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Outlines of an Optical Method of Measuring Thermal Conductivities of Fluids

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The relative lack of data on the thermal conductivity of liquids may be ascribed to a certain inconvenience of the methods of measurement in this field. An optical hot wire arrangement is shown to be expedient to an extent, which would hardly have been anticipated. It is necessary to know the change of refractive index with temperature. Many methods, not discussed in this paper, present themselves for this determination.

The analogy between the transport of heat and of matter by diffusion is not limited to the fundamental laws, but also exists in the possibilities of measuring by optical methods. This was very early realized in connection with interference and schlieren observations. Whereas in the field of diffusion and sedimentation [1], electrophoresis [2], and thermodiffusion [3] the practical importance of the optical principles in modern experimental technique is settled, the same cannot, as far as known, be said of thermal conductivity. There is a pronounced need for developments in this latter field, and optical procedures should be investigated besides the electric, thermometric, and calorimetric methods in vogue. The electric arrangement referred to, is especially the "hot wire resistance thermometer" method of Eucken and Englert and of Pfriem [4], which has been the object of a complementary, very careful study in this Institute [5-7]. This is, in part, identical with the Piranie pressure gauge, which is used also for thermal conductivity measurements (von Ubisch[8]). Through all these works, a considerable experience has been won regarding *the state of a liquid or a gas around a vertical hot wire*, characterized by a telescopic symmetry of the convections within certain limits of experimental conditions. In the ideal case, the thermal and optical properties in the horisontal direction around the wire are unaffected by these convections. We will be solely concerned with this "convection free" situation. An elaborate study, among other things of the necessary length of the wire and the permissible output of heat from the wire as a function of viscosity and thermal dilatation, is still lacking.

The curvature of light which propagates in a horisontal plane and passes the region of heat flow around the wire will be the optical basis for the measurement. The phenomenon will be seen from the standpoint of geometrical optics. A refinement according to wave optics can be performed along well known principles. As shown below, the theory and the measurements give a surprisingly simple result. One distinct angle of deflection is observed on each side of the wire. In order to resolve this simple phenomenon in its finer details, if requisite, a wave optical theory will be required; the technically important case of *a hot wall in air* was investigated by optical interferometry well 25 years ago [9,10].

As far as a constant deviation is concerned, there is no need for using methods like the scale or the schlieren arrangements. These methods have been criticized by Gosting; scale method [11], schlieren method [12]. In the *former* case, the criticism is based upon a creditable but incomplete theoretical attempt by Adler and Blanchard, which evidently cannot rival in conclusive evidence with the severe experimental test [13], compare Ref. [14]. (A somewhat modified experimental procedure has been proposed for greater convenience [15].) In the *latter* case, the criticism is limited to the region of maximum deviation of light, in which nobody uses the schlieren method for to some extent exact purposes, owing to the lack of definition of the image which is immediately evident to the experimenter. Hence, the self-warning property [13] is a common characteristic of these methods.

THE THERMAL CONDITIONS

A very thin metal wire is extended in an electrically isolating stationary fluid of thermal conductivity λ and diffusivity $a = \lambda/c\varrho$ (c specific heat at constant pressure, ϱ density). The wire is electrically heated, and represents a linear heat source Q_0 per unit of length and of time (t). Counted from a zero time $t = 0$ ($t < 0$, $Q_0 = 0$), the time derivative of temperature (T) at a radial distance r from the source is [4]

$$\frac{\partial T}{\partial t} = \frac{Q_0}{4\pi\ \lambda t} \exp(-r^2/4at) \tag{1}$$

The heat passing one cm^2 of a coaxial cylindrical surface element at a distance r is, in time dt

$$\mathrm{d}Q = \frac{Q_0}{2\pi r} [\exp(-r^2/4at)]\mathrm{d}t \tag{2}$$

The thermal conductivity is defined according to

$$\mathrm{d}Q = -\lambda \frac{\partial T}{\partial r} \mathrm{d}t \tag{3}$$

(2) and (3) yield

$$\frac{\partial T}{\partial r} = -\frac{Q_0}{2\pi\ \lambda r} \exp(-r^2/4at) \tag{4}$$

