

Dynamic Lightscattering

1 Introduction

As the name implies, dynamic lightscattering analyses the temporal behaviour of light scattered by a sample fluid, enabling a number of properties of the sample to be determined. The theoretical foundations of this method were laid in the beginning of the century; but the high resolution required to detect and measure the small frequency shifts and narrow spectral linewidths of the scattered light impose stringent demands on both the light source and detection system.

Only with the development of the laser in the 1960's and the concurrent widespread use of photomultipliers as detection elements, did measurements become feasible. The continuous improvement of these components and the introduction of the digital correlator as a means of measuring spectral linewidths, has improved the accuracy and simplified the operation of method. Today, dynamic lightscattering finds many and increasing applications in the fields of physics, chemistry and biology such as the measurement of diffusion and diffusion-related properties or molecular characteristics and structural changes in fluids.

2 Overview

The process primarily involved in dynamic light scattering is known as rayleigh scattering. As discussed in the introductory chapter on scattering processes, rayleigh scattering deals with particles which are small compared to the wavelength of incident light such that their interaction does not appreciably change the phase or amplitude of the light wave. Typical scatters are the molecules of the fluid itself, but microscopic suspended particles also fulfill the rayleigh critereon. The effect was first observed by Tyndall (1869) who studied the scattering of light on aerosols, and was able to explain the color of the sky and the polarization of scattered light. Rayleigh (1871,1881) cast these observations into theoretical form and showed that the scattered light intensity was proportional to the square of the particle diameter and inversely proportional to the fourth power of the wavelength of light.

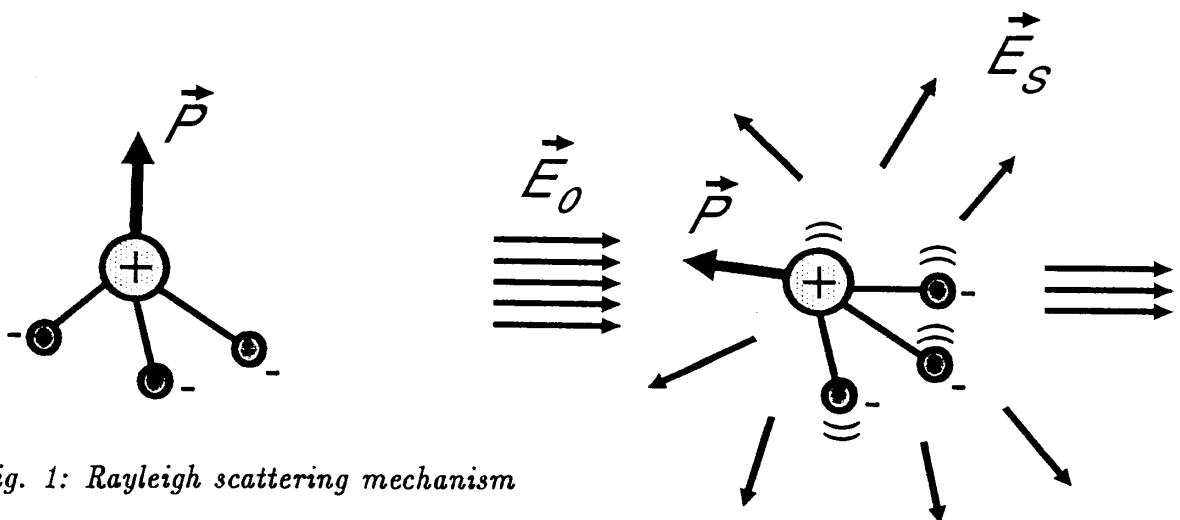
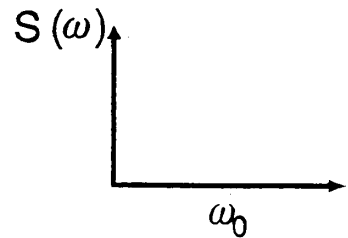
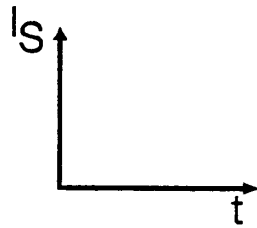
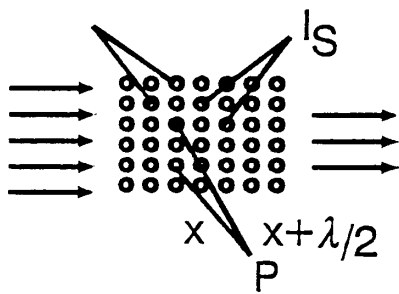


Fig. 1: Rayleigh scattering mechanism

Classical electromagnetic wave theory can be used to describe the scattering process involved. In the presence of an electric field \vec{E} , the individual molecules are polarized, the positive and negative charges being distorted, aligning themselves in the direction of the applied field. A resulting dipole moment \vec{P} parallel to the direction of the field is induced, creating an oscillating dipole which radiates electromagnetic energy \vec{E}_S in all directions. The magnitude of the resultant radiation field \vec{E}_S is dependent on the molecular polarizability α , $\vec{E}_S = \alpha \cdot \vec{E}$. This polarized scattered light is of the same frequency as the incident light, a characteristic of rayleigh scattering.

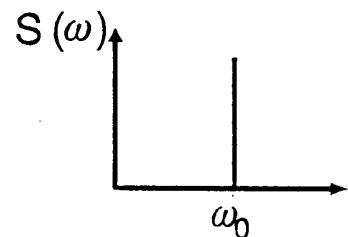
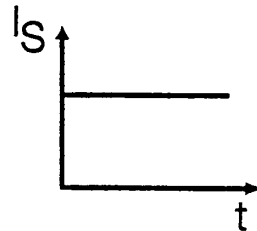
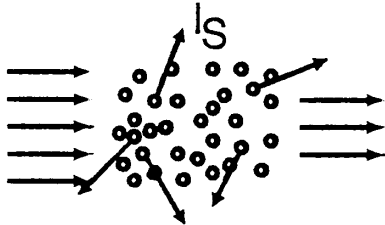
In classical rayleigh theory, the molecules are treated as independent scatterers. Thus the resultant intensity of scattered light is simply the sum of the individual contributions of the molecules. While this theory can predict the scattered intensities of dilute gases quite accurately, it fails in the fluid region, the predicted intensities being more than an order of magnitude larger than actually measured. The explanation lies in the fact that the individual scattering contributions in fluids and dense gases interact, making an exact estimate of the overall intensity very difficult. This problem was solved in the early 1900's by Smoluchowski (1908) and Einstein (1910) who developed the "fluctuation theory of light scattering". The concept can be demonstrated by a simple "gedanken experiment".

lattice structure



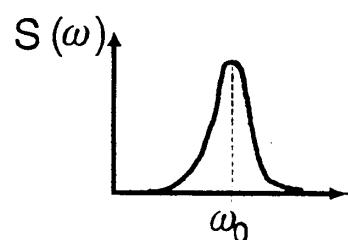
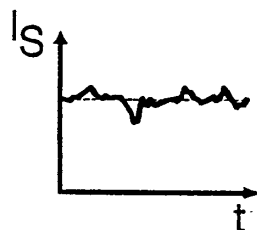
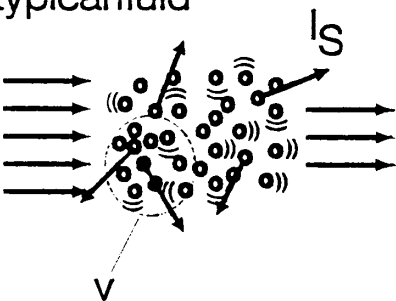
(2a)

motionless fluid



(2b)

typical fluid



(2c)

Fig. 2: Demonstration of the fluctuation theory of light scattering.

If we assume the molecules of a substance to be motionless and ordered in a strict lattice structure, an incident monochromatic light beam of frequency ω_0 will produce no resultant scattering intensity I_s due to destructive interference (Fig. 2a). By observing a scattering center at any point P in space, we will always find another which is half a wavelength apart such that both contributions cancel. The light beam is only visible in the forward direction.

