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Knudsen-Effect Errors with Transient Line-Source Measurement in Fluids

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This paper decribes the Knudsen-effect errors of the transient line-source method used for accurate measurements of the thermal conductivity and thermal diffusivity of fluids. The analysis demonstrates that the instrument can be used with a good accuracy ($>0.5\%$) to lower densities than previously thought. The principal errors are illustrated by measurements on propane in the temperature range 250–300 K at densities less than 9 $kg \cdot m^{-3}$.

KEY WORDS: Knudsen effect; propane; thermal conductivity; thermal diffusivity; transient line-source method.

1. INTRODUCTION

The evolution of modern transient line-source techniques for thermal conductivity measurements can be traced from early experiments by Pittman [1], Haarman [2], and Mani [3]. Extensive evaluation of the applicable theory by Kestin and his co-workers [4–9] and succeeding investigators [10–13] has enabled these workers and others [14–27] to perform measurements on a variety of fluids. Provided that the ranges of pressure and temperature are such that the fluid density is large, highly precise measurements are possible.

Simultaneous thermal diffusivity measurements by the same technique are, in theory, also possible [25–30]. For dense fluids, however, these results have always been less than satisfactory [27–29]. Few measurements

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in dilute gases have been reported and these show short time behavior attributed to time-dependent Knudsen effects [31].

This paper reviews the Knudsen-effects errors proposed thus far and examines their validity for dilute-gas thermal conductivity and diffusivity determinations. Measurements on propane [24] are used to illustrate the discusion and demonstrate that the instrument can, in fact, be used to much lower fluid densities that previously thought for both these measurements.

2. THEORY

The operation of a transient line-source cell in a medium of constant thermal diffusivity, α, for sufficiently long times, $t \gg a^2/4\alpha$ (5–1000 ms), with small-diameter wires ($2a = 5\text{-}20\ \mu$m), can be accurately represented as

$$\Delta T(a, t) = T(a, t) - T_0 = \frac{q}{4\pi\lambda}\left[\ln\left(\frac{4\alpha t}{a^2 C}\right) + 0\right] \tag{1}$$

where, with a well-designed cell and appropriate corrections for ΔT, the terms 0 are vanishingly small.

This is a linear relationship in ΔT versus $\ln(t)$, with the thermal conductivity, λ, being obtained as

$$\lambda = \frac{q/4\pi}{d(\Delta T)/d[\ln(t)]} = \frac{q/4\pi}{A} \tag{2}$$

where A represents the slope of the ΔT versus $\ln(t)$ straight line.

$$\Delta T = A \ln(t) + B \tag{3}$$

Equations (1) and (2) may be combined to yield

$$\alpha = \frac{a^2 C}{4t} \exp\left\{\frac{d[\ln(t)]}{d(\Delta T)} \Delta T\right\} \tag{4}$$

which, with Eq. (3), results in

$$\alpha = \frac{a^2 C}{4t} \exp[\ln(t) + B/A] \tag{5}$$

Results at densities greater than about $10\ \text{kg} \cdot \text{m}^{-3}$ do, in fact, display the linear behavior described above (Fig. 1). Experiments conducted at lower densities (Fig. 2), however, display two apparently linear regions, which for the conditions shown, result in what may be described as short and long time regions, $50 < t < 265$ ms and $t > 265$ ms. It is speculated that this behavior results due to transient Knudsen or temperature-jump effects.

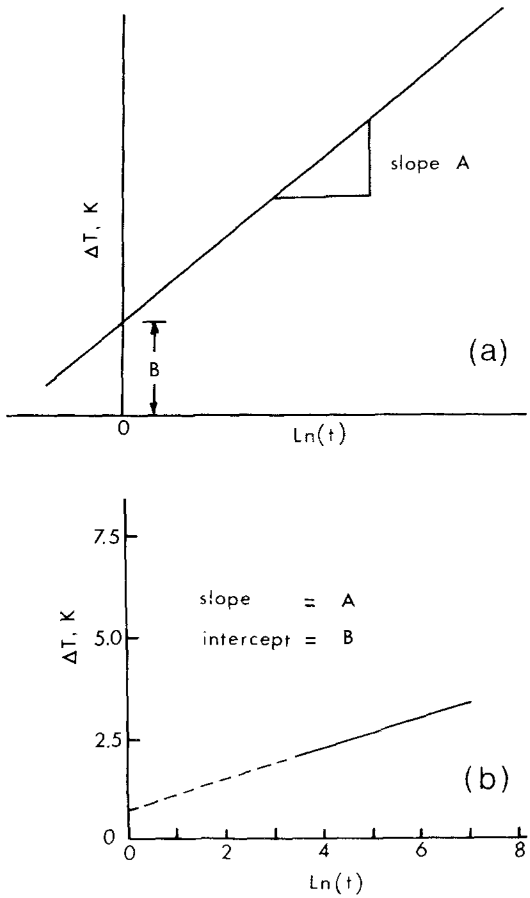

Fig. 1. Plot of ΔT versus $\ln(t)$ (t in ms) for dense fluids. (a) Schematic representation. (b) Experimental—propane at 70.5 MPa and 252.7 K.

