Light scattering by impurities at a liquid interface*

U. M. Titulaer† and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 23 October 1975)

We discuss the scattering of light by anisotropic impurities located at a fluid interface. Our aim is to determine which type of information about the arrangement and motion of the impurities can be obtained from precise light scattering experiments. Since the paper is intended to be exploratory rather than exhaustive, we concentrate our attention on the simplest nontrivial case; a number of possible complications are discussed in a more qualitative way.

I. INTRODUCTION

There is considerable chemical and biological interest in determining the arrangement and motion of impurity molecules that are constrained to lie in a fluid interface. This paper is devoted to an analysis of the possibilities for obtaining information about such systems by precise light scattering measurements. The work was motivated by an interest in assessing the prospects for new applications of modern laser light scattering techniques.[1,2] To our knowledge there are no reported experiments of the type considered here, and our results are presented in the hope of stimulating new experiments.

The model we adopt for the impurity–interface system is not the most general that can be constructed; the absence of data does not justify treatment of the most complicated case. Rather, we will exhibit the type of information that might be obtained under favorable experimental circumstances. We do consider particles with anisotropic polarizabilities, for simplicity cylindrically symmetric, since for such particles light scattering experiments provide information about orientational distributions and rotational relaxation. The corresponding, but more general, treatment of light scattering from anisotropic particles in bulk fluids has been presented by Steele and Pecora.[3] Since the results of our calculations for the scattering cross sections at different angles and polarizations are complicated, we summarize here the main qualitative conclusions of our inquiry.

(1) For a low concentration of impurities, one can determine two parameters of the orientational distribution of a single particle at the interface. In addition, some information about the degree of submersion of the impurities may be obtained. This requires determination of the total scattered intensity at several angles and polarizations.

(2) At higher concentrations similar scattering measurements can provide information about the correlations in position and orientation of the impurities. The information can be expressed in a finite number of averaged products of spherical harmonics of order 0 and 2, depending on the molecular orientation angles, over the two-particle joint distribution of positions and orientations. Since the experiment provides Bessel transforms of these functions for wave vectors up to twice that of the incoming light, one will only be able to determine a few moments of these averaged distributions, unless the correlations are of unusually long range. The moments can be connected to some generalized susceptibilities of the assembly of impurities with respect to aligning forces.

(3) When the frequency distribution of the scattered light can be resolved, one may obtain information about the time dependent analogues of the correlation functions mentioned in the preceding paragraph. In particular, measurements at low concentration provide information about the diffusion of the impurities along the interface and some information about their rotational relaxation. Measurements at higher concentration yield information about correlations in the motion of different particles.

The most serious limitation of the simple model adopted here is our assumption that the interface remains flat, and that the degree of submersion of the impurities is fixed and independent of its orientation. In fact, fluctuations will distort the interface and induce relative motion between the impurity and the interface. This will influence the observed light scattering, particularly its frequency spectrum. This question is discussed briefly in the last section.

The treatment in this paper is also restricted to low or moderate impurity concentrations, since we neglect the field scattered by other impurities relative to the incoming field. It is possible to take such effects into account, but then the relatively simple relationship between the scattered light and the distribution function for the impurities is lost.

II. THE SCATTERING AMPLITUDE FOR A SINGLE SCATTERER NEAR AN INTERFACE

The presence of an interface in the immediate vicinity of a scatterer causes some modifications in the familiar expression for the scattering cross section of a polarizable particle. We will consider a geometry in which the interface coincides with the x–y plane and the wave vector of the incident light lies in the x–z plane and makes an angle $\pi-\theta_0$ with the z axis. The two principal modes of polarization are the parallel one, with the electric field parallel to the interface, in this case along the y axis, and the oblique one, with the electric field in the plane of incidence. The explicit form of the three unit vectors (the direction of propagation $\hat{k}$ and the two polarization vectors) are given in Table I, for the incident beam and for a beam leaving the surface in the direction (θ, ϕ). The scatterers are treated as

TABLE I. The unit vectors in the direction of the wave vector and of the two principal directions of polarization for both the incoming and the scattered light. Quantities pertaining to the incoming light are designated with a subscript zero. The expressions in column 2, 3, and 4 are the x-, y-, and z component of the unit vector in column 1.

$\hat{\mathbf{a}}$	a_x	a_y	a_z
$\hat{k}_0$	$\sin\theta_0$	0	$-\cos\theta_0$
$\hat{e}_{P,0}$	0	1	0
$\hat{e}_{O,0}$	$-\cos\theta_0$	0	$\sin\theta_0$
$\hat{k}$	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$
$\hat{e}_P$	$-\sin\phi$	$\cos\phi$	0
$\hat{e}_O$	$\cos\theta\cos\phi$	$\cos\theta\sin\phi$	$-\sin\theta$

point particles with a polarizability tensor that is invariant under rotations around the molecular axis:

$$\boldsymbol{\alpha} = \alpha\mathbf{I} + \beta(\hat{\mathbf{R}}\hat{\mathbf{R}} - \tfrac{1}{3}\mathbf{I}), \qquad (2.1)$$

where $\hat{\mathbf{R}}$ is a unit vector along the molecular axis with polar components (Θ, Φ). The tensor $\boldsymbol{\alpha}$ is an *effective* polarizability tensor; it may differ from the polarizability tensor of the isolated molecule due to local field effects and modifications of the solvent in the neighborhood of the impurity.

The Maxwell field near the surface can be obtained from the field of the incoming wave by application of the Fresnel formulas.[4] For our purposes it is convenient to write them in the form

$$E_x = \frac{2n\cos\theta_0'}{n^2\cos\theta_0 + n\cos\theta_0'}\, E_{x0} \equiv \mathfrak{x}_0\, E_{x0}, \qquad (2.2a)$$

$$E_y = \frac{2\cos\theta_0}{\cos\theta_0 + n\cos\theta_0'}\, E_{y0} \equiv \mathfrak{y}_0\, E_{y0}, \qquad (2.2b)$$

$$E_z = \frac{2n_c^2\cos\theta_0}{n^2\cos\theta_0 + n\cos\theta_0'}\, E_{z0} \equiv \mathfrak{z}_0\, E_{z0}, \qquad (2.2c)$$

or

$$\mathbf{E} \equiv \mathfrak{R}_0 \cdot \mathbf{E}_0, \qquad (2.2d)$$

where n is the refractive index of the fluid, θ_0' is the angle of the refracted beam with the normal to the surface, as determined by Snell's law ($\sin\theta_0 = n\sin\theta_0'$), and n_c^2 has the value n^2 in the upper medium and 1 in the lower medium. For a partially submerged scatterer Eq. (2.2) applies with $n_c^2 = p + n^2(1-p)$, where p is the submerged fraction.

The induced dipole moment μ of the scatterer is given by

$$\boldsymbol{\mu} = \boldsymbol{\alpha}\cdot\mathbf{E}, \qquad (2.3)$$

with α and $\mathbf{E}$ given by Eq. (2.1) and (2.2), respectively. The field emitted by this dipole may be expressed conveniently in terms of the Hertz vector $\Pi(\mathbf{r})$,[5]

$$\mathbf{E}^{sc}(\mathbf{r}) = \nabla\times\nabla\times\Pi(\mathbf{r}). \qquad (2.4)$$

For a dipole at the origin in a homogeneous medium, the Hertz vector is

$$\Pi(\mathbf{r}) = r^{-1}\exp(ikr)\,\boldsymbol{\mu}. \qquad (2.5)$$

The form of $\Pi(\mathbf{r})$ appropriate for a dipole source in the vicinity of an interface was derived by Sommerfeld.[6] His expression is rather complicated, but the asymptotic form for large r may again be expressed in the form (2.5), but with μ replaced by

$$\boldsymbol{\mu}^{\text{eff}}(\theta,\phi) = \mathfrak{R}'(\theta,\phi)\cdot\boldsymbol{\mu}, \qquad (2.6)$$

which depends on the direction (θ, ϕ) of the vector $\mathbf{r}$ [the notation anticipates a relation between $\mathfrak{R}'$ and the matrix $\mathfrak{R}_0$ in Eq. (2.2d), which is yet to be established].

When μ is normal to the surface, μ^{eff} is also normal to the surface; its value depends on the position of the emitter with respect to the surface, but the various cases can be combined in the formula

$$\mu_z^{\text{eff}} = \frac{2n_c^2\cos\theta}{n^2\cos\theta + n\cos\theta'}\,\mu_z \equiv \mathfrak{z}\mu_z, \qquad (2.7)$$

where n_c^2 has the same meaning as in Eq. (2.2c), and θ' is related to θ by Snell's law ($\sin\theta = n\sin\theta'$). For μ parallel to the surface, but perpendicular to $\mathbf{r}$, μ^{eff} is again parallel to μ and given by

$$\mu_{y'}^{\text{eff}} = \frac{2\cos\theta}{\cos\theta + n\cos\theta'}\,\mu_{y'} \equiv \mathfrak{y}\mu_{y'}, \qquad (2.8)$$

where y' denotes the direction perpendicular to $\mathbf{r}$ and $\hat{\mathbf{z}}$. For a μ directed along the projection of $\mathbf{r}$ on the surface (the x' direction), Sommerfeld gives an expression for μ^{eff}, which has both an x' and a z component[7]:

$$\mu_{x'}^{\text{eff}} = \frac{2\cos\theta}{\cos\theta + n\cos\theta'}\,\mu_{x'}, \qquad (2.9a)$$

$$\mu_z^{\text{eff}} = \frac{2\sin\theta\cos\theta(n^2-1)}{(\cos\theta + n\cos\theta')(n^2\cos\theta + n\cos\theta')}\,\mu_{x'}. \qquad (2.9b)$$

