

Semi-Empirically Based Assessment for Predicting Dilute Gas Transport Properties of F_2 and Ar–F_2 Fluids

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The purpose of this paper is to extract information about intermolecular pair interaction potential energy and then predict the dilute gas transport properties of Ar–F_2 and F_2 systems. The potential energies of the two aforementioned systems have been compared with the LJ (12-6) and m-6-8 model potentials. A rather accurate correlation for the viscosity coefficients of each system, which encompasses a temperature range $200\,K < T < 3273.15\,K$, was reproduced from the calculated intermolecular potential energies. The predicted viscosities of Ar–F_2 and F_2 systems deviate from the literature data to within 1 and 2%, respectively. Furthermore, the calculated potential energies were used to present smooth correlations for other transport properties.

Recent developments of software packages for process design have generated a great deal of activity in a number of chemical engineering fields. Such design packages invariably require the thermophysical properties of different process streams and recent tests have indicated that the accuracy of thermophysical properties is paramount.[1,2] However, it has been recognized that it is impractical to carry out direct measurements of all of the properties of all possible systems. Consequently, in order to substitute direct measurements as much as possible, prediction schemes are being developed based on the results of kinetic theory and a limited number of experimental data of high accuracy. The highly developed kinetic theory for dilute monoatomic and polyatomic gases, on one hand, and increasingly powerful computers, on the other, have formed the basis for extensive work on the correlation and prediction of transport properties, especially in the dilute gas regime.[3–6]

From a theoretical point of view, thermophysical properties of any pure substance are predicted by intermolecular forces that operate between the molecules of that substance. Similarly, thermophysical properties of a mixture depend on the intermolecular forces that operate between the molecules of the mixture. The case of a mixture, however, is necessarily more complicated because consideration must be given not only to interaction between molecules belonging to the same component, but also to the interaction between dissimilar molecules. Therefore, to interpret and correlate thermodynamic and transport properties of fluids, it is necessary to have some understanding of the nature of intermolecular forces.[7] The general method of inferring molecular interactions was essentially trial and error. That is, a model potential was adopted with a certain number of adjustable parameters, which were varied until a good fit was obtained to a given set of experimental data. The major problem here is that, as the number of adjustable parameters increases, difficulties for fixing them with experiments arise. In addition, this procedure does not produce a unique potential.

The purpose of this paper is to describe an iterative inversion method for generating spherical pair potential energies without introducing any disposable model potential for F_2 and for Ar–F_2 gaseous systems from the corresponding states correlation of gas viscosity coefficients.

In order to establish the credential of our inverted potential energies of F_2 and Ar–F_2 systems, it is necessary to test their ability to reproduce transport properties in a wide variety of experimental accuracies. Therefore, in this paper, we examine the low-density transport properties of these systems using the inverted potential energies. The reason for selecting these systems is that, on the one hand transport properties of these systems in literature are scarce (it may arise from this fact that fluorine is so toxic and reactive that its physical properties are difficult to measure), and on the other Ar and F_2 are potentially important cryogenics fluids and such properties are needed. For example, fluorine is the most chemically reactive element of the periodic table and has widespread applications in modern industry and technology. Some of its applications can be placed in the following categories: 1) the nuclear power industry for the production of uranium hexafluoride, which is needed for the separation of ^{235}U by gaseous diffusion, of ^{235}U, 2) the manufacture of sulfur hexafluoride, which is widely used in power generation and distribution industries as an insulator on gas filled circuit breakers and as the main insulation for power transmission in high voltage coaxial cables, 3) the development of a high power laser which burns hydrogen and fluorine gases to form hot hydrogen fluoride molecules which emit infrared light at a wave length of 2.7 μm.

It is of importance to mention that the practical way to calculate transport properties, including viscosity and diffusion coefficients as well as the thermal diffusion factor from a pair potential energy, is to use the kinetic theory expressions based on the Chapman–Enskog solution of the Boltzmann equation.[7,8] The calculated viscosities of fluorine agree with litera-

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ture data within 2% in the temperature range of 200 K < T < 3273.15 K. The thermal conductivity of an Ar–F_2 mixture is calculated from the Ross et al.[9] solution of the Wang Change–Uhlenbeck–de Boer kinetic equation.[10] In the case of an Ar–F_2 system, the predicted interaction viscosity, η_{12}, binary diffusion coefficients, D_{12}, and equimolar thermal conductivity, λ are correlated with smooth equations.

