, we now impose an extensional flow field on the monomers:

$$\mathbf{v}_0=\gamma(-x,-y,2z) \tag{3.10}$$

with γ the elongational strain rate. The Deborah number $\text{De}=\gamma\tau$ is normally assumed to be the critical index for significant flow deformation of the internal structure. When De exceeds 1, non-Newtonian flow behavior is observed, while for De small compared to 1, the polymer liquid should obey the Navier-Stokes law. We will always assume the Deborah number to be small compared to 1.

We will assume that the material parameters are all concentration dependent:

$$\lambda(c)\approx\lambda_g+\left[\frac{\partial\lambda}{\partial c}\right]_g\delta c \ , \tag{3.11a}$$

$$\mu(c)\approx\mu_g+\left[\frac{\partial\mu}{\partial c}\right]_g\delta c\ , \tag{3.11b}$$

$$\tau(c)\approx\tau+\left[\frac{\partial\tau}{\partial c}\right]_g\delta c\ , \tag{3.11c}$$

$$\Lambda(c)\approx\Lambda+\left[\frac{\partial\Lambda}{\partial c}\right]_g\delta c\ , \tag{3.11d}$$

where δc is again a concentration fluctuation. Both $(\partial\lambda/\partial c)_g$ and $(\partial\mu/\partial c)_g$ are to be assumed positive since an increased monomer concentration of gels means increased moduli, as discussed in the Introduction. Note that we included also the concentration dependence of dynamical parameters like the relaxation time (and thus of the effective viscosity $\eta_{\text{eff}}\propto\tau k_BT/\xi_e^3$). Since increased monomer concentration must mean increased viscosity, we also will assume $(\partial\tau/\partial c)_g$ to be positive.

In the presence of flow, we first must everywhere replace the $\partial/\partial t$ operator by $d/dt=\partial/\partial t+\mathbf{v}\cdot\nabla$. Taking the divergence of Eq. (3.1) and combining Eqs. (3.1), (3.2), and (3.5) then gives, to lowest order in δc, an *advection-diffusion* equation:

$$\frac{\partial\delta c}{\partial t}+\mathbf{v}_0\cdot\nabla\delta c=D_c\nabla^2\delta c-(\Lambda c_0/\eta_s)\partial_i\partial_j\sigma_{ij}\ . \tag{3.12}$$

We will start by initially ignoring all advection terms. For relaxation rates small compared to τ^{-1}, the solution of Eq. (3.3) is then the purely viscous stress:

$$\sigma\approx2\mu(c)\tau(c)\mathbf{A}+\lambda(c)\tau(c)\mathbf{1}(\nabla\cdot\mathbf{v}) \tag{3.13}$$

with $\mathbf{v}$ the flow velocity field, $\mathbf{1}$ the unit tensor, and $A_{ij}=\frac{1}{2}(\partial v_i/\partial x_j+\partial v_j/\partial x_i)$ the strain-rate tensor. The effective viscosities in Eq. (3.13) are of order η_{eff}, but of course concentration dependent. Assume now that the flow velocity is the sum of the background flow $\mathbf{v}_0$ plus an infinitesimal part $\mathbf{v}'$ due to concentration fluctuations. Inserting this in Eq. (3.13) and expanding to lowest order in concentration gives

$$\sigma\approx2\mu_g\tau\mathbf{A}_0+2\mu_g\tau\mathbf{A}'+\lambda_g\tau\mathbf{1}(\nabla\cdot\mathbf{v}')$$
$$+2\left[\mu_g\left[\frac{\partial\tau}{\partial c}\right]_g+\left[\frac{\partial\mu}{\partial c}\right]_g\tau\right]\mathbf{A}_0\delta c \tag{3.14}$$

with the strain-rate tensor decomposed in the same way as the flow velocity so

$$\mathbf{A}_0=\begin{bmatrix}-\gamma&0&0\\0&-\gamma&0\\0&0&2\gamma\end{bmatrix}.$$

Inserting Eq. (3.14) into Eq. (3.12), using Eq. (3.5), and again neglecting advection, gives to lowest order in δc

$$\frac{\partial\delta c}{\partial t}=D_c\nabla^2\delta c+2\,\text{De}(\Lambda c_0/\eta_s)\left[\mu_g\left[\frac{\partial\ln\tau}{\partial c}\right]+\left[\frac{\partial\mu}{\partial c}\right]_g\right]$$
$$\times\left[\frac{\partial^2\delta c}{\partial x^2}+\frac{\partial^2\delta c}{\partial y^2}-2\frac{\partial^2\delta c}{\partial z^2}\right]. \tag{3.15}$$

