International Journal of Thermophysics, Vol. 15, No. 2, 1994

A Dilatometric Method to Measure the Thermal Diffusivity of Nonmetallic Liquids

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Received October 5, 1993

A new method to measure the thermal diffusivity of liquids is presented. It requires determination of the time dependence of the thermal expansion of the liquid when it is subjected to a heat source at the top of the cell containing the liquid. The high accuracy of the method (about 3%) is due to an essential reduction of convective currents and also to the absence of temperature detectors, which generally introduce unwanted perturbations on the thermal field.

KEY WORDS: dilatometry; thermal diffusivity.

1. INTRODUCTION

The standard method to measure the thermal diffusivity of liquids is the hot wire method [1], in which the heat source is a resistive wire, used at the same time as a temperature sensor. A proper analysis of the time behavior of the temperature of the wire embedded in the liquid can give either the thermal conductivity or the thermal diffusivity of the liquid itself. Very sophisticated experimental arrangements and data analysis programs have been developed to reduce the error sources due to the finite size of the cell containing the liquid and to the convective currents taking place during the measurement [2–5].

In the present paper, we propose a new method which provides an alternative solution to the above problems. Such a method is based on an original idea already used for solids: The temperature field in the specimen is determined by measuring its thermal expansion [6–8]. Through the

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0195-928X/94/0300-0215$07.00/0

analysis of the sample dilation and of the temperature measured at the heat source, it is possible to obtain the thermal diffusivity. The high sensitivity of the detection apparatus and the elimination of unknown thermal losses provide measurements with an accuracy of about 3% for low-conducting solid materials.

The dilatometric technique turns out to be applicable to measurements on liquids by using the experimental apparatus shown in Fig. 1. The sample is contained in a cell (L) bounded by a Pyrex glass tube (G), by a copper disk (D), and by an Invar support (I). A thermocouple (T_0) inserted in D records the temperature of the copper disk, which can be heated by the thermofoil heater (H). The temperature recorded by the thermocouple is the temperature of the whole disk, since owing to the high thermal diffusivity of copper, the thermal field can be considered uniform in D. The cell (L) is connected, through the two Invar nozzles (A and B), to the liquid reservoir (R) and to the rotative pump (P), respectively. One first evacuates the cell (A closed and B open) and then introduces the liquid (B closed and A open). Finally, B is closed, and hereafter in this way any thermal expansion of the liquid in L is automatically transmitted to the mercury contained in the U tube. A nickel wire (C_1) embedded in mercury

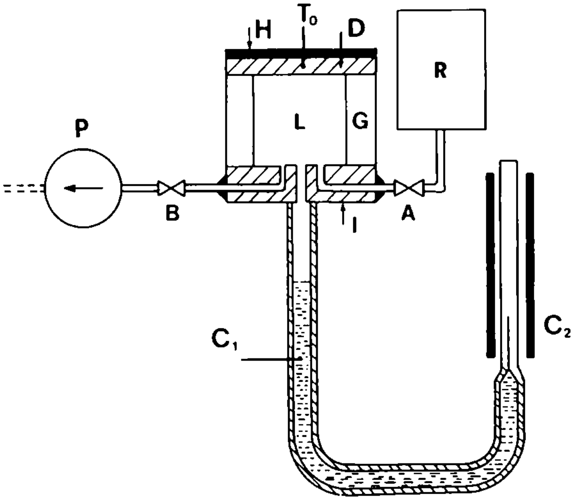

Fig. 1. Experimental setup. The liquid is contained in the cell (L) bounded by the Pyrex tube (G), the copper disk (D), and the Invar support (I). T_0 is the thermocouple recording the temperature of D heated by H. Nozzles A and B connect the cell to a reservoir (R) and a pump (P). C_1 and C_2 are the electrodes of the capacitive system.

allows an electrical connection with the electronic equipment (see below). At the other end, the U tube communicates with a fused silica capillary tube 0.050 cm in internal diameter and 0.5 cm in external diameter. The capillary is surrounded by a thin hollow cylinder of aluminum (C_2), forming a cylindrical capacitor with the mercury of the capillary tube. Its capacitance can be detected by connecting the electric wire (C_1) and the electrode (C_2) to the electronic equipment composed by a GenRad bridge and a lock-in amplifier. When the thermofoil heater is working the fluid in L undergoes a thermal expansion, resulting in a rise in the mercury level in the capillary. This produces a change in capacitance, which is detected with a high sensitivity (1 part in 10^6) by the lock-in amplifier.