However, from Eq. (2.4) one sees that only the components of μ^{eff} perpendicular to $\mathbf{r}$ have physical meaning, and it is easy to see that an alternative form,

$$\mu_{x'}^{\text{eff}} = \frac{2n\cos\theta'}{n^2\cos\theta + n\cos\theta'}\,\mu_{x'} \equiv \mathfrak{x}\mu_{x'}, \qquad \mu_z^{\text{eff}} = 0, \qquad (2.10)$$

differs from Eq. (2.9a) by a vector parallel to $\mathbf{r}$. Therefore, we may write instead of Sommerfeld's expression (2.6), with $\mathfrak{R}'$ given by Eqs. (2.7), (2.8), and (2.9),

$$\boldsymbol{\mu}^{\text{eff}} = \mathfrak{R}(\theta,\phi)\cdot\boldsymbol{\mu}, \qquad (2.11)$$

with $\mathfrak{R}$ defined by Eqs. (2.7), (2.8), and (2.10). The matrix $\mathfrak{R}$ is obtained from $\mathfrak{R}_0$ in Eq. (2.2) by replacing θ_0 by θ and rotating the coordinate system over an angle ϕ around the z axis:

$$\mathfrak{R}_0 = \mathfrak{R}(\theta_0, 0). \qquad (2.12)$$

By combining the results of this section, in particular Eqs. (2.5), (2.11), (2.3), and (2.2), we find for the strength of the scattered electric field for sufficiently large r ($kr \gg 1$)

$$\begin{aligned}\mathbf{E}^{sc}(\mathbf{r}) &= k^2 r^{-1}\exp(ikr)(\mathbf{I} - \mathbf{rr})\cdot\mathfrak{R}(\theta,\phi)\cdot\boldsymbol{\alpha}\cdot\mathfrak{R}(\theta_0, 0)\cdot\mathbf{E}_0 \\ &\equiv r^{-1}\exp(ikr)\mathbf{A}(\theta,\phi;\theta_0,0)\cdot\mathbf{E}_0. \end{aligned}\qquad (2.13)$$

We will call $\mathbf{A}$ the scattering amplitude matrix. In terms of $\mathbf{A}$, the scattering cross section for an incoming field with direction $(\pi - \theta_0, 0)$ and polarization $\hat{\mathbf{e}}_0$ and a scattered field with direction (θ, ϕ) and polarization $\hat{\mathbf{e}}$ is given by

$$\frac{d\sigma}{d\Omega} = |\hat{\mathbf{e}} \cdot \mathbf{A} \cdot \hat{\mathbf{e}}_0|^2 = k^4 |\hat{\mathbf{e}} \cdot \mathfrak{R}(\theta, \phi) \cdot \boldsymbol{\alpha} \cdot \mathfrak{R}(\theta_0, 0) \cdot \hat{\mathbf{e}}_0|^2 . \tag{2.14}$$

For the case $n = 1$, the matrix $\mathfrak{R}$ becomes equal to the unit matrix and the expression assumes the familiar form

$$\frac{d\sigma}{d\Omega} = k^4 |\hat{\mathbf{e}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{e}}_0|^2 \tag{2.15}$$

for light scattering by a polarizable molecule in the dipole approximation. The relation (2.13) between the matrices describing the modification of the incoming and the scattered field by the presence of the interface could have been expected on the basis of Lorentz's reciprocity theorem,[8] which states that the scattered signal stays the same when the positions (and polarizations) of light source and light detector are interchanged.

III. POLARIZED INCOHERENT SCATTERING

In this section we will discuss the expression (2.15) in somewhat more detail for different choices of the polarization vectors. In addition, we will consider averages over an ensemble of scatterers with different orientations of the molecular axes, described by a probability distribution $f(\Theta, \Phi)$. The result thus obtained will also be equal to $1/N$ times the scattering cross section for N scatterers on a surface with a spacing large compared to the coherence distance of the incoming radiation. Corrections for closer spacing of the scatterers are considered in the next section.

We will determine the scattering amplitude A, defined in Eq. (2.14), for initial and final polarizations either parallel to the interface or oblique, using the polarization vectors of Table I and the expressions (2.2), (2.7), (2.8), and (2.10) for the distortion factors. In this way we obtain

$$A_{PP} = k^2 \mathfrak{y}_0 \mathfrak{y} [\alpha \cos\phi - \tfrac{1}{2}\beta \cos\phi (\cos^2\Theta - \tfrac{1}{3}) - \tfrac{1}{2}\beta \sin^2\Theta \cos(2\Phi - \phi)] , \tag{3.1a}$$

$$A_{PO} = k^2 \mathfrak{y}_0 \{\mathfrak{x}' [\alpha \sin\phi - \tfrac{1}{2}\beta \sin\phi (\cos^2\Theta - \tfrac{1}{3}) + \tfrac{1}{2}\beta \sin^2\Theta \sin(2\Phi - \phi)] - \mathfrak{z}' \sin\Theta \cos\Theta \sin\Phi\} , \tag{3.1b}$$

$$A_{OP} = k^2 \mathfrak{y} \{\mathfrak{x}_0' [\alpha \sin\phi - \tfrac{1}{2}\beta \sin\phi (\cos^2\Theta - \tfrac{1}{3}) - \tfrac{1}{2}\beta \sin^2\Theta \sin(2\Phi - \phi)] + \mathfrak{z}_0' \sin\Theta \cos\Theta \sin(\Phi - \phi)\} , \tag{3.1c}$$

$$\begin{aligned} A_{OO} = k^2 \{ & - \alpha(\mathfrak{x}_0' \mathfrak{x}' \cos\phi + \mathfrak{z}_0' \mathfrak{z}') + \beta(\tfrac{1}{2}\mathfrak{x}_0' \mathfrak{x}' \cos\phi - \mathfrak{z}_0' \mathfrak{z}')(\cos^2\Theta - \tfrac{1}{3}) - \tfrac{1}{2}\beta \mathfrak{x}_0' \mathfrak{x}' \sin^2\Theta \cos(2\Phi - \phi) \\ & + \beta \mathfrak{z}_0' \mathfrak{x}' \sin\Theta \cos\Theta \cos(\Phi - \phi) + \beta \mathfrak{x}_0' \mathfrak{z}' \sin\Theta \cos\Theta \cos\Phi\} , \end{aligned} \tag{3.1d}$$

where we used the abbreviations

$$\begin{aligned} \mathfrak{x}' &= \mathfrak{x} \cos\theta , & \mathfrak{x}_0' &= \mathfrak{x}_0 \cos\theta_0 , \\ \mathfrak{z}' &= \mathfrak{z} \sin\theta , & \mathfrak{z}_0' &= \mathfrak{z}_0 \sin\theta_0 . \end{aligned} \tag{3.2}$$

Another useful quantity is obtained by choosing the final polarization in such a way that the isotropic component of $\boldsymbol{\alpha}$ does not contribute. For initial polarization parallel to the interface we have to choose the final polarization along the vector $\hat{\mathbf{e}}_O \cos\gamma - \hat{\mathbf{e}}_P \sin\gamma$ with $tg\gamma = (\mathfrak{x}'/\mathfrak{y}) tg\phi$ The corresponding amplitude is

$$\begin{aligned} A_{PD} = {} & (\mathfrak{x}'^2 \sin^2\phi + \mathfrak{y}^2 \cos^2\phi)^{-1/2} \beta k^2 \mathfrak{y}_0 \mathfrak{y} \\ & \times (-\tfrac{1}{2}\mathfrak{x}' \sin^2\Theta \sin 2\Phi + \mathfrak{z}' \sin\Theta \cos\Theta \sin\Phi \cos\phi) . \end{aligned} \tag{3.3}$$

The amplitude A_{OD} is not particularly simple and therefore not given explicitly.

In order to obtain the scattering cross sections one must square the expressions (2.2) and (2.3) and average the result over the probability distribution $f(\Theta, \Phi)$ for the orientation of the molecular axis. This is most easily done by rewriting Eqs. (3.1) and (3.2) in terms of spherical harmonics, as is done in the Appendix.

When we assume that $f(\Theta, \Phi)$ is independent of Φ, as is to be expected from symmetry considerations, then $f(\Theta, \Phi)$ enters into the final expressions only through the quantities

$$\begin{aligned} q_l &= \iint f(\Theta, \Phi) P_l(\cos\Theta) \sin\Theta d\Theta d\Phi \\ &= [4\pi/(2l+1)]^{1/2} \iint f(\Theta, \Phi) Y_{l0}(\Theta, \Phi) \sin\Theta d\Theta d\Phi \end{aligned} \tag{3.4}$$

for $l = 2$ and 4. These coefficients vanish for an isotropic distribution and assume the value unity when all molecules are aligned along the z axis. In terms of the quantities (3.4) we obtain for the cross section per scatterer with specified initial and final polarization

$$\sigma_{PP} = k^4 \mathfrak{y}_0^2 \mathfrak{y}^2 \{\cos^2\phi [\alpha^2 - \tfrac{2}{3}\alpha\beta q_2 + \beta^2(\tfrac{1}{45} + \tfrac{2}{63} q_2 + \tfrac{2}{35} q_4)] + \beta^2(\tfrac{1}{15} - \tfrac{2}{21} q_2 + \tfrac{1}{35} q_4)\} , \tag{3.5a}$$

$$\sigma_{PO} = k^4 \mathfrak{y}_0^2 \mathfrak{x}'^2 \{\sin^2\phi [\alpha^2 - \tfrac{2}{3}\alpha\beta q_2 + \beta^2(\tfrac{1}{45} + \tfrac{2}{63} q_2 + \tfrac{2}{35} q_4)] + \beta^2(\tfrac{1}{15} - \tfrac{2}{21} q_2 + \tfrac{1}{35} q_4)\} + k^4 \mathfrak{y}_0^2 \mathfrak{z}'^2 \beta^2 (\tfrac{1}{15} + \tfrac{1}{21} q_2 - \tfrac{4}{35} q_4) , \tag{3.5b}$$

$$\sigma_{OP} = k^4 \mathfrak{x}_0'^2 \mathfrak{y}^2 \{\sin^2\phi [\alpha^2 - \tfrac{2}{3}\alpha\beta q_2 + \beta^2(\tfrac{1}{45} + \tfrac{2}{63} q_2 + \tfrac{2}{35} q_4)] + \beta^2(\tfrac{1}{15} - \tfrac{2}{21} q_2 + \tfrac{1}{35} q_4)\} + k^4 \mathfrak{z}_0'^2 \mathfrak{y}^2 \beta^2 (\tfrac{1}{15} + \tfrac{1}{21} q_2 - \tfrac{4}{35} q_4) , \tag{3.5c}$$

