THERMAL CONDUCTIVITY OF MULTATOMIC GASES AT LOW DENSITIES

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UDC 536.45

It is shown that divergence between measurement results and calculations by the Mason–Monchik theory are caused by imperfection of the model potentials used.

Maitland et al. [1] studied the applicability of the nonlinearized Mason–Monchik theory [2, 3] to determination of the contribution of internal degrees of molecular freedom to the thermal conductivity of multiatomic gases. It was shown that at a temperature of 300 K, at which measurements are most reliable, the divergence between calclation and experiment increases in direct proportion to the quantity c_{rot}/Z_{rot} (where c_{rot} and Z_{rot} are the heat capacity and number of collisions necessary for establishment of equilibrium of rotational degrees of freedom). For nitrogen and methane ($c_{rot}/Z_{rot} \approx 0.2$) the deviation comprises 2-3%, while for ethane and ethylene ($c_{rot}/Z_{rot} \approx 0.5$) it increases to 5-8%. Since experimental data of [4] were used for Z_{rot}, the cause of the divergence was ascribed to imperfection of the Mason–Monchik theory.

There are two reasons why this conclusion is not convincing. First, the paired model potentials (including multiparameter ones) used in the calculations do not consider the internal structure of multiatomic molecules. As is well known [5], the interaction potential of multiatomic molecules averaged over all possible orientations remains spherically symmetrical, but of necessity must contain a new parameter characterizing the nonsphericity of the molecules. Second, in a sequential theory, the relaxation time of rotational degrees of molecular freedom, like their other properties, should be determined by the intermoelcular interaction potential. Only when these conditions are satified can be functional relationship be established between Mason–Monchik theory for the thermal conductivity coefficient of multiatomic gases and intermolecular forces, as is the case for viscosity and the second virial coefficient. Naturally, calculated relaxation time values should also agree with the corresponding experimental results.

In the present study the paired model potential (12-7, δ) [6, 7] will be used to describe the thermophysical properties of multiatomic gases. This model describes the thermodynamic [8, 9] and transport [10, 11] properties of monatomc and biatomic gases as well as their mixtures [12, 13] over the entire measurement range in a consistent manner. Use of the (12-7, δ) potential for multiatomic molecules of arbitrary symmetry is complicated by uncertainty in choosing the value of the molecular "core" r_e, and consequently, the nonsphericity parameter $\delta = (r_e/\sigma)^2$.

In [14] the value chosen for the "core" of multatomic molecules was the quantity

$$r_e = \sqrt{\frac{4I_m}{m}} = \sqrt{\frac{4(I_A + I_B + I_C)}{nm}},$$

where $I_m = (I_A + I_B + I_C)/n$ is the mean moment of inertia of the molecule; I_A, I_B, and I_C are the main moments of inertia, and n is the number rotational degrees of freedom. For homonuclear biatomic molecules ($n = 2$, $I_m = I_A = I_B = 1/4\ mr_B^2$) the "core" is equal to the equilibrium distance between nuclei. For multiatomic molecules the value of r_e is calculated from experimental data on rotational constants [15]. Molecules which have identical structure and similar internuclear distances, but greatly different moments of inertia (for example, methane and carbon tetrafluoride) will have significantly different "core" values, and thus different nonsphericity parameters δ. Constants of the (12–7, δ) potential for 10 nonpolar multiatomic molecules with quite different symmetries are presented in Table 1.

For such a definition of the nonsphericity parameter of the molecule in the (12-7, δ) potential the corresponding mean number of collisions necessary for establishing equilibrium of rotational degrees of freedom is described by the theoretical expression of O'Neal and Brokaw [16]:

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 53, No. 6, pp. 983-986, December, 1987. Original article submitted January 12, 1987.

TABLE 1. Constants of (12-7, δ) Potential for Multiatomic Gases

Gas	ε/k, K	$\sigma\cdot 10^8$, cm	$r_e\cdot 10^8$, cm	δ	T_B, K
H_2	53,0	2,820	0,7418	0,0692	
CO_2	440	3,532	1,982	0,3149	750
N_2O	456	3,510	1,912	0,2967	800
CF_4	280	4,175	2,006	0,2309	545
SF_6	388	4,735	2,256	0,2270	760
CH_4	208	3,566	0,896	0,0631	516
C_2H_6	364	4,120	1,592	0,1493	800
C_3H_8	468	4,600	2,093	0,2070	944
C_2H_4	334	3,900	1,390	0,1270	759
C_3H_6	464	4,452	2,009	0,2036	941

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*T_B, Boyle temperature.