This gradient corresponds to a refractive index gradient of

$$\frac{\partial n}{\partial r} = -\left(\frac{\partial n}{\partial T}\right)_p \frac{Q_0}{2\pi\ \lambda r} \exp(-\ r^2/4at) \tag{5}$$

In a practical measuring device, the temperature gradient should be as low as possible, and $(\partial n/\partial T)_p$ may be regarded as constant (or nearly constant) and approximated to the value at the temperature of the medium in bulk at the beginning of an experiment (or at the average temperature within the gradient, if needed). This derivative has to be determined in a separate experiment. — For less accurate purposes, it is noted that the equation of Dale and Gladstone, $(n-1)/\varrho$ = const., gives

$$\frac{\mathrm{d}n}{\mathrm{d}T} = -\ (n-1)\gamma \tag{6}$$

and that of Lorenz and Lorentz $(n^2-1)/\varrho\ (n^2+2)$ = const.

$$\frac{\mathrm{d}n}{\mathrm{d}T} = -\frac{(n^2-1)(n^2+2)}{6n}\ \gamma \tag{7}$$

γ being the coefficient of cubic expansion.

A direct determination of $\partial n/\partial r$, eqn (5), it not easy; it would be measured by the light curvature of rays of incidence *parallel* to the wire. Terminal anomalies make such a procedure seem less advantageous than an incidence transversal to the thread.

THE OPTICAL CONDITIONS

The curvature of light [16] is, according to Snellius' law, always towards regions of higher refractive index. Fig. 1 shows a horizontal section with two cylindrical surfaces S_1 and S_2 of radius $r_1 = r + \mathrm{d}r$ and $r_2 = r$. An incident light ray from the left is deviated at these surfaces in the direction which removes it from the vertical wire at O *. A parallel beam is thus split up in two parts deviated each to its side of the wire. — A ray passing near O is strongly bent in this region; a ray passing at a longer distance from O has a more moderate curvature, but along a greater section of its path. It will appear that this tends to make the resulting deviation independent of the condition of incidence (y_0).

The indices of refraction are, on the two sides of S_1, n and $n' = n + \mathrm{d}n$. By the construction (Fig. 1) is seen that OA $= r_1 \sin b_1 = r_2 \sin i_2$. Further, by Snellius' law we obtain $n \sin i_1 = n' \sin b_1$. These two relations yield $nr_1 \sin i_1 = n'r_2 \sin i_2$; more generally, C being a constant along the ray,

$$nr \sin i = C \tag{8}$$

We are interested in the differential deviation $\delta = b_1 - i_1$ at the surface S_1. Writing Snellius' law $n \sin i_1 = (n + \mathrm{d}n) \sin (i_1 + \delta)$ and omitting vanishing

* The only ray which would be undeviated is one originally directed towards O. — In practice, the interference phenomenon caused by the wire is considered to be of vanishing intensity.

