Rayleigh scattering and flow birefringence measurement in colloidal solutions

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(Received 13 November 2003; published 14 January 2005)

A unique method for measuring the birefringence intensity of colloidal solutions which become anisotropic under the action of orienting flow is described. When a laser beam crosses a liquid-containing asymmetrical particle orientated by the flow, the scattered intensity in a direction perpendicular to the wave vector of the incident light shows nodes and antinodes. The distance between two antinodes is related to the phase difference between the eigenpolarizations of the medium and thus to the birefringence of the medium.

DOI: 10.1103/PhysRevE.71.011503 PACS number(s): 83.50.Ax, 42.25.Lc, 71.15.Ap

In a perfectly transparent and homogeneous medium, a plane wave will propagate in the direction of its wave vector without diffusion on the sides. When the medium contains particles or small regions, the index of refraction of which is slightly different from the index of the surrounding medium, the optical homogeneity is lost: light will not only propagate in the direction of the wave vector $\boldsymbol{k}$ but will be scattered in every direction in space according to Rayleigh theory.

This scattering phenomenon is also observed in colloidal solutions of anisotropic particles. When subjected to the action of orienting flows, and when the particles also have an asymmetrical shape, the solution becomes anisotropic and shows flow-induced birefringence. Although the scattering and the birefringence both result from the polarization of the medium under the action of the incident field $\boldsymbol{E}_i$ and thus might be correlated, we shall assume that the field in the anisotropic medium is the sum of an elliptical vibration propagating in the same direction as the light incident on the medium plus the scattered field. The linearity of Maxwell's equation allows to treat separately the two phenomena.

Our aim is to find the amplitude, or the intensity of the scattered light, in a medium propagating an elliptical vibration. To do so we have to solve Maxwell's equation in the medium that we shall assume to consist of a homogeneous isotropic medium (refraction index n_1, permittivity ϵ_1) containing anisotropic particles (principal indexes of refraction tensor $\boldsymbol{n}_p$ and principal permittivities tensor $\boldsymbol{\epsilon}_p$). To solve this problem we shall simply follow the development given by Fuller [1] for anisotropic particles in vacuum. We assume that the time dependence of the electric field $\boldsymbol{E}_i$ is a harmonic function of t and that the space is free of charges; The amplitude of the scattered field is given by

$$\boldsymbol{E}_S = k_1^2 \int_V d\boldsymbol{x}' \frac{\exp ik_1 r}{4\pi r} \exp(-ik_S \cdot \boldsymbol{x}')(\boldsymbol{I} - \boldsymbol{uu}) \times [n_r^2(\boldsymbol{x}') - \boldsymbol{I}]\boldsymbol{E}(\boldsymbol{x}'). \quad (1)$$

k_1 is the magnitude of the incident wave vector, $\boldsymbol{k}_S$ is the wave vector of the scattered field, and $\boldsymbol{k}_S = k_S \boldsymbol{u}$, where $\boldsymbol{u}$ is a unit vector. The distance between the particle and the point where the scattered wave is observed is r. $\boldsymbol{I}$ is the unit tensor and $\boldsymbol{n}_r$ the tensor of the relative refraction indexes of the particle,

$$\boldsymbol{n}_r = \frac{\boldsymbol{n}_p}{n_1} = \sqrt{\frac{\boldsymbol{\epsilon}_p}{\epsilon_1}}. \quad (2)$$

$\boldsymbol{E}(\boldsymbol{x}')$ is the internal field in the medium, sum of the incident field $\boldsymbol{E}_i(\boldsymbol{x}')$, and the field resulting from the polarization $\boldsymbol{E}'(\boldsymbol{x}')$. Replacing the index of refraction by the permittivity in Eq. (1), the vector $[\boldsymbol{n}_r^2(\boldsymbol{x}') - \boldsymbol{I}] \cdot \boldsymbol{E}(\boldsymbol{x}')$ becomes

$$\frac{1}{\epsilon_1}[\boldsymbol{\epsilon}(\boldsymbol{x}') - \boldsymbol{I}\epsilon_1]\boldsymbol{E}(\boldsymbol{x}'). \quad (3)$$