The use of the mercury capillary tube as a mechanical amplifier of the liquid thermal dilation does not perturb the temperature field inside the cell and, for this reason, represents an ideal temperature detector provided that we are able to correlate the dilation to the field itself. This is certainly possible because, if the measurement time is short enough, the heat diffusing from D does not appreciably arrive at the Invar support I, and consequently the problem essentially involves heat diffusion from a hot base into a long cylinder surrounded by an annular vessel of different material. The mathematical solution of this problem is discussed in Section 2.

We impose boundary conditions of zero flux at both the upper and the lower base of the cylinder (due to the reasons explained above) and show that, for reasonable values of the Newton coefficient describing the heat exchange between the outer surface of the annular vessel and the environment, the perturbation produced by this exchange on the thermal field inside the liquid can be rendered negligibly small by a proper choice of the vessel thickness.

Finally, by the same apparatus we also avoid the problem of convective currents, these being drastically reduced, because the thermal gradient inside the cell and the gravitational field are set in opposite directions.

2. THEORY

We solve the diffusion equation for a system consisting of a homogeneous cylinder of liquid having length l, surrounded by a vessel with known physical properties. The two media are in contact with the copper disk D in which, owing to the high thermal conductivity of copper, the temperature can be considered independent of the spatial coordinates and, consequently, a function of only one variable (time): Its time behavior is detected by the thermocouple T_0.

Let k be the conductivity and μ the product $c\rho =$ (specific heat) $\times$ (density) for the liquid under study. We subdivide the whole time interval into many small intervals, in each of which the temperature of the copper disk can be considered constant. Let us indicate by T_i the temperature of the copper disk in the time interval between t_i and t_{i+1} and by $\theta_i^{i+1}(\vec{r}, t)$ the corresponding temperature at any point $\vec{r}$ of the system (liquid + vessel), assuming the vessel to be described by the same values of μ and k characterizing the liquid. θ_i^{i+1} is referred to as the unperturbed field; it obviously satisfies the diffusion equation[2]

$$-k\nabla^2\theta + \mu\frac{\partial\theta}{\partial t} = 0 \tag{1}$$

With reference to cylindrical coordinates (r, z, ϕ), the z axis being directed downward with the origin at the upper base of the cylinder, the solution of Eq. (1) must satisfy the boundary condition at the outer surface of the vessel $(r = R)$, namely,

$$-k\left(\frac{\partial\theta}{\partial r}\right)_R = h\theta \tag{2}$$

and the condition of zero heat flux at the lower base

$$-k\left(\frac{\partial\theta}{\partial z}\right)_{z=l} = 0 \tag{3}$$

This follows from the condition that, during the time of measurement, no appreciable heat arrives at $z = l$. At the upper base $(z = 0)$ the temperature of the liquid at any time is assumed to be the same as the temperature of the copper disk: In fact, the temperature jump through the contact between a metal and a low-conducting medium is negligibly small, as experimentally shown by the authors in previous works [6, 7]. Consequently our assumption is valid for all the dielectric liquids but would certainly fail for liquid metals.

In terms of the diffusivity $\alpha = k/\mu$, the solution satisfying Eqs. (2) and (3) can be written in the form

$$\theta_i^{i+1}(r, z, t) = T_{i+1} + \sum_{nm} c_{nm}^i \phi_{nm} e^{-\alpha q_{nm}^2 t} \tag{4}$$

where

$$\phi_{nm} = \sin(\omega_n z)\, J_0(\nu_m r) \tag{5}$$

$$q_{nm}^2 = \omega_n^2 + \nu_m^2 \tag{6}$$

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[2] Definitions of symbols are given under Nomenclature, at the end of the text.