If the molecules are next assumed to be randomly orientated as they would be in any typical fluid, but still motionless, then there is some resultant scattered intensity of constant value. This intensity is however less than that predicted by the rayleigh theory since there is still a great amount of destructive interference. The frequency spectrum of the scattered light $S(\omega)$ reveals a sharp line at the incident light frequency ω_0 if rayleigh scattering is the only process involved (Fig. 2b).

In fluids however, the molecules are constantly in random motion, known as thermal - or Brownian Motion. Light scattered off these molecules will fluctuate in intensity. The resultant spectrum is still centered about the incident frequency but now broadened somewhat due to the characteristics of the molecular motion (Fig. 2c).

If we now observe a volume element v in Fig. 2c, small enough to be considered microscopic, but large enough to contain a sufficient number of molecules, the thermal motion will cause the number density to fluctuate in time, even for fluids in a macroscopic state of equilibrium.

By considering a large number of molecules as are in the element v , we may overlook its particle nature and treat the fluid as a continuum. The paths and positions of the molecules need not be taken into account and macroscopic thermodynamic properties such as density can be used to describe the fluctuations. Thus we measure small density fluctuations about macroscopic equilibrium values in fluids

$$\rho(t) = \rho_0 + \Delta\rho(t), \quad (1)$$

where ρ_0 denotes the constant macroscopic equilibrium density and $\Delta\rho(t)$ the fluctuating component. Other thermodynamic properties such as pressure, entropy and temperature fluctuate as well. These fluctuations are in essence dissipative (that is, decaying towards "macroscopic equilibrium"), the forces governing these processes are characteristic properties of the fluid. The concept of a continuum and small fluctuations about equilibrium values allows us to apply the hydrodynamic equations of motion (laws of conservation of mass, momentum and energy) to investigate the temporal behaviour of the fluctuations in fluids. This yields transport properties as thermal diffusivity a , the diffusion coefficient D for mixtures, the sound absorption coefficient β and the speed of sound C_S . Finally, Onsagers law of reciprocal relations states that the laws governing the fluid behaviour on a microscopic scale are identical to those laws governing the macroscopic thermodynamic behaviour, so that by investigating the temporal behaviour of microscopic fluctuations we can extract the transport properties of the fluid.

The fluid may also be seeded with suspended particles small enough to fulfill the rayleigh criterion. Depending on their mass, the particles follow the thermal motion of the fluid molecules in a dampened form. A temporal investigation of light scattered off these particles reveals their respective diffusion coefficients through the fluid, and finally, the size and mass distribution of the particles themselves.

3 Light Scattering Theory

The application of dynamic light scattering has been extended to several fields of science. Depending on the experimental characteristics and on what property is to be measured, the assumptions and theoretical approaches differ, making a general treatment of light scattering theory far too large a task within the scope of this contribution. For this reason we restrict ourselves to translational diffusion, treating an important application: the measurement of thermal diffusivity of fluids.

Even with these restrictions, the theoretical considerations involving light scattering are rather extensive in nature which is why we only emphasize the important aspects here, with the objective of supplying an overview. A detailed derivation can be found in standard literature such as Berne & Pecora (1976), Chu (1974), Cummins & Pike (1977) and Pecora (1985).

3.1 Scattering Geometry. Assumptions

Although light scattering theory can be described by a molecular approach, eg. Fixmann (1955) and Zwanzig (1964), fluctuation theory is more commonly used since it treats the fluid as a continuum, allowing the use of macroscopic thermodynamics. The results are consistent with molecular theory for the applications treated here.

Figure 3 depicts a model of the geometry used in light scattering theory. Usually the laser beam is focused into the fluid and the scattered light is observed at a far point P at an angle Θ by means of a detector.

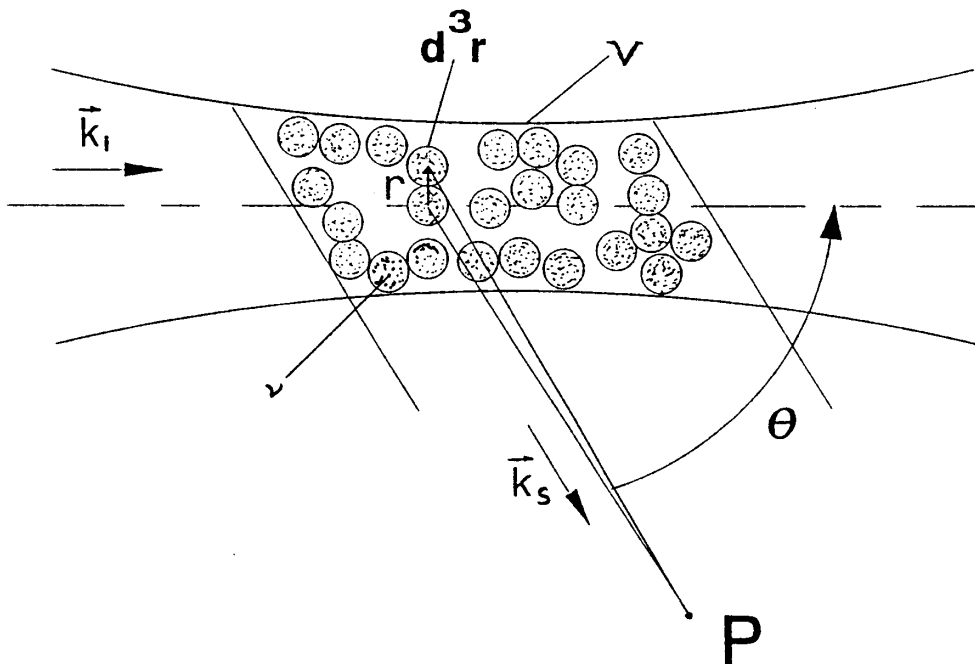


Fig. 3: Light scattering geometry

The scattering volume V is defined by the optics of light source (by how narrow the laser beam can be focussed down to a point), and by that of the detection system (characterized by the solid angle Ω). V consists of a large number of imaginary microscopic volumes v which, in analogy to Fig. 2c, contain the actual molecules that produce the scattering.

The fluid is assumed to be isotropic. v is still small compared to the incident wavelength ($v \ll \lambda^3$), so that the incident electric field is homogenous over the volume. Since v is treated as a continuum (the molecules in fluids and dense gases being packed closely together), the molecular polarizability responsible for rayleigh scattering is replaced by the corresponding macroscopic property, the dielectric constant ϵ . The thermal motion of the molecules causes the dielectric constant of v to fluctuate as ($\epsilon(t) = \epsilon_0 + \Delta\epsilon(t)$), with ϵ_0 being the macroscopic dielectric constant and $\Delta\epsilon(t)$ signifying the fluctuation of ϵ . $\Delta\epsilon$ is assumed to be scalar, meaning that we do not consider depolarized light scattering. The resultant scattered intensity at the far point P is the sum of all scattering contributions of the microscopic volumes v , each of which is treated as an independent scatterer; ie. the scattering contributions of each element v are uncorrelated. Generally, the fluctuations in the dielectric constant $\Delta\epsilon(r, t)$ are a function of temperature T and density ρ of the fluid. However, for gases and fluids in a moderate range of temperatures, the temperature dependence can be neglected and $\Delta\rho(r, t)$ is only a function of ρ . Thus, fluctuations in the dielectric constant, which ultimately cause fluctuations in the scattered light intensity, directly reflect the microscopic density fluctuations within the fluid.