The new term entering in the diffusion equation is entirely due to the concentration dependence of the effective viscocity and, by construction, unrelated to any advection effects. The mode dispersion $\omega^-(\mathbf{k})=(\Lambda/\eta_s)E_{\text{eff}}(\mathbf{k})k^2$ of this anisotropic diffusion equation has an angle-dependent diffusion constant $D_c(\mathbf{k})=(\Lambda/\eta_s)E_{\text{eff}}(\mathbf{k})k^2$ with an effective "modulus"

$$E_{\text{eff}}(\mathbf{k})=E'-2\,\text{De}c_0\left[\mu_g\tau^{-1}\left[\frac{\partial\tau}{\partial c}\right]_g+\left[\frac{\partial\mu}{\partial c}\right]_g\right]$$
$$\times[3(k_z/k)^2-1]\ . \tag{3.16}$$

The similarity of this result with Eq. (2.13), the effective longitudinal modulus of a gel, is immediately apparent. The Deborah number in Eq. (3.16) plays a role analogous to that of the strain in Eq. (2.13). Recalling that the material parameters generally have a power-law dependence on concentration, it follows from Eq. (3.16) that the Deborah number required to see strong flow effects on the mode spectrum is of order E'/μ_g. For theta solvents, this number is of order $N^{-1/2}$ so *strong flow effects on the fluctuation spectrum are expected long before we reach the non-Newtonian regime* De>1. The anisotropic collective diffusion spectrum again will hybridize with strain relaxation for wave vectors in excess of $[\tau(\Lambda/\eta_s)E_g]^{-1/2}$.

To find the experimental signature of flow deformation of fluctuations, recall [39] that the dynamic structure factor $S(\mathbf{k},\omega)$ of a semidilute solution is the sum of two Lorentzians associated with the two branches of the mode spectrum:

$$S(\mathbf{k},\omega)=\{(c_0^2k_BT\Lambda/\eta_s)k^2/[\pi\omega^+(\mathbf{k})]\}\{\omega^+(\mathbf{k})/[\omega^2+\omega^+(\mathbf{k})^2]+\tau^{-1}/[\omega^2+\omega^-(\mathbf{k})^2]\}\ . \tag{3.17}$$

The second term, associated with the hybridized collective diffusion branch $\omega^-(k)$, dominates. Using Eq. (3.17) and performing an integration over all frequencies produces the static structure factor:

$$S(\mathbf{k})\approx k_BTc_0^2/\{E_{\text{eff}}(\mathbf{k})[1+J(k\xi)^2]\}\ \text{(no advection)}\ .$$

The $J(k\xi)^2$ term was added "by hand" to allow for the usual exponential decay of correlations (J is of order 1). This static structure factor of a polymer liquid in extensional flow is mathematically of exactly the same form as the equilibrium structure factor of the strained gel [Eq. (2.12)]. The equiintensity contours thus must produce butterfly patterns. The butterfly effect becomes dramatic when De$\approx E'/\mu_g$ so, as expected, for semidilute solutions it should be most prominent for the case of theta solvents. As mentioned, butterfly effects indeed are observed in extensional flow of semidilute solutions [29] where they were assumed to be due to heterogeneities. We propose that flow deformation of thermally produced concentration fluctuations may be a more natural explanation.

Our analysis consistently neglected advection terms. It has been the experience of other problems involving advection of fluctuations [41] that for Deborah numbers small compared to 1, the Maxwell construction Eq. (1.11) accurately predicts the effects of advection on the structure factor. Applying the Maxwell construction on the result we just obtained gives, to first order in the Deborah number:

$$S(\mathbf{k})\approx k_B T c_0^2 \Big/ \left[E'[1+J(k\xi)^2]-2\,\mathrm{De}\left\{ c_0 \left[\mu_g \tau^{-1} \left(\frac{\partial\tau}{\partial c} \right)_g + \left(\frac{\partial\mu}{\partial c} \right)_g \right] - JE'(k\xi)^2 \right\} [3(k_z/k)^2-1] \right] . \tag{3.18}$$

The condition that the Maxwell effect does not suppress our butterfly pattern is that the coefficient in curly brackets is positive. Just as for gels, we have found two competing effects but for wave vectors comparable to, or less then, the correlation length, and for theta solvents the butterfly effect is always guaranteed to "win" since $c_0(\partial \ln\tau/\partial c)_g$ is of order 1 while μ_g/E' is large compared to 1. We thus may conclude that the Maxwell effect is not important for low Deborah numbers and that the butterfly effect should be a generic feature of semidilute solutions in theta solvents in extensional flow.