ω_n being fixed by the condition given by Eq. (3) as

$$\omega_n = \left(n + \frac{1}{2}\right)\frac{\pi}{l} \tag{7}$$

and ν_m by the condition given by Eq. (2), or

$$k\nu_m J_1(\nu_m R) + hJ_0(\nu_m R) = 0 \tag{8}$$

By imposing time continuity

$$\theta^i_{i-1}(r, z, t_i) = \theta^{i+1}_i(r, z, t_i) \tag{9}$$

and using the orthogonality properties of the functions ϕ_{nm}, one easily obtains the following recurrence relation:

$$c^i_{nm} - c^{i-1}_{nm} = (T_i - T_{i+1})\frac{(\phi_{nm}, 1)}{(\phi_{nm}, \phi_{nm})}e^{\alpha q^2_{nm} t_i} \tag{10}$$

for $i > 1$, where (ϕ, ψ) means the scalar product

$$(\phi, \psi) = \int_0^R r\,dr \int_0^l \phi\psi\,dz \tag{11}$$

The expression of c^0_{nm} is deduced from the condition of zero temperature at $t = 0$, namely,

$$c^0_{nm} = -T_1\frac{(\phi_{nm}, 1)}{(\phi_{nm}, \phi_{nm})} \tag{12}$$

Putting

$$\theta^{i+1}_i(t_{i+1}) = \theta_{i+1} \tag{13}$$

one easily deduces, from Eqs. (4), (10), and (12), the following general expression of the unperturbed temperature field:

$$\theta_i = T_i + \sum_{p=1}^{i}(T_{p-1} - T_p)\sum_{nm}\frac{(\phi_{nm}, 1)}{(\phi_{nm}, \phi_{nm})}\phi_{nm}e^{-\alpha q^2_{nm}\tau(i+1-p)} \tag{14}$$

where τ is the constant

$$\tau = t_{i+1} - t_i \tag{15}$$

Let us now try to solve the diffusion equation in the nonhomogeneous medium consisting of the central cylinder of liquid and of the surrounding vessel. By proper choice of the material, the difference in diffusivity and conductivity between the liquid and the vessel can be greatly reduced and a perturbation theory correspondingly developed. The temperature field in the system (liquid + vessel) is now written $\theta(r, z, t) + \theta'(r, z, t)$, where $\theta(r, z, t)$ is the unperturbed solution given previously and θ' is the perturbation. The diffusion equation to be solved is

$$-(k + k')\nabla^2(\theta + \theta') + (\mu + \mu')\frac{\partial(\theta + \theta')}{\partial t} = 0 \tag{16}$$

where k and μ refer to the liquid and k' and μ' are zero for $r < a$, where a is the inner radius of the vessel: conversely, for $a < r < R$ one has $k' = k_V - k$ and $\mu' = \mu_V - \mu$, the index V referring to the vessel. We assume the contribution of the term

$$k'\nabla^2\theta' + \mu'\frac{\partial\theta'}{\partial t} \tag{17}$$

to be negligible and solve the equation

$$-k\nabla^2\theta' - k'\nabla^2\theta + \mu\frac{\partial\theta'}{\partial t} + \mu'\frac{\partial\theta}{\partial t} = 0 \tag{18}$$

The solution of Eq. (18) in the time interval (t_i, t_{i+1}) is written in the form

$$(\theta')_i^{i+1} = \sum_{nm} \psi^i_{nm} e^{-\alpha q^2_{nm} t} \tag{19}$$

Substituting Eqs. (4) and (19) into Eq. (18), we obtain the equation

$$\nabla^2\psi^i_{nm} + q^2_{nm}\psi^i_{nm} = c^i_{nm}\lambda(r)\, q^2_{nm}\phi_{nm} \tag{20}$$

where

$$\lambda(r) = \frac{k'}{k} - \frac{\mu'}{\mu} = \begin{cases} \dfrac{\mu_V}{\mu}\left(\dfrac{\alpha_V}{\alpha} - 1\right) = \lambda_0 & \text{for} \quad a < r < R \\ 0 & \text{for} \quad r < a \end{cases} \tag{21}$$

having introduced the thermal diffusivity $\alpha_V = k_V/\mu_V$.

The solution of Eq. (20) can be written as

$$\psi^i_{nm} = \sum_{n'm'}{}^{*} A^i_{nm,n'm'}\phi_{n'm'} + r^i_{nm}\phi_{nm} \tag{22}$$

where the symbol * means that $m' = m$ must be excluded from the sum.