3. KNUDSEN EFFECTS

The basic working Eq. (1) constitutes a series expansion for small values of $r^2/4\alpha t$ and supposes that the cylindrical wire of radius, a, assumes a uniform temperature which is equal to that in the conduction medium at $r = a$. Provided that departures from the basic solution (1) are small, a complete detailed solution to date has not been necessary, and indeed it would represent a formidable task since it would require a solution of the Boltzmann equation [32].

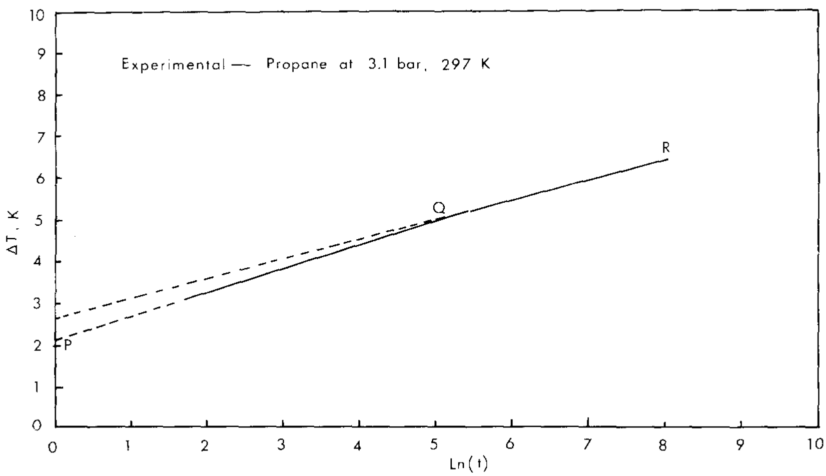

Fig. 2. Plot of ΔT versus $\ln(t)$ (t in ms) for low-density fluids. Propane at 0.31 MPa and 297 K.

The attempts made thus far [4, 5] have described the temperature jump at the wire with the Smoluchowski equation [2, 33],

$$T_w(a, t) - T(a, t) = -g \left. \frac{\partial T}{\partial r} \right|_{r=a} \tag{6}$$

where T_w is the wire temperature, T is the temperature of the adjacent gas, and g is stated to be an empiric, time-independent factor proportional to the molecular mean free path, Λ.

The Smoluchoswki equation is, however, applicable only where molecular velocities can be represented by Maxwell's velocity distribution [32]; that is, it should represent a good approximation for "long" times when thermal gradients are small. In cases where the thermal gradients are not small, that is, at "small" times, the velocity distribution function $f_1^{(0)}$, must be modified by use of the second and nonuniform approximation

$$f_1 = f_1^{(0)}[1 + \phi_1^{(1)}] \tag{7}$$

where

$$\phi_1^{(1)} = A(C_1) C_1 \,\text{Grad}[\ln(T)] \tag{8}$$

with $A(C_1)$ and C_1 obtained from the Boltzmann equation [32].

We thus have a situation such that at $t = 0$, the medium and wire are in equilibrium and the molecular velocities are uniform. The temperatures are represented, in fact scaled, with the mean free path of the cell, and not the wire. At time $t = 0^+$, the wire commences heating and there results a time-dependent accommodation as a result of the very large temperature gradient initially etablished ($dT/dr > 5000\ \mathrm{K \cdot m^{-1}}$ at 6 ms and $1400\ \mathrm{K \cdot m^{-1}}$ at 265 ms) and the accommodation is now scaled to the wire size. With time the volume of thermally disturbed fluid increases and the rate of increase in wire temperature decreases, providing conditions more appropriate to a time-independent accommodation coefficient.

Knuden or noncontinium effects are usually associated with very low pressures [31]. Their effects have been stated to be of the order of 0.3% in He at $P = 1$ bar and 300 K for a wire of $a = 2.5\ \mu$m [5], i.e., $\mathrm{Kn} = 0.003$.

Considering first the situation where the temperature jump is nearly independent of time, the solution may be rewritten with an added temperature difference, δT_k; thus [5]

$$\begin{aligned} \Delta T_w(a, t) &= \Delta T(a, t) + [T_w(a, t) - T(a, t)] \\ &= \frac{q}{4\pi\lambda}\left[\frac{2g_0}{a} + \ln\frac{4\lambda t}{a^2 C}\right] \end{aligned} \tag{9}$$

This result illustrates that the principal effect of the Knudsen temperature jump in this region is to shift all points on the ΔT versus $\ln(t)$ diagram upward by the constant amount

$$\delta T_k = \frac{q}{4\pi\lambda}\left(\frac{2g_0}{a}\right) \tag{10}$$

without changing its slope; that is the reported value of λ. The intercept B is, however, shifted resulting in an incorrect experimental value for α. Second-order corrections to λ for this time region have been obtained [5] and are not considered further here.

