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APPLICATIONF OF INTENSITY CORRELATION SPECTROSCOPY TO LIGHT SCATTERING FROM FLUIDS

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The term intensity correlation spectroscopy (ICS) designates the technique by which relevant properties of a scattering medium illuminated by a light beam are derived from the measurement of the correlation function of the intensity of the scattered light. In the last few years ICS has found many areas of applications in physics, chemistry, biology, and engineering. Its understanding requires an acquaintance with the statistics of light fields, theories of light scattering, and some knowledge of optical and electronic instrumentation. Detailed treatments of the ICS technique and of its must significant applications can be found in Refs. 1 and 2 and articles quoted therein. We shall discuss here a few important points, with the aim of making clear the basic principles of ICS.

1. - Properties of correlation functions [3]

The statistical properties of any random process (such as an optical field) can be characterized by joint probability distributions or (and) correlation functions of any order. In practical cases, relevant information on optical fields is obtained by measuring only the lowest order correlation functions $G^{(1)}$ and $G^{(2)}$, defined as follows;

$$G^{(1)}(\vec{r}_1,\vec{r}_2,\tau) = \langle E^{+}(\vec{r}_1,t)\; E(\vec{r}_2,t+\tau)\rangle \qquad (1)$$

$$G^{(2)}(\vec{r}_1,\vec{r}_2,\tau) = \langle I(\vec{r}_1,t)\; I(r_2,t+\tau)\rangle \qquad (2)$$

where E and $I = |E|^2$ are respectively the electric field and the intensity of the optical beam.

Quite generally it can be said that the spatial properties of correlation functions reflect merely the geometry of the source (the scattering volume in a light scattering experiment). We are here more interested in the time dependence of $G^{(1)}$ and $G^{(2)}$ which contains information about the dynamics of source fluctuations. We put therefore $\vec{r}_1 \equiv \vec{r}_2$. Furtermore we consider only stationary fields, so that $G^{(1)}$ and $G^{(2)}$ depend only on the time delay τ.

Properties of $G^{(1)}(\tau)$:

$$G^{(1)}(0) = \langle I\rangle;\quad |G^{(1)}(\tau)| \leq G^{(1)}(0)\quad;\quad \lim_{\tau\to\infty} G^{(1)}(\tau) = 0$$

Properties of $G^{(2)}(\tau)$

$$G^{(2)}(0) = \langle I^2\rangle;\lim_{\tau\to\infty} G^{(2)}(\tau) = \langle I\rangle^2;\; |G^{(2)}(\tau) - \langle I\rangle^2| \leq G^{(2)}(0) - \langle I\rangle^2$$

We recall also the definition of the optical spectrum $S^{(1)}(\omega)$

$$S^{(1)}(\omega) = \int G^{(1)}(\tau) \quad e^{i\omega\tau} \, d\tau \tag{3}$$

If $S^{(1)}(\omega)$ is a symmetric function with respect to the central frequency ω_o, and we write the field as

$$E(t) = E_o(t) \, e^{-i\left[\omega_o t + \varphi(t)\right]} \qquad (E_o(t) \text{ real})$$

the correlation functions can be expressed as

$$G^{(1)}(\tau) = \langle I \rangle \, e^{i\omega_o\tau} f(\tau) \tag{4}$$

$$G^{(2)}(\tau) = \langle I \rangle^2 \, (1 + g(\tau)) \tag{5}$$

where $f(\tau)$ and $g(\tau)$ are real.

The following relation holds for gaussian fields

$$g(\tau) = f^2(\tau) \tag{6}$$

Note that the knowledge of $G^{(2)}$ does not give completely $G^{(1)}$ even for gaussian fields. The information about the central frequency ω_o is lost.

2. - Light scattering: generalities [4]

A schematic light scattering experiment is sketched in fig. 1. A monocromatic plane wave, linearly polarized, is incident upon a perfectly uniform transparent medium.

An optical detector in the position P reveals the presence of a nonzero light intensity, generally weak, propagating in directions other than that of the reflected and refracted beam. This is what is called scattered light.