Substituting Eq. (22) into Eq. (20) and taking the scalar product of both sides of Eq. (22) by $\phi_{n''m''}$, one obtains

$$A^i_{nm,n''m''}=\frac{c^i_{nm}q^2_{nm}(\phi_{n''m''},\lambda(r)\,\phi_{nm})}{(q^2_{nm}-q^2_{n''m''})(\phi_{n''m''},\phi_{n''m''})}=\frac{c^i_{nm}q^2_{nm}\delta_{nn''}\lambda_{mm''}}{(q^2_{nm}-q^2_{n''m''})(\phi_{n''m''},\phi_{n''m''})} \tag{23}$$

where

$$\lambda_{mm''}=\frac{l}{2}\int_a^R \lambda(r)\,J_0(v_m r)\,J_0(v_{m''}r)\,r\,dr$$

Using Eqs. (22) and (23), the perturbation field [Eq. (19)] can be rewritten as

$$\begin{aligned}(\theta')^{i+1}_i=&\sum_{nm}\sum_{n'm'}{}^{*}\frac{c^i_{nm}q^2_{nm}\delta_{nn'}\lambda_{mm'}}{(q^2_{nm}-q^2_{n'm'})(\phi_{n'm'},\phi_{n'm'})}\,\phi_{n'm'}e^{-\alpha q^2_{nm}t}\\&+\sum_{nm}r^i_{nm}\phi_{nm}e^{-\alpha q^2_{nm}t}\end{aligned} \tag{24}$$

It is now possible to obtain the coefficients r^i_{nm} by imposing the time continuity of $(\theta')^i_{i-1}$ and $(\theta')^{i+1}_i$ at $t=t_i$. Using Eq. (11) for the coefficients c^i_{nm}, one can easily find the following recurrence relation:

$$\begin{aligned}r^i_{nm}-r^{i-1}_{nm}=&-\sum_{n'm'}{}^{*}(T_i-T_{i+1})\\&\times\frac{(\phi_{n'm'},1)}{(\phi_{n'm'},\phi_{n'm'})}\,\frac{q^2_{n'm'}\delta_{nn'}\lambda_{mm'}}{(q^2_{n'm'}-q^2_{nm})(\phi_{nm},\phi_{nm})}\,e^{\alpha q^2_{nm}t_i}\end{aligned} \tag{25}$$

The coefficient r^0_{nm} is determined by imposing zero temperature at $t=0$, or $\sum_{nm}\psi^0_{nm}=0$:

$$r^0_{nm}=T_1\sum_{n'm'}{}^{*}\frac{(\phi_{n'm'},1)\,q^2_{n'm'}}{(\phi_{nm},\phi_{nm})(\phi_{n'm'},\phi_{n'm'})}\,\frac{\delta_{nn'}\lambda_{mm'}}{(q^2_{n'm'}-q^2_{nm})} \tag{26}$$

Solving the recurrence relation for r^i_{nm} and substituting the explicit expression of the coefficients c^i_{nm} in Eq. (23) for $A^i_{nm,n'm'}$ provides the following expression for the perturbative term:

$$\begin{aligned}\theta'_i=&\sum_{p=1}^{i}(T_{p-1}-T_p)\sum_{n}\sum_{n'm'}{}^{*}\frac{(\phi_{nm'},1)\,q^2_{nm'}\lambda_{mm'}}{(\phi_{nm},\phi_{nm})(\phi_{nm'},\phi_{nm'})}\,\frac{\phi_{nm}}{(q^2_{nm'}-q^2_{nm})}\\&\times\{\exp[-\alpha q^2_{nm'}\tau(i+1-p)]-\exp[-\alpha q^2_{nm}\tau(i+1-p)]\}\end{aligned} \tag{27}$$

where we have put $\theta'_{i+1}=\theta'^{i+1}_i(t_{i+1})$.

