The Quantum-Mechanical Treatment of Voscosity Coefficient of Helium by Use of a Rigid Sphere Model with Attractive Force.

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1. Introduction.

In the former reports[1),(2)], it was studied if the quantum-mechanical effect can fill up the gap between theoretical and experimental temperature dependency of the viscosity coefficient, and it was concluded definitely that the effect is short of explaining the gap in case of helium, so far as the rigid elastic sphere model is concerned. Therefore, the next step to be taken will be the introduction of molecular interaction in the calculation, as Massay and Buckingham[3)] already did by use of Slater's potential. However, it was obliged to conclude that the concordance attained by them was limited in some narrow temperature-range, because the evaluation on higher temperatures was hindered by the cumbersome numerical integration. The final aim of the theory, therefore, has not been attained yet.

It is the object of the present paper to introduce a relatively less complicated model in the calculation, with the view to investigate the contribution of the molecular attraction on the collision phenomena. The well-known "Sutherland" model was adopted, assuming the potential form of inverse cube-law-force was the attractive potential to be utilized, i. e.,

$$V(r) = \infty, \quad \text{if } r < r_0 \quad \text{and} \quad \beta/r^2, \quad \text{if } r > r_0 \qquad (1)$$

where β denotes a constant and r_0 is the least distance of the molecular encounter.

The above attraction potential was adopted mainly for convenience's sake of the calculation, even though it is slightly improper as compared with the potential form of the sixth order, now aknowledged generally.

In the present report, the calculation was carried out on helium, keeping other assumptions as similarly as in the former report.[2)]

II. Theoretical Formula.

(1) K. Hirota, A. Takahashi, and T. Yoshitomi, this Bulletin, **20** (1947), 1.

(2) K. Hirota, this Bulletin **19** (1944), 102.

(3) H.S. Massay and R. A. Buckingham, *Proc. Roy. Soc.*, A, **168** (1938), 304.

The aim of this paper can be reduced to a mathematical problem of evaluating the term (R) which is dependent on molecular interaction in Chapman-Enskog's formula[4] of the viscosity by use of such a model as (1):

$$\eta = \frac{10\kappa^2 T^3}{\mu}\left(\frac{4\pi\kappa T}{\mu}\right)^{\frac{3}{2}} \frac{1+\varepsilon_1+\varepsilon_2+\cdots}{\pi R} \tag{2}$$

where

$$R = \frac{1}{2}\int_0^\infty Q_\eta v^7 e^{-\frac{\mu v^2}{\kappa T}} dv \tag{3}$$

ε_ν: the ν-th order approximation term; Q_η: viscosity "Cross-section"; κ: Boltzmann's constant; μ and v: reduced mass and velocity of the colliding molecules, respectively; T: absolute temperature.

In the treatment, the first order approximation term (ε_1) was only calculated, while the higher order approximation terms (ε_2, ε_3, etc.) were neglected, according to the conclusion in the previous paper[1] that they are small irrespective to the model adopted.

The viscosity cross-section is given by[5]

$$Q_\eta = \frac{2\pi}{k}\sum_n \{1+\tilde{\varepsilon}^n\}\left\{\sin^2\delta_n \frac{4n^3-6n^2-2n+2}{(2n+1)(2n+3)} - \cos(\delta_n-\delta_{n-2})\sin\delta_n \sin\delta_{n-2}\frac{2(n+1)(n+2)}{2n+3}\right\} \tag{4}$$

where $k = \frac{2\pi\mu v}{h}$ and $\tilde{\varepsilon}$ equals to 0, 1, −1 according as the statistics is Boltzmann's, Bose-Einstejn's or Fermi-Dirac's, respectively, and −1 was utilized throughout in this paper, because collisions of similar molecules were only dealt with. Summation was carried out with respect to all the scattered de Broglie's waves, and δ_n's are their phases which are to be determined from the solution of the wave equation with the boundary condition (1), i.e., the wave amplitude is zero at the molecular distance of r_0.

As the field is symmetrical to the centre of the scattering molecules, the problem is reduced to the solution of the radial part of the wave function u:

$$\frac{d^2u}{dr^2} + \left\{k^2 + \frac{n(n+1)}{r^2} - \frac{8\pi^2\mu}{h^2}V(r)\right\}u = 0 \tag{5}$$

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

(5) Cf. Chapman and Cowling, *ibid.*, Chapt. 17.

where r is the radial distance from the molecular centre of the colliding molecules.

Under the assumptions of (1),

$$\frac{d^2u}{dr^2}+\left\{k^2+\frac{n(n+1)-\gamma}{r^2}\right\}u=0 \qquad (5')$$

where $\gamma=8\pi\mu\beta/h^2$ at $r>r_0$ and 0 at $r<r_0$, the general solution is given by

$$U=\sqrt{r}\{AJ_{\nu+}(kr)+BJ_{\nu-}(kr_0)\} \qquad (6)$$

where ν_+ and ν_- denote $\nu_\pm=\frac{1}{2}(-1\pm\sqrt{(2n+1)^2+8})$, respectively.

