ESTIMATE OF THE QUANTUM CORRECTION TO THE TRANSPORT COEFFICIENTS OF MONATOMIC GASES

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Quantum corrections to the transport coefficients of all monatomic gases are calculated. The temperature range in which these corrections are important is found more accurately. The calculated results are compared with experiment.

The application of quantum mechanics to the description of the interaction of molecules in gases permits the calculation of the transport coefficients (viscosity and thermal conductivity) for high, intermediate, and very low temperatures. It is possible to take account not only of diffraction effects related to the wave properties of the colliding molecules of the gas, but also symmetry effects related to the kind of statistics obeyed by an ensemble of molecules of the gas. Both these effects contribute a quantum correction to the values of the transport coefficients.

Somewhat contradictory opinions are expressed in the literature [1-3] as to the temperature at which quantum effects begin to be important. We have estimated the quantum corrections to the transport coefficients of all monatomic gases, and, in particular, have determined more accurately the temperature range in which this correction must be taken into account in practical calculations.

The transport coefficients (the thermal conductivity λ and the viscosity η) of monatomic gases were calculated by the formulas of the rigorous kinetic theory of gases [2]

$$\lambda = 1.9891 \cdot 10^{-4} \frac{\sqrt{\frac{T}{M}}}{\sigma^2 \Omega^{(2,2)^*}(T^*)} \left[\text{cal/cm} \cdot \text{sec} \cdot \text{deg}\right], \tag{1}$$

$$\eta = 266.93 \cdot 10^{-7} \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)^*}(T^*)} \left[\frac{\text{g}}{\text{cm} \cdot \text{sec}}\right]. \tag{2}$$

The parameters σ and ε for the gases considered were taken from [2] where they are tabulated for the Lennard-Jones potential on the basis of experimental data on viscosity

$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{3}$$

The starting points for the quantum mechanical calculation of the collision integral is the solution of the radial wave equation for two interacting molecules. Using the parameters of the Lennard-Jones potential this equation can be written in the form

$$\frac{d^2}{dr^{*2}}(r^*\psi) + \left[\varkappa^{*2} - \frac{l(l+1)}{r^{*2}} + \frac{16\pi^2}{\lambda^{*2}}\left(\frac{1}{r^{*12}} - \frac{1}{r^{*6}}\right)\right](r^*\psi) = 0, \tag{4}$$

where $r^* = r/\sigma$; $\varkappa^* = \varkappa\sigma$.

The solution of this equation permits an estimate of the phase shift of the wave function ψ, i.e., the probability of the reflection of a molecule by an angle χ in a collision. The collision cross section $Q(\chi)$ and the related normalized collision integral [1]

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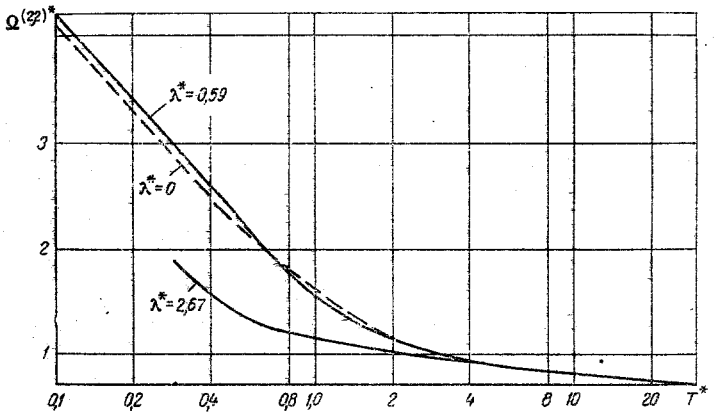

Fig. 1. Collision integral $\Omega^{(2,2)*}$ as a function of the reduced temperature.

$$\Omega^{(2,2)*} = \int_0^1 \alpha^5 (-6 \ln \alpha)^3 Q(\chi)\, d\alpha. \tag{5}$$

can be calculated from the phase shift.

Using the results of a numerical integration of this equation [4] the normalized collision integral $\Omega^{(2,2)*}$ can be constructed as a function of the reduced temperature for various values of the de Boer parameter.

Figure 1 shows three curves. The first of these ($\lambda^* = 0$) corresponds to no quantum correction, i.e., to a classical calculation of the collision integral. The second curve ($\lambda^* = 0.59$) is characteristic of the neon, and the third ($\lambda^* = 2.67$) of helium.

The curve corresponding to $\lambda^* = 0.59$ is only slightly different from the curve for $\lambda^* = 0$, and, consequently, the quantum correction to the transport coefficients for Ne is rather small.

Since the values of the de Boer parameter for the other gases lie between 0.59 and zero, it should be expected that the quantum correction will be as small for them as for neon.

Using data on the normalized collision integral of real gases and data on the normalized collision integral in the classical case it is possible to calculate the relative correction to the collision integral, and from Eqs. (1) and (2) the quantum correction to the transport coefficients themselves.