$$\begin{aligned} \sigma_{PP} = {} & k^4 \mathfrak{x}_0'^2 \mathfrak{x}'^2 \{\cos^2\phi [\alpha^2 - \tfrac{2}{3}\alpha\beta q_2 + \beta^2(\tfrac{1}{45} + \tfrac{2}{63} q_2 + \tfrac{2}{35} q_4)] + \beta^2(\tfrac{1}{15} - \tfrac{2}{21} q_2 + \tfrac{1}{35} q_4)\} + k^4(\mathfrak{x}_0'^2 \mathfrak{z}'^2 + \mathfrak{z}_0'^2 \mathfrak{x}'^2)\beta^2(\tfrac{1}{15} + \tfrac{1}{21} q_2 - \tfrac{4}{35} q_4) \\ & + k^4 \mathfrak{z}_0'^2 \mathfrak{z}'^2 [\alpha^2 + \tfrac{4}{3}\alpha\beta q_2 + 4\beta^2(\tfrac{1}{45} + \tfrac{2}{63} q_2 + \tfrac{2}{35} q_4)] + k^4 \mathfrak{x}_0' \mathfrak{z}_0' \mathfrak{x}' \mathfrak{z}' \cos\phi [2\alpha^2 + \tfrac{2}{3}\alpha\beta q_2 + \beta^2(\tfrac{2}{45} - \tfrac{2}{63} q_2 - \tfrac{16}{35} q_4)] , \end{aligned} \tag{3.5d}$$

and

$$\sigma_{PD} = k^4 \mathfrak{y}_0^2 \mathfrak{y}^2 [\mathfrak{x}'^2 \sin^2\phi + \mathfrak{y}^2 \cos^2\phi]^{-1} \beta^2 [\mathfrak{x}'^2 (\tfrac{1}{15} - \tfrac{2}{21} q_2 + \tfrac{1}{35} q_4) + \mathfrak{z}'^2 (\tfrac{1}{15} + \tfrac{1}{21} q_2 - \tfrac{4}{35} q_4) \cos^2\phi] . \tag{3.6}$$

In Eq. (3.4) and (3.5) we assumed that α and β are real quantities; this means that the frequency of the scattered light should not coincide with any of the absorption frequencies of the impurity.

In analyzing experimental data for the scattering cross sections we may consider the distortion factors $\mathfrak{y}_0, \mathfrak{y}, \mathfrak{x}_0'$, and $\mathfrak{x}'$ as completely known functions of θ and θ_0; the factors $\mathfrak{z}_0'$ and $\mathfrak{z}'$ contain the factor n_c^2, which contains the submersion factor p, and is therefore in general not known *a priori*. A complete experiment yields the following five quantities:

$$\begin{aligned}
d_1 &= \tfrac{1}{15}\beta^2 - \tfrac{2}{21}\beta^2 q_2 + \tfrac{1}{35}\beta^2 q_4 ,\\
d_2 &= n_c^4(\tfrac{1}{15}\beta^2 + \tfrac{1}{21}\beta^2 q_2 - \tfrac{4}{35}\beta^2 q_4) ,\\
d_3 &= \alpha^2 - \tfrac{2}{3}\alpha\beta q_2 + \tfrac{1}{45}\beta^2 + \tfrac{2}{63}\beta^2 q_2 + \tfrac{2}{35}\beta^2 q_4 ,\\
d_4 &= n_c^8(\alpha^2 + \tfrac{4}{3}\alpha\beta q_2 + \tfrac{4}{45}\beta^2 + \tfrac{8}{63}\beta^2 q_2 + \tfrac{8}{35}\beta^2 q_4) ,\\
d_5 &= n_c^4(\alpha^2 + \tfrac{1}{3}\alpha\beta q_2 - \tfrac{2}{45}\beta^2 - \tfrac{4}{63}\beta^2 q_2 - \tfrac{4}{35}\beta^2 q_4) .
\end{aligned} \tag{3.7}$$

The quantity d_1 follows from σ_{PP} at $\phi = \pm 1/2\pi$; once d_1 is known, d_3 follows from σ_{PP} at any other ϕ, and d_2 from σ_{PO} or σ_{OP} at $\phi = 0$ (or any other ϕ, when the known value of d_3 is used); d_4 and $(d_2 + d_5)$ then follow from the ϕ dependence of σ_{OO} at fixed θ_0 and θ. Notice that a complete experiment requires only measurements at one fixed value of θ_0 and θ; variation of these two quantities yields no independent information, but may serve to confirm the model used for describing the impurities.

From the quantities $d_1, \ldots, d_5$ we can determine the five unknowns α, β, n_c^2, q_2, and q_4. This is perhaps done most easily by assuming a value for n_c^2; this reduces (3.7) to five linear equations with unknowns α^2, β^2, $\alpha\beta q_2$, $\beta^2 q_2$, and $\beta^2 q_4$. One then varies n_c^2 until the condition $\beta^2\,(\alpha\beta q_2)^2 = \alpha^2(\beta^2 q_2)^2$ is met. In choosing between multiple solutions one may employ the conditions

$$\begin{aligned}
&|\beta| \leq 3|\alpha| ; \quad 1 \leq n_c^2 \leq n^2 ;\\
&-\tfrac{1}{2} \leq q_2 \leq 1 ; \quad -\tfrac{3}{7} \leq q_4 \leq 1 ,
\end{aligned} \tag{3.8}$$

which follow immediately from the various definitions.

When one drops the requirement that α and β are real, one must make the substitutions

$$\begin{aligned}
&\alpha^2 \to |\alpha|^2 ; \quad \beta^2 \to |\beta|^2 ;\\
&\alpha\beta \to \mathrm{Re}(\alpha^*\beta) .
\end{aligned} \tag{3.9}$$

Now the system of Eqs. (3.7) is underdetermined. In order to extract the required information, one may combine measurements at different frequencies, provided the ratio β/α varies with frequency. In that case each new frequency introduces four new equations (the ratio d_1/d_2 is frequency independent), and three new unknowns: $|\alpha(\omega_i)|^2$, $|\beta(\omega_i)|^2$, and $\mathrm{Re}[\alpha^*(\omega_i)\beta(\omega_i)]$.

Now a practical method to determine all required quantities is to solve for $|\alpha(\omega_i)^2|$, $q_2\,\mathrm{Re}[\alpha^*(\omega_i)\beta(\omega_i)]$, and $|\beta(\omega_i)|^2(\frac{1}{45} + \frac{2}{63}q_2 + \frac{2}{35}q_4)$ from $d_3(\omega_i)$, $d_4(\omega_i)$, and $d_2(\omega_i) - d_5(\omega_i)$, with an assumed fixed n_c^2, and subsequently to adjust n_c^2 until the value of $|\beta(\omega_2)|/|\beta(\omega_1)|^2$ agrees with the one determined from $d_1(\omega_2)/d_1(\omega_1)$. Once n_c^2 is determined the system of Eq. (3.7) determines all required quantities.

IV. COHERENT SCATTERING

In the preceding section we calculated the scattering cross section of an assembly of impurities by adding the contributions from the individual scatterers. This treatment is justified when the distance between the scatterers is large compared to the coherence length of the light, or when the positions and orientations of the scatterers are completely uncorrelated. Moreover, we neglected any contributions of multiple scattering (or, alternatively, of modifications of the local field by the presence of other impurities). Complications of the latter kind will not be considered in this paper, except briefly in the concluding section. In the present section we will review the modifications of the results of Sec. III due to interference between light scattered by different impurities.

In the limit when the distance from the scattering region to the detector is large compared to the dimensions of the scattering region, the scattering cross section for N scatterers is [cf. Eq. (2.15)]

$$\frac{d\sigma}{d\Omega} = \sum_{i,j=1}^{N} e^{i(\mathbf{k}-\mathbf{k}_0)(\mathbf{r}_i-\mathbf{r}_j)}\,\hat{\mathbf{e}}\cdot\boldsymbol{\alpha}_j^*\cdot\hat{\mathbf{e}}_0\hat{\mathbf{e}}\cdot\boldsymbol{\alpha}_i\cdot\hat{\mathbf{e}}_0 , \tag{4.1}$$

where $\mathbf{k}$ and $\mathbf{k}_0$ are the wave vectors of the scattered and incoming light, respectively; $\hat{\mathbf{e}}$ and $\hat{\mathbf{e}}_0$ are the polarization directions; and $\mathbf{r}_i$ and $\boldsymbol{\alpha}_i$ are the position and the effective polarizability tensor of the ith molecule. We assume that the polarizability tensors $\boldsymbol{\alpha}_i$ are all of the form (2.1), with identical constants α and β, but each with its own orientation of the molecular axis $\hat{\mathbf{R}}_i \approx (\Theta_i, \Phi_i)$.

It is convenient to separate the cross section Eq. (4.1) into two parts, an *incoherent* part consisting of the terms with $i = j$ and a *coherent* part consisting of the terms with $i \neq j$. The ensemble average of the incoherent part contains only the distribution function for the orientation of a single molecule, and it is equal to the quantity calculated in the preceding section, apart from a factor N. The ensemble average of the coherent part contains the two-particle distribution function $f_2(\mathbf{r}_1, \Theta_1, \Phi_1; \mathbf{r}_2, \Theta_2, \Phi_2)$, which gives the probability of simultaneously finding impurities at specified positions in the interface $z = 0$ with the specified orientations. The function f_2 is normalized such that

$$\int \cdots \int f_2\, d^2\mathbf{r}_1 d^2\mathbf{r}_2 \sin\Theta_1\, d\Theta_1\, d\Phi_1 \sin\Theta_2\, d\Theta_2\, d\Phi_2 = N(N-1). \tag{4.2}$$

Notice that we assumed that all impurities are located exactly at the interface, and that the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are treated in Eq. (4.2) as two-dimensional vectors.

