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Spectrum of light scattered from a viscoelastic gel[*]

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We report measurements of the spectrum of light scattered from thermally excited displacement fluctuations in polyacrylamide gels. These measurements have been carried out on the polarized scattered light as a function of scattering angle and temperature for 5% and 2.5% polyacrylamide gels using the methods of optical mixing spectroscopy. We also present a theory for the amplitude and time dependence of the thermally excited longitudinal and transverse displacements of the gel fiber network. These displacements are responsible, respectively, for the polarized and depolarized scattered light. The correlation function for the displacements having wave vector q is predicted for these gels to have the form of an exponential decay: $\exp(-\Gamma t)$. The decay rate is given by $\Gamma = G_l q^2/f$ or $G_t q^2/f$, where f is the frictional force per unit volume on the fiber network as it moves with unit velocity relative to the gel liquid. G_l is the longitudinal compressional modulus for longitudinal displacements and G_t is the shear modulus for transverse displacements of the fiber network. We have measured, using macroscopic methods, the friction factor f, and the elastic moduli G_l, G_t and compared the numerical predictions of the theory with the experimental measurements of the correlation function of the scattered light intensity. The theory is quite successful in predicting the size and q dependence of the decay rate of the time correlation function of the scattered light. Conversely, these experiments demonstrate that the correlation function of the light scattered from thermal fluctuations of the gel fiber network provides a detailed quantitative characterization of the viscoelastic properties of gels.

INTRODUCTION

A gel looks like a crystal when it is stationary, but when it is subject to shear it deforms easily. However, when subject to hydrostatic pressure it is quite incompressible. These half-liquidlike and half-solidlike properties can be understood if we consider its structure—that of a liquid held in a fibrous network of polymers by the extremely large friction between the liquid and the fiber or polymer network.

Understanding the viscoelastic properties of gels has substantial medical and biochemical importance. In the eye, for example, the lens and vitreous humor are gels. Changes in the viscoelastic properties of the lens leads to the loss of accommodation range.[1] Also the "liquefaction" of the vitreous is believed to play an important role in retinal detachment.[1] In both cases the ability to measure the viscoelastic properties of gels *in situ* would have substantial clinical applicability.

Gels are also extensively used in biochemistry as matrices for gel chromatography and electrophoresis. They are also adopted as matrices for crystalization of many substances because the rates of crystalization are greatly enhanced if the reactions are performed in gel matrices.[2] To quantitatively characterize such gel matrices, the knowledge of the viscoelastic properties of gels would be very valuable.

Traditional methods for measuring the viscoelastic properties of gels generally depend on mechanical devices. Measurements of the shear modulus[3] and birefringence[4] of gels have been made by static methods. The only dynamic measurements that have been made measure the propagation of shear waves through gels.[5] In these measurements the liquid in the gel moves *with* the fiber network not against it and accordingly the damping is largely due to the inelastic flexing of the polymers in the fiber network. These measurements of shear damping give information about the motions of the individual polymers that form the fiber network rather than about the collective motion of the network structure. From the shear wave velocity we get the shear modulus of the gel as a whole.

In this paper we present measurements of the correlation function of the light scattered from thermally excited density fluctuations in the fiber network of the polyacrylamide gel. The correlation times are long, typically 10^{-3}–10^{-4} sec, so that we have employed the technique of optical mixing spectroscopy to measure the correlation function of the scattered light. Prins has previously reported measurements of the spectrum of light scattered from agarose and poly(vinylalcohol) gels.[6]

We also present a detailed theory which permits the calculation of the correlation function of the scattered light. This theory predicts the existence, characteristic time constant, and intensity of collective excitations of the fiber network.

The gel is characterized by two kinds of bulk

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wing easily derivable $J_k(\zeta)$ and J'_k

Methods of Theoretical Physics p. 393.
Chem. Phys. **45**, 4556 (1966). ublished).

coefficients: (a) the elastic constants of the fiber network and (b) the friction factor connecting the velocity of the network relative to the gel liquid and the resistive force provided by the gel liquid. We have been able to measure these coefficients macroscopically and have compared the results with the values determined from the time correlation functions of the scattered light. The agreement between the spectroscopic and the macroscopic determinations of these coefficients is very encouraging.

We find that the measurements of the correlation and the intensity of light scattered from gels can provide detailed and accurate information on the elastic properties of the fiber network alone and on the viscous interaction between the network and the gel liquid. We believe that the light scattering spectroscopy of gels can be used as a convenient diagnostic tool for the accurate characterization of gels both in biochemical and medical applications.

THEORY

Let us consider that gels consist of: (a) a fiber network which gives elasticity to gel, and (b) a liquid which occupies the rest of the space in the gel (the gel liquid). We are concerned with structural fluctuations of the fiber network rather than that of the gel liquid. Of course, the gel liquid undergoes thermal fluctuations in its structure and these affect the fiber network. Thus we can consider four kinds of modes in the structural fluctuations of the fiber network: the fiber network can move with ($\uparrow\uparrow$) or against ($\uparrow\downarrow$) the gel liquid in the form of either a longitudinal or a shear wave (see Table I). Because of the large differences between the characteristic times of these modes, we can separate them in such a scheme as Table I: First, let us consider the longitudinal modes. In our light scattering experiments on polyacrylamide gels, we observe modes of type I with relaxation times $\tau \sim 10^{-3}$ sec for fluctuations with wave vector $|q| = 10^5$ cm^{-1}. The time of the corresponding fluctuation of type III can be estimated by the frequency and the damping time of sound waves in pure water. This frequency and damping time can be measured from the line shift and the linewidth of Brillouin scattered light in pure water.[7] The times are about 10^{-9} sec for the frequency and 10^{-7} sec for the damping in 90° scattering. Thus if we are concerned with the time evolution of type I modes, the fluctuations of type III modes in the gel liquid are averaged out, and we can consider the gel liquid to be a nonfluctuating medium.

In the case of shear waves, type II modes have about the same relaxation time as type I modes as will be shown later ($\tau \sim 10^{-3}$ sec, for $|q| = 10^5$ cm^{-1}). On the other hand, the corresponding type IV shear

wave propagates with a frequency $\omega = 10$ MHz which can be calculated from $\omega = \sqrt{\mu/\rho_w} q$, using the gel density ($\rho_w \sim 1$ g/ml) and the shear modulus ($\mu \sim 10^4$ dyn/cm^2 by our measurements).

