The Quantum Mechanical Treatment of Viscosity by Use of the Rigid Elastic Sphere Model. I. The Viscosity Coefficient of Gaseous Helium and Neon.

By Kozo HIROTA.

(Received April 4, 1944.)

Introduction. Now it has been shown necessary by several authors(1) to apply quantum mechanics in the theory of transport phenomena in gaseous substances, as was suggested by Professor Mizushima,(2) if the gases were at low temperatures, or if the molecular weights were small. Among the papers within which the problems were dealt quantitatively, the first is due to Massay and Mohr(1a) who applied the treatment to the viscosity coefficient of helium and hydrogen which can be expected to show the conspicuous difference between quantal and classical method, because of the smallness of the molecular weight. They showed that, in spite of assuming the molecules to be rigid elastic spheres, the temperature variation of the viscosity coefficient can be given more correctly by the quantal method than by the classical ones, though the coincidence left much to be desired from quantitative point of view, especially for hydrogen, the molecule of which was the softer of the two. Using a proper intermolecular potential, this gap was later filled up, as expected, by Massay and Buckingham(1c) for helium, and by Miyako(1f) for hydrogen. On the other hand, the similar idea has been applied to another problem, such as in the calculation of the second virial coefficient of the gases by several authors(1c)(1f)(3) and the effectiveness of such quantal method has been confirmed. So it seems now evident that the importance of the method leaves no doubt.

It is aimed in the present paper to treat more extensively the viscosity coefficient by this method, to see to what degree the quantum effect contributes to reconcile the discrepancy hitherto found between the classical theory and the experiment in comparatively heavier gases. To meet this aim, the rigid elastic sphere model was adopted for the simpleness of calculation on one hand, and for the re-examination of the result of Massay and Mohr on the other, because it was criticised by Uehling that it included some numerical errors. So neon, a comparatively light and hard spherical molecule next to the hydrogen and helium, has been selected as well as helium, as the object of the present research.

---

(1) (a) Massay and Mohr, *Proc. Roy. Soc.*, A**141** (1933), 433; (b) *ibid.*, **144** (1934), 188; (c) Massay and Buckingham, *ibid.*, **168** (1938), 378; (d) Uehling, *Phys. Rev.*, **46** (1938), 917; (e) Halpern and Gwathmey, *ibid.*, **51** (1937), 994; (f) Miyako, *Proc. Phys.-Math. Soc. Japan*, [3] **24** (1942), 852.

(2) Mizushima, *J. Chem. Soc. Japan*, (in Japanese), **53** (1932), 512.

(3) (a) Gropper, *Phys. Rev.*, **51** (1937), 1108; (b) Beth and Uhlenbeck, *Physica*, **4** (1937), 915.

In case of the rigid sphere model, the general formulation was given by Massay and Mohr, so it was used without any change.(4) However, their numerical values were insufficient for our purpose in many respects, so it was obliged to extend their calculation of the phases in more details, not only up to the higher overtones but also in more figures.

The General Formulation. According to the classical theory of Chapman and Enskog, the viscosity coefficient η at the temperature T is given as,

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

and

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

where Q=viscosity "cross-section";
κ=Boltzmann's constant;
μ=reduced mass;
v=velocity of the colliding molecules;
ε=a small term which denotes the interaction of the molecules.(5)

Q_η is given as,

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

where $\tilde{\varepsilon}$ is equal to 0,1,–1 according as the statistics is Boltzmann's, Bose-Einstein's or Fermi-Dirac's, respectively, and n is the number of the waves and δ_n's are the phases which are to be determined from the solution u of the Schrödinger equation:

$$\frac{d^2u}{dr^2} + \left\{k^2 - \frac{n(n+1)}{r^2} - \frac{8\pi^2\mu}{h^2}V(r)\right\}u = 0, \tag{4}$$

where the notations are ordinary ones.

Under the assumption of rigid sphere molecules,

$$V(r) = 0, \text{ if } r > r_0, \text{ and } V(r) = \infty, \text{ if } r \leq r_0, \tag{5}$$

where r_0 is the sum of the radii of the colliding molecules, Q_η which is designated hereafter as Q_{η_0} equals to $2/3\pi r_0^2$ and the solution is given by

---

(4) See, Chapman and Cowling, "Mathmatical Theory of Non-Uniform Cases," Cambridge (1940); Mott and Massay, "Theory of Atomic Collisions," London (1932).

