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LIGHT SCATTERING AS A MEASURING METHOD FOR ISOTHERMAL COMPRESSIBILITY AND THERMAL DIFFUSIVITY

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Abstract

Thermal diffusivity and isothermal compressibility may be measured with a light scattering method without influencing the equilibrium state of the sample. No temperature or pressure gradient is needed. A short summary of theory is given. Experimental mounting is explained and measurements of overcritical thermal diffusity of CO_2 are presented.

NOMENCLATURE

a	: Thermal diffusivity, m^2/s
E	: Electric field vector, V/m
I_o	: Incident light intensity, W
$I_{\theta,\phi}$	: Scattered light intensity, W
k	: Wave vector, $1/m$
k_B	: Boltzmann constant, Ws/K
k_T	: Isothermal compressibility, bar^{-1}
n_o	: Refractive index, -
p	: Pressure, bar
r	: Distance, m
R	: Rayleigh's ratio, m^{-2}
s	: Entropie, Joule/K
T	: Temperature, K
u	: Velocity of fluid, m/s
v_o	: Velocity of sound, m/s
V	: Volume, m^3
Γ	: Sound attenuation, m^2/s
ε	: Dielectric constant, As/Vm
ζ	: Bulk viscosity, Kg/ms
η	: Shear viscosity, kg/ms
θ	: Angle, grd
κ	: Ratio of specific heat, -
λ	: Thermal conductivity, W/mK
λ_o	: Wavelength of light, m
ϱ	: Density, kg/m^3
ϕ	: Angle
ω	: Frequency, s^{-1}
ω_o	: Frequency of laser light, s^{-1}
$d\Omega$	: Solid angle,
$\Delta\omega_{1/2}$	: Halfwidth of frequency spectrum, s^{-1}

APPLICATION OF LIGHT SCATTERING MEASUREMENTS

Measuring isothermal compressibility and thermal diffusivity of a fluid, one usually produces a temperature or a pressure gradient in a sample, but in some cases gradients are not allowed or wanted. We measure thermal diffusivity and isothermal compressibility very near to the liquid-gas critical point and in isochoric subcooled liquids, which is important for boiling. Here we are only able to measure, if the properties of the sample are not changed. A small change in temperature or pressure would produce another, non-critical state, or in the case of a subcooled liquid a sudden change to thermodynamic equilibrium with two phases. With a light scattering method measurements are possible, because only a light beam is needed, which does not influence the sample.

THEORY OF THE MEASURING METHOD

The light scattering method was developed by Benedek et al. about 1965 [1]. A detailed explanation of the theory is given in references [2], [3] and [4].

Imagine a sample of a fluid, which is in thermodynamic equilibrium. In it exists microscopic deviations of equilibrium, so called fluctuations. The linearized hydrodynamic equations are applied to these fluctuations:

$$\begin{aligned} &\dot{\varrho}_1 + \varrho_o \nabla u = 0 \\ &\varrho_o \dot{u} = -\nabla p_1 + \eta \nabla\nabla u + (\zeta + \tfrac{1}{3}\eta)\nabla\nabla u \\ &\varrho_o T_o \dot{s}_1 = \lambda \nabla^2 T_1 \end{aligned} \quad (1)$$

index 0: equilibrium values
index 1: deviation from equilibrium.

The dielectric constant ε depends on density and temperature, therefore the fluctuations of density and temperature appear in fluctuations of the dielectric constant ε. Now ε is the mean property if radiation interacts with a dense medium. Therefore the light, which interacts with a dense medium, will be varied and this variation will be in connection with the fluctuations. If a polarized light beam with the electric field vector E in z direction (see figure 1) and wavelength λ_o interacts with matter in a volume V with refractive index n_o a part of the incident intensity I_o will be scattered and a part transmitted. Within a small solid angle $d\Omega$ at point P at a distance r of the scattering volume, light will appear with the intensity $I_{\theta,\phi}$.