The volume change of the liquid at time t_i is

$$\Delta_i = 2\pi\beta \int_0^l dz \int_0^a [\theta_i(r, z) + \theta'_i(r, z)]\, r\, dr \tag{28}$$

where β is its thermal expansion coefficient. Using Eqs. (14) and (27) and putting $v_m R = x_m$, one finally obtains

$$\begin{aligned}\Delta_i = {} & \beta\pi a^2 l T_i + \frac{4\beta l R^2}{\pi} \sum_{p=1}^{i} (T_{p-1} - T_p) \\ & \times \sum_{nm} \frac{1}{(n+\frac{1}{2})^2}\, \sigma_m \exp\left[-\frac{\alpha\tau}{R^2}\, \kappa_{nm}(i+1-p)\right] \\ & + \frac{4\beta l R^2 \lambda_0}{\pi} \sum_{p=1}^{i} (T_{p-1} - T_p) \sum_{n} \sum_{n'm'}{}^{*} \frac{\gamma_{mm'}}{(n+\frac{1}{2})^2}\, \frac{\kappa_{nm'}}{x_{m'}^2 - x_m^2} \\ & \times \left\{\exp\left[-\frac{\alpha\tau}{R^2}\, \kappa_{nm'}(i+1-p)\right] - \exp\left[-\frac{\alpha\tau}{R^2}\, \kappa_{nm}(i+1-p)\right]\right\}\end{aligned} \tag{29}$$

where

$$\kappa_{nm} = \left(n + \frac{1}{2}\right) \pi \frac{R}{l} + x_m^2$$

$$\sigma_m = \frac{\int_0^1 y J_0(x_m y)\, dy \int_0^{a/R} y J_0(x_m y)\, dy}{\int_0^1 y J_0^2(x_m y)\, dy}$$

$$\gamma_{mm'} = \frac{\int_0^{a/R} y J_0(x_m y)\, dy \int_0^1 y J_0(x_{m'} y)\, dy}{\int_0^1 y J_0^2(x_m y)\, dy \int_0^1 y J_0^2(x_{m'} y)\, dy} \int_{a/R}^1 y J_0(x_m y)\, J_0(x_{m'} y)\, dy$$

In our experimental apparatus, the temperature T_i and the expansion of the liquid are recorded simultaneously, through the signals given by the thermocouple T_0 and by the capacitance cell, respectively. The capacitive signal is easily converted into a volume change through a simple calibration procedure in which one observes, in a preliminary experiment, the change of the electric signal ΔV corresponding to an increase in the mercury level Δd from a lower to an upper mark in the capillary, as produced by the heating of the liquid. Since the capacitance is a linear function of the mercury height in the capillary, one can determine in this way the coefficient $\varepsilon = \Delta V / \Delta d$ and hereafter deduce, for any small change of capacitance signal, δV, the corresponding volume change of the liquid, $\delta\Omega$, through the relation

$$\delta\Omega = \frac{S}{\varepsilon}\, \delta V \tag{31}$$

where S is the area of the capillary cross section. In our apparatus, we had $\Delta d = 5$ cm and the error in the calibration coefficient ε was of the order 0.5%.

After the calibration experiment, when the system has again reached thermal equilibrium, one can proceed to the measurement of the liquid thermal diffusivity.

In Fig. 2 we show the temperature and the capacitance signal corresponding to the heating experiment on a sample of ethyl alcohol, performed in air at 15°C.

Determining for each time t_i, by a simple analysis of these curves, the experimental values of T_i and Δ_i, we impose a guess value of the diffusivity $\alpha = k/\mu$ and calculate through Eq. (42) the square sum

$$\delta = \sum_{i=1}^{N} (\Delta^i_{\text{exp}} - \Delta^i_{\text{th}})^2 \tag{32}$$

where N is the number of intervals of width τ into which the total time interval has been subdivided, while Δ^i_{exp} and Δ^i_{th} refer to the experimental and theoretical values of the volume change, respectively, at time t_i.

The value of the liquid diffusivity is determined by looking for the value of α producing the minimum δ.

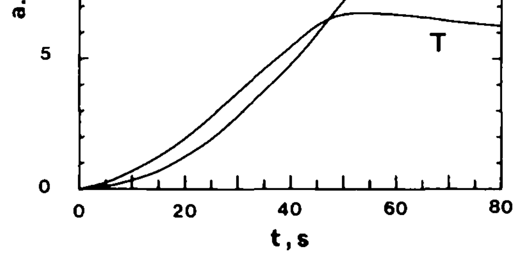

Fig. 2. V and T are the signals coming from the capacitive system and from the thermocouple T_0, respectively. Note that the units on the y axis are arbitrary. The actual temperature increase in D is 3.2°C.

