Particle size from optical anisotropy effects in scattered light

J. C. Ravey and P. Mazeron
Laboratoire de Biophysique Moléculaire, Université de Nancy I, ERA CNRS No.828, B.P. No.239, 54506 Vandoeuvre les Nancy Cedex, France
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An original light-scattering method often suitable for the case of anisotropic particles is explained. Two particular values of the scattering angle θ are needed: θ_m, the angular position of the minimum of the H_h component, and θ_0, the angular value for which $H_h = V_v$. This method has been successfully applied to the case of copolymer single crystals.

Keywords Light scattering; optical anisotropy; size determination; copolymer single crystals

INTRODUCTION

In relation to light scattering by anisotropic particles within the Rayleigh–Gans–Debye approximation, a formalism has been developed some years ago by Ravey[1–3]. Its originality lies in the use of the general properties of the so-called I_{pqr} integrals which allow the four components of the scattered light V_v, H_v, V_h and H_h to be written down easily. The expressions obtained in this way are valid for scatterers of any shape of revolution. Often without needing any numerical computations, they can be used to throw light onto some interesting properties which can provide fast and/or easy experimental methods for the determination of the shape[4], of the optical anisotropy[5] or of electrical parameters[6–8] if the particles are oriented by means of an electric field.

Thus, the measurement of the ratio $(H_h - H_v)/H_v$ at $\theta = 90°$ (generally knowledge of its sign is sufficient) is a very sure way of ascertaining the particle shape (prolate or oblate spheroid). Likewise, the study of the angular position of the minimum of the H_h component may be useful for the algebraic determination of the optical anisotropy δ if the shape is known, or for the shape determination if δ is known. Both these methods have been successfully applied to various suspensions of particles[9,10].

What we want to consider now is another optical anisotropy effect. The V_v component is believed to be generally greater than the H_h component for any scattering angle θ. This may often be wrong. As shown below, the components of the scattered light depend among other things on the optical anisotropy, the shape and the size of the scatterers. For appropriate values of these parameters, H_h is actually greater than V_v and this circumstance may provide a new tool for the measurement of optical properties. It is the purpose of this paper to investigate that possibility.

GENERAL THEORETICAL RELATIONS

In Appendix I are briefly recalled the definitions of the I_{pqr} integrals together with the complete expressions for V_v and H_h (equations (7)). A theoretical examination of a few particular cases will be a good opportunity to show the interesting consequences arising from the properties of the I_{pqr} functions and to throw some light onto the basis of our method. This approach is straightforward and does not need any numerical computation.

Isotropic particles ($\delta = 0$)

The following well known relation holds for $\delta = 0$:

$$H_h = I_{000}\cos^2\theta = V_v\cos^2\theta \tag{1}$$

so that H_h is always smaller than V_v except for $\theta = 0$.

Very large particles

For brevity, two cases of interest can be considered: the disc ($\omega = -1$) and the rod ($\omega \to \infty$), both deduced from the spheroid model whose semi-axes are a, a and pa. Their anisometry ω is defined by $\omega = p^2 - 1$. The asymptotic behaviour of the scattered intensities can be obtained most easily from the properties of the corresponding I_{pqr} functions:

Large discs of radius R. All the I_{pqr} become negligible, I_{p00} excepted:

$$I_{p00} \to 2/H^2 \qquad \text{for any } p$$

where

$$H = 4\pi\frac{R}{\lambda}\sin\frac{\theta}{2}$$

and λ is the wavelength in the medium.

Large rods of length L. All the I_{pqr} become negligible, I_{00r} excepted:

$$I_{00r} \to \frac{2}{H}\mathrm{Si}(2H)\frac{(2r)!}{2^{2r+1}r!r!}$$

where

$$H = 2\pi\frac{L}{\lambda}\sin\frac{\theta}{2}$$

and Si(x) is the sine-integral function.