(5) For repulsive force which is proportional to $1/r^n$, $\varepsilon=0$, when $n=5$, and as n increases ε rises only to 0.016 for $n=\infty$, this limiting case corresponds to the rigid elastic sphere, (*cf.* Kennard," Kinetic Theory of Gases", 147, New York (1939), Chapman and Cowling, *ibid.*, 218).

$$u = \sqrt{r}\left\{AJ_{n+1/2}(kr) + BJ_{n-1/2}(kr_0)\right\}, \tag{6}$$

and

$$\delta_n = \arctan\,(-1)^n\left\{J_{n+1}(kr_0)/J_{n-1/2}(kr_0)\right\}, \tag{7}$$

where k is given by the relation: $v=kh/2\pi\mu$.

Calculation of the Viscosity Cross-section. Phase values δ_n calculated by (7) for various kr_0 are shown in table 1a and 1b. Half order Bessel function $J_\nu(x)$ necessary for the procedure was calculated in case that the existing tables of it were inadequate for our purpose.(6)

The viscosity cross-section was then evaluated by (3), putting $\tilde{\varepsilon}= +1$, or 0 according as the collision was between similar or dissimilar molecules, respectively. In table 2, Q_η/Q_{η_0}, the ratio of the quantal "cross-section" to that of the classical one, is tabulated against kr_0, together with those by Massay and Mohr and by Uehling for the purpose of comparison.

As is shown in the table, it has been found that the result of Massay and Mohr is rather correct than that of Uehling, so far as the collision between similar molecules is concerned.(7) However, it can be concluded that some numerical errors really exist in the result Massay and Mohr in the dissimilar case; i.e., $Q_\eta/Q_{\eta_0}=a$) inclined to coincide in both similar and dissimilar cases when kr_0 is larger than 7 in the present studies, while the reversed result was found in the study of Massay and Mohr.

It is noteworthy that the value of a does not diminish so rapidly, e.g., it is 1.039 even at $kr_0=50$; quantum theoretical values are yet larger by 4% than the classical ones.(8) Therefore it must be remembered that for comparatively small and light molecules such as methane, ammonia and neon the quantum effect will affect the values of molecular diameters slightly, even if they are evaluated from the data at ordinary temperatures. Judging from the tendency of the decrease of the ratio a at larger kr_0, it was hoped to determine the value when a was larger than 50. However, as it was too tedius to do so, the plan was given up, and the values were determined, if necessary, by the interpolation from the curve and approximated formula, which gave the relation between kr_0 and a. For, over the range from $kr_0=7$ tc ∞, the calculated viscosity cross-section can be represented by

$$a = Q_\eta/Q_{\eta_0} = 1+\frac{A}{kr_0}+\frac{B}{(kr_0)^2}, \tag{8}$$

in which $A=1.90$, $B=4.00$ for both similar and dissimilar cases.(9)

---

(6) The table of $J_\nu(x)$ calculated will be published in the Bull. of the Central Laboratory of South Manchuria Railway Co. (in Japanese).

(7) Uehling did not calculate the dissimilar case.

(8) The value of kr_0 calculated from the mean velocity of helium at 100°C corresponds to about 50.

(9) Halpern and Gwathmey(1e) proposed such an approximate formula but their constants are not concordant with those here obtained, because their source of the determination is probably based upon the results of Massay and Mohr.

Table 1a. Values of the Phases $(-\delta_n)$.

