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The Quantum-Mechanical Contributions of the Terms Arising from Higher Order Approximations on Gaseous Viscosity and Thermal Conductivity.

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I. Introduction. Since the study of Massay and Mohr,(1) gaseous viscosity was often treated and discussed quantum-mechanically by several authors, among whom the senior author(2) is included. However, perfect agreement between theory and experiment has not been obtained, even by the adjustment of the intermolecular potential as tried by Massay and Buckingham(3) and Uehling and Hellund.(3) Such result may be due to two following reasons. Firstly the effect due to ternary collisions, the role of which becomes conspicious at low temperature, was not taken into account. Secondly they applied viscosity formula of the first order approximation in spite of the suspicion that the contributions arising from the higher order ones may not be neglected. In the works published by the senior writer the same formula was also adopted. Then it will be the next step to know quantitatively to what degree these two effect contribute quantum-mechanically, before we carry on the detailed treatment, e.g., introduction of some complicated model.

It is the aim of the present paper to clarify the first effect on viscosity on one hand and, applying its basic numerical value, to the thermal conductivity which has never been studied quantum-mechanically on the other. Helium which will show probably most marked effect was adopted as the object of the research by use of two models, i. e. that of rigid elastic sphere and that of Slator's potential.

II. Theoretical Formula. i) *Viscosity:* According to the rigorous theory of Chapman and Enskog, the gaseous viscosity η is expressible with respect to every types of the adopted model by the formula :(4)

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(1) H. S. Massay and C B.C. Mohr, *Proc. Roy. Soc.* A **141,** (1933) 434.

(2) H. Hirota, *Bull Chem. Soc. Japan,* **19,** (1944) 109.

(3) H. S. Massay and R. A. Buckingham, *Proc. Roy. Soc.,* A **168,** (1938) 378; **169,** (1939) 304; E. A. Uehling and E. J. Hellund. *Phys. Rev.,* **54,** (1938) **479.**

(4) Chapman and Cowling, " Mathematical Theory of Non-uniform Gases," Cambridge (1939).

$$\eta = \frac{5}{8}\,\frac{kT}{\Omega^{(2)}(2)}\,(1+\varepsilon_1+\epsilon_2+\cdots\cdots\cdots) \qquad 1)$$

Small terms ϵ_i's arising from the higher order approximations and will be called i-th order approximation terms. The first and second approximation-terms are expressed, respectively, by use of the usual notation which is the same as the previous papers (Cf. Chapman and Cowling, ibid.) as:

$$\varepsilon_1 = b_{12}^2 \Big/ \begin{vmatrix} b_{11} & b_{21} \\ b_{12} & b_{22} \end{vmatrix}, \qquad 2\,\mathrm{a})$$

and

$$\varepsilon_2 = b_{11} \begin{vmatrix} b_{21} & b_{22} \\ b_{31} & b_{32} \end{vmatrix}^2 \Big/ \begin{vmatrix} b_{11} & b_{21} \\ b_{12} & b_{23} \end{vmatrix} \begin{vmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{52} & b_{33} \end{vmatrix}, \qquad 2\,\mathrm{b})$$

where $b_{11} = 4\Omega^{(2)}(2)$, $b_{12} = b_{21} = 7\Omega^{(2)}(2) - 2\Omega^{(2)}(3)$,

$$b_{22} = \frac{301}{12}\Omega^{(2)}(2) - 7\Omega^{(2)}(3) + \Omega^{(2)}(4)$$

$$b_{13} = b_{31} = \frac{63}{8}\Omega^{(2)}(2) - \frac{9}{2}\Omega^{(2)}(3) + \frac{1}{2}\Omega^{(2)}(4),$$

$$b_{23} = b_{32} = \frac{1365}{32}\Omega^{(2)}(2) - \frac{321}{10}\Omega^{(2)}(3) + \frac{25}{8}\Omega^{(2)}(4) - \frac{1}{4}\Omega^{(2)}(5),$$

