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REFERENCE STATE IN TRANSIENT THERMAL CONDUCTIVITY MEASUREMENTS

A new, unambiguous way of defining the reference temperature, T_r, for the thermal conductivity of fluids measured with the transient hot wire technique is presented. The analysis shows that a previous evaluation of the reference temperature is only exact for a particular set of circumstances which are seldom realized in practice. In extreme cases the two evaluations of the reference temperature can lead to differences of as much as 1 K, causing an uncertainty of about ± 0.3 % in the absolute values of the thermal conductivity of liquids.

INTRODUCTION

In recent years the transient hot-wire method has emerged as the most accurate technique for the measurement of the thermal conductivity of liquids [1, 2]. However, there remain a small number of minor aspects of the technique which must be considered in order to achieve the highest accuracy under all conditions. Among these is the evaluation of the so called "reference temperature". This is a correction that arises from the variation of the fluid properties with temperature during the measurement. According to this correction the thermal conductivity measured in an experiment is assigned to a reference temperature, T_r, which is different from the equilibrium, initial temperature of the fluid, T_0. The paper presents a new analysis of this problem leading to an unambiguous way of determining the reference temperature for a certain set of experimental data.

THE REFERENCE TEMPERATURE PROBLEM

The transient hot-wire technique for the measurement of the thermal conductivity of fluids is based on the solution of the Fourier equation

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T \qquad (1)$$

subjected to the boundary conditions [3]

$$T(r,t) = T_0 \quad \text{for } t < 0 \qquad (2)$$

$$-\frac{q}{4\pi\lambda} = \lim_{r \to 0} \left(r \frac{\partial T}{\partial t}\right) \text{ for } t > 0 \text{ and } r = 0 \qquad (3)$$

$$T(r,t) = T_0 \quad \text{for } t > 0 \text{ and } r = \infty \qquad (4)$$

In equations (1) to (4), T_0 is the equilibrium temperature of the fluid prior to a measurement, q is the heat dissipation per unit lenght of the wire and ρ, C_p and λ are, the density, heat capacity and thermal conductivity of the fluid respectively. The solution of this equation yields, for the temperature rise of the fluid at a radial position r_1,

$$\Delta T^{id}(r_1, t) = T(r_1, t) - T_0 = \frac{q}{4\pi\lambda} \ln \frac{4kt}{r_1^2 C} \quad (5)$$

where k is the thermal diffusivity of the fluid. To account for unavoidable departures between the ideal model and any real instrument several minor corrections, δT_i, must be added to the measured temperature rise, ΔT_w, of the thin metallic wire (the practical heat source), in order to recover ΔT^{id} so that [3-8]

$$\Delta T^{id} = \Delta T_w + \sum_i \delta T_i \quad (6)$$

However, one of the departures of the real instrument from the ideal model cannot be dealt with in this way. It is an assumption of the ideal model that the physical properties of the fluid are independent of temperature and for real fluids this is not valid. Nevertheless, because of the relatively mild dependence of the properties on temperature, it is possible to represent the properties by linear functions of temperature within the range ΔT. Thus we write

$$\lambda(T, \rho) = \lambda(T_0, \rho_0)(1 + \chi\Delta T) = \lambda_0(1 + \chi\Delta T) \quad (7)$$

and

$$\rho C_p(T, \rho) = \rho C_p(T_0, \rho_0)(1 + \phi\Delta T) = \rho_0 C_{p_0}(1 + \phi\Delta T) \quad (8)$$

The Fourier equation may then be solved again including the linear dependences subject to the modified boundary conditions

$$\lim_{r \to 0} \left(r \frac{\partial T}{\partial r}\right) = -\frac{q}{2\pi\lambda_0(1 + \chi\Delta T)} \quad (9)$$

The solution is

$$\ln\left[\frac{4k_0 t}{r_1^2 C}\right] = -\frac{q}{4\pi\lambda_0}(\chi - \phi)\ln 4 + \frac{4\pi\lambda_0}{q}\Delta T + \frac{2\pi\lambda_0}{q}\chi(\Delta T)^2 \quad (10)$$

Thus, owing to the temperature dependence of the fluid physical properties, a small curvature occurs in a plot of lnt against ΔT. In practice this curvature is so small that it lies within the precision of individual measurements of ΔT and lnt. Furthermore, if the average gradient of the curve, b, between two times t_1 and t_2 is evaluated, it is readily shown from Eq (10) that

$$b = \frac{4\pi\lambda(T_r, \rho_r)}{q} \quad (11)$$

where

$$T_r = T_0 + \frac{1}{2}\{\Delta T(t_1) + \Delta T(t_2)\} \quad (12)$$

and

$$\rho_r = \rho(T_r, P_0) \quad (13)$$

If it were practicable to determine the mean slope experimentally Eq. (12) would always be exact within the linear approximations (6) and (7). However, in practice the experimental data points $(\Delta T_i, \ln t_i)$ are subjected to a linear regression in order to provide a least squares estimate of the slope. In general, this slope must differ from the true mean slope and in such circumstances Eqs (11) and (12) are not exact.

