LITERATURE CITED

1. L. Bergman, Ultrasound [Russian translation], Moscow (1957).
2. W. P. Mason (editor), Physical Acoustics, Vol. 1, Pt. B, Academic Press (1964).
3. Yu. M. Babikov and D. S. Rasskazov, Organic and Silicone Heat-Transfer Agents [in Russian], Énergiya, Moscow (1975).

ACTION OF QUANTUM EFFECTS ON THERMAL CONDUCTIVITY OF LIGHT GASES (HELIUM-3, HELIUM-4, AND HYDROGEN)

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Expressions are found for quantum corrections considering symmetry effects expressed in terms of collision integrals, and their contribution to the thermal-conductivity coefficient of gases is calculated. It is shown that quantum effects for light gases are insignificant at temperatures above 20°K.

The study of gas transfer properties at low temperatures and high pressures is of practical interest because of the use of the phenomenon of superconductivity in many scientific and industrial fields. Experimental study of such properties is complicated by large material expenditures, the limited number of objects for study (isotopes of helium and hydrogen), and severe methodological difficulties.

The literature offers isolated experimental data on the transfer properties of helium-3, helium-4, hydrogen, and their mixtures at low temperatures, usually at atmospheric pressure.

Together with the experimental methods of studying transfer properties, there exist two theoretical approaches to describing such properties. The first of these is the thermodynamic approach, based on the quantum theory of irreversible transfer phenomena [1], in which one initially establishes linear phenomenological relationships between the Fourier components of the corresponding flux densities $I^{(p)}(q;\ \omega)$ and the forces acting on the equilibrium system $X^{(p)}(q;\ \omega)$ in the form

$$I^{(p)}(q;\ \omega) = L^{pp'}(q;\ \omega) X^{(p)}(q;\ \omega),$$

where $L^{pp'}(q;\ \omega)$ are kinetic coefficients; $I^{(p)}(q;\ \omega) = \int dx e^{iqx} \int dt e^{i\omega t} \times I^{(p)}(x,\ t)$. Then general formulas are found for $L^{pp'}(q;\ \omega)$ commencing from a microscopic (quantum mechanical) description of the macroscopic system. Finally the values of these quantities are calculated as functions of temperature.

In particular, for the thermal-conductivity coefficient the relationship [2]

$$\lambda = \beta^{-1} \int_0^\infty dt \int_0^\beta d\lambda^* < I^{(p)}(x,\ 0)\, I^{(p')}(x,\ t + i\lambda^*) >, \tag{1}$$

may be obtained, where $\beta = (kT)^{-1}$; t, time; $I(x,\ t) = e^{-iHt} I(x,\ 0)$. Equation (1) is valid for both classical and quantum systems.

The viscosity coefficient is determined from the expression

$$\eta = \lim_{N,V\to\infty} \frac{1}{VkT} \int_0^\infty dt < I(0)\, I(t) > = \frac{n}{kT} \int_0^\infty dt \int dp^* \frac{p_x^* p_y^*}{m} \Phi(p^*,\ q,\ t) - $$
$$- \frac{n^2}{kT} \int_0^\infty dt \int dp_1^* dp_2^* dr_{12} \frac{r_{12,x}}{2} \frac{\partial \varphi (r_{12})}{\partial r_{12,y}} \Phi(p_1^*,\ q_1,\ p_2^*,\ q_2,\ t), \tag{2}$$

p_i^*, q_i characterize the momentum and position of the i-th particle; $r_{ij} = q_i - q_j$; $\varphi(r_{ij})$ is the intermolecular interaction potential; V, volume;

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$$I(0)=\sum_{i=1}^{\infty}\frac{p_{ix}^{*}p_{jx}^{*}}{m}-\frac{1}{2}\sum\sum_{i\neq i}^{N} r_{ij,x}\frac{\partial\varphi(r_{ij})}{\partial r_{ij,y}}.$$

