Measurements of heat transfer in microemulsions by laser-induced thermal blooming

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In this letter, we describe a variation of the well-known thermal blooming technique used for the measurement of the thermal conductivity in fluids. An IR microsecond laser pulse is used to develop the thermal effect. The decay of the thermal lens is analyzed by a cw nonabsorbed auxiliary wave. This dual-beam technique is for the first time used for studying selective heat transfer in microemulsions.

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Two classical methods have already been used for the study of heat conduction in liquids. In forced Rayleigh scattering,[1] an interferometric grating is generated in a thin absorbing sample by creating interference between two light beams coming from the same laser. The induced phase grating is probed by an auxiliary nonabsorbed wave. Such a technique has been used to measure the thermal conductivity in pure liquids,[2] in liquid crystals,[3] and in five-component microemulsions.[4] In the cw thermal lens technique,[5,6] a refractive index change is induced along the ray path by a laser wave, leading to a self-defocusing effect. The time evolution of the thermal focal length allows the measurement of heat conductivity in the medium.[6-10]

We present here an application of a variation of the thermal lens technique to the study of thermal relaxation in liquids. This method is based on the study of the transient thermal blooming induced by an IR microsecond pulse, the decay of the thermal lens being analyzed by a probe nonabsorbed cw laser wave.

This dual-beam method seems to be well adapted to the thermal relaxation of liquids characterized by (i) the selective absorption in the near-IR part of the spectrum present in some liquids, (ii) the weakness of such absorption, and (iii) a time scale in the millisecond range. Indeed, in spite of its two considerable advantages—a well-defined analysis wave vector and a great sensitivity (detection of optical fluxes on a dark background)—the forced-Rayleigh technique, which requires strong absorbance in thin layers, cannot be used with weakly absorbing samples.

We now briefly discuss the choice of the laser used for heating. The emission at 1060 nm of the neodymium glass laser seems to be well adapted to condition (i). The mode-locked and Q-switched modes lead to very short pulses, associated with high values of electrical field. Such pulses can induce nonlinear effects (such as breakdown, stimulated Brillouin and Raman scattering, etc.) which could disturb the medium and give spurious results. Beside, the free-running mode, giving light pulses which can extend up to 1 ms, do not seem to be well adapted to the study of relaxation with time scales in the range of a few tens of milliseconds. The theoretical treatment presented below requires pulses effectively much shorter. Moreover, long-time laser emissions, or cw lasers, favor convection effects, which are not desired in this work.[11] So we have chosen one of the free-running oscillations of the neodymium glass laser. Such a microsecond laser pulse develops the "bloom" in the sample, and the thermal conductivity properties of the fluid are analyzed by studying the decay of the induced thermal lens. Figure 1 illustrates our experimental setup.

The inductive wave is given by a neodymium glass laser oscillator, operated at 1060 nm. TEM_{00} is selected by a pinhole (diameter $\phi = 2$ mm) inserted in the optical cavity. Since the analysis depends upon the assumption of a Gaussian transverse distribution of the heating energy, such a selection was carefully controlled. A Pockels cell is used as an optical shutter selecting one of the free-running oscillations of the oscillator.[12] The pulse duration is about 1 μs (at half-height). The absence of any fast modulation (or spiking) of the impulsion must be noted. After amplification, the energy of the pulse is about 10 mJ and the highest value of the associated electric field is about 2×10^6 V m^{-1}. The probe wave is given by a cw weak-power He-Ne laser ($P\sim 1$ mW).

The radius of its beam waist (about 150 μm in the cell) is controlled by a beam expander (L_3 in Fig. 1) in order to

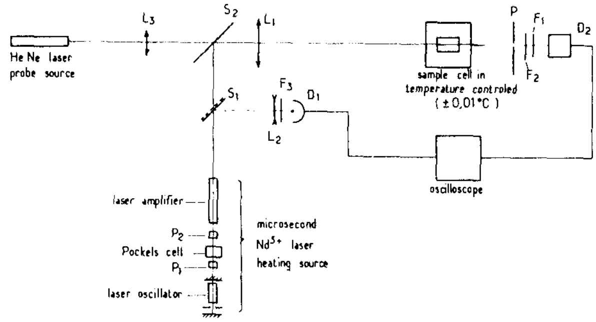

FIG. 1. Experimental setup: S_1 beam splitter; S_2 highly reflecting mirror at 1060 nm; L_1, L_2, L_3, lenses; P pinhole, $\phi = 1$ mm; F_1, F_2, F_3, interferential filters; P_1,P_2, Glan polarizer; D_1, fast photocell, D_2, pin photodiode.

TABLE I. Experimental values of specific heat ρC_p, thermal diffusivity, and thermal conductivity of the system AOT/water/carbon-tetrachloride at 25.0 ± 0.1 °C.

Sample	Volume fraction of dispersed phase	C_p J g^{-1} K^{-1} (± 0.04)	ρC_p J cm^{-3} K^{-1} (± 0.03)	$10^3 D_{th}$ cm^2 s^{-1} (± 0.03)	$10^3 \Lambda$ J cm^{-1} s^{-1} K^{-1} (± 0.04)
M	0.48	1.55	2.09	0.32	0.67
1	0.36	1.34	1.88	0.66	1.25
2	0.24	1.17	1.71	0.68	1.17
3	0.12	1.00	1.55	0.63	0.96
4	0.08	0.96	1.46	0.80	1.17
5	0.06	0.92	1.46	0.85	1.21
6	0.05	0.92	1.42	0.87	1.25
CCl_4	0	0.84[b]	1.38	0.77	1.04[a]

[a]from D. Solimi, J. Appl. Phys. 37, 3314 (1966).

