Prediction of Thermal Conductivity for Dense Fluids and Fluid Mixtures

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Murad and Gubbins (1977) have developed a corresponding states correlation for the thermal conductivity of dense fluids based on the shape factor method. The method in its present form requires extensive computer programming. In this note we present the shape factor method for thermal conductivity in a form that is easy to use. The simplifications to the procedure include: (a) the use of empirical equations for the shape factors of the fluids involved, in place of the iteration procedure used before; (b) the use of plots for the thermal conductivity and equation of state data of the reference fluid, in place of the equations of Goodwin (1974) and Hanley et al. (1975); and (c) the use of a simple approximation procedure for mixtures, which avoids iterations. This simplified method has almost the same accuracy as the original procedure (Murad and Gubbins, 1977), which within the range of the correlation was accurate to within 4-5%. For mixtures involving hydrocarbons and nonpolar or mildly polar inorganic constituents this is a considerable improvement over previous methods, particularly at higher pressures. As for other shape factor correlations, the method is not suitable for predictions involving strongly polar, hydrogen-bonded solvents (MeOH, H_2O, NH_3, etc.) and does not account for anomalous behavior in the immediate vicinity of the critical point.

The unknown thermal conductivity of a fluid α at T and P can be related to the known thermal conductivity of a reference fluid o by the equation

$$\lambda_\alpha[P,T] = \left(\frac{T^c_o}{\theta_{\alpha,o}T^c_\alpha}\right)^{1/6}\left(\frac{P^c_\alpha\psi_{\alpha,o}}{P^c_o}\right)^{2/3}\left(\frac{M_\alpha}{M_o}\right)^{-1/2} \times\lambda_o\left[\frac{PP^c_o}{P^c_\alpha\psi_{\alpha,o}}, \frac{TT^c_o}{T^c_\alpha\theta_{\alpha,o}}\right] \tag{1}$$

where subscript o refers to the reference fluid and $\theta_{\alpha,o}$ and $\psi_{\alpha,o}$ are state-dependent shape factors. As can be seen from Eq. 1, these shape factors have the effect of making the effective critical parameters of fluid α state-dependent in such a way as to ensure conformality. We have previously calculated these factors by comparing Eq. 1, together with the equality of the compressibility factors, $Z_\alpha = Z_o$, with experimental data. Such calculations were carried out for saturated hydrocarbons, carbon dioxide, nitrogen, n-octane, i-octane, benzene, and carbon tetrachloride, and we have presented empirical equations for the shape factors of each substance in terms of reduced temperature and density (Murad and Gubbins, 1977, Appendix). These equations for $\theta_{\alpha,o}$ and $\psi_{\alpha,o}$ assume the availability of PVT data for fluid α. If such data is unavailable a predictive technique must be used. One such accurate method is that of Leach et al. (1966).

A reference fluid must be chosen for which accurate thermal conductivity and equation of state data are available. We use methane as the reference fluid in this work. Thermal conductivity data for methane is shown in Figure 1, and PVT data is given in Figure 2. If necessary the range of Figures 1 and 2 can be extended using the empirical equations of Goodwin (1974) and Hanley et al. (1975); computer programs to do these calculations, and also the PVT calculations using the method of Leach et al. (1966), are available from S. Murad.

EXAMPLE: PURE FLUIDS

To further clarify the technique, we now carry out a sample calculation for the thermal conductivity of butane at 478°K, 138 × 10^5 N/m². The density is 0.374 g cm^{-3}. Using Eq. A1 and A2 of Murad and Gubbins (1977):

$$\theta_{\alpha,o} = 1.525; \quad \psi_{\alpha,o} = 1.224$$

$$\frac{TT^c_o}{T^c_\alpha\theta_{\alpha,o}} = 140.5°\text{K} \; ; \frac{PP^c_o}{P^c_\alpha\psi_{\alpha,o}} = 136.3 \times 10^5 \text{ N/m}^2$$