Thus these four modes can be separated if we adopt an appropriate time region. We shall not concern ourselves with type III modes (longitudinal sound waves in liquids), since their properties are decided by the complex compressibility of the gel liquid rather than by that of the fiber network. Type IV modes have been discussed by other authors.[5] We would like to study in this paper the other two modes, I and II, which give us information about the viscoelastic properties of gels much more directly than modes III and IV in which the gel liquid and fiber network move together.

Since we are only concerned with modes where the fiber network moves against the gel liquid, we may assume that the viscous properties of gels are due to the friction between the fiber network and the gel liquid. Compared to this the damping caused by the inelastic flexing of the fiber network is considered to be negligible. We also consider the fiber density to be uniform, and treat the gel as a continuous medium since the distance between cross-linked points is generally much shorter than the wavelength of the probing light.

The fiber network consists of a cross-linked polymer which is treated as a Gaussian network where Hooke's law is valid over a certain range of deformation.[8] It has been shown that in such a Gaussian network the bulk modulus and the shear modulus are proportional to the absolute temperature.[8] An example of a Gaussian network is a rubber. However, it is interesting to observe the elastic constant of the 5% polyacrylamide fiber network is between 10^3 and 10^5 times smaller than that of a rubber.

Let us introduce a displacement vector $u(r, t)$ which represents the displacement of a point r in the fiber network from its average location at time t. The ensemble average value of the vector is zero,

$$\langle u(r, t) \rangle = 0. \tag{1}$$

The state of a gel is uniquely determined if one

knows the vect... can calculate t... displacement v... Fourier transf... z and q is the w... used the fact th... As will be show... $= 0$, if $j \neq k$. W... one can calcula... from any linear... tion between di... physical quantit...

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The stress ten... ment vector u as...

$$\sigma_{ik} = K\nabla \cdot u\delta_{ik} ...$$

where

$$u_{ik} \equiv \tfrac{1}{2}[(\partial u_k/\partial x ...$$

The first term in... by a volume chan... stress caused by ... ficients K and μ a... the fiber network... efficients are exp... absolute tempera...

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TABLE I. Modes of the structural fluctuations of gels.

	Liquid	Network	Liquid	Network
Longitudinal	(I) $\uparrow$	$\downarrow$	(III) $\uparrow$	$\uparrow$
Transverse	(II) $\uparrow$	$\downarrow$	(IV) $\uparrow$	$\uparrow$

knows the vector **u** for every point **r** in the gel. One can calculate the space time correlations of the displacement vector $\langle u_j(\mathbf{r}, t)u_j^*(\mathbf{r}', t')\rangle$ and its Fourier transform $\langle u_j(\mathbf{q}, t)u_j(\mathbf{q}, t')\rangle$ where $j = x$, y, z and **q** is the wave vector of the fluctuation, and we used the fact that **u** is real and that $u_j(\mathbf{q}) = u_j^*(-\mathbf{q})$. As will be shown in the Appendix, $\langle u_j(\mathbf{q}, t)u_k(\mathbf{q}, 0)\rangle = 0$, if $j \neq k$. With these space–time correlations one can calculate the time correlation resulting from any linear response experiment if the relation between displacement vector **u** and the applied physical quantity is known. [9]

We consider a small deformation of a unit cube of the fiber network with density ρ. The displacement vector obeys the following linear equation:

$$\rho(\partial^2/\partial t^2)\mathbf{u} = \nabla \cdot \tilde{\sigma} - f(\partial/\partial t)\mathbf{u}, \tag{2}$$

where $\tilde{\sigma}$ is a stress tensor whose component σ_{ik} gives the force along the k axis on a unit plane perpendicular to the i axis. Equation (2) is nothing but the representation of Newton's second law. The term on the left represents the mass times the acceleration of a unit cube of the fiber network. The terms on the right-hand side represent the forces exerted on the cube. The first one is the net force of the internal stresses and is expressed as the difference of two internal stresses on the two opposing walls of the cube. Thus it is given by the divergence of the stress tensor. The second term is the drag friction by the gel liquid. In analogy with the Stokes' formula $\mathbf{F} = -6\pi R\eta(\partial \mathbf{u}/\partial t)$ for a sphere with a radius R, we may assume that the force is proportional to the relative velocity $\partial \mathbf{u}/\partial t$ between the fiber network and the gel liquid and that the friction constant f is proportional to the viscosity η of the gel liquid. The quantity f can be measured by fixing the fiber network and measuring the liquid flow rate through the fiber network for a given pressure applied to the liquid alone. Indeed this method was used to measure macroscopically the constant f as will be shown later (Fig. 1).

The stress tensor $\tilde{\sigma}$ is related to the displacement vector **u** as follows[10]:

$$\sigma_{ik} = K\nabla \cdot \mathbf{u}\delta_{ik} + 2\mu(u_{ik} - \tfrac{1}{3}\nabla \cdot \mathbf{u}\delta_{ik}), \tag{3}$$

where

$$u_{ik} \equiv \tfrac{1}{2}[(\partial u_k/\partial x_i) + (\partial u_i/\partial x_k)]. \tag{4}$$

The first term in Eq. (3) shows the stress produced by a volume change, and the second term is the stress caused by shear deformation. The coefficients K and μ are the bulk and shear modulus of the fiber network alone, respectively. These coefficients are expected to be proportional to the absolute temperature as mentioned above.

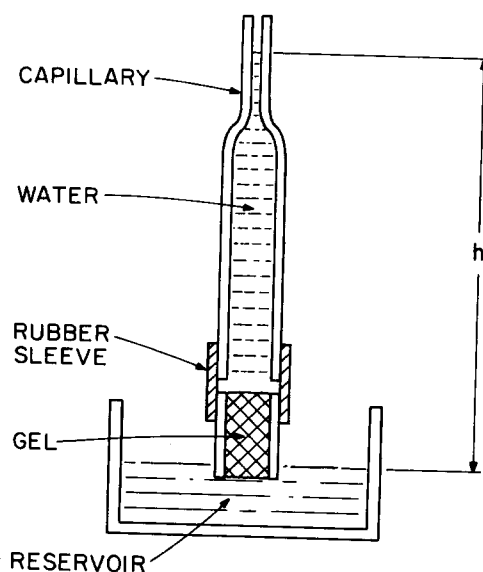As will be shown later, the relaxation time of a

FIG. 1. Measurement technique for determining the friction between the fiber network and the gel liquid. The volume flow rate of water was measured in the capillary tube.

density fluctuation of the fiber network has the same form $[\tau_g = (D_g q^2)^{-1}]$ as that of thermal diffusion $\tau_T = (D_T q^2)^{-1}$. Here **q** is the wave vector of the fluctuation. Since the thermal diffusion constant is $D_T = 1.4 \times 10^{-3}$ cm^2/sec for water while $D_g = 2 \times 10^{-7}$ cm^2/sec for polyacrylamide gels, the thermal diffusion can be seen to be much faster than the relaxation rate of the fiber network structure. Thus in the time scale characteristic to the density fluctuation of the fiber network, the temperature can be assumed to be constant and the process is isothermal. Accordingly, we can adopt isothermal values for K and μ.