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Substituting these asymptotic expressions into those of H_h and V_v, the difference $H_h - V_v$, or better the ratio $(H_h - V_v)/V_v$, can be written as follows:

For large discs:

$$\frac{H_h - V_v}{V_v} \left(\frac{\delta+2}{1-\delta}\right)^2 \left(\frac{3\delta}{\delta+2} - \sin^2\frac{\theta}{2}\right)\cos^2\frac{\theta}{2} \qquad (2)$$

For large rods:

$$\frac{H_h - V_v}{V_v} \rightarrow \frac{4-2\delta+\frac{11}{8}\delta^2}{1+\delta+\frac{11}{8}\delta^2}\cos^2\frac{\theta}{2}\left(\frac{(-\delta)3(1+\frac{1}{8}\delta)}{4-2\delta+\frac{11}{8}\delta^2} - \sin^2\frac{\theta}{2}\right) \qquad (3)$$

These two relations mean that a θ value exists for which the asymptotic values of H_h and V_v become equal. Let us denote by θ'_0 that root of the expressions in brackets in (2) and (3), which exists provided that δ is positive for discs and negative for rods, that is to say when $(\delta\omega)$ is negative.

Slightly anisotropic particles ($\delta \ll 1$)

The terms containing δ^2 may be dropped in (7) (see Appendix I), so that we get

$$\frac{H_h - V_v}{2\cos^2(\theta/2)} \simeq 3\delta(I_{100} - I_{001}) - 2I_{000}\sin^2\frac{\theta}{2} \qquad (4)$$

Perhaps for sufficiently low θ values, the second term may be so small that the difference $H_h - V_v$ will have the sign of $\delta(I_{100} - I_{001})$, that is to say the sign of $(-\delta\omega)$ by virtue of a property of the I_{pqr} integrals[1-3]. Then, again if $\delta\omega$ is negative, $H_h - V_v$ could be positive or zero for a particular θ_0 value.

Therefore, what is to be emphasized is that this event might arise for small particles and for large particles too, provided they are anisotropic ones, with a proper value of their optical anisotropy.

To sum up, every time $\delta\omega$ is negative, it could be possible to find a value θ_0 of the scattering angle, for which $H_h = V_v$, and hence to deduce some optical characteristic or some physical parameter of the scatterer. A more systematic study of this phenomenon was performed and since the I_{pqr} integrals cannot be solved analytically, numerical processings were involved.

DISCUSSIONS AND RESULTS

Let ρ be the radius of gyration of the scatterer and w the dimensionless quantity $w = 4\pi\rho/\lambda$. In *Figure 1* are displayed some typical variations of $(H_h - V_v)/V_v$ as a function of the scattering angle θ for various optical anisotropies, for rods ($p \rightarrow \infty$) and discs ($p \rightarrow 0$).

According to the former discussion, curves A and B correspond to scatterers with a positive value of their product $\delta\omega$ and decrease monotonically from zero so that H_h is never greater than V_v. The other three curves exhibit the opposite behaviour. Curve C has been calculated for a rod whose optical anisotropy is negative ($\delta = -0.10$). It can be seen that that curve increases at first until a maximum is reached, and then decreases in such a way that $H_h = V_v$ for $\theta_0 = 25.6°$. The fact that the initial slope of the curve is positive should be noted, because it is specific to such rods ($\delta\omega < 0$): as soon as this slope is positive, H_h will be equal to V_v for a certain value θ_0. A series expansion of $H_h - V_v$ in the vicinity of small θ leads to the following

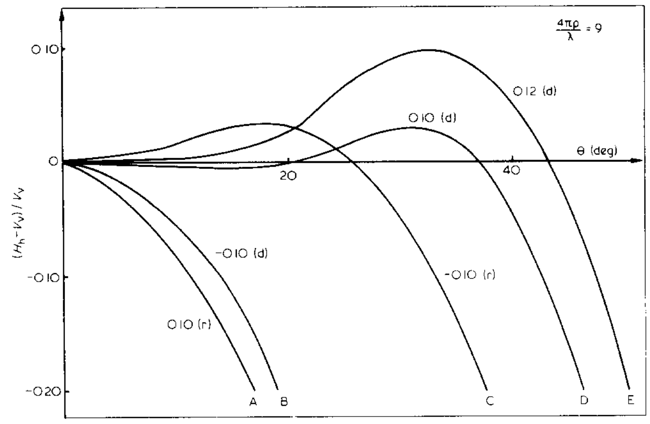

Figure 1 Typical variations of the ratio $(H_h - V_v)/V_v$ as a function of the scattering angle θ for rods (r) and discs (d), according to several optical anisotropy values (δ). The parameter size is $w = 9$

