$g(f) = (f - 2)/f$. This result differs from those of a number of previous theories, for which g was found to be unity and independent of network connectivity. It confirms the inference of Duiser and Staverman, drawn from the behavior of first-order micronetworks, and agrees with the value $g = \frac{1}{2}$ obtained by Edwards for the case of networks formed by random tetrafunctional cross-linking.

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Harmonically Bound Particle Model for Quasi-Elastic Light Scattering by Gels

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ABSTRACT: The intensity fluctuations of the scattered light in time reflect the dynamics of the scattering entities. In the case of a gel, the initial amplitude of the intensity autocorrelation function has been found to be greatly reduced compared to that of its "sol" state. The initial amplitude seems to correlate with the constraint imposed on the motion of a macromolecule in its "gel" state. Assuming each macromolecule in the "gel" state to behave as a harmonically bound particle executing independent Brownian motion about a stationary mean, and including the presence of additional static scattering due to spatial structuring of the Rayleigh scatterers, the intenstiy autocorrelation function is derived. Three physical parameters may then be deduced from autocorrelation measurements, *i.e.*, a chain elastic constant which can be related to the equilibrium storage or shear modulus, the conventional diffusion coefficient or frictional constant, and the fraction of static scattering in addition to that prescribed by Rayleigh scattering. Quantitative measurements were done on polyacrylamide gels. The equilibrium storage moduli deduced from light scattering experiments were compared with those determined by unilateral compression measurements.

It has been observed that the initial amplitude of the normalized intensity autocorrelation function of the scattered light, *i.e.*, $g^{(2)}(0)$, is drastically reduced going from the "sol" to the "gel" state for actin–heavymeromyosin complexes[1] and agarose.[2] For freely diffusing particles, the normalized intensity autocorrelation function may be written as[3]

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2 = 1 + \exp(-2DK^2\tau) \quad (1)$$

where $g^{(1)}(\tau)$ represents the normalized autocorrelation function of the optical field; D is the translational diffusional coefficient; K is the amplitude of the scattering vector, $(4\pi\eta_0/\lambda_0)\sin\theta/2$, where η_0 is equal to the refractive index of the scattering medium, λ_0 is the wavelength of the incident light in vacuum and θ is the scattering angle, and τ is the delay time.

Hence, the theoretical value of $g^{(2)}(0)$ from eq 1 is 2 for any scattered optical field that is Gaussian with zero mean. However, measured estimators of $g^{(2)}(\tau)$ are limited by incomplete spatial coherence at the detector so that experimentally, an instrument constant, α, should be included in eq 1 and in practice, $0 < \alpha < 1$.

$$g^{(2)}(\tau) - 1 = \alpha \exp(-2DK^2\tau) \quad (2)$$

α can be determined from measurements on polystyrene latex spheres or similar monodisperse free diffusing particles. Consequently, if $g^{(2)}(0) - 1$ for a scattering system is observed to be significantly less than α, as is the case for our measurements on gels so far, it may be concluded that the representation $g^{(1)}(\tau) = e^{-\Gamma\tau}$ is inadequate.

Carlson and Fraser[1] have proposed a simple modl for scattering molecules in the gel state which assumes each molecule as harmonically bound and executing Brownian motion. A collection of such identical, independent harmonically bound particles, each executing Brownian motion about a stationary mean position, is considered to be a simple model for a gel. It is reasonable to expect the gel particles, *i.e.*, the macromolecular chains, to execute only limited motions about a stationary mean, with the "harmonic" constraint provided by its closely packed neighbors. In the case of covalently cross-linked gels, the cross-links themselves may also affect the motions of the chains. Tanaka, Hocker, and Benedek[4] have developed a continuum theory for gels that makes no provision for the large static scattering due to spatial correlation of the Rayleigh scatterers which is usually observed in gels. In this paper, we present a revised version of the theory proposed by Carlson and Fraser and an experimental test of it. A sample of our experimental data was also fitted with an equation conforming to the continuum theory but with an added provision for the static scattering. The results are discussed in the last section.