3.2 Temporal and spatial behaviour of scattered light

Classical wave theory can be used to describe the temporal and spatial behaviour of rayleigh scattering. The electromagnetic radiation obeys Maxwells-Equations

$$\nabla \cdot \vec{D} = 0 \quad (2a)$$

$$\nabla \cdot \vec{B} = 0 \quad (2b)$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (2c)$$

$$\nabla \times H = \frac{\partial \vec{D}}{\partial t} \quad (2d)$$

whereby we assume no isolated charges and currents (the volume charge density ρ and free current density σ are zero). \vec{D} denotes the electric displacement and \vec{B} the magnetic field respectively. Since the detector, responding to light intensity I , is usually a square law detector ($I = |\vec{E}|^2$), we are primarily interested in variations of the electric field. The incident electromagnetic wave is written in its complex form

$$E(\vec{r}, t) = E_0(\vec{r}, t) \cdot e^{i(\vec{k}\vec{r} - \omega t)}. \quad (3)$$

$E_0(\vec{r}, t)$ is a complex amplitude, \vec{k} the wave vector with $|\vec{k}| = \frac{2\pi}{\lambda}$ and ω the angular frequency of the wave. The scattering geometry is that of figure 3 with the incident wave \vec{k}_i being polarized perpendicular to the scattering plane. The resultant scattered field \vec{E}_s at a far point P is the superposition of all fields radiated from volume elements $d^3r(v)$ at a position \vec{r} with respect to the scattering center (random walk in three dimensions). E_S can, after a rather lengthy calculation, be expressed as

$$E_S(\vec{R}, t) = \frac{-E_0 k_s^2}{4\pi R \epsilon_0} \cdot e^{i(\vec{k}_s \cdot \vec{R} - \omega t)} \int_{\mathbf{V}} e^{i\vec{q}\vec{r}} \Delta\epsilon(\vec{r}, t) d^3r. \quad (4)$$

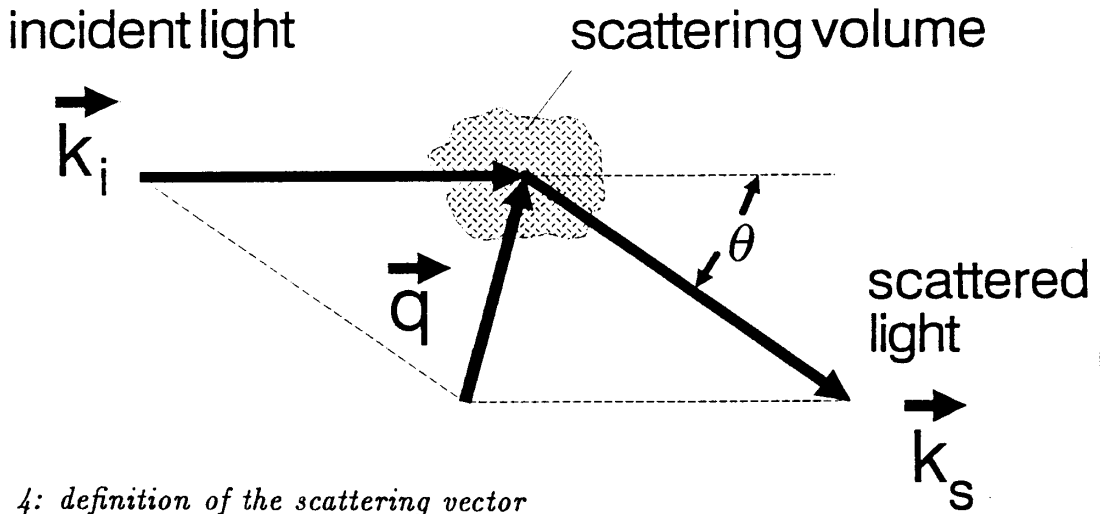


Fig. 4: definition of the scattering vector

\vec{q} , shown in figure 4, represents the scattering vector and defines the scattering geometry. It results from the difference between the incident and scattered wave vectors $\vec{q} = \vec{k}_i - \vec{k}_s$. The product $\vec{q} \cdot \vec{r} = (\vec{k}_i - \vec{k}_s) \cdot \vec{r}$ is the phase delay that results from the path difference between light scattered from a volume element v at \vec{r} relative to one at the origin (Fig.5 and Fig.3).

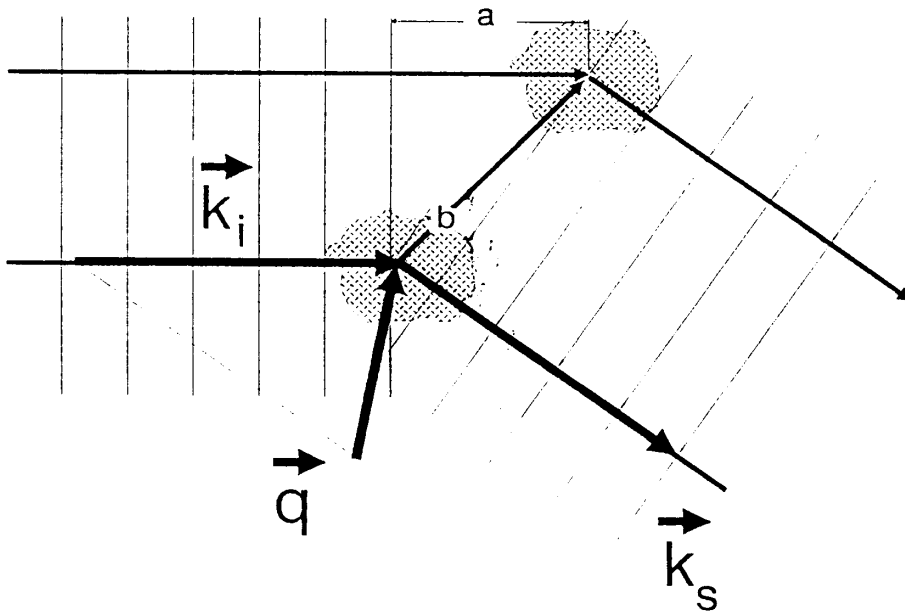


Fig. 5: section of the scattering geometry

If we assume elastic light scattering, then $|\vec{k}_i| = |\vec{k}_s|$ and the "value" of q (see fig.4) becomes:

$$|\vec{q}| = \frac{4\pi n}{\lambda_L} \cdot \sin\left(\frac{\Theta}{2}\right), \quad (5)$$

where λ_L is the wavelength of light in vacuum and n the refractive index of the fluid. The scattered field (E_S) therefore consists of a monochromatic carrier wave $E_0 \cdot e^{i(\vec{k}_s \cdot \vec{R} - \omega t)}$

modulated in amplitude and phase by the integral $\int_{\mathbf{V}} e^{i\vec{q}\vec{r}} \cdot \Delta\epsilon(\vec{r}, t) d^3r$ which constitutes the fluctuating signal. The integral is actually the spacial fourier transform of the dielectric constant fluctuations $\Delta\epsilon(\vec{r}, t)$ into \vec{q} -space (the component of the fluctuations in \vec{q} direction)

$$\Delta\epsilon(\vec{q}, t) = \int_{\mathbf{V}} \Delta\epsilon(\vec{r}, t) \cdot e^{i\vec{q}\vec{r}} d^3r. \quad (6)$$

Equation 4 can therefore be written as

$$E_s(\vec{R}, t) = \frac{-E_0 k_s^2}{4\pi R \epsilon_0} \cdot e^{i(\mathbf{k}_s R - \omega_s t)} \cdot \Delta\epsilon(\vec{q}, t) \quad (7)$$

The information of the fluctuating dielectric constant, and, since $\Delta\epsilon$ is only a function of the density ρ , of the density fluctuations $\Delta\rho(\vec{q}, t)$ is thus contained in the temporal fluctuations of the scattered light signal $\vec{E}_s(\vec{R}, t)$.

3.3 Correlation Functions

The afore-mentioned microscopic fluctuations represent a stochastic process resulting from the random motion of the molecules or particles. The signal possesses typical characteristics of a noise pattern. To obtain the information on transport properties present in the fluctuating density signal we can analyse its temporal behavior by digital correlation. Another possibility is to decompose the signal into its frequency components by fourier transformation with a spectrum analyser, obtaining its power spectrum. Most experiments today are performed with digital correlators since these instruments are fast and introduce no noise of their own, thus possessing an efficiency of 100%. Modern spectrum analysers can obtain the spectral information with a comparable speed, however they invariably introduce a bandwidth error into measurements. We therefore concentrate on the concept of time correlation functions and digital correlators in this section. A typical fluctuating signal, in this case the fluctuating part of the microscopic density $\Delta\rho(t)$ in fluids, is shown in figure 6.