n/kr_0	50	40	30	25	20
0	$16\pi-0.2655$	$13\pi-0.8407$	$10\pi-1.4159$	$8\pi-0.1328$	$6\pi+1.1504$
1	$15\pi+1.3258$	$12\pi+0.7541$	$9\pi+0.1882$	$7\pi+1.4781$	$6\pi-0.3704$
2	$15\pi-0.2055$	$12\pi-0.7657$	$9\pi-1.3159$	$7\pi-0.0127$	$5\pi+1.3004$
3	$14\pi+1.4256$	$11\pi+0.8760$	$8\pi+0.3550$	$7\pi-1.4634$	$5\pi-0.1200$
4	$14\pi-0.0654$	$11\pi-0.5905$	$8\pi-1.0822$	$6\pi+0.2680$	$5\pi-1.4897$
5	$14\pi-1.5361$	$10\pi+1.1056$	$7\pi+0.6550$	$6\pi-1.1012$	$4\pi+0.3334$
6	$13\pi+0.1551$	$10\pi-0.3147$	$7\pi-0.7136$	$5\pi+0.7113$	$4\pi-0.9332$
7	$13\pi-1.2753$	$9\pi+1.4320$	$6\pi+1.0926$	$5\pi-0\ 5759$	$3\pi+0.9946$
8	$12\pi+0.4561$	$9\pi+0.0625$	$6\pi-0.2086$	$4\pi+1.3202$	$3\pi-0.1655$
9	$12\pi-0.9336$	$9\pi-1.2814$	$6\pi-1.4748$	$4\pi+0.1173$	*$3\pi-1.2706$
10	$11\pi+0.8416$	$8\pi+0.5418$	$5\pi+0.4356$	$4\pi-1.0425$	$2\pi+0.8225$
11	$11\pi-0.5107$	$8\pi-0.7515$	$5\pi-0.7602$	$3\pi+0.9833$	$2\pi+0.1684$
12	$10\pi+1.3024$	$7\pi+1.1250$	$4\pi+1.2220$	$3\pi-0.0876$	$2\pi-1.0973$
13	$10\pi-0.0054$	$7\pi-0.1154$	$4\pi-0.0988$	$3\pi-1.1126$	$\pi+1.1778$
14	$10\pi-1.2925$	$7\pi-1.3283$	$4\pi-0.9871$	$2\pi+1.0514$	$\pi+0.3777$
15	$9\pi+0.5829$	$6\pi+0.6266$	$3\pi+1.1051$	$2\pi-0.7557$	$\pi-0.3514$
16	$9\pi-0.6622$	$6\pi-0.5329$	$3\pi+0.0978$	$\pi+1.5602$	$\pi-1.0060$
17	$8\pi+1.2523$	$5\pi+1.4767$	$3\pi-0.8714$	$\pi+0.7895$	1.5611
18	$8\pi+0.0528$	$5\pi+0.3724$	$2\pi+1.3419$	$\pi+0.0769$	1.0742
19	$8\pi-1.1281$	$5\pi-0.7036$	$2\pi+0.4556$	$\pi-0.5745$	0.6824
20	$7\pi+0.8538$	$4\pi+1.3903$	$2\pi-0.3873$	$\pi-1.1600$	0.3808
21	$7\pi-0.2837$	$4\pi+0.3710$	$2\pi-1.1846$	1.4665	0.1936
22	$7\pi-1.3990$	$4\pi-0.6770$	$\pi+1.2063$	1.0276	0.0817
23	$6\pi+0.6491$	$3\pi+1.5658$	$\pi+0.5051$	0.6702	0.0289
24	$6\pi-0.4208$	$3\pi+0.6379$	$\pi-0.1442$	0.3982	0.0091
25	$6\pi-1.4681$	$3\pi-0.2585$	*$\pi-0.7382$	0.2103	0.0024
26	$5\pi+0.6493$	$3\pi-1.1225$	$\pi-1.2731$	0.0965	0.0005
27	$5\pi-0.3518$	$2\pi+1.1881$	1.3966	0.0380	
28	$5\pi-1.3281$	$2\pi+0.3915$	0.9925	0.0129	
29	$4\pi+0.8611$	$2\pi-0.3698$	0.6607	0.0038	
30	$4\pi-0.0669$	$2\pi-1.0946$	0.4055	0.0010	
31	$4\pi-0.9691$	$\pi-1.3604$	0.2235		
32	$3\pi+1.2957$	$\pi+0.7136$	0.1167		
33	$3\pi+0.4451$	$\pi+0.1084$	0.0519		
34	$3\pi-0.3787$	$\pi-0.4527$	0.0097		
35	$3\pi-1.1750$	$\pi-0.9672$	0.0020		
36	$2\pi+1.1988$	$\pi-1.4321$			
37	$2\pi+0.4597$	1.2974			
38	$2\pi-0.2491$	0.9426			
39	$2\pi-0.9270$	0.6486			
40	$\pi+1.5679$	0.4152			
41	$\pi+0.9567$	0.2444			
42	$\pi+0.3794$	0.1301			
43	$\pi-0.1611$	0.0621			
44	$\pi-0.6629$	0.0265			
45	$\pi-1.1218$	0.0101			
46	$\pi-1.5411$	0 0035			
47	1.2295	0.0012			
48	0.9078				
49	0.6373				
50	0.4208				
51	0.2598				
52	0.1467				
53	0.0656				
54	0.0352				
55	0.0149				
56	0.0058				
57	0.0021				
58	0.0007				
59	0.0002				

---

* These values differ from those of Massay and Mohr over the range of calculation error.

Table 1b. Values of the Phases $(-\delta_n)$.