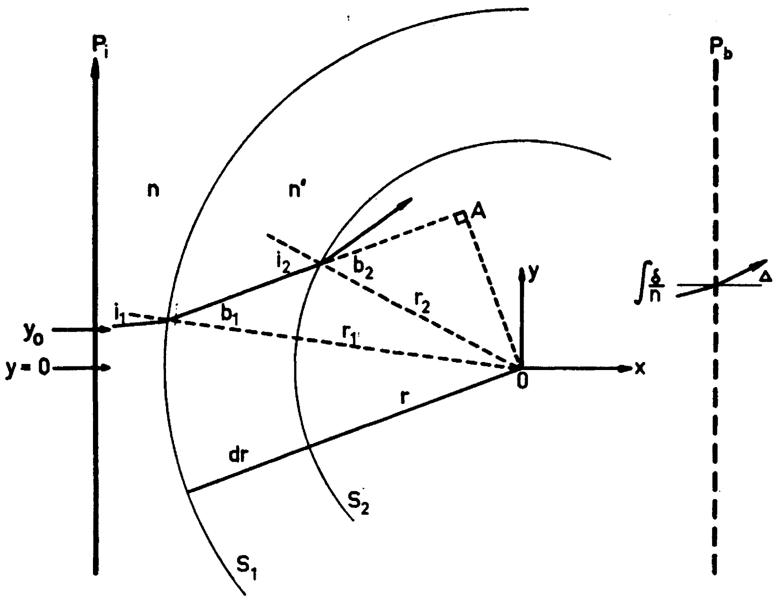

Fig. 1. Horizontal section of the cell, showing the liquid enclosed between P_i and P_b, with the linear source at O, and the direction of light from left to right.

terms, $\sin \delta = -(\mathrm{d}n/n) \operatorname{tg} i_1$. Approximating $\sin \delta$ by δ, and omitting index 1, yields

$$\delta = -\frac{1}{n}\frac{\partial n}{\partial r} \operatorname{tg} i \, \mathrm{d}r \tag{9}$$

We introduce i from eqn (8):

$$\delta = -\frac{1}{n}\frac{\partial n}{\partial r} \frac{C \, \mathrm{d}r}{\sqrt{n^2r^2 - C^2}} \tag{10}$$

$\partial n/\partial r$ is given by eqn (5), so we have obtained $\delta = f(r)\mathrm{d}r$ which shall be integrated for different ordinates of incidence y_0 of the cartesian system (x, y of Fig. 1). We will assume

1) a parallel beam of light with an incidence at right angles to the plane P_i and issuing at the plane P_b

2) a temperature gradient which does not reach the planes P_i and P_b, ensuring an integration from $x = -\infty$ to $x = +\infty$

3) refractive indices outside the region between P_i and P_b to be unity

4) that in eqn (8), r and i change significantly along the path of a light ray but neither n nor y. (Owing to $r^2 = x^2 + y^2$, y is of interest in this connection.)

From the approximations 1) and 4) is seen that, along the ray, $y = y_0 = r \sin i$. With this approximation eqn (8) gives $C = ny_0$. Hence, eqn (10) becomes

$$\delta = -\frac{1}{n}\frac{\partial n}{\partial r}\frac{y_0\,\mathrm{d}r}{\sqrt{r^2-y_0^2}} \tag{11}$$

The approximations made, all imply that the total angle of deviation between P_i and P_b, Δ, is supposed to be very small, that is the refractive index gradient is feeble. We will eventually have to demand this from other reasons too, in order to avoid disturbing convections. — It is seen that the argument of eqn (11) becomes infinite at $r = y_0$. This is the point at which the ray passes as near the wire as possible, that is where r is a minimum and $\mathrm{d}r = 0$.

Introducing $\partial n/\partial r$ by eqn (5), and x as independent variable by $r^2 = x^2 + y_0^2$

$$\delta = \frac{1}{n}\left(\frac{\partial n}{\partial T}\right)_p \frac{y_0 Q_0}{2\pi\lambda}\frac{\mathrm{d}x}{x^2 + y_0^2}\exp[-(x^2 + y_0^2)/4at] \tag{12}$$

We will integrate this expression in order to obtain the total angle of deviation Δ. The angle in question shall represent the total deviation of the ray, counted from before entering the cell at P_i and after leaving it at P_b, that is in air of refractive index approximately equal to unity. Strictly speaking, all the small angles of Fig. 1 would have to be divided by n (as indicated at the plane P_b), in order to be referred to a specified angle of incidence *in air*. Hence, we obtain Δ directly from eqn (12), as if there were no refraction at P_b

$$\delta = \frac{1}{n}\left(\frac{\partial n}{\partial T}\right)_p \frac{y_0 Q_0}{2\,\pi\lambda}\int_{-\infty}^{+\infty}\frac{\mathrm{d}x}{x^2 + y_0^2}\exp\,[-(x^2 + y_0^2)/4at] \tag{13}$$