TABLE 2. Values of Z_{rot}, f_{tran}, f_{in}, and Transport Coefficients for Multiatomic Gases at T = 300 K

Gas	$\mu\cdot 10^8$, [Pa·sec]			$x=\frac{c_{in}}{R}$	Z_{rot}	f_{tran}	f_{in}	$\lambda\cdot 10^5$, [W/(m·K)]		
	[20]	[1]	calc.					[21]	[1]	calc.
H_2	895	895	894	0,970	9,764	2,392	1,398	18300	18530	18230
CO_2	1496	1500	1488	1,976	1,599	2,094	1,483	1660	1680	1707
N_2O	1488	1493	1477	2,157	1,596	2,090	1,473	1730	1748	1761
CF_4	—	1747	1732	4,930	2,832	2,096	1,377	1650	1598	1626
SF_6	1540*	1533	1526	9,224	2,270	2,031	1,363	1367*	1296	1357
CH_4	1106	1114	1106	1,529	9,003	2,333	1,386	3420	3462	3442
C_2H_6	933	930	913	3,845	3,285	2,141	1,399	2140	2181	2170
C_3H_8	823	823	819	6,398	2,001	2,007	1,387	1820	—	1835
C_2H_4	1028	1031	1015	2,676	3,983	2,190	1,416	2060	2163	2127
C_3H_6	865	—	856	5,275	2,047	2,018	1,398	1760	—	1759

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*From generalized experimental data [22].

$$Z_{rot}^{-1}=\frac{5\pi}{12}\frac{\delta}{(1+\delta)^2\Omega^{(2.2)}}\exp\left(\frac{\varepsilon}{kT}\right),$$

where $\Omega^{(2.2)}$ is the collision integral.

It should be noted that in Parker's theory [17], in contrast to [16] the effect of the rigid "core" of multiatomic molecules is not considered ($\varphi = \infty$ at $r \leq r_e$).

Calculations of Z_{rot} values for 10 nonpolar multiatomic molecules at a temperature of 300 K are presented in Table 2. As a rule, calculated and experimental data from [4, 16] agree with the intermeasurement divergence of the various authors.

The nonlinearized Mason–Mönchik theory [2, 3] was then used to calculate the thermal conductivity coefficient of the multiatomic gases:

$$\lambda=\frac{R\mu}{m}\left[f_{tran}\frac{c_{tran}}{R}+f_{in}\frac{c_{in}}{R}\right], \tag{1}$$

where

$$f_{tran}=\frac{5}{2}\left[1-\frac{10}{3\pi}\left(1-\frac{2}{5}\frac{\rho D}{\mu}\right)\frac{y}{Z_{rot}A}\right]; \tag{2}$$

$$f_{in}=\frac{\rho D}{\mu}\left[1+\frac{5}{\pi}\left(1-\frac{2}{5}\frac{\rho D}{\mu}\right)\frac{y}{xZ_{rot}A}\right];$$

$$A = 1 + \frac{2y}{\pi x Z_{\mathrm{rot}}}\left(\frac{5}{3}x + \frac{\rho D}{\mu}\right), \quad (2)$$

with $x = c_{in}/R$, $y = c_{rot}/R$.

