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Pair Interaction Potential Energy Function for H_2-H_2 from the Viscosity of Normal Hydrogen in the Limit of Zero Density

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An iterative inversion procedure is used to obtain the effective isotropic part of the pair-interaction potential for H_2-H_2 from the correlation equation for the zero density collision integral of hydrogen, proposed by Assael and coworkers. The Lennard-Jones (12-6) potential energy function is chosen as the initial model potential prerequisite for the method . The comparison of the measured potential with that of HFD-type potential was carried out over a wide range of temperature, *i.e.*, from 20 to 2200 K. The results of this work can satisfactorily be applied in evaluation of both orientation-average viscosity collision integrals and the dimensionless ratios which are essential parameters in the calculation of other transport properties.

Key Words: Interaction potential, Collision integrals, Inversion method, Correlation equation of viscosity.

INTRODUCTION

A traditional approach having a long history in determination of neutral-neutral interaction potentials from macroscopic properties is the use of a mathematical model potential containing a few parameters which are adjusted in some way until a reasonable agreement is attained between theoretical and experimental properties. Nevertheless, the parameter determined from the equilibrium properties such as second virial coefficients and Joule-Thomson coefficients are slightly different from those obtained from nonequilibrium properties such as viscosity and self-diffusion. In particular, the force-fitting data brings about inadequate analytical functions and leads to wrong results. Morecver, the function resulting from this procedure may not be precise and unique. The main weakness of the procedure mentioned is that it is often difficult to find a suitable and sufficiently flexible potential unless including several adjustable parameters; otherwise, the available data cannot fix them uniquely, meanwhile, leaving the potential in doubt unless data for many physical properties are available for simultaneous analysis[1].

The central problem in molecular physics is how to calculate the intermole-

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cular potential energy[2-8]. To date, there is no direct way to measure the intermolecular potential and what is generally carried out is measurement of some macroscopically observable quantities which have some functional dependence on the intermolecular forces. What remains is, thus, how to extract information about these forces by analyzing the results of measurements. Every macroscopic property, which contains two very restricted conditions, is suitable for obtaining the potential energy. These are, namely, (1) an accurate statistical mechanical theory connecting the intermolecular forces to the macroscopic properties must be available, and (2) the forces must not be buried under too many layers of theory.

It has long been recognized that measurements of the temperature-dependent properties of gases such as transport coefficients contain information about the intermolecular potential energy function over a wide range of separation distance. The problem lies in extracting this information from the measurements. Hence, it has led to search for an inversion scheme.

By paying meticulous attention to details of the chronological order of the development of the inversion method, the implicit inversion method was started by Jonah and Rowlinson[9]. In fact, the first explicit inversion of viscosity data was due to Dymond[10]. The theoretical source of information about the nature of intermolecular potential energy is based on quantum mechanics (*i.e.*, the *ab initio* method). In the case of evaluation of intermolecular potential energy from experimental sources, there exist, in general, two independent approaches. The first approach, carried out by Barker *et al.*[11], is based on the assumption that some specific potential functions and the optimization of the parameters are contained in the functions, so that experimental and calculated data come into a reasonable agreement. The second approach, developed by Smith and coworkers[12,13] is the inversion procedure, by which the potential energy is determined without any assumption about the intermolecular potential energy functions. The detail of this procedure will be explained in the next section. The principal sources of the experimental data have been molecular beam scattering, determination of the vibration-rotational fine structure of molecules, and accurate measurements of transport and equilibrium properties. Of all the sources considered in this work we have forced our attention to the determination of the intermolecular potential energy from transport properties, namely, viscosity, by using the inversion approach. Among the transport properties, the measurement of viscosity is more accurate than the others; in addition, viscosity measurement is experimentally more practical than, say, diffusion measurement.

The technique of inversion of thermo-physical properties is obtaining pair potentials has been applied with considerable success to monatomic species (inert gas)[14,15], polyatomic gases[16] and the mixtures of polyatomic and noble gases[17-22].

By the way, the viscosity and thermal conductivity of normal hydrogen in the limit of zero density by Assael *et al.*[23] has been formulated. It has been proved that this technique is capable of correlating transport properties of hydrogen, over a temperature range, with an accuracy commensurate to the best measurements.

We have considered the experimental reduced viscosity collision integral obtained by the Assael *et al.*[23] correlation, Hattikudar[24] correlation and Aziz[25]

relations, and performed an inversion to determine the reduced potential energy curve corresponding to these collision integrals. Comparison of these results with the HFD-type independently known potential of McConvile[26] is shown.