B. Stretched gels

We will now apply the dynamical formalism developed for liquids to the case of stretched gels. We can use some of the earlier results if we keep in mind (i) that there are two length scales (the Flory radius and the correlation length) and (ii) that we must account for the transverse mode spectrum. Starting with Darcy's law [Eq. (3.1)] and the Navier-Stokes equation for the solvent [Eq. (3.6)], they remain valid provided we replace ξ by R_F in the Stokes friction coefficient and in the permeability. We can however no longer use the Maxwell model for the stress tensor since (shear) elastic stress no longer can relax. We will use instead the stress tensor $\sigma=\partial F/\partial\epsilon$ with F the free energy used in our discussion of the equilibrium properties [Eq. (2.2)]:

$$\sigma=\lambda(\psi)\epsilon_{ii}\mathbf{1}+2\mu(\psi)\epsilon+C_c\psi\mathbf{1} . \tag{3.19a}$$

The force density $\mathbf{f}=\nabla\cdot\sigma$ is then

$$\mathbf{f}=(\lambda_g+\mu_g)\nabla\nabla\cdot\mathbf{r}+\mu_g\nabla^2\mathbf{r}+C_c\nabla\psi+2\left(\frac{\partial u}{\partial\psi} \right)_g \epsilon_0\cdot\nabla\psi \tag{3.19b}$$

with the bias shear strain ϵ_0 used in Sec. II. Recall that both purely elastic and purely osmotic (i.e., "liquid") effects are lumped together in the fluctuation free energy Eq. (2.2) so we should *not* add a separate osmotic pressure as in Eq. (3.2).

We still need a dynamical equation for the internal order parameter. For a single blob in good solvent, the amplitude r of the Zimm mode obeys (in the Kirkwood approximation [42])

$$\zeta\frac{\partial r}{\partial t}=-Kr \tag{3.20}$$

with $K\propto k_B T/R_F^2$ and $\zeta=6\pi\eta_s R_F$ the blob friction constant. The relaxation time $\tau=\xi/K$ is of order 10^{-5} sec in good solvents. The natural continuum generalization of the Zimm model for a collection of blobs attached to the "basis" of a random network is clearly

$$\frac{\partial\psi}{\partial t}=-(R_F/\zeta)\frac{\delta F}{\delta\psi} \tag{3.21}$$

with F the free energy and assuming we have one blob per volume R_F^3. Using Eq. (2.2) for F in Eq. (3.21) gives a conventional time-dependent Ginzburg-Landau equation for a nonconserved order parameter, except that now there are coupling terms connecting ψ to the strain tensor:

$$\zeta\frac{\partial\psi}{\partial t}=-R_F\left[B\psi-M\nabla^2\psi+C_c\epsilon_{ii}+\left(\frac{\partial\lambda}{\partial\psi} \right)_g \epsilon_{ii}^2 + 2\left(\frac{\partial\mu}{\partial\psi} \right)_g \epsilon_{ij}^2 \right] . \tag{3.22}$$

The terms in Eq. (3.22) which are of second order in the strain can at this point be neglected but they must be included when we later discuss the effect of bias strains.

1. Mode dispersion (zero bias)

To simplify the discussion of the gel mode spectrum, we first investigate the dynamics in the absence of an applied strain, in which case our results must be consistent with known results on the longitudinal and transverse mode spectra of gels. For the longitudinal modes, the solvent velocity $\mathbf{u}$ is still negligible. Combining Eqs. (3.1) and (3.19) gives, with $\delta c/c_0=-\nabla\cdot\mathbf{r}$,

$$\eta_s\frac{\partial\delta c}{\partial t}=\Lambda\nabla^2(E_g\delta c-c_0C_c\psi) , \tag{3.23a}$$

$$\zeta\frac{\partial\psi}{\partial t}=-R_F\{B\psi-C_c\delta c/c_0\} , \tag{3.23b}$$

where we neglected terms which were small for wave vectors small compared to the Flory length. Looking again for modes proportional to $e^{i\mathbf{k}\cdot\mathbf{r}-\omega(k)t}$, the mode spectrum is found to obey

