Dynamics of Cellulose Whiskers Spatially Trapped in Agarose Hydrogels

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ABSTRACT: The motion of cellulose whiskers trapped in agarose hydrogels is measured by depolarized dynamic light scattering (DDLS) under conditions of optical heterodyning, in which the rigid polymer network provides a static depolarized reference signal. At low concentration in free suspension, the rotational relaxation rate Θ of the whiskers is decoupled from the osmotic properties of the suspension. When incorporated inside a gel, however, as the agarose concentration increases, Θ first increases beyond that in the free suspension, reflecting a reduced amplitude of rotational fluctuations of the whiskers due to the repulsive interactions with their surroundings. At the same time, the dynamic light scattering Rayleigh ratio R_{VH} obtained from DDLS decreases with increasing gel concentration. At high gel concentrations, however, Θ tends to decrease due to the steric hindrance of the network. Except at the lowest whisker concentrations, Θ is governed by the same fluctuations as those associated with R_{VH}.

Introduction

The motion of molecules in confined media is of interest both from a theoretical standpoint[1−7] and for practical applications, which range from chromatography to drug release. When large molecules are trapped inside a swollen network, their rate of translational diffusion tends to decrease. Dynamic light scattering (DLS) studies show that this reduction stems from entropy loss due to the restriction in configuration space, rather than from increased hydrodynamic friction.[7] On the other hand, for the rotational properties of large trapped anisotropic particles, equivalent information is lacking. Theoretical models predict that the rotational diffusion rate of confined molecules should decrease.[1,3] In free suspensions, depolarized dynamic light scattering (DDLS) has been used to study tobacco mosaic virus (TMV) and copolymer micelles,[8] while the rotational motion of short chains has been measured by interferometry.[9] In these cases the relaxation rate increased with increasing concentration. This counterintuitive behavior was attributed to long-range electrostatic interactions between the molecules. Earlier, Ouano and Pecora[10] found that the small molecule chlorobenzene, when trapped in poly(methyl methacrylate), displays two rotational relaxation rates, one of which is similar to that in free chlorobenzene; the second, corresponding to sites with a smaller cage, is significantly faster. The correlation time of the more confined molecules is reduced because they execute only small angular fluctuations before striking their cage wall.

In this article we discuss the rotational and translational dynamics of rodlike particles (cellulose whiskers) in a confined medium. These highly anisotropic crystallites are stabilized by sulfate groups at the surface via attractive/repulsive electrical double-layer forces.[11] Trapped in a rigid gel, their translational dynamics has been investigated by DLS.[12] In free suspension, the rotational properties of cellulose whiskers have previously been explored with DLS[13] and transient electric birefringence.[14]

Agarose hydrogels are composed of rigid bundles of chains whose motion is effectively frozen; although this system scatters light strongly, the dynamic component is vanishingly small. In a dynamic light scattering measurement, therefore, the intrinsically static structure of the agarose network provides a constant reference signal that heterodynes the light scattered by the motion of guest molecules in the gel. In ref 12, it was found that the product of the translational diffusion coefficient D and the fluctuating polarized scattered intensity R_V was independent of the gel concentration as long as the length of the whiskers was smaller than the mesh size of the agarose network. As the average mesh size becomes smaller with increasing agarose concentration, for a given length of rodlike particle, the quantity $R_V D$ was observed to decrease, showing that in this regime frictional effects begin to be felt.

For rotational diffusion, the situation is different, since the rotation of anisotropic molecules in free suspension is in principle unrelated to their light scattering intensity. The same assertion is not necessarily true, however, when such molecules are spatially confined. The effect of coupling of large molecules to their surroundings remains an unresolved issue. Cush et al.[15] found that the rotational diffusion coefficient of TMV in solutions of un-cross-linked dextran decreases monotonically with dextran concentration. These authors, however, did not report corresponding measurements of the scattered intensity. It is easy to imagine, following ref 10, that large anisotropic molecules could undergo restricted angular rotation before they encounter the surrounding matrix; further rotation would occur with a time constant that depends only on the gel relaxation. In this paper DDLS measurements are reported on the rotational diffusion of whiskers trapped in an agarose gel, the structure of which does not relax. To separate hydrodynamic from thermodynamic effects in such a motion, measurements must be made both of the rotational relaxation rate and of the scattering intensity.