	15	10	7	5	4
1	$5\pi-0.7080$	$3\pi+0.5752$	$2\pi+0.7168$	$\pi+1.8584$	$\pi+0.8584$
2	$4\pi+0.9294$	$3\pi-0.8959$	$2\pi-0.7121$	$\pi+0.4850$	$\pi-0.4674$
3	$4\pi-0.5079$	$2\pi+0.8752$	$\pi+1.1450$	$\pi-0.6847$	$\pi-1.5387$
4	$3\pi+1.2637$	$2\pi-0.3925$	$\pi+0.0106$	1.5033	0.8091
5	$3\pi-0.0379$	$2\pi-1.5551$	$\pi-0.9653$	0.7863	0.3087
6	$3\pi-1.2699$	$\pi+0.5344$	1.3723	0.3211	0.0780
7	$2\pi+0.7112$	$\pi-0.4013$	0.7559	0.0920	0.0122
8	$2\pi-0.3761$	$\pi-1.2121$	0.3403	0.0175	0.0020
9	$2\pi-1.3871$	1.2544	0.1154	0.0022	
10	$\pi+0.8231$	0.7300	0.0280	0.0002	
11	$\pi-0.0241$	0.3584	0.0048		
12	$\pi-0.7829$	0.1415	0.0006		
13	$\pi-1,4430$	0.0428	0.00007		
14	1.1423	0.0099			
15	0.6996	0.0020			
16	0.3772				
17	0.1719				
18	0.0641				
19	0.0193				
20	0.0048				
21	0.0010				
22	0.0002				

Table 1c. Values of the Phases $(-\delta_n)$.

	3	2.5	2	1.5	1	0.5	0.25
1	$\pi-0.1416$	$\pi-0.6416$	$\pi-1.1416$	1.5000	1.0000	0.5000	0.2500
2	$\pi-1.3907$	1.3097	0.8928	0.5172	0.2146	0.0364	
3	0.8412	0.5203	0.2641	0.0944	0.0172	0.00065	
4	0.2908	0.1297	0.0409	0.0075	0.0005		
5	0.0610	0.0174	0.0032	0.00029			
6	0.0072	0.0011	0.00014				
7	0.0005	0.00006					

Table 2. Q_η/Q_{η_0}: Ratio of the quantal viscosity cross-section to that of the classical one, in case of the rigid elastic sphere molecule.

(Sim. C.=Simmilar Case; Dis. C.=Dissimilar Case.)

	Authors				
kr_0	Hirota		Massay-Mohr		Uehling
	Sim. C.	Dis. C.	Sim. C.	Dis. C.	Sim. C.
0.0	8.000	4.000	—	—	8.00
0.25	7.834	3.914	—	—	7.82
0.5	7.342	3.709	—	—	7.32
1	5.530	3.115	—	—	5.54
1.5	3.585	2.556	—	—	3.56
2	2.287	2.168	2.28	2.17	2.28
2.5	1.866	1.953	—	—	—
3	1.757	1.780	1.76	1.78	1.76
4	1.596	1.570	—	—	1.60
5	1.466	1.468	1.47	1.41	1.48
7	1.327	1.329	—	—	1.34
10	1.234	1.229	1.23	1.14	1.22
15	1.150	1.149	—	—	—
20	1.113	1.110	1.11	1.06	1.16
25	1.088	1.097	—	—	—
30	1.070	1.070	1.07	1.04	1.06
40	1.049	—	—	—	—
50	1.039	—	—	—	—

The Viscosity Coefficient without Any Molecular Interaction. According to (3), η's of helium and neon were calculated over wide temperature ranges,(10) the term ε, which would be supposed to be small as similarly as in the classical theory, being omitted for the convenience of comparison with those of Massay-Mohr and Uehling.(11)

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

T°K	$\eta_{obs.}$	$\eta_{calc.}$				
		Hirota		Massay-Mohr	Uehling	Classical
		$r_0 = 2.1$Å	$r_0 = 2.0$Å	$r_0 = 2.1$Å	$r_0 = 2.1$Å	Method*
1090	471.3	378.8	415.8	—	—	386
879	408.7	337.9	370.7	—	—	347
680	343.6	994.6	323.2	—	—	313
473	267.2	241.2	264.8	—	—	255
273.1	187.0	177.9	194.9	177	193.3	193
170.5	139.2	136.3	148.9	135	129.4	154
88.8	91.8	93.4	101.8	92	89.7	110
15.0	29.5	30.5	32.6	30	29.7	46

* Proportional constant in the relation $\eta \infty \sqrt{T}$ was adjusted from the experimental value at 100°C.

Table 4. Viscosity Coefficient of Neon ($\times 10^7$).