$$b_{33} = \frac{25137}{256}\Omega^{(2)}(2) - \frac{1755}{32}\Omega^{(2)}(3) + \frac{381}{32}\Omega^{(2)}(4) - \frac{9}{8}\Omega^{(2)}(5) + \frac{1}{16}\Omega^{(2)}(6) + \frac{1}{2}\Omega^{(4)}(4),$$

$$\Omega^{(l)}(r) = \sqrt{\pi}\int_0^\infty e^{-V^2}\,V^{2r+2}\,\phi^{(l)}\,dV,$$

$$\phi^{(l)} = \frac{v}{2\pi}\,Q_\eta^{(l)}(v), \qquad V = \sqrt{\frac{M}{2kT}}\,v.$$

(M: mass of a colliding particle; v: its velocity.)

$Q_\eta^{(l)}$ has the dimension of square of length and $Q_\eta^{(2)}$ corresponds to the so-called viscosity "cross-section" of rigid elastic sphere. Classical quantity of $Q_\eta^{(l)}$, which will be hereafter denoted as $Q_{\eta_0}^{(l)}$, is given by $\frac{\pi}{2} r_0^2 \left[2 - \frac{1}{l+1}(1+(-1)^l)\right]$ $(l = 1, 2\cdots\cdot)$, r_0 denoting the molecular diameter. Thus $Q_{\eta,0}^{(2)}$ and $Q_{\eta,0}^{(4)}$, which are concerned in the present paper, equal to $\frac{2}{3}\pi r_0^2$ and $\frac{4\pi}{5} r_0^2$, repsectively. Quantum-mechanically, $Q_\eta^{(l)}$ depends upon the velocity of colliding particles (v), so it will be denoted as $Q_\eta^{(l)}(v)$, if necessary. $Q_\eta^{(l)}(v)$ and $Q_\eta^{(4)}(v)$ are given by the following formula in the cases of the similar collisions:

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(5) Chapman and Cowling, ibid., p. 169.

$$Q^{(2)}_{\eta}(v) = \frac{4\pi}{k^2}\sum_n \Big\{\sin\delta_n \frac{4n^3+6n^2-2n-2}{(2n+1)(2n+3)} - \cos(\delta_n-\delta_{n-2})\sin\delta_n \sin\delta_{n-2}\frac{2(n+1)(n+2)}{2n+3}\Big\}, \qquad 3\text{ a)}$$

and

$$\begin{aligned}Q^{(4)}_{\eta}(v) = \frac{4\pi}{k^2}\sum_n \Big\{&(2n+1)\sin^2\delta_n - \frac{1}{2n+1}\Big[\frac{n^2(n-1)^2}{2n-1}\sin^2\delta_{n-2} \\ &+ \frac{(4n^3+6n^2-1)}{(2n-1)(2n+3)}\sin^2\delta_n + \frac{(n+1)^2(n+2)^2}{(2n+3)^2}\sin^2\delta_{n+2} \\ &+ \frac{(4n^3+6n^2-1)(n+1)n}{(2n-1)^2(2n+3)}\sin\delta_n\sin\delta_{n+2}\cos(\delta_{n+2}-\delta_n) \\ &+ \frac{(4n^3+6n^3-1)(n+1)(n+2)}{(2n-1)^2(2n+3)^2}\sin\delta_n\sin\delta_{n+2}\cos(\delta_{n+2}-\delta_n) \\ &+ \frac{n(n-1)(n+1)(n+2)}{(2n-1)(2n+3)}\sin\delta_{n-2}\sin\delta_{n+2}\cos(\delta_{n+2}-\delta_{n-2})\Big]\Big\}\end{aligned} \qquad 3\text{ b)}$$

where $k = \frac{\pi M v}{h}$ and δ_n is the phases of n–th waves. In the former paper δ_n has been calculated extensively in case of rigid elastic sphere models, and $Q^{(2)}_{\eta}$ of this model was shown to vary in such a way that it becomes larger as the velosity is decreased. This tendency is concordant qualitatively with the experimental results of the temperature effect on viscosity, though yet insufficient quantitatively.