It should be noted that Eqs. (1), (2) were obtained with the assumption that the diffusion transport coefficients of internal degrees of freedom are equal to the self-diffusion coefficient, and moreover, that the term c_{osc}/Z_{osc} may be neglected in comparison to c_{rot}/Z_{rot}, i.e.,

$$c_{\mathrm{in}}/Z_{\mathrm{in}} = \frac{c_{\mathrm{rot}}}{Z_{\mathrm{rot}}} + \frac{c_{\mathrm{osc}}}{Z_{\mathrm{osc}}} \approx \frac{c_{\mathrm{rot}}}{Z_{\mathrm{rot}}}.$$

The well-known result of the kinetic theory of gases [18] was used for the dimensionless ratio $\rho D/\mu$:

$$\frac{\rho D}{\mu} = \frac{6}{5}A^*,$$

where $A^* = \Omega^{(2.2)}/\Omega^{(1.1)}$ is the ratio of the collision integrals. Thus a theoretically justifiable relationship has been established between the thermal conductivity coefficients of multiatomic gases and the (12-7, δ) paired model potential. In principle, this makes it possible to use experimental data on thermal conductivity together with data on viscosity and the second virial coefficient to determine two other constants of the (12-7, δ) potential (the depth of the potential well ε and the "diameter" of the molecule σ). In the present study these constants (see Table 1) were defined in the usual manner: by combined analysis of experimental data on the second virial coefficient [19] and viscosity [20]. A comparison of calculated and experimental values of the second virial coefficients of methane, ethane, and propane was performed in [14].

The divergence between calculation and experiment (Table 2) is within the limits of experimental uncertainty (for viscosity the mean divergence is ±0.8%, with a maximum of 2.1%, for thermal conductivity, ±1.5 and 5.4% respectively).

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METHODS FOR MEASUREMENT OF THERMAL CONDUCTIVITY AND SPECIFIC HEAT AT MODERATE, LOW, AND CRYOGENIC TEMPERATURES

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UDC 681.2:536.083

Physical principles and schematic diagrams of automated devices for measurement of thermophysical properties of materials and components in the temperature range 100-700 K are presented.

Recent decades have been characterized by an increased interest in study of thermophysical properties of materials which must operate over wide temperature ranges. To create highly efficient dynamic methods and equipment for experimental determination of thermal conductivity and specific heat of industrial materials used in refrigeration and cyrogenic technology, in 1977 at the Leningrad Refrigeration Industry Technological Institute a separate scientific-research laboratory operating in close contact with the State Thermophysical Instrument Engineering Committee was organized. In the following 10 years this laboratory has performed a series of interesting studies, many of which resulted in creation of a new generation of domestic thermophysical equipment provided with direct readout units or systems for automated control of experiments and computer processing of measurement results. Their operating specifications are not exceeded by the best available foreign products, and some are beginning to enter regular industrial production.

Devices intended for measurements under normal climatic conditions form an independent group of developments. Despite the wide range of thermophysical measurement methods available under normal climatic conditions, there is still a necessity for developing new devices which consider more fully structural specifics and use conditions of modern technical materials. Thus the laboratory developed a group of direct readout instruments for use with specimens of the most universal form — disks 15-40 mm in diameter with thicknesses of 0.5-20 mm [1].

A generalized schematic diagram of the thermal cell used in these devices is shown in Fig. 1. Measurements are made with this device using the principle of heating of a disk with uniform initial temperature field with boundary conditions of the first sort. The thermal cell is based on two massive metallic blocks 1, 3, one of which is at room temperature (temperature of the medium), while the second is heated by heater 4 to a temperature 5-15 K above that of the medium. During experiment the blocks are located in contact with the planar faces of the specimen 2, and the thermal fluxes passing through them into the specimen $q_u(\tau)$ and $q_\ell(\tau)$ (see Fig. 2) are recorded by two gradient thermometers 5 and 6, installed in the working area of the blocks.

This experimental regime is convenient for a number of reasons. In particular, it makes it unnecessary to record the nonsteady state temperature field of the specimen or maintain constant temperature levels on its plane faces. To determine thermal conductivity it is only necessary to know the temperature head between the blocks (within the specimen) and the steady state thermal flux passing through the specimen $q_c = q(\tau_c)$. In turn, to determine specific heat of the specimen it is sufficient to establish the quantity of heat accumulated within the specimen over the time of the experiment, by integrating over time the difference in the indications of the thermometers $Q = \int_0^{\tau_c} (q_u - q_\ell)/d\tau$, i.e., to calculate the shaded area in Fig.

Refrigeration Industry Technological Institute, Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 53, No. 6, pp. 987-994, December, 1987. Original article submitted April 21, 1987.

0022-0841/87/5306-1452$12.50