Kinetic Theory of Gases

The kinetic theory expressions for the viscosity (η), diffusion coefficient (D), and isotopic thermal diffusion factor (α_0) of single substances in terms of collision integrals, read as:[7]

$$\eta = \frac{5}{16}\frac{(\pi mkT)^{1/2}}{\pi\sigma^2\Omega^{*(2,2)}} f_\eta, \tag{1}$$

and

$$D = \frac{3}{8}\frac{(\pi mkT)^{1/2}}{\pi\sigma^2\Omega^{*(1,1)}} f_D, \tag{2}$$

$$\alpha_0 = \frac{15}{2}\frac{(6C^* - 5)(2A^* + 5)}{A^*(16A^* - 12B^* + 55)}(1 + k_0), \tag{3}$$

where

$$f_\eta = 1 + (3/196)(8E^* - 7)^2, \tag{4}$$

$$f_D = 1 + (1/8)(6C^* - 5)^2/(2A^* + 5), \tag{5}$$

$$k_0 = \frac{1}{9}(7 - 8E^*)\left[\frac{2A^*}{(35/4) + 7A^* + 4F^*}\left(H^* + \frac{[A^*(7 - 8E^*) - 7(6C^* - 5)][(35/8) + 28A^* - 6F^*]}{42A^*(2A^* + 5)}\right) - \frac{5}{7}\left(H^* + \frac{7}{5}\frac{(6C^* - 5)}{(2A^* + 5)} - \frac{3}{10}(7 - 8E^*)\right)\right]. \tag{6}$$

The collision diameter σ is defined as the separation distance when the intermolecular potential function is equal to zero. ρ is the number density. In the above equations the reduced collision integral $\Omega^{*(l,s)}$ may be defined by:

$$\Omega^{*(l,s)} = \frac{\Omega^{(l,s)}}{\pi\sigma^2}, \tag{7}$$

In expressions 1, 2, 3, 4, 5, and 6, m is the molecular mass and A^*, B^*, C^*, E^*, F^*, and H^* are the collision integral ratios, which may be defined as:

$$A^* = \frac{\Omega^{*(2,2)}}{\Omega^{*(1,1)}}, \tag{8}$$

$$B^* = \frac{[5\Omega^{*(1,2)} - 4\Omega^{*(1,3)}]}{\Omega^{*(1,1)}}, \tag{9}$$

$$C^* = \frac{\Omega^{*(1,2)}}{\Omega^{*(1,1)}}, \tag{10}$$

$$E^* = \frac{\Omega^{*(2,3)}}{\Omega^{*(2,2)}}, \tag{11}$$

$$F^* = \frac{\Omega^{*(3,3)}}{\Omega^{*(1,1)}}, \tag{12}$$

$$H^* = (3B^* + 6C^* - 35/4)(6C^* - 5)^{-1}. \tag{13}$$

It should be mentioned that because the viscosity and diffusion coefficients are concerned with transporting momentum and mass, respectively, and therefore do not involve an internal degree of freedom, the Chapman–Enskog theory retains in its useful form, but the collision integrals must be averaged over all possible relative orientations occurring in collisions. If we assume that all relative orientations are equally probable, the averaged value of $\Omega^{*(l,s)}$, takes the following form:

$$\langle\Omega^{(2,2)}(T)\rangle = \frac{1}{4}\int_0^\infty\int_0^{2\pi}\int_0^\infty \times \gamma^6\{(1 - \cos^2\varphi)b\mathrm{d}b\mathrm{d}\psi\}\exp(-\gamma^2)\mathrm{d}\gamma^2. \tag{14}$$

This expression is called the Mason–Monchick approximation.[11] In the above equation $\gamma = (m/2kT)^{1/2}w$, kT is the molecular thermal energy, ψ is the azimuthal angle, w is the relative velocity, and b is the impact parameter. For the sake of simplicity, $\Omega^{*(l,s)}$ is used instead of $\langle\Omega^{*(l,s)}\rangle$.