The terms of higher order approximation are calculated by Chapman in cace of rigid elastic sphere model; i. e., $\varepsilon_1 = 0.01485$, $\varepsilon_2 = 0.00103$, $\varepsilon_3 = 0.00012$ $(\varepsilon_1+\varepsilon_2+\varepsilon_3 = 0.01600)$. As these terms are small and independent upon temperature, it may be considered that no serious change will occur in the arguement as usually done, even if they are neglected. However, it cannot be admitted quantum-mechanically that these terms are practically independent upon temperatures. Such conclusion gives us the reason to carry on the present research which tries to clarify the degree of contribution of the terms.

ii) *Thermal conductivity*: The gaseous thermal conductivity is given(*), using the similar notation as Eq. (1), by

$$\lambda = \frac{25}{16} C_v \frac{kT}{\Omega^{(2)}(2)}(1+\varepsilon_1'+\varepsilon_2'+\cdots\cdots); \qquad 4)$$

here C_v denotes the molecular specific heat at constant volume and ε_i' the i-th order approximation term; ε_1' is shown as,

$$\varepsilon_1' = a_{12}^2 / (a_{11}a_{22}-a_{12}^2) \qquad 5)$$

(*) Cf. Chapman and Cowling, p. 169.

where $a_{11}=b_{11}$, $a_{12}=b_{12}$ and $a_{22}=b_{22}=\frac{35}{24}b_{11}$.

Theoretically, it is convenient to discuss thermal conductivity by a quantity f defined by

$$f=\lambda/(\eta\cdot C_v)\,. \qquad 4\text{ a)}$$

As C_v is constant in case of rigid elastic sphere model, and with respect to the same model, $\varepsilon_1'=0.02273$, $\varepsilon_2'=0.00209$ and $\varepsilon_3'=0.00031$ ($\varepsilon_1'+\varepsilon_2'+\varepsilon_3'=0.02513$) for all temperatures classically. Thus f_1 equals to $2.5\frac{1+\varepsilon_1'}{1+\varepsilon_1}$, according to the formulas (1) and (3), and the higher order approximation gives us also practically the similar constant value (2.5), because the factor $(1+\varepsilon_1')/(1+\varepsilon_1)$ neaaly equals to one, (in case of the above model, 1.00885). Though the conclusion holds well at ordinary temperatures, it was denied at low temperatures at least for helium by Eucken and later by Weber(6); 2.51 at 2.73° K, 2.23 at 81° K and 2.02 at 21° K.(†)

It will be interesting to investigate the quantal contribution on f as well as viscosity itself. In the present paper it was tried only by means of the same simplest model as done in the study of viscosity, though more difinite conclusion may be obtained, if some other specific model be adopted.

iii) *Terms determined in this paper*: Three terms ε_1, ε_2 and ε_1' were determined actually because procedure of the further approximation is very difficult numerically. The conclusion will, however, be nearly sufficient for the object of study even at this stage of approximation. Because the values here obtained are found to be comparable order of magnitude with the classical ones and their temperature dependencies are not so large, the contribution of the further terms thus being negligibly small.

III. **Calculation and Discussion of ε_1 and ε_1' in Case of Rigid Elastic Sphere Model.** i) *Assumptions and Calculations*: It was assumed that the diameter of helium was 2.0 A or 2.1 A, similary as in the former papers.(2) Though the basic numerical results of Bessel function of half-integers ($J_{\nu+\frac{1}{2}}(x)$ already obtained were utilized as much as possible, it was obliged newly to perform trouble calculations complimentarily and also to take more figures down one or two places in order to determine $\Omega^{(l)}(\alpha)$ ($\alpha=2,3,4\ldots,7$) accurately. Integration of the latter values was performed graphically, so their ranges of error occurred in the final values

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(6) A Eucken, *Phys. Zeits.*, **14**, (1913) 324; Weber, *Ann. der Physik*, **54**, (1918) 325, 437, 481; **82**, (1927) 479.

(†) Cf. course other molecules, which have the internal degrees of freedom, lower values may be expected as suggested by Eucken. Such discussion will be omitted in the present treatment.

were not clear (ambiguous figures were shown by a small style in the table).