A relation can be deduced, which gives the intensity and frequency of scattered light as function of thermodynamic and geometric properties [5]. One has to connect relations of electrodynamics with the linearized hydrodynamic equations and statistic mechanics. The solution of this problem for the Rayleigh's ratio

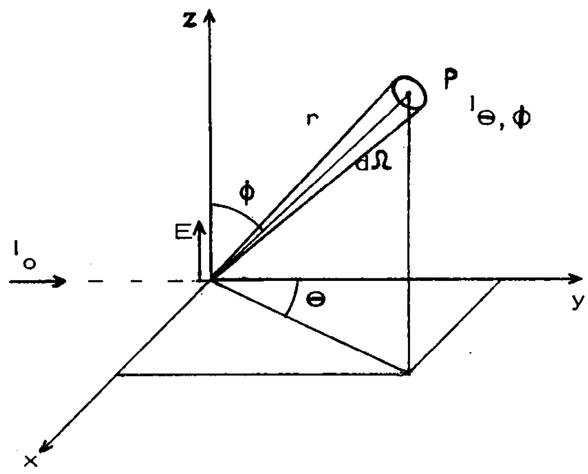

Fig. 1: Incident intensity I_o with E vector in z direction. Scattered intensity $I_{\Theta,\Phi}$ at point P.

$$R_{\Theta,\Phi} = \frac{I_{\Theta,\Phi}\, r^2}{I_o\, V^2} \qquad (2)$$

as a function of frequency shift ω and the scattering wave vector k

$$|k| = \frac{4\pi}{\lambda_o n_o} \sin\frac{\Theta}{2} \qquad (3)$$

is given by

$$R(k,\omega) = \left[\frac{\pi^2}{\lambda_o^4} \sin^2\Phi \left(\varrho \frac{\partial \varepsilon}{\partial \varrho}\right)_T k_B T \cdot k_T \right] \cdot$$

$$\cdot \left\{ \left(1 - \frac{1}{k}\right) \frac{2ak^2}{(ak^2)^2 + \omega^2} + \frac{1}{k}\left[\frac{\Gamma k^2}{(\Gamma k^2)^2 + (\omega + v_o k)^2} + \right.\right.$$

$$\left.\left. + \frac{\Gamma k^2}{(\Gamma k^2)^2 + (\omega - v_o k)^2}\right]\right\} \qquad (4)$$

The graph of this function, which is symmetric to ω_o, is plotted in figure 2.

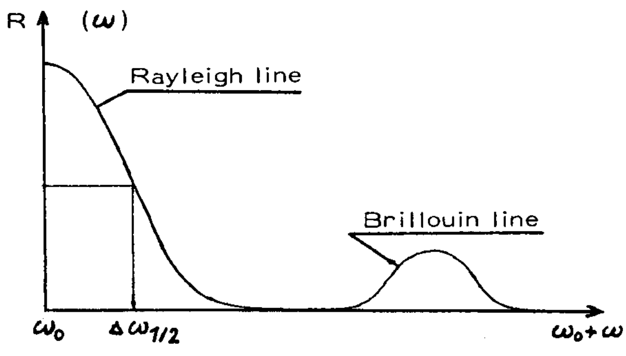

Fig. 2: Frequency spectrum of Rayleigh- and Brillouin scattered light; k = const.

The value of the maximum is determined by the term in the first brackets (equ. 4). Wavelength, angle, density, Boltzmann constant and temperature are knwon. The term $(\partial\varepsilon/\partial\varrho)_T$ may be calculated with

$$\varepsilon = n_o^2 \qquad (5),$$

because the relation between refractive index and density is given by the Lorenz-Lorentz law. Therefore the isothermal compressibility may be calculated from the value for $\omega = 0$.

The term $(2ak^2)/((ak^2)^2 + \omega^2)$ produces the Rayleigh line. This graph is determined by a halfwidth $\Delta\omega_{1/2}$:

$$\Delta\omega_{1/2} = a\,k^2 \qquad (6).$$

If the Rayleigh line is known by experiment, one may calculate the thermal diffusivity. Mc. Intyre and Sengers [2] describe a method to calculate other properties from equation (4), but this is not of interest here.