The kinetic theory expression for the viscosity of mixtures reads as:

$$\eta_{\mathrm{mix}} = -\frac{\begin{vmatrix} \mathrm{H}_{11} & \mathrm{H}_{12} & \cdots & \mathrm{H}_{1\nu} & x_1 \\ \mathrm{H}_{21} & \mathrm{H}_{22} & \cdots & \mathrm{H}_{2\nu} & x_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mathrm{H}_{\nu1} & \mathrm{H}_{\nu2} & \cdots & \mathrm{H}_{\nu\nu} & x_\nu \\ x_1 & x_2 & \cdots & x_\nu & 0 \end{vmatrix}}{\begin{vmatrix} \mathrm{H}_{11} & \mathrm{H}_{12} & \cdots & \mathrm{H}_{1\nu} \\ \mathrm{H}_{21} & \mathrm{H}_{22} & \cdots & \mathrm{H}_{2\nu} \\ \vdots & \vdots & \ddots & \vdots \\ \mathrm{H}_{\nu1} & \mathrm{H}_{\nu2} & \cdots & \mathrm{H}_{\nu\nu} \end{vmatrix}}, \tag{15}$$

where,

$$\mathrm{H}_{ii} = \frac{{x_i}^2}{\eta_i} + \sum_{\substack{k=1 \\ k\neq i}}^{\nu}\frac{2x_ix_k}{\eta_{ik}}\frac{m_im_k}{(m_k + m_i)^2}\left(\frac{5}{3{A_{ik}}^*} + \frac{m_k}{m_i}\right), \tag{16}$$

$$\mathrm{H}_{ij}(i \neq j) = -\frac{2x_ix_j}{\eta_{ij}}\frac{m_im_j}{(m_i + m_j)^2}\left(\frac{5}{3{A_{ik}}^*} - 1\right), \tag{17}$$

$$\eta_{ij} = \frac{5}{16}\left[\left(\frac{2m_im_j}{m_i + m_j}\right)\frac{kT}{\pi}\right]^{1/2}\frac{1}{{\sigma_{ij}}^2{\Omega_{ij}}^{*(2,2)}(T_{ij}{}^*)}. \tag{18}$$

$\mathrm{A}_{ij}{}^*$ is the ratio of collision integrals (Eq. 8), x is the mole fraction of components, and η_{ij} is the interaction viscosity. Subscript i represents the heavier component and subscript j represents the lighter component of the i–j pair.

Diffusion in multi-component mixtures is entirely described in terms of the binary diffusion coefficients, D_{ij},

$$D_{ij} = \frac{3}{8}\left[\left(\frac{m_i + m_j}{2m_im_j}\right)\frac{kT}{\pi}\right]^{1/2}\frac{kT}{P}\frac{1 + \Delta_{ij}}{{\sigma_{ij}}^2{\Omega_{ij}}^{*(1,1)}(T_{ij}{}^*)}, \tag{19}$$

where P is the pressure and Δ_{ij} is a higher order correction term of the binary diffusion coefficient, which can be defined as

$$\Delta_{ij} \approx 1.3(6{C_{ij}}^* - 5)^2\frac{\mathrm{a}_{ij}x_{ij}}{1 + \mathrm{b}_{ij}x_{ij}}, \tag{20}$$

where ${C^*}_{ij}$ is the collision integral ratio for the i–j pair given by Eq. 10 and

$$\mathrm{a}_{ij} = \frac{\sqrt{2}}{8[1 + 1.8(m_j/m_i)]^2}\frac{{\Omega_{ij}}^{*(1,1)}(T_{ij}{}^*)}{{\Omega_{jj}}^{*(2,2)}(T_j{}^*)},$$

$$\mathrm{b}_{ij} = 10\mathrm{a}_{ij}[1 + 1.8(m_j/m_i) + 3(m_j/m_i)^2] - 1,$$

$$x_{ij} = \frac{x_i}{x_i + x_j}. \tag{21}$$

The expression for the thermal-diffusion factor of a binary mixture is:

$$\alpha_T = (6C^*_{ij} - 5)\left(\frac{x_1 S_1 - x_2 S_2}{x_1^2 Q_1 + x_2^2 Q_2 + x_1 x_2 Q_{12}}\right)(1 + k_T), \tag{22}$$

where k_T is a higher order correction term for the thermal-diffusion factor. This term is usually negligible compared with experimental uncertainties in α_T. The other quantities in Eq. 22 are:

$$S_1 = \frac{m_1}{m_2}\left(\frac{2m_2}{m_1 + m_2}\right)^{1/2}\frac{\sigma_{11}^2\Omega_{11}^{*(2,2)}}{\sigma_{12}^2\Omega_{12}^{*(1,1)}} - \frac{4m_1m_2A_{12}^*}{(m_1 + m_2)^2} + \frac{15m_2(m_1 - m_2)}{2(m_1 + m_2)^2}, \tag{23}$$

