

On The Calculation of Viscosity Coefficients for H₂ Obeying Hartree-Fock-Dispersion (HFD)-type Potential

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Summary: The Hartree-Fock-Dispersion (HFD) intermolecular pair potential describing the spherical interaction for H₂ proposed by McConville has been used to calculate the viscosity coefficients for H₂ theoretically.

Since, other transport properties data for hydrogen rather than viscosity coefficients are scarce, we present the viscosity collision integrals with an uncertainty commensurate with the experimental accuracy. Eventually this accuracy in the viscosity collision integrals is also exist in the other collision integrals needed for obtaining related thermophysical properties. Three consecutive integrals for the calculation of viscosity collision integral have been carried out numerically. We come into force to adopt the aforesaid potential, since, it has been modified to reproduce accurately the equilibrium bulk properties such as second virial coefficients. Consequently, there is no doubt about the application of aforementioned potential to calculate the transport properties for H₂, because the calculated results are clearly adequate with experimental ones and has shown good agreement.

Introduction

The knowledge of intermolecular potentials opens the way to (the calculation of) many observable properties for macroscopic as well as microscopic systems. In the first category are various bulk gas and condensed matter properties. Measured gas phase properties which depend directly on the intermolecular potential are virial coefficients, viscosity and diffusion coefficients, thermal conductivity [1-3]. In the second category are the spectra of van der Waals molecules [4,5] and molecular beam scattering cross sections [6,7], elastic or inelastic state-to-state or differential.

By the mean, the pair interaction potential of hydrogen is important for studies of Earth's upper atmosphere and aeronautical applications, design and development of future air craft such as National Aero - Space Plant (NASP) and studies of preliminary heating of the fuel and combustion processes for air - heating, hydrogen -burning, etc.

Accurate determination of the potential interaction of H₂-H₂ has proven to be a challenging and interesting problem. Several attempts to calculate the H₂- H₂ interaction potential energy were made. Determination of intermolecular potentials from the velocity dependence of the elastic scattering cross section has become an important technique. The first

attempt to measurement the elastic differential cross section of H₂-H₂ go back to Dondi *et al.* [8] Gengenbach and Hahn performed similar experiment by measuring the absolute value of H₂-H₂ cross section at several beam velocities [9]. Farrar and Lee were also used a similar method for the evaluation of para -H₂-para-H₂ interaction potential [10] and Gengenbach *et al.* measured the absolute integral cross sections for n-H₂-n-H₂ at primary particle velocities between 1270 and 9650 m/sec with a 77K target[11].

Up to the authors knowledge various pair interaction potential for H₂ has been reported in the literature [11-17,68-70]. Several potential functions have been reported to fit physical properties of hydrogen. McConville [15] has calculated for five of these functions and obtained second virials, bound state energy differences, total and differential scattering cross sections to compare the experimental data. He found that none of the previously proposed potential can represent more than two of the above properties. He used the Hartree-Fock dispersion (HFD) form proposed by Ahlrich *et al.* [71], but by changing the damping constant, D, a consistent representation is found for all the data by him.

However, in general, there are two contacts with the relation between thermophysical properties

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and interaction potential: From potential function toward thermophysical properties (or collision integrals) and vice versa.

There is also a large literature on some of the attempts, for example, in the forward direction, but we do not attempt to review these here. By paying meticulous attention to details of some these papers, not in the chronological order of their development, most of the available tabulation of collision integrals are for the classical limit only, but this suffices for most gas pairs. The collision integrals for both repulsive and attractive inverse - power potentials have been summarized, [19,20]. Those for the repulsive exponential potential have been given [20-22]. Collision integrals have been tabulated for the screened Coulomb potential which is used as a model for the interaction of neutral atoms at high energies (or of ions in a plasma) [23-24]. Collision integrals for the Lennard-Jones (12-6) potential have been calculated by Kim and Ross [25], Cohen *et al.* [18], Clifton [36] and by Munn *et al.* [26]. The (9-6) - in general Lennard - Jones (n-m)-potential [27], the (16-6) and (18-6) potentials [28] have been treated. Collision integrals for (28-7) potential have been calculated by McCoubrey and Singh [29] and also by Smith *et al.* [27]. Mason calculated collision integrals for modified Buckingham (MB) or (exp-6) potential - which is similar to the (n-6) potential, but uses an exponential instead of an inverse-power potential repulsion [30]. Scharmm has presented the calculation of the viscosities of gases from the open shell potentials [33]. Taylor has calculated transport collision integrals for hydrogen - helium assuming an (exp-6) spherical interaction potential [35]. The H₂-H₂ interactions have been assumed to obey the (exp-6) potential and the coefficient of viscosity has been computed by Clifton [36]. Tables of collision integrals for the Morse potential - which contains two exponential terms, one repulsive and one attractive - have been given by Smith and Munn [31]. L. A. Viehland *et al.* proposed tables of transport collision integrals for (n,6,4) ion-neutral potentials [32]. Calculation of reduced transport collision integrals for Lennard - Jones (n-6) have been found by Lin and Hsu [34] and for Lennard - Jones (12-6) by Neufeld *et al.* [37]. Ely and Hanely calculated collision integrals for a non - spherical m-6-8 potential energy function [38]. On the other hand, the exact calculation of the transport collision integrals for a realistic model of the intermolecular pair potential of helium and nitrogen are reported [39].

