

THERMAL LENS EFFECT APPLIED IN THERMAL DIFFUSION DETERMINATIONS FOR MOLECULAR LIQUIDS

BY J. SKUPIŃSKI, J. BUCHERT, S. KIELICH

Nonlinear Optics Division, Institute of Physics, A. Mickiewicz University, Poznań*

J. R. LALANNE AND B. POULIGNY

University of Bordeaux I and C.N.R.S. Research Center Paul Pascal, University Domain, 33405-Talence, France

(Received March 20, 1984; revised version received October 2, 1984)

Thermal defocussing of a focussed laser beam in a liquid is considered for the case when the time during which the medium undergoes heating by the beam is comparable to the thermal relaxation time τ_c . The experimentally determined space-time temperature distribution function permitted the determination of τ_c and the thermal diffusivity of acetone, ethyl alcohol, benzene, bromobenzene, carbon tetrachloride, nitrobenzene, toluene and water.

PACS numbers: 42.60.Kg, 42.65.-k, 66.10.Cb

1. Introduction

The phenomenon consisting in a temperature gradient-induced change in refractive index of the medium has first been observed in 1964 by R. C. Leite, R. S. Moore and J. R. Whinnery [1]: the temperature gradient perpendicular to the propagation direction of the laser beam modifies the index of the medium. Obviously, these modifications affect the geometry of the beam and, in particular, its divergence. When dealing with the effect, the nonlinear medium is equivalently represented by a lens (positive or negative) of focal length varying with the time, often referred to as a "thermal lens". The phenomenon is dependent on the amount of energy absorbed by the medium, the temperature-variation of the index, and the heat transfer process within the medium. The solution of the heat transfer equation involves the quantity τ_c , referred to as the characteristic time, or thermal relaxation time. Its magnitude is dependent as follows on the physical properties of the medium and the experimental geometry [2]:

$$\tau_c = \frac{w_0^2 \rho c_p}{8k} = \frac{w_0^2}{8D}, \quad (1)$$

* Address: Instytut Fizyki, Uniwersytet A. Mickiewicza, Grunwaldzka 6, 60-780 Poznań, Poland.

with: w_0 the radius of the incident beam, ρ the density of the medium, c_p its specific heat at $p = \text{const}$, k its thermal conductivity coefficient, and $D = k/(\rho c_p)$ its thermal diffusivity coefficient.

Denoting by t_h the time interval during which the medium undergoes heating by the laser beam we have to deal, depending on τ_c , with the following three cases:

- 1° $t_h \gg \tau_c$ — the stationary case, considered and observed by S. A. Akhmanov, D. P. Krindach, A. P. Sukhorukov, A. V. Migulin, R. V. Khokhlov [3, 4, 5];
- 2° $t_h \ll \tau_c$ — the heating time of the medium by the beam of a pulse laser is so short, compared to the relaxation time, that the vanishing of the temperature gradient can be considered on omission of the heating time. The respective experimental setup has been applied to the study of emulsions by J. R. Lallanne, E. Sein, J. Buchert and S. Kielich [6, 7];
- 3° $t_h \approx \tau_c$ — heating for a sufficiently long time requires the use of a cw low power laser and a shutter. Here, the theory involves heat diffusion from the focus in the process of heating and on removal of heating. This, in fact, is the case of our present experimental study.

2. Determination of the temperature distribution function in the medium and the intensity variations in the probe beam

As stated above, the thermal lens effect is caused by the temperature gradient arising in the medium. Hence, the dynamics of the process is directly related to the problem of heat transfer. In cylindrical coordinates (r, z, φ) , the equation of thermal diffusivity in a homogeneous medium takes the form:

$$\rho c_p \frac{\partial T(r, z, t)}{\partial t} - k \Delta T(r, z, t) = Q(r, z, t), \quad (2)$$

where $T(r, z, t)$ is the temperature distribution function, and $Q(r, z, t)$ the amount of heat absorbed by the medium on the assumption that $\partial T/\partial \varphi = 0$ for sufficiently small values of r .