3. DISCUSSION AND CONCLUSIONS

To discuss the effect of the heat exchange between the outer surface of the vessel and the environment, as described by Newton's law [Eq. (2)], we performed a computer experiment, determining for a given vessel thickness the theoretical dilation of the liquid corresponding to a given value of the diffusivity ($\alpha = 0.0010\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$) and a given Newton coefficient ($h = 10$ for solid in contact with air; see Ref. 9, p. 5). At this point we treated the theoretical dilation as an experimental function, Δ'_{exp}, to be inserted into Eq. (32), and determined the value of α producing the minimum δ under the assumption $h = 0$. The difference $\delta\alpha$ between the value of α determined in this way and the original value of α gives the error introduced by neglecting heat exchange with the environment. In Table I we give the relative change $\delta\alpha/\alpha$ corresponding to different thicknesses ($d = R - a$) of the vessel, taking $a = 0.7$ cm and $l = 4$ cm (as in our experimental setup).

We deduce from Table I that for a thickness greater than 0.2 cm, the presence of heat exchange at the lateral wall of the cell produces an error lower than 1% in the value of the thermal diffusivity and, therefore, can be neglected. This conclusion holds *a fortiori* if the cell operates in vacuum: In fact, the value used for h was pessimistically high, as referring to Pyrex glass in contact with air: The heat exchange obviously can be reduced by putting the vessel in a vacuum chamber.

Another source of uncertainty coming from the cell wall is related to the dilation of the cell itself, which introduces an error in the measurement of the volume change of the liquid. This problem can be avoided if the cell wall is made of fused silica or low-expansion glass ceramic (Zerodur). In our case, the cell was obtained from a Pyrex tube: Since the volume expansion coefficients of Pyrex and of the liquid (ethyl alcohol in our case) are 0.93×10^{-5} and 1.01×10^{-3}, respectively [11], we expect a correction of the order of 1% to be added to Eq. (29) for the volume change of the liquid. Since the correction is small, it can be evaluated by assuming the

Table I. Values of $\delta\alpha/\alpha$ Obtained in the Computer Experiment Described in the Text

d (cm)	$\delta\alpha/\alpha$ (%)
0.05	2.0
0.10	1.5
0.20	1.0
0.30	0.5

temperature field in the Pyrex wall depending only on z and t and solving the diffusion equation as in Ref. 6. The correction resulting in this way turns out to be less than 1.5%.

To analyze the curves in Fig. 2 we used the values $\mu_V/\mu = 1.02$ and $\alpha_V = 6.23 \times 10^{-3}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$ deduced from the interpolation at 15°C of the specific heat data [10] and density data of ethyl alcohol [11] and from data on Pyrex glass as given by the Shott Company (Shott Pyrex glass, $k = 1.16 \times 10^{-3}\ \mathrm{J} \cdot \mathrm{cm}^{-1} \cdot \mathrm{s}^{-1} \cdot {}^\circ\mathrm{C}^{-1}$, $c = 0.84\ \mathrm{J} \cdot \mathrm{g}^{-1} \cdot {}^\circ\mathrm{C}^{-1}$, $\rho = 2.23\ \mathrm{g} \cdot \mathrm{cm}^{-3}$). The value of the diffusivity of ethanol resulting from the minimization of Eq. (32) (including the correction due to the thermal expansion of the cell) was $1.13 \times 10^{-3}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, in agreement with the value of 1.05×10^{-3} coming from thermal conductivity measurements [11].

Since we imposed the condition given by Eq. (3) on account of the fact that during the time of measurement ΔT no appreciable heat arrives at the base of the cell (Invar support), we expect the final value of α to be independent of l, provided that this length is higher than a critical length l_c, roughly representing the space covered by the heat front during ΔT. As the time required to go from $z = 0$ to $z = l$ is approximately $l^2/\pi^2\alpha$ [12], we have $l_c \cong \pi \sqrt{\alpha\, \Delta T}$. For $\Delta T = 80$ s, l_c turns out to be of the order of 1 cm, so that the use of our cell with $l = 4$ cm is widely justified. We repeated the minimization procedure for $l = 5$ cm and $l = 6$ cm and did not find significant differences in the final values of α. A further point to be considered is the possible source of error coming from the calibration of the capacitive system.