Theory

Upon application of the Ornstein and Uhlenbeck distribution function for the highly overdamped case,[5] Carlson and Fraser have derived an expression for the normalized intensity autocorrelation function[1]

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\bar{I}^2} = 1 - \exp(-2\Gamma_0) + \exp(-2\Gamma_0\tau_0) \tag{3}$$

where $\Gamma_0 = DK^2/\gamma$, with γ (sec^{-1}) being the ratio of the chain elastic constant, k (dyn/cm), to the frictional constant, f (dyn sec/cm); and $\tau_0 = 1 - \exp(-\gamma\tau)$. However, in their calculations, uncorrelated Rayleigh scattering has been assumed which in effect has neglected the presence of a large component of static scattering by gels due to interparticulate interference[6] and microscopic inhomogeneities.[7] This additional component may act as a local heterodyning source which in turn may contribute to the lowering of the initial amplitude in addition to that due to constrained motion. We shall include in the intensity an additional term, I_x, which is time independent and essentially constant for scattering angles from 30 to 110° to account for the additional static scattering. Hence the average intensity may be expressed in terms of three components

$$\bar{I} = I_x + I_0 + I_s$$

where I_0 and I_s are the time independent and time dependent components from the constrained Brownian particles.[1] Expressing the static component as a fraction of the total intensity, $\beta = I_x/\bar{I}$, gives for the other two components

$$I_0 = (1 - \beta)\bar{I}\exp(-\Gamma_0) \tag{4}$$

$$I_s = (1 - \beta)\bar{I}[1 - \exp(-\Gamma_0)] \tag{5}$$

and the intensity autocorrelation function is

$$\langle I(t)I(t+\tau)\rangle = \langle [I_x + I_0 + I_s g_s^{(1)}(t)][I_x + I_0 + I_s g_s^{(1)}(t+\tau)]\rangle \tag{6}$$

where $g_s^{(1)}(\tau)$ has been shown to be[1]

$$g_s^{(1)}(\tau) = \frac{\exp(-\Gamma_0\tau_0) - \exp(-\Gamma_0)}{1 - \exp(-\Gamma_0)} \tag{7}$$

The final expression for the normalized intensity autocorrelation function and its initial amplitude after applying eq 4, 5, and 7 to 6 and performing the multiplications is

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\bar{I}^2} = 1 + 2\beta(1-\beta) \times [\exp(-\Gamma_0\tau_0) - \exp(-\Gamma_0)] - (1-\beta)^2\exp(-2\Gamma_0) + (1-\beta)^2\exp(-2\Gamma_0\tau_0) \tag{8}$$

$$g^{(2)}(0) = 1 + (1-\beta)^2 + 2\beta(1-\beta)[1 - \exp(-\Gamma_0)] - (1-\beta)^2\exp(-2\Gamma_0) \tag{9}$$

Of course, in the limit of ideal Rayleigh scatterers, $\beta \rightarrow 0$, the above expressions simplify to those derived by Carlson and Fraser.[1]

Consequently, intensity autocorrelation measurements at different angles should yield the frictional factor, f (or equivalently the diffusional coefficient, D), as well as the chain elastic constant, k. One may then apply Gaussian chain statistics to derive the theoretical shear modulus from the two parameters (see Discussion section).

A series of polyacrylamide gels copolymerized in water and ethylene glycol have been studied in order to test this model. For comparison, compression measurements were also performed on gels prepared from the same monomer mixtures to determine the moduli independently.