result: for a given δ value, that initial slope becomes positive if w is larger than w_{min} whose expression is

$$w_{min} = -\frac{7}{\delta}\left(\frac{5+\delta^2}{7+2\delta}\right)^{1/2} \qquad (5)$$

Then, this relation means that H_h can be equal to V_v if the rod has at least this minimum size.

The behaviour of discs is not so simple. Curves D and E prove that, in that case, the initial slope is relevant only in a first approximation, to know whether H_h could be equal to V_v or not. A rigorous expression giving w_{min} cannot be obtained here. Let us also note (see curve D) that when the initial slope is negative, H_h may be equal to V_v for two θ_0 values. For the sake of clarity, only the largest θ_0 will be considered in the remainder of this paper. It should correspond to the most easily measurable one in light scattering experiments.

On *Figures 2* and *3* are displayed numerical results of the θ_0 values for rods and discs, as a function of the scatterer size (w), for a set of δ values. The asymptotic values (large particles) have been obtained from the relations (2) and (3). The w_{min} values for rods come from relation (5). For discs, these w_{min} had to be computed

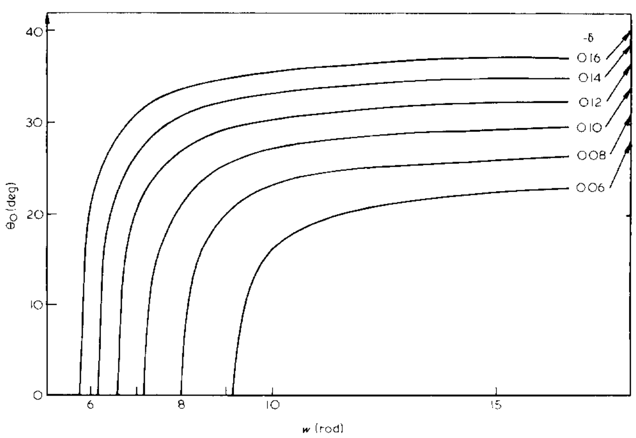

Figure 2 The scattering angle θ_0 for which $H_h = V_v$ as a function of the parameter size $w = 4\pi\rho/\lambda$ for rods with various negative δ values. The arrows indicate the asymptotic values

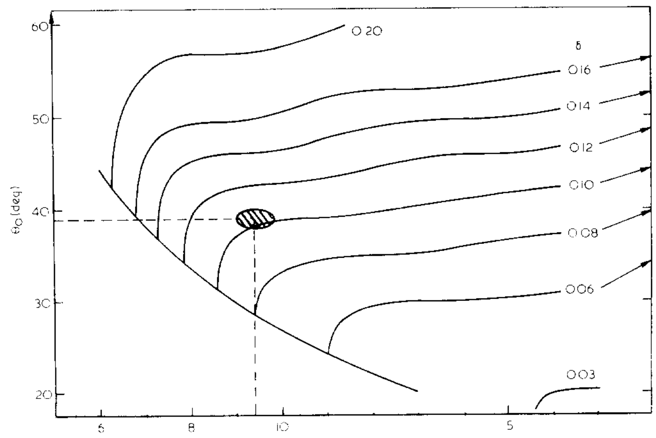

Figure 3 Same as *Figure 2* but for discs with various positive δ values. The hatched area is the experimental point for copolymer crystals