The scattering cross sections may be expressed in terms of the quantities

$$\begin{aligned}
g_{LM;L'M'}(\mathbf{r}, \mathbf{r}') = 4\pi \iiiint & f_2(\mathbf{r}, \Theta_1, \Phi_1; \mathbf{r}', \Theta_2, \Phi_2)\tilde{\mathcal{Y}}_{LM}(\Theta_1, \Phi_1)\\
& \times \tilde{\mathcal{Y}}_{L'M'}(\Theta_2, \Phi_2) \sin\Theta_1\, d\Theta_1\, d\Phi_1 \sin\Theta_2\, d\Theta_2\, d\Phi_2 ,
\end{aligned} \tag{4.3}$$

where $\tilde{\mathcal{Y}}_{LM}$ are the *real* spherical harmonics (with $\tilde{\mathcal{Y}}_{L,+|M|}$ containing the factor $\cos M\Phi$ and $\tilde{\mathcal{Y}}_{L,-|M|}$ containing the factor $\sin M\Phi$) in a coordinate system with z axis normal to the interface and x axis along the vector $\mathbf{r}'$

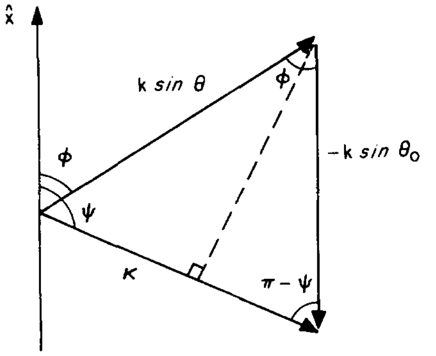

FIG. 1. The two-dimensional scattering vector κ, its azimuthal angle ψ, and their relation to the quantities k, θ_0, θ, and ϕ. The relations (4.7) and (4.8) express simple geometrical relations in this figure. [Equation (4.8) is obtained by equating two expressions for the length of the dashed line.] All vectors in this figure lie in the plane of the interface.

$-\mathbf{r}$. The factor 4π is chosen such that $g_{00;00}(\mathbf{r}, \mathbf{r}')$ is the customary two-particle distribution function. In view of the definition and the supposed invariance of the ensemble of scatterers under translations and rotations that leave the interface invariant, the functions $g_{LM;L'M'}(\mathbf{r}, \mathbf{r}')$ depend only on $|\mathbf{r}-\mathbf{r}'|$; moreover,

$$g_{LM;L'M'}(|\mathbf{r}-\mathbf{r}'|) = (-1)^{M+M'} g_{L'M';LM}(|\mathbf{r}-\mathbf{r}'|) . \qquad (4.4)$$

Finally we may assume that, certainly in the absence of magnetic interactions between the impurities, the function f_2 is invariant under the simultaneous change in sign of Φ_1 and Φ_2. This implies that $g_{LM;L'M'}$ vanishes unless M and M' are either both negative or both nonnegative.

By using the expressions derived in the Appendix for the scattering amplitudes in terms of the spherical harmonics, Eq. (A2), we can now express the coherent part of the scattering amplitude in terms of the functions (4.3); the functions $g_{LM;L'M'}$ always occur in the combination

$$\int \exp[i(\mathbf{k}_0-\mathbf{k})\cdot\mathbf{r}]\, g_{LM;L'M'}(r) f(\chi) r\, dr\, d\chi , \qquad (4.5)$$

where $f(\chi)$ is some function of the angle χ between $\mathbf{r}$ and the projection of $\mathbf{k}_0$ on the interface. The χ integration can be carried out; for this purpose we write

$$(\mathbf{k}_0-\mathbf{k})\cdot\mathbf{r} = -\kappa r\cos(\chi-\psi) , \qquad (4.6)$$

with κ the length of the projection of $\mathbf{k}-\mathbf{k}_0$ on the interface and ψ its angle with the projection of $\mathbf{k}_0$ on the interface (see Fig. 1),

$$\kappa = k[\sin^2\theta_0 + \sin^2\theta - 2\sin\theta_0\sin\theta\cos\phi]^{1/2} , \qquad (4.7)$$

$$\sin\theta_0\sin\psi = \sin\theta\sin(\psi-\phi) , \qquad (4.8)$$

and use the standard integral formula[9]

$$\int_0^{2\pi} \exp[-i\kappa r\cos\alpha]\cos n\alpha\, d\alpha = 2\pi(-i)^n J_n(\kappa r) , \qquad (4.9a)$$

$$\int_0^{2\pi} \exp[-i\kappa r\cos\alpha]\sin n\alpha\, d\alpha = 0 , \qquad (4.9b)$$

with J_n the Bessel function of nth order.

The final expressions for the averaged coherent scattering cross section will therefore contain the quantities

$$j^{(n)}_{LM;L'M'}(\kappa) \equiv 2\pi\int_0^\infty g_{LM;L'M'}(r) J_n(\kappa r) r\, dr . \qquad (4.10)$$

In terms of these, quantities for various cross sections may be expressed as

$$d\sigma_{PP}/d\Omega = Nk^4\mathfrak{y}_0^2\mathfrak{y}^2[\cos^2\phi D_3^0 + \cos\phi\cos(2\psi-\phi)D_1^2 + D_1^0 + \cos(4\psi-2\phi)D_1^4] , \qquad (4.11a)$$

$$d\sigma_{PO}/d\Omega = Nk^4\mathfrak{y}_0^2\mathfrak{x}'^2[\sin^2\phi D_3^0 + \sin\phi\sin(2\psi-\phi)D_1^2 + D_1^0 - \cos(4\psi-2\phi)D_1^4] + Nk^4\mathfrak{y}_0^2\mathfrak{z}'^2[D_2^0 + \cos 2\psi D_2^2] - Nk^4\mathfrak{y}_0^2\mathfrak{x}'\mathfrak{z}'\sin\phi\sin\psi D_1^1 , \qquad (4.11b)$$

$$d\sigma_{OP}/d\Omega = Nk^4\mathfrak{x}_0'^2\mathfrak{y}^2[\sin^2\phi D_3^0 - \sin\phi\sin(2\psi-\phi)D_1^2 + D_1^0 - \cos(4\psi-2\phi)D_1^4] + Nk^4\mathfrak{z}_0'^2\mathfrak{y}^2[D_2^0 + \cos(2\psi-2\phi)D_2^2]$$
$$+ Nk^4\mathfrak{x}_0'\mathfrak{z}_0'\mathfrak{y}^2\sin\phi\sin(\psi-\phi)D_1^1 , \qquad (4.11c)$$

$$d\sigma_{OO}/d\Omega = Nk^4[\mathfrak{x}_0'^2\mathfrak{x}'^2\cos^2\phi D_3^0 + \mathfrak{z}_0'^2\mathfrak{z}'^2 D_4^0 + 2\mathfrak{x}_0'\mathfrak{z}_0'\mathfrak{x}'\mathfrak{z}'\cos\phi(D_5^0 + D_2^0)] + Nk^4\mathfrak{x}_0'^2\mathfrak{x}'^2[D_1^0 + \cos(4\psi-2\phi)D_1^4]$$
$$+ 2Nk^4\mathfrak{x}_0'\mathfrak{z}_0'\mathfrak{x}'\mathfrak{z}'\cos(2\psi-\phi)D_2^2 + Nk^4\{(\mathfrak{z}_0'^2\mathfrak{x}'^2 + \mathfrak{x}_0'^2\mathfrak{z}'^2)D_2^0 + [\mathfrak{z}_0'^2\mathfrak{x}'^2\cos(2\psi-2\phi) + \mathfrak{x}_0'^2\mathfrak{z}'^2\cos 2\psi]D_2^2\}$$
$$- Nk^4[\mathfrak{x}_0'^2\mathfrak{x}'^2\cos\phi\cos(2\psi-\phi)D_1^2 + \mathfrak{x}_0'\mathfrak{z}_0'\mathfrak{x}'\mathfrak{z}'\cos(2\psi-\phi)D_2^3] + Nk^4(\mathfrak{x}_0'\mathfrak{x}'\cos\phi + \mathfrak{z}_0'\mathfrak{z}')[\mathfrak{z}_0'\mathfrak{x}'\cos(\psi-\phi) + \mathfrak{x}_0'\mathfrak{z}'\cos\psi]D_1^1 , \qquad (4.11d)$$

and, for the completely depolarized direction of polarization,

$$d\sigma_{PD}/d\Omega = Nk^4\mathfrak{y}_0^2\mathfrak{y}^2[\mathfrak{x}'^2\sin^2\phi + \mathfrak{y}^2\cos^2\phi]^{-1}[\mathfrak{x}'^2(D_2^0 - \cos 4\psi D_1^4) + \mathfrak{z}'^2\cos^2\phi(D_3^0 + \cos 2\psi D_2^2)] . \qquad (4.12)$$

In Eqs. (4.11) and (4.12) we used the abbreviations

$$D_1^0 = \tfrac{1}{30}|\beta|^2(j^{(0)}_{22;22} + j^{(0)}_{2-2;2-2}) , \qquad (4.13a)$$

$$D_2^0 = \tfrac{1}{30}|\beta|^2(j^{(0)}_{21;21} + j^{(0)}_{2-1;2-1}) , \qquad (4.13b)$$

$$D_3^0 = |\alpha|^2 j^{(0)}_{00;00} - \frac{2}{3\sqrt{5}}\,\mathrm{Re}(\alpha^*\beta) j^{(0)}_{00;20} + \tfrac{1}{45}|\beta|^2 j^{(0)}_{20;20} , \qquad (4.13c)$$

$$D_4^0 = |\alpha|^2 j^{(0)}_{00;00} + \frac{4}{3\sqrt{5}}\,\mathrm{Re}(\alpha^*\beta) j^{(0)}_{00;20} + \tfrac{4}{45}|\beta|^2 j^{(0)}_{20;20} , \qquad (4.13d)$$

$$D_5^0 = |\alpha|^2 j^{(0)}_{00;00} + \frac{1}{3\sqrt{5}}\,\mathrm{Re}(\alpha^*\beta) j^{(0)}_{00;20} - \tfrac{2}{45}|\beta|^2 j^{(0)}_{20;20}, \tag{4.13e}$$

$$D_1^1 = \frac{2}{\sqrt{15}}\,\mathrm{Im}(\alpha^*\beta) j^{(1)}_{00;21}, \tag{4.13f}$$

$$D_1^2 = \frac{2}{\sqrt{15}}\,\mathrm{Re}(\alpha^*\beta) j^{(2)}_{00;22} - \frac{2}{15\sqrt{3}}|\beta|^2 j^{(2)}_{20;22}, \tag{4.13g}$$

$$D_2^2 = \tfrac{1}{30}|\beta|^2 (j^{(2)}_{21;21} - j^{(2)}_{2-1;2-1}), \tag{4.13h}$$

$$D_3^2 = \frac{2}{\sqrt{15}}\,\mathrm{Re}(\alpha^*\beta) j^{(2)}_{00;22} + \frac{4}{15\sqrt{3}}|\beta|^2 j^{(2)}_{20;22}, \tag{4.13i}$$

$$D_1^4 = \tfrac{1}{30}|\beta|^2 (j^{(4)}_{22;22} - j^{(4)}_{2-2;2-2}). \tag{4.13j}$$

A complete experiment allows one to determine these ten quantities as functions of κ for the values $0<\kappa<2k$. For example, σ_{PD} allows one to determine D_1^0, D_2^0, D_1^4, and D_2^2. When these are known, σ_{PP} determines D_3^0 and D_1^2, and σ_{PO} or σ_{OP} determines D_1^1. The remaining three quantities, D_4^0, D_5^0, and D_3^2, then follow from analysis of the part of σ_{OO} that is not yet accounted for by the terms already determined.