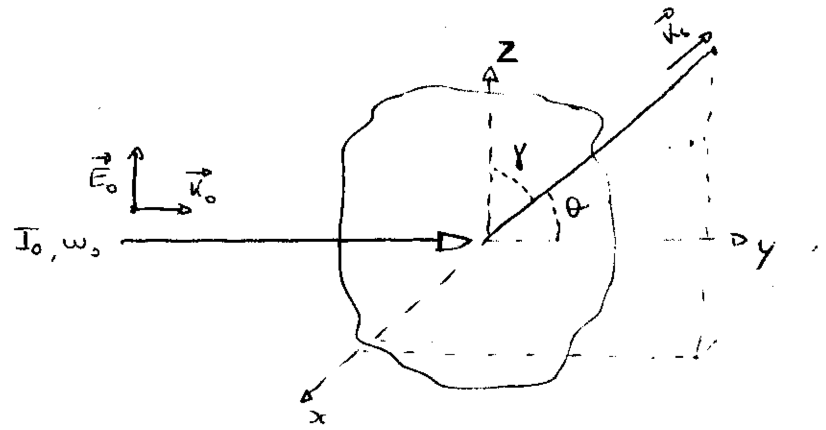

Fig. 1 - Schematic light scattering experiment. The incident beam propagates along the y axis and is linearly polarized along the z axis; ω_0 and I_0 are respectively its angular frequency and its intensity. The scattered light is observed at the point P having polar coordinates (R, θ, γ). θ is the angle between $\vec{k}_0$ and $\vec{k}_s$. The effective volume V which contributes to the scattered field collected at P does not include the entire sample, but it is rather defined by the cross section of the incident beam and the detection optics. The distance R is taken to be much larger than the linear size of the scattering volume V.

The physical origin of the scattering process, can be understood in the following way. The illuminated medium interacts with the inci-

dent electric field at optical frequency through a electric polarizability per unit volume $\chi(\vec{r}, t)$;For sake of simplicity the medium is assumed to be optically isotropic (χ is a scalar quantity) and linear (χ independent of the amplitude of the incident field).
The polarization induced in each element of the illuminated volume is oscillating at the same frequency of the incident field, [illegible]. The field radiated by each volume element follows the well-known dipole radiation pattern. The field collected by a detector placed in the position R is the sum, with appropriate phases, of the contributions from each volume element. It is easy to show that, if $\chi(\vec{r}, t)$ is independent of $\vec{r}$, we get destructive interference in any direction, apart from that of the refracted beam. If, however, χ is a fluctuating function of $\vec{r}$, all the elementary contributions to the scattered field will not completely cancel out, and we do expect a nonzero scattered intensity.

The polarizability χ can always be written as

$$\chi(\vec{r}, t) = \langle \chi \rangle + \delta\chi(\vec{r}, t)$$

where $\langle \chi \rangle$ is the average part, independent of $\vec{r}$ and t for a homogeneous medium in stationary conditions, and $\delta\chi(\vec{r}, t)$ is the fluctuating part, which has zero average. From the intuitive considerations given above, it is clear that scattering is produced by $\delta\chi(\vec{r}, t)$.

The theoretical computation gives the following expression for the scattered field Es (R, t):

$$E_s(R,t) = \frac{1}{\langle \varepsilon \rangle} \vec{k}_s \cdot (\vec{k}_s \cdot \vec{E}_0) \frac{V\, e^{i(\vec{k}_s \cdot \vec{R} - \omega_0 t)}}{4\,\pi\,R} \delta\varepsilon\,(\vec{k}, t) \qquad (7)$$

where $\varepsilon = 1 + \chi$ is the relative dielectric constant of the medium, V is the volume, $\vec{k}_s$ is the wave vector of the scattered field, and $\delta\varepsilon\ (k,t)$ is defined by the Fourier transformation:

$$\delta\varepsilon\,(k,t) = \frac{1}{V} \int_V \delta\varepsilon\,(\vec{r},t)\, e^{-i\,\vec{k}\cdot\vec{r}}\, d^3r\ . \qquad (8)$$

The vector $\vec{k}$, as shown in fig. 2, is defined by:

$$\vec{k} = \vec{k}_s - \vec{k}_0 \qquad (9)$$

Eqs. (7-9) indicate that of all the Fourier components of the fluctuation in dielectric constant only that particular component whose wave vector is the difference between the wave vectors of the scattered and incident light is responsible for scattering in the direction of observation. It is interesting to observe that this is completely equivalent to say that the scattering process has to satisfy the Bragg condition for the reflection of the incident beam by a tridimensional grating characterized by a reciprocal vector $\vec{k}$.