From Figure 2 $\rho_o = 24.75$ mol l^{-1}, which corresponds to ρ^r_o =

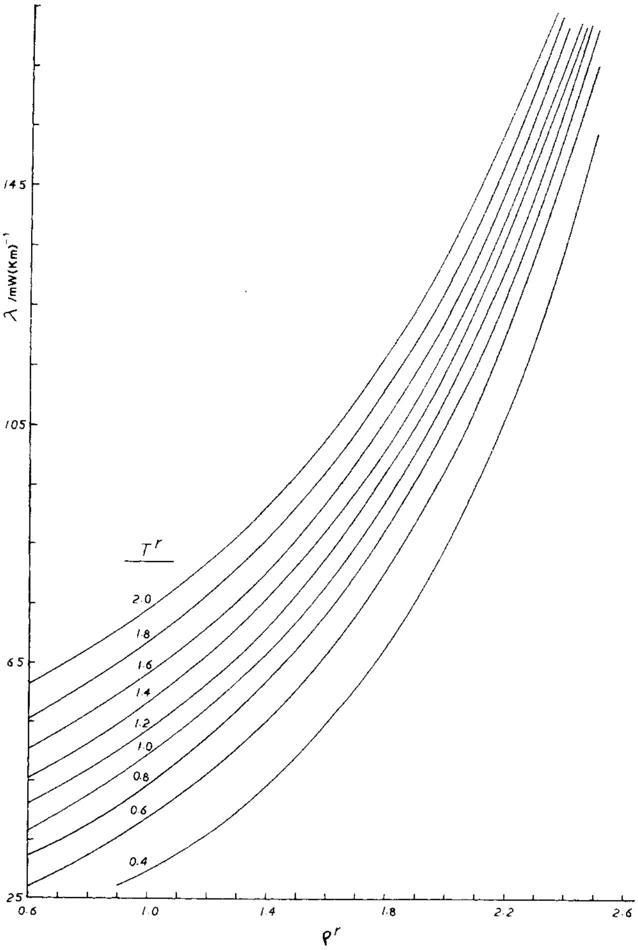

Figure 1. Thermal conductivity of CH_4 as a function of reduced density and temperature.

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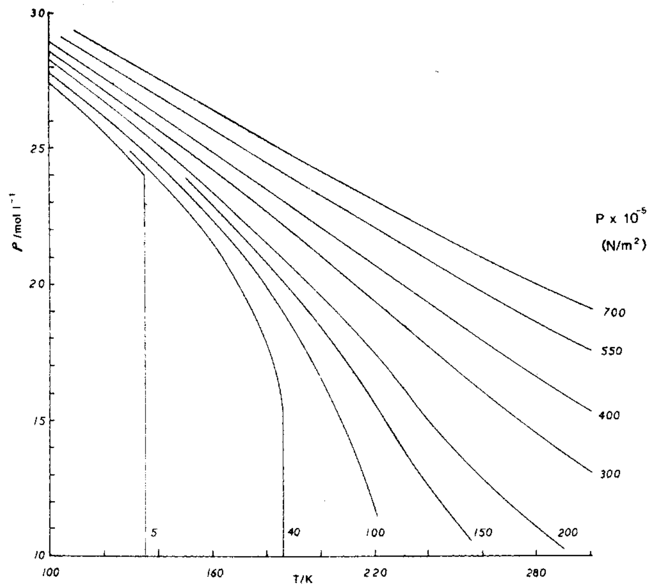

Figure 2. $P\rho T$ relationship for methane.

2.475; T^r_o = 140.5/190.55 = 0.74. From Figure 1, at these state conditions, λ_o = 165 mW(Km)$^{-1}$, and finally using Eq. 1

$$\lambda_\alpha = 71.0 \text{ mW(Km)}^{-1}$$

The experimental value from Carmichael and Sage (1964) is 67.5 mW(Km)$^{-1}$.

EXTENSION TO MIXTURES

To extent the shape factor approach to mixtures we use pseudo-critical reduced temperatures and pressures. These are given by

$$T^{r'} = \frac{T \sum\limits_{\alpha\beta} x_\alpha x_\beta \eta_{\alpha\beta} \left[\left(\frac{T^c_\alpha}{P^c_\alpha} \right)^{1/3} + \left(\frac{T^c_\beta}{P^c_\beta} \right)^{1/3} \right]^3}{\sum\limits_{\alpha\beta} x_\alpha x_\beta \eta_{\alpha\beta} \left[\left(\frac{T^c_\alpha}{P^c_\alpha} \right)^{1/3} + \left(\frac{T^c_\beta}{P^c_\beta} \right)^{1/3} \right]^3 \xi_{\alpha\beta} [T^c_\alpha T^c_\beta]^{1/2}} \tag{2}$$

$$P^{r'} = \frac{P \left(\sum\limits_{\alpha\beta} x_\alpha x_\beta \eta_{\alpha\beta} \left[\left(\frac{T^c_\alpha}{P^c_\alpha} \right)^{1/3} + \left(\frac{T^c_\beta}{P^c_\beta} \right)^{1/3} \right]^3 \right)^2}{8 \sum\limits_{\alpha\beta} x_\alpha x_\beta \eta_{\alpha\beta} \left[\left(\frac{T^c_\alpha}{P^c_\alpha} \right)^{1/3} + \left(\frac{T^c_\beta}{P^c_\beta} \right)^{1/3} \right]^3 \xi_{\alpha\beta} \, [T^c_\alpha T^c_\beta]^{1/2}} \tag{3}$$

