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Note

Corrections to the Smooth Hard-Sphere Theory of Thermal Conductivity for Internal Energy Transport: Application to Methane

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Thermal conductivities have been calculated for dense fluid methane from the exact smooth hard-sphere expression valid for monoatomics with core sizes derived from fitting self-diffusion and viscosity data. The results are lower than experimental values by about 16% at all densities greater than the critical density. This difference is attributed to the effect of internal energy transport on this property.

KEY WORDS: core sizes; Enskog; hard-sphere theory; methane; thermal conductivity.

1. INTRODUCTION

The exact smooth hard-sphere theory of transport properties has been shown [1] to give a very satisfactory interpretation of viscosity and thermal conductivity data for argon and viscosity and self-diffusion data for the pseudospherical molecular fluid methane at densities greater than the critical density, with a property-independent set of temperature-dependent core sizes for each molecule. Corrections to the approximate Enskog theory [2] given by Easteal et al. [3] were used for diffusion and corrections for viscosity were derived from fitting methane and argon results and for thermal conductivity from fitting argon data. Although internal energy transport in a polyatomic molecule has no effect on the viscosity and self-diffusion, it can give rise to a significant increase in the thermal conductivity.

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The magnitude of this effect can be theoretically calculated in the case of a dilute gas but there is no corresponding theory for the dense gas or liquid. Recent correlations of liquid *n*-alkane thermal conductivities [4, 5] have been based on the assumption that the density dependences of the translational and internal contributions are the same. In order to test this assumption, it is necessary to restrict attention to pseudospherical molecular fluids under conditions where the hard-sphere theory can be expected to apply. In this paper, the thermal conductivity of dense fluid methane is calculated on the basis of the hard-sphere theory for monatomics with core sizes determined from a simultaneous fit to viscosity and self-diffusion data. The results are compared with experimental thermal conductivities and the differences are discussed in terms of the effects of internal energy transport on this property.

2. CALCULATION

The exact hard-sphere expression $\lambda_{\mathrm{HS,M}}$ for the thermal conductivity of a monatomic species is given by

$$\lambda_{\mathrm{HS,M}} = (\lambda/\lambda_{\mathrm{E}})(\lambda_{\mathrm{E}}/\lambda_0)\,\lambda_0 \tag{1}$$

where $(\lambda/\lambda_{\mathrm{E}})$ represents the correction to the approximate Enskog theory for the effect of correlated molecular motions, and $\lambda_{\mathrm{E}}/\lambda_0$ is the ratio of the Enskog dense hard-sphere fluid thermal conductivity coefficient to the dilute hard-sphere value

$$\lambda_{\mathrm{E}}/\lambda_0 = [1/g(\sigma) + 1.2\, b_0/V + 0.755\, g(\sigma)(b_0/V)^2] \tag{2}$$

where $g(\sigma)$ is the radial distribution function at contact [6] and b_0 is given by $2\pi N\sigma^3/3$ for spheres of diameter σ in a volume V.

In the first approximation, λ_0 is given by

$$\lambda_0 = \frac{25 c_{\mathrm{v}}}{32\pi\sigma^2}\left(\frac{\pi kT}{m}\right)^{1/2} \tag{3}$$

where m is the molecular mass and c_{v} is the molecular heat capacity at constant volume.

For a polyatomic molecular fluid, it is necessary to include the effects of internal energy contributions to the thermal conductivity. Up to moderate densities it is assumed [7] that the thermal conductivity can be written as the sum of two terms

$$\lambda = \lambda_{\mathrm{M}} + \lambda_{\mathrm{int}} \tag{4}$$

where λ_M and λ_{int} are the contributions from translational and internal degrees of freedom. The internal contribution, which is considered to be carried by a diffusion mechanism, can be related [8] to the coefficient of self-diffusion, D, and the molecular internal heat capacity at constant volume

$$\lambda_{int} = c_{v,int} nD \tag{5}$$

where n is the number density.

It should be noted that this contribution to the thermal conductivity at any constant temperature will decrease significantly as the density increases.