For DDLS in gels, a first requirement is to ascertain whether the conditions of optical heterodyning that usually prevail in

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dynamic light scattering measurements from gels are relevant to depolarized light. In their measurements of TMV dispersed in dextran, Cush et al. elegantly sidestepped this difficulty, as the depolarized light from the matrix, due to the optical activity of the dextran, was much weaker than that scattered by the TMV.[15] In general, however, it is a basic requirement of heterodyning that the electric fields of the signal and the reference have the same polarization. In standard DLS experiments on polymer gels, the light scattered by the guest molecules is optically heterodyned by that scattered by the network, since both retain the same polarization as the incident light. In a depolarized light scattering experiment the situation is less clear since the polarization of the light scattered by the network is undetermined. For the special case of zero angle scattering optical heterodyning with depolarized light can be achieved, since the local oscillator may be provided either by the light scattered by immobilized anisotropic particles[16] or, artificially, by inserting a quarter wave plate between the sample and the analyzer.[17] To our knowledge, however, no measurements have been reported at large scattering angles from highly anisotropic (and highly depolarizing) particles such as whiskers. After a brief outline of the theoretical and experimental aspects of the present investigation, therefore, the first part of this paper is devoted to investigating the heterodyning of light scattered from gels in depolarized conditions.

Theoretical Background

In normal DLS measurements on gels the incident light is polarized vertically, while the detector receives scattered light with all polarizations (V geometry). The resulting fluctuating electric field $\mathbf{E}_f(t)$ scattered by mobile guest molecules in the gel is mixed with the static field from the network, $\mathbf{E}_s$, giving for the total scattered light intensity

$$I_{tot}(t) = I_V(t) + I_s + \mathbf{E}_s\cdot\mathbf{E}_f^*(t) + \mathbf{E}_s^*\cdot\mathbf{E}_f(t) \quad (1)$$

where $I_V(t) = \mathbf{E}_f(t)\cdot\mathbf{E}_f^*(t)$, $I_s = \mathbf{E}_s\cdot\mathbf{E}_s^*$, and the asterisk denotes the complex conjugate. For simplicity, it is assumed that the static light intensity I_s from the gel is constant during the observation time.

For the depolarized configuration (VH geometry), in which a horizontally adjusted analyzer is placed before the detector, two different situations can arise. In the first, I_s is composed only of vertically polarized light, transmitted, for example, by the imperfections of the analyzer. The horizontally polarized electric field from the dynamic component, $\mathbf{E}_f$, is then orthogonal to $\mathbf{E}_s$, i.e.,

$$\mathbf{E}_s\cdot\mathbf{E}_f^*(t) = E_sE_f^*(t)\cos\phi \quad (2)$$

where ϕ, the angle between the polarization of the fluctuating and the static fields, is $\pi/2$. In this case, the last two terms in eq 1 are identically zero. The normalized intensity correlation function then becomes

$$G_{inc}(\tau) = [I_s^2 + 2I_s\langle I_{VH}\rangle + \langle I_{VH}\rangle^2(1 + \beta g^2(\tau))]/\langle I_{tot}\rangle^2 = 1 + X^2\beta\, g^2(\tau) \quad (3)$$

where $X = \langle I_{VH}\rangle/I_{total}$, $I_{VH}(t) = E_f(t)E_f^*(t)$, with $I_{total} = \langle I_{VH}\rangle + I_s$, β is the optical coherence factor of the detection, and $g(\tau)$ is the field correlation function. The angular brackets denote time averages. Equation 3 is an expression of the Siegert relation

$$G(\tau) = 1 + \beta|g(\tau)|^2 \quad (4)$$

which applies when the electric field is a zero-average Gaussian variable, i.e., when there is no static field with a constant phase. The factor $X^2 < 1$ in eq 3 implies that an incoherent light source is also present in addition to the fluctuating field.

A second situation occurs when the gel matrix scatters enough depolarized light to mix coherently with that from the mobile guest (i.e., the cellulose whiskers). The normalized coherent intensity correlation function $G_{coh}(\tau)$, calculated from eq 1, is then given by the expression for heterodyne mixing with polarized light[18]

$$G_{coh}(\tau) = 1 + \beta[2X(1 - X)g(\tau)|\cos\phi| + X^2g^2(\tau)] \quad (5)$$

where X is found from the condition $g(0) = 1$. Equation 5 differs from the standard expression in that the heterodyne term explicitly includes the cosine of the angle between the polarization of the fluctuating and static fields. In the fully polarized situation, $\phi = 0$; equally, if the reference and the fluctuating field are both fully depolarized, $\phi = 0$. The last term in the square brackets in eq 5 (homodyne term) exhibits no ϕ dependence since it involves only the product of E_f by itself. The relative intensity of the dynamically scattered depolarized light is then given by