Experimental Section

Sample Preparation. The polyacrylamide gels were prepared by copolymerization of acrylamide (AC) and *N,N'*-methylenebisacrylamide (MBAC) (Eastman Kodak Co., N.Y., recrystallized) in water using ammonium persulfate and sodium bisulfite (Baker Chemical Co., N.J.) as initiators. Each monomeric mixture was purged with nitrogen and a portion of it was filtered through 0.22 μ Millipore filter paper directly into a 1-cm optical-glass cell (Hellma Cells, Inc., N.Y.) which has been prerinsed with refluxing acetone in a special apparatus for about 2 hr to eliminate dust.[8] The other portion was put into a cylindrical Teflon mould of about 1.7 cm in diameter and 1 cm in thickness. Then the samples were sealed and allowed to polymerize at room temperature (about 24°) for at least 24 hr before taking measurements. For sample 1506E with ethylene glycol rather than water as solvent, H_2O_2 was used as initiator and the temperature was regulated at 60° during polymerization. The gels so prepared were clear with no visual turbidity. As a control for free diffusion measurements, a 5% acrylamide aqueous solution with *no* cross-linking agent was allowed to polymerize at 45° using again the persulfate–bisulfite couple as initiator, resulting in a very viscous liquid (sample 500).

Unilateral Compression and Rayleigh Ratio Determination. The compression measurements and Rayleigh ratio determinations at small angles were performed at the Polymer Research Laboratory of Syracuse University. The procedures and instruments have been described by Wun and Prins.[7] The compressing Teflon plate was fitted with a motor-driven screw micrometer. The force was measured by means of an inductive transducer attached to a carrier wave amplifier and recorder. A recording was made of the force until a constant value was obtained in 2 to 4 hr. The modulus G was determined by a least-squares computer fit to the equation

$$\sigma_t = G[(L/L_0)^2 - (L_0/L)] \tag{10}$$

in which L_0 and L are the initial and compressed thickness of the sample respectively and σ_t is the true stress, *i.e.*, force per unit area of strained cross section: $A = A_0(L_0/L)$; the modulus is given by[9]

$$G = \nu q_0^{-2/3} q^{2/3} k_b T \tag{11}$$

where ν is the number of chains per cubic centimeter of gel; $q_0^{-2/3}$ is the ratio of the average chain dimension at the dry state to that of the unperturbed, swollen state, *i.e.*, $\langle r^2\rangle d/\langle r^2\rangle_{0,s}$ and is equivalent to the so-called isotropic dilation factor; q is the volume degree of swelling; k_b is the Boltzman constant; and T is the temperature in degrees Kelvin.

The Rayleigh ratio was determined by using the filtered solvent as a blank and its Rayleigh ratio subtracted from the gel data. Corrections for reflections, refractions, turbidity, and use of the neutral density filters were calculated as described by Stein[10] with the aid of a computer program to yield corrected Rayleigh ratios.

Intensity Autocorrelation Measurements. The light source was a He–Ne laser (Model 125, Spectra Physics, Mountainview, Calif) with a wavelength of 632.8 nm. The spectrometer and autocorrelator for our intensity autocorrelation mesurements have been described before.[11,12] Basic theoretical and technical information for this experimental technique has been reported by Foord, *et al.*,[13] and Jakeman, Oliver, and Pike.[14]

Results and Discussion

Figures 1 and 2 illustrate typical autocorrelation functions with varying initial amplitudes measured with the same collection optics. Sample 500, which is 5% polyacrylamide in aqueous solution, serves as a control for free diffusion and the measured $g^{(2)}(0)$ values are about the same as that for polystyrene latex particles for all scattering angles measured. Sample 506 (see footnote *a* in Table I for compositions of samples), which is a gel containing 6% (relative to monomer) of MBAC, has only about a third of the initial amplitude as that of sample 500 at 68° and only about ⅙ at 29°. In general, $g^{(2)}(0)$ of the gel samples measured decreases monotonically with decreasing scattering angles and is practically zero at angles below 20°. Such strong angular dependence of $g^{(2)}(0)$ at the range of scattering angles 20–110° seems to rule out the possibility that simple heterodyning with the local static scattering alone can account