$$[\omega_L(k)-(\Lambda/\eta_s)E_gk^2][\omega_L(k)-\tau^{-1}] - k^2(C_c^2/B)\tau^{-1}(\Lambda/\eta_s)=0 \tag{3.24}$$

with $\tau^{-1}=R_FB/\zeta$. Mathematically, this mode dispersion has the same "hybridized" form as that of a semidilute solution [Eq. (3.8)]. To make the mapping formally, first define $E'=E_g-C_c^2/B$ and $E_g'=C_c^2/B$ and then use these quantities to eliminate E_g and B, after which we recover Eq. (3.8). The new effective osmotic modulus E' is of course just our familiar gel longitudinal modulus encountered in the discussion of the statics (Sec. II). In the interesting regime where $E'/E_g \ll 1$, $E_g' \approx E_g$.

The discussion of the longitudinal mode dispersion of a gel is from here on completely analogous to that of a semidilute solution. There are again two branches:

$$\omega^-(k) \approx (\Lambda/\eta_s)E'k^2/[1+\tau(\Lambda/\eta_s)E_gk^2] , \tag{3.25a}$$

$$\omega^+(k) \approx [\tau^{-1}+(\Lambda/\eta_s)E_gk^2] . \tag{3.25b}$$

The lower branch shown is, for small k, the well-known collective diffusion spectrum of a gel with a diffusion constant $D_c=(\Lambda/\eta_s)E'$. It was found experimentally by Tanaka, Hocker, and Benedek [20]. For larger wave vectors Eq. (3.25) predicts some new results: collective diffusion should first hybridize with order-parameter relaxation and then saturate to a dispersionless relaxation spectrum with a relaxation rate $\tau^{-1}E'/E_g$. Also, there should be a "forbidden" gap in the relaxation spectrum for rates in the range $\tau^{-1}E'/E$ to τ^{-1} followed by order-parameter relaxation for higher relaxation rates.

Should the new effects be observable? The crossover takes place around $k_{\rm co} \approx [\eta_s/(\Lambda\tau E_g)]^{1/2}$, just as for semidilute solutions. For pure Zimm relaxation $k_{\rm co} \approx R_F^{-1}$ so for gels in good solvents with highly swollen coils, hybridization should *not* play an important role and the new effects are not important. If, however, we reduce solvent quality, then the relaxation time is expected to be increased, in analogy with the case of theta solvents discussed earlier. The crossover wave vector $k_{\rm co}$ could become much smaller and hybridization may become important in light-scattering experiments on gels made of high molecular weight chains between cross links. Possible origins of anomalously long stress-relaxation time in gels which may lead to observable hybridization effects could be the presence of dangling chains and topological entanglements between different network chains [43]. Both effects depend strongly on the conditions under which the network was formed. Theoretical estimates of the stress-relaxation time are quite difficult, although information about it can be obtained from mechanical relaxation studies.

Turning to the transverse modes, we now must allow for transverse solvent flow so we must include the full Navier-Stokes equation. The coupled equations for transverse solvent and monomer velocities ($\mathbf{u}_T$ and $\mathbf{v}_T$, respectively) are

$$\rho_0\frac{\partial \mathbf{u}_T}{\partial t}=\eta_s\nabla^2\mathbf{u}_T+(\eta_s/\Lambda)(\mathbf{v}_T-\mathbf{u}_T) , \tag{3.26a}$$

$$(\eta_s/\Lambda)(\mathbf{v}_T-\mathbf{u}_T)=\mu_g\nabla^2\mathbf{r}_T \tag{3.26b}$$

with $\nabla\cdot\mathbf{u}_T=\nabla\cdot\mathbf{v}_T=0$ and with $\partial\mathbf{r}_T/\partial t=\mathbf{v}_T$. Note that the internal order parameter does not enter. These two coupled equations for $\mathbf{v}_T$ and $\mathbf{u}_T$ are identical to those of the de Gennes–Pincus theory of transverse modes in semidilute polymer solutions [44] (applied to gels). The mode spectrum for the two propagating (degenerate) transverse modes is

$$k \approx i[\omega(k)/c_t][1+\omega(k)(\eta_s/\mu_g)]^{-1/2} \tag{3.27}$$

with $c_t=(\mu_g/\rho_0)^{1/2}$ the transverse velocity of sound (assuming $k \ll R_F^{-1}$ and $\mu_g \ll \eta_s^2/\Lambda\rho_0$). Note that $\omega(k)$ has both an imaginary part (corresponding to transverse sound propagation) and a real part (corresponding to transverse sound damping). We thus conclude that for the case of good solvents, the dynamic mode spectrum of our theory reduces to well-known results while for gels with reduced solubility it predicts the type of mode hybridization encountered in theta solvents.