In Eq. (3) the term in brackets represents the excess of polarization due to presence of anisotropic particles in the isotropic substratum. We shall assume that the three principal indexes of the particle are not too different from the index of the surrounding medium n_1 so that

$$\frac{n_{pi}}{n_1} \simeq 1, \quad \text{where } i = 1,2,3.$$

In that case, following van de Hulst [2] the internal field $\boldsymbol{E}(\boldsymbol{x}')$ is not too different from the incident electric field since the contribution to the internal field due to the polarization is small; $\boldsymbol{E}(\boldsymbol{x}')$ then reduces to

$$\boldsymbol{E}_i(\boldsymbol{x}') = \boldsymbol{n}_i E_0 \exp(i\boldsymbol{k}_1 \cdot \boldsymbol{x}'),$$

$\boldsymbol{n}_i$ is a unit vector and we assume for now that the incident light in the medium is linearly polarized in the direction of $\boldsymbol{n}_i$. In an anisotropic medium, this is usually not the case, light is elliptically polarized and the end of $\boldsymbol{E}_i$ describes an ellipse; however, as we shall see in the following, when the phase difference introduced by the anisotropic medium equals $m\pi$ the polarization becomes linear and $\boldsymbol{E}_i$ keeps a fixed direction in space. The scattered amplitude is written as

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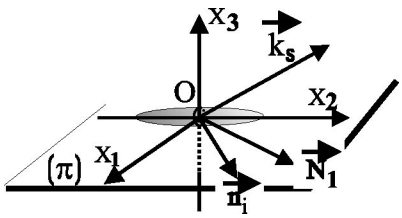

FIG. 1. Coordinates system: OX_1, OX_2, OX_3 principal axis of the particles.

$$\boldsymbol{E_S} = k_1^2 \int_V d\boldsymbol{x}' \frac{\exp ik_1 r}{4\pi r} \exp[-i(\boldsymbol{k}_1 - k_S)\cdot \boldsymbol{x}'] \times (\boldsymbol{I} - \boldsymbol{uu})\left(\frac{\boldsymbol{n}_p^2(x')}{n_1^2} - \boldsymbol{I}\right)\boldsymbol{n}_i E_0. \quad (4)$$

All the vectors and tensors in Eq. (4) are expressed in the principal axis coordinates system OX_1X_2 (see Fig. 1), thus $\boldsymbol{n_p}$ is a diagonal tensor, the elements of which are three scalar quantities; $\boldsymbol{u}$ and $\boldsymbol{n_i}$ are unit vectors and do not depend on the variable $\boldsymbol{x}'$.

The vector $(\boldsymbol{I}-\boldsymbol{uu})[(\boldsymbol{n}_p^2/n_1^2)-\boldsymbol{I}]\boldsymbol{n}_i$ is thus independent of $\boldsymbol{x}'$ and can be removed from the integral.

In the following we shall call $\boldsymbol{N}_1$ the vector,

$$\boldsymbol{N}_1 = \left(\frac{\boldsymbol{n}_p^2}{n_1^2} - \boldsymbol{I}\right)\boldsymbol{n}_i. \quad (5)$$

It can easily be shown that

$$(\boldsymbol{I} - \boldsymbol{uu})\boldsymbol{N}_1 = \boldsymbol{u} \times (\boldsymbol{u} \times \boldsymbol{N}_1).$$

Finally, the amplitude of the scattered field takes the simper form,

$$\boldsymbol{E_S} = k_1^2 E_0 \frac{\exp(ik_1 r)}{4\pi r}[\boldsymbol{u} \times (\boldsymbol{u} \times \boldsymbol{N}_1)]S, \quad (6)$$

where $S=\int_v d\boldsymbol{x}' \exp(-i\boldsymbol{q}\cdot\boldsymbol{x}')$. When $\boldsymbol{N}_1$ is parallel to $\boldsymbol{u}$, the scattered amplitude and consequently the scattered intensity, is zero; thus for an observer looking in the direction $\boldsymbol{N}_1$, he should see no scattered light: an antinode will appear in the scattered pattern. It should be remembered that usually $\boldsymbol{n}_i$ and consequently $\boldsymbol{N}_1$ do not keep a fixed direction since the polarization is elliptical and the observer will see an average intensity $\langle \boldsymbol{E_S} \boldsymbol{E_S^*} \rangle$ different from zero; however, as already quoted, when the phase difference equals $m\pi$ the vibration becomes linear, $\boldsymbol{N}_1$ has a time-independent direction, and the scattered intensity is zero in that direction.