The transport properties of pure helium, pure neon and mixtures of them have been calculated by the obtaining the reduced collision integrals for the Born - Mayer potential function [40]. The calculation of collision integrals have been carried out using a new potential function for the ground singlet state of the alkali diatomics [41-42]. Finally, some references to the rather wide body of recent and not-so-recent studies of H₂ is presented here. For example, low temperature second virial coefficients of para-H₂ gas [43], absorption spectra of H₂-H₂ pairs [44], viscosity and thermal conductivity of normal hydrogen [45], scattering and transport cross sections of hydrogen [46] and transport properties of hydrogen [47]. On the other hand, some sample of the efforts in the backward direction also have been done by INVERSION method [17,48-51] or by obtaining interaction potential functions from multiproperty fits to experimental data [52-55].

Theory

The collision integrals, which carry the information of the two - body interaction, are also therefore functions of the intermolecular potential between any two given particles [57]. In present work, the two - body interaction will be taken to be between particles.

Once the interaction potential is known, transport properties can be obtained from the Chapman-Enskog solution [56] of the integro-differential Boltzmann-kinetic equation. According to the aforesaid method of solution the Boltzmann equation the transport properties (viscosity, thermal conductivity, diffusion coefficients and thermal diffusion ratio) can all be calculated if the reduced collision integrals, $\Omega^{(l,s)*}$, are known. These collision integrals are Boltzmann factors of transport cross sections, $Q^{(l)*}$, and defined in the standard source book [57].

$$\Omega^{(l,s)*}(T^*) = \frac{2}{(S+1)!} \int_0^\infty e^{-(G^*/T^*)} Q^{(l)*}(G^*) \left(\frac{G^*}{T^*}\right)^{2S+1} d\left(\frac{G^*}{T^*}\right)$$

(1)

$$Q^{(1)*}(G^*) = \frac{4}{[2l+1-(-1)^l]} \int_0^\pi (1-\cos^l \chi) b^* db^* \quad (2)$$

$$\chi = \pi + 2b^* \int_{R_c^*}^\infty \frac{d\left(\frac{1}{R^*}\right)}{[1-U^*(R^*)/G^* - b^{*2}/R^2]^{1/2}} \quad (3)$$

In these equations G^* is the reduced kinetic energy of collision, T^* ($\equiv k_B T/\epsilon$) the reduced temperature, b^* the reduced impact parameter, R^* ($\equiv R/R_m$) the reduced distance between molecules and k_B is Boltzmann constant. The potential strength is characterized by a potential minimum well depth, ϵ , and the potential range by an scaling potential parameter, R_m . The later scaling interaction parameter, R_m , may be the intermolecular separation at which the potential energy is a minimum. Thus the reduced kinetic energy is the actual kinetic energy of collision (in the center of mass frame or reference), divided by ϵ . In (3) χ is angle deflection of the relative velocity at collision, the lower limit of integration R_c is the reduced closest distance of approach, equal to largest value of R^* for which the expression in the denominator of Eq.(3) vanishes.

It is worthwhile to remark that low density is necessary and sufficient condition for computation the reduced collision integrals to confirm the existence of binary collision and the validity of its approximation.