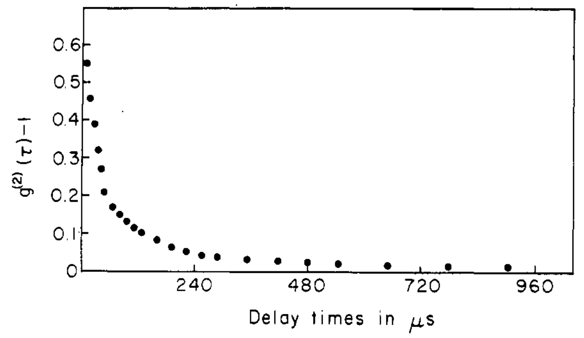

Figure 1. Sample intensity autocorrelation function of 5% polyacrylamide in aqueous solution (sample 500) measured at $\theta = 83°$, with the ordinate being normalized to the theoretical background (see text). All experiments were regulated at 25 ± 0.2°. The apparent diffusion coefficient is 3.3×10^{-7} cm^2/sec.

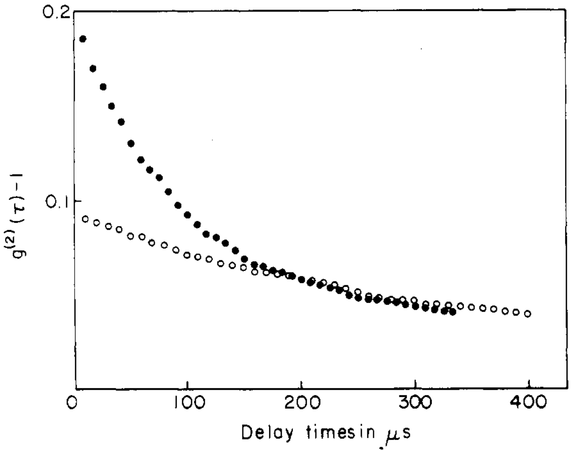

Figure 2. Sample intensity autocorrelation functions of 5% polyacrylamide gel (sample 506) at different scattering angles: (●) $\theta = 68°$; (○) $\theta = 29°$.

for the observed lowering of the initial amplitudes for as illustrated in Figure 3, the intensity appears to level off beyond 20°.

Figure 3 is a semilogarithmic plot of the Rayleigh ratios at $\theta = 2$ to 22° for sample 1506E. Its strong angular dependence at small angles indicates the presence of significant interparticulate and microscopic inhomogeneity effects as mentioned earlier. This is quite typical for scattering from gels.[7,15,16]

The two parameters β and D/γ in eq 9 can be deduced by measuring the initial amplitudes of the autocorrelation functions at two different scattering angles and normalizing with respect to the instrument constant α, determined to be 0.67 for our experimental conditions. The $g^{(2)}(0) - 1$ values are determined by extrapolation of the first point $\tau = 1$ to $\tau = 0$ and normalized with respect to the theoretical background given by the square of the total number of counts divided by the total number of measuring bins.[14] The random errors involved in measuring $g^{(2)}(0) - 1$ are determined to be 0.02 by repeated measurements. Also, the autocorrelation functions were observed to decay to the theoretical background to within 2% in all cases. Pairs of measurements at various angles for the same sample were used to iterate for sets of values of β and D/γ and they were found to agree with 5%. If one ignores any small difference between the bulk and local viscosities within a macromolecular network, then the chain elastic constant, k, can be calculated from a given value of D/γ, that is

$$\begin{aligned} D/\gamma &= (k_bT/f)/(k/f) \\ k &= k_bT/(D/\gamma) \end{aligned} \tag{12}$$