The collision integrals

Once the interaction potential is known, transport properties can then be obtained from the Chapman-Enskog solution of the integral-differential Boltzmann kinetic equation. The transport properties (viscosity, thermal conductivity, diffusion coefficients and thermal diffusion factor) 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 are defined in the standard source books[6,7].

The collision integrals, which carry the information of the two-body interaction, are functions of the intermolecular potential between any two given particles[6–8]. In the present work, the two-body interaction will be taken to be between particles. The collision integral $\Omega^{(l,s)}$ is the first member of a family of consecutive integrals that arise in the kinetic theory derivations[6–8].

$$\Omega^{(l,s)} = [(s+1)!\,(kT)^{s+2}]^{-1} \int_0^\infty Q^{(l)}(E) e^{-E/kT} E^{s+1}\, dE \tag{1}$$

where E is the relative energy of colliding partner, and $Q^{(l)}(E)$ is a transport cross-section that classically is given by the equation

$$Q^{(l)}(E) = 2\pi\{1 - [1 + (-1)^l / 2(l+1)]\}^{-1} \int_0^\infty (1 - \cos^l \theta) b\, db \tag{2}$$

in which θ is the relative deflection angle between two colliding partners of energy E and impact parameter b at the gas temperature.

The deflection angle θ is calculated as a function of b and E from the classical equation of motion.

$$\theta(b, E) = \pi - 2b \int_0^\infty 1 - b^2/r^2 - V(r)/E]^{-1/2}\, dr/r^2 \tag{3}$$

where the distance of closest approach r_0 is the outermost root of

$$1 - b^2/r_0^2 - V(r_0)/E = 0 \tag{4}$$

Numerical differentiation and use of the recursion relation can generate collision integrals higher than that mentioned.

$$\Omega^{*(l,s+1)} = \Omega^{*(l,s)} \left[1 + \frac{1}{(s+2)} \frac{d \ln \Omega^{*(l,s)}}{d \ln T^*} \right] \tag{5}$$

where the reduced collision integral is defined by

$$\Omega^{*(l,s)} = \frac{\Omega^{(l,s)}}{\pi\sigma^2} \tag{6}$$

where σ is length scaling factor so that $V(\sigma) = 0$. Reduced temperature (T^*) is defined as

$$T^* = kT/\varepsilon \tag{7}$$

ε is energy scaling factor.

The Hartree-Fock Dispersion Potential

Hartree-Fock dispersion potentials were proposed by several investigators. They used a combination of the self-consistent field Hartree-Fock, semi-empirical estimate of the correlation energy, and empirically determined dispersion coefficients C_6, C_8 and C_{10} to determine an intermolecular potential such as

$$V(r) = \varepsilon V^*(x) \tag{8}$$

$$V^*(x) = Ae^{-(\alpha x)} - (C_6/x^6 + C_8/x^8 + C_{10}/x^{10})F(x) \tag{9}$$

where

$$F(x) = e^{[-D/x-1)^2]} \qquad x < D \tag{10}$$

$$F(x) = 1 \qquad x \geq D \tag{11}$$

and $x \equiv r/r_m$. It is noteworthy that the potential strength is characterized by a potential minimum well depth, ε, and the potential range by a scaling distance parameter, r_m. The later parameter, r_m, may be the intermolecular separation at which the potential energy is minimum. The aforesaid potential has a normal form identical to that of HFD-A. The HFD-B potential differs in form of the HFD-A in the repulsive part having an additional parameter β as $A \exp(-\alpha x + \beta x^2)$. The HFD-C potential has a repulsive component similar to that of $Ax^\gamma \exp(-\alpha x)$.

The inversion method

The kinetic theory of gases yields theoretical expressions for the viscosity, thermal conductivity and other transport properties of gases, the results of which are in reasonably good agreement with experiment. The rigorous kinetic theory treatment of transport properties in gases is grossly complicated from mathematical and physical viewpoints. The rigorous expressions underlying transport phenomena in gases were worked out in 1860 and 1870 by Maxwell and Boltzmann, but it was not until 1917 when Chapman and Enskog worked out independently and solved the equations.