$$I_{VH} = X\langle I_{total}\rangle \sin\theta/Tr \quad (6)$$

where θ is the scattering angle and Tr is the transmittance of the sample. Normalizing I_{VH} with respect to the signal from a reference sample (toluene) yields the Rayleigh ratio of the depolarized dynamic light scattering

$$R_{VH} = I_{VH}R_{tol}/I_{VH,tol} \quad (7)$$

where R_{tol} and $I_{VH,tol}$ are respectively the Rayleigh ratio and the relative scattering intensity of toluene measured in the same conditions. According to whether X obeys eq 3 or eq 5, different values of R_{VH} are obtained. Comparison of these values therefore constitutes a test of the coherence or otherwise of I_s.

Owing to polydispersity, the field correlation functions $g(\tau)$ of the whisker samples investigated here were not single-exponential decays. For this reason, the relaxation rate was defined by the first cumulant

$$\Gamma = -\mathrm{d}[\ln(g(\tau))]/\mathrm{d}\tau|_{\tau\to 0} \quad (8)$$

Since $g(\tau)$ is determined by its functional relationship to $G(\tau)$, the apparent diffusion coefficient $D_{app} = \Gamma/q^2$ also depends on whether $g(\tau)$ obeys eq 3 or eq 5. This provides a further test of the coherence of I_s.

Experimental Section

Whisker/agarose gels were prepared in 10 mm diameter thin wall glass tubes, using deionized water as reported previously.[12] Whiskers in agarose gels of concentrations $c_{gel} = 0$, 2, 6, and 16 g/L were studied. To avoid effects of phase separation, and also due to the very low signals, higher values of c_{gel} were not investigated.

Depolarized dynamic light scattering measurements were made at 25 °C with a Glan-Thompson analyzer (extinction coefficient better than 10^{-5}), an ALV-5000 multi-tau correlator, and a Spectra Physics 2020 laser operating at 488 nm. Measurements were made at scattering angles between 30° and 140°. Tests for heterodyning were made with an ALV 5022F goniometer equipped with fiber-optic coupling and an avalanche diode, working with a 22 mW HeNe laser. Depolarization ratios for various free whisker concentrations and angles between 30° and 140° were measured with a Brookhaven BI-200 spectrogoniometer and a Coherent laser operat-

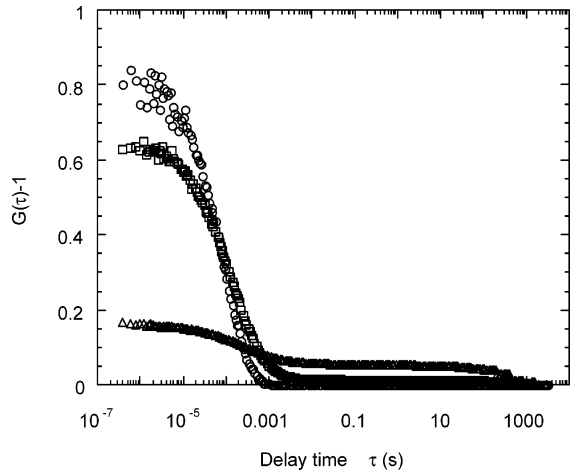

Figure 1. Reduced depolarized intensity correlation functions $G(\tau) - 1$ at the same whisker content $c_w = 0.2$ g/L for free whisker suspension (○) and for whiskers in the gel (□, $c_{gel} = 2$ g/L; Δ, $c_{gel} = 6$ g/L). Scattering angle $\theta = 90°$.

ing at 633 nm. On extrapolation to zero concentration, the value found for the depolarization ratio was 0.021, a result that is an order of magnitude greater than for TMV.[15]

Results and Discussion

In the system studied here, agarose, like dextran,[15] is optically active, the value of the activity coefficient being $[\alpha] = -49°$ at 589 nm.[19] This yields a rotation of the polarization in the forward direction of about −1.7 arc minutes for an agarose solution of concentration 6 g/L when the optical path is 10 mm. In the gel state, however, since the intrinsic optical activity is negligible compared to that due to the random domain structure of the network, the resulting rotation is random and much larger. For a 6 g/L gel, for example, in an average of 10 different sample positions the rotation of the polarization at 90° scattering angle was determined to be $-0.1 \pm 2.9°$. A similar dispersion was found for a whisker-free gel with an agarose concentration of 18 g/L. These results therefore suggest, in the present experiments, that random optical activity of the gel matrix and immobilized clusters of whiskers trapped in the gel may both contribute to the horizontally polarized heterodyning reference field $\mathbf{E}_s$.