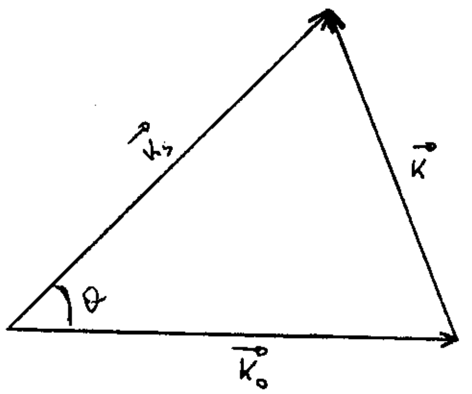

Fig. 2 - Triangle of wave vectors. If $k_s \simeq k_0$, the triangle is practically isosceles.

Eq. (7) has been derived by using a perturbation approach which takes $\delta\chi(\vec{r}, t)$ to be small compared to $\langle\chi\rangle$ and which assumes the attenuation of the incident field to be negligible over the whole length of the scattering volume. Multiple scattering effects are, therefore, assumed to be very weak.

The scattered field $\vec{E}_s(\vec{R}, t)$ is a random function of position ~~in space~~ and time with a zero average. The time-dependent fluctuations of $\vec{E}_s$ exactly mirror the fluctuations in dielectric constant of wave vector k. Fluctuations in dielectric constant are generally much slower than an optical period, that is, the energy associated with an elementary excitation in the medium is much smaller than the energy of the incident optical photon. As a consequence, the energy conservation theorem tells us that the energy of the scattered photon is practically the same as that of the incident one. By putting $|\vec{k}_s| = |\vec{k}_0| \doteq k_0$, the momentum conservation relation (9) gives $k = 2k_0 \sin \theta/2$ where θ is the angle between $\vec{k}_0$ and $\vec{k}_s$ (see fig. 2).

The space-dependent fluctuations of $\vec{E}_s$ depend only, in usual cases, on the geometry of the experiment. Indeed, if we compare $\vec{E}_s(\vec{R}, t)$ with $\vec{E}_s(\vec{R} + \delta\vec{R}, t)$, where $\delta\vec{R}$ is a displacement on the sphere of radius R centered at the origin of the coordinate system, we find that both amplitude and phase of $\vec{E}_s$ are different since the relative phases of the scattered fields from each volume element change by moving from $\vec{R}$ to $\vec{R} + \delta\vec{R}$. The coherence area A_c of the scattered field is qualitatively defined as the area (on the sphere of radius R) over which the scattered field is appreciably uniform in amplitude and phase. A more precise definition would imply the use of a spatial correlation function for the scattered field. The coherence area is given by:

$$A_c \simeq \frac{\lambda^2 R^2}{A_s(\theta, \gamma)}$$

where $A_s(\theta, \gamma)$ is the area intersected on the scattering volume by a plane perpendicular to R and passing through the center of the scattering volume. It is evident from this definition that A_c depends upon the observation direction, that is, the angles θ and γ.

The ratio λ^2 / A_s is called the coherence solid angle. Eq.(10) can be interpreted as an extension of the well known result for a one-dimensional grating of size a, which gives a diffraction angle λ/a and, therefore, a spot size $\lambda R/a$ at a distance R.

The scattered field $\vec{E}_s(\vec{R},t)$ at a given point is a random function of time. A complete characterization of it is given by the set of correlation functions:

$$G_m(t_1,\ldots,t_{2m}) = \langle E_s^*(t_1)\ldots$$

$$\ldots E_s^*(t_m)\ E_s(t_{m+1})\ldots E_s(t_{2m})\rangle$$

where m runs from 1 to infinity. By using Eq.(7) a one-to-one correspondence between the correlation functions of the field and those of the dielectric constant can be established.