For simplicity, we shall restrict our calculation to a wave propagating in the Oz direction (the same as OX_3) and look at the scattered light in a direction perpendicular to Oz in the plane π; thus any $\boldsymbol{u}$ has two components in the frame of the principal axis. As shown in Eq. (5), in an anisotropic medium, $\boldsymbol{N}_1$ is not parallel to $\boldsymbol{n}_i$, the unit vector defining the direction of the incident field except when the light incident on the medium is linearly polarized in one of the two eigenpolarization directions. But this case is of no practical interest since the polarization will remain linear through all the sample. The scattering particles are not only anisotropic but also have asymmetrical shape. The surrounding medium is a solvent (usually water) and the solution is subjected to flow in a shearing cell. We shall assume that the mean refraction index of the particle is not too different from the index of the solvent so that structural contribution to the birefringence can be neglected. This assumption relies on the stress optical rule which applies to the samples studied in this work, at least in the range of shear rates investigated.

Under the action of the hydrodynamical field, all the particles will take, on average, the same orientation and the solution will become birefringent; as concerns light propagation it will behave exactly like a biaxial crystal with three principal axes that we shall assume to be the same as the system $OX_1X_2X_3$ fixed to a single particle (this assumption relies on the fact that all the particles in the medium will take the same average orientation). In the case of Couette flow, the average orientation is characterized by the so-called extinction angle χ defined as the smallest angle between the direction of the flow and one of the principal direction (also called neutral line) in the plane of the flow. Good examples of such anisotropic liquids are micellar solutions which often show very strong birefringence even under rather weak shearing conditions [4]. In that case the classical method of Senarmont [3] often is useless. We shall see that the pattern of the scattered intensity will lead to a very simple way of finding the birefringence of these solutions. The birefringence Δn is related to the phase difference $\phi(z)$ between the two eigenpolarizations of the medium by the simple relation

$$\Delta n = \frac{\phi(z)\lambda}{2\pi z}, \quad (7)$$

where λ is the wavelength of the light and z the thickness of the sample.

In a purely birefringent medium, the eigenpolarizations are two linearly polarized vibrations at right angles which propagate at different velocities ($v_1 \neq v_2$); thus any linearly polarized light incident upon the anisotropic medium can be resolved in these two linear vibrations which oscillate in phase at the entrance of the medium but show a phase difference $\phi(z)$ after traveling a certain distance z inside; thus the vibration $\boldsymbol{E}_i$ is elliptical except for $\phi = m\pi$. In these cases the vibrations are linear and their direction is one of the two directions given by

$$\boldsymbol{n}_i = \boldsymbol{u}_1 \cos\alpha \pm \boldsymbol{u}_2 \sin\alpha, \quad (8)$$

where $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$, respectively, are unit vectors along OX_1 and OX_2 and α is the angle between $\boldsymbol{E}_i$ and OX_1.

These are the directions of the two diagonals of the rectangle containing the ellipse that will give the two directions in which we shall observe antinodes in the scattered pattern. Figure 2 is a view of the Couette cell used in these Rayleigh scattering experiments. The outer wall is made of glass while the inner cylinder is manufactured in a dark black material to prevent unwanted reflections. The height of the cell is 73 mm and the width of the gap 1.5 mm. An antinode is clearly seen in the upper part of the cell approximately at 2/3 of the height. Two birefringent samples have been prepared for

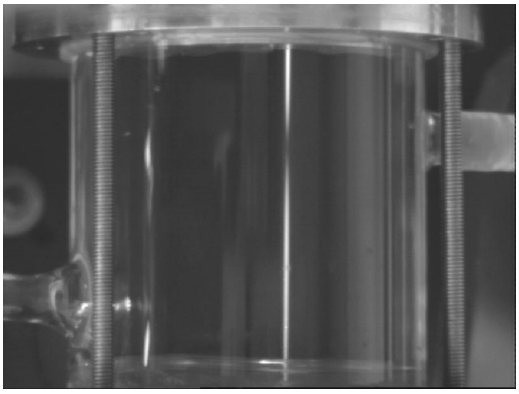

FIG. 2. Glass Couette cell with the inner cylinder rotating and laser beam crossing a colloidal solution in a direction parallel to the vorticity; a node corresponding to a phase difference of π is clearly seen in the upper half of the cell.

these experiments: a solution of CTAB/NaSal at 30/230 mmol and a solution of CTAB/$NaNO_3$ at 300/405 mmol.

In Fig. 3 some of the different states of polarization that exist in the anisotropic medium have been sketched together with the image of the laser beam in a direction in which antinodes can be observed. As light enters the cell (top of Fig. 3) and propagates in the anisotropic medium, its polarization goes through all the different states and periodically becomes linearly polarized when the phase retardation equals $m\pi$; the directions of vibrations are then given by Eq. (8) and antinodes are observed in these particular directions; the first one is encountered for $\phi=\pi$ (see the left part of Fig. 3), the second one for $\phi=2\pi$, and so on (right part of Fig. 3).