Substituting Eqs. (3) and (4) into Eq. (2), we obtain an equation for the displacement vector,

$$\rho(\partial^2/\partial t^2)\mathbf{u} = \mu\Delta\mathbf{u} + (K + \tfrac{1}{3}\mu)\nabla(\nabla \cdot \mathbf{u}) - f(\partial\mathbf{u}/\partial t). \tag{5}$$

At this point let us introduce the Fourier transform of the displacement vector,

$$\mathbf{u}(\mathbf{q}, \omega) = [(2\pi)(2\pi)^{3/2}]^{-1} \int_{-\infty}^{\infty} \int \mathbf{u}(\mathbf{r}, t) \times \exp[-i(\mathbf{q} \cdot \mathbf{r} + \omega t)] d\mathbf{r} dt, \tag{6}$$

and seek an equation for it. Since the gel is isotropic the fluctuation should not depend on the direction of the vector **q**. Thus, we can choose the z axis in **q** space as a direction of **q** without loss of generality,

$$\mathbf{q} = (0, 0, q). \tag{7}$$

Substituting Eq. (6) into Eq. (5), we find

$$\rho\omega^2 u_z - if\omega u_z - \rho c_l^2 q^2 u_z = 0 \tag{8}$$

and

$$\rho\omega^2 u_j - if\omega u_j - \rho c_t^2 q^2 u_j = 0, \qquad (9)$$

where $j = x$, y and c_l and c_t are defined by

$$c_l = \sqrt{(K + \tfrac{4}{3}\mu)/\rho} \qquad (10)$$

and

$$c_t = \sqrt{\mu/\rho}. \qquad (11)$$

These correspond to the longitudinal and transverse sound velocities, respectively, in the fiber network. In a 5% polyacrylamide gel the velocity c_l is very slow (about 10 m/sec) because of its very small elastic constants.

From now on we need not write the suffices l and t of c_l and c_t, since Eqs. (8) and (9) have the same forms. In order to get nontrivial solutions for u_j's the following relation should exist between ω and q:

$$\rho\omega^2 - if\omega - \rho c^2 q^2 = 0. \qquad (12)$$

This gives

$$i\omega = -(f/2\rho)(1 \pm \sqrt{1 - 4\rho^2 c^2 q^2/f^2}) \qquad (13)$$

$$= -(\tau_0)^{-1}(1 \pm \sqrt{1 - \omega_0^2 \tau_0^2}), \qquad (14)$$

where

$$\tau_0 = 2\rho/f \qquad (15)$$

and

$$\omega_0 = cq. \qquad (16)$$

The meaning of τ_0 and ω_0 can be easily understood if we consider a case where $\omega_0 \tau_0 \gg 1$. In this case we obtain from the equation (14) two frequencies,

$$i\omega = \pm i\omega_0 - (\tau_0)^{-1}. \qquad (17)$$

This shows that $\omega_0 = cq$ is a sound frequency with a wave vector q, and τ_0 is the relaxation time of the wave due to the friction between the fiber network and the gel liquid. Generally $i\omega$ is a complex number. If it has an imaginary part the wave propagates, but if it is purely real the wave does not propagate. Equation (14) shows that if $\omega_0 \tau_0 > 1$, we obtain propagating sound waves, and if $\omega_0 \tau_0 \lesssim 1$, we get nonpropagating waves.

In the case of polyacrylamide gels $\omega_0 \tau_0 \sim 10^{-4}$ as will be shown later, and Eq. (14) becomes

$$-i\omega = \begin{cases} 2/\tau_0 \equiv (\tau_f)^{-1} \\ \tfrac{1}{2}\tau_0\omega_0^2 \equiv (\tau_s)^{-1} \end{cases} \qquad (18)$$

and accordingly there are no propagating modes. The faster decay time τ_f in Eq. (18) could have been obtained from Eq. (5) by neglecting the elastic term. In this way we recognize that τ_f is the velocity relaxation given by Stokes' formula $\rho\ddot{u} = F = -f\dot{u}$. The slower decay time τ_s could have

been obtained if we had eliminated the acceleration term in Eq. (5). Noticing $\mathbf{u} \propto e^{iqz}$, we get from Eq. (5) with $\rho\partial^2\mathbf{u}/\partial t$ set equal to zero that

$$f(\partial\mathbf{u}/\partial t) = G(\partial^2\mathbf{u}/\partial z^2), \qquad (19)$$

where G is $K + \tfrac{4}{3}\mu$ for a longitudinal wave and μ for a transverse wave. Equation (19) shows that the displacement diffuses along the z axis with a diffusion constant $D_g = G/f$. This constant has a form similar to that of the diffusion coefficient of a macromolecule in solution: $D_m = kT/\zeta$, where $\zeta = 6\pi\eta a$ (a is the radius of the molecule, η is the viscosity of the medium, and T is the temperature). The denominators are similar for both D's, but the numerators are the elastic constant G in gels and the temperature kT in the macromolecule. While the movement of a macromolecule is caused by the collisions with small molecules in solution and is directly related to temperature, the movement of the fiber network is due to its own elasticity. On taking the Fourier transform of Eq. (19), we see that a fluctuation of wave vector q dies away with a time constant $1/\tau_s = Gq^2/f$, as is given in Eq. (18), since $\omega_0^2 \tau_0/2 = Gq^2/f$.