The heating beam and probe beam propagate co-axially along the z -axis. Assuming both beams as radially Gaussian at the input into the cuvette holding the liquid, we have:

$$E(r, z = 0, t = 0) = E_0 \exp\left(-\frac{r^2}{w_0^2}\right),$$

and

$$Q(r, z = 0, t = 0) = Q_0 \exp\left(-\frac{2r^2}{w_0^2}\right), \quad (3)$$

where E is the electric field of the heating beam and w_0 its radius at E_0/e . Let L be the length of the cuvette, i.e. $z \in [0, L]$. We then have for the emergent beam:

$$Q(r, z, t = 0) = Q_0(z) \exp\left(-\frac{2r^2}{w_0^2}\right), \quad (4)$$

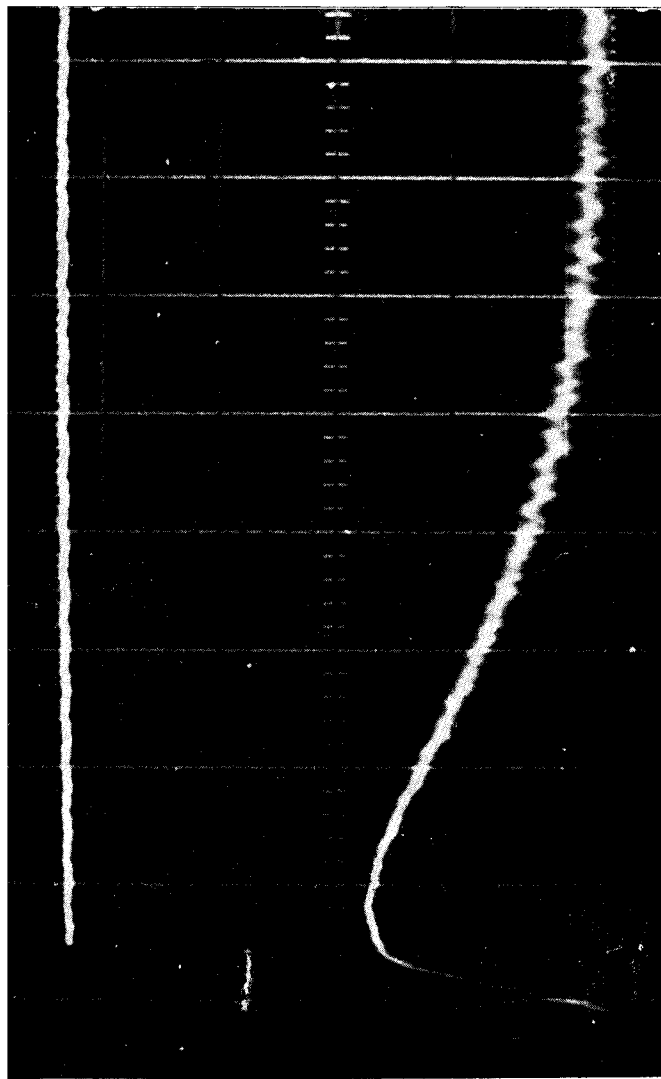


Fig. 3. Oscillogram of the change in intensity of the probe beam on the area of the circular hole, πa^2 (lower curve), and measurement of the heating time $t_{sh} = 25$ ms (upper curve), for benzene

where $Q_0(z) = \frac{0.48\alpha P_0}{\pi\omega_0^2} \exp(-\alpha z)$ [cal cm⁻³ s⁻¹], α the light absorption coefficient of the liquid [cm⁻¹], and P_0 the power of the incident heating beam [W]. The numerical coefficient 0.48 has the dimension cal · W⁻¹ · s⁻¹ (to convert the power in watts to calories per second).

For small values of the variable r (i.e. near the optical axis) and on the above initial conditions the standard solution [8] of the parabolic Eq. (2) has the form:

$$T(r, z, t) = \frac{Q_0(z)\tau_c}{\rho c_p} \left\{ Ei \left[-\frac{2r^2}{w_0^2} \right] - Ei \left[-\frac{2r^2}{w_0^2(1+t/\tau_c)} \right] + \frac{t}{t+\tau_c} \exp \left[-\frac{2r^2}{w_0^2(1+t/\tau_c)} \right] \right\}. \quad (5)$$