2. Mode dispersion (with strain bias)

Having ascertained that in the absence of strain our theory is in good agreement with the known mode dispersion of gels, we now turn on the strain. Assuming, as before, an extensional strain, $\epsilon_{xx}=\epsilon_{yy}=-\epsilon$ and $\epsilon_{zz}=2\epsilon$, the equations of motion become more complex because the transverse and longitudinal modes are now coupled. The time-dependent amplitudes of the longitudinal and transverse modes of wave vector $\mathbf{k}$ obey

$$\begin{aligned}
&\rho_0\frac{\partial \mathbf{u}_{T1,2}}{\partial t}=-k^2\eta_s\mathbf{u}_{T1,2}+(\eta_s/\Lambda)(\mathbf{v}_{T1,2}-\mathbf{u}_{T1,2}) ,\\
&(\eta_s/\Lambda)(\mathbf{v}_{T1}-\mathbf{u}_{T1})=-k^2\mu_g\mathbf{r}_{T1} ,\\
&(\eta_s/\Lambda)(\mathbf{v}_{T2}-\mathbf{u}_{T2})\\
&\qquad=-k^2\mu_g\mathbf{r}_{T2}+6i\epsilon\left[\frac{\partial\mu}{\partial\psi}\right]_g[k_z(k_x^2+k_y^2)^{1/2}/k]\psi\mathbf{e}_2 ,\\
&\eta_s\frac{\partial r_L}{\partial t}=\Lambda\left\{-E_gk^2r_L\right.\\
&\qquad\left.+i\left[C_c+2\epsilon\left[\frac{\partial\mu}{\partial\psi}\right]_g(3k_z^2/k^2-1)\right]k\psi\right\} ,\\
&\zeta\frac{\partial\psi}{\partial t}=-R_F\left[B\psi+i\left\{\left[C_c+2\epsilon\left[\frac{\partial\mu}{\partial\psi}\right]_g(3k_z^2/k^2-1)\right]kr_L\right.\right.\\
&\qquad\left.\left.-6\epsilon\left[\frac{\partial\mu}{\partial\psi}\right]_g k_z\mathbf{z}\cdot\mathbf{r}_{T2}\right\}\right] .
\end{aligned} \tag{3.28}$$

We decomposed the polarization of the transverse modes along two unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ in the plane perpendicular to $\mathbf{k}$, with $\mathbf{e}_1$ perpendicular to $\mathbf{z}$ and with $\mathbf{e}_2$ perpendicular to $\mathbf{e}_1$ (and $\mathbf{k}$):

$$\begin{aligned}
&\mathbf{e}_1=(-k_y,k_x,0)/(k_x^2+k_y^2)^{1/2} ,\\
&\mathbf{e}_2=(\mathbf{k}/k)\times\mathbf{e}_1 .
\end{aligned} \tag{3.29}$$

The amplitude r_{T1} of the $\mathbf{e}_1$ polarization is not affected by the bias strain so we recover the de Gennes–Pincus result [44] for the T_1 spectrum. The mode dispersion for the remaining modes is, to second order in the strain bias,

$$\rho_0[\omega-\omega^T(k)][\omega-\omega^{*T}(k)][\omega-\omega^-(\mathbf{k})][\omega-\omega^+(\mathbf{k})]$$
$$=36(R_F/\zeta)\epsilon^2\left[\frac{\partial\mu}{\partial\psi}\right]_g^2(k_z/k)^2$$
$$\times(k_x^2+k_y^2)[\omega-(\Lambda/\eta_s)E_gk^2]\ . \qquad (3.30)$$

Here, $\omega^T(k)$ is the (complex) de Gennes–Pincus spectrum while $\omega^{-,+}(\mathbf{k})$ is the hybridized collective-diffusion–internal-relaxation spectrum Eq. (3.25) except that (to first order in ϵ) we must replace E' by the anisotropic angle-dependent longitudinal modulus

$$E'(\mathbf{k})=E'-(2C_c/B)\epsilon\left[\frac{\partial\mu}{\partial\psi}\right]_g(3k_z^2/k^2-1)\ . \qquad (3.31)$$

Note the similarity with angle-dependent osmotic modulus encountered for semidilute solutions [Eq. (3.16)]. Note also that for $\epsilon=0$, we recover the usual mode spectrum.