In general, we find that the time correlation has the form,

$$\langle u_j(\mathbf{q}, t) u_j(\mathbf{q}, 0) \rangle = \langle u_j(\mathbf{q})^2 \rangle [A_s \exp(-t/\tau_s) + A_f \exp(-t/\tau_f)], \qquad (20)$$

where $A_s + A_f = 1$. Using the values of A_s, A_f, and $\langle u_j(\mathbf{q})^2 \rangle$ calculated in the Appendix, we find that $|A_s/A_f| \gg 1$ and that

$$\langle u_z(\mathbf{q}, t) u_z(\mathbf{q}, 0) \rangle = \frac{VkT}{(2\pi)^3(K + 4/3\mu)} \frac{1}{q^2} \times \exp\left(-\frac{(K + 4/3\mu)q^2 t}{f}\right) \qquad (21)$$

for longitudinal fluctuations and

$$\langle u_j(\mathbf{q}, t) u_j(\mathbf{q}, 0) \rangle = [VkT/(2\pi)^3\mu](1/q^2)\exp(-\mu q^2 t/f) \qquad (22)$$

for transverse ones, where $\mathbf{q} = (0, 0, q)$ and $j = x$, y.

In the heterodyne spectrum of the polarized light and depolarized light, one measures the time correlation functions of the electric field scattered by the longitudinal and transverse fluctuations, respectively. The calculation of the correlation function of the scattered electric field can be made in the same way as for Brillouin scattering.[7] We should note, however, that the processes we consider are isothermal rather than adiabatic as in the case of Brillouin scattering. At a point of a distance R from the illuminated volume, we obtain

$$\langle E_{\text{pol}}(\mathbf{q}, t) E_{\text{pol}}(\mathbf{q}, 0) \rangle$$

$$= \frac{I_0}{c}\left(\frac{\omega_0}{c}\right)^4 \text{s...}$$

$$\times \exp\left(-\frac{(\ldots}{\ldots}\right.$$

for polarized s...

$$\langle E_{\text{dep}}(\mathbf{q}, t) E_{\text{dep}}(\mathbf{q},$$

$$= \frac{I_0}{c}\left(\frac{\omega_0}{c}\right)^4 \text{s...}$$

for the depolari... cident intensity length, and ϕ is tion of the inci... tion. ϵ and ϵ_D ... elements of the ... $(\partial\epsilon/\partial\rho)_T$ can be ... refraction n of a... tration ρ, since ... can be obtained ... u_{xy} to a gel and ... light passing thr... ratio of the depo... measured in the ... $I_D/I_P = (\epsilon_D/\epsilon)^2$, a... a function of u_{xy}.

In homodyne m... for our measure... obtain a time co... tric field but of t... However, becaus... the electric field ... intensity is given ... functions in Eq. ... the decay constan... and $(2\mu/f)q^2$ for ... tering, respectiv...

Thus from the ... light, in principle ... $(K + \tfrac{4}{3}\mu)/f$ and $\mu/$... ments of the scatt... by putting $t = 0$ in ... the quantities $K + \tfrac{?}{?}$... inhomogeneities i... work which scatte... tensity, however, ... contribution to the ... relation function. ... total intensity expr... be determined fro... tion function at $t = $... polarized and depo... we can in principle ... parameters of a ge... the present experi... intensity was quite ...

$$= \frac{I_0}{c} \left(\frac{\omega_0}{c} \right)^4 \frac{\sin^2\phi}{4\pi R^2} \left(\frac{\partial\epsilon}{\partial\rho} \right)^2_T \rho^2 \frac{LkT}{K+4/3\mu}$$

$$\times \exp\left(-\frac{(K+4/3\mu)q^2 t}{f} \right) \qquad (23)$$

for polarized scattering and

$$\langle E_{dep}(\mathbf{q}, t) E_{dep}(\mathbf{q}, 0) \rangle$$

$$= \frac{I_0}{c} \left(\frac{\omega_0}{c} \right)^4 \frac{\sin^2\phi}{4\pi R^2} \left(\frac{\partial\epsilon_D}{\partial u_{xy}} \right)^2_T \frac{LkT}{\mu} \exp\left(\frac{-\mu q^2 t}{f} \right) \qquad (24)$$

for the depolarized scattering. Here I_0 is the incident intensity of the light, L is the illuminated length, and ϕ is the angle between the polarization of the incident light and the scattering direction. ϵ and ϵ_D are the diagonal and off-diagonal elements of the dielectric tensor. The quantity $(\partial\epsilon/\partial\rho)_T$ can be obtained by measuring the index of refraction n of a gel while changing the gel concentration ρ, since $\epsilon = n^2$. The quantity $(\partial\epsilon_D/\partial u_{xy})_T$ can be obtained by applying a shear deformation u_{xy} to a gel and measuring the depolarization of a light passing through the gel along the z axis. The ratio of the depolarized vs polarized light intensity measured in the forward direction is given by $I_D/I_P = (\epsilon_D/\epsilon)^2$, and therefore we can obtain ϵ_D as a function of u_{xy}.

In homodyne mixing spectroscopy which we used for our measurements of polyacrylamide gels, we obtain a time correlation function not of the electric field but of the intensity of the scattered light. However, because of the Gaussian properties of the electric field, the correlation function of the intensity is given by the square of the correlation functions in Eq. (23) or (24) of the field.[11] Thus the decay constants $\Gamma = 1/\tau$ become $2[(K + \frac{4}{3}\mu)/f]q^2$ and $(2\mu/f)q^2$ for polarized and depolarized scattering, respectively.

Thus from the time correlations of the scattered light, in principle we can obtain the ratios $(K+\frac{4}{3}\mu)/f$ and μ/f. From the intensity measurements of the scattered light, which can be obtained by putting $t = 0$ in Eqs. (23) and (24), we can obtain the quantities $K + \frac{4}{3}\mu$ and μ. Of course, there are inhomogeneities in the structure of a polymer network which scatter light. This scattered light intensity, however, is time independent and has no contribution to the time dependent part of the correlation function. Thus the contribution to the total intensity expressed in Eqs. (23) and (24) can be determined from the intercept of the correlation function at $t = 0$. Consequently, by using only polarized and depolarized scattering techniques, we can in principle determine all the viscoelastic parameters of a gel: K, μ, and f. However, in the present experiments the depolarized scattering intensity was quite small because $(\partial\epsilon_D/\partial u_{xy})_T$ is

very small for our gel, and we could not observe the depolarized scattered light spectrum.

EXPERIMENTS

Macroscopic Measurements

In order to obtain values for the bulk parameters used in the theory, we made measurements of the frictional and elastic constants for 2.5% and 5% polyacrylamide gels prepared from Canalco premixed reagents.