Reduced intensity correlation functions $G(\tau) - 1$ in VH mode are shown in Figure 1 for three samples with the same whisker concentration ($c_w = 0.2$ g/L), in free suspension, and trapped in two agarose gels ($c_{gel} = 2$ and 6 g/L). The relaxation times lie between 10^{-4} and 10^{-3} s. For the 6 g/L sample, the long relaxation time of about 100 s is due to slow changes in the static speckle pattern of the gel that are unrelated to the fluctuations of the whiskers of interest here. This feature is subtracted from the field correlation function before evaluating the cumulant in expression 8. The value of $G(0) - 1$, which depends on the sample and on its position, is smaller than the coherence factor β of the optics ($\beta = 0.80$ in VH). Reduced initial values of $G(\tau)$ are a symptom of optical heterodyning but do not constitute a proof of it.

Figure 2 shows the results of measurements made at 90° scattering angle on a 6 g/L agarose gel with whisker concentration 0.1 g/l, obtained by rotating the sample in the goniometer housing to positions of differing speckle brightness. In Figure 2a the values of the fraction of dynamically scattered light, $X = \langle I_{VH} \rangle / I_{total}$, are plotted, calculated for each speckle from eq 5 and assuming $\phi = 0$. In Figure 2b the corresponding dynamic intensity measurements R_{VH} are shown, using either eq 3 or eq

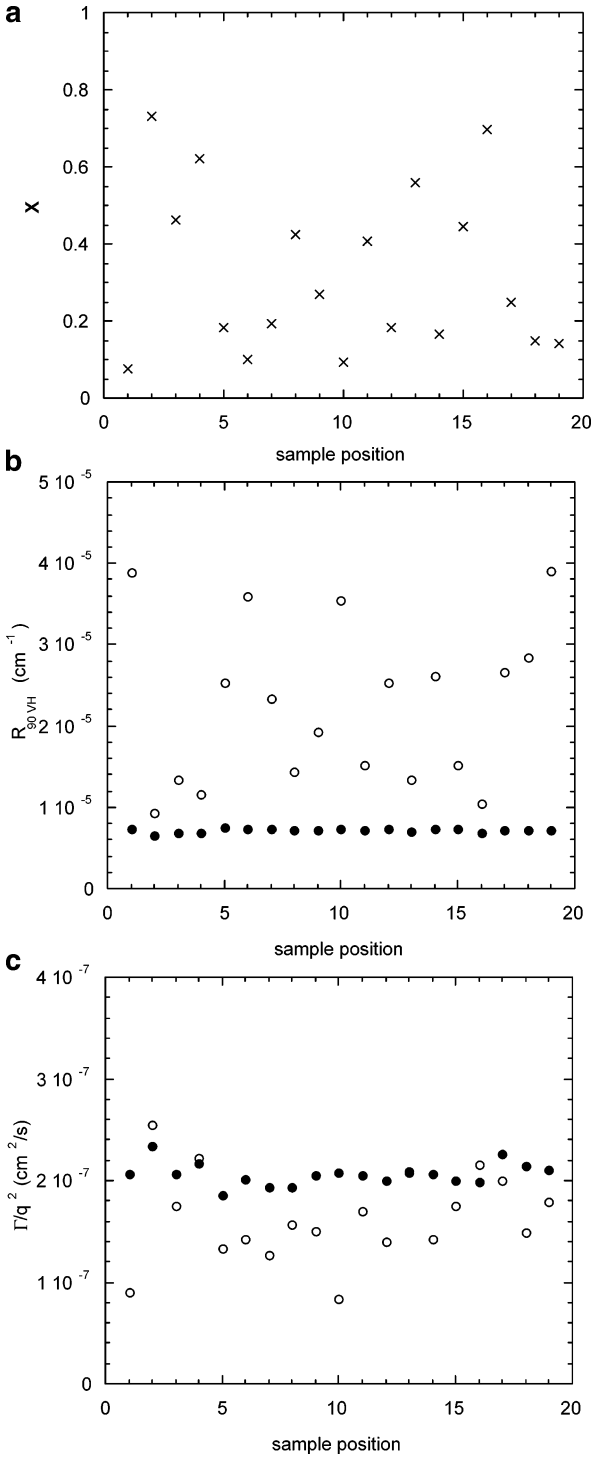

Figure 2. (a) Values of dynamic intensity ratio $X = \langle I_{VH} \rangle / I_{total}$, measured at 90° for different sample positions in an agarose gel with $c_w = 0.1$ g/L and $c_{gel} = 6$ g/L. (b) Depolarized dynamic scattering intensity R_{VH} calculated for these positions using eq 3 (○) and eq 5 (●). (c) Effective diffusion coefficient Γ/q^2 deduced from the same depolarized scattering measurements at 90° for the different sample positions. Data analyzed using eq 3 (○) and eq 5 (●).