The obtained ε_1 and ε_1' values together with $\frac{b_{22}}{b_{11}}$, $\frac{b_{12}}{b_{11}}$ etc., are shown in table 2. The constants used consistently in the present series of papers are shown in table 1.

Table 1. Universal Constants Employed in the Present Series of the Research. (by K. Shiba)

Planck's Constant (h)	6.624×10^{-27}	erg. sec
Temperature of the Ice Point	273.16° K	
Joul's Constant	4.1858×10^{7}	erg. cal.
Avogadro's Number	6.023×10^{-7}	
Boltzmann's Constant (**k**)	1.3804×10^{-16}	erg. deg.$^{-1}$

ii) *Discussions*: As shown in the table 2, the lower is the temperature, the smaller is ε_1, it increases asymptotically to the classically to the classical values as the temperature rises. Such temperature dependency of viscosity conforms with the tendency due to the quantal effect on "cross-section", though the degree of the improvement by the term ε_1 is not so large.

The variation due to molecular radius (Cf. the result of r_0 2.0 and 2.1 A) seems also to be small. The theoretical viscosity was redetermined by multiplying the first approximation term by the factor $1+\varepsilon_1$ (assuming molecular radius $r_0 = 2.1$ A, in which case the coincidence of theory and experiment was the better in lower temperatures). The comparison, which is given by table 3, denotes that the introduction of the second approximation terms do not fulfil our object yet to obtain the perfect agreement between theory and experiment.

Nextly the term $(1+\varepsilon_1')/(1+\varepsilon_1)$ tablated in the last column of table 2 will be discussed. It is nearly constant from 89° to 1090° K and also practically equal to the classical one. So for every monoatomic molecules, f will be 2 53, so far as the rigid elastic sphere model is concerned. Thus even if the contribution and quantal correction of the term $\frac{1+\varepsilon_1'}{1+\varepsilon_1}$ are taken into consideration, there is practically few improvement in the divergency from the experimental values. Therefore the result on the thermal conductivity also suggests it to be necessary that some new way of attack is to be tried.

Table 2. Numerical Results for the Helium Gas.

Radius of Helium	Temp. (°K)	b_{12}/b_{11} $(=a_{12}/a_{11})$	b_{22}/b_{11} $(=a_{22}/a_{11}=35/24)$	ε_1	ε_1'	$\frac{1+\varepsilon_1'}{1+\varepsilon_1}$
2.0 Å	15	-0.13_1	4.2	0.004_6	0.007_1	1.002_5
	88.5	-0.20_7	4.2	0.010_3	0.0_16	1.006
	273.1	-0.21_7	4.2_5	0.011_2	0.018	1.006
	680	-0.23_2	4.2_5	0.012_8	0.020	1.007
	1090	-0.24_6	4.2_5	0.0144	0.022	1.007
2.1 Å	273	-0.21_8	4.2_6	0.0114	0.017	1.006
Classical Case	For all temp.	−0.25 (=−1/4)	4.27 (=205/48)	0.01485	0.02273	1.008

Table 3. Gaseous Viscosity of Helium. $\eta(\times 10^6)$

Temp. (°K)	η(Obs)	η(Calc.) First Approx.		η(Calc.) Second Approx.		Classical*
		r=2 1 A	2.0	2.1	2.0	——
15.0	29.5	30.5	32.5	30.8	32.9	46
88.8	91.8	93.4	101.8	94.4	102.9	110
273.1	187.0	177.9	194.9	180.0	197.3	193
680	343.6	294.6	323.2	298.4	326.7	313
1090	471.3	378.8	415.8	384.3	420.5	386

* Atomic radius was adopted properly, so as to obtain the perfect coincidence of at 373° K.