For a dilute gas the viscosity given by the rigorous expression for the viscosity, η, of a dilute gas by the Chapman-Enskog solution of Boltzmann equation is[7]

$$\eta(T) = \frac{5}{16\sigma^2} \frac{(mk_BT/\pi)^{1/2}}{\langle\Omega^{(2,2)*}\rangle} f_\eta \tag{12}$$

where m is the molecular mass, k_B the Boltzmann constant, and f_η is a "second order Kihara" correction factor for the calculation of transport properties which normally differs from unity by only 1 per cent[8]. We have set the value of f_η equal to unity. By dilution, we mean that the rates of transport of mass, momentum and energy are controlled by binary molecular collision. In other words, it means at sufficiently low densities that only two-body collisions need to be considered.

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

$$\langle\Omega^{(2,2)*}(T^*)\rangle = \frac{1}{\pi}\int_0^{\pi}\int_0^{1}\int_0^{1} \Omega^{(2,2)*}(T^*, \varphi, \theta_1, \theta_2)\, d\varphi\, d(\cos\theta_1)\, d(\cos\theta_2) \quad (13)$$

Writing the collision integrals in the form of eqn. (13) is tantamount, by the way, to assuming that the post-averaging approximation has been used throughout the entire temperature range, albeit keeping in mind that this approximation has been applied since our studies 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 eqn. (13). It is worthwhile to note that most of the interaction in a collision occurs near the distance of closest approach during which the relative orientation does not change much, so that one relative orientation dominates each collision. Strictly speaking, the Chapman-Enskog kinetic theory of gases applies only to monoatomic gases (molecules 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, the 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 monoatomic gases may be applied to polyatomic molecules with considerable success. On the other hand, viscosity and diffusion involve, respectively, momentum and mass transfer; then they should not be affected significantly in the first approximation by internal degrees of freedom and hence can serve as one of the best sources of information for the intermolecular forces in polyatomic gases.

The viscosity coefficients of H_2 have been correlated in the limit of zero density by Assael *et al.*[23]

$$\langle\Omega^{(2,2)*}\rangle = \exp\,[0.354125 - 0.427581(\ln(T^*)) + 0.149251\{\ln(T^*)\}^2 - 0.037174\{\ln(T^*)\}^3 + 0.003176\{\ln(T^*)\}^4 \quad [0.6 \le T^* \le 42] \quad (14)$$

The inversion technique initiates by estimating of G_η, inversion function, from an initial model potential such as Lennard-Jones (12-6). The inversion function is a function of the reduced temperature (T^*) alone[13]. We have estimated this function using Lennard-Jones (12-6) model as the based initial model[27]. Hischfelder and Eliason[28] have applied the inverse power potential, $V^* = A/r^m$, where A is a constant having both positive and negative values, and r is inter-nuclear distance, to calculate the transport properties of molecules that interact with an inverse power law. It has been shown that for such molecules there is a relation between temperature and r, as below:

$$r = (kT/A)^{-1/m}F(m) \quad (15)$$

where $F(m)$ is a function of m only, and kT has its usual meaning. Then, the interaction potential energy at the separation of r would be in the form of

$$V^* = kT[F(m)]^{-m} \quad (16)$$

Practically, G(m) is chosen such that

$$V^* = kT[G(m)] \tag{17}$$

$G(m)$ is called inversion function and is a number determined only by m and the sign of A. For repulsive forces with m = 8–18, G lies in the range 0.86–0.82. For long range attractive forces when A is negative and $m = 6$, $G = -0.58$. Realistic potentials contain both repulsive and attractive terms and can be imagined to be comprised of a number of simple inverse power terms so that the effective exponent m is a continually changing function of separation. For realistic potentials, therefore, G is a temperature-dependent function $G(T)$ ranging from 0.85 at high temperatures when repulsive forces dominate, to a limiting value of –0.58 at very low temperatures where repulsive forces determine the viscosity and the r^{-6} term is the most important. Despite this temperature variation, $G(T)$ is remarkably similar for all realistic potentials and it is the stability of this function that leads to the effectiveness of the inversion method[12]. The procedure is to calculate an approximation $G_0(T)$ from a simple model potential $V_0(r)$ such as the Lennard-Jones (12-6) function. Then we can write

$$V^{(1)}(r) = G_0(T)kT \tag{18}$$

and to obtain points on a new potential function $V^{(1)}(r)$ which proves to be closer to the true potential than $V^{(0)}(r)$. A new inversion function $G_1(T)$ may be calculated from $V^{(1)}(r)$ and the process is repeated for a number of iterations (two iterations in the present case). However, in order to perform the calculation, an estimate of the well depth ε/k is required. In practice, a number of trial values of ε/k are employed and the one that leads to inversion potential and best accommodates the data is selected. For the present procedure we obtain the potential with a mean deviation of better than 1%.