For the purpose of devising a measurement strategy one may use Fig. 1 to determine the values of θ_0 and θ that correspond to the desired values of κ, ψ, and ϕ.

In the preceding discussion we have assumed that α, β, and n_c^2 are known quantities, measured from the incoherent part of the cross section in the way pointed out in Sec. III. The coherent and incoherent parts of the cross section cannot be separated when one considers only measurements at a single density of scatterers; one sees by comparing Eqs. (3.5), (3.6), (4.11), and (4.12) that the quantities to be determined occur in the combinations $d_1+D_1^0$, $d_2+n_c^4 D_2^0$, $d_3+D_3^0$, $d_4+n_c^8 D_4^0$, and $d_5+n_c^4 D_5^0$. However, the coherent quantities depend on the density of scatterers, and they vanish in the low density limit. A separation of coherent and incoherent contributions to the scattering cross section is therefore possible when one is able to vary the density of scatterers.

The behavior of the functions $j^{(l)}_{LM;L'M'}(\kappa)$ for low κ is of particular interest since it can be tied to various thermodynamic quantities for the assembly of scatterers via thermodynamic sum rules.[10] As a preliminary to discussing the low-κ behavior, we note that the functions $j^{(0)}_{L0;L'0}(\kappa)$ contain a $\delta(\kappa)$ term due to the fact that the underlying functions $g_{L0;L'0}(r)$ approach the constant value $\rho[(2L+1)(2L'+1)]^{1/2} q_L q_{L'}$, for large r [cf. Eq. (3.4)], where ρ is the number of scatterers per unit area. In practice, this δ function is replaced by a peak with a width which is the inverse of coherence length or the dimension of the scattering region, whichever is smallest. The nonsingular part of $j^{(l)}_{LM;L'M'}$ will be of the order $(\kappa l_{LM;L'M'})^l$ for small κ, where $l_{LM;L'M'}$ is the range of the correlation function.

The small-κ behavior can therefore only be measured with any accuracy when $l_{L0;L'0}$ is small compared to both the coherence length and the dimensions of the scattering volume.

The $\kappa\to 0$ limit of $j^{(0)}_{00,00}$ is related to the difference between the "isothermic compressibility" of the assembly of scatterers and the corresponding ideal gas value.[11] Similarly, the $\kappa\to 0$ limit of $j^{(0)}_{20,20}$ is related to the excess in the susceptibility of the assembly of scatterers to an aligning force with 2, 0 tensor character over the isolated particle value. The $\kappa\to 0$ limit of $j^{(0)}_{00,20}$ relates to the cross effect, i.e., the change in 2, 0 alignment due to an increase in the pressure, or the change in pressure due to a 2, 0 aligning force. The combinations of j functions D_1^0 and D_2^0, respectively, are related in the $\kappa\to 0$ limit to the excess susceptibility for aligning forces with a tensor character described by any linear combination of either $\mathcal{Y}_{22}$ and $\mathcal{Y}_{2-2}$ (for D_1^0) or $\mathcal{Y}_{21}$ and $\mathcal{Y}_{2-1}$ (for D_2^0) with respect to a coordinate system with space fixed axes, of which the z axis is normal to the interface. (In order to find this relation one has to transform from the system with x axis along $\mathbf{r}$, in which the functions $g_{LM;L'M'}$ are defined, to the space-fixed system in which the aligning force is described.) These susceptibilities are independent of the precise linear combinations chosen, owing to the invariance of the ensemble of scatterers under rotations in the plane of the interface. Physical interpretations for the low-κ values of the other j functions may be given, but the matter will not be pursued here any further.

In order to estimate the relative importance of the various terms in the coherent cross sections (4.11) and (4.12) one must know something about the forces exerted by the scatterers on one another. For example, when these forces do not depend on the orientation of the scatterers, there is no mechanism for establishing orientational correlations, and all D_n^l except D_3^0, D_4^0, and D_5^0 vanish. Moreover, one has the relations

$$\begin{aligned} j^{(0)}_{00;20} &= q_2 j^{(0)}_{00;00}, \\ j^{(0)}_{20;20} &= (q_2)^2 j^{(0)}_{00;00}. \end{aligned} \tag{4.14}$$

In particular, this means that the completely depolarized cross sections have no coherent part in this special case.

V. FREQUENCY RESOLVED SCATTERING

In this section we shall discuss the frequency dependence of the scattering that arises from the translation and rigid rotation of the impurities at the interface.

The explicit expressions for the differential cross section for frequency resolved scattering can be obtained along the same lines as those for the total elastic scattering in Secs. III and IV. The analogue of the starting equation (4.1) is

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \sum_{i,j=1}^{N} e^{i(\mathbf{k}-\mathbf{k}_0)[\mathbf{r}_i(0)-\mathbf{r}_j(t)]} \times \hat{\mathbf{e}}\cdot \boldsymbol{\alpha}_j^*(t)\cdot \hat{\mathbf{e}}_0\, \hat{\mathbf{e}}\cdot \boldsymbol{\alpha}_i(0)\cdot \hat{\mathbf{e}}_0, \tag{5.1}$$

where $d^2\sigma/d\Omega d\omega$ is the cross section for scattering in the direction Ω with a frequency shift ω. It is easy to check that

$$\int_{-\infty}^{+\infty} \frac{d^2\sigma}{d\Omega d\omega}\, d\omega = \frac{d\sigma}{d\Omega}, \tag{5.2}$$

with the rhs given by Eq. (4.1), in view of the identity

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\, d\omega = \delta(t)\,. \qquad (5.3)$$

The subsequent development closely parallels that of Sec. IV; one introduces the two-point correlation function

$$f_2(\mathbf{r}_1, \Theta_1, \Phi_1;\mathbf{r}_2, \Theta_2, \Phi_2;t)\,,$$

which specifies the probability of finding a particle at $\mathbf{r}_1$ with orientation (Θ_1, Φ_1) at time 0 and a particle at $\mathbf{r}_2$ with orientation (Θ_2, Φ_2) at time t. It is convenient to drop the requirement, made in the definition of the corresponding function $f_2(\mathbf{r}_1, \Theta_1, \Phi_1;\mathbf{r}_2, \Theta_2, \Phi_2)$ in Sec. IV, that the two particles be different, and make the distinction between coherent and incoherent parts of the scattering cross section at a later stage in the development.

Next we define

$$g_{LM;L'M'}(\mathbf{r}, \mathbf{r}', t) = 4\pi\iiiint f_2(\mathbf{r}_1, \Theta_1, \Phi_1;\mathbf{r}', \Theta_2, \Phi_2; t)\tilde{\mathcal{Y}}_{LM}(\Theta_1, \Phi_1)\tilde{\mathcal{Y}}_{L'M'}(\Theta_2, \Phi_2)\sin\Theta_1\, d\Theta_1\, d\Phi_1 \sin\Theta_2\, d\Theta_2\, d\Phi_2\,, \qquad (5.4)$$

with the coordinate axes for the spherical harmonics as in Eq. (4.3). When f_2 depends only on $|\mathbf{r}' - \mathbf{r}'|$, the same is true for $g_{LM;L'M'}$. If, moreover, f_2 is independent of the choice of the zero in time and invariant under time inversion, we have

$$g_{LM;L'M'}(|\mathbf{r} - \mathbf{r}'|, t) = (-1)^{M+M'} g_{L'M';LM}(|\mathbf{r} - \mathbf{r}'|, t)\,. \qquad (5.5)$$

Finally, when f_2 is invariant under a simultaneous change in sign of Φ_1 and Φ_2, i.e., under reflection with respect to the plane through $\mathbf{r} - \mathbf{r}'$ normal to the interface, $g_{LM;L'M'}$ vanishes unless M and M' are either both negative or both nonnegative.

When all these conditions are met $d^2\sigma/d\Omega d\omega$ has exactly the same form for the different choices of polarization as $d\sigma/d\Omega$ in Eqs. (4.11) and (4.12), with the single modification that the $j^{(n)}_{LM;L'M'}(\kappa)$ in Eq. (4.13) are replaced by

$$j^{(n)}_{LM;L'M'}(\kappa, \omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\int_0^{\infty} r\, dr\, g_{LM;L'M'}(r, t) J_n(\kappa r)\,. \qquad (5.6)$$

We remind the reader that the functions $g_{LM;L'M'}(r, t)$ contain both a coherent and incoherent part; as a consequence, integration over frequency of the expressions obtained by substituting Eq. (5.6) for $j^{(n)}_{LM;L'M'}$ in Eq. (4.13) results in

$$\int d\omega\, D^{(n)}_m(\kappa, \omega) = D^{(n)}_m(\kappa) + n_c^{-4l(m)} d_m \delta_{n,0}\,, \qquad (5.7)$$

with d_m defined in Eq. (3.7), and $l(m) = 0$ for $m = 1$ or 3; $l(m) = 1$ for $m = 2$ or 5, and $l(m) = 2$ for $m = 4$. Unlike the incoherent contributions to the frequency-integrated differential cross section, the incoherent contributions to the frequency-resolved cross sections do depend on the scattering vector κ.