The phase difference between two consecutive antinodes appearing in the direction of observation is 2π while it is only π between two consecutive antinodes found in the direction of the two diagonals of the rectangle containing the ellipse. Thus, by merely measuring the distance between two antinodes, the birefringence intensity can be readily computed with the help of Eq. (7).

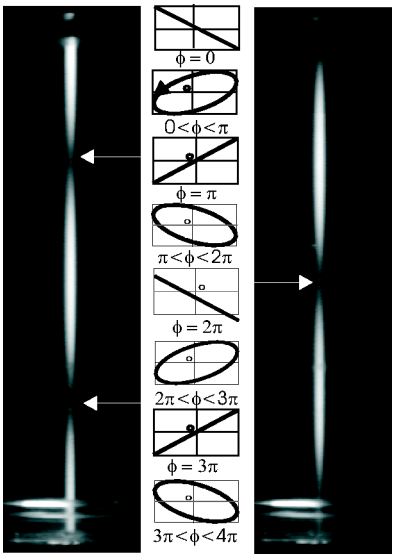

FIG. 3. Variation of the state of polarization of light in the gap of a Couette cell and scattered intensity in two directions in the plane $(\boldsymbol{v}, \boldsymbol{\nabla v})$ perpendicular to the vorticity. Nodes and antinodes corresponding to phase difference of $m\pi$ are clearly observed.

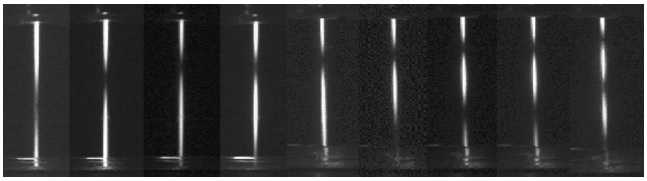

FIG. 4. Changes in the Rayleigh scattering pattern when the shear rate is gradually increased in the gap of a Couette cell (the figures give the values of the shear rate in S^{-1}). Light propagates from top to bottom over a length of 73 mm.

One can follow on Fig. 4 the evolution of the scattered intensity pattern when the shear rate is increased in a Couette cell. Light is traveling from top to bottom and antinodes corresponding to phase retardation of $m\pi$ are clearly observed in the vorticity direction. Considering the first antinode for each value of the shear rate we notice that the length of the bright needlelike part gets shorter and shorter as $\dot{\gamma}$ increases, thus clearly showing the change in the birefringence intensity; for the highest values of $\dot{\gamma}$ second-order antinodes corresponding to $k=1,2,\ldots$, start to appear. In order to measure conveniently the distance between the entrance and the first antinode, or between two consecutive antinodes, the patterns are analyzed in a gray level scale, the intensity profile is readily drawn, and the quantitative measurements performed.

Figure 5 presents experimental results of birefrigence intensity measurements performed with the two different techniques: measurement of the distance between two antinodes in the pattern of the scattered intensity and the method of Senarmont. This latter merely consists of finding the ellipticity ψ of the vibration which has traveled a definite distance (the height or length of the shearing device) in the material. ψ is half the phase difference ϕ introduced between the two eigenpolarizations. These variations are plotted as a function of the shear rate $\dot{\gamma}$ and as can be seen this sample already shows high birefringence even under rather weak shearing conditions. The plot speaks for itself: the agreement between both sets of results is fairly good, especially in the low shear rates domain.

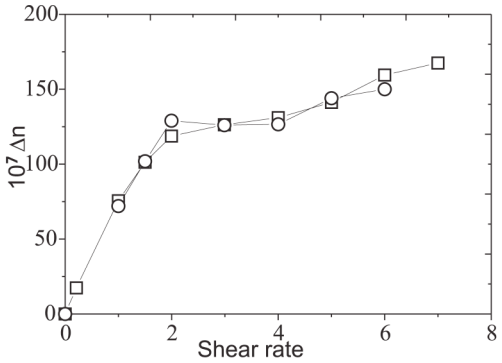

FIG. 5. Birefringence intensity $\Delta n(\times 10^7)$ vs the shear rate: open squares correspond to the method of Senarmont and open circles to the scattering pattern method.