The integral reduces to a simple from by assuming $x^2 + y_0^2 = r^2 \ll 4\,at$, an assumption which is strongly supported by the experimental results *. Hence

$$\Delta = \frac{1}{n}\left(\frac{\partial n}{\partial T}\right)_p \frac{y_0 Q_0}{2\pi\lambda}\left|\frac{1}{y_0}\sin^{-1}\frac{x}{\sqrt{x^2 + y_0^2}}\right|_{-\infty}^{+\infty}$$

from which

$$2\Delta = -\frac{Q_0}{\lambda n}\left(\frac{\partial n}{\partial T}\right)_p \tag{14}$$

EXPERIMENTAL CONDITIONS

The total angle of deflection, 2Δ may be measured either by photography, see Fig. 5, or with a screw micrometer eyepiece as used in our observations,

* In eqn (5), this approximation leads to a logarithmic decrease of temperature within the region nearest to the wire.

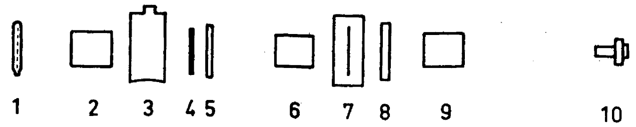

Fig. 2. 1. straight wire lamp, 2. condenser lens, 3. water cell, 4. light filter, 5. fine vertical slit, 6. lens with focal plane at 5, 7. trough with the vertical wire suspended in the liquid to be measured, 8. broad vertical diaphgram, 9. lens, 10. micrometer screw eyepiece adjusted to the slit 5.

see Fig. 2. The arrangement is an Abbe schlieren or Gouy interference device with parallel light passing the cell 7. The eyepiece 10 is adjusted to the focal plane of the lens 9 *.

The diaphragm 8 was 3—4 mm broad. The slit 5 is seen as a central line at the beginning of the experiment, which disappears altogether after in induction time of less than 10 seconds. Instead of this, two distinct lines appear (Fig. 5), the distance of which was read off by the eyepiece micrometer 10 $\times$. It corresponds to 2 Δ of eqn (14). The real angle was obtained by comparison with the deviation caused by a glass prism with a *double* deviation angle of 0.01208 radians (red light).

The readings were independent of a diminished breadth of the diaphragm 8. Of course, the lines are finally getting unsharp.

The electric circuit and measurement was the simplest possible, see Fig. 3.

The proportionality of 2 Δ to Q_0 (eqn 14) has been tested, see Fig. 4. The good linearity observed, and the excellent stability of the eyepiece readings with time is very advantageous for the purpose of determining the coefficient of heat conduction. — An estimation of the systematic error is not possible for the present.

In our experiments, the angle of deviation 2 Δ varied from 2′ to 10′. — It is interesting to compare 2 Δ/Q_0 of eqn (14) for some substances at 20°C, see Table 1. For the measurement, a high value of 2 Δ/Q_0 is desirable. The step from glycerine to water is, in this respect, greater than that from water to a gas like air. The method might eventually be extended to gases of ordinary or elevated pressures, although the optically useful region around the wire is very narrow in such a case. Hence, the optical requirements become very special, and no test has been made.

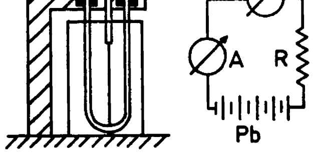

Fig. 3. The vertical wire (0.1 mm Pt) is shown at the left, immersed in the liquid container, a plane parallel glass cuve. The electrical circuit is the simplest possible, by application of a big battery (Pb) of variable voltage, and a high resistance mVVmeter.

* With this adjustment, a screening diaphragm 8 is needed in order to get a clear double line in the eyepiece. However, a re-focusing according to the actual value of Q_0 shows that a double line can be obtained *in absence of the screen.* This gives an insight into the optical properties of the wire surroundings which is not covered by the simple treatment given in this article.