At time $t = 0$, the fluid is in thermal equilibrium with the wire and surroundings and there is no accommodation effects since the wire does not begin to depart from the fluid temperature until $t = 0^+$. The accommodation coefficient from $t = 0^+$ to time τ_k is time dependent, increasing in value until $g(\tau_k) = g_0$. It is in this time period, $0^+ < t < \tau_k$, that the average radial temperature gradient decreases as greater and greater volumes of fluid are thermally disturbed. Although, as stated previously, a rigorous correction theory will require the solution of the Boltzmann's equation using the second-order nonuniform velocity distribution function approximation, the experimental evidence permits an empirical, albeit, intuitive approach.

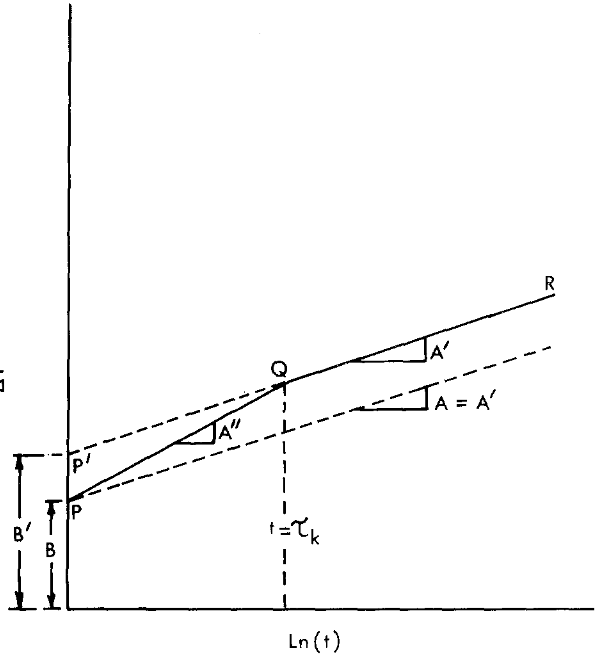

Fig. 3. Plot of ΔT versus $\ln(t)$ for low-density fluids; schematic representation.

Figure 3 illustrates the temperature-rise ΔT versus $\ln(T)$ behavior for the two types of Knudsen effects described here. The errors introduced by these effects can be corrected by fitting the data before and after τ_k so to determine τ_k, and the diffusivity α, by extrapolation. Thermal conductivity data for $t > \tau_k$ are used to determine the slope, A', and the intercept, B'. The true slope (A) and corrected intercept (B) are then obtained from

$$A = A' \tag{11a}$$

and

$$B = B' - (A'' - A')\ln(\tau_k) \tag{11b}$$

thus permitting evaluation of the correct λ and α as well as the accommodation coefficient and the time τ_k.

4. EXPERIMENT

Measurements made on propane illustrate the results obtained with a compensating transient line-source instrument reported earlier [24, 26].

Figure 1 displays dense-gas behavior with no accommodation effects apparent. In this case the resulting values of λ and α are for $T = 252.72$ K, $P = 705.35$ bar, $\rho = 0.619\ \text{g} \cdot \text{cm}^{-3}$;

$$\lambda = 159.886\ (\pm 0.032)\ \text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

$$\alpha = 1.25 \times 10^{-7}\ \text{m}^2 \cdot \text{s}^{-1}$$

where $A = 0.37027$, $B = 0.71770$, and the correlation coefficient for the straight-line fit from $t = 100$ to 850 ms is 0.999998. At lower densities (Fig. 2), at a Knudsen number of approximately 0.003, the bilinear behavior described is clearly present yielding from the above analysis;

$$P = 3.10\ \text{bar} \qquad \lambda = 19.5\ \text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

$$\rho = 5.86\ \text{kg} \cdot \text{m}^{-3} \qquad \alpha = 1.78 \times 10^{-6}\ \text{m}^2 \cdot \text{s}^{-1}$$

$$T = 296.85\ \text{K} \qquad C_p = 1738\ \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$$

$$\tau_k = 265\ \text{ms}$$

$$g_0 = 3.2 \times 10^{-5}\ \text{ms}$$

For $t < \tau_k$ the data used are from the third measurement point (58 ms, $\Delta T = 4.413$ K) to the eighth (183 ms, $\Delta T = 5.054$ K). The values of the slope and intercept obtained for this range were

$$A = 0.5562 \pm 0.0102$$

$$B = 2.164 \pm 0.048$$

For $t > \tau_k$ the data used the 47th (1158 ms, $\Delta T = 5.9623$ K) to 50th (1233 ms, $\Delta T = 5.9919$ K) points. The values of slope and intercept obtained we now

$$A = 0.4707 \pm 0.004$$

$$B = 2.642 \pm 0.030$$

5. CONCLUSION

The Knudsen-effect errors of the transient line-source technique have been reviewed and experimental evidence for a time-dependent accommodation coefficient has been introduced an explained. This work demonstrates the potential for simultaneous measurement of low-density thermal conductivity and thermal diffusivity values with the present instrument.

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