In an alternative and purely empirical approach, Menashe et al. [4] assumed that the density dependence of the internal energy contribution to the thermal conductivity could be taken as identical to that of the translational contribution. If this is correct, then the ratio of the experimental thermal conductivity for a dense hard-sphere polyatomic fluid to the value calculated assuming that the fluid is monatomic will be given by the zero-density ratio, namely,

$$\lambda_{HS}/\lambda_{HS,M} = 1 + 0.352 c_{v,int}/k \tag{6}$$

In order to establish which of these approaches gives the better description of the density dependence of the thermal conductivity for a polyatomic fluid, it is necessary to consider a pseudospherical molecular fluid for which the core size σ at different temperatures has been unambiguously determined by an independent method. This is important because a small change in the core size can lead to a large variation in the calculated transport properties [9]. The simplest such molecule is methane, for which a recent application of the exact smooth hard-sphere theory to the simultaneous fit of the dense fluid self-diffusion and viscosity data has led [1] to a common set of temperature-dependent core sizes. The corresponding close-packed volumes, V_0, equal to $N\sigma^3/\sqrt{2}$, were satisfactorily represented by the equation

$$V_0 = \sum_{i=0}^{i=3} a_i (T/100)^i \tag{7}$$

with V_0 in $\text{cm}^3 \cdot \text{mol}^{-1}$ and the temperature, T, in K. Values of the coefficients a_i, with units of $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-i}$, are given in Table I.

Values for the thermal conductivity of methane at densities greater than the critical density have been calculated using Eqs. (1) to (3) with the corrections to Enskog theory given [1] by

$$\lambda/\lambda_E = \sum_{j=0}^{j=3} a_j (V_0/V)^j \tag{8}$$

with the coefficients in Table I.

Table I. Coefficients in Eqs. (7) and (8)

	a_0	a_1	a_2	a_3
V_0	29.4922	−9.5901	2.8727	−0.31763
λ/λ_E	1.1413	−1.4499	4.8872	−5.4163

It is found that the calculated values are, as expected, lower than experiment but the differences increase by as much as 100% for liquid methane as the density increases up to the highest pressures. This demonstrates that Eq. (5) is not applicable at densities above the critical density. The calculated values are compared directly with experimental thermal conductivities [10] in Fig. 1. The region in the immediate neighborhood of the critical temperature has not been included. At temperatures of 235 and 275 K, which are in the extended critical region, there

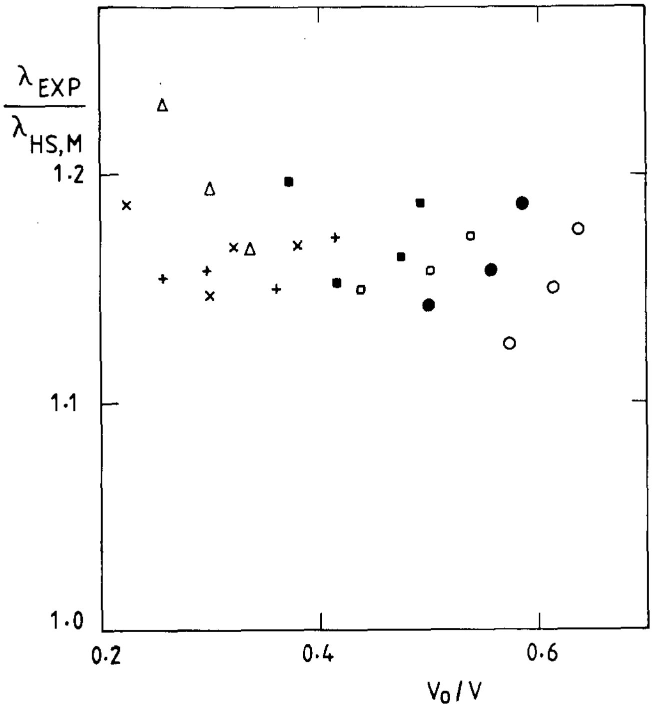

Fig. 1. Ratio of experimental methane thermal conductivities to values calculated by the smooth hard-sphere expression at different reduced densities: ○, 110 K; ●, 135 K; □, 155 K; ■, 175 K; +, 235 K; x, 275 K; △, 310 K.

is an enhancement in the experimental values and this has been subtracted from the measured values in making the comparison with the calculations since the hard-sphere theory cannot account for this. The results indicate clearly that, on the basis that methane can be considered a hard-sphere fluid, the ratio of the experimental thermal conductivities to the values calculated with neglect of internal energy contributions is indeed density independent and approximately equal to 1.16. On the assumption that this can be represented by an equation similar to Eq. (6), then substitution of appropriate heat capacity values [11] leads to the result that for methane at densities greater than critical,

$$\lambda_{\mathrm{HS}}/\lambda_{\mathrm{HS,M}} = 1 + 0.07 c_{\mathrm{v,int}}/k \tag{9}$$

3. CONCLUSION

Analysis of the thermal conductivity coefficient data for methane at densities greater than the critical density on the basis of the exact hard-sphere theory, neglecting effects of internal motion, leads to the result that the experimental values are higher than the calculated coefficients by approximately 16% at all densities. Although this still awaits a rigorous theoretical interpretation, it nevertheless supports the idea that the density dependence of the internal part of the thermal conductivity is the same as that for the translational part and indicates that the internal part is not carried solely by a purely diffusive mechanism at these densities.

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