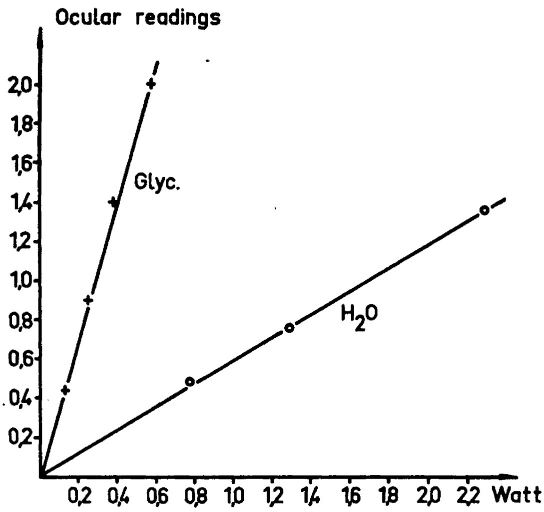

Fig. 4. The proportionality between the ocular readings (line distance in the ocular) and the total energy output from the wire is shown for water and glycerine.

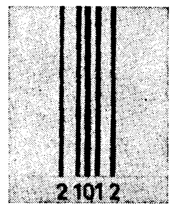

Fig. 5. From photographic exposures of the central line (0) and two double lines (1,1 and 2,2) on an Ilford H.P.S. Plate. Line O: exposure time 7.5 sec., $Q_0 = 0$. Lines 1,1: 15 sec., $Q_0 = 0.00657$ watt/cm. Lines 2,2: 15 sec., $Q_0 = 0.0183$ watt/cm. Voltage of accumulator: 0, 6 and 10, respectively. Substance: colourless liquid paraffin. Light source: straight wire lamp without filter.

A higher energy output Q_0 in the case of water was necessary in order to ensure a sufficient resolving power for this substance, with its exceptionally small $\partial n/\partial T$ and great λ. A refinement of the method of observation is, of course, possible; this would be necessary for an application to water around 4°C (where the risk for convection is specially small), owing to the small value of $\partial n/\partial T$. — The stability in the case of water at 20°C was much better than expected; convections have been observed only when the wire was quite evidently non vertical.

Available experimental data for the calculation of $(\mathrm{d}n/\mathrm{d}T)_p$ are, even for water, not quite satisfactory. The uncertainty is at least $\pm$ 2 % if estimated without a critical examination of the values of different authors.

Table 2 illuminates further our conditions and presents result on λ as compared with the exact data obtained by Gillam [6].

Additionally, the following data are of interest:

1) The liquid column had the dimensions 4 × 4 × 14 cm, the exact length of the wire was 12.70 cm. The highest effect used for water, 2.28 watt on the whole wire, corresponds to a temperature rise of 10°C/h if no loss of heat occurred to the surroundings.

2) The final reading is normally obtained in 20—30 sec. A high Q_0 and a low λ may increase the induction period considerably. A test of the stability

Table 1.

	$10\lambda^3$ cal/cgs	n	-10^4 $(dn/dT)_p$ ~D-line		$(-1/\lambda n)$ $(dn/dT)_p$ = $= 2\Delta/Q_0$
n-Octanol	0.40	1.429	4.0	(average 18−80°C)	0.70
Glycerine	0.675	1.473	2.79?	(from eqn 7)	0.28
Water	1.44	1.333	0.92	(average from lit.)	0.048
Air (1 at)	0.057	1.00027	0.0100		0.017

Table 2.