The above method was used to calculate the quantum corrections to the thermal conductivity and viscosity of monatomic gases. Bose – Einstein statistics were used for helium, neon, argon, and krypton,

TABLE 1. Quantum Corrections† (in %) to Transport Coefficients of Monatomic Gases [$\delta = 100\% (\lambda_{qu} - \lambda_{cl}) / \lambda_{cl} = 100\% (\eta_{qu} - \eta_{cl}) / \eta_{cl}$]

T, °K	δ_{He}	δ_{Ne}	δ_{Ar}	δ_{Kr}	δ_{Xe}
3	52				
5	61				
10	37				
20	14	−0,27			
40	3,91	1,65			
60	1,59	1,57	−0,01	−0,38	
80	0,81	1,10	+0,01	−0,31	−0,09
100	0,46	0,59	0,24	−0,16	−0,10
150	0,21	0,35	0,35	0,12	−0,09
200	0,14	0,10	0,35	0,18	0,13
300	0,04	0,06	0,25	0,17	0,12
500	0,03	0,001	0,06	0,06	0,08

†The calculation was performed for a reduced temperature $T^* \geq 0.3$. The upper limit of the temperature 300 °K corresponds to a reduced temperature T^* of 50 for He, 14 for Ne, 4 for Ar, 2.6 for Kr, and 2.2 for Xe.

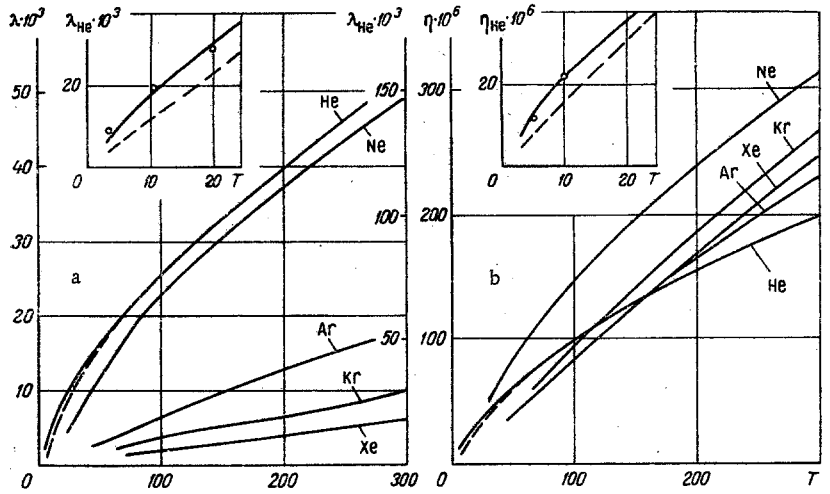

Fig. 2. Thermal conductivity (a) and viscosity (b) of monatomic gases in the temperature range 3-300°K. λ is in W/m · deg and T is in °K.

and Fermi–Dirac statistics, for xenon. The results of the calculation are listed in Table 1. Analysis of these results shows that the quantum correction does not exceed 0.3% for all monatomic gases at room temperature. The correction decreases with increasing temperature. For decreasing temperatures the quantum correction increases and oscillates in sign, as can be seen from Fig. 1 and Table 1.

Direct calculation of the thermal conductivity and viscosity using Eqs. (1), (2), and (5), and data for the collision integral (1), (4) are shown in Fig. 2a and b. The open curves in these figures are for the thermal conductivity and viscosity calculated by classical theory. The solid curves are calculated by quantum theory.

In addition to the calculated curves, the measured values of the transport coefficients reported by a number of authors [5-7] are shown in these figures. The experimental values and the quantum theory calculations are in relatively good agreement.

In conclusion, it should be noted that quantum corrections are very important for helium; for neon these corrections begin to matter only below 200°K, and for argon, krypton, and xenon the quantum corrections are of the order of tenths of a percent even at very low temperatures (down to $T^* = 0.3$).

NOTATION

T	is the temperature of the gas, °K;
M	is the molecular weight of the gas;
σ	is the molecular collision diameter;
$\Omega^{(2,2)*}$	is the normalized collision integral;
$T^* = kT/\varepsilon$	is the reduced temperature;
ε	is the parameter of the molecular interaction potential;
$\varkappa$, l	are the quantum numbers characterizing the relative kinetic energy and the angular momentum for binary collisions;
$\lambda^* = \lambda/\sigma = h/\sigma\sqrt{mc}$	is the de Boer parameter, equal to the ratio of the de Broglie wavelength λ of the relative motion of two molecules with relative kinetic energy ε to the collision diameter σ;
λ_{qu}, η_{qu}	are the transport coefficients calculated by quantum theory;
λ_{cl}, η_{cl}	are the transport coefficients calculated classically.

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