IV. **Calculations and Discussions of ε_2.** The second approximation term ε_2 was then calculated only at 15° and 273.1° K, due to the complicated procedure of its calculation, especially due to the occurrence of the term $Q^4_\eta(v)$ included in $\Omega^{(4)}_i(v)$ or in b_{33}. $'Q^{(4)}_i(v)$ given by Eq. (3 b) was calculated and ratios of these to $Q^{(4)}_{\eta,0}$ are tabulated against kr_0 in table 4.

Table 4. $Q^{(4)}_\eta \,/\, Q^{(4)}_{\eta,0}$

kr_0	0.5	1	1.5	2	3	4	5	10
$Q^{(4)}_\eta \,/\, Q^{(4)}_{\eta,0}$	7.37	5.61	3.45	2.19	1.80	1.65	1.67	1.68

The final results obtained were shown in table 5 with those of classical ones.

Table 5. The Second Approximation Term ε_2.

Method of Calculation	Temperature	b_{13}/b_{11}	b_{23}/b_{11}	b_{33}/b_{11}	ε_2
Quantal Method	15° K	0.0038	−0.721	8.55	0.00009
	273.1	−0.0024	−1.093	8.67	0.00077
Classical Method	Indep.	−0.03125	−1.273	11.61	0.00103
	on Temp.	(−1/32)	(163/128)	(11889/1024)	

It is found that quantum-mechanical value of ε_2 at ordinary temperature is of the same order as classical one at 273° K, while it becomes smaller at lower temperatures. However, their absolute values being small as compared with the second approximation term ε_1, it may almost be negligible for the usual discussions.

V. **Calculations and Discussions for Some Special Model.** Judging from the above results, it will be interesting to calculate ε_1 and ε_1' in such a case where some model of molecular interaction nearer to the actual molecule than the rigid elastic sphere is introduced.

Massay and Buckingham(3) calculated the viscosity at low temperatures by use of 1.3 times of Slator's potential(7) : i.e.,

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(7) On the reason of the factor 1.3, Cf. *Proc. Roy. Soc.* A **169,** (1939) 204.

$$V(r) = 7.7 \times 10^{-10} \exp (r/0.217 - 1.47 \times 10^{-12} r^6) \text{ erg},$$

r being the distance between the centres of helium atoms, and found that the agreement at temperatures above 15° K is quite good though the calculated values are slightly too large, while below 15° K the agreement becomes less satisfactory and the discrepancy is in the opposite sence; Exper. value was 12.67×10^{-6}, while calc. value 10.7×10^{-6} at 4.23° K.(8)

The present authors used their δ_n values and calculated ε_1 and ε_1' at 4.23° K and tested if the above descrepancy might be decreased. The result is, $a_{12}/a_{11} = b_{12}/b_{11} = 0.73$, $b_{22}/b_{11} = 4.1$, $a_{22}/a_{11} = 2.6$, so $\varepsilon_1 = 0.001$ and $\varepsilon_1' = 0.002$ by Eqs. (2 a) and (4); that is by use of the present model, the terms of the second order approximation ε_1 and ε_1' are also positive and very small, if compared with the classical values (0.014 and 0.227, respectively). Therefore, there occurred few improvement in viscosity as compared with that of the rigid elastic sphere model. (Cf. table 2.), so that the discrepancy of 20% cannot be almost diminished.

One way of settling the above difficulty is to obey the conclusion that it is necessary to find some suitable potential function as asserted by Massay and Buckingham; Hellund really suggested(9) that the intermolecular potential of helium determined emperically from the data of viscosity is fairly more complicated than that of Slator. However it will be rather reasonable that the effect due to ternary collison becomes more important, especially for the viscosity at lower temperatures. Simple calculation showed us that the reasoning is plausible.

Summary

The quantum-mechanical contribution of the terms arising from higher order approximation on viscosity and thermal conductivity has been calculated by use of the rigorous formula of Chapman and Enskog. The contributions are found in both properties to be so slight that it may be negligible with respect to both models adopted (rigid elastic sphere and Slator's potential).

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(8) Theoretical value calculated by us was 10.4×10^{-6}. The difference will be ascribed to the error arising from the numerical integration.

(9) E. J. Hellund, *Phys. Rev.*, **58**, (1940) 278.