To evaluate this error we proceed in analogy with the discussion of the heat losses from the lateral surface of the vessel. In other words, we first assume α, h, d, and a, calculate the theoretical dilation of the liquid as a function of time, and alter each value of this function by a factor 1.005, corresponding to a supposed change of 0.5% in the calibration parameter ε. Treating the resulting values as experimental dilations (Δ^i_{exp}), we determine the liquid diffusivity through the usual minimization of δ. In this way we see that the new value of α differs from the original one by about 0.7%. From the above discussion we deduce that our dilatometric technique allows, in principle, measurements of the thermal diffusivity of liquids with an accuracy better than 1%.

At this point, however, it is necessary to discuss the corresponding accuracy required for the parameters μ, μ_V, and α. We repeated the analysis of the curves in Fig. 2, first giving a change of 10% in the ratio μ_V/μ (that is, putting $\mu_V/\mu = 1.122$), and found through the minimization procedure $\alpha = 1.12\ 10^{-3}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$. In the second step, we changed the value of α_V by 10% and again found $\alpha = 1.12\ 10^{-3}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$. Thus an uncertainty as high as 10% in our knowledge of μ_V/μ and α_V is still consistent with the accuracy claimed for α. This feature is a consequence of the fact that μ_V/μ and α_V enter only the perturbative term of the solution (θ'), which is small with respect to the unperturbed term θ.

A final comment concerns the presence of convective currents inside the cell. As said previously, we resorted to an experimental arrangement in which the thermal gradient and the gravitational field are set in opposite directions. Such a device has been used to reduce convective currents in classical experiments concerning the measurement of thermal conductivity in fluids (flat plate method; see Ref. 13). Even if a full elimination of such currents is probably not obtained, we have arguments to assess that their effect is small. In fact, for a given data record pertaining to a total measurement time of 80 s, we applied our analysis to a shorter time interval $(0, t_i)$ extracted from the same record ($t_i = 40$ s) and deduced the corresponding value of the thermal diffusivity. The deviation of this value from the result referring to the total range is contained within 5%. The essential point is, however, that if the analysis is applied to another data record of 80 s pertaining to an independent measurement, the deviation, though still contained within 5%, is not systematically found to be of the same sign as in the previous measurements: Actually, the deviations corresponding to several records referring to the same time extension and the same temperature are found to be randomly scattered with positive or negative sign. Now convective currents arising as a consequence of the applied gradient should progressively increase with time during the experiment, and consequently their effect on the apparent value of α corresponding to the total time interval should always be of the same sign with respect to the value corresponding to shorter time intervals. The absence of such a result in our measurements shows that the effect of the above currents is certainly small with respect to the intrinsic source of uncertainty in our measurements, which is essentially attributed to the instability connected with an imperfect thermostatation of the cell. This uncertainty masked the relevant accuracy predicted for the method and was estimated by comparing the values of the diffusivity deduced from all the records mentioned previously and referring to the same temperature conditions and the same time extension of the measurements (80 s): The resulting diffusivities were scattered with a spread of ±3% around the mean value as obtained from the analysis of 10 independent experiments (including calibration procedures) performed on the same sample. The above value is therefore assumed as an indication of the present accuracy of the method: The fact that, for each record, the discrepancy between the value of α corresponding to 40 and to 80 s was found to be somewhat higher (±5%) reflects the uncertainty connected with insufficient information on the thermal behavior of the sample in the case of the data referring to the shorter time interval. Our efforts are now concentrated on imposing the thermostatation of the cell so as to eliminate an error which is not pertinent to the method and reduces its nominal accuracy.

NOMENCLATURE

k	Thermal conductivity
c	Specific heat
ρ	Density
μ	$c\rho$ = specific heat × density
h	Newton coefficient
α	Thermal diffusivity
T, θ	Temperature
ΔV	Electric signal
ε	Calibration coefficient
$\Delta\Omega, \Delta_{\mathrm{exp}}, \Delta_{\mathrm{th}}$	Volume change of the liquid

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