The correlation functions Φ_S are defined in the general form:

$$\Phi_s(p_1^{*},\ q_1,\dots,p_s^{*},\ q_s,\ t)=\lim_{N,V\to\infty}\frac{V^s}{N!Z_N}\int dp_{s+1}^{*}\,dq_{s+1}\dots$$

$$\dots dp_N^{*}\,dq_N\,e^{-tH}I(0)\,e^{-\beta H}.$$

Expanding the correlation functions in a series and limiting ourselves to the case of binary collisions, it may be shown [3] that Eq. (2) coincides with the analogous equation obtained by Chapman–Enskog theory [4].

The second approach to describing transfer properties at low temperatures is connected with solving the classical Boltzmann equation. Uehling and Uhlenbeck offered an intuitive generalization of the classical Boltzmann equation to the quantum case (i.e., a correction to the Boltzmann equation in the presence of quantum effects). Such a description with the limitations $p^{*}\gg\hbar/\bar{l}$ and $kT\gg\hbar/\tau$ permits the particles to be considered classical, i.e., simultaneously possessing a coordinate and quasimomentum. Quantum effects are produced by the symmetry properties of the multiparticle wave function characterizing the wavelike propagation of a perturbation, and are statistical in nature.

A number of studies have considered the influence of quantum effects on transfer properties [4-10]. In particular, it was demonstrated in [4] that "at room temperature diffraction effects reach a measurable magnitude in helium and hydrogen but are insignificant in heavy gases. At low temperatures quantum corrections produced by these effects become significant for helium and hydrogen, and are completely detectable in heavy gases also. Symmetry effects become significant only at very high densities or very low temperatures."

A numerical evaluation of the contribution of quantum effects to the thermal conductivity and viscosity of light gases is of interest. Such an evaluation permits establishment of the temperature range in which the behavior of transfer properties will differ significantly from classical behavior.

Solution of the Boltzmann equation by the Chapman–Enskog method leads to an equation for the thermal conductivity and viscosity coefficients in the form [4]

$$\lambda=25c_vT(16\Omega^{(2,2)})^{-1}[1\pm nh^3(2\pi mkT)^{-3/2}\delta_\lambda^{(1)}]=\lambda_0(1\pm\varepsilon_\lambda),$$

$$\eta=5kT(8\Omega^{(2,2)})^{-1}[1\pm nh^3(2\pi mkT)^{-3/2}\delta_\eta^{(1)}]=\eta_0(1\pm\varepsilon_\eta).$$

The quantities ε_λ and ε_η which consider the contributions of symmetry effects to the thermal-conductivity and viscosity coefficients are determined by the equations

$$\varepsilon_\lambda=\pi^{3/2}n\bar{\lambda}^3\delta_\lambda^{(1)},\qquad(3)$$

$$\varepsilon_\eta=\pi^{3/2}n\bar{\lambda}^3\delta_\eta^{(1)}.\qquad(4)$$

We express $\delta_\lambda^{(1)}$ and $\delta_\eta^{(1)}$ in terms of standard collision integrals.

In the first approximation

$$\delta_\eta^{(1)}=2^{-7/2}\left[4-\frac{128}{3^{3/2}}\frac{\Gamma^{(2,2)}}{\Omega^{(2,2)}}\right],$$

$$\delta_\lambda^{(1)}=2^{-7/2}\left[7-\frac{128}{3^{3/2}}\frac{\Gamma^{(2,3)}+6\Gamma^{(2,2)}}{9\Omega^{(2,2)}}\right],$$

where

$$\sqrt{\frac{2\pi\mu}{kT}}\,\Gamma^{(n,t)}=\int_0^\infty e^{-\frac{4}{3}\gamma^2}\gamma^{2t+3}Q^{(n)}\,d\gamma,$$

$\gamma^2=\hbar^2\varkappa^2/2\mu kT$; $\varkappa$, a quantum number characterizing the relative kinetic energy in paired collisions; $Q^{(n)}$, effective section.