$$Q_1 = \frac{2}{m_2(m_1 + m_2)}\left(\frac{2m_2}{m_1 + m_2}\right)^{1/2}\frac{\sigma_{11}^2\Omega_{11}^{*(2,2)}}{\sigma_{12}^2\Omega_{12}^{*(1,1)}} \times \left[\left(\frac{5}{2} - \frac{6}{5}B_{12}^*\right)m_1^2 + 3m_2^2 + \frac{8}{5}m_1m_2A_{12}^*\right], \tag{24}$$

$$Q_{12} = 15\left(\frac{m_1 - m_2}{m_1 + m_2}\right)^2\left(\frac{5}{2} - \frac{6}{5}B_{12}^*\right) + \frac{4m_1m_2A_{12}^*}{(m_1 + m_2)^2}\left(11 - \frac{12}{5}B_{12}^*\right) + \frac{8}{5}\frac{(m_1 + m_2)}{(m_1m_2)^{1/2}}\frac{\sigma_{11}^2\Omega_{11}^{*(2,2)}}{\sigma_{12}^2\Omega_{12}^{*(1,1)}}\frac{\sigma_{22}^2}{\sigma_{12}^2}\frac{\Omega_{22}^{*(2,2)}}{\Omega_{12}^{*(1,1)}}. \tag{25}$$

The expressions for S_2 and Q_2 are obtained from those of S_1 and Q_1 by interchanging subscripts 1 and 2. The sign convention for α_T requires that subscript 1 denotes the heavier component. In the basic development of the theory of Chapman–Enskog, only binary elastic collisions between the molecules are considered and also molecules are considered to be without internal degrees of freedom. Since the internal degrees of freedom of polyatomic molecules involve transporting energy in gases, this theory can not be employed to predict thermal conductivity.

The theoretical expressions for the thermal conductivity of dilute, multi-component polyatomic gas mixtures were first derived from a solution of the kinetic theory equation found by Wang Change–Uhlenbeck,[10] employing expansion vectors that depend separately upon the translational and the internal contributions to the heat flux.

A simplified version of the thermal conductivity of an atom–diatom mixture in the limit of zero density was developed by Schreiber et al.:[12]

$$\lambda_{mix} = -\frac{\begin{vmatrix} L_{AA} & L_{AB} & x_A \\ L_{AB} & L_{BB} & x_B \\ x_A & x_B & 0 \end{vmatrix}}{\begin{vmatrix} L_{AA} & L_{AB} \\ L_{AB} & L_{BB} \end{vmatrix}}, \tag{26}$$

where

$$L_{AA} = \frac{x_A^2}{\lambda_A} + \frac{25x_Ax_B}{8A_{AB}^*\lambda_{AB}}\left(\frac{R}{C_{pA}^0}\right)^2\left[\frac{25}{4}y_B^4 + \frac{15}{2}y_A^4 - 3y_B^4B_{AB}^* + 4y_A^2y_B^2A_{AB}^* + \left(\frac{C_{pA}^0}{R} - 2.5\right)\right], \tag{27}$$

$$L_{BB} = \frac{x_B^2}{\lambda_B} + \frac{x_Ax_B}{2A_{AB}^*\lambda_{AB}} \times \left(\frac{25}{4}y_A^4 + \frac{15}{2}y_B^4 - 3y_A^4B_{AB}^* + 4y_A^2y_B^2A_{AB}^*\right), \tag{28}$$

$$L_{AB} = -\frac{5x_Ax_By_A^2y_B^2}{4A_{AB}^*\lambda_{AB}}\left(\frac{R}{C_{pA}^0}\right)\left(\frac{55}{4} - 3B_{AB}^* - 4A_{AB}^*\right), \tag{29}$$

where λ_A is the thermal conductivity of the molecular species A, λ_B is the thermal conductivity of the atomic species B, and λ_{AB} is the interaction thermal conductivity.

In Eqs. 27 and 29, C_{pA}° is for the isobaric heat capacity of molecule A of an ideal gas, which is calculated from statistical thermodynamics. R is the gas constant and A_{AB}^* and B_{AB}^* are collision integral ratios defined by the Eqs. 8 and 9. x_q stands for the mole fraction of species q and y_q is the mass ratio of species q, obtained from the ratio:

$$y_q^2 = \frac{M_q}{M_A + M_B}, \tag{30}$$

where M_q is the molar mass of species q. The interaction thermal conductivity λ_{AB} is calculated by the following relation:

$$\lambda_{AB} = \frac{15}{8}R\left(\frac{M_A + M_B}{M_AM_B}\right)\eta_{AB}. \tag{31}$$

In the present study, the functional correlation equations obtained from the extended law of corresponding states of viscosity for Ar, and also for F_2, along with the inversion method were used to establish effective isotropic pair potential energies of Ar–F_2 and F_2 systems. These correlation equations are given in Refs. 13 and 14.