Given a set of reduced viscosity coefficient collision integrals, $\langle\Omega^{*(2,2)}(T^*)\rangle$ over a wide range of reduced temperature from the correlation equations on the one hand, and estimating the G_η function from initial model potential Lennard-Jones (12-6) on the other, it is possible, to transform a pair of datum ($\langle\Omega^{*(2,2)}\rangle$, T^*) to plot V/ε *vs.* r/σ on the potential energy curve and hence we can marshal two steps of inversion procedure, *viz.*,

$$V/\varepsilon = V^* = G_\eta(T^*) \tag{19}$$

$$r/\sigma = r^* = (\Omega^{*(2,2)})^{1/2} \tag{20}$$

equations (19) and (20) are central equations in the inversion scheme.

The new potential is a closer approximation to the true potential energy than the potential of the initial model. The new $G_\eta(T^*)$ can be obtained from square interpolation among new potentials. These new potentials have been used to calculate the improved collision integrals. Numerical integration has been carried out for the evaluation of the integral equations (1)–(3) with these new potentials. The above process is repeated until convergence occurs. The convergence criteria are judged by: (i) the extent to which the calculated collision integrals are in accordance with reduced viscosity coefficient collision integrals determined by

the correlation equation proposed by Assael *et al.*[23], *i.e.*, eqn. (14), Aziz *et al.*[25] and Hattikudar *et al.*[24] In this work, the three consecutive integrals are evaluated within an accuracy of 0.1%. This accuracy is obtained by comparing the calculated values of collision integral with the experimental ones in each iteration. (ii) the degree to which the intermolecular potential energies obtained by inversion method reproduce thermophysical properties within the experimental accuracies. (iii) the degree to which the potentials are unchanged from one iteration to the next. It should be noted that the rate of convergence of iterations reflects the differences of detail between the initial model $V_0^*(r^*)$ and true model $V^*(r^*)$. Our results converged after two iterations and are introduced and discussed in the next section.

RESULTS AND DISCUSSION

The most striking result of this work is to obtain an effective potential which will reproduce the kinetic theory of gas phase transport properties (collision integrals and their dimensionless ratios). The wide availability of thermophysical properties makes them as a potentially important source of information about intermolecular potential.

It is noteworthy that, in principle, the collisions at low energies do not follow classical mechanics. The resulting quantum deviations are usually described by a reduced de Broglie thermal wavelength known as the de Boer parameter

$$\Lambda^* \equiv h/\sigma(m\varepsilon)^{1/2} \tag{21}$$

where the symbols have their usual meanings. Quantum effects at low temperatures are quite large for second virial coefficients, but are much less important for transport coefficients[29]. No systematic calculations of quantum deviations of transport coefficients as a function of A^* and T^* have been carried out for realistic interaction potentials, and all the correlations presented in the relevant literature correspond to classical limit[30]. It is worthwhile to be noted that one can show

$$\Omega^{(2,2)*} = \Omega_0^{(2,2)*} + \Lambda^{*2}\Omega_1^{(2,2)*} + \Lambda^{*4}\Omega_2^{(2,2)*} \tag{22}$$

The calculations of the quantum corrections, $\Omega_1^{*(2,2)}$ and $\Omega_2^{*(2,2)}$, are rather complicated, and have never been carried out for any realistic potential function[29]. However, the effects are fairly small and are thus not of major importance for the temperature range we used; henceforth our calculations were entirely classical. It should also be mentioned that full quantum-mechanical calculations of collision integrals have been carried out for Lennard-Jones (12-6) potential model[31–33]. We think that the quantum effect caused a slight deviation in the value of viscosity collision integral from the expected accuracy (*i.e.*, 1%)[34]. Moreover, due to quantum effect, the average per cent deviations of the calculated viscosity collision integrals are fairly small for the used temperature.

We have used our reasonably effective isotropic potential to obtain the improved collision integrals necessary for the calculation of transport properties.