It follows from Eq. (3.30) that there is *no* stress-induced hybridization between the transverse and the internal modes. The reason is that the transverse modes are propagating so they can never be degenerate with the purely overdamped ψ mode. As a result, we can use simple perturbation theory to include the mode mixing. The collective-diffusion mode branch of Eq. (3.30) is given by

$$\omega(\mathbf{k})\approx(\Lambda/\eta_s)\left[E'(\mathbf{k})-(4/B)\epsilon^2\left[\frac{\partial\mu}{\partial\psi}\right]_g^2\{[3\cos^2(\theta)-1]^2-9(E_g/\mu_g)\cos^2(\theta)\sin^2(\theta)\}\right]k^2/[1+\tau(\Lambda/\eta_s)E_gk^2] \qquad (3.32)$$

with θ the angle between the wave vector and the strain direction. In complete analogy with the case of semidilute solutions we encounter, to lowest order in the strain, an effective diffusion constant $D_{\text{coll}}(\mathbf{k})\approx(\Lambda/\eta_s)E'(\mathbf{k})$ which is controlled by the anisotropic longitudinal modulus. The collective diffusion constant has decreased along the strain direction and increased in the perpendicular direction. The collective mode spectrum saturates—because of hybridization—at larger wave vectors. The crossover wave vector has not been affected by the applied strain.

The second-order term in Eq. (3.32) is due to strain-induced mixing between collective diffusion and the transverse modes. If the second-order term becomes comparable to the first-order term, then the butterfly pattern is severely deformed which, in general, happens when the strain ϵ becomes of order one.

The dispersion law Eq. (3.32) is our key result in this section. Experimentally, it can be directly checked through dynamical light scattering. The dynamic structure factor $S(\mathbf{k},\omega)$ can be found by inserting Eq. (3.32) in Eq. (3.17). The collective-diffusion constant measured this way should exhibit an "inverse" butterfly pattern with $D_{\text{coll}}(\mathbf{k})\approx(\Lambda/\eta_s)E'(\mathbf{k})$, i.e., it should be inversely proportional (for small wave vectors) to the equilibrium static structure factor $S(\mathbf{k})$ [Eq. (2.12)]. On the other hand, the quenched-fluctuation theory of the stress-induced butterfly pattern predicts only anomalies at zero frequency and should show no such anomaly in the diffusion constant. Although dynamic light scattering on swollen, stretched gels has already been done [45], we are unaware of direct light-scattering measurements of the static structure factor under these conditions. A combination of both static and dynamic measurements on uncharged deformed gels is needed to provide a comprehensive test of our theory (a separate treatment is required for polyelectrolyte gels in which the counterion osmotic pressure plays an important role [46]).

An alternative experimental test of the theory is provided by a measurement of the time evolution of the static structure factor following the imposition of a strain at $t=0$. Assume that at $t=0$ we have a concentration fluctuation spectrum $S_0(\mathbf{k})$ given by Eq. (1.1). Apply instantaneously an extensional strain ϵ. This will advect the concentration fluctuations and produce a structure factor:

$$S(\mathbf{k},t=0+)=S_0[(1+\epsilon)\mathbf{k}]\ . \qquad (3.33)$$

This structure factor necessarily exhibits isointensity contours consistent with the "strong self-affinity" assumption discussed in the Introduction [Eqs. (1.8)–(1.10)]. Immediately afterwards, relaxation processes will start to deform these contours. The "high-frequency" $\omega^+(k)$ part of the branch is isotropic and will not change the geometrical shape of the contours significantly. The "low-frequency" branch $\omega^-(\mathbf{k})$, which is strongly anisotropic, will take longer to develop. To find its time evolution, note that the amplitude $c(\mathbf{k},t)$ of a concentration wave with wave vector $\mathbf{k}$ must, in a harmonic theory, obey a Langevin equation of motion:

$$\frac{\partial c(\mathbf{k},t)}{\partial t}=-\omega^-(\mathbf{k})c(\mathbf{k},t)+\eta(\mathbf{k},t)\ , \qquad (3.34)$$