Provided the system is in macroscopic equilibrium ($\rho_0 = \text{const}$), the signal will fluctuate about a mean value $\langle \Delta\rho \rangle$ given by

$$\langle \Delta\rho \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \Delta\rho(t) dt, \quad (8)$$

in this case $\langle \Delta\rho \rangle = 0$. T is the integration time. Generally, at a certain time t_1 , $\Delta\rho$ will differ from the same signal a variable time τ later, $\Delta\rho(t_1) \neq \Delta\rho(t_1 + \tau)$. if τ is chosen to be small ($\tau \rightarrow 0$), then the signal will not have changed appreciably during τ and the correlation between both terms is large. If τ is increased, the deviation is more likely to increase, and if this comparison is repeated often, the correlation is lost. A measure of this correlation can be expressed in a correlation function $G(\tau)$ which is defined as

$$G(\tau) = \langle \Delta\rho(t_1) \cdot \Delta\rho(t_1 + \tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \Delta\rho(t_1) \cdot \Delta\rho(t_1 + \tau) dt \quad (9)$$

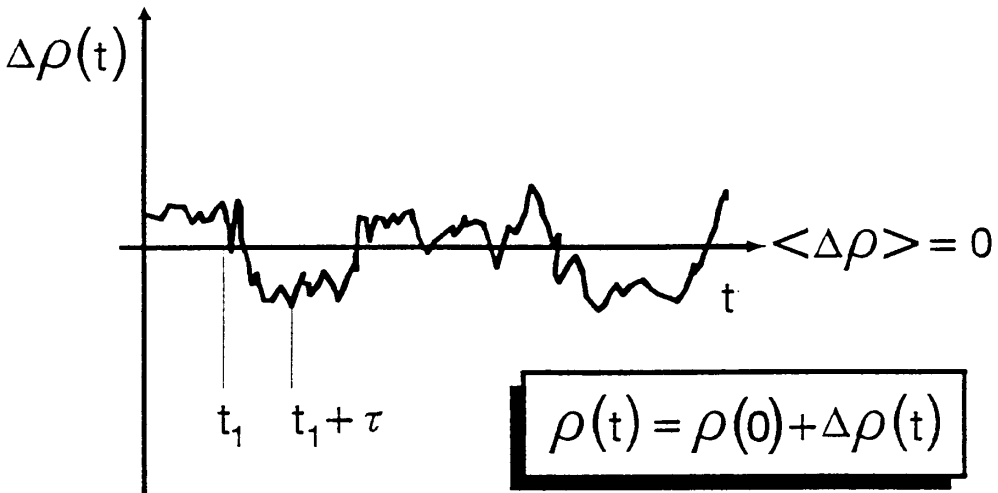


Fig. 6: Fluctuating density signal

The brackets $\langle \rangle$ denote the temporal averaging. If this process is repeated very often ($T \rightarrow \infty$), then the correlation function becomes independent of the starting time t , and only a function of τ .

$$G(\tau) = \langle \Delta \rho(0) \cdot \Delta \rho(\tau) \rangle \quad (10)$$

$G(\tau)$ is a measure of the mutual relationship in a signal. If the signal is completely random, then the correlation function will remain flat (ie. uncorrelated), even after long times $T \rightarrow \infty$. For nonperiodic signals as is the case here, $G(\tau)$ is a decaying function for τ varying from 0 to infinity (Figure 7).

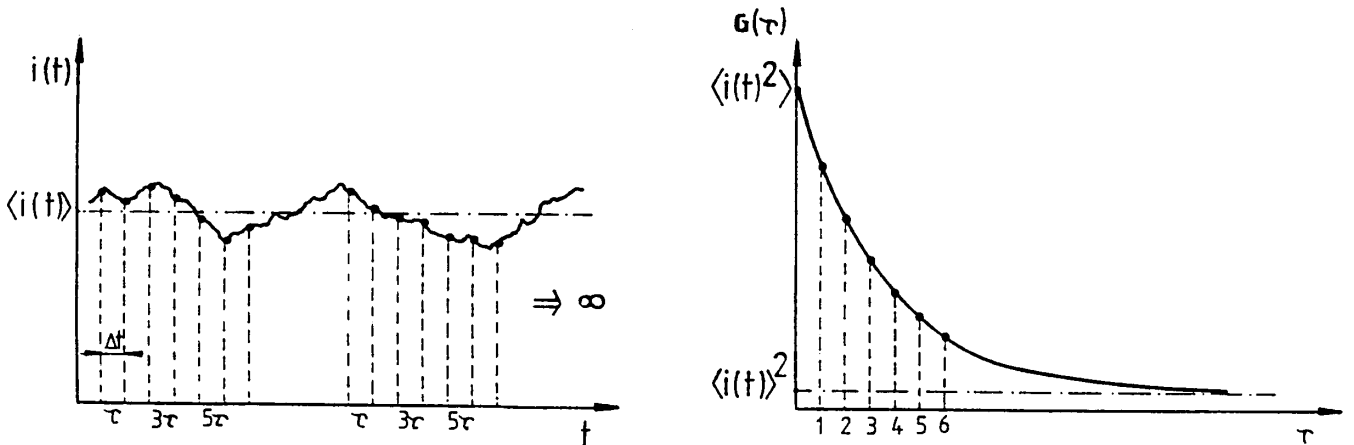


Fig. 7: Typical correlation function of a non-periodic signal

If we correlate the signal over a long period ($T \rightarrow \infty$) for $\tau \rightarrow 0$ (ie. almost no time lag between the two signals to be correlated), then the value of the correlation function is simply the square of the signal

$$G(\tau)_{\tau \rightarrow 0} = \langle \Delta \rho(0) \cdot \Delta \rho(0) \rangle = \langle \Delta \rho(0)^2 \rangle. \quad (11)$$

For long delay times $\tau \rightarrow \infty$, the signal contributions are totally uncorrelated with their respective averages being the mean value of the fluctuation

$$\tau \rightarrow \infty \langle \Delta \rho(0) \rangle = \langle \Delta \rho(\tau) \rangle = \langle \Delta \rho \rangle. \quad (12)$$

Thus the correlation function drops to the square of the mean signal

$$G(\tau)_{\tau \rightarrow \infty} = \langle \Delta \rho(0) \cdot \Delta \rho(\tau) \rangle = \langle \Delta \rho \rangle \langle \Delta \rho \rangle = \langle \Delta \rho \rangle^2. \quad (13)$$

Usually, the correlation function is required in its normalized form $g(\tau)$, as shown in figure 8, which is simply $G(\tau)$ divided by its initial value $G(0)$.

$$g(\tau) = \frac{G(\tau)}{G(0)} = \frac{\langle \Delta \rho(0) \cdot \Delta \rho(\tau) \rangle}{\langle \Delta \rho(0)^2 \rangle} \text{ with } 0 < g(\tau) < 1. \quad (14)$$