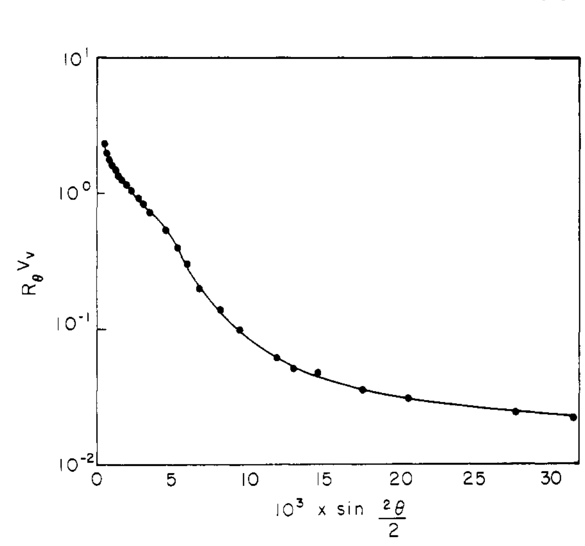

Figure 3. The logarithm of the Rayleigh ratios (measured with vertical polarizer and vertical analyzer) as a function of scattering angles. The range is 2–22°. The sample is 1506E. Note the strong angular dependence at small angles and its leveling off at higher angles.

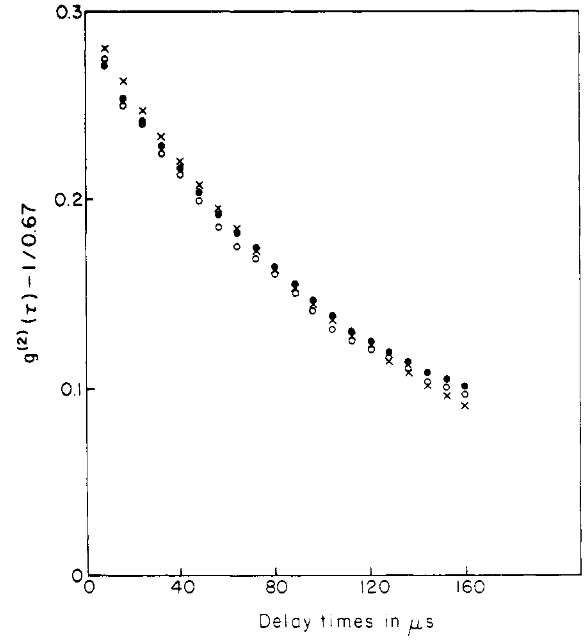

Figure 4. Comparison of the theoretical fits using eq 8 (●) and using eq 19 (×) to the experimental data (○) for sample 506 at $\theta = 68°$.

To determine D, or f, the data were iterated for a given D/γ until the deviations between the experimental and theoretical points for a set of D and γ values reached the minimum. The average deviation was found to be between 5 and 10%. Figure 4 illustrates a typical comparison of the two. The initial D values were determined by force fitting the data to single exponentials even though the cumulant analysis[17] as well as the variance ratio test[18] indicated that all the autocorrelation functions for the gel samples were not single exponentials.

To obtain an estimate of the storage or shear modulus from k, one notes that for a Gaussian chain, the retractive force, F, can be written as[19]

$$F = (\delta A/\delta r)_{T,V} = 3k_bTr/\langle r^2\rangle_0 \tag{13}$$

where A is the Helmoltz free energy, r is the end-to-end distance, and $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance of a Gaussian chain. Hence, for small de-

Table I
Summary of Results

Sample[a]	Chains/cm³ [b]	θ, deg	$g^{(2)}(0) - 1/0.67$	β	k, dyn/cm	f, (dyn sec)/cm	G_s, dyn/cm²	G, dyn/cm² [c]
256	1.17×10^{19}	104.8	0.97	0.52	2.48×10^{-4}	1.11×10^{-7}	5.8×10^{3}	
		90.0	0.94					
		28.7	0.51					
		25.4	0.40					
		21.9	0.39					
		14.8	0.31					
506	2.34×10^{19}	68.1	0.27	0.51	2.34×10^{-3}	9.36×10^{-8}	7.8×10^{4}	$(2.65 \pm 0.13) \times 10^{4}$
		28.7	0.14					
		21.9	0.054					
1506	7.02×10^{19}	104.8	0.23	0.35	14.0×10^{-3}	4.84×10^{-8}	3.6×10^{5}	$(1.36 \pm 0.07) \times 10^{5}$
		90.0	0.13					
		82.6	0.099					
1506E	7.02×10^{19}	103.8	0.88	0.51	4.34×10^{-3}	5.74×10^{-6}	4.4×10^{6}	$(8.17 \pm 0.40) \times 10^{5}$
		90.0	0.66					
		83.0	0.27					