where the Gaussian noise source $\eta(\mathbf{k},t)$ has a noise spectrum consistent with the fluctuation dissipation theorem. To solve Eq. (3.34), we must specify the initial conditions. The initial value $c(\mathbf{k},t=0)$ is taken to be a Gaussian random variable with a spectrum $\langle|c(\mathbf{k},t=0)|^2\rangle=S(\mathbf{k},t=0+)$. The resulting time evolution of the static structure factor is

$$S(\mathbf{k},t)=S(\mathbf{k},t=0+)e^{-2\omega^-(\mathbf{k})t}+S(\mathbf{k})(1-e^{-2\omega^-(\mathbf{k})t}) \qquad (3.35)$$

with $S(\mathbf{k})$ the static structure factor given by Eq. (2.12). Notice that $S(\mathbf{k},t)$ is the one-time ($\langle|c(\mathbf{k},t)|^2\rangle$) density-density correlation function (and not the dynamic structure factor which is a two-time $\langle|c(\mathbf{k},0)c^*(\mathbf{k},t)|\rangle$ correlation function).

The resulting time evolution of the intensity contours is shown in Fig. 3. The self-affine pattern seems to

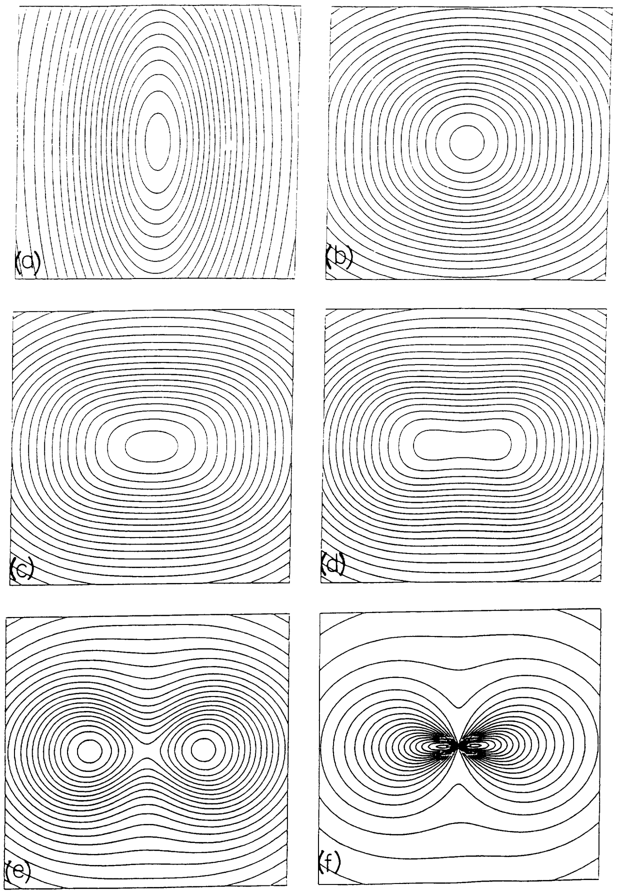

FIG. 3. Contour plots of the structure factor in the $(Q_z, Q_\perp)$ plane (z is the horizontal axis), taken at different times. Time is measured in units of the relaxation time τ of the scalar order parameter ψ: (a) $t=0$, (b) $t=2$, (c) $t=3$, (d) $t=4$, (e) $t=10$, and (f) $t=10^5$. The applied strain $\epsilon=0.3$ and the coupling constant is $\delta=0.3$.

smoothly transform to the butterfly pattern. This progression qualitatively reproduces the experimental observations of [12]. There is however a surprise during the later stages: for late times, Eq. (3.35) predicts *maxima* in the scattering intensity along the stretching direction (see Fig. 3). With time, these maxima move in towards the origin $\mathbf{k}=0$ after which the equilibrium butterfly pattern $S(\mathbf{k})$ is obtained. Such maxima have indeed been reported in one case. The appearance of the maxima is due to "interference" between the butterfly anisotropy of $S(\mathbf{k})$ and the anisotropy of $\omega^{-}(\mathbf{k})$ so it should be a good diagnostic of the applicability of our dynamic description. The maxima suggest that during the evolution of a gel, after stress is applied, it passes through a stage where there is a modulation in the concentration with a wavevector along the strain direction. Indeed, it can be shown that our theory predicts that the decomposed phase has a concentration modulation of this type with a wave vector of order the system size.