Pair Potential Energy from the Viscosity Data

As was mentioned earlier, the traditional fitting procedures failed to infer a unique potential. This failure encouraged Smith and his co-workers,[15–18] to introduce a more direct method of determining the potential from transport coefficient data known as the inversion method. Because the details of this procedure have been given elsewhere,[4–6] we outline this method briefly here.

The necessary requirement to perform the inversion procedure is the determination of G, the inversion function, from an initial intermolecular potential energy, such that the following equations can be applied:

$$\frac{u}{\varepsilon} = u^* = GT^*, \tag{32}$$

$$\frac{r}{\sigma} = r^* = (\Omega^{*(2,2)})^{1/2}, \tag{33}$$

for inverse power potential functions, where G is a numerical constant. In this work, G is estimated from the Lennard–Jones (12-6) model potential, following Viehland et al.[19]

The inversion procedure begins by employing the experimental viscosity collision integral from corresponding states correlation equations to invert data points $(\Omega_{exp.}^{*(2,2)}, T^*)$ to their corresponding values $(u/\varepsilon, r/\sigma)$ on the potential energy curve

through Eqs. 32 and 33.[20] The new potential is a closer approximation to the true potential energy than the potential of the initial model. The new potential is used to calculate collision integrals from the following relations:

$$\theta = \pi - 2b\int_{r_m}^{\infty} \frac{r^{-2}\mathrm{d}r}{\left\{1-\left(\frac{b^2}{r^2}\right)-\left[\frac{2u(r)}{mw^2}\right]\right\}^{1/2}}, \quad (34)$$

$$Q^{(l)}(E) = 2\pi\left[1-\frac{1+(-1)^l}{2(1+l)}\right]^{-1}\int_0^{\infty}(1-\cos^l\theta)b\mathrm{d}b, \quad (35)$$

$$\Omega^{(l,s)}(T) = [(s+1)!(kT)^{s+2}]^{-1}\int_0^{\infty} Q^{(l)}(E)\exp(-E/kT)E^{s+1}\mathrm{d}E, \quad (36)$$

where l and s specify weighting factors related to the mechanism of transport by molecular collisions, viscosity, and thermal conductivity, which have $l = 2$ and $s = 2$, and for diffusion, which has $l = 1$ and $s = 1$. θ is the scattering angle, $Q^{(l)}(E)$ is the transport collision integral, b is the impact parameter, E is the relative kinetic energy of colliding partners, w is the relative velocity of colliding molecules, and r_m is the closest approach of two molecules.

The above process was repeated until convergence occurs. The convergence condition is judged by the extent to which the calculated collision integrals are in accord with those obtained from the corresponding states correlations and by the degree to which the intermolecular potential energies obtained by the inversion reproduce thermophysical properties consistent with the experimental values. The present results converged after two iterations and the results are given in the next section.

Results and Discussion

In this work, an iterative inversion procedure was used to determine isotropic intermolecular pair potential energies for Ar–F_2 and F_2 systems.

In the case of a noble gas-molecule (Ar–F_2) system, a corresponding states correlation for viscosity collision integral, $\Omega^{*(2,2)}$, proposed by Najafi et al.[13] and Najafi et al.[14] for Ar and F_2, respectively, was employed to calculate the interaction functional $\Omega_{12}^{*(2,2)}$ by the use of an arithmetic mean rule. We applied the two-iterative inversion procedure, outlined in the previous section, to the interaction viscosity collision integral $\Omega_{12}^{*(2,2)}$ to establish the unlike pair potential energy for the Ar–F_2 system. Furthermore, we followed the same procedure to determine the pair interaction potential of F_2 using the viscosity collision integrals given by Najafi et al.[14] In Fig. 1, the interaction potential energy of the Ar–F_2 system is compared with the LJ (12-6) model potential (initial model potential). Moreover, Figure 2 illustrates a comparison between the inverted potential energy of the F_2 system with the LJ (12-6) and m-6-8[21] model potentials. As Figures 1 and 2 depict, the inverted potential energies deviate from the LJ (12-6) and m-6-8 model potentials in the short-range region.