The calculation of the collision integrals involves three consecutive integral, all of which were carried out numerically. It may also be pointed out that there are various proposal for the calculation of collision integral [58-59]. It should also be noted that we adopted the procedure proposed by Barker *et al.* [60]. The angle deflection is integrated by trapezium rule. The cross-section and the collision integrals are evaluated by using a five point Gauss-Legendre quadrature [61-63].

Calculation of Viscosity Coefficients

The rigorous kinetic theory treatment of transport in gases is extremely complicated mathematically and physically. The rigorous expression underlying transport phenomena in gases were worked out by Maxwell and Boltzmann, but it was not until Chapman and Enskog, working out independently, solved the equations.

For a dilute gas the viscosity is given by the rigorous expression Chapman-Enskog solution of Boltzmann-kinetic equation

$$\eta = \frac{5}{16\sigma^2} \frac{(mk_B T / \pi)^{1/2}}{\langle \Omega^{(2,2)*} \rangle} f_\eta \quad (4)$$

where f_η is higher-order kinetic-theory correction that deviates only slightly from unity, m is molecular mass, σ is a Scale factor for molecular size.

Strictly speaking, the Chapman -Enskog kinetic theory of gases applies only to monatomic gases (molecular with no internal degrees of freedom for which the interaction potential is spherically symmetric). Inelastic collisions occur between molecules with internal degrees of freedom. In these collisions kinetic energy is no longer conserved, albeit clearly mass and momentum are conserved. Consequently, the viscosity and diffusion are not appreciably affected by the presence of the internal degree of freedom, and the theory of monatomic gases may be applied to polyatomic molecules with considerable success [17,49-51].

$\langle \Omega^{(2,2)*} \rangle$ is orientation-averaged reduced viscosity collision integral which is defined in general form as :

$$\langle \Omega^{(l,s)*} \rangle = \frac{1}{8\pi} \int_{-1}^1 d(\cos \theta_1) \int_{-1}^1 (\cos \theta_2)^{2s} d\Omega^{(l,s)*}(\theta_1, \theta_2, \phi, \tau^*) \quad (5)$$

Since our knowledge does not support a weighting factor for orientation more complicated than that giving equal weights to all orientations. The assumption of equal weights of all orientations is also considered in. (5). It is worthwhile to be noted that the most of the interaction in a collision occurs near the distance of closest approach during which the relative orientation dose not change much, so that one relative orientation dominates each collision.

We evaluated aforementioned consecutive integrals for the HFD type potential of H_2 proposed by McConville. First of all, we reduce the pair-interaction potential as following form:

$$U(R) = \epsilon U^*(x)$$

$$U^*(X) = Ae^{-\alpha X} - f(X) \sum_{n=6}^{10, \text{neven}} \left(\frac{C_n}{X^n} \right)^*$$

$$f(x) = e^{-(D/x - 1)^2}, \quad x < D$$

$$f(x) = 1.0, \quad x \geq D \quad (6)$$

Where the reduced potential parameters for HFD intermolecular potential is reported in Table I.

Table-I. Reduced Potential for the Hartree-Fock-Dispersion (HFD) Intermolecular potential for H₂-H₂

A	1.1464×10 ³
α	11.4790
C ₆ *	1.4759
C ₈ *	0.6104
C ₁₀ *	0.3191
D	1.31
ε/k _B (K)	34.71
R _m (Å)	3.438
σ(Å)	3.0194
κ=R/R _m	

By insertion of Eq(6) in Eqs (3,2 and 1) and numerically integrating, one find reduced collision integral. From the obtained reduced viscosity collision integral, we find the viscosity coefficient for H₂ by Eq(4).

The expression of $\langle \Omega^{(2,2)*} \rangle$ in the low temperature region ($T^* < 1$) has not been obtained, since (i) the experimental information on viscosity at low temperatures is not available and (ii) the existence of several long - range contribution to the interaction potential whose effects on the low-temperature properties that can neither be calculated nor separated.