3. - Light scattering: macomolecular solutions [5]

In a macroscopic system in thermal equilibrium at a temperature T, local fluctuations of the dielectric constant are caused by fluctuations in the thermodynamic parameters describing the state of the system. For instance, in a pure fluid the value of $\delta\varepsilon(\vec{r},t)$ is mainly determined by local density fluctuations. We will discuss now a specific example, that is light scattering from a suspension of non-interacting macromolecules, small compared with the wavelength of light. For such a system, containing N_s macromolecules in the scattering volume

$$\delta\varepsilon(\vec{r}, t) = \Delta\varepsilon_r \sum_{i=1}^{N_s} \delta\left[\vec{r}-\vec{r}_i(t)\right] \tag{11}$$

where $\Delta\varepsilon_r$ is the difference in relative dielectric constant between a macromolecule and the solvent, and $\vec{r}_i(t)$ is the position of the macromolecule i at time t. Equation 7 then becomes (taking $\vec{k}_s \perp \vec{E}_o$)

$$E(\vec{R}, t) = \frac{E_o k_o^2}{4\pi \langle\varepsilon\rangle R} e^{i(k_s R - \omega_o t)} \Delta\varepsilon_r \sum_{i=1}^{N_s} \exp\left[i\vec{K}\cdot\vec{r}_i(t)\right] \tag{12}$$

This result can also be obtained directly by regarding each macromolecule as an elementary dipole radiator. The electric field correlation function is given by

$$G^{(1)}(\tau) = \frac{|E_o|^2 k_o^4 \Delta\varepsilon_r^2}{16\pi^2 \langle\varepsilon\rangle^2 R^2} e^{i\omega_o\tau} \sum_i \sum_j \left\langle \exp\left\{ i\vec{K}\cdot\left[\vec{r}_i(t) - \vec{r}_j(t+\tau)\right]\right\}\right\rangle \tag{13}$$

For independent scatterers, the position of particle i will at all times be uncorrelated with the position of particle j. Thus only the terms for i = j will contribute to the double sum of Eq. 13. For random walk diffusion under the influence of Brownian motion it is easy to show that

$$G^{(1)}(\tau) = \langle I_s \rangle \exp(i\omega_o\tau) \exp(-DK^2\tau) \tag{14}$$

where $\langle I_s \rangle$ is the average scattered intensity and D is the translational diffusion coefficient of the macromolecule. An intuitive justification of this result comes from the fact that $(DK^2)^{-1}$ is roughly the time taken by a macromolecule to diffuse a distance $1/k$.

If N_s is not too small, the scattered field, being the superposition of many statistically independent contributions, is gaussian. The intensity correlation function is therefore immediately derived from Eqs. 14 and 6, and reads

$$G^{(2)}(\tau) = G^{(1)}(\theta)^2 + \left| G^{(1)}(\tau) \right|^2 =$$

$$= \langle I_s \rangle^2 \left[1 + \exp(-2 D k^2 \tau) \right] \tag{15}$$

4. - The intensity correlation technique

Let us evaluate in a typical case the correlation time $\tau_c = (Dk^2)^{-1}$. For a spherical particle, D is given by the Einstein-Stokes relation

$$D = \frac{K_B \quad T}{6 \pi \eta r} \tag{16}$$

where K_B is the Boltzmann constant, T the absolute temperature, η the viscosity of the solvent, and r the radius of the particle.

By considering a room temperature aqueous solution of spherical macromolecules with $r \simeq 20$ Å, we find $D \simeq 10^{-6}$ cm^2/sec. If the optical source is a He-Ne laser ($\lambda = 6328$ Å) and the scattering angle is $\theta = 60°$, the correlation time comes out to be around 10^{-4} sec.