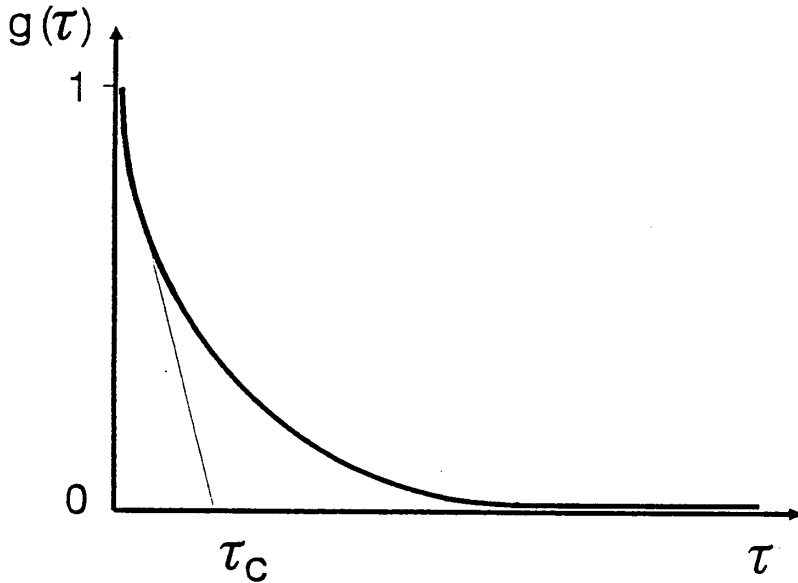


Fig. 8: Normalized correlation function with characteristic decay time

The exact form of the correlation function depends on the physical process under study. As will be shown in the next section $g(\tau)$ is usually a decaying exponential function for dissipative fluctuations about equilibrium

$$g(\tau) = \exp(-\tau/\tau_c) \quad (15)$$

The value τ_c is the characteristic decay time of the exponential function (figure 8) and contains the actual information on the transport coefficient. $g(\tau)$ represents the statistical mean behaviour of the microscopic density fluctuations.

In practice, digital correlators are used to measure $g(\tau)$. These instruments, which are basically fast CPUs, possess a large number of sampling channels or stores (I), which represent distinct points of the correlation function. The delay time τ is discretized as intervals of Δt and counted by a running parameter j with $j = 1 \dots I$ (number of channels)

$$\tau = j\Delta t (j = 1 \dots I). \quad (16)$$

Δt represents the fundamental sample time of the correlator. Thus, each successive channel represents an increasing time lag τ in the correlation function. The actual correlation is achieved by means of shift registers (one for each channel). The momentary value of the signal $i(t)$ arriving at the correlator, is multiplied by the delayed signal distribution in each shift register $i(t + j\Delta t j = 1 \dots I)$ before being added to the contents of the individual sampling channels. Figure 7 schematically demonstrates idealized measurements with a 7-channel correlator. The correct setting of the sample time Δt is very important when correlating, as this defines the "time window" within which the fluctuation should decay to zero.

Another method of extracting information from the density fluctuations is to fourier transform $G(\tau)$ into its frequency components ($\tau \rightarrow \omega$)

$$S_{\Delta \varrho}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \Delta \varrho(0) \cdot \Delta \varrho(\tau) \rangle e^{i\omega\tau} dt, \quad (17)$$

obtaining the power spectral density of the signal. This transformation is known as the Wiener-Khintchine theorem and is shown in figure 9.

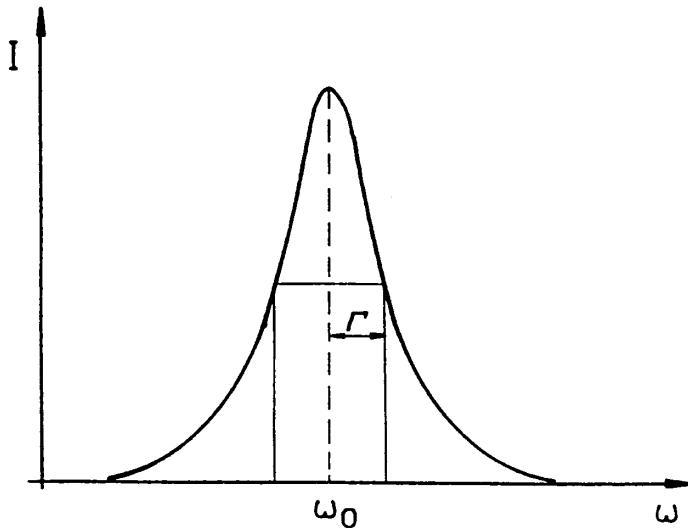


Fig. 9: Typical power spectrum

The form of this curve, arising from dissipative fluctuations (ie. an exponential decaying correlation function), is a Lorentzian distribution centered at the incident laser frequency

ω_0 with a linewidth Γ . Γ is a direct measure of the dissipative process involved. Since the power spectrum and the corresponding correlation function are fourier transform pairs, Γ is directly related to the characteristic decay time

$$\Gamma = \frac{1}{\tau_c}. \quad (18)$$

In practice, spectrum analysers are used to obtain the integrated power density of the signal at a set frequency ω . By tuning the filter through a frequency range, the power spectral density is measured.

3.4 Hydrodynamic fluctuation theory

Up to this point, we have shown that the fluctuating electric field (or intensity of scattered light) contains information on density fluctuations in a fluid arising from the collective motion of the molecules. Temporal investigation of the signal by means of correlation, or frequency decomposition by spectrum analysis, reveals the characteristic behaviour of the fluctuations. What is still required is the connection between the microscopic fluctuations and macroscopic transport phenomena. In this derivation, we are considering fluctuations arising from the collective motion of large numbers of molecules (volume elements v), allowing us to treat the fluid as a continuum. Molecular interactions such as collision times and interparticle distances are thus avoided, only relatively long-lived and long-ranged fluctuations being considered. Macroscopic laws, such as the hydrodynamic laws of motion should then be able to describe the temporal behaviour of the fluctuations. The basis of this theory is the regressional hypothesis of Onsager (1931) which states that the spontaneous fluctuations amongst the individual microscopic volume elements v "regress" back to equilibrium according to the same equations which describe the macroscopic relaxational process.

The laws of hydrodynamics are the laws of conservation of mass, momentum and energy stated here in their general form:

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \vec{u}) = 0 \quad (\text{mass}) \quad (19a)$$

$$\frac{\partial(\rho \vec{u})}{\partial t} + \text{div}(\rho \vec{u} \vec{u}) + \text{grad}P + \text{div}(\vec{\tau}) = 0 \quad (\text{momentum}) \quad (19b)$$

$$\rho \frac{\partial e}{\partial t} + \text{div}(\rho \vec{u} e) - \lambda \nabla^2 T + \text{div}(p \vec{u}) + \text{div}[\vec{\tau} \cdot \vec{u}] = 0 \quad (\text{energy}) \quad (19c)$$

where \vec{u} is a velocity vector, $\vec{\tau}$ the stress tensor, e is the sum of the internal and kinetic energies and λ the thermal conductivity. The fluctuations of these properties are determined for instance by substituting $\rho_0 + \Delta\rho$ for the density ρ or $\vec{u}_0 + \Delta\vec{u}$ for the velocity \vec{u} . By assuming that these fluctuations are small about equilibrium values, the above equations can be linearized, resulting in 5 equations (conservation of momentum is a vector equation) with 7 variables. Two of the scalar variables can be eliminated by applying local equilibrium thermodynamic equations of state. Usually density and temperature are chosen as the independent variables. The resulting linearized hydrodynamic equations are solved by Fourier-Laplace analysis (Mountain 1966), the fluctuations such as

density $\Delta\rho(\vec{r}, t)$ being space- ($\vec{r} \rightarrow \vec{q}$) and time-transformed ($t \rightarrow s$), obtaining $\Delta\rho(\vec{q}, s)$. The correlation function of these fluctuations describes the light scattering spectrum. For density fluctuations the solution is obtained in the form of a correlation function and by Laplace inverting ($s \rightarrow t$) as

$$g(\tau) = \frac{\langle \Delta\rho(\vec{q}, 0) \cdot \Delta\rho(\vec{q}, \tau) \rangle}{\langle \Delta\rho(\vec{q}, 0) \cdot \Delta\rho(\vec{q}, 0) \rangle} = \left[\frac{c_p - c_v}{c_v} \right] \cdot \exp(-\alpha q^2 \tau) + \frac{c_v}{c_p} \cdot \exp(-\beta q^2 \tau) \cos(C_s q \tau). \quad (20)$$

c_p and c_v denote the specific isobaric and isochoric heat capacities respectively. α is the thermal diffusivity, β the sound absorption coefficient and C_s the local speed of sound. The spectral density can be obtained by a fourier transform ($\tau \rightarrow \omega$) of equation 20, according to equation 17. The result is presented schematically in figure 10.