Friction Constant

The system drawn in Fig. 1 permits the macroscopic determination of the friction factor f. It is designed to determine both the force per unit volume on the gel liquid and the velocity w (or equivalently the volume flow rate $\dot{V}$) of the gel liquid relative to the fiber network. From examinations of Fig. 1 and the definition of f as appeared in Eq. (2) we obtain

$$f = \frac{\rho_w g(h - h')A/(LA)}{w} .$$

The quantity in the numerator is the net force per unit volume on the gel liquid. Here ρ_w is the water density, g is the acceleration of gravity, h is the height of the water column above the reservoir level, and h' is the distance the water is pulled up the capillary by surface tension alone. L and A are the length and the cross-sectional area of the gel, respectively. Since the volume flow rate $\dot{V}$ is wA, we obtain

$$f = \rho_w g(h - h')A/L\dot{V}. \qquad (25)$$

The flow rate $\dot{V}$ is measured by observing the rate at which the level falls in the calibrated capillary.

In our experiments with 5% and 2.5% polyacrylamide gels we found that

$$\rho_w g(h - h')_5 = 5.6 \times 10^4 \ (\text{dyn/cm}^2),$$

$$\rho_w g(h - h')_{2.5} = 7.0 \times 10^3 \ (\text{dyn/cm}^2),$$

$$A = 0.20 \ (\text{cm}^2),$$

$$L = 2.0 \ (\text{cm}),$$

$$\dot{V}_5 = 2.5 \times 10^{-8} \ (\text{cm}^3/\text{sec}),$$

$$\dot{V}_{2.5} = 2.0 \times 10^{-7} \ (\text{cm}^3/\text{sec}),$$

where the subscripts 5 and 2.5 denote the 5% and 2.5% gels, respectively. From these parameters Eq. (25) gives $f_5 = 2.2 \times 10^{11}$ dyn·sec/cm^4 and $f_{2.5} = 3.5 \times 10^9$ dyn·sec/cm^4.

Elastic Constants

There are two elastic constants involved in the fiber network. In polarized light scattering one needs to know the longitudinal elastic constant

$K + \frac{4}{3}\mu$ as has been shown in Eq. (21). However, because of the large viscosity between the fiber network and the gel liquid, when a gel is compressed uniaxially only a very small amount of water is expected to flow out of the fiber network. Indeed for pressures low enough to avoid damaging the gel, it would take about a month to get a 20% contraction. Thus, for practical purposes one can only measure the elastic constant under the condition of no change in volume. One can get from any elastic measurement with zero volume change only the shear modulus μ. Despite this we can make a deduction as to the value of K because of the very weak structure of the fiber network. The shear modulus of the fiber network is about 10^3–10^5 times smaller than that of rubber, and indeed is similar to that of a sponge. If we compress a sponge uniaxially, its length decreases along the direction of compression, but the sides do not move out. Without its fluid to help it maintain a constant volume, a gel is much like a sponge, and accordingly a uniaxial compression applied to the fiber network alone would be expected to make it shrink along the direction of compression, and not to make it spread out. The above reasoning leads us to expect that for the fiber network in a gel the Poisson's ratio is nearly zero.

The Poisson's ratio σ of a uniaxially compressed material is defined by

$$\sigma = \frac{\Delta d/d}{\Delta l/l},$$

where l and d are the length and the diameter of the compressed cylinder (see Fig. 2). If $\sigma = 0$, a single elastic constant, the Young's modulus

$$E = \frac{\Delta P}{\Delta l/l}$$

of the fiber network determines its elasticity. Since K and μ are related to E and σ by the equations[10]

$$K = E(1-\sigma)/3(1+\sigma)(1-2\sigma)$$

and

$$\mu = E/2(1-\sigma), \tag{26}$$

we conclude that when $\sigma = 0$, $K = E/3$, and $\mu = E/2$. Thus by measuring μ alone we can also obtain K. The longitudinal elastic constant $K + \frac{4}{3}\mu$ can readily be shown to be 2μ.

The measurement of μ was made by pressing on a cylinder of gel and measuring the contraction $\Delta l/l$. Since there is no volume change

$$\Delta l/l = 2(\Delta d/d) \tag{27}$$

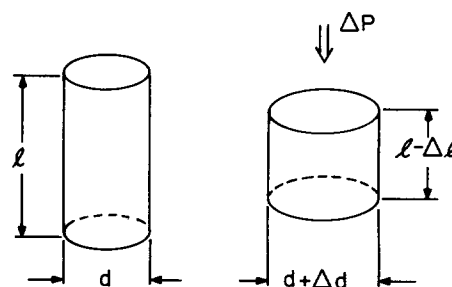which was easily checked in our experiment. Here we should notice that the condition of no volume

FIG. 2. Method for determining the elastic constant μ.

change does not mean that the Poisson's ratio σ of the *polymer network* is $\frac{1}{2}$, but that σ of the *whole* gel, including the gel liquid, is $\frac{1}{2}$ because of the enormous friction mentioned above.

The work done by the pressure ΔP in compressing the gel is given by

$$\frac{1}{2}\Delta P(\pi d^2/4)\Delta l, \tag{28}$$

where we assume the contraction is small so that there will be a linear relation between the contraction l and the pressure ΔP. The elastic energy H_E in a deformation in which there is no volume change is the third term of Eq. (A1) in the Appendix. In obtaining this relation we used the fact that for the deformation shown in Fig. 2, $\nabla \cdot \mathbf{u} = 0$ and $u_{ik} = \delta_{ik}u_{ii}$. Also the values of u_{ii} are $u_{xx} = u_{yy} = \Delta d/d$ and $u_{zz} = \Delta l/l$. Thus

$$H_E = \frac{1}{4}\mu\, l\pi d^2 [(\Delta l/l)^2 + 2(\Delta d/d)^2], \tag{29}$$

where $l\pi d^2/4$ is the volume of the gel. Using Eqs. (27)–(29), we find

$$\mu = \frac{1}{3}\Delta P(l/\Delta l). \tag{30}$$

In our measurements we find the value of μ_5 and $\mu_{2.5}$ to be 2.6×10^4 and 2.2×10^2 (dyn/cm^2), respectively.

The comparisons of the values of f and μ for 5% and 2.5% gels are made in Table II. It is interesting that by changing the concentration by a factor of 2, the bulk parameters change by about two orders of magnitude. The large changes in bulk coefficients are probably due to the decrease in the number of cross links between polymers.