The derivation of this formula is given by Mott and Massay.[6]

Taking the boundary condition $u=0$ at r_0 into consideration, we obtain

$$\delta_n=\operatorname{arctg}(-1)^n\{J_{\nu+}(kr_0)/J_{\nu-}(kr_0)\} \qquad (7)$$

where

$$v=(kh')/(2\pi\mu) \qquad (8)$$

III. Calculation and Results.

The numerical constants adopted in the calculation are as follows. The value of r_0 was assumed as 2.0 Å, because it was the best one in case of rigid elastic sphere models. The value of β was assummed as 8.9×10^{-32} c. g. s. and 1.12×10^{-32} for case A and B, respectively. They correspond to the assumption that the least energy at the distance of the molecular contact is, respectively, 800 and 1000 cal. Probably the least energy of attraction in the actual potential curve will exist within the two values. In other words, the attractive potential of liquid helium is estimated as such from the thermodynamic properties.

The procedure of calculation was perfectly similar to the case of rigid elastic sphere except the cumbersome evaluation of the Bessel function of non-integral orders. This most difficult procedure of the calculation was, however, simplified by the extrapolation of the values of Bessel functions $J_m(z)$ calculated by us.[7]

Thus it became possible to calculate the ratio of the quantal cross-section to that of the classical value $(Q_n/Q_{\eta 0})$ in each two cases. The

(6) "Atomic Collisions", Oxford (1933), Chap. 1.

(7) Generally ν's in (6) become irrational numbers, so they are evaluated only when m equals to 0.0, $\pm$ 0.1, $\pm$ 0.2. $\pm$ 0.3, ..., $\pm$ 4.9, 5.0. It was found that values larger than $m=5$ were unnecessary in the present object.

results are shown by Table 1 together with that by use of a rigid elastic sphere model, as the function of kr_0. As is known the attractive potential made the effective collisional area larger, and the ratio is fairly near to that of a rigid elastic sphere model in case of small attractive potential (case B). It is also found that the larger the kr_0, the less is the effect, and in case of large attractive potential (case A), it is needless to calculate the values higher than $kr_0 > 10$, because they are practically equal to that of a rigid elastic sphere model.

By use of the values of case A, η was calculated according to (2), those of similar collisions being used. It was found that the effect of the attractive potential became marked at lower temperatures, and at 88.8°K the effect does not bring any change of figures (101.8×10^{-6}). However, it is clearly shown that introduction of such attractive potential contributes, to some extent, to fill up the gap hitherto found in case of rigid elastic sphere models. (cf. the last column of Table 2.)

Table 1. Effective "Cross-section" (Q_η/Q_{τ_0}).

	Similar Collision			Dissimilar Collision		
kr_0	Rigid E. Sp. Model	Sutherland Model		Rigid E. Sp. Model	Sutherland Model	
		Case A.	Case B.		Case A.	Case B.
0.	8.000			4.000		
0.5	7.342			3.709		
1	5.535	6.673	5.63	3.108	3.64	3.18
1·5	3·585	3.727	—	2.556	2.500	—
2	2·287	2.163	2.271	2.168	2.217	2.17
2.5	1.866	1.895	—	1.653	1.973	—
3	1.757	1.960	1.795	1.780	2.075	1.809
4	1.596	1.638	1.599	1.570	1.642	1.598
5	1.466	1.448	1.462	1.468	1.498	1.464
7	1.327	1.332	—	1.329	1.345	—
10	1.234			1.229		
15	1.150			1.149		
20	1.113			1.110		
25	1.088			1.097		
30	1.070			1.070		
40	1.049			—		
50	1.039			—		

N. B. (Case A. the least energy of attractive force 800 cal.
Case B. ..... 1000 cal.

On the other hand, it was found that larger values of β can make the η-values at 15°K smaller as much as we desire, though they cannot do so at 89°K at the same time. Such tendency can be amended, if

Table 2. Calculated and Experimental Values of Viscosity Coefficient of Helium.

T°K	Viscosity Obser.	Classical Value	Viscosity R. E. Sp. $r_0=2.0$ A	calculated Model $r_0=2.1$ A	Sutherland M. $r_0=2.0$ A
1090	471.3	368	415.8	378.8	(415.8)
879	408.7	347	370.7	—	(370.7)
680	343.6	313	323.2	294.6	(323.2)
473	267.2	255	264.8	—	(264.8)
273.1	187.0	193	194.9	198.9	(194.9)
170.5	139.2	154	148.9	—	(148.9)
88.8	91.8	110	101.5	93.4	(101.8)
15.0	29.5	46	32.5	30.5	31.9

N. B. Values in parenthesis are the same as in the 4-th column.

we adopt a slower inclination of the repulsive potential. Thus we can got generally to a fairly good concordance of the theory and experiment, so far as monoatomic molecule is concerned.

Summary.

By use of a rigid sphere molecule model with attractive force of inverse cube law the viscosity coefficient of helium was calculated quantum-mechanically. It was found that the gap hitherto known between theory and experiment has become smaller at low temperatures than in case of no attractive force.

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