5. The consistency of the results obtained from eq 5 shows that the field of the local oscillator is fully coherent. In Figure 2c a similar result is found from the variation of Γ/q^2 as a function of sample position. (Note that for two points (1,10) in Figure 2c the ratio of Γ/q^2 is slightly greater than 2, while for three others (2, 4, 16) it is slightly less than unity. These deviations from the theoretical range (≥ 1, ≤ 2) are due to small differences in the way the cumulants were evaluated in eqs 3 and 5.) The

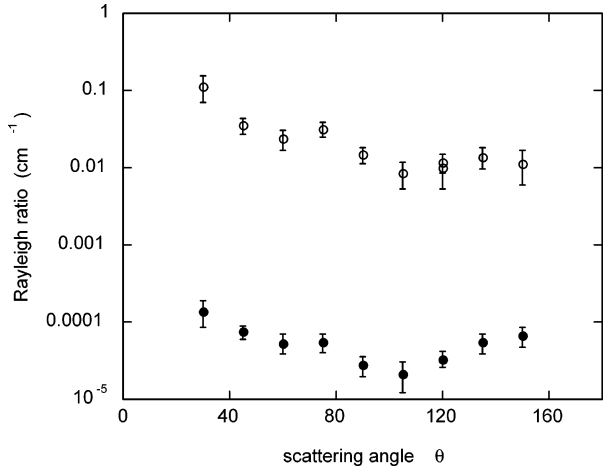

Figure 3. Scattering intensity from 6 g/L whisker-free agarose gel in V (○) and VH geometry (●) as a function of scattering angle. Each point is an average of 10 measurements taken for different discrete sample positions. The error bars are the standard deviations corresponding to each data set.

reduced scatter obtained with eq 5 confirms the coherence of the static component. It follows that in these experiments the local oscillator field E_s is the depolarized light scattered directly from the gel matrix itself.

Figure 3 shows the integrated intensity scattered by a whisker-free agarose gel of concentration 6 g/L. For each scattering angle θ the points are averages over 10 different sample positions. In the absence of analyzer (V geometry, open circles) the signal is 3 orders of magnitude larger than that with an analyzer adjusted with its polarization axis in the horizontal plane (VH geometry, filled circles). Comparison of Figures 2b and 3 shows that the residual intensity of static depolarized light is sufficient to heterodyne the dynamic component when whiskers are present.

To place the present discussion in the perspective of nonergodicity, a digression is appropriate here. This question, raised more than a decade ago,[20,21] is concerned with restricted motion of the scattering centers in partially free systems such as gels. It was pointed out that if the scattering centers in a gel execute limited excursions of amplitude δ around their mean position, then only a small number of configurations in phase space are explored. The corresponding fluctuations in the phase of the scattered electric field, $q\delta$, are then insufficient, by time averaging alone, to ensure proper statistical averaging for the diffusion coefficient of the particles to be deduced. The remedy consists in making a spatial (ensemble) average over observations from a large number of different positions of the sample. The debate on nonergodicity, however, diverted attention from the underlying physics of the molecular motions in gels. In particular, it has not been widely understood why in many cases the heterodyne approach, such as employed in the present and in previous articles, yields consistent and satisfactory results for the dynamics of gels without resorting to the machinery of ensemble averaging.[6,7,12]

Although the topic merits a more extensive discussion than can be given here, a brief explanation is in order. First, it must be emphasized that the model of a polymer gel consisting of identical scattering centers, each undergoing restricted diffusion, bears little resemblance to the structure of most real polymer gels. When swollen in a diluent, soft polymer gels exert an osmotic swelling pressure by virtue of their mobile network chains. Although each chain is limited in the amplitude of its spatial excursion, the strong overlap among chains belonging to different cross-link nodes makes them indistinguishable. A scattering experiment on such a system is therefore incapable of distinguishing between the motion of one tethered chain segment and that of its neighbor. In other words, the network chains appear to be able to migrate throughout the sample and are hence effectively ergodic. At distance scales larger than the correlation length of these local motions, however, cross-links, or more generally clusters of cross-links, which account for their solidlike properties, give rise to the characteristic static speckle pattern of gels. Since these clusters neither overlap nor mutually interpenetrate, they are nonergodic, and ensemble averaging becomes essential if they are the subject of the investigation. Such averaging yields the full intermediate scattering function of the sample. In some cases, however, e.g. when it is required to investigate the dynamics of a sample, the properties of the clusters are of secondary interest since, as their low mobility implies, their contribution to the overall osmotic properties of the gel is insignificant.