Table II. Reduced collision Integrals for H₂; $\Omega^{(l,j)*} = \Omega^{(l,j)} / \pi\sigma^2$

T(K)	$\Omega^{(1,1)*}$	$\Omega^{(1,2)*}$	$\Omega^{(1,3)*}$	$\Omega^{(1,4)*}$	$\Omega^{(1,5)*}$	$\Omega^{(2,2)*}$	$\Omega^{(2,3)*}$	$\Omega^{(2,4)*}$	$\Omega^{(2,5)*}$
273	0.717	0.622	0.626	0.599	0.578	0.819	0.778	0.748	0.720
293	0.705	0.652	0.617	0.590	0.569	0.807	0.767	0.738	0.710
300	0.701	0.649	0.614	0.587	0.566	0.804	0.764	0.735	0.707
313	0.695	0.643	0.608	0.582	0.561	0.797	0.758	0.729	0.701
333	0.685	0.634	0.600	0.574	0.553	0.787	0.749	0.721	0.693
353	0.676	0.626	0.592	0.567	0.546	0.778	0.741	0.713	0.685
373	0.668	0.619	0.585	0.560	0.539	0.770	0.733	0.706	0.678
423	0.650	0.602	0.569	0.544	0.524	0.752	0.716	0.689	0.662
473	0.634	0.588	0.555	0.530	0.510	0.736	0.701	0.674	0.647
523	0.620	0.575	0.543	0.518	0.498	0.722	0.682	0.660	0.634
573	0.608	0.563	0.532	0.507	0.487	0.709	0.675	0.648	0.623
623	0.597	0.553	0.521	0.497	0.477	0.698	0.664	0.637	0.612
673	0.587	0.543	0.512	0.488	0.468	0.687	0.654	0.627	0.602
773	0.569	0.526	0.495	0.471	0.452	0.669	0.635	0.608	0.584
873	0.553	0.511	0.481	0.457	0.438	0.652	0.619	0.592	0.569
1073	0.527	0.486	0.457	0.433	0.414	0.625	0.591	0.565	0.542
1173	0.516	0.476	0.446	0.423	0.404	0.613	0.579	0.553	0.530
1273	0.507	0.466	0.437	0.414	0.395	0.602	0.569	0.542	0.519
1773	0.467	0.428	0.399	0.377	0.357	0.558	0.525	0.499	0.419
2273	0.438	0.399	0.369	0.343	0.317	0.525	0.491	0.460	0.438
2773	0.414	0.374	0.340	0.306	0.269	0.496	0.457	0.418	0.404
3273	0.393	0.349	0.308	0.265	0.220	0.468	0.421	0.372	0.369

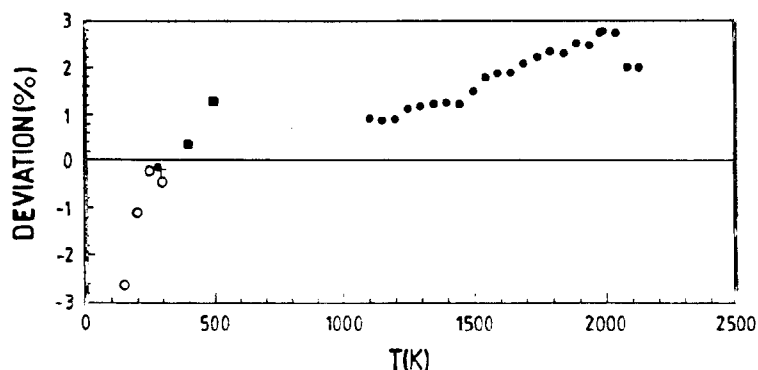


Fig. 1: Deviation plot for the viscosity of H_2 as a function of temperature, with $\text{Deviation (\%)} = 100(\eta_{\text{cal}} - \eta_{\text{exp}}) / \eta_{\text{exp}}$. The experimental points are: (■) H. L. Johanston and K. E. McCloskey [64], (●) L. Bornstein [65], (□) A. Van Itterbeek and A. Claes [66], (○) J.M.J. Coremans *et al.* [67].

Results and Discussions

The kinetic theory of gases yields theoretical expressions for the viscosity, thermal conductivity and other transport properties of gases and results are in reasonably good agreement with experiment [48-51].

The comparison between calculated viscosity coefficient, η_{cal} , and experimental one, η_{exp} , shows that the results are in excellent agreement and clearly adequate.

We prefer to use the modern HFD potential form, recognizing that in the cases treated it must be regarded to be an "effective" (Spherical) potential; thus the internal degrees of freedom of H_2 have been ignored for the present purpose. For the hydrogen interaction we used this potential with the parameters proposed by McConville [15]. Reduced collision integrals for H_2 have been tabulated in Tables II. Deviation plot for the calculated viscosity of H_2 has been depicted in Figure 1.

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