APPARATUS

The sample cell consists of a cylindrical glass tube (20 mm in height, 10 mm outer and 4 mm inner diameter), the axis is parallel to z direction (see fig. 3). Scattered light is measured in the x-y plane, therefore sin $\Phi = 1$. As light source a cohorent light with a very narrow spectral width is needed. For this investigation a Siemens LG 641 He Ne laser is used. A lens L 1 (f = 150 mm) focusses the laserbeam on the center of the sample cell and the scattered light at an angle Θ is measured. The lens L 2 (f = 65 mm) focusses the scattering volume on an aperture A of 50 µm. Now there is the problem of measuring the Rayleigh scattered light. It is impossible to measure the frequency shift directly, because a resolution $\Delta\omega/\omega_o$ of about 10^{-10}– 10^{-12} is needed, where $\Delta\omega$ is the frequency shift and ω_o the frequency of laser light. But it is possible to measure the frequency shift by an optical mixing method [3]. Here only a short simplified explanation shall be given. Consider there is not a spectrum of light like in figure 2, but only light of frequency ω_o and of frequency $\omega_o + \omega$, where $\omega_o \gg \omega$. Mixing the two oscillations gives an oscillation with frequency ω – a light beating. Experimentally of course one obtains a great number of beating frequencies – a light beating spectrum. It is assumed a special cohorent light source and a small solid angle dΩ. The light illuminates the photocathode of a photomultiplier (R C A 8645). The photomultiplier's output consists of a dc term from the unshifted light and an ac term from the oscillations. The spectrum of the obtained electric oscillations is analysed by a common spectrum analyser (H P 8552 B, 8556 A, 141 T). Between photo-

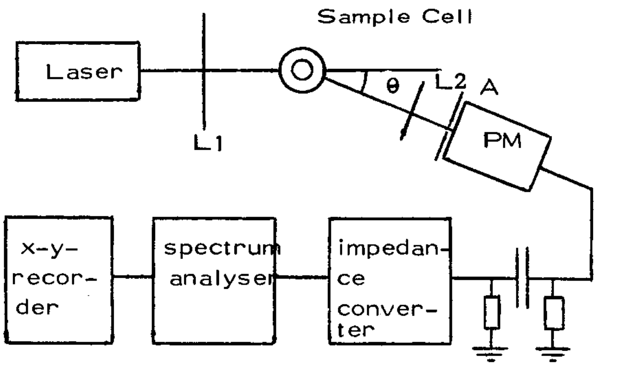

Fig. 3: Apparatus, L 1, L2 lenses; A aperture; PM photomultiplier.

multiplier and spectrum analyser a dc blocking and an impedance converter (S G 310) is needed. The spectrum analyser's output is plotted on a x-y-recorder.

EXPERIMENTAL RESULTS

Results of measurements are shown in figure 4 where the thermal diffusivity of CO_2 is plotted versus temperature difference $T - T_c$.

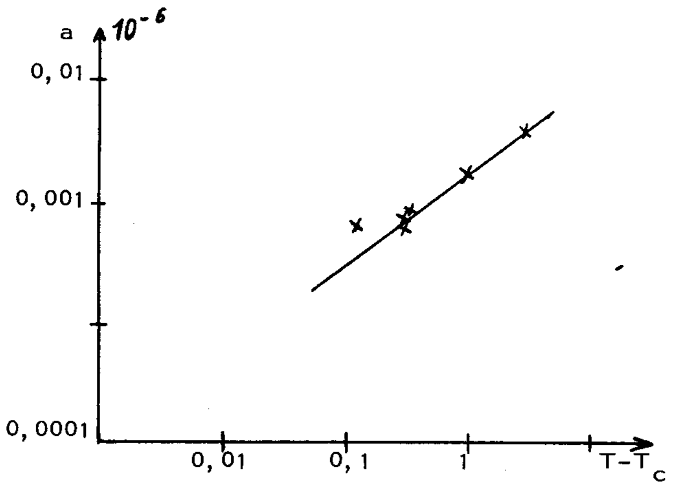

Fig. 4: Thermal diffusivity of CO_2 ($\varrho \approx \varrho$ critical) versus $T - T_{critical}$.

As other authors [3] an exponent of 0.73 is obtained. The deviation for low temperatures can be explained from deviations of isochoric state, because of density gradients over the height of the sample cell. The deviations from the isochoric state leads to a greater thermal diffusivity. Figure 4 shows that thermal diffusivity seems to become zero approaching the critical point. Measurements of isothermal compressibility seem to show that thermal conductivity becomes infinite with $\lambda \propto (T - T_c)^{0,6}$.

The error of the light scattering method, resulting essentially from angle measurements, seems to be less than 5 percent.

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