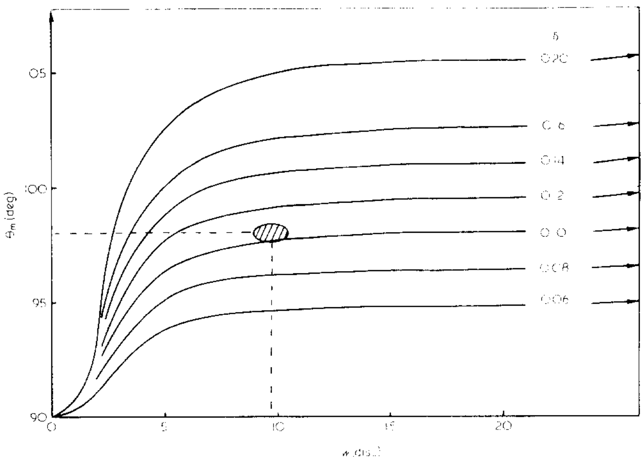

Figure 5 Same as *Figure 2* but for θ_m, the scattering angle for which the H_h component for discs is minimum. The hatched area is the experimental point for copolymer crystals

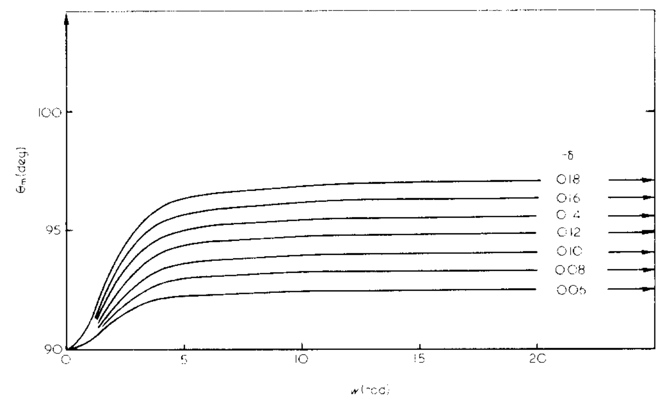

Figure 4 Same as *Figure 2* but for θ_m, the scattering angle for which the H_h component for rods is minimum

numerically. The following conclusions can be drawn:

(a) θ_0 may not exist even though $\delta\omega$ is negative. This event arises when the size of the scatterer is smaller than $w_{min}(\delta)$.

(b) Generally speaking, the lower the optical anisotropy of the scatterer, the larger its size must be and conversely.

(c) For a given δ value, θ_0 is generally an increasing function of w, strongly at first and then more moderately (but with the occurrence of small undulations for the discs). Even when $w = 15$, the asymptotic values are far from being reached.

Having measured θ_0 experimentally, the use of these curves must then lead to knowledge of the size of the scatterer if δ is known (and *vice versa*), with an accuracy depending on the slope of these $\theta_0(w)$ curves. That is why it is interesting to use a complementary method, namely the angular determination of the minimum of the H_h component. As already known, this θ_m occurs at scattering angles less than $\pi/2$ when $\delta\omega$ is positive and greater than $\pi/2$ when $\delta\omega$ is negative. *Figures 4* and *5* correspond to this latter case. These θ_m curves as a function of w greatly resemble the previous θ_0 curves. However, their asymptotic limits are reached within a few per cent for size parameter values as low as $w = 5$ for a rod and $w = 10$ for a disc, which is not the case for the θ_0 curves.

Let us recall these asymptotical expressions which bind θ_m to δ:

$$3\sin^4\frac{\theta_m}{2}\left(4 - 2\delta + \tfrac{11}{8}\delta^2\right) - (1-\delta)^2 - \sin^2\frac{\theta_m}{2}\left(4 - 5\delta + \delta^2\right) = 0 \quad (6a)$$

for any rod with $w > 5$; and

$$\sin^2\frac{\theta_m}{2} = \frac{1+2\delta}{\delta+2} \quad (6b)$$

for any disc with $w > 10$.

Then it may be verified that the precision reached for δ is about 5% if $|\delta|$ is about 0.15 and when θ_m is experimentally measured within half a degree, provided the size is large enough.