A second aspect of this discussion has to do with distinguishable particles trapped in the gel that execute limited spatial excursions, with correspondingly small phase shifts $q\delta \leq 1$ in their scattered electric field. Naturally, if only a small number of such particles is present in the scattering volume, the scattered field explores only a limited region of q-space. An ensemble average of the intensity correlation function is then indeed necessary. In many cases of particles trapped in gels, however, including the system studied here, the scattering volume (usually about 10^6 μm^3) contributing to the observed coherence area contains a very large number of such particles, each contributing a fluctuating field with a different phase according to its mean position $\mathbf{r}_j$. For example, at the lowest concentration of whiskers measured in this investigation, the scattering volume contains several million particles. Provided that the phase fluctuation $q\delta_j$ of each whisker j is independent and not vanishingly small, as their number increases the total resultant field from all the moving particles quickly tends to the sum of a constant field, plus a zero-mean fluctuating field whose phase spans many radians. In such a case, the fluctuating field observed at each value of q is thus already a (micro)ensemble average, even if it is accompanied by an additional static (nonergodic) field from the gel inhomogeneities. To measure the dynamics of such a system, further ensemble averaging is not necessary. To measure the static component, however, full ensemble averaging over the whole sample is of course required. For completeness, it should be added that an underlying assumption in this procedure is that the composition of the observed scattering volume is representative of the whole sample; i.e., phase separation does not occur. The above argument implies that the need for ensemble averaging in gels may be less general than is commonly believed.

Returning to the present measurements, Figure 4 shows the angular dependence of the relaxation rate Γ at the same whisker concentration, both in free suspension and in two concentrations of gel. The relaxation rate Γ of the depolarized light is[22]

$$\Gamma = Dq^2 + 6\Theta \tag{9}$$

where Θ is the rotational diffusion coefficient of the whisker rods. In confined or concentrated systems, the assumption of decoupling between translational and rotational motion, inherent in eq 9, fails. It was shown in ref 3, however, that this assumption nevertheless remains valid at short times τ. As the first cumulant Γ is defined in eq 8 for the limit $\tau \rightarrow 0$, it seems reasonable to expect that eq 9 is a satisfactory approximation. As can be seen in Figure 5, for the three whisker concentrations,

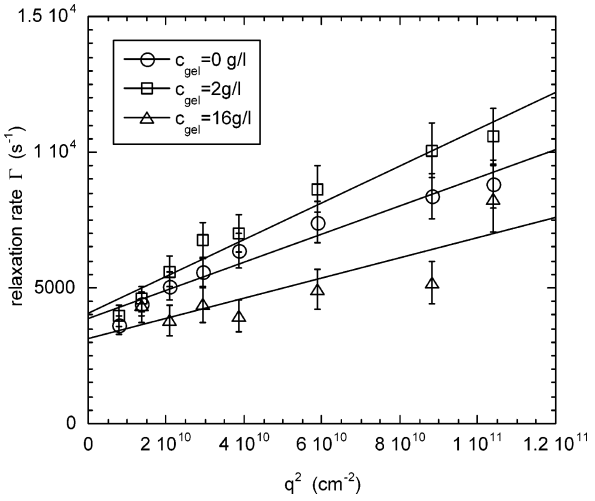

Figure 4. Relaxation rate Γ of the first cumulant plotted as a function of q^2 at the same whisker content $c_w = 3.25$ g/L.

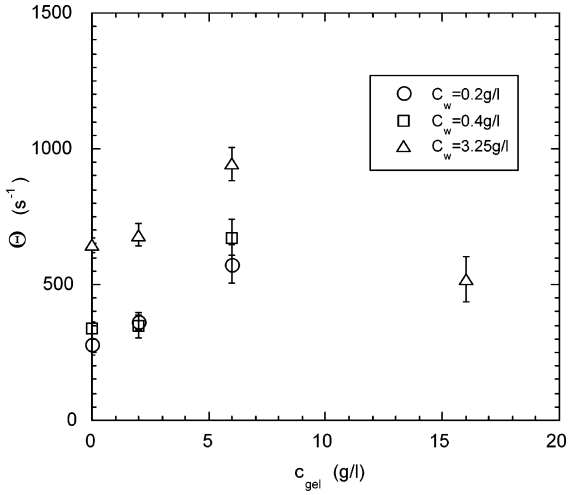

Figure 5. Variation of rotational diffusion coefficient Θ with agarose concentration c_{gel}: ○, $c_w = 0.2$ g/L; □, $c_w = 0.4$ g/L; △, $c_w = 3.25$ g/L.