Here $\xi_{\alpha\beta}$ and $\eta_{\alpha\beta}$ are values for the binary interaction parameters which are listed for a number of mixtures elsewhere (Murad and Gubbins, 1977). Two parameters f and q are now introduced which are given by

$$f_{\alpha\alpha.o}(P,T,\{x\}) = \frac{T^c_\alpha}{T^c_o} \theta_{\alpha.o}(P'_r, T'_r) \tag{4}$$

$$q_{\alpha\alpha,o}(P,T,\{x\}) = \frac{P^c_\alpha}{P^c_o} \psi_{\alpha.o}(P'_r, T'_r) \tag{5}$$

The double α subscript shows that these parameters are for α molecules interacting with α molecules. The parameters for α molecules interacting with β molecules are given by

$$f_{\alpha\beta.o} = \xi_{\alpha\beta}(f_{\alpha\alpha.o} f_{\beta\beta.o})^{1/2} \tag{6}$$

$$\frac{f_{\alpha\beta.o}}{q_{\alpha\beta.o}} = \eta_{\alpha\beta} \left[\frac{1}{2} \left(\frac{f_{\alpha\alpha.o}}{q_{\alpha\alpha.o}} \right)^{1/3} + \frac{1}{2} \left(\frac{f_{\beta\beta.o}}{q_{\beta\beta.o}} \right)^{1/3} \right]^3 \tag{7}$$

For the mixture f and q are given by

$$\frac{f_{x.o}}{q_{x.o}} = \sum_{\alpha\beta} x_\alpha x_\beta \frac{f_{\alpha\beta.o}}{q_{\alpha\beta.o}} \tag{8}$$

$$\frac{f^2_{x.o}}{q_{x.o}} = \sum_{\alpha\beta} x_\alpha x_\beta \frac{f^2_{\alpha\beta.o}}{q_{\alpha\beta.o}} \tag{9}$$

$$\frac{q^{2/3}_{x.o}}{M_x^{1/2} f^{1/6}_{x.o}} = \sum_{\alpha\beta} x_\alpha x_\beta \frac{q^{2/3}_{\alpha\beta.o}}{M^{1/2}_{\alpha\beta} f^{1/6}_{\alpha\beta.o}} \tag{10}$$

where

$$M_{\alpha\beta} = 2 \left(\frac{1}{M_\alpha} + \frac{1}{M_\beta} \right)^{-1} \tag{11}$$

The thermal conductivity of the mixture is finally given by

$$\lambda[P,T,\{x\}] = f^{-1/6}_{x,o} q^{2/3}_{x,o} \left(\frac{M_x}{M_o} \right)^{-1/2} \lambda_o \left[\frac{P}{q_{x,o}}, \frac{T}{f_{x,o}} \right] \tag{12}$$

EXAMPLE: MIXTURES

To further clarify the method we now do a sample calculation for the thermal conductivity of a N_2/C_2H_6 mixture at 348°K, 507 × 10^5 N/m^2, and X_{N2} = 0.598. From Eqs. 2 and 3
$T^{r'}$ = 1.784; $P^{r'}$ = 12.169
From Figure 2, $\rho^{r'}$ = 1.57.
From Eqs. 4 and 5, together with Eqs. A5 and A6 of Murad and Gubbins (1977) for N_2, $f_{NN,o}$ = 0.6910; $q_{NN,o}$ = 0.6781.
From Eqs. 4, 5, together with Eqs. A1 and A2 of Murad and Gubbins (1977) for C_2H_6, $f_{EE.o}$ = 2.4278 and $q_{EE.o}$ = 1.1575.
From Eqs. 6 and 7 $f_{NE.o}$ = 1.2305 and $q_{NE.o}$ = 1.1575.
From Eqs. 8, 9 and 10 $f_{x.o}$ = 1.3796, $q_{x.o}$ = 0.9718 and M_x = 34.1595, and finally from Figure 1 and Eq. 12,
λ_x = 71.8 mW(Km)$^{-1}$
λ_{exp} from Gilmore and Comings (1966) is 71.3 mW(Km)$^{-1}$.