[a] Samples 256, 506, and 1506 represent gels prepared by copolymerizing 2.5, 5.0, and 15 wt % acrylamide, respectively, in water, all having the same weight ratio of MBAC to AC in the mixture: 6 to 100. Sample 1506E has the same monomer and cross-linker composition as that of 1506 but the solvent is ethylene glycol instead. [b] The chain densities were estimated from the monomeric compositions assuming 100% conversion. [c] Sample 256 could not be obtained in a reasonably sturdy form for conventional compression measurement. For the other samples, the force was measured to within ±1/g and the length of ±0.01 mm.

formations, the Gaussian chain may be viewed as a spring with zero initial length with the elastic constant given by

$$k = 3k_bT/\langle r^2\rangle_0 \qquad (14)$$

The equilibrium storage modulus, G_s, of a network is in general very much dependent on the network structure. However, pertaining to the very crude approximation that the network is composed of a collection of identical Gaussian free chains (ν chains per cubic centimeter), the modulus may be expressed in terms of the chain elastic constant as[19,20]

$$G_s = k\nu\langle r^2\rangle_0/3 \qquad (15)$$

For an estimate of $\langle r^2\rangle_0$ from our data, it is noted for a random coil, in the absence of any excluded volume effect, the frictional constant is related to $\langle r^2\rangle_0$ by[21]

$$f = (0.271)(6\pi\eta_0)\langle r^2\rangle_0^{1/2} \qquad (16)$$

where η_0 is the viscosity of the medium and hence

$$G_s = k\nu f^2/78.3\eta_0^2 \qquad (17)$$

With recourse to eq 11, if one assumes that

$$q_0^{-2/3} = \langle r^2\rangle_d/\langle r^2\rangle_{0,s} \sim (V_d/V_s)^{2/3} = q^{-2/3} \qquad (18)$$

where V_d and V_s are the volume of the dry and swollen network respectively, the modulus G from compression measurements also approaches to the approximation by νk_bt, which then becomes equivalent to G_s. In general, some assumption has to be made regarding this so-called "memory parameter," $q_0^{-2/3}$, in order to derive any molecular parameter from equilibrium compression and swelling measurements on gels. Table I summarizes the results.

In comparing G_s (from light scatterings) and G (from compression measurements) in Table I, it is important to note that the chain density, ν, used in calculating G_s, was estimated from stoichiometry of the monomeric compositions assuming 100% conversion. In practice, of course, the conversion is seldom complete and the chain density is usually lower in the network formed which may account for the higher values of G_s compared to G. In fact, the much larger difference between G_s and G for sample 1506E may indicate that the copolymerization is much less efficient in ethylene glycol than in water as indeed the hydroxyl groups are known to be chain transfer agents for acrylamide polymerization.[22] Also much shorter chains would be formed in that case which explains why the modulus is higher than that in water. Using the permeability measurements on polyacrylamide gels by White,[23] one can also compare the frictional constants determined by the two independent methods, even though the cross-linker concentrations are slightly lower in his case (5% instead of 6%).

Table II
Comparison of Frictional Constants

Sample	f(this study)	f(White)
256	1.1×10^{-7}	1.3×10^{-7}
506	9.4×10^{-8}	5.7×10^{-8}
1506	4.8×10^{-8}	4.6×10^{-8}

The frictional constant within the same medium is higher for gels with lower concentration of cross-links because the effective dimension of the chain is larger. It is interesting to note that the fraction of static scattering β is lower the higher the concentration of the gel for a given solvent which is consistent with the observation of Wun and Prins[7] that for highly swollen gels, nonrandom cross-linking giving rise to large local fluctuations in refractive indices becomes the dominant contribution to light scattering. It was found that higher concentration of monomers or cross-linkers present during the cross-linking process led to less nonrandom cross-linking locally. While the usual concentration enhancement for Rayleigh scatterers is included in I_0 of eq 4, β, which is I_x/I, seems to reflect other contributions due to the spatial structure of the scattering elements.