The general expression for the incoherent (single particle) cross section is still rather complicated owing to the possibility of coupling between the rotational and translational degrees of freedom. However, in the absence of such coupling one obtains rather simple results, since the joint probability distribution $f_2^{(s)}(\mathbf{0}, \Theta_1, \Phi_1;\mathbf{r}, \Theta_2, \Phi_2; t)$ for finding a particle at $\mathbf{0}$ with orientation (Θ_1, Φ_1) at time 0 and at $\mathbf{r}$ with orientation (Θ_1, Φ_1) at time t, factorizes into

$$f_2^{(s)} = f_2^{(s,t)}(\mathbf{0}, \mathbf{r}; t) f_2^{(s,r)}(\Theta_1, \Phi_1; \Theta_2, \Phi_2; t)\,, \qquad (5.8)$$

where the angles Φ_1 and Φ_2 are measured with respect to a fixed direction in the interface, rather than with respect to the vector $\mathbf{r}$ (in fact, it follows from symmetry under rotations around the z axis that the choice of the origin of Φ is immaterial). Moreover, $f_2^{(s,t)}(\mathbf{0}, \mathbf{r}; t)$ depends only on $|\mathbf{r}|$, and it will be denoted as $f_2^{(s,t)}(r, t)$. In order to make the separation (5.8) unambiguous we require

$$\iiiint f_2^{(s,r)} \sin\Theta_1\, d\Theta_1\, d\Phi_1 \sin\Theta_2\, d\Theta_2\, d\Phi_2 = 1\,. \qquad (5.9)$$

The function $f_2^{(s,r)}$ is related to the eigenvalues $-\lambda_n$ and the eigenfunctions $h_n(\Theta, \Phi)$ of the evolution operator $\mathfrak{D}$ for the single particle orientational distribution function defined by

$$\frac{d}{dt} f_1(\Theta, \Phi; t) = \mathfrak{D} f_1(\Theta, \Phi; t) \qquad (5.10)$$

by the relation

$$f_2^{(s,r)}(\Theta_1, \Phi_1;\Theta_2, \Phi_2; t) = \sum_n h_n^*(\Theta_1, \Phi_1) h_n(\Theta_2, \Phi_2)\, e^{-\lambda_n |t|}\,. \qquad (5.11)$$

The eigenvalues and eigenvectors of $\mathfrak{D}$ have the following properties:

(1) With the exception of the simple eigenvalue 0 associated with the equilibrium distribution $h_0(\Theta, \Phi) = f_{eq}(\Theta)$ all eigenvalues $-\lambda_n$ have negative real parts; the complex ones occur in mutually conjugate pairs and the corresponding eigenfunctions may be chosen complex conjugates. Moreover,

$$\iint h_n(\Theta, \Phi) \sin\Theta\, d\Theta\, d\Phi = \delta_{n,0}\,. \qquad (5.12)$$

(2) In view of the invariance of $\mathfrak{D}$ under rotations around the z axis, the functions $h_n(\Theta, \Phi)$ may be chosen to have the form

$$h_n^{(M)}(\Theta, \Phi) = \sum_{L=|M|}^{\infty} C^{(M)}_{n,L} \mathcal{Y}_{LM}(\Theta, \Phi) \qquad (5.13)$$

with a single value of M and $\sum_L |C^{(M)}_{n,L}|^2 = 1$. For $n = 0$ in particular [cf. Eq. (3.4)]

$$h_0^{(0)}(\Theta, \Phi) = \sum_{L=0}^{\infty}\left(\frac{2L+1}{4\pi}\right)^{1/2} q_L \mathcal{Y}_{L0}(\Theta, \Phi)\,. \qquad (5.14)$$

We now introduce the functions

$$g^{(s)}_{LM;L'M'}(r,t)=4\pi\iiiint \mathcal{Y}_{LM}(\Theta_1,\Phi_1)\mathcal{Y}_{L'M'}(\Theta_2,\Phi_2)f_2^{(s,t)}(r,t)f_2^{(s,r)}(\Theta_1,\Phi_1;\Theta_2,\Phi_2;t)\sin\Theta_1\,d\Theta_1\,d\Phi_1\sin\Theta_2\,d\Theta_2\,d\Phi_2\,, \tag{5.15}$$

with Θ_i, Φ_i chosen with respect to a fixed coordinate frame with z axis perpendicular to the interface. For these functions one easily derives

$$g^{(s)}_{00;LM}(r,t)=f_2^{(s,t)}(r,t)\delta_{M,0}(2L+1)^{1/2}q_L\,, \tag{5.16}$$

$$g^{(s)}_{LM;L'M'}(r,t)=f_2^{(s,t)}(r,t)\delta_{M,M'}\,\tilde{g}^{(M)}_{LL'}(t)\,, \tag{5.17}$$

with

$$\tilde{g}^{(M)}_{LL'}(t)=\delta_{M0}[(2L+1)(2L'+1)]^{1/2}q_L q_{L'}+\sum_n{}' C^{(M)*}_{n,L}C^{(M)}_{n,L'}\exp[-\lambda_n|t|]\,, \tag{5.18}$$

and $C^{(M)}_{n,L}$ as in Eq. (5.13); the prime in the summation means that the $n=0$ term, that occurs only for $M=0$, has to be omitted, since it has already been written explicitly.

The incoherent contribution to the frequency resolved cross section can be expressed in terms of the quantities [cf. Eqs. (5.1), (5.4), and (5.17)],

$$g^{(s)}_{LM;L'M'}(\kappa,\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\exp[i\omega t]\,d\omega\int_0^{\infty}d^2\mathbf{r}\exp[-i\kappa\cdot\mathbf{r}]f_2^{(s,t)}(r,t)\delta_{M,M'}\tilde{g}^{(M)}_{LL'}(t)\equiv\delta_{M,M'}f_2^{(s,t)}(\kappa,\omega)*\tilde{g}^{(M)}_{LL'}(\omega)\,, \tag{5.19}$$

where the symbol $*$ denotes the convolution

$$f(\omega)*g(\omega)=2\pi\int d\omega' f(\omega-\omega')\,g(\omega')\,, \tag{5.20}$$

and $\tilde{g}^{(M)}_{LL'}(\omega)$ is given by

$$\tilde{g}^{(M)}_{LL'}(\omega)=\delta_{M,0}[(2L+1)(2L'+1)]^{1/2}q_L q_{L'}\delta(\omega)+\frac{1}{2\pi}\sum_n{}' C^{(M)*}_{n,L}C^{(M)}_{n,L'}\left[\frac{1}{i\omega+\lambda_n}-\frac{1}{i\omega-\lambda_n}\right], \tag{5.21}$$

as follows from Eq. (5.18).

The function $f_2^{(s,t)}(\kappa,\omega)$ depends on the assumptions made for the motion of the impurities in the interface. When we assume simple diffusive motion:

$$f_2^{(s,t)}(r,t)=\rho(4\pi D|t|)^{-1}\exp[-r^2/4D|t|] \tag{5.22}$$

(with ρ the density of scatterers), then

$$f_2^{(s,t)}(\kappa,\omega)=\frac{\rho}{2\pi}\left[\frac{1}{i\omega+D\kappa^2}-\frac{1}{i\omega-D\kappa^2}\right], \tag{5.23}$$

and

$$g^{(s)}_{LM;L'M'}(\kappa,\omega)=\frac{\rho}{\pi}\,\delta_{M,M'}\left\{\frac{D\kappa^2}{\omega^2+D^2\kappa^4}\,q_L q_{L'}[(2L+1)(2L'+1)]^{1/2}\delta_{M,0}+\sum_n{}' C^{(M)*}_{n,L}C^{(M)}_{n,L'}\frac{D\kappa^2+\mathrm{Re}(\lambda_n)}{[\omega+\mathrm{Im}(\lambda_n)]^2+[D\kappa^2+\mathrm{Re}(\lambda_n)]^2}\right., \tag{5.24}$$

where the second term vanishes when either L or L' is zero, as a consequence of Eq. (5.12).

Moreover, since complex eigenvalues occur in conjugate pairs with complex conjugate eigenfunctions, the functions $g^{(s)}_{LM;LM}(\kappa,\omega)$ are even in ω.

The final result for the incoherent part of $d^2\sigma/d\Omega d\omega$ has the same form as Eqs. (3.5) and (3.6) with the substitutions

$$\alpha^2\rightarrow\pi^{-1}\alpha^2 D\kappa^2[\omega^2+D^2\kappa^4]^{-1}\,, \tag{5.25a}$$

$$\alpha\beta q_2\rightarrow\pi^{-1}\alpha\beta q_2\,D\kappa^2[\omega^2+D^2\kappa^4]^{-1}\,, \tag{5.25b}$$

$$\beta^2[\tfrac{1}{45}+\tfrac{2}{63}q_2+\tfrac{2}{35}q_4]\rightarrow\beta^2(45\pi)^{-1}g^{(s)}_{20;20}(\kappa,\omega)\,, \tag{5.25c}$$

$$\beta^2(\tfrac{1}{15}-\tfrac{2}{21}q_2+\tfrac{1}{35}q_4)\rightarrow\beta^2(30\pi)^{-1}[g^{(s)}_{22;22}(\kappa,\omega)+g^{(s)}_{2-2;2-2}(\kappa,\omega)]\,, \tag{5.25d}$$

$$\beta^2(\tfrac{1}{15}+\tfrac{1}{21}q_2-\tfrac{4}{35}q_4)\rightarrow\beta^2(30\pi)^{-1}[g^{(s)}_{21;21}(\kappa,\omega)+g^{(s)}_{2-1,2-1}(\kappa,\omega)]\,, \tag{5.25e}$$

with $g^{(s)}_{2M;2M}(\kappa,\omega)$ defined by Eq. (5.24). As was to be expected, the integral of the quantities on the right over all ω yields the quantities on the left in the expressions (5.25).