ACKNOWLEDGMENT

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NOTATION

f = corresponding states parameter
M = molecular weight
P = pressure
P^r = P/P^c
q = corresponding states parameter
T = temperature
T^r = T/T^c
V = volume
x = mole fraction
$\{x\}$ = mole fractions of all components
Z = PV/RT

Greek Symbols

θ, ψ = shape factors
λ = thermal conductivity
ξ, η = unlike parameters in Eqs. 2, 3, 6 and 7
ρ = density
ρ^r = ρ/ρ^c
ω = Pitzer acentric factor

Subscripts

α, β = general components
$\alpha\alpha, o$ = parameter for substance α relative to reference substance
o = reference substance value
x = mixture value
x, o = parameter for mixture relative to reference substance

Superscripts

c = critical value
r = reduced value

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Deviations of Actual Minimum Fluidization Velocities from Theoretical Predictions at Different Temperatures

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The incipient fluidization velocity is one of the fundamental parameters in modeling fluidized bed processes. Although most fluidized bed applied in industry operate well above room temperature, there is, in general, little known about fluidization at elevated or high temperatures. Only few studies reporting data on the variation of onset of fluidization with temperature can be found in the literature.

With temperature increase the density and viscosity of a gas change in a definite, well known way. In dependence on the type of material, the particle diameter and density are also affected by temperature. Unfortunately, accurate data on the thermal expansion at high temperatures can be found in the literature only for very few materials. Some calculations showed that this effect should be small. It is assumed in the present work that the effect of temperature on the particle diameter and density is negligible. Recent works of Desai et al. (1977) and Doheim and Collinge (1978) suggest a possible influence of temperature on properties of the solid particle bed.

Effort to separate the effect of temperature on the properties of gas from those of particle bed led to a simple linear equation (Desai et al., 1977):

$$\log G_{mf} = -a \log T + b \qquad (1)$$

Originally, this equation was developed for laminar gas flow region, where viscous effect predominate, i.e., approximately for $Re_{mf} < 2$.

A practical meaning of Eq. 1 is apparent. When the coefficient a is known, the minimum fluidization velocity at temperature of interest can be predicted from a single measurement at room temperature.

Theoretically, the coefficient a in Eq. 1 depends only on the properties of fluidizing medium, i.e., $a = a(\mu_g, \rho_g)$. Its value shows how the incipient velocity changes when temperature varies. The other coefficient $b = b(d_p, \epsilon, \psi$, gas species) combines effects of material constants, particle bed characteristics and gas properties as well.

The values of the coefficient $(a)_{\text{exp}}$ reflect actual overall changes in the minimum fluidization velocities U_{mf} with temperature found by experiments. This offers a rational basis for verification of the theoretical predictions.

The gas density is inversely proportional to the absolute temperature and the viscosity of air is given with accuracy better than 3% by the relation:

$$\mu_g = 1.81 \times 10^{-5}\left[\frac{T}{293}\right]^{0.66} \qquad (2)$$

It follows from this that the theoretical value of a for air is about 1.66 in the laminar flow region ($Re_{mf} < 2$). For turbulent flow ($Re_{mf} > 1000$), where inertia effects predominate, the expected value of a is 0.5. In the transition flow region ($2 < Re_{mf} < 1000$) the coefficient a should decrease with increasing Reynolds numbers. With respect to the illustrative form of Eq. 1, it is convenient to evaluate the effect of temperature on G_{mf} also in the transition or turbulent region with the aid of this relation.

The purpose of the present work is to find by experiments in a wide temperature range the coefficients a and b in Eq. 1 for various materials and different particle sizes. The experimental values are compared with values $(a)_{\text{calc}}$ and $(b)_{\text{calc}}$ predicted from different equations for U_{mf} summarized in Table 1.

EXPERIMENTAL

Materials. The minimum fluidization velocity was determined from pressure drop—gas velocity data measured at different temperatures. Bed materials were chosen with respect to their occurrence in a fluidized bed for combustion of brown coal and simultaneous SO_2 removal. The particle and bed properties of limestone, lime, brown coal ash and corundum used in the work are presented in Table 2. The last material was chosen as a comparing standard for its well defined physical properties. The particles of coal ash were almost flake-like, the particles of limestone and lime were of irregular shapes, nevertheless, they appeared quite isometrical when examined by a microscope. The particles of sintered corundum were ellipsoidal ones with a smooth surface.

Apparatus. Measurements of U_{mf} were performed in a 0.085 m I.D. steel, electrically heated reactor the height of which was $H_K = 0.5$ m. The fluidizing air was well preheated to a desired temperature prior to being introduced through a plate distributor into the bed of particles. Temperature in the bed was measured by the thermocouple Pt—Rh10 Pt. The pressure drop across the bed was measured by means of a pressure probe and U-tube manometer.

Procedure. The particle bed of height $H = D_K$ was heated to a desired temperature and the flow rate of air was gradually reduced from a well fluidized state to a static bed. The pressure drops and corresponding air flow rates were recorded and the minimum fluidization velocity was then determined from the plot pressure drop vs. velocity of air. The measurements of U_{mf} were carried out on eight levels of temperature in the range 20-890°C. In the case of limestone temperatures up to 450°C

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