Knowing δ, it is now possible by using the curves of *Figures 2* and *3* to determine the size parameter. θ_0 may be estimated within one degree and, for $\Delta\delta/\delta = 5\%$, an accuracy ranging from 5 to 10% on w may generally be expected if the experimental point lies on the quasi-linear part of the curve which is moderately increasing. By way of illustration of this method, single crystals of the copolymer poly(ethylene oxide)–polystyrene suspended in *p*-xylene have been used[9]. For these disc-like particles whose dimension is 0.65 μm (from electron microscopy) the calculated size parameter w is about 10 ± 1, when the mercury green radiation is used ($\lambda = 0.546\,\mu$m). Then the use of the asymptotic expression (6b) could seem a little questionable. This is why we prefer a graphical determination of w and δ. The experimental values we have found are $\theta_m = 98°$ and $\theta_0 = 39°$. Taking into account the experimental errors visualized in *Figures 5* and *3*, the (δ, w) couple which fits best both theoretical diagrams is: $\delta = +0.105 \pm 0.005$ and $w = 9.5 \pm 1$. This is in excellent agreement with the directly measured w value and with previous determinations of δ[5,10].

Note that in this example, the shape of the scatterer was known *a priori*. If it were not the case, a previous determination of the ratio $(H_h - H_v)/H_v$ at $\theta = 90°$ should have been advantageously used for that purpose[4].

In short then, it may be possible to deduce the size of an anisotropic scatterer by means of only two angular determinations: θ_m, and θ_0, if any. But yet, the non-existence of a θ_0 value may be used to determine the upper limit of that size if δ is known. Some advantages of the method are noticeable: First, only one suspension of particles is needed to deduce the size. This aspect is particularly important in the case of molecular aggregates whose structure depends on the solute concentration. Secondly, it may be applied for rather large particles, contrary to the Zimm plot technique whose extrapolations become so close to zero that neither the molecular weight nor the radius of gyration can be attained. In addition, since only two θ values have to be measured, this method is not at all time-consuming. When studies of the size evolutions during a time-dependent process are involved, its quickness makes it the more suitable because the difference $H_h - V_v$ can be modulated as we have already done for the $H_h - H_v$ difference[4], and then directly measured.

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APPENDIX I

The I_{pqr} *integrals and the components* H_h *and* V_v

Let g_1 and g_2 be the two principal optical polarizabilities excess of a scatterer in a given solvent. The optical anisotropy δ is defined as

$$\delta = \frac{g_1 - g_2}{g_1 + 2g_2}$$

and may be positive or negative. Here the subscript 1 refers to the revolution axis.

Consider the usual reference frame (s, s', z) built on the exterior s and interior s' bisectors of the scattering angle θ. The normalized interference factor of a revolution scatterer is $R(\phi)$ where ϕ is the angle of its revolution axis with s. $\beta_1, \beta_2, \beta_3$ being the direction cosines of that axis in the frame (s, s', z), the I_{pqr} expression is as follows:

$$I_{pqr} = \frac{1}{4\pi}\iint R(\phi)\beta_1^{2p}\beta_2^{2q}\beta_3^{2r}\,d\Omega$$

the integrals being extended over all space. Their properties have been indicated in our previous papers[1-3].

The general expressions for V_v and H_h are:

$$\begin{aligned} V_v &= 9\delta^2 I_{002} + 6\delta(1-\delta)I_{001} + (1-\delta)^2 I_{000} \\ H_h &= 9\delta^2[I_{200}\cos^4(\theta/2) + I_{020}\sin^4(\theta/2) - \tfrac{1}{2}I_{110}\sin^2\theta] \\ &\quad + 6\delta(1-\delta)\cos\theta\,[I_{100}\cos^2(\theta/2) - I_{010}\sin^2(\theta/2)] \\ &\quad + (1-\delta)^2 I_{000}\cos^2\theta \end{aligned} \tag{7}$$

For isotropic orientation, we have $I_{pqr} = I_{prq}$.