It should be mentioned that the correlation equation for F_2[14] is restricted to $T^* > 0.8$. The most important consequence of restricting the correlation to $T^* > 0.8$, is that the viscosity in this temperature range produces an effective average spherical potential energy function. In this temperature range, all orientation dependence effects on the transport properties are weak. Consequently, in order to integrate Eqs. 34, 35, and 36 over

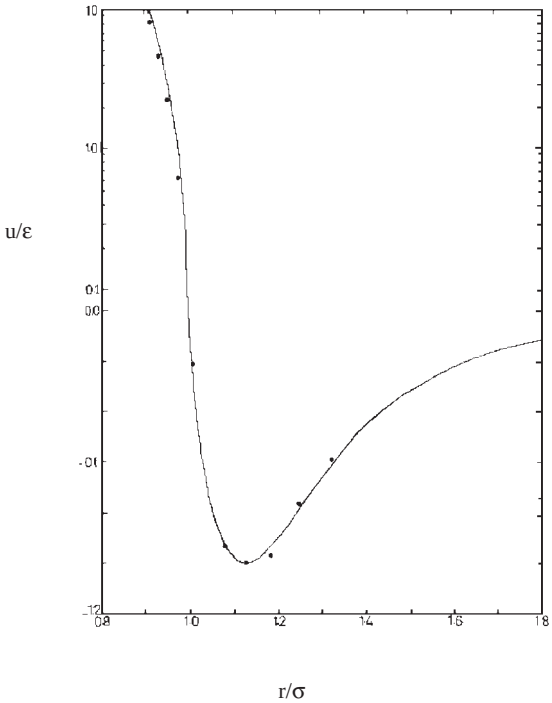

Fig. 1. The reduced effective pair potential energy versus reduced intermolecular distance for the Ar–F_2 system. The results of inversion of the viscosity data are shown by (●). The solid line (—), shown for comparison is, the LJ (12-6) model potential.

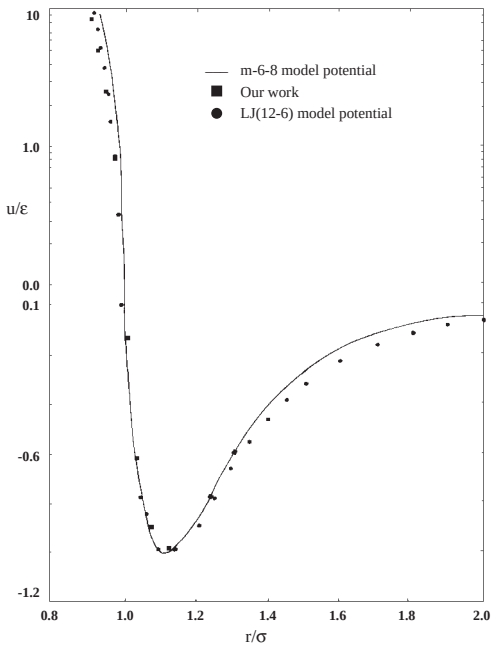

Fig. 2. The reduced effective potential energy for the pure F_2 system. The results of inversion of the viscosity data are shown by (■). The solid line (—), shown for comparison, is the m-6-8 model potential.[21] The LJ (12-6) model potential is shown by (●).

Table 1. The Reduced Collision Integrals and Their Ratios for the Ar–F_2 System

$\log T^*$	$\Omega^{*(1,1)}$	A^*	B^*	C^*	E^*	F^*
−0.1	1.5530	1.1208	1.2248	0.8423	0.8796	0.9187
0.0	1.3952	1.1166	1.1989	0.8483	0.8808	0.9217
0.1	1.2605	1.1105	1.1718	0.8584	0.8877	0.9282
0.2	1.1481	1.0489	1.1477	0.8713	0.8988	0.9377
0.3	1.0555	1.1012	1.1284	0.8854	0.9117	0.9492
0.4	0.9799	1.1002	1.1152	0.8991	0.9244	0.9610
0.5	0.9177	1.1016	1.1075	0.9110	0.9355	0.9720
0.6	0.8659	1.1049	1.1041	0.9205	0.9443	0.9817
0.7	0.8218	1.1095	1.1036	0.9276	0.9506	0.9899
0.8	0.7831	1.1149	1.1046	0.9324	0.9548	0.9968
0.9	0.7482	1.1207	1.1064	0.9355	1.0000	1.0026
1.0	0.7161	1.1265	1.1087	0.9372	0.9585	1.0073
1.1	0.6859	1.1323	1.1123	0.9379	0.9591	1.0107
1.2	0.6570	1.1386	1.1178	0.9374	0.9595	1.0130
1.3	0.6289	1.1460	1.1254	0.9358	0.9593	1.0146
1.4	0.6011	1.1542	1.1332	0.9332	0.9578	1.0165
1.5	0.5734	1.1622	1.1380	0.9301	0.9543	1.0195
1.6	0.5459	1.1677	1.1364	0.9277	0.9489	1.0239
1.7	0.5191	1.1680	1.1264	0.9272	0.9424	1.0289
1.8	0.4939	1.1608	1.1083	0.9295	0.9367	1.0331
1.9	0.4713	1.1458	1.0846	0.9353	0.9339	1.0352
2.0	0.4520	1.1245	1.0588	0.9442	0.9355	1.0347