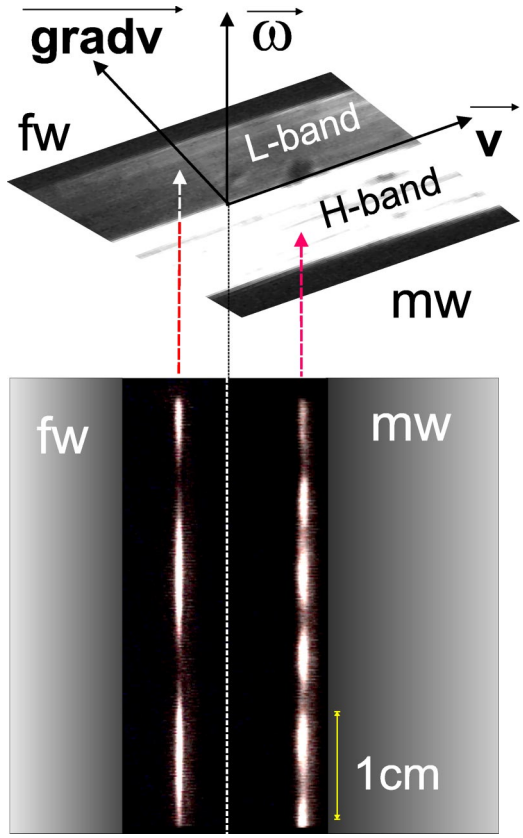

FIG. 6. (Color online) Two views of the gap in a Couette cell: the top one in the $(\boldsymbol{v}, \boldsymbol{\nabla v})$ plane, bottom one in the $(\boldsymbol{\omega}, \boldsymbol{\nabla v})$ plane. mw, fw mean moving and fixed wall, $\boldsymbol{\omega}$ is the vorticity direction.

Apart from this simple way of measuring the phase retardation of an anisotropic solution without first having to know the orientation of the medium χ, as necessary in the method of Senarmont, this technique also allows for the determination of the angle of extinction. For a given direction of rotation of the moving cylinder, one of the principal axes (OX_2, for example) will make the angle χ with the line of flow which is the reference for the angles in the case of Couette flow; for the reverse direction, OX_2 will take the symmetrical orientation with respect to the line of flow: thus the angle between the directions in which we observe two antinodes for the same shear rate will be twice the angle χ. In Fig. 6 we report scattering patterns obtained with the second solution ($CTAB/NaNO_3$) in which shear banding occurs. The shear rate is 20 s^{-1} in a gap 1.5-mm wide. Two different views of the gap are proposed: the top one is taken in the plane $(\boldsymbol{v}, \boldsymbol{\nabla v})$, the bottom one is a cross section in the plane $(\boldsymbol{\omega}, \boldsymbol{\nabla v})$. To realize the top view, a thin beam of parallel monochromatic polarized light illuminates the whole gap which appears divided in two layers (h and l band [6]) as predicted by the theory [5]; in the bottom view, a polarized laser beam is sent successively through both bands. In the l band (left part of Fig. 6, the pattern is a sequence of thin bright needlelike segments separated by antinodes; the phase retardation between two consecutive nodes in the same direction $\boldsymbol{u}$ being 2π, the birefringence intensity is readily computed. In the h band, near the moving wall (see the right part of Fig. 6), the thin segments are changed into much closer bright blobs, indicating that the birefringence is several times higher than in the l band. Moving the beam towards the frontier between the two layers (dotted line) does not significantly alter the distance between antinodes in both layers; this tends to confirm that the shear rate is constant but different in the h and l bands as predicted by the theory.

In summary, this paper presents a very simple method for the determination of the anisotropic properties of a solution containing asymmetrical particles. It will allow for an easy and simple way of measuring the flow-induced phase retardation without having to know at first the orientation of the medium which is a prerequisite in the method of Senarmont. But it will also lead to the orientation angle χ as previously mentioned. However, this method will not give the sign of the shear-induced retardation. This technique will also prove to be interesting in transient optical experiments when the phase retardation ϕ often reaches several times 2π, especially when the time-dependent behavior of the optical properties shows complicated features like overshoots, sigmodal relaxation, or damped oscillations. In that case, the analysis of the periodical signal of the transmitted intensity $[I/I_0 = \sin^2(\phi/2)]$ does not allow for the calculation of ϕ without ambiguity in particular during the relaxation of the steady state. Besides, this method is also very useful in shear banding experiments in order to find the birefringence of the shear-induced phase, measurements which were not made before. It will prove to be helpful each time the phase retardation induced in an anisotropic medium exceeds 2π like in many surfactants systems, liquid crystals, or polymer melts.

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