It can be shown that

$$\delta_\lambda^{(1)}=2^{-7/2}\left[7-3.464\left(2+\frac{\Omega^{(2,3)*}}{\Omega^{(2,2)*}}\right)\right],$$

$\delta_\eta^{(1)}=-0.598$, independent of temperature.

TABLE 1. Quantum Corrections to Helium-4 Thermal-Conductivity Coefficient

T, °K	4	5	10	20	40	60	80	100	150	200	300	500
δ, %	76	71	49	20	4	1.6	0,8	0,46	0,2	0,15	0,04	0,03

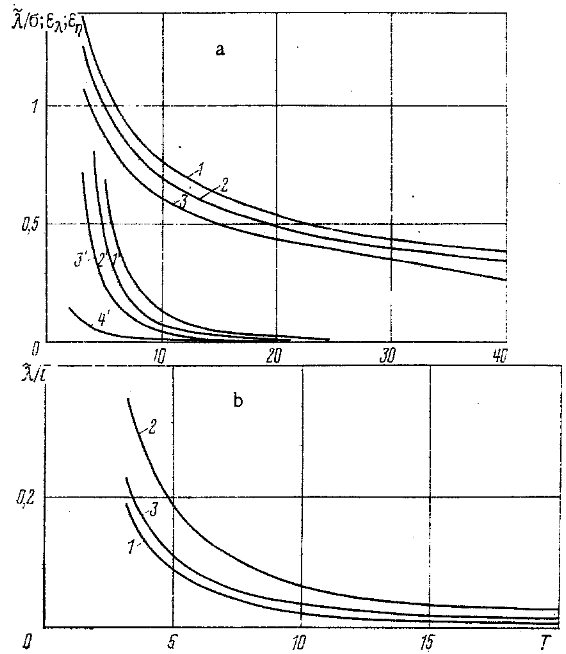

Fig. 1. Temperature dependence of quantities ε_λ [a: 1) $\tilde{\lambda}/\sigma$, H_2, 2) $\tilde{\lambda}/\sigma$, He^3, 3) $\tilde{\lambda}/\sigma$, He^4, 1') $\varepsilon_\lambda \cdot 10$, H_2, 2') $\varepsilon_\lambda \cdot 10$, He^3, 3') $\varepsilon_\lambda \cdot 10$, He^4, 4') ε_η, He^4; and b: 1) He^4; 2) H_2; 3) He^3] helium and hydrogen isotopes.

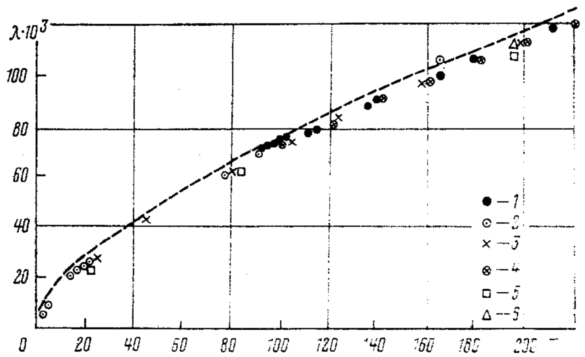

Fig. 2. Comparison of theoretical and experimental results on thermal conductivity of helium-4: 1) data of [11]; 2) [12]; 3) [13]; 4) [14]; 5) [15]; 6) [16]. $\lambda \cdot 10^3$, W/m·°K; T, °K.

Using Eqs. (3), (4) with collision integrals for the Lennard-Jones (12-6) potential [17] the values of the quantum corrections to thermal conductivity and viscosity of gases were calculated. Their temperature dependence is shown in Fig. 1a. The hypothetical quantum correction considering symmetry effects for the thermal-conductivity coefficient of hydrogen below 20.28°K is also presented to illustrate the effect of molecular weight on the magnitude of the quantum correction. For p = 1 atm the symmetry effects are insignificant, since $\tilde{\lambda}/\bar{l} < 1$ (Fig. 1b), and become apparent at p = 10 atm and higher.