We expand the integral-exponential function $Ei(-x)$ in the series: $Ei(-x) = \ln(\gamma x) - x + x^2/4 + \dots$, where $\gamma = 0.5772\dots$ (Euler's constant). On retaining the first two terms of the expansion, we have with regard to Eq. (5):

$$T(r, z, t) = T_0(z) \left\{ \left[\ln(1+t/\tau_c) - \frac{2r^2}{w_0^2} \frac{t}{t+\tau_c} \right] + \frac{t}{t+\tau_c} \exp \left[-\frac{2r^2}{w_0^2(1+t/\tau_c)} \right] \right\}, \quad (6)$$

whence, by (4) and (1), we have

$$T_0(z) = \frac{Q_0(z)\tau_c}{\rho c_p} = \frac{0.48\alpha P_0\tau_c}{\pi w_0^2 \rho c_p} e^{-\alpha z} = \frac{0.06\alpha P_0}{\pi k} e^{-\alpha z},$$

the amplitude of the temperature distribution expressed in [deg]. The expression (6) represents the space-time temperature distribution in the medium. The first term in square brackets (that in ln) determines the rise in temperature due to heating. However, it should be kept in mind that the heating time is comparable to the thermal relaxation time τ_c leading simultaneously to heat transfer (the exponential term). On removal of heating, the temperature distribution varies as the result of heat transfer only. It is thus necessary to take into consideration the heating time t_{sh} (the time during which the shutter is open) in Eq. (6). The function (6), $T(r, z, t)$ is valid for $t \leq t_{sh}$; during the time interval from 0 to t_{sh} it attains the value

$$T(r, z, t = t_{sh}) = T'_0(r, z, t' = 0),$$

where $t' = t - t_{sh}$. With this notation, the effect of heat transfer in the medium on removal of heating is described by the function

$$T(r, z, t') = T'_0 \frac{\exp \left[-\frac{2r^2}{w_0^2(1+t'/\tau_c)} \right]}{1 + \tau_c/t'}.$$

From the solution of the wave equation, and taking into account the slowly variable amplitude and the Fresnel term defining the nonlinear change in phase, we obtain the intensity distribution in the probe beam [3]:

$$I(r, \theta, t) = I_0 \left| \int_0^a r J_0(k_0, \theta, r) \exp \left\{ -\frac{r^2}{\sigma_0^2} + ik_0 \right. \right. \\ \left. \left. \times \left[-\frac{r^2}{R_0} + \int_0^L \delta n(r, z, t) dz \right] \right\} dr \right|^2, \quad (7)$$

where R_0 — radius of phase divergence, J_0 — Bessel function, σ_0 is the radius of the probe beam (Gaussian in shape and having the angle of divergence θ), and $k_0 = (2\pi)/\lambda_0$ its wave number. The function describing the change in refractive index $\delta n(r, z, t)$ of the liquid is of the form

$$\delta n(r, z, t) = \frac{\partial n}{\partial T} \delta T(r, z, t) \begin{cases} \delta T = T(r, z, t) & \text{for } t \leq t_{sh}, \\ \delta T' = T'(r, z, t') & \text{for } t > t_{sh}. \end{cases} \quad (8)$$

If the probe beam is not divergent, $\theta = 0$ and $J_0(k_0, 0, r) = 1$. When studying the changes in intensity in the probe beam close to the optical axis (for small values $2a$ of the diameter of the hole in front of the detector), the wave can be assumed as plane ($R_0 \rightarrow \infty$), considerably simplifying Eq. (7). The function thus simplified served as the basis for our numerical computations.

Fig. 1 shows the numerically obtained relative changes in intensity distribution, for the following initial data: $P_0 = 0.1$ W, $w_0 = 0.03$ cm (heating beam $\lambda = 514.5$ nm), $\sigma_0 = 0.075$ cm, $k_0 = 99291.8$ cm $^{-1}$ (probe beam $\lambda_0 = 6.32.8$ nm), $R_0 = 9000$ cm (since $R_0 \rightarrow \infty$), $t_{sh} = 20, 40, 60, 80, 100$ ms, $L = 3$ cm, $\alpha = 2 \times 10^{-2}$ cm $^{-1}$, $\rho = 1.20$ g \cdot cm $^{-3}$, $c_p = 0.364$ cal g $^{-1}$ K $^{-1}$. In agreement with our expectations, the value of the subintegral function is dependent on the time of heating t_{sh} whereas the heating process (the shape