Optical Mixing Spectroscopy

Polyacrylamide gels were prepared in the same way as for the gels in the macroscopic measurements. After mixing, the gels were allowed to stand at room temperature for at least 1 day to allow sufficient time for the gelation process to come to completion. Only one gel was used for each set of measurements reported in this paper.

TABLE II. Exp
and optical mixing

| f (dyn·sec/cm^4) |
| 2μ (dyn/cm^2) |
| $D_{\text{calc}} = 2\mu/f$ (10^{-7} cm^2/s |
| $D_{\text{exptl}} = \Gamma/2q^2$ (10^{-7} cm |

The risk of da by measuring th prepared. For the cells were p perature could b in the range 5–7 areas was colle onto a photomul scaled autocorr correlation func photomultiplier.

The data from by the method of for a distributio possible to calcu cumulants of the able to measure variance $V = \sqrt{\overline{\Gamma^2}}$ order cumulants simplify the disc cern ourselves the variance and to the inhomoge scribed in a subs to note that the d quite well, with generally less th correlation funct

Figure 3 show for a 5% polyacry and 25 °C. The l ponential fit to th fit,[12] we found $\overline{\Gamma}/$ value is also give ance V of the fit $V = 0.43$. The rm of the correlation is expected to be the points shown

The last row in measurements of 5% polyacrylamid correlation functi tions. These mea scattering angle o temperature of 25 to coincide with th measurements we

TABLE II. Experimental data by macroscopic methods and optical mixing spectroscopy.

	5% Gel	2.5% Gel
f (dyn·sec/cm^4)	$2.2 \pm 0.3 \times 10^{11}$	$3.5 \pm 0.1 \times 10^9$
2μ (dyn/cm^2)	$5.2 \pm 0.3 \times 10^4$	$4.4 \pm 0.9 \times 10^2$
$D_{calc} = 2\mu/f$ (10^{-7} cm^2/sec)	2.4 ± 0.4	1.3 ± 0.3
$D_{exptl} = \Gamma/2q^2$ (10^{-7} cm^2/sec)	2.4 ± 0.1	1.6 ± 0.1

The risk of damaging the samples was minimized by measuring them in the cells in which they were prepared. For the light scattering measurements the cells were placed in a cell holder whose temperature could be maintained at any temperature in the range 5–70 °C. Light from a few coherence areas was collected at the desired angle and imaged onto a photomultiplier. A 18-channel double-scaled autocorrelator was used to measure the correlation function of the photocurrent from the photomultiplier.

The data from the autocorrelator were analyzed by the method of cumulants.[12] This method allows for a distribution of decay rates Γ and makes it possible to calculate some of the lowest-order cumulants of the distribution. In our case we were able to measure the average decay rate $\overline{\Gamma}$, the variance $V = \sqrt{\overline{\Gamma^2} - \overline{\Gamma}^2 / \overline{\Gamma}}$, and sometimes higher-order cumulants of this distribution. In order to simplify the discussion in this paper, we will concern ourselves with $\overline{\Gamma}$ only. The significance of the variance and higher-order moments is related to the inhomogeneities in the gel and will be described in a subsequent publication. It is important to note that the data could be fit to one exponential quite well, with the largest deviation of the data generally less than 1% of the initial value of the correlation function.

Figure 3 shows the measured correlation function for a 5% polyacrylamide gel at 90° scattering angle and 25 °C. The line represents the best single exponential fit to the data. By making a two cumulant fit,[12] we found $\overline{\Gamma}/2q^2 = 2.38 \times 10^{-7}$ cm^2/sec. This value is also given in Row 4 of Table II. The variance V of the fit for the data in Fig. 1 is $V = 0.43$. The rms error of this two-cumulant form of the correlation function (not shown in Fig. 3) is expected to be about one-third the diameter of the points shown in Fig. 3.

The last row in Table II is a summary of our measurements of $D_{exptl} \equiv \Gamma/2q^2$ for a 2.5% and a 5% polyacrylamide gel from the decay rate of the correlation function of the photocurrent fluctuations. These measurements were made with a scattering angle of 90° ($q^2 \sim 3.5 \times 10^{10}$ cm^{-2}) and a temperature of 25 °C. The temperature was chosen to coincide with the temperature at which the bulk measurements were made. There are two con-

tributions to the error in D_{exptl}. Whereas the variation of any measurement made on any given gel sample was about 1%, we found that the gel-to-gel variations of the measurements made for a particular polyacrylamide concentration varied by about 5%. In Row 3 of Table II are the calculated values of $D_{calc} = 2\mu/f$ using the elastic constant μ and the friction factor f which we measured macroscopically and listed in Rows 1 and 2 of Table II. The agreement between D_{calc} and D_{exptl} obtained by optical mixing spectroscopy is very good and provides strong support of the theory.

In order to further check the theory, we investigated the validity of the equation $\Gamma = 4(\mu/f)q^2$ by measuring the dependence of the decay rate Γ on scattering angle. The results of these measurements are shown in Fig. 4 where the mean decay rate of the gel fluctuation $\overline{\Gamma}$ is plotted against the square of the scattering vector q for a polyacrylamide gel at 25 °C. The straight line on the figure shows the values predicted by the theory $\overline{\Gamma}/2q^2 = 2\mu/f$ and the bulk measurements of f and μ. One can conclude that indeed the decay rate is proportional to the square of the scattering vector as anticipated in the theory section.

We also have measured the temperature dependence of the decay rate Γ in a 5% polyacrylamide gel. The results of the measurements are shown in Fig. 5. The circles represent measurements made as the temperature of the gel was increased
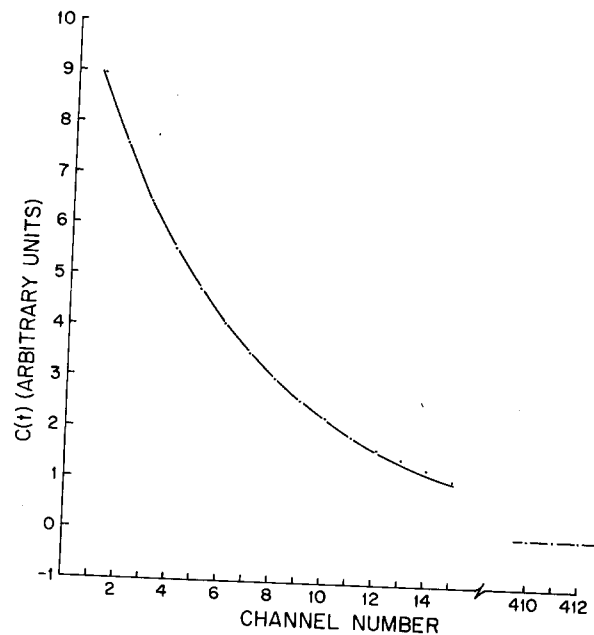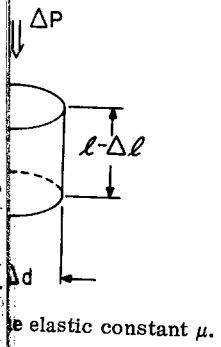