IV. CONCLUSIONS

We presented a theory of the combined effects of strain and concentration fluctuations in gels swollen in excess solvent. According to our view, the behavior of gels on mesoscopic scales cannot be understood in terms of a purely "solid" or a purely "liquid" picture and, therefore, we constructed a model which incorporates both aspects of gel behavior by combining the macroscopic theory of elasticity of solids with a microscopic order parameter which describes the fluctuations of the size and the local stress of individual polymer chains in the network. The introduction of microscopic "liquidlike" degrees of freedom leads to the breakdown of the geometrical relation between concentration and strain (the strong-affinity assumption), on length scales comparable to the size of network chains. Although this relation is recovered in the macroscopic limit, the presence of microscopic degrees of freedom affects the long-wavelength density fluctuations in the gel. In particular, when the symmetry is broken by externally applied strain, the coupling between microscopic and hydrodynamic degrees of freedom produces butterfly patterns akin to those observed in SANS experiments. We analyzed the dynamics of concentration fluctuations and showed that following the externally applied deformation, the structure factor evolves with time from the initial affine profile to the final butterflylike one, in qualitative agreement with experimental observations. Other predictions of our theory such as the explicit predictions for the mode dispersion are yet to be tested. The close connection between the dynamics of deformed gels and that of semidilute polymer solutions subjected to elongational flow was also demonstrated. The agreement between our static and dynamic results and experimental observations appears to support our assertion that the observed butterfly patterns originate in thermal fluctuations rather than in quenched inhomogeneities in the gel, at least in the range of length scales probed by SANS. Still, the more general issue of the relative importance of quenched vs annealed concentration inhomogeneities in the physics of gels remains open and comprehensive experimental studies of static and dynamic scattering from gels which probe all length scales in the $10-10^4$-Å range are clearly needed.

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APPENDIX

To find the relation between our order parameter and the monomer concentration, let $g_R(r)$ be the density-density correlation function of a single N monomer self-avoiding blob of mean radius R. It is well known that $g_R(r)$ obeys a scaling form

$$g_R(r)=(N/R^3)G(r/R) \tag{A1}$$

with $G(x) \propto 1/x^{4/3}$ for $x \ll 1$ and $G(x) \approx 0$ for $x \gg 1$. Its Fourier transform

$$F_R(q)=\int d^3r\, e^{i\mathbf{q}\cdot\mathbf{r}} g_R(r) \tag{A2}$$

behaves in the small-q limit as

$$F_R(q)\approx N[1-\Gamma(qR)^2] \tag{A3}$$

with Γ a numerical factor of order 1. Now consider a random network of such blobs, with the center of mass of the ith blob at $\mathbf{r}_i$. For a gel at swelling equilibrium, we expect from the c^* theorem that the blobs are not greatly deformed so the equilibrium monomer concentration $c_0(r)$ should be approximately

$$c_0(\mathbf{r})=\sum_i g_R(\mathbf{r}-\mathbf{r}_i)\ . \tag{A4}$$

In the presence of fluctuations, we allow the positions of the blobs to be displaced (by the strain displacement vector) and we allow the blob radius to be altered (by the internal order parameter):

$$\mathbf{r}_i \Longrightarrow \mathbf{r}_i+\mathbf{u}_i\ , \tag{A5}$$

$$R \Longrightarrow R_F(1+\psi_i)$$

(with R_F the Flory radius) so the monomer concentration is

$$c(\mathbf{r})=\sum_i g_{R_F(1+\psi_i)}(\mathbf{r}-\mathbf{r}_i-\mathbf{u}_i)\ . \tag{A6}$$

Define the Fourier transform

$$c(\mathbf{q})=\int d^3r\, e^{i\mathbf{q}\cdot\mathbf{r}} c(r)\ . \tag{A7}$$

Linearizing Eq. (A6) gives

$$c(\mathbf{q})=c_0(\mathbf{q})+iF_{R_F}(q)\sum_i \mathbf{q}\cdot\mathbf{u}_i e^{i\mathbf{q}\cdot\mathbf{r}_i} + R_F\partial F_{R_F}(q)/\partial R_F \sum_i \psi_i e^{i\mathbf{q}\cdot\mathbf{r}_i}\ . \tag{A8}$$

Going to the long-wavelength limit, where the summations over units of volume R_F^3 can be treated as integrations, gives

$$c(\mathbf{r})/c_0 \approx 1-\epsilon_{ii}+\Gamma R_F^2\nabla^2\psi+O(\nabla^4\psi) \tag{A9}$$

which is Eq. (2.4).

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