As is evident from Fig. 1a, diffraction effects, characterized by the ratio $\tilde{\lambda}/\sigma$ become quite small at temperatures above 20°K. Table 1 shows the temperature dependence of the quantity $\delta, \% = \frac{\lambda_q - \lambda_c}{\lambda_c} \cdot 100$, where λ_c is the thermal-conductivity coefficient calculated by classical theory and λ_q is the same quantity determined by quantum theory. It is evident that with growth in temperature quantum effects produce an ever smaller contribution to thermal conductivity and become practically insignificant at p = 1 atm above 20°K.

A comparison of theory with experimental results on thermal conductivity of helium-4 at p = 1 atm are presented in Fig. 2. The theoretical results were obtained by Chapman–Enskog theory with consideration of quantum effects, with the calculations using the Lennard-Jones potential.

In conclusion, we must note that the transfer properties of light gases and their mixtures at very low temperatures and high pressures have in fact not been studied, and in that case it is impossible to give a numerical evaluation of the influence of quantum effects.

NOTATION

$\hbar = h/2\pi$, Planck's constant; k, Boltzmann's constant; c_V, heat capacity of gas; T, temperature; λ, thermal-conductivity coefficient; n, numerical gas molecule density; m, mass of molecule; σ, diameter; $\bar{l}$, mean molecular free path length; $\Omega^{(2.2)}$, collision integral; $\Omega^{(2.2)*}$, reduced collision integral; $\tilde{\lambda}$, de Broglie wavelength; μ, reduced mass of molecule; p*, momentum; τ, free path time; r, intermolecular distance.

LITERATURE CITED

1. P. S. Zyryanov and M. I. Klinger, Quantum Theory of Electron Transfer Phenomena in Crystalline Semiconductors [in Russian], Nauka, Moscow (1976).
2. J. Chester, Theory of Irreversible Processes [Russian translation], Nauka, Moscow (1966).
3. E. G. D. Cohen and M. H. Ernst, Phys. Lett., 5, 192 (1963).
4. J. O. Hirschfelder, et al., Molecular Theory of Gases and Liquids, Wiley-Interscience (1964).
5. S. Chapman and T. Cowling, Mathematical Theory of Non-Uniform Gases, 3rd ed., Cambridge University Press (1970).
6. E. G. D. Cohen, M. J. Offenhaus, J. M. J. Van Zeeuwen, B. W. Roos, and J. De Boer, Physica, 22, No. 9 (1956).
7. V. S. Zuev (editor), Thermodynamics of Gases [in Russian], Mashinostroenie, Moscow (1970).
8. E. A. Mason and W. E. Rice, J. Chem. Phys., 22, No. 3 (1954).
9. V. S. Yargin and G. I. Belashova, Inzh.-Fiz. Zh., 27, No. 6 (1974).
10. V. I. Aleinikova, Author's Abstract of Candidate's Dissertation, A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR (1976).
11. A. G. Shashkov, N. A. Nesterov, V. M. Sudnik, and V. I. Aleinikova, Inzh.-Fiz. Zh., 30, No. 4 (1976).
12. G. B. Ubbink and W. J. de Haas, Physica, 10, 465 (1943).
13. I. F. Golubev and I. B. Shpagina, Grazov. Prom-st', 40, No. 8 (1966).
14. A. L. Johnston and E. R. Grilly, J. Chem. Phys., 14, 233 (1946).
15. A. Eucken, Phys. Z., 14, 324 (1913).
16. W. Kannulik and E. Carman, Proc. Phys. Soc., 65, B, 701 (1952).
17. A. G. Shashkov and T. N. Abramenko, Thermal Conductivity of Gas Mixtures [in Russian], Énergiya, Moscow (1970).