Analysis of the frequency-resolved scattering cross section for incoherent scattering along the lines of those described in Secs. III and IV allows the determination of the quantities at the right in (5.25). From either one of the first two, one can determine the diffusion coefficient D.

The latter three for $\kappa\rightarrow 0$ give the relaxation functions $g^{(0)}_{22}(\omega)$, $[g^{(1)}_{22}+g^{(-1)}_{22}]$, and $[g^{(2)}_{22}+g^{(-2)}_{22}]$, which are sums of Lorentzians in the approximation of this section. For finite κ all these peaks are broadened by the identical amount $D\kappa^2$. We expect that $\mathrm{Im}(\lambda_n)<[D\kappa^2+\mathrm{Re}(\lambda_n)]$ for most cases, and accordingly the spectrum will consist of overlapping Lorentzians. The precise decomposition of such experimental spectra is notoriously difficult. Nevertheless, these predictions are probably the most severe test of the various approximations made in this paper, in particular of the assumption that the interface and the position of the impurities with respect to the interface do not fluctuate to any appreciable extent, as well as of the assumption that the translation and rotation of the impurities are decoupled. We will return to this point in the next section.

VI. CONCLUDING REMARKS

As stated in the Introduction, the calculations presented in this paper are meant as an illustrative example of the kind of information about impurities at an interface, that may be obtained from precise light scattering measurements. It was not our intention to give an exhaustive treatment of all effects that might occur in such situations. In the present section we will list the assumptions and approximations made in the paper, and we will briefly comment on the way in which a violation of these assumptions might manifest itself in a scattering experiment, and the way our treatment might be modified in order to correct for them.

A. Assumptions about the individual scatterers

We treated the scatterers as point particles with cylindrically symmetric polarization tensors. When the dimensions of the particle become nonnegligible with respect to the wavelength of the light, the incoherent cross sections will depend on $\mathbf{k}-\mathbf{k}_0$, and the coherent cross sections contain convolutions of this molecular form factor with the Fourier transform of the correlation functions. Effects of this kind can be accounted for by means of the formalism developed, e.g., by Steele and Pecora.[3] Their formalism also allows one to treat the case in which the polarizability tensor is no longer cylindrically symmetric.

B. Assumptions about the ensemble of scatterers

We assumed in Secs. IV and V that the distribution functions for position and orientation of the scattering particles possess a number of symmetry properties: invariance under translations, rotations and reflections that leave the interface invariant, and stationarity in time. These conditions will be obeyed in most experimental situations, and violations are rather easy to detect. The invariance under rotations may be violated for very concentrated systems, where the impurities form an ordered surface phase; this may be detected simply by checking the invariance of various cross sections under simultaneous rotation of the directions of the incoming and the detected scattered beam around the normal to the interface. Deviations from invariance under reflection may occur when magnetic effects are nonnegligible. In such a case the angular dependence of the coherent part of the scattering is more complicated than the one described in Secs. IV and V, owing to contributions from $g_{LM;L'M'}$ with different signs of M and M'. Moreover, one would expect a dependence of the scattering cross sections on the value of an externally applied magnetic field.

C. Assumptions about the surface and the position of the scatterers with respect to the surface

Throughout this paper we treated the interface as perfectly flat and the degree of submersion of the scatterers as fixed and independent of the orientation of the scatterers. For fluids with sufficiently high surface tension and specific gravity, the fluctuations in the position of the surface will be small compared to the wavelength of the light. Similarly, the distance of the scatterers from the interface will be small compared to the wavelength, provided the force that keeps the impurity near the interface is sufficiently strong. Consequently, neglecting the z component of the position of the scatterers seems fully justified in most circumstances.

An additional dependence on the surface fluctuations enters through the distortion factors in the matrices $\mathfrak{R}$ and $\mathfrak{R}'$. In a more complete theory they would be calculated with respect to the instantaneous, fluctuating, direction of the normal to the surface, and subsequently averaged over fluctuations in the surface orientation. The effect is expected to be small for not too low surface tension and specific gravity; it is of second order in the amplitude of the surface waves. Moreover, in the coherent and time-resolved scattering it exhibits the characteristic space- and time dependence of the surface waves. Since the surface waves themselves scatter light whenever the refractive index of the fluid differs from unity,[12] their effect will be easy to estimate; in fact, light scattering by surface waves will cause a background, which has to be subtracted before the effects described in this paper can be determined. Difficulties may occur in this separation process when the scattering impurities interact with the surface waves, i.e., when their position and orientation exhibit oscillations in phase with those waves. In such cases interference between the light scattered by the waves and by the impurities may occur; they may be separated, however, when the frequency dependence of the refractive index differs from that of the polarizability $\alpha(\omega)$ of the impurities.

Probably the most serious limitation of our model (at least for low impurity concentration) is the assumption that the submerged fraction of the impurity is constant and independent of the orientation of the impurity. When the submerged fraction depends appreciably on the orientation, only our results for the *PP* polarization remain reliable. All other cross sections contain contributions involving rather complicated averages over the angular orientations, due to the Θ dependence of the distortion factors $\mathfrak{z}$ and $\mathfrak{z}_0$. When the fluctuations in the degree of submersion are independent of the orientation, then the theory presented in this paper needs only relatively minor modifications. In the expressions of Sec. III the quantities n_c^4 and n_c^8 must be replaced by $\langle n_c^4\rangle$ and $\langle n_c^8\rangle$, respectively; the latter is no longer the square of the former, and the analysis needed to extract all information from a complete scattering experiment becomes more complicated. However, it now yields information on the fluctuations in the submersion factor. The analysis can be performed, by combining measurements at different frequencies of the incoming light (cf. the discussion at the end of Sec. III), provided the ratio $\alpha(\omega)/\beta(\omega)$ varies with frequency.

The coherent and the frequency-resolved cross sections will contain the modified correlation functions

$$g^{(p,q)}_{LM;L'M'}(\mathbf{r},\mathbf{r}';t)=4\pi\iiiint f_2(\mathbf{r},\Theta_1,\Phi_1;\mathbf{r}',\Theta_2,\Phi_2;t)\,n_c^{2p}(\mathbf{r},0)n_c^{2q}(\mathbf{r}',t)\tilde{\mathcal{Y}}_{LM}(\Theta_1,\Phi_1)\tilde{\mathcal{Y}}_{L'M'}(\Theta_2,\Phi_2)\sin\Theta_1\,d\Theta_1\,d\Phi_1\sin\Theta_2\,d\Theta_2\,d\Phi_2, \tag{6.1}$$

where $n_c(\mathbf{r},t)$ contains the submersion factor of the particle at $\mathbf{r}$ at time t. When either p or q is zero, the new functions are simply proportional to the old ones:

$$g^{(p,0)}_{LM;L'M'}(\mathbf{r},\mathbf{r}';t)=\langle n_c^{2p}\rangle g_{LM;L'M'}(\mathbf{r},\mathbf{r}';t)\,. \tag{6.2}$$

Inspection of the expressions (A2) for the scattering amplitudes shows that $g_{2\pm2;2\pm2}$ is never modified, while $g_{2\pm1;2\pm1}$ is always replaced by $g^{(1,1)}_{2\pm1;2\pm1}$, since $\mathcal{Y}_{2\pm1}$ is always accompanied by a factor $\mathfrak{z}_0$ or $\mathfrak{z}$. The functions $\mathcal{Y}_{00}$ and $\mathcal{Y}_{20}$ have either two such factors or none. Consequently, $g_{00;00}$ may remain unmodified or it may be replaced by $g^{(2,2)}_{00;00}$; similarly $g_{00;20}$ and $g_{20;20}$. Finally, $g_{00;21}$ may be replaced by either $\langle n_c^2\rangle g_{00;21}$ (this is the only place where $\langle n_c^2\rangle$ rather than $\langle n_c^4\rangle$ or $\langle n_c^8\rangle$ appears in the theory) or by $g^{(2,1)}_{00;21}$. It turns out that a complete analysis of the experiments yields the nth Bessel transforms, analogous to the ones defined in Eq. (4.10), of both the modified and the unmodified g functions, for the values of n occurring in Eq. (4.13). For all functions except the $g^{(p,q)}_{00;21}$ this analysis requires combining measurements at different frequencies, and it is therefore not feasible when $\alpha(\omega)/\beta(\omega)$ is independent of the frequency ω.

The effect of fluctuations in the degree of submersion may be seen most clearly in the frequency-resolved incoherent scattering, when the conditions of the last part of Sec. V (no coupling between translation and rotation) are satisfied. In this case the quantities in Eqs. (5.25a)–(5.25c) remain unmodified in $d^2\sigma_{PP}/d\Omega d\omega$, $d^2\sigma_{PO}/d\Omega d\omega$, and $d^2\sigma_{OP}/d\Omega d\omega$, but some of these terms are convoluted with the Fourier transform of $\langle n_c^4(0)n_c^4(t)\rangle$ in $d^2\sigma_{OO}/d\Omega d\omega$. The quantity in Eq. (5.25e) is always convoluted with the Fourier transform of $\langle n_c^2(0)n_c^2(t)\rangle$; this may not be easy to detect, since no independent information on the unconvoluted form is available.

D. Local-field and concentration effects

In Sec. II we assumed that the induced dipole moment of the impurity may be expressed as $\boldsymbol{\alpha}\cdot\mathbf{E}$, with $\mathbf{E}$ the Maxwell field at the site of the impurity. This needs some justification; the field at the site of the scatterer is not in general equal to the Maxwell field, and the apparent dipole moment may include some contributions from dipole moments induced by the emitting dipole in its surroundings. In the context of the present paper it is important to distinguish between modifications due to the solvent and modifications due to other impurities.