FIG. 3. The measured correlation function of a 5% polyacrylamide gel at 25 °C with a scattering angle of 90°. The line represents the best single exponential fit to the data. One channel corresponds to 10 μsec.

by steps from 15 to 65°C. The squares show the measurements made as the temperature was then reduced from 65 to 15°C. The lack of hysteresis implies that no structural changes are occurring in the fiber network over this temperature range. The dashed line represents theoretical variations of the decay rate divided by q^2. This line was obtained from the following considerations: According to the theory of the elasticity of Gaussian polymers,[8] the elastic constants K and μ of the gel fiber network are expected to be directly proportional to kT, provided that no structural changes occur in the fiber network. The friction factor f is taken to be directly proportional to the viscosity of pure water. Thus, we can compute the temperature variation of $2\mu/f$ from its value at 25°C using the relation $D(T) = 2\mu(T)/f(T) = (2\mu/f)_{25°C} \times (T/298)[\eta(25°C)/\eta(T)]$.

We observe that the experimental results for $D(T)$ agree qualitatively with the theory. However, the data do significantly depart from the theoretical prediction as the temperature rises above $\sim 40°C$. This suggests that μ may not be strictly proportional to kT or that f is not strictly proportional to the viscosity of pure water.

FIG. 5. Temperature dependence of diffusion constant $D = \Gamma/2q^2$ in 5% polyacrylamide gel. The circles show the points taken with temperature increasing, while squares show those taken with temperature decreasing. The dotted line is the predicted $D = 2\mu/f$ by the theory using the measured bulk coefficients μ and f at 25°C and their predicted temperature dependences.
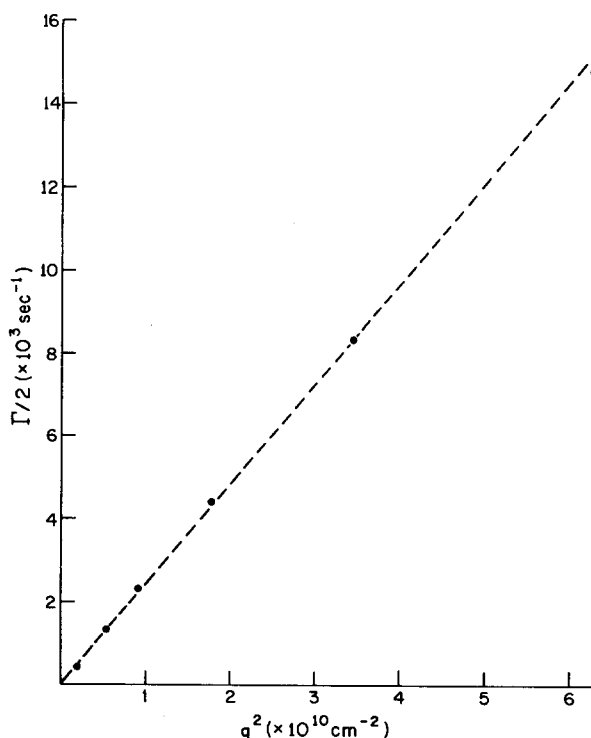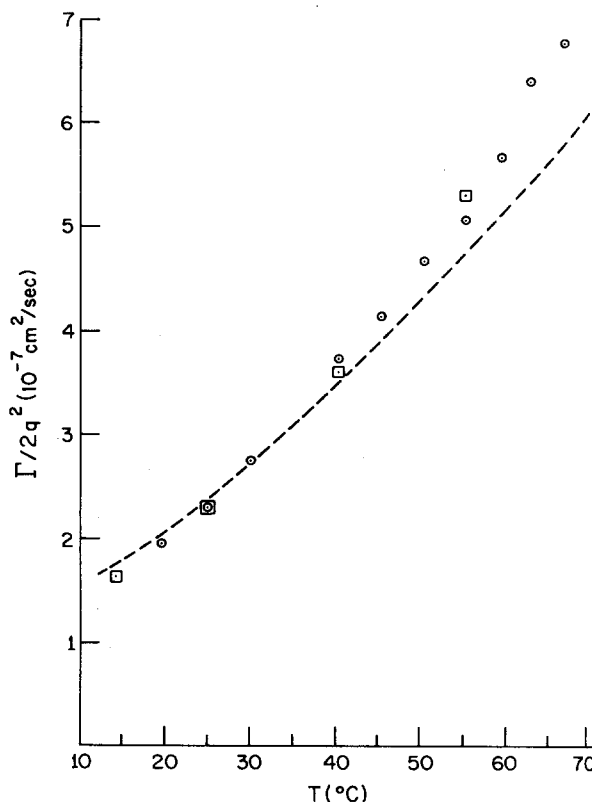

FIG. 4. q^2 dependence of the relaxation rate $\Gamma/2 = (2\mu/f)q^2$ of the time correlation of scattered light in a 5% polyacrylamide gel at 25°C. Dotted line shows the predicted curve by the theory using the bulk coefficients μ and f.

CONCLUSION

From these measurements we can see that optical mixing spectroscopy can be used to provide detailed and accurate measurements of the elastic properties of the fiber network and on the viscous interaction between the fiber network and the gel liquid for simple gels.

Whereas μ and f can be measured separately by macroscopic means, these measurements are time consuming and relatively inaccurate. Accurate measurements of $2\mu/f$ can be made using optical mixing spectroscopy in less than 2 min. This opens the door to the possibility of watching the time evolution of the gel structure during gelation.

Extensions of the theory and the experiments to cover other gels, the process of gelation, and to discover the precise meaning of nonexponentiality of the correlation function are currently under way.