IMPROVED ANALYSIS

In order to provide an improved analysis of the problem of the reference temperature it is necessary to relate the least squares estimate of the slope, obtained by linear regression of a set of N experimental data points, to the thermal conductivity at a specific temperature. In other words, we seek the two points of eq. (10) between which its average gradient is equal to the slope of the experimental linear regression. In order to carry this through we first write the solution (10) in the form

$$\ln t = A + B(\Delta T) + C(\Delta T)^2 \quad (14)$$

If data $(\Delta T_i, \ln t_i)$ which conform to this equation are represented by the linear relationship

$$\ln t = A' + B'\Delta T \quad (15)$$

by means of a linear regression, then it is easily shown that the slope B′ is equal to the average slope of curve (14) between the points $\Delta T_m(t_m)$ and $\Delta T_n(t_n)$, i. e.

$$B' = \frac{\ln(t_m/t_n)}{\Delta T_m - \Delta T_n} \tag{16}$$

with

$$\Delta T_m = \frac{1}{2}\{[Y^2 - 4X]^{1/2} - Y\} \tag{17}$$

$$\Delta T_n = -\frac{1}{2}\{[Y^2 - 4X]^{1/2} + Y\} \tag{18}$$

where

$$X = \frac{(\Sigma\Delta T_i^2)^2 - \Sigma\Delta T_i^3\Sigma\Delta T_i}{N\Sigma\Delta T_i^2 - (\Sigma\Delta T_i)^2} \tag{19}$$

$$Y = \frac{N\Sigma\Delta T_i^3 - \Sigma\Delta T_i^2\Sigma\Delta T_i}{N\Sigma\Delta T_i^2 - (\Sigma\Delta T_i)^2} \tag{20}$$

This average slope then defines a thermal conductivity at a temperature T_r through the equation

$$\frac{\ln(t_m/t_n)}{\Delta T_m - \Delta T_n} = \frac{4\pi\lambda_0}{q}\{1 + \frac{1}{2}\chi(\Delta T_m + \Delta T_n)\}\frac{4\pi\lambda(T_r, \rho_r)}{q} \tag{21}$$

where

$$T_r = T_0 + \delta T_1{}^* = T_0 + \frac{1}{2}[\Delta T_m(t_m) + \Delta T_n(t_n)] \tag{22}$$

so that

$$\delta T_1{}^* = \frac{1}{2}\,\frac{N\Sigma(\Delta T_i)^3 - \Sigma(\Delta T_i)^2\Sigma\Delta T_i}{N\Sigma(\Delta T_i)^2 - (\Sigma\Delta T_i)^2} \tag{23}$$

The interpretation of this result is made simpler if it is rewritten in the form

$$\delta T_1{}^* = \frac{\sum\limits_{i=1}^{N}\sum\limits_{j\neq i}^{N}(\Delta T_i - \Delta T_j)^2\ \frac{1}{2}\ (\Delta T_i + \Delta T_j)}{\sum\limits_{i=1}^{N}\sum\limits_{j\neq i}^{N}(\Delta T_i - \Delta T_j)^2} \tag{24}$$

The correction to the equilibrium temperature therefore depends upon the distribution of the experimental points and is a weighted average of the arithmetic mean of pairs of points with a distribution function

$$\xi(\Delta T_i, \Delta T_j) = (\Delta T_i - \Delta T_j)^2 \tag{25}$$

This makes it clear that when the points are uniformly distributed in ΔT(i.e.$\Delta T_{i+1} - \Delta T_i =$ = constant) $\delta T_1{}^*$ reduces to

$$\delta T_1{}^* = \frac{1}{2}(\Delta T_1 + \Delta T_N) \tag{26}$$

involving just the first and last temperature rises observed in a run. It is this result which has been universally employed in the evaluation of the reference temperature to date, even when the distribution of points was not uniform [3].

In many measurements the differences between the reference temperature defined by Eqs. (11) and (22) are very small (~ 0.1K) [9], and are thus negligible. However, in some measurements made in our laboratory [10, 11] the distribution of points is distinctly non-uniform and a reanalysis shows that the difference between the two reference temperatures can be as large as 1 K. A difference of this magnitude contributes an error of ± 0.3 % to the reported value of the thermal conductivity. It is therefore important in such cases to employ the proper form of the reference temperature defined by Eq. (22).

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RESUMO

Apresenta-se uma nova definição de temperatura de referência nas medidas de condutibilidade térmica de fluidos pelo método do fio aquecido, a qual evita alguma ambiguidade da definição anterior.

A presente análise demonstra que a definição anterior só é exacta em certas condições particulares, raramente conseguidas na prática. Em condições extremas de trabalho as duas análises conduzem a resultados para T_r *que podem diferir de 1 K, o que introduz uma incerteza de cerca de ± 0,3 % nos valores absolutos da condutibilidade térmica de líquidos.*