Table 2. The Reduced Collision Integrals and Their Ratios for the F_2 System

$\log T^*$	$\Omega^{*(1,1)}$	A^*	B^*	C^*	E^*	F^*	H^*
−0.1	1.5297	1.1105	1.2189	0.8448	0.8842	0.9174	−0.3561
0.0	1.3770	1.1098	1.1958	0.8512	0.8865	0.9223	−0.5168
0.1	1.2464	1.1073	1.1719	0.8610	0.8928	0.9296	−0.4115
0.2	1.1368	1.1046	1.1497	0.8731	0.9025	0.9390	−0.2611
0.3	1.0140	1.1030	1.1318	0.8862	0.9139	0.9502	−0.1179
0.4	0.9713	1.1031	1.1188	0.8989	0.9250	0.9619	−0.0005
0.5	0.9094	1.1049	1.1103	0.9103	0.9351	0.9732	0.0925
0.6	0.8576	1.1079	1.1056	0.9196	0.9432	0.9830	0.1631
0.7	0.8133	1.1119	1.1038	0.9268	0.9494	0.9914	0.2179
0.8	0.7747	1.1166	1.1039	0.9319	0.9537	0.9982	0.2589
0.9	0.7400	1.1216	1.1053	0.9354	0.9564	1.0037	0.2912
1.0	0.7082	1.1268	1.1077	0.9374	0.9581	1.0079	0.3163
1.1	0.6784	1.1323	1.1114	0.9381	0.9591	1.0110	0.3385
1.2	0.6500	1.1386	1.1172	0.9377	0.9599	1.0131	0.3638
1.3	0.6223	1.1461	1.1246	0.9362	0.9598	1.0147	0.3905
1.4	0.5950	1.1546	1.1321	0.9336	0.9582	1.0168	0.4121
1.5	0.5677	1.1626	1.1368	0.9307	0.9545	1.0198	0.4187
1.6	0.5407	1.1676	1.1353	0.9283	0.9488	1.0240	0.3961
1.7	0.5144	1.1673	1.1256	0.9278	0.9423	1.0287	0.3416
1.8	0.4897	1.1596	1.1074	0.9301	0.9368	1.0328	0.2632
1.9	0.4674	1.1444	1.0835	0.9359	0.9343	1.0350	0.1883
2.0	0.4485	1.1232	1.0578	0.9448	0.9361	1.0346	0.1379

the given range, it was necessary to extrapolate $u(r)$ in the long-range region (low temperatures). The extrapolating function we used was $u(r) = -C_6/r^6$, where C_6 is the dispersion coefficient and r is the intermolecular distance. C_6 was estimated from the last data point in the attractive region. Then, the integration over the whole range, using the inverted pair interaction potential along with those obtained from the extrapolation function, was performed and the improved viscosity collision integrals were evaluated. These quantities are required for the computation of the transport properties. Tables 1 and 2 list the results of calculated collision integrals in conjunction with their ratios obtained from Eqs. 8, 9, 10, 11, and 12, for Ar–F_2 and Eqs. 8, 9, 10, 11, 12, and 13 for F_2 systems, respectively. The crucial benefit of the ratios of the collision integrals obtained from the inversion of the corresponding states of viscosity is that they are expected to be more accurate than those obtained from other corresponding states because the measurement of viscosity is more practical and

Table 3. The Predicted Dilute Gas Transport Properties of an Equimolar Mixture of Ar–F_2 System