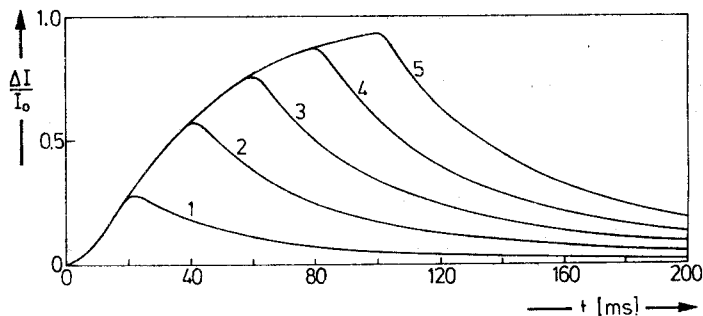


Fig. 1. Dynamics of the relative intensity distribution $\Delta I/I_0$ in the probe beam in the process of thermal defocussing (calculated). 1 — $t_{sh} = 20$ ms; 2 — $t_{sh} = 40$ ms; 3 — $t_{sh} = 60$ ms; 4 — $t_{sh} = 80$ ms; 5 — $t_{sh} = 100$ ms

TABLE I
Literature data* and our experimental results for some selected molecular liquids

Liquid	ρ [g · cm ⁻³]	c_p [cal/g · K]	$k \cdot 10^4$ [cal/cm · s · K]	$D^{\text{calc}} \cdot 10^4$ [cm ² /s]	$\alpha \pm 0.003$ for 514.5 nm [1/cm]	t_{sh} [ms]	τ_c [ms]	$D^{\text{exper}} \cdot 10^4$ [cm ² /s]
Acetone	0.790	0.515	3.84	9.44	0.023	25	120	9.37
Ethyl alcohol	0.795	0.577	4.3	2.37	0.024	25	103	10.93
Benzene	0.879	0.406	3.8	10.65	0.041	25	104	10.82
Bromobenzene	1.490	0.236	2.6	7.39	0.021	25	153	7.35
Carbon tetrachloride	1.590	0.201	2.5	7.82	0.052	25	119	9.45
Nitrobenzene	1.203	0.364	3.8	8.68	0.030	25	130	8.65
Toluene	0.860	0.422	3.6	9.92	0.074	35	106	10.61
Water	1.000	0.998	14.0	14.02	0.133	25	83	13.55

* *Landolt-Börnstein Tables*, New Series, V1, part a, Springer-Verlag, Berlin 1974; J. P. Gordon, R. C. C. Leite, R. S. Moore, S. P. S. Porto, J. R. Whinnery, *J. Appl. Phys.* **36**, 3 (1965).

of the growing part of the curves) remains the same for a given liquid and given conditions of experiment. On removal of heating (at $t > t_{sh}$), heat transfer is a function of the amount of heat already absorbed. On the assumption of $t_{sh} \rightarrow \infty$ the curve describing the process of heating (the envelope) tends asymptotically to unity and visualizes the attainment of equilibrium between the process of heating and that of heat transfer to the environment (steady state).

3. Experimental setup, and results of measurements

The experimental setup is shown in Fig. 2. The argon laser 1 generates the heating beam (of power 100 mW at the input into the cuvette, and of wavelength 514.5 nm). The heating time, controlled by the shutter of the photographic camera 2, ranged from 20 to

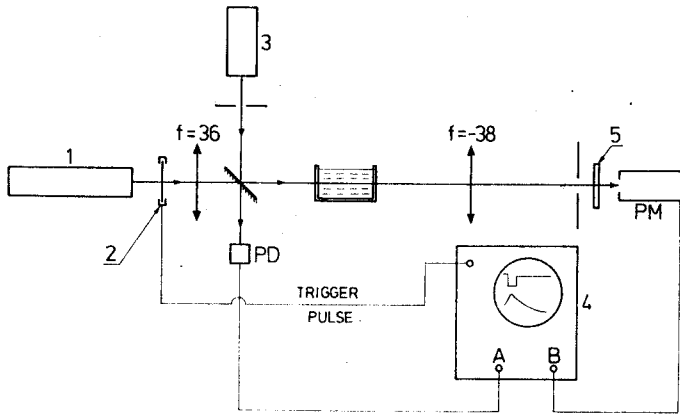


Fig. 2. Diagram showing the measuring setup

40 ms and was determined oscillographically for each exposition by the photodiode PD, triggered by the pulse of the heating beam. The latter, focussed by a lens of $f = 36$ cm, attained a diameter of $2w_0 = 0.06$ cm at the input into the cuvette. The power density achieved in the cuvette of length $L = 3$ cm amounted to 35 W cm^{-2} . On emerging from the cuvette, the heating beam was cut off by the interference filter 5, so that it was not recorded by the photomultiplier PM. The oscilloscope 4 was released, at the moment the shutter opened, by the triggering switch of the flash bulb in the camera. The non-divergent beam from the He-Ne laser 3, of wavelength $\lambda_0 = 632.8 \text{ nm}$, diameter $2\sigma_0 = 0.15$ cm, and power about 1 mW, was directed into the cuvette co-axially with the heating beam by means of a plane dielectric mirror ($T = 0\%$ for λ_0). On traversing the cuvette and the lens of focal length $f = -38$ cm, the probe beam attained a diameter of about 2.5 cm (without heating). The circular diaphragm, of diameter $2a = 0.25$ cm, was placed in front of the photo-multiplier.