Collision integrals in conjunction with their ratios are shown in Table-1. The ratios of collision integrals have been calculated by the following equations:

$$A^* \equiv \frac{\langle \Omega^{(2,2)*} \rangle}{\langle \Omega^{(1,1)*} \rangle}, \tag{23}$$

$$B^* \equiv \frac{5\langle \Omega^{(1,2)*} \rangle - 4\langle \Omega^{(1,3)*} \rangle}{\langle \Omega^{(1,1)*} \rangle}, \tag{24}$$

$$C^* \equiv \frac{\langle \Omega^{(1,2)*} \rangle}{\langle \Omega^{(1,1)*} \rangle}, \tag{25}$$

$$E^* \equiv \frac{\langle \Omega^{(2,3)*} \rangle}{\langle \Omega^{(2,2)*} \rangle}, \tag{26}$$

$$F^* \equiv \frac{\langle \Omega^{(3,3)*} \rangle}{\langle \Omega^{(1,1)*} \rangle}, \tag{27}$$

TABLE-1
THE DIMENSIONED SCALING PARAMETERS σ AND ε/K_B FOR H_2-H_2

H_2-H_2	σ (Å)	ε/k(K)
Potential obtained by the inversion method	2.8430	30.06

Calculation of other properties are considerably eased by introducing Table-2. In this work, the three consecutive integrals are evaluated using the Gatland version[35] of the computer program developed by O'Hara and Smith[36]. It may also be pointed out that the integral of the deflection angle is integrated by trapezium rule. The cross-section and the collision integrals are evaluated by using a Gauss-Legendre quadrature (numerical integration)[37-39]. Therefore, toward the eventual goal of a fundamental and unambiguous methodology of the inversion procedure, the objective of the present paper is to understand that the application of the aforesaid method appears to be reasonable. The present work reveals the undoubted power of the inversion method to obtain information about intermolecular forces from correlation formula of viscosity collision integrals. In this work, we chose the HFD-type potential. Since the HFD-type potential model was generated on a sound experimental basis, so the selection of the HFD-type potential as the reference system is quite reasonable. The results are shown in Fig. 1. The values of the dimensioned scaling potential parameters obtained in this work are given in Table-1. The results obtained here cover the range from the potential energy minimum inwards to a repulsion of the well depth. In this work, the potential well depth could be obtained as the relative value with respect to a convenient reference system. Comparison of the results obtained can be made

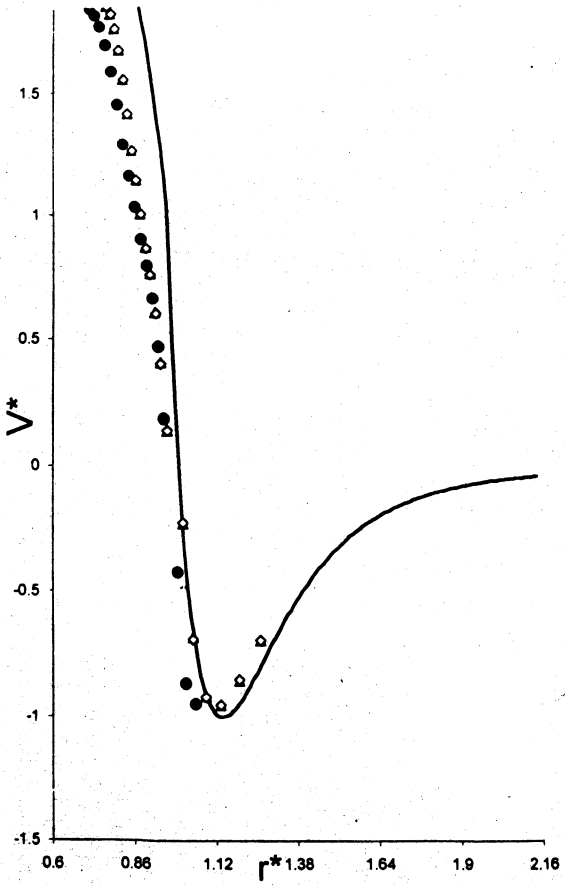

Fig. 1. Reduced pair interaction potential for H_2-H_2 (•) results obtained by the inversion of the Assael *et al.*[23] correlation equation for collision integrals, (Δ) inversion of the Hattikudar's relation[24], (◊) inversion of the Aziz's relation and (—) the HFD-type potential[26]