Table 1. Rotational (Θ) and Translational (*D*) Diffusion Coefficients at Infinite Dilution from VH and VV Geometry, and Average Whisker Length *L* and Diameter *d*, Calculated from Broersma[23] and Tirado[24] (Precision in Θ ca. 10%)

agarose concn			Broersma		Tirado	
c_{gel} (g L^{-1})	Θ (s^{-1})	D (cm^2 s^{-1})	L (nm)	d (nm)	L (nm)	d (nm)
0	309	5.5×10^{-8}	356	7.5	347	10.2
2	356	6.0×10^{-8}	349	5.7	341	7.6

Θ initially increases with increasing agarose concentration c_{gel}. Only at high gel concentration does it start to decrease due to steric hindrance from the network. In the present case, confinement of the whiskers in the gel matrix by exclusion from regions of small pore size increases their concentration elsewhere, thereby enhancing the repulsion between the individual particles and causing the rotational diffusion rate to increase.[8−10] Similarly, at low whisker concentrations, Θ is independent of c_w, but it increases at high c_w where repulsive interactions become significant. This result is consistent with measurements made in a lower range of c_w,[11] where interparticle interactions are weaker.

Table 1 lists the values of the effective length L and diameter d of the whiskers calculated from Θ and D using the theories of Broersma[23] and Tirado[24] for cylindrical rods. Although Tirado's expressions are expected to be valid for $2 \leq L/d \leq 30$, the values of L and d obtained using these relations agree well with those found from Broersma's model. We also note that comparison with the length of the single cotton whiskers found from electron microscopy ($L = 170$ nm)[25] indicates that this batch of whiskers is on average aggregated.

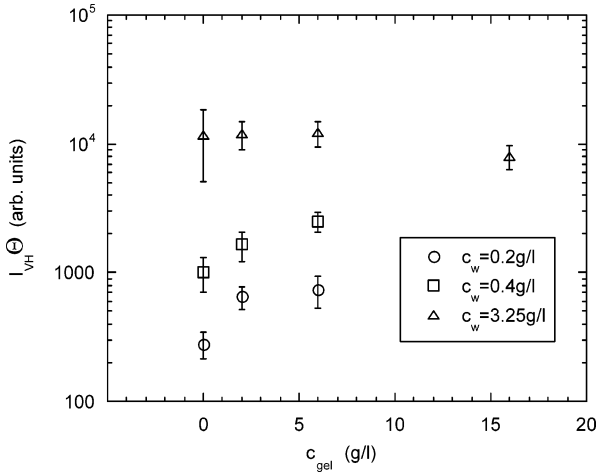

Figure 6. Variation of $I_{VH}\Theta$ with agarose concentration c_{gel}. In the free suspension ($c_{gel} = 0$), $I_{VH}\Theta$ is an increasing function of c_w (○, $c_w = 0.2$ g/L; □, $c_w = 0.4$ g/L; △, $c_w = 3.25$ g/L).

In polarized light scattering a relationship holds between the mutual diffusion coefficient D for an assembly of interacting particles and the Rayleigh ratio of the scattered light R_V, which can be expressed in the form[26,27]

$$R_V D = Kc(\partial c/\partial \Pi)(\partial \Pi/\partial c)/f = Kc/f \qquad (10)$$

Here, K is the light scattering contrast factor, c the mass concentration, and f the friction coefficient of the interacting particles in the solution. The product $R_V D$ is thus independent of the osmotic susceptibility $\partial c/\partial \Pi$.

In the case of rotational diffusion the situation is different: the intensity of depolarized light scattered by dilute suspensions of anisotropic molecules depends only on their concentration and is independent of their rate of rotation. In the free suspension the intensity of the dynamically scattered depolarized light cannot exceed that for complete end-over-end tumbling of the particles. With increasing concentration, however, coupling between molecules develops. Spatial confinement due to neighboring whiskers or to the surrounding gel matrix restricts the amplitude of their rotational motion, thus reducing the intensity of the dynamically depolarized light. Under these conditions, it becomes reasonable to propose a relation analogous to eq 10, namely

$$R_{VH}\Theta = K_{VH}c_w/f_r \qquad (11)$$

where the subscripts VH and r refer to depolarized light scattering and to rotational motion and where c_w is the concentration of the anisotropic particles in suspension. In eq 11 it is indifferent whether the dynamic scattering intensity I_{VH} or the toluene-normalized quantity R_{VH} is used, the only difference being in the value of the proportionality constant K_{VH}. Figure 6 shows how the product of the intensity and the rotational diffusion coefficient, $I_{VH}\Theta$, depends on the agarose concentration c_{gel} as well as on the whisker concentration c_w. These results are summarized in Figure 7, where the normalized quantity $I_{VH}\Theta/c_w = K_{VH}/f_r$ is plotted as a function of $c_{gel} + kc_w$. In this representation, the multiplying factor k for c_w in the coordinate variable is chosen to reveal the trend below the