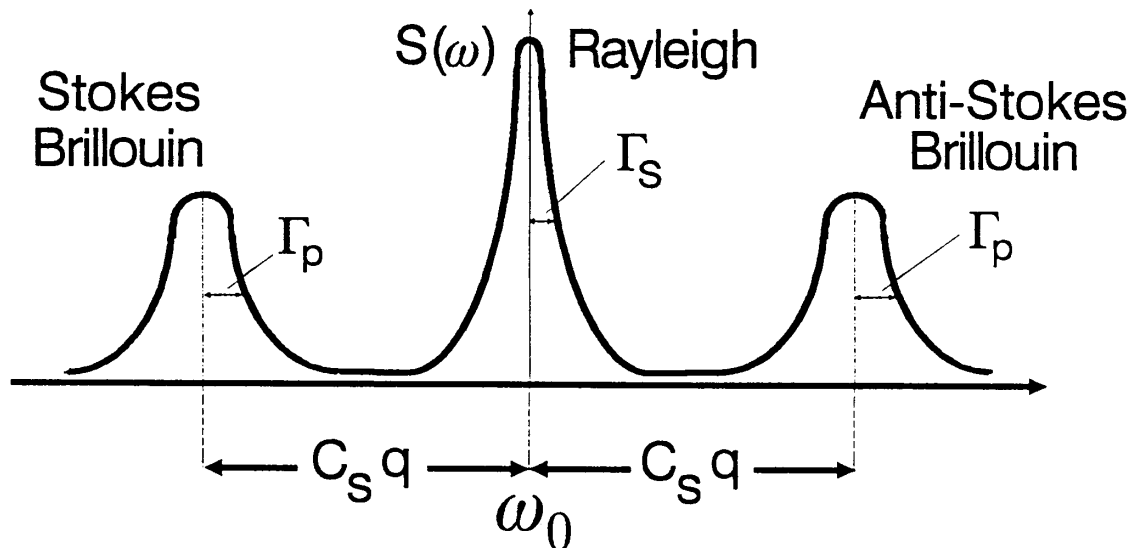


Fig. 10: Spectrum of light scattered off density fluctuations

The spectrum of light scattered from density fluctuations is the sum of three Lorentzian distributions. The strongest contribution results from the central or Rayleigh line, which peaks at the incident light frequency. The broadening of this spectrum, as expressed by its half-width at half-maximum, is a direct measure for the rate of diffusion, which, for pure fluids is the thermal diffusivity α (the half-width is in general denoted by Γ as in figure 9). The rayleigh contribution to the spectrum is often interpreted as local entropy fluctuations at constant pressure.

The next two terms represent a doublet, also known as the Brillouin doublet. This contribution can be interpreted as local adiabatic pressure fluctuations which give rise to sound

waves travelling through the fluid. Light scattered off these waves is slightly frequency shifted in both directions in analogy to the doppler-effect, the amount of frequency shift being dependent on the local speed of sound and the scattering vector. This scattering process is known as Brillouin scattering and has been briefly described in the general scattering section of this book. As with the Rayleigh spectrum, the Brillouin spectrum also possesses a dissipative element (the sound waves decay), a measure of which is the sound absorption coefficient β . Thus the thermal diffusivity a , diffusion coefficient D (for mixtures), the speed of sound C_s , and the sound absorption coefficient β can be obtained by investigating the spectrum of light scattered off local density fluctuations in fluids. In this contribution we only deal with the Rayleigh spectrum investigating diffusion and diffusion related properties.

4 Experimental Methods

There are two methods which can be employed in dynamic light scattering experiments; those which directly measure the intensity of the scattered light are known as the single beam, self-beat or homodyne method while those which superimpose a second reference beam or a local oscillator with the scattered light are called dual beam or heterodyne method. Essentially the major components used in both setups are identical, the primary difference lies in the optical detection of the light.

4.1 Homodyne Method

Figure 11 shows a typical experimental setup of a light scattering apparatus employing the homodyne detection method. We will first treat the major components before dealing with the characteristics of the light detection.

Frequency stabilised (etalon) argon-ion lasers are often used as light sources in such experiments due to their high stability and output power, typical required power values lying between 1 - 600mW, depending on the scattering ability of the fluid. For experiments with large scattering intensities, such as light scattered off particles or when investigating the critical region of fluids, lower light levels of a few milliwatts suffice, making helium-neon lasers applicable.

As the theory of light scattering assumes Gaussian statistics of the incident light, the laser beam is usually directed through a beam expander before it is focussed into the scattering volume, the beam being polarized with the polarization vector perpendicular to the scattering plane. The intensity of the scattered light is then observed at the variable angle Θ by means of a photomultiplier tube. Recent advances made with avalanche photodiodes which possess a higher quantum efficiency and other advantages such as compact dimensions, also make these instruments useful for detection (Lightstone 1988).

In order to reduce self correlation effects (after-pulse and dead time effects) which appear at short delay times τ , two photomultipliers can be used in cross correlation, the disadvantage being a reduction of the signal due to beam splitting.

The important factor which determines the signal to noise ratio S/N and thus the detection capability of the light scattering apparatus is the amount of power scattered into a single coherence area A_{COH} . A_{COH} defines an area over which signal contributions arising from different parts of the scattering volume V are correlated, and is inversely related to the dimensions of V . The laser beam should therefore be focussed down to small diameters, typically $< 0.1\text{mm}$. The elements of the optical system, pinhole (5), lens

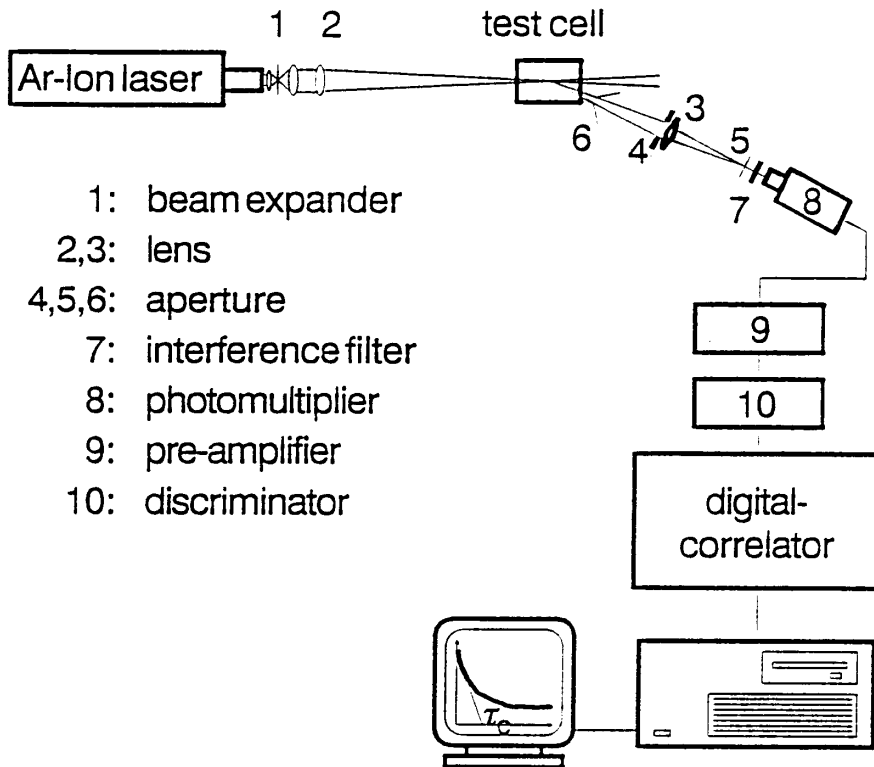


Fig. 11: Experimental setup in light scattering experiments

(3) and aperture (4) determine the number of coherence areas detected by the photomultiplier and thus the light intensity, as well as the angular resolution of the apparatus. These elements have to be chosen carefully as large apertures reduce the informational content of the signal as manifested by a smaller spread of the exponential function. Although S/N itself is not influenced by these measures, the evaluation of the exponential function becomes more prone to error and run times increase substantially in this case (eg. Cummins 1977).