The modifications due to the solvent do not cause any trouble for an impurity in the bulk phase. Then their only effect is to replace the "true" susceptibility of the impurity by an effective one. On symmetry grounds it is reasonable to assume that the local field $\mathbf{E}_l$ is related to the Maxwell field $\mathbf{E}$ by a relation of the type

$$\mathbf{E}_l=(A\mathbf{I}+B\hat{\mathbf{R}}\hat{\mathbf{R}})\cdot\mathbf{E}\,. \tag{6.3}$$

In this case the effective susceptibility $\boldsymbol{\alpha}$ is related to the true susceptibility $\boldsymbol{\alpha}_0$ by the relation

$$\boldsymbol{\alpha}=(A\mathbf{I}+B\hat{\mathbf{R}}\hat{\mathbf{R}})\cdot\boldsymbol{\alpha}_0\cdot(A\mathbf{I}+B\hat{\mathbf{R}}\hat{\mathbf{R}}). \tag{6.4}$$

(Note that $\boldsymbol{\alpha}$ has the form $\alpha\mathbf{I}+\beta\hat{\mathbf{R}}\hat{\mathbf{R}}$ when $\boldsymbol{\alpha}_0$ has such a form.) The fact that the same factor appears twice (once to convert the Maxwell field into the local field and once to convert the molecular induced dipole moment into an effective one including moments induced by the central dipole in its surroundings) is another consequence of Lorentz's reciprocity theorem.[8] The polarizability $\boldsymbol{\alpha}$ used in this paper is the one defined by Eq. (6.4), and we hope this accounts for the local field effects due to the solvent. It is not clear, however, that this procedure remains correct for an impurity located near the surface. In that case one might expect different local field factors for vertical and horizontal components of the field. As long as this difference does not depend on the orientation of the impurity, this asymmetry factor will combine with the distortion factors $\mathfrak{z}_0$ and $\mathfrak{z}$ and cause the factor n_c^2 to be replaced by an "effective" quantity $\tilde{n}_c^2$. The only noticeable effect will be a possible violation of the inequality $1\leqslant\tilde{n}_c^2\leqslant n^2$. Even fluctuations of the asymmetry factor due to fluctuations in the distance from the impurity to the surface may be handled by a minor modification of the theory in this paper, along the lines suggested in the preceding subsection. Any dependence of the asymmetry on the orientation of the impurity would, however, require a major modification of our scheme.

A major modification is also required when the concentration of impurities near the surface becomes so high that the scattered field of the other impurities is no longer negligible compared to the incoming field. A theory that enables one to treat this situtation was provided recently by Vlieger and Bedeaux.[13] Their theory gives expressions for the "local field factors" due to other impurities in terms of the distribution functions of "surface susceptibilities."

In this connection we should point out that the treatment given in this paper is mainly appropriate for low impurity concentrations. For higher concentrations it would be preferable to employ a "phenomenological," rather than a "molecular" theory, and use as a starting point not the clean surface, but the surface covered with a uniform layer of impurities. The Fresnel factors for such a case were evaluated by Bedeaux and Vlieger[14]; in a subsequent paper[15] they related the surface material coefficients appearing in these Fresnel factors to the distribution functions of the elementary scatterers. It is far from trivial to relate phenomenological and molecular theories, even for the case of scattering by bulk liquids,[16] and the subject will not be pursued here any further.

APPENDIX

The expressions (3.1) and (3.3) may be rewritten in terms of the real spherical harmonics,

$$\mathcal{Y}_{00}=\frac{1}{\sqrt{4\pi}}, \tag{A1a}$$

$$\mathcal{Y}_{20}=\sqrt{\frac{45}{16\pi}}\left(\cos^2\Theta-\tfrac{1}{3}\right), \tag{A1b}$$

$$\mathcal{Y}_{2\pm1}=-\sqrt{\frac{15}{4\pi}}\sin\Theta\cos\Theta\genfrac{}{}{0pt}{}{\cos}{\sin}\Phi, \tag{A1c}$$

$$\mathcal{Y}_{2\pm2}=\sqrt{\frac{15}{4\pi}}\sin^2\Theta\genfrac{}{}{0pt}{}{\cos}{\sin}2\Phi. \tag{A1d}$$

In Eqs. (A1c) and (A1d) the positive sign corresponds to the cosine and the negative sign to the sine.

Now we give the formulas for the expressions corresponding to Eqs. (3.1) and (3.2) in terms of the functions (A1), but for a coordinate system rotated over an angle χ (in this form they will be needed in Sec. IV):

$$A_{PP}=k^2\mathfrak{y}_0\mathfrak{y}\left[\sqrt{4\pi}\,\alpha\cos\phi\mathcal{Y}_{00}-\sqrt{\frac{4\pi}{45}}\beta\cos\phi\mathcal{Y}_{20}-\sqrt{\frac{4\pi}{15}}\beta\cos(2\chi-\phi)\mathcal{Y}_{22}+\sqrt{\frac{4\pi}{15}}\beta\sin(2\chi-\phi)\mathcal{Y}_{2-2}\right], \tag{A2a}$$

$$\begin{aligned}A_{PO}=k^2\mathfrak{y}_0\mathfrak{x}'\Bigg[&\sqrt{4\pi}\,\alpha\sin\phi\mathcal{Y}_{00}-\sqrt{\frac{4\pi}{45}}\beta\sin\phi\mathcal{Y}_{20}+\sqrt{\frac{4\pi}{15}}\beta\sin(2\chi-\phi)\mathcal{Y}_{22}\\&+\sqrt{\frac{4\pi}{15}}\beta\cos(2\chi-\phi)\mathcal{Y}_{2-2}\Bigg]+k^2\mathfrak{y}_0\mathfrak{z}'\left[\sqrt{\frac{4\pi}{15}}\beta\sin\chi\mathcal{Y}_{21}+\sqrt{\frac{4\pi}{15}}\beta\cos\chi\mathcal{Y}_{2-1}\right],\end{aligned} \tag{A2b}$$

$$\begin{aligned}A_{OP}=k^2\mathfrak{x}_0'\mathfrak{y}\Bigg[&\sqrt{4\pi}\,\alpha\sin\phi\mathcal{Y}_{00}-\sqrt{\frac{4\pi}{45}}\beta\sin\phi\mathcal{Y}_{20}\\&-\sqrt{\frac{4\pi}{15}}\beta\sin(2\chi-\phi)\mathcal{Y}_{22}-\sqrt{\frac{4\pi}{15}}\beta\cos(2\chi-\phi)\mathcal{Y}_{2-2}\Bigg]+k^2\mathfrak{z}_0'\mathfrak{y}\left[-\sqrt{\frac{4\pi}{15}}\beta\sin(\chi-\phi)\mathcal{Y}_{21}-\sqrt{\frac{4\pi}{15}}\beta\cos(\chi-\phi)\mathcal{Y}_{2-1}\right],\end{aligned} \tag{A2c}$$

$$\begin{aligned}A_{OO}=\;&k^2(\mathfrak{x}_0'\mathfrak{x}'\cos\phi+\mathfrak{z}_0'\mathfrak{z}')\sqrt{4\pi}\,\alpha\mathcal{Y}_{00}-k^2(\mathfrak{x}_0'\mathfrak{x}'\cos\phi-2\mathfrak{z}_0'\mathfrak{z}')\sqrt{\frac{4\pi}{45}}\beta\mathcal{Y}_{20}-k^2\mathfrak{x}_0'\mathfrak{x}'\sqrt{\frac{4\pi}{15}}\beta[\cos(2\chi-\phi)\mathcal{Y}_{22}\\&-\sin(2\chi-\phi)\mathcal{Y}_{2-2}]-k^2\mathfrak{z}_0'\mathfrak{x}'\sqrt{\frac{4\pi}{15}}\beta[\cos(\chi-\phi)\mathcal{Y}_{21}-\sin(\chi-\phi)\mathcal{Y}_{2-1}]-k^2\mathfrak{x}_0'\mathfrak{z}'\sqrt{\frac{4\pi}{15}}\beta[\cos\chi\mathcal{Y}_{21}-\sin\chi\mathcal{Y}_{2-1}],\end{aligned} \tag{A2d}$$

and, for the completely depolarized amplitude

$$A_{PD}=(\mathfrak{x}'^2\sin^2\phi+\mathfrak{y}^2\cos^2\phi)^{-1/2}k^2\mathfrak{y}_0\mathfrak{y}\beta\left[\mathfrak{x}'\sqrt{\frac{4\pi}{15}}(\mathcal{Y}_{22}\sin2\chi+\mathcal{Y}_{2-2}\cos2\chi)+\mathfrak{z}'\sqrt{\frac{4\pi}{15}}\cos\phi(\mathcal{Y}_{21}\sin\chi+\mathcal{Y}_{2-1}\cos\chi)\right]. \tag{A2e}$$

In order to determine the incoherent cross sections we must express the products $\mathcal{Y}_{LM}\mathcal{Y}_{L'M'}$ in terms of single $\mathcal{Y}_{L''M''}$. In view of the symmetry of the ensemble, we need to consider only those products that yield terms $\mathcal{Y}_{L''0}$. Apart from those containing a factor $\mathcal{Y}_{00}$, these are only the squares of $\mathcal{Y}_{2M}$ functions:

$$\mathcal{Y}_{20}^2=\frac{3}{7\sqrt{\pi}}\mathcal{Y}_{40}+\frac{\sqrt{5}}{7\sqrt{\pi}}\mathcal{Y}_{20}+\frac{1}{\sqrt{4\pi}}\mathcal{Y}_{00}, \tag{A3a}$$

$$\mathcal{Y}_{2\pm2}^2=\frac{1}{14\sqrt{\pi}}\mathcal{Y}_{40}-\frac{\sqrt{5}}{7\sqrt{\pi}}\mathcal{Y}_{20}+\frac{1}{\sqrt{4\pi}}\mathcal{Y}_{00}+\cdots, \tag{A3b}$$

$$\mathcal{Y}_{2\pm1}^2=-\frac{2}{7\sqrt{\pi}}\mathcal{Y}_{40}+\frac{\sqrt{5}}{14\sqrt{\pi}}\mathcal{Y}_{20}+\frac{1}{\sqrt{4\pi}}\mathcal{Y}_{00}+\cdots, \tag{A3c}$$

where we omitted terms in Eqs. (A3b) and (A3c) containing $\mathcal{Y}_{LM}$ with $M\neq0$. After substitution of Eq. (A3) in the squares of the expressions (A2) the results (4.11) and (4.12) are obtained in a completely straightforward manner.

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[*] Supported in part by the National Science Foundation.

[†] Present address: Institut für Theoretische Physik A, RWTH, 51 Aachen, Germany, Templergraben 55.

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