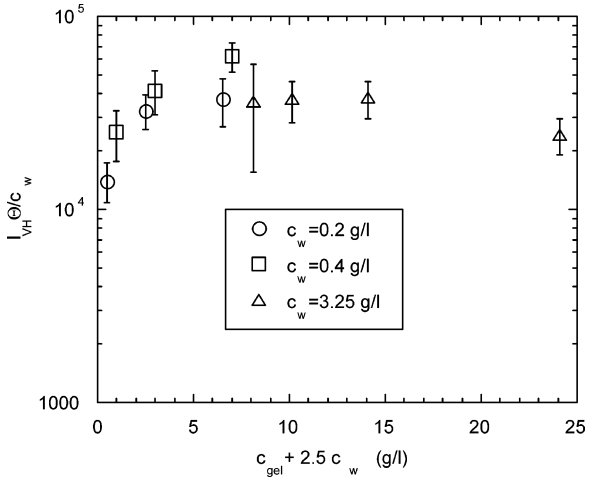

Figure 7. Variation of $I_{VH}\Theta/c_w$ with total concentration $c_{gel} + 2.5c_w$: ○, $c_w = 0.2$ g/L; □, $c_w = 0.4$ g/L; △, $c_w = 3.25$ g/L.

plateau behavior. Above $c_w \approx c_{gel}/k$, the plateau behavior of $I_{VH}\Theta/c_w$ shows that it is independent both of the gel concentration c_{gel} and of the whisker concentration c_w. This threshold behavior applies both to whiskers trapped in the gel as well as to those in the most concentrated free whisker suspension. At the highest agarose concentration ($c_{gel} = 16$ g/L), however, frictional forces between the whiskers and the network become significant, thus yielding a smaller value of $I_{VH}\Theta/c_w$ for this point. It is notable that a similar increase in the friction coefficient was found for the translational diffusion of whiskers in agarose gels at $c_{gel} \geq 10$ g/L.[12] In Figure 7 it can also be seen that for free suspensions at low whisker concentration $I_{VH}\Theta/c_w$ also falls below the plateau value. This result is consistent with free whisker rotation in dilute suspensions, where electrostatic repulsion from neighboring particles is negligible. In more concentrated suspensions, and in the gels, a change of regime occurs in which interparticle interactions dominate the osmotic pressure and, by limiting the available volume, control the rotational relaxation rate. The picture that emerges from these observations is that whiskers trapped in the gel undergo angular fluctuations of limited amplitude. As the size of their cage becomes smaller with increasing gel concentration, the amplitude of the fluctuations (i.e., the depolarized scattering intensity) diminishes, and the collision rate with the cage walls (i.e., the apparent rotational diffusion coefficient) accordingly increases. This implies a situation in which full rotation of the whiskers occurs rarely or not at all. The present results thus appear to be more consistent with the model of limited angular rotation of Ouano and Pecora[10] rather than the theoretical models in which the rotation is complete but merely slowed.[1,3]

Conclusions

When cellulose whiskers are trapped in a gel (agarose hydrogel), the light scattered by the whiskers is heterodyned by depolarized light from the agarose network. The rotational relaxation rate Θ of the whiskers increases with increasing concentration of both the whiskers and the gel. In contrast, the depolarized dynamic scattering intensity I_{VH} decreases with increasing gel concentration. The principal finding of this investigation is that over an extended range of gel concentration the quantity $I_{VH}\Theta/c_w$ is independent of the agarose concentration. The amplitude of the restricted angular rotation of the whiskers confined in the gel is thus inversely proportional to their relaxation rate. In the free suspension above a certain threshold concentration c_w the same plateau behavior is also observed for $I_{VH}\Theta/c_w$; at low c_w the rotational relaxation rate Θ remains independent of I_{VH}. At high agarose concentrations, however, $I_{VH}\Theta/c_w$ starts to decrease due to the steric hindrance of the matrix.

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