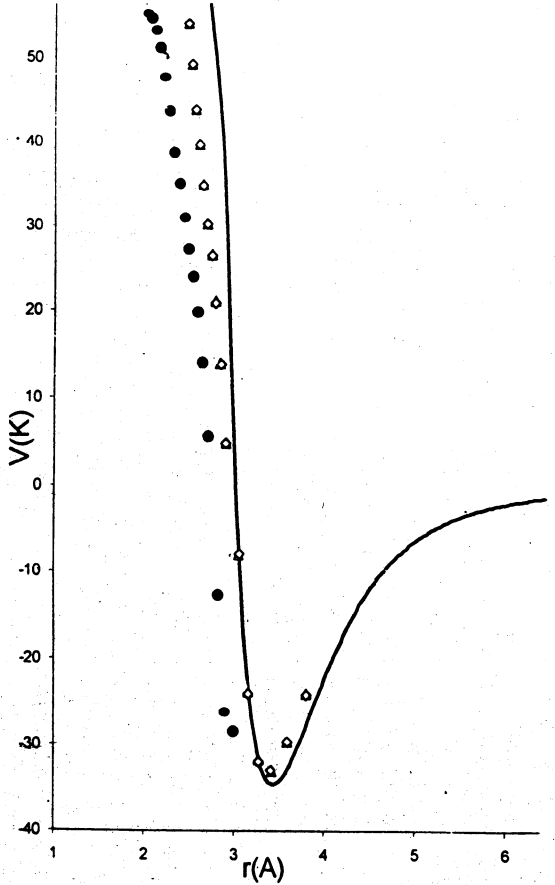

Fig. 2. Pair interaction potential for H_2-H_2 (the symbols are same as in Fig. 1)

with HFD-type and this is shown in Figs. 1 and 2. We could observe some discrepancies between the potential energy from the inversion procedure, that we claimed to be reliable, and the potential energy obtained by McConvile. Such discrepancy is more explicit in the short-range region than in the other regions. On the other hand, the relation of Assael *et al.*[23] correlates properties of hydrogen at low density over a wide temperature range with excellent accuracy. Therefore, our inverted potential is more accurate than those obtained by the other methods.

TABLE 2
DIMENSIONLESS COLLISION INTEGRALS AND RELATED RATIOS FOR H_2-H_2

$\log_{10} T^*$	$\langle\Omega^{(2,2)*}\rangle$	A*	B*	C*	E*	F*
0.0	1.44384	1.08006	1.11412	0.834456	0.88237	0.90248
0.1	1.30856	1.08712	1.11104	0.862908	0.90304	0.92732
0.2	1.20570	1.09299	1.11014	0.884802	0.91849	0.94595
0.3	1.12479	1.09795	1.10965	0.901008	0.93016	0.96025
0.4	1.05920	1.10257	1.10882	0.912787	0.93896	0.97188
0.5	1.00445	1.10718	1.10761	0.921329	0.94543	0.98179
0.6	0.95735	1.11176	1.10629	0.927558	0.95002	0.99031
0.7	0.91570	1.11616	1.10526	0.932121	0.95321	0.99740
0.8	0.87807	1.12037	1.10520	0.935386	0.95561	1.00289
0.9	0.84372	1.12487	1.10712	0.937498	0.95770	1.00679
1.0	0.81214	1.13018	1.11123	0.938332	0.95931	1.00956
1.1	0.78243	1.13633	1.11579	0.938010	0.95940	1.01249
1.2	0.75301	1.14181	1.11694	0.937184	0.95692	1.01674
1.3	0.72220	1.14381	1.11089	0.937079	0.95208	1.02227
1.4	0.68928	1.13960	1.09650	0.939028	0.94677	1.02766
1.5	0.65515	1.12811	1.07595	0.943806	0.94347	1.03109
1.6	0.62185	1.11045	1.05329	0.951269	0.94395	1.03154
1.7	0.59165	1.08931	1.03230	0.960494	0.94862	1.02926
1.8	0.56627	1.06783	1.01533	0.970224	0.95658	1.02532
1.9	0.54645	1.04851	1.00318	0.979328	0.96617	1.02086
2.0	0.53205	1.03273	0.99549	0.987053	0.97574	1.01671

Conclusion

A conclusion central to our study is that it seems to describe an interesting example of the application of the inversion method to calculate the intermolecular potential energy curve for an important prototypical system. The inverted potential can be used to obtain reduced collision integrals and their dimensionless ratios which are necessary to calculate other transport properties. This can be obtained with more accuracy than is possible by a correlation formula analysis

of such properties, primarily because viscosity measurements are more accurate than the measurement of other properties. Table-2 contains such results.

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