In general, the gels contain macromolecular chains with broad distributions of sizes. It is implicitly assumed in our model that the whole network may be replaced by identical chains of the same average length while in principle, a distribution of diffusion coefficients or chain elastic constants

Table III

	D, cm^2/sec	$f = k_bT/D$, (dyn sec)/cm	β or B
Using eq 8	4.40×10^{-7}	9.36×10^{-8}	0.51
Using eq 19	3.16×10^{-7}	13.0×10^{-8}	0.83
Lit.value (Permeability measurement)[23]		5.7×10^{-8}	

should be incorporated into eq 8. However, such distribution is rarely known for gels. In view of the crudeness of our model at this stage and all the approximations involved in deducing the physical parameters, the results are encouraging.

Tanaka, Hocker, and Benedek have recently reported expressions for the light scattering of gels based on a continuum theory in which the effects of interparticulate interferences and microscopic inhomogeneities were neglected and the amplitude of the autocorrelation function was not considered. It has been demonstrated here that the additional static scattering due to the spatial structure in gels is not negligible. The autocorrelation functions for this series of gels and other hydrogels studied[24] were found to be *not* single exponentials according to the cumulant analysis and variance ratio test. However, it may be argued that it is this large portion of static scattering acting as a local heterodyning source which leads to the lowering of the initial amplitude of the autocorrelation function. This seems unlikely since we have observed a pronounced angular dependence of the initial amplitude between 20 and 110° (see Table I) while the time-averaged intensity tends to level off to an almost constant value at angles beyond 20° (see Figure 3). For better insights, a sample of our normalized data was fitted with the following equation

$$g^{(2)}(\tau) - 1/\alpha = 2B(1 - B)\exp(-DK^2\tau) + (1 - B)^2\exp(-2DK^2\tau) \quad (19)$$

which conforms with the theory proposed by Tanaka, Hocker, and Benedek[4] but with an added static fraction, B (analogous to β in eq 8), to account for the observed low $g^{(2)}(0)$ values, thus leading to a double-exponential expression for the intensity autocorrelation function. B was first determined by solving eq 19 at $\tau = 0$ with the corresponding initial amplitude value measured experimentally. Then the D value was iterated with eq 19 until the average deviation between the theoretical and experimental autocorrelation function was minimized. Figure 4 illustrates the comparison for sample 506 at $\theta = 68°$. In this case, the minimal average deviation from the experimental data (open circles) for using eq 8 (solid circles) and using eq 19 (crosses) is about the same (5 and 7%, respectively), but the shapes of the two functions are noticeably different. The parameters deduced from the two different fits are compared in Table III.

Our model constitutes an alternative corpuscular approach on the molecular level. It attributes the observed decrease in the initial amplitudes of the autocorrelation functions for gels to the decreasing amplitudes of diffusive motion of the macromolecules under the constraints of their nearby neighbors. An additional constant, the static contribution to the scattered intensity, is stipulated to account for the much higher level of static scattering observed for gels compared to polymers in solution. As our model is presently only concerned with the dynamical aspects of the gel systems, details of the static term which is related to the gel structure have not been considered. However, with the application of this model, a second physical parameter, the average elastic constant of the chains, can be derived from light intensity autocorrelation measurements in addition to the time constant. With further application of some statistical model for the macromolecular network, the equilibrium storage modulus may also be deduced from the elastic constant. Of course, how well a macroscopic parameter like the storage modulus can be deduced from the molecular parameter k depends on the adequacy of the network theory that one applies as well as the adequacy of this model. That the distribution of chain lengths within the gel system is usually broad and unknown constitutes a serious difficulty. Stipulating a Gaussian or other appropriate distribution function into the calculation might be an improvement. Another obvious improvement is to include also coupling of the motions of these harmonically bound particles. Studies on better characterized gel systems with uniform chain lengths and uniform chain distributions in space will also be more illuminating. This is presently under consideration in our laboratory.

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