T°K	$\eta_{obs.}$	$\eta_{calc.}$				
		Quantal method (Hirota)		Classical method**		
		(a)	(b)	(c)	(d)	Kotani
		$\begin{cases} C=0 \\ r_0 = 2.52\text{ Å} \end{cases}$	$\begin{cases} C=55 \\ r_0 = 2.30\text{Å} \end{cases}$	$C=0$	$C=56$	
1100	721	612	700	599	687	690.9
775	580.2	—	573	503	565	596.1
473	424.8	376	427	392	423	425.2
273	298.1	298	298	(298)	(298)	296.2
195	236.7	250	234	252	236	—

** In (c) and (d), values in parenthesis were used for the determination of the proportional constants.

Helium: Adjusting the molecular diameter, the best result was obtained when it was selected as 2.0 Å. As is shown in the third column of table 3, it is concordant with experiment within 12% between 15°–1090°K. For the comparison, the values calculated by use of $r_0=2.10$ Å, as similarly as in the studies of Massay-Mohr and Uehling, are shown in the first and second columns. It is evident that the concordance here obtained is clearly better than those obtained according to the law derived classically that η is proportional to $\sqrt{T}$ (the seventh column).

---

(10) In case of helium, it was obliged to integrate graphically when the temperature was too low. To diminish the error in such cases, Q_{η_0} was separated into Q_{η_0} and $Q_\eta Q_{\eta_0}$, and only the term including the latter factor was integrated graphically.

(11) This neglection is equivalent to regard the molecular diameter smaller by 1%.

Neon: Table 4 gives the calculated result for neon. Here, the agreement between the experimental values and the calculated ones was not so good as for helium. Considering that the molecule is regarded to be softer in this case than helium, this is probably due to the inadequateness of the use of the rigid sphere model for the quantitative treatment of the viscosity. Thus it seems neccessary, in order to obtain better agreement, to introduce a more proper potential, instead of (5), in the determination of so-called "cross-section" by (3), (4). However, the following conventional method of attack was adopted for the time being to see the contribution of the quantal effect, a rigorous improvement being postponed to the next occasion.

The Viscosity Coefficient with the Sutherland Term. For practical purpose such viscosity formula which includes a factor $1/(1+C/T)$ is often used, C being a constant, because it fairly reproduces the temperature variation of the experiments (Compare the fifth and the sixth columns of table 4). The meaning of the factor usually called Sutherland term is regarded as the introduction of the term due to the attracting potential between molecules, as it is proved theoretically.(12) However, as is suspected from the incomplete basis of the correction, this improved formula is still imcapable for the wide temperature ranges.(13) The circumstances will be seen in the seventh column of table 3 in case of helium.

Though the corrections due to Sutherland and the quantal effect contribute in such a direction to the viscosity(2) that the apparent molecular diameters increase when the temperature lowers, they are not perfectly equal. So the introduction of a term similar to the former into the quantal treatment was then tried, to increase the concordance between the experiment and the theory for neon, the result being given in the fourth column in table 4. The trial was found so successful that the agreement became comparable even with those obtained by Kotani(14) who took also the attracting potential of the Sutherland type: $V(r)=\infty$, $r<r^{\circ}$ and $V(r)=-\mu/r^6$, $r\geq r_0$ (μ is a constant), into consideration for the calculation, though he did by the classical method. On the other hand, the concordance was not so improved by the same procedure for helium, but a tendency that C must be selected always less than about 20 was found. This latter result seems interesting because C obtained in the classical case has several reasons that it may be too large,(15) considering that the attracting potential of helium is weak.

These conclusions tell us that the rigid elastic sphere model is insufficient to reproduce the experimental value accurately even if both corrections due to the attraction potential and the quantum mechanical effect are added; in other words, the phase values must be determined from (4), putting a proper potential into V.

---

(12) Kennard, *loc. cit.*, 154.

(13) Jeans, "Dynamical Theory of Gases", 4th Ed., London (1925) 286; Chapman and Cowling, *ibid.*, 222.

(14) Kotani, *Proc. Phys.-Math. Soc. Japan*, [3] **24** (1942), 76.

(15) Usually the value determined from the data at the ordinary temperature is 56. This discrepancy will be discussed in a following paper.

Summary.

1) According to the formula of Massay and Mohr, the viscosity cross-section has been calculated quantum-mechanically in more details than they did, using the rigid elastic sphere model.

2) The viscosity coefficients of neon and helium have been calculated over wide temperature ranges, and it has been found that the concordance between theory and experiment is yet insufficient, though it is better than the result of the classical method.

3) The agreement has been improved, if the "Sutherland term" is introduced in the formula to take the intermolecular potential in consideration.

4) The criticism of Uehling to Massay and Mohr's result has been found rather inappropriate, so far as the similar collision is concerned.

The author wishes to express his sincere thanks to Dr. Y. Tanaka and to T. Arimori of our laboratory for their encouragement throughout this research.

Department of Inorganic Chemistry, Central Laboratory,
South Manchuria Railway Company, Dairen.