21°C	Q_0 watt/cm	$2\Delta/Q_0$ (exp.) cgs/cal	-10^4 $(1/n)$ $(dn/dT)_p$	10^3 λ(opt.) cal/cm sec degree	10^3 λ(Gillam [6])
Glycerine	0−0.045	0.269	(1.89)	(0.70)	0.675
Water	0−0.180	0.0460	0.69 ± 2 %	(1.50)	1.44

of the ocular reading over a long period of time was made with glycerine. 0.56 watt was used over the wire, corresponding to the upper limit of Q_0 in Table 2. The line distance was constant over the measured period of 1 ½ h. The lowest value of 5.02 was obtained after 3 and 90 min; the highest value measured was 5.05. The difference is within the accidental errors of the readings. — In the case of mixtures, effects of thermodiffusion may be obtained, and the readings should be made as early as possible.

3) When the current is switched off, the double line disappears and the central line is restored in a time of the order of 5 seconds to several minutes. A new measurement may be started immediately, without stirring of the liquid.

4) With a suitable form of the terminal connections of the wire, a correction for a *low* electrical conductivity of the liquid should be easy to perform.

5) A cylindrical lens may be used in order to decrease the magnification in the direction of the wire, so that an average deviation may be observed in the ocular. However, it is advantageous to use only a narrow middle section of the wire region, where the terminal anomalies are as small as possible.

ELECTROLYTES

Although no experiments on conducting solutions have hitherto been made, there is no doubt as to the possibility of covering the field of most ordinary electrolytes by the use of an electrically isolated wire.

Another possibility is interesting: to use the wire as an electrode and a cylindrical second electrode at a distance around it, and to feed the system with alternating current. It is easily seen that the joule heat evolved per unit of volume of the liquid is inversely proportional to the square of the distance from the wire. This should be compared to the much slower, logarithmic decrease of temperature in the neighbourhood of the heated wire according to our equations. Hence, by electrolytic heating, only the nearest surrounding of the wire will become appreciably heated directly by the current. — The detailed optical properties of this system, with thermal conduction, has not yet been calculated. However, a simple consideration convinces of that the conductivity even of a thin wire (preferably made of silver) is so much greater than the conductivity of the solution, that hardly any difficulties can arise in obtaining an *even distribution* of the heat effect along the wire. The procedure might be of special interest in cases of very corrosive liquids, molten salts *etc.*, for which an isolating coating of the wire would be difficult to procure. — The optical observations must be made through apertures in the outer electrode.

The arrangement outlined would eventually be another technique for a variety of experiments on the transports of ions and heat.

CONCLUSIONS

In connection with the hot wire arrangement (Schleiermacher and others) an *optical* method has been examined which enables a simple and rapid measuring of coefficients of heat conduction of transparent liquids with considerable exactitude. The experimental test and fundamental theory given, do not allow a final judgement of the attainable accuracy. A separate determination of the change of refractive index with temperature is needed.

The hot wire *resistance thermometer* method, used previously for precision determinations, utilizes the resistance change during the first 20—60 seconds after switching on the current. This valuable method is a typically non stationary procedure. It has many advantages, *e.g.* that of being sufficiently independent of a temperature jump at the wire surface (Eucken). A condition for this seems to be that such a jump does not appreciably depend upon temperature. The optical method described is thermally (quasi-) stationary and *optically stationary*. This greatly simplifies the measuring device. The temperature jump is eliminated, as the method is based on a constant heat source, and not upon the heat flow between surfaces of fixed temperatures. This is especially pronounced in our case, owing to the stationarity mentioned.

The magnitude of the necessary joule heat supply (given the optical arrangement), increases with increasing thermal conductivity and decreasing thermal expansion of the liquid. This did not prevent measurements to be performed with water, using an output of 0.18 watt/cm without disturbances detectable by the method itself. Nevertheless, the procedure may be refined in different directions. Electrolytes can be included.

The method is unsuitable for solids in general. Already the frequent lack of transparency is preventive. By the great simplicity of the method, it may be valuable in improving the evident lack of data in the field of liquids and molten salts, in which essential informations are to be expected.*

* *Note added in proof:* Extended experimental work, and theoretical considerations by O. Bryngdahl, have disclosed fallacies in this work which will become corrected in further publications. Essential for the method is that the stability of the liquid has been established, the disturbances being slower than the restoring by thermal conduction.

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