Different optical systems with varying angular, on- and cross-axis resolutions can be used to project the light generated in the scattering volume onto the surface of the photomultiplier (Cheung 1988). Dual pinhole, single imaging lense or dual imaging lense systems are typically employed. After amplification and passing through a discriminator, the signal $i(t)$ is fed into a digital correlator in the form of discrete photocount events within a certain sampling intervall Δt . Improvements in correlation techniques and correlator features (such as size, speed, number of channels) are continuous. In particular, the ability of correlators to work in parallel (or more) modes with logarithmic time scales allows a simultaneous determination of many diffusive processes with different time scales, particle sizing being a typical application. The obtained correlation function $g(\tau)$ is then analyzed, usually by a nonlinear least-squares fit, resulting in a direct determination of diffusivity.

The derivation of light scattering theory in sections 3.2 to 3.4 has shown that the correlation function of the density fluctuations is an exponential function, the characteristic decay time τ_c being related to diffusivity $\tau_c = 1/aq^2$. Furthermore, the electric field and the density fluctuations are directly related as

$$\Delta\rho(\vec{R}, t) \sim \Delta\epsilon(\vec{R}, t) \sim \vec{E}_s(\vec{R}, t). \quad (21)$$

The normalized correlation function of the scattered electric field therefore directly measures diffusivity

$$g_1(\tau) = \frac{\langle |\vec{E}_s(0)| \cdot |\vec{E}_s(\tau)| \rangle}{\langle |\vec{E}_s(0)|^2 \rangle} = \exp(-aq^2\tau). \quad (22)$$

Photomultipliers however, are square-law detectors and only respond to intensity fluctuations

$$I_S(t) = \vec{E}_S(t) \cdot \vec{E}_S^*(t), \quad (23)$$

the "*" denoting the complex conjugate value of the field. Thus it is not the so-called first-order correlation function $g_1(\tau)$ that is measured in homodyne experiments, but the second-order correlation function $g_2(\tau)$

$$g_2(\tau) = \frac{\langle |E_S(0)|^2 \cdot |E_S(\tau)|^2 \rangle}{\langle |E_S(0)|^2 \rangle^2} = \frac{\langle I_S(0) \cdot I_S(\tau) \rangle}{I_S^2} \quad (24)$$

with $\langle |E_S(0)|^2 \rangle^2 = I_S^2$.

The informational content of $g_1(\tau)$ is not lost in $g_2(\tau)$, provided that the scattered light has a Gaussian distribution; which requires that the total scattered intensity arises from a large number of statistically independent subregions (as assumed in section 3.1). The statistical properties of the higher moments are then only a function of the first - order correlationfunction.

$$g_2(\tau) = 1 + g_1(\tau)^2. \quad (25)$$

The correlation function now takes the form

$$g_2(\tau) = 1 + [\exp(-aq^2\tau)]^2 = 1 + \exp(-2aq^2\tau), \quad (26)$$

or, if not normalized,

$$G_2(\tau) = I_S^2 + I_S^2 \exp(-2aq^2\tau). \quad (27)$$

In homodyne experiments, we therefore measure the square of the signal $\vec{E}_S(\vec{R}, t)$ and the resulting exponential decay is multiplied by a factor of 2. The homodyne method is generally employed when the scattered light intensities are high and no other stray sources of light are present. This condition can be achieved by means of an additional pinhole (6) which effectively screens out these sources such as the flare of the cell windows.

4.2 Heterodyne method

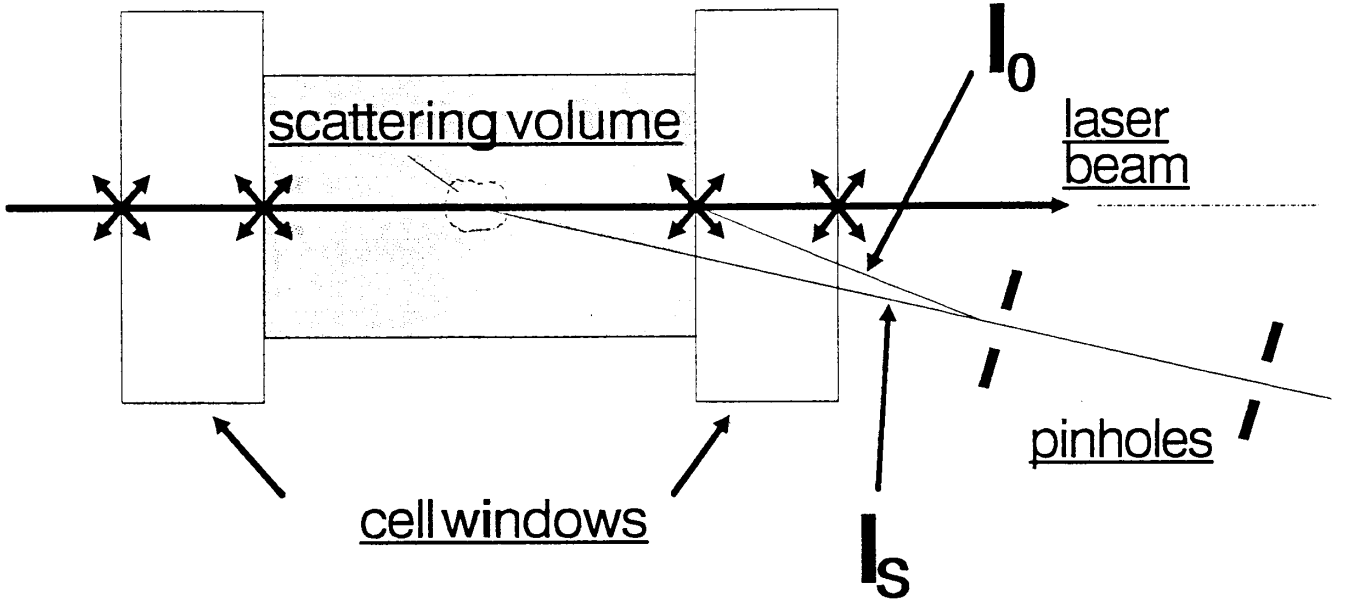


Fig.12: Optical paths of the heterodyne method

At low fluctuation intensities, signal enhancement is achieved by superimposing a second coherent beam or local oscillator of constant intensity with the scattered light beam. While this can be done in numerous manners such as beam splitting before and after scattering, an effective method is to include light scattered from the interior window surface in the field of view of the pinhole (Fig.12).

The electric field arriving at the detector is then the sum of the scattered field \vec{E}_S and the local oscillator \vec{E}_{LO} . Again, since photomultipliers respond to intensity, the second-order correlation function (not normalized) becomes:

$$G_2(\tau) = \langle |E_S(0) + E_{LO}(0)|^2 \cdot |E_S(\tau) + E_{LO}(\tau)|^2 \rangle. \quad (28)$$

Multiplying out this expression results in 16 terms. By assuming E_{LO} to be constant, that is $E_{LO}(0) = E_{LO}(\tau)$, and E_{LO} and E_S to be statistically independent, equation 28 is reduced to three terms

$$G_2(\tau) = \langle I_{LO}^2 \rangle + \langle 2I_{LO}(E_S(0)E_S^*(\tau)) \rangle + \langle I_S(0)I_S(\tau) \rangle. \quad (29)$$