[b]from *Handbook of Chemistry and Physics* (Chemical Rubber, Cleveland, 1974).

obtain the largest effect, after focalization by lens L_1. The energy is detected by a photodiode D_2 (signals of a few millivolts), through a pinhole P (diameter 1 mm), while a photocell D_1 monitors the heating pulse energy. Both electric signals are sent on a Tektronix 7904 scope equipped with a Polaroid camera.

The sample cell is about 4 cm long. We have used silica and plates for the large value of its thermal conductivity (about 13 times that of the studied liquids). Such a difference leads to well-defined boundary conditions which are included in the theoretical treatment of the problem. Let us also note that the induced increase of the temperature in the sample is relatively weak[13] and cannot give any significant experimental uncertainty owing to the temperature dependence of the thermal diffusivity.

The temperature distribution is obtained from the heat conduction equation, neglecting convection effect, and approximating the heating laser pulse by a Dirac function $\delta(t)$:

$$-\frac{1}{D_{th}}\frac{\partial}{\partial t}(\Delta T) + \nabla^2(\Delta T) = -\frac{1}{\Lambda} A \exp(-2r^2/\omega_0^2)\exp(-bz)\delta(t). \quad (1)$$

The propagation of optical waves occurs on the $0z$ axis. D_{th} is the thermal diffusivity constant of the sample; ΔT the induced temperature change; Λ the thermal conductivity ($D_{th} = \Lambda/\rho C_p$, where ρ is the density of the liquid and C_p the specific heat); A is a constant; $\exp(-r^2/\omega_0^2)$ takes into account the radial distribution of TEM_{00}; ω_0 is the radius of the heating wave to the $1/e$ height; and b is the absorption coefficient at 25 °C and at 1060 nm. By solving this equation with the boundary condition $\Delta T = 0$ for $z = 0$ and $z = L$ ($L = 4$ cm is the length of the cell), we find the induced temperature distribution. Then, assuming that the first-order defocusing is given by the quadratic term in r^2,[14] we find the focal length f_{th} of the induced thermal lens:

$$\frac{1}{f_{th}} = -\frac{L(\partial n/\partial T)\Delta T_0 Y(t)[1+\exp(-bL)]}{n\pi\omega_0^2(D_{th}t/\omega_0^2+\frac{1}{8})^2} \times \sum_{\substack{m=1 \\ (m\ \text{odd})}}^{\infty} \frac{\exp[-D_{th}t(m\pi/L)^2]}{(Lb)^2+(m\pi)^2}; \quad (2)$$

$Y(t)$ is the Heaviside function ΔT_0 is given by $\Delta T_0 = 0.12\, bW_0/\rho C_p\omega_0^2$, where W_0 is the total energy of the inductive pulse. Then, a Fresnel transform leads to the expression of the intensity received by the detector:

$$I = I_0\left(1 - \exp - \frac{2R^2}{d^2\omega_p^2(\lambda^2/\pi^2\omega_p^4 + 1/f'^2)}\right), \quad (3)$$

where ω_p is the beam waist of the probe (wavelength λ), R is the diameter of the detector pinhole, and f' is given by

$$1/f' = n/f_{th} + 1/d, \quad (4)$$

where d is the distance between the sample and the detector.

By fitting the experimental response of the detector with the theoretical formula (3), we can evaluate the diffusivity coefficient of the medium.

We report now the first application of such a thermal blooming technique to the study of heat transport in inversed micelles containing water (microemulsions). Microemulsions are composed, in the simplest case, of water, oil, and amphiphilic molecules.[15] They can, in first approximation, be described as small spheres (about 2 nm in diameter) with a polar core slightly absorbing at 1060 nm, surrounded by an amphiphilic monolayer, in an apolar continuum completely transparent at the neodymium laser wavelength (carbon tetrachloride). The T jump is selectively induced in the polar core and the analysis of the time decay of the thermal effect leads to information about heat transfer at the interface. Table I reports our main experimental results.

The inversed micelles containing water are described under the term "dispersed phase." The volume fraction ϕ of such micelles is calculated to be in the range 0.05–0.48. The specific heat C_p has been obtained from auxiliary measurement described elsewhere.[11]

Values of D_{th}, in the range $(3\text{–}9)\times 10^{-4}$ cm^2 s^{-1}, are obtained with acceptable accuracy (within 10%). They must be compared to recent ones obtained by the forced-Rayleigh method on a more complex system.[4] D_{th} is found to vary more strongly with ϕ than in that work. Another important point is that extrapolated values, at $\phi = 0$, of both thermal diffusivity ($D_{th} = 9.9\times 10^{-4}$ cm^2 s^{-1}) and thermal conductivity ($\Lambda = 1.38\times 10^{-3}$ J cm^{-1} s^{-1} K^{-1}) are largely different from values tabulated for pure carbon tetrachloride (respectively 7.7×10^{-4} $cm^2\,s^{-1}$ and 1.04×10^{-3} $J\,cm^{-1}\,s^{-1}\,K^{-1}$). Moreover, a relatively large domain of volumic fraction ($\phi<0.1$), where Λ seems to vary linearly with ϕ, is evidenced for the first time. It allows the determination of the intrinsic value of the thermal conductivity of the interface.

In conclusion, we briefly describe in this letter an application of short-pulse-induced thermal blooming to the study of heat transfer in liquids and more precisely, in microemulsions. Such a technique does not require the use of absorbing centers (dyes), which are often incorporated in systems studied by forced Rayleigh scattering, without any proof for not disturbing them. Such preliminary results, if confirmed, can be used for microscopic calculations of thermal relaxation within the micelles and heat transfer through the liquid-liquid interface.

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