Here we calc
$\langle u_j(q, t)u_j(q, t)\rangle$
z, and q is the
factors A_s and
$\langle \dot{u}_j(q)u_j(q)\rangle$ as v

The Hamilton

$$H = \frac{1}{2}\rho \sum_j \int$$

$$+ \frac{1}{2}K \int \Big|$$

$$+ \mu \sum_{j,k} \int$$

$$+ H_{int} + H$$

where the first
fiber network, t
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$$u_j(\mathbf{r}) = (2\pi)^{-3/}$$

Then,

$$u_{ik} = \frac{1}{2}[(\partial u_k/\partial$$

$$= [i/2(2\pi)^3$$

$$\times \exp(iq\cdot$$

The Hamiltonian

$$H = (\frac{1}{2}\rho/z)\int \dot{u}($$

$$+ \frac{1}{2}K\int \sum_i$$

$$+ \mu \sum_{i,k} \int \Big|$$

$$+ H_{solv} + H_i$$

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$$(A_s/\tau_s + A_f/\tau_f)$$

ACKNOWLEDGMENTS

APPENDIX

Here we calculate the same time correlation $\langle u_j(\mathbf{q}, t)u_j(\mathbf{q}, t)\rangle$ and $\langle \dot{u}_j(\mathbf{q}, t)u_j(\mathbf{q}, t)\rangle$, where $j = x$, y, z, and $\mathbf{q}$ is the wave vector of the fluctuation. The factors A_s and A_f in Eq. (20) are calculated using $\langle \dot{u}_j(\mathbf{q})u_j(\mathbf{q})\rangle$ as will be shown later.

The Hamiltonian of the gel has the form,[10]

$$H = \frac{1}{2}\rho \sum_j \int |\dot{u}_j(\mathbf{r})|^2 d\mathbf{r}$$
$$+ \frac{1}{2}K \int |\nabla \cdot \mathbf{u}|^2 d\mathbf{r}$$
$$+ \mu \sum_{j,k} \int |u_{jk} - \frac{1}{3}\nabla \cdot \mathbf{u}\delta_{jk}|^2 d\mathbf{r}$$
$$+ H_{int} + H_{solv} , \qquad (A1)$$

where the first represents the kinetic energy of the fiber network, the second the bulk energy, the third the shear energy. H_{solv} is the energy of the gel liquid and H_{int} is the interaction energy between the fiber network and the liquid. Let us Fourier-transform the deformation vector u_j,

$$u_j(\mathbf{r}) = (2\pi)^{-3/2} \int u_j(\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{q} \qquad (A2)$$

Then,

$$u_{ik} = \frac{1}{2}[(\partial u_k/\partial x_i) + (\partial u_i/\partial x_k)]$$
$$= [i/2(2\pi)^{3/2}] \int [q_i u_k(\mathbf{q}) + q_k u_i(\mathbf{q})]$$
$$\times \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{q}. \qquad (A3)$$

The Hamiltonian becomes

$$H = (\frac{1}{2}\rho/z)\int \dot{u}(\mathbf{q})^2 d\mathbf{q}$$
$$+ \frac{1}{2}K \int \sum_l [q_l u_l(\mathbf{q})]^2 d\mathbf{q}$$
$$+ \mu \sum_{i,k} \int \left[\frac{1}{2}(q_i u_k + q_k u_i) - \frac{1}{3}\left(\sum_l q_l u_l\right)\delta_{ik}\right]^2 d\mathbf{q}$$
$$+ H_{solv} + H_{int} , \qquad (A4)$$

since u is real so that $\mathbf{u}(\mathbf{q}) = \mathbf{u}^*(-\mathbf{q})$.

Since the energy of the interaction between the fiber network and the gel liquid is a function of only their relative velocity, $\dot{u}$, and is independent of their absolute position u, we may assume that H_{int} is independent of u. Thus there is no term which contains the product of $\dot{u}_j(\mathbf{q})$ and $u_j(\mathbf{q})$, and there is no correlation between $u_j(\mathbf{q})$ and $\dot{u}_j(\mathbf{q})$, so

$$\langle \dot{u}_j(\mathbf{q})u_j(\mathbf{q})\rangle = 0. \qquad (A5)$$

From Eq. (20) in the text and Eq. (A5) we obtain

$$(A_s/\tau_s + A_f/\tau_f)\langle u(\mathbf{q})^2\rangle = 0. \qquad (A6)$$

Also, $A_s + A_f = 1$. Thus we find

$$A_f = \tau_f/(\tau_f - \tau_s) \text{ and } A_s = \tau_s/(\tau_s - \tau_f), \qquad (A7)$$

where

$$|A_s| \gg |A_f| \sim 10^{-5}|A_s| \qquad (A8)$$

in the case of 5% polyacrylamide gel and one can neglect the term with the fast decay.

Next let us calculate $\langle u_j(\mathbf{q})^2\rangle$. In order to compute $\langle u_j(\mathbf{q})^2\rangle$, we have to find the energy $H(j, \mathbf{q})$ associated with a single value of $\mathbf{q}$ in reciprocal space. The volume in $\mathbf{q}$ space associated with the point $\mathbf{q}$ is $|d\mathbf{q}| = (2\pi)^3/V$, where V is the illuminated volume of the gel. If we integrate the expression (A4) over one such volume, we obtain

$$H(j, \mathbf{q}) = [(2\pi)^3/2V][(K + \mu/3)q_j^2 + \mu \mathbf{q}^2]u_j(\mathbf{q})^2 \qquad (A9)$$

and we can calculate

$$\langle u_j(\mathbf{q})^2\rangle = \int u_j^2(\mathbf{q})\exp[-\beta H(j, \mathbf{q})]du_j(\mathbf{q})/$$
$$\int \exp[-\beta H(j, \mathbf{q})]du_j(\mathbf{q})$$
$$= VkT/\{(2\pi)^3[(K + \frac{1}{3}\mu)q_j^2 + \mu\mathbf{q}^2]\}, \qquad (A10)$$

where $\beta = kT$. Thus for $\mathbf{q} = (0, 0, q)$,

$$\langle u_z(\mathbf{q})^2\rangle = VkT/[(2\pi)^3(K + \frac{4}{3}\mu)q^2], \qquad (A11)$$

$$\langle u_{x \text{ or } y}(\mathbf{q})^2\rangle = VkT/[(2\pi)^3\mu q^2]. \qquad (A12)$$

There is no term which is a product of two different components of the displacement vector, because in each term $q_j u_k q_k u_j$ with $j \neq k$, at least one of the q_j or q_k is zero.

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