$\langle I_{LO}^2 \rangle$ or simply I_{LO}^2 is the background term. The correlation function $\langle (E_S(0)E_S^*(\tau)) \rangle$ is, from hydrodynamic theory, equal to $I_S \exp(-aq^2\tau)$, and the last term is the afore-mentioned homodyne correlation function (eq. 27). The resulting correlation function can therefore be written as

$$G_2(\tau) = (I_{LO} + I_S)^2 + 2I_{LO}I_S \exp(-aq^2\tau) + I_S^2 \exp(-2aq^2\tau), \quad (30)$$

which is the addition of two exponential functions, a heterodyne term ($2I_{LO}I_S \exp(-aq^2\tau)$) and a homodyne term ($I_S^2 \exp(-2aq^2\tau)$), differing in their decay rates by a factor

of two. Since the signal detected at the photomultiplier is always a superposition of light scattered off other objects (cell walls, windows, dust etc.), equation 30 represents the general form of the correlation function for both methods. The simultaneous evaluation of two exponential functions is always difficult and prone to error. Thus, the homodyne technique assumes that the intensity of stray light I_{LO} is negligible ($I_S \gg I_{LO}$) reducing eq. 30 to eq. 27, while the heterodyne method assumes ($I_{LO} \gg I_S$) reducing eq. 30 to

$$G_2(\tau) = (I_S + I_{LO})^2 + 2I_{LO}I_S \exp(-aq^2\tau). \quad (31)$$

This condition can be assured by varying the intensity of I_{LO} with respect to I_S , for example by shifting the scattering volume closer to the window surface.

Heterodyning can be a very effective method for measuring diffusivities and diffusion coefficients at further distances from the critical point, especially in the liquid region. In those regions where intensity fluctuations are very weak, a gain in the statistical accuracy of an order of magnitude may be achieved [47]. Heterodyning however requires coherent mixing of the scattered light and reference beam signals. The sensitivity is comparable to that of a Michelson interferometer. While the alignment problem can be circumvented by positioning the scattering volume and local oscillator source very close together, the sensitivity to intensity fluctuations in I_0 and external vibrations remains. These sources of error are difficult to avoid completely. Due to the weak signal I_S , run times lie between 1-3 hours.

5 Measurement of thermal diffusivity

As was already mentioned in the beginning of this contribution, dynamic light scattering offers numerous applications in physics, chemistry and biology, a detailed overview being given for example by Pecora(1988). Since even a brief treatment of these applications would exceed the scope of this contribution, we will only describe an application from the field of physics, the measurement of thermal diffusivity a of pure fluids.

The behaviour of microscopic density fluctuations can be described, as shown, by the hydrodynamic equations of motion. The resulting spectrum consists of entropy fluctuations at constant pressure (Rayleigh spectrum) and pressure fluctuations at constant entropy (Brillouin spectrum). The fluctuations in entropy represent a purely dissipative mode of heat transfer. Since entropy is primarily a function of temperature T , the decay of these fluctuations is expressed by the instationary fourier heat law

$$\frac{\partial}{\partial t} \Delta T(\vec{r}, t) = a \nabla^2 (\Delta T(\vec{r}, t)) \quad (32)$$

which is basically the law of conservation of energy (eq. 19c) assuming $p = const.$. The solution of this equation, after performing the necessary Fourier- transform into q -space and integrating the differential equation, is the exponential function

$$\Delta(\vec{q}, t) = \Delta T(\vec{q}, 0) \exp(-aq^2t). \quad (33)$$

The decay of temperature gradients in macroscopic as in microscopic systems follows a simple exponential behaviour. The measurement of the characteristic decay time τ_c by means of correlation directly yields the thermal diffusivity

$$\tau_c = \frac{1}{aq^2}. \quad (34)$$

Substituting for the scattering vector \vec{q} , we obtain

$$a = \frac{1}{\tau_c \left[\frac{4\pi n}{\lambda_L} \sin\left(\frac{\Theta}{2}\right) \right]^2} \quad (35)$$

which is the equation determining thermal diffusivity. τ_c is obtained from a regression analysis of the correlation function. The scattering angle Θ has to be determined along with the refractive index n of the fluid, although the error made by assuming $n = const = 1$ is under 1% for $\Theta < 10^\circ$ C (Kruppa(1991)). The incident wavelength of light λ_L is usually kept constant.

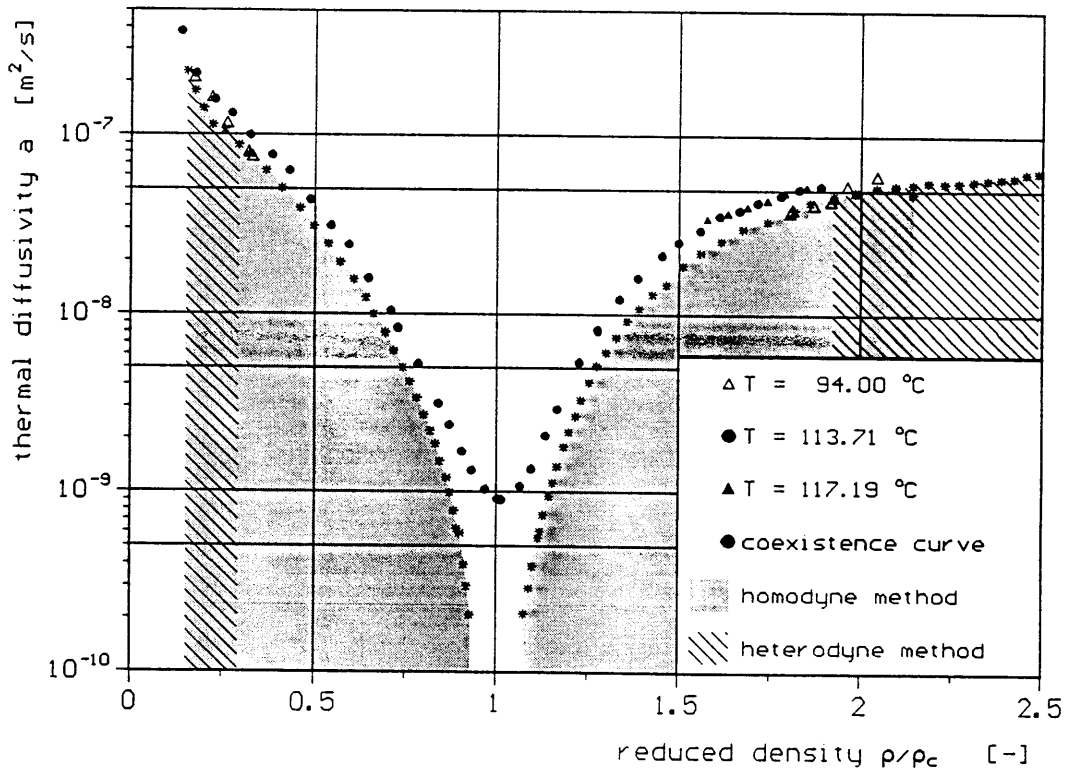


Fig. 13: Thermal diffusivity measurements of the refrigerant R152a

Figure 13 shows typical measurement of the alternative refrigerant R152a along the coexistence curve and several sub- and supercritical isotherms plotted against the reduced density ρ/ρ_c . ρ_c denotes the critical density of the fluid. Measurements were made using both methods described earlier. In the extended critical region characterized by $0.3 < \rho/\rho_c < 1.8$, where scattering intensities are relatively large, the homodyne method was employed. The measurements lying outside this region were obtained by the heterodyne method. The accuracy of these measurements is dependent upon the investigated

region of state and lies between 0.5% and 2.0 %. In the gas region at lower densities (typically $\rho/\rho_c < 0.2$), this method is subject to increasing errors due to low density fluctuations and resulting low scattered light intensities and therefore cannot be applied. When compared with other conventional methods of measuring thermal diffusivity or thermal conductivity, such as the instationary hot wire technique or the parallel plates method, dynamic light scattering offers three major advantages.

- 1) The investigated substance is in a state of thermodynamic equilibrium with no temperature gradients being present in the fluid.
- 2) The measurement is absolute. No lengthy calibrations are necessary, since only the decay time and not the spread or the position of the exponential function is required.
- 3) The time required for a measurement point is relatively short, even for heterodyne experiments.

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