The time-evolution of the intensity at the centre of the probe beam as obtained on the oscilloscope (Fig. 3) and fed to the computer, in conjunction with the curves calculated

from Eq. (7), permitted (by means of least square methods) the determination of the thermal relaxation time τ_c and then, with Eq. (1), that of the thermal diffusivity coefficient

$$D^{\text{exper}} = \frac{w_0^2}{8\tau_c}$$

In addition to our experimental results, Table I gives the values of the thermal diffusivity coefficient, calculated with the data tabulated applying the relation:

$$D^{\text{calc}} = \frac{k}{\rho c_p}$$

The absorption coefficients α for the heating and α_0 for the probe beam were determined with a UV-VIS spectrometer. From a comparison of D^{calc} and D^{exper} , the present method of determining the thermal diffusivity coefficient by following the change in optical properties of the medium under the influence of the induced gradient of temperature can be said to be correct.

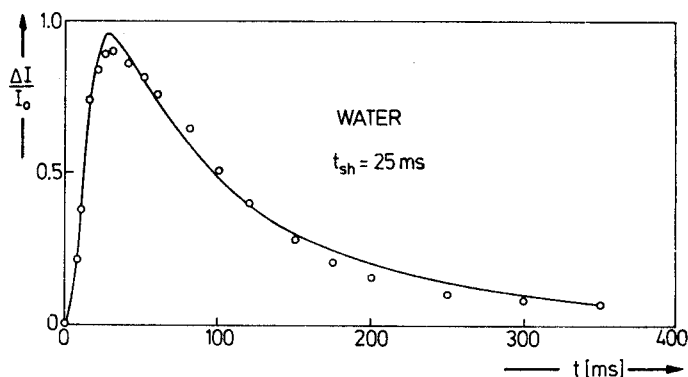


Fig. 4. Shape of the relative change in intensity on the area πa^2 of the circular hole as calculated from Eq. (7) (solid line). Little circles — experimental points

The theoretical considerations of this paper are in good agreement with the experimental results, as shown in Fig. 4, where the (continuous) curve was calculated with Eq. (7) and the little circles are experimental points. The example is for water, exposed to the heating beam for 25 ms.

4. Conclusions

The above proposed method of measuring the thermal relaxation time and determining the thermal diffusivity coefficient of molecular liquids belongs to the group of methods based on the study of the optical properties of the medium. It eliminates the need to determine the density of the liquid, its specific heat, or thermal conductivity coefficient. The

experimental difficulties reduce to the elimination of mechanical instabilities of the setup and to the achievement of strict co-axiality of the two beams. Also, some inconvenience arises from the necessity of determining the absorption coefficient for the heating beam.

REFERENCES

- [1] R. C. Leite, R. S. Moore, J. R. Whinnery, *Appl. Phys. Lett.* **5**, 141 (1964).
- [2] P. Calamettes, C. Laj, *Phys. Rev. Lett.* **27**, 239 (1971).
- [3] S. A. Akhmanov, D. P. Krindach, A. P. Sukhorukov, R. V. Khokhlov, *Pisma v Zh. Eksp. Teor. Fiz.* **6** (2), 509 (1967).
- [4] S. A. Akhmanov, A. P. Sukhorukov, R. V. Khokhlov, *Zh. Eksp. Teor. Fiz.* **50**, 1537 (1966).
- [5] S. A. Akhmanov, D. P. Krindach, A. V. Migulin, A. P. Sukhorukov, R. V. Khokhlov, *IEEE J. Quant. Electron.* **QE-4**, 568 (1968).
- [6] E. Sein, J. R. Lalanne, J. Buchert, S. Kielich, *J. Coll. Interf. Sc.* **72**, 363 (1979).
- [7] J. R. Lalanne, E. Sein, J. Buchert, S. Kielich, *Appl. Phys. Lett.* **36**, 973 (1980).
- [8] M. S. Carslaw, J. C. Jaeger, *Operational Methods in Applied Mathematics*, Dover Pub. Inc., New York 1963.