We could evaluate alternatively the linewidth $\Delta\nu_c$ of the optical spectrum of the scattered light. From Eqs. 3 and 14 we obtain a Lorentzian spectrum, with $\Delta\nu_c = \frac{1}{2\pi\tau_c} \simeq 2$ KHz.
Besides the problem of the required frequency stability of the laser source, it is clear that such a narrow linewidth cannot be measured with the available optical instrumentation.
We recall in fact that the smallest obtainable instrumental width of a Fabry-Perot interferometer is around 1 MHz. The measurement of $G^{(2)}(\tau)$ is simply performed by sending the scattered beam to a photodetector and by electronically processing the electric current at the output of the detector. Weak light beams are generally detected by high-gain photomultiplier tubes which yield a current pulse for each photon absorbed by the photodensitive surface. If the optical signal to be analyzed is so intense that many photons are absorbed within the response time of the photodetector, the output electric current i(t) can be considered as an analog signal proportional to the intensity of the light beam. If we assume that i(t) is a stationary random variable, its autocorrelation function $R(\tau)=\langle i(t)i(t+\tau)\rangle$ depends only on the delay τ and can be evaluated by a time average. In practice, $R(\tau)$ is measured by sampling i(t) periodically and performing the appropriate multiplications among the samples. Since it is easier and faster from an electronic point of view to perform multiplications among digital signals, the result of each sampling operation is quanti-

zed through an analog-to-digital converter. Several correlators based on this technique are now commercially available.They generally work at a maximum sampling frequency of 4 MHz, but real time operation is possible only at sampling frequencies lower than a few kilohertz.

If, however, the optical signal is so weak that it is very unlikely to detect more than one photon within the response time of the photodetector, the output electric current consists of a random train of nonoverlapping pulses. In this case the efficiency of correlators utilizing analog-to-digital conversion is very low, and it is more convenient to exploit the fact that the signal is already in digital form. Several photon correlators have been built in the last few years. A detailed description of their design and operation can be found in Refs. 6 and 7.

It should be recalled that the same information obtained from the intensity correlation function can be gathered by measuring the photocurrent power spectrum which is the Former transform of the correlation function. This was indeed the technique employed in the original applications of electronic spectroscopy to light scattering. Spectral analysis is still widely used for velocimetry applications (fluid mechanics and electrophoresis) because it gives directly the velocity distribution of the scatterers [2].

In usual light scattering experiments the scattered field has gaussian statistical properties, so that the time behavior of $G^{(1)}$ can be derived from the measured $G^{(2)}(\tau)$. It should be mentioned, however, that a direct measurement of $G^{(1)}$ can be performed also by the intensity correlation technique. Indeed if the scattered light under investigation is mixed on the photodetector surface with some of the unscattered light which acts as a local oscillator, and the intensity of the local oscillator is made much larger than the average scattered-intensity, it can be shown that the time dependent part of the intensity correlation is proportional to $\cos\left[(\omega_o - \omega_s)\tau\right]|G^{(1)}(\tau)|$ ~~$G^{(1)}$~~ , where w_o and w_s are respectively the frequency of the incident beam and the central frequency of the scattered field. The reference-beam technique is particularly useful when the scattered field is not gaussian or is frequency shifted with respect to the incident field.

Since ICS introduces electronic instead of optical delays, there is practically no upper limit to the available time delays. The response time of the photodetector puts however a lower limit to the delay. A very interesting feature of ICS is that requirements on the temporal coherence of the optical source are much less severe than in the case of interferometric measurements. If Eq. 7 is written as

$$E_s(t) = E_o(t)\ a(t)\ , \qquad (17)$$

where a(t) is proportional to the amplitude of the appropriate Fourier component of the fluctuating polarizability of the scattering medium, and if we take into account that $E_o(t)$ and $a(t)$ are statistically independent, the correlation functions of $E_s(t)$ are expressed by

$$G_s^{(1)}(\tau) = G_o^{(1)}(\tau)\ G_a^{(1)}(\tau) \quad \text{and} \qquad (18)$$

$$G_s^{(2)}(\tau) = G_o^{(2)}(\tau)\ G_a^{(2)}(\tau)\ , \qquad (19)$$

where $G_o^{(1)}(\tau) = \langle E_o^*(t)\, E_o(t+\tau)$, $G_a^{(1)}(\tau) = \langle a^*(t)\, a(t+\tau)\rangle$, and so on. The function $\left| G_o^{(1)}(\tau)\right|$ is constant if τ is much shorter than the coherence time τ_{co} of the source, and goes to zero for $\tau \gg \tau_{co}$. Therefore $G_a^{(1)}(\tau)$ can be derived from the measured $G_s^{(1)}(\tau)$ only when its decay time is $\lesssim \tau_{co}$. Quite different is the situation for the measurement of $G^{(2)}$, because $G_o^{(2)}(\tau)$ becomes asymptotically a constant for large delays. Hence, provided the source is intensity stabilized, no matter how broad is its optical spectrum, $G_s^{(2)}$ is proportional to $G_a^{(2)}$. The only limitation to the spectral width of the source comes from the fact that Eq. 7 is valid only if the scattering volume is smaller than the coherence volume of the source.

5.- Applications

We list below the main applications of ICS.

a) Fluids in thermal equilibrium :

Physical chemistry of macromolecules in solution: polymers, biological macromolecules, micelles. Information on size, shape, hydration, molecular weight, interaction, association-dissociation equilibria, motility of living microorganisms (bacteria, sperm cells).

Dense fluids : single and multicomponent systems. Measurement of thermal diffusivity and mass diffusion coefficients. Study of phase transitions [8].

Fluid interfaces : velocity of propagating surface waves (ripplons). Information on surface tension and shear viscosity.

Plasmas and gases : velocity distribution of ions, electrons, atoms. Information on temperature and other parameters.

b) Flowing fluids (Laser Doppler velocimetry) [2]

Hydrodynamics : laminar and turbolent flows, convective instabilities.

Aerodynamics : wind tunnels

Combustion and flames

Blood flow

Electrophoresis : macromolecular motion under the action of an electric field.

With regard to applications b), we

only mention here the principle on which Laser Doppler Velocimetry is based. If we consider Eq. 12 and assume that the N_s particles are moving with a constant velocity $\vec{v}$, the position $\vec{r}_j(t)$ can be written as $\vec{r}_j(t) = \vec{r}_{oj} + \vec{v}\,t$. As a consequence the scattered field is frequency shifted with respect to the incident field of a quantity $\Delta\nu_D = \frac{\vec{K}\cdot\vec{v}}{2\pi}$.

We have not here the space to give even a sketchy treatment of all application a). The following short discussion is confined to macro molecular solutions.

Macromolecules with a linear size much smaller than $1/K$ are essentially point scatterers, and only motion of their centres of mass will contribute to the time-dependence of scattered light fluctuations.

If we further assume the scatterers to be non-interacting and identical, $G^{(1)}(\tau)$ is exponential (sec Eq. 14) with a decay time $\tau_c = (DK^2)^{-1}$. The translational diffusion coefficient D is a parameter of some importance for the following reasons. First of all it can be used to determine the molecular weight of the macromolecule through the Svedberg equation [5], once the sedimentation coefficient is known. Furthermore D provides a direct measure of the friction coefficient f_o through the relation $D = (K_B\ T/f_o)$. For spherical particles f_o is, in turn, given by the Stokes relation (cf. Eq. 16)

$$f_o = 6\pi\eta R_H \tag{20}$$

where R_H is the radius of the particle in solution, the so-called hydrodynamic radius. Note that when the macromolecule is hydrated r_H does not coincide with the radius of the dry macromolecule, and the comparison of r_H withe the dry radius gives information on

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the degree of solvation. For non-spherical particles a form factor has to be included into Eq. 20. Therefore configurational changes in the macromolecule produced by any variation of the environment, such as temperature or pH, can be detected by measuring changes of D. A typical application is the study of the reversible denaturation of small proteins.

The treatment becomes more complicated if macromolecular polydispersity and (or) interactions are taken into account. We refer to the specialized literature for a full discussion of these points. We just mention here that, from the experimental point of view, polydispersity appears as a departure of $G^{(1)}(\tau)$ from the single exponential behavior and interactions give rise to a concentration dependence of the diffusion coefficient D.

A large variety of macromolecules have been studied in the last few years by ICS. The list includes naturally occurring and man-made polymers in water and other organic solvents, many macromolecules of biological interest, such as proteins, viruses, phages, microorganisms such as bacteria and sperm cells. Very recently ICS has been applied to micelles which are colloidal aggregates formed by surfactant molecules [9].

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