T /K	η /μPas	D_{12} /10^{-4} m^2 s^{-1}	α_T	λ /10^{-3}(w/mk)
200	16.019	0.0896	0.0049	21.08
250	19.586	0.1364	0.0067	25.96
273.15	21.187	0.1611	0.0082	28.17
293.15	22.474	0.1833	0.0074	30.06
300	22.906	0.1912	0.0080	30.70
313.15	23.734	0.2067	0.0085	31.89
333.15	24.990	0.2315	0.0090	33.73
353.15	26.217	0.2575	0.0094	35.54
373.15	27.363	0.2840	0.0098	37.32
423.15	30.191	0.3557	0.0108	41.70
473.15	32.839	0.4332	0.0114	45.94
523.15	35.380	0.5168	0.0121	50.07
573.15	37.816	0.6061	0.0125	54.07
623.15	40.124	0.7004	0.0129	57.93
673.15	42.393	0.8005	0.0133	61.70
723.15	44.568	0.9055	0.0135	
773.15	46.666	1.0152	0.0137	
873.15	50.752	1.2505	0.0141	
973.15	54.609	1.5030	0.0143	
1073.15	58.353	1.7751	0.0145	
1173.15	61.947	2.0640	0.0146	
1273.15	65.438	2.3701	0.0147	
1773.15	81.709	4.1470	0.0147	
2273.15	96.485	6.3052	0.0143	
2773.15	110.158	8.8227	0.0139	
3273.15	123.303	11.6829	0.0132	

Table 4. The Predicted Dilute Gas Transport Coefficients of the Pure F_2 System

T/K	η /μPas	D /10^{-4} m^2 s^{-1}	α_0
200	16.24	0.1861	0.1773
250	19.79	0.2884	0.2389
273.15	21.38	0.4028	0.4584
293.15	22.66	0.3438	0.4200
300	23.09	0.3874	0.4069
313.15	23.92	0.4330	0.3816
333.15	25.19	0.4808	0.3430
353.15	26.39	0.5323	0.3358
373.15	27.55	0.5873	0.3489
423.15	30.42	0.7357	0.3819
473.15	33.07	0.8953	0.4047
523.15	35.66	1.0683	0.4262
573.15	38.11	1.2522	0.4422
623.15	40.47	1.4473	0.4554
673.15	42.78	1.6547	0.4685
723.15	44.97	1.8709	0.4767
773.15	47.11	2.0969	0.4841
873.15	51.27	2.5835	0.4976
973.15	55.19	3.1058	0.5051
1073.15	59.01	3.6684	0.5125
1173.15	62.64	4.2643	0.5160
1273.15	66.18	4.8971	0.5192
1773.15	82.54	8.5654	0.5240
2273.15	97.29	13.0217	0.5189
2773.15	110.95	18.2198	0.5097
3273.15	123.82	24.1272	0.4986

accurate than the measurements of other transport properties, such as diffusion and thermal conductivity. Generally, the existence of numerical tables of collision integrals and their ratios considerably ease calculations of the other properties.

A stringent assessment of any potential energy is its ability to reproduce thermophysical properties with acceptable accuracies. In this respect, transport properties of two systems, F_2 and Ar/F_2, have been generated from the present recommended potential energies.

To calculate mixture transport properties, we needed to know binary potential parameters σ_{12} and ε_{12}. None of these parameters for the Ar–F_2 system were found from transport properties in the literature. This lack encouraged us to test the most widely used combining rule known as the Lorentz–Berthelot rule, in which the collision diameter is taken to be the arithmetic mean, and the well depth to be the geometric mean of those for the pure species:

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2, \tag{37}$$

$$\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2}. \tag{38}$$

It is crucial to mention that Maitland and Wakeham[22] outlined that the experimental values of σ_{12} agree reasonably with the prediction of Eq. 37. Then, we applied the aforementioned combining rule to predict transport properties as follows.

To calculate the viscosity coefficients of the two systems, Ar–F_2 and F_2, we employed Eqs. 1, 4, 11, 15, 16, 17, and 18 obtained from the Chapman–Enskog version of the kinetic theory.[7,8] Tables 3 and 4 contain the viscosity values of an equimolar mixture of Ar–F_2 and pure F_2, respectively, in the temperature range 200 K $< T <$ 3273.15 K.

Table 5. Least-Square Coefficients for Eqs. 39, 40, and 41

Parameters in Eq. 39	
a_η	0.630948
b_η/K	−53.5025
c_η/K^2	−4.60794
d_η	−0.28872
Parameters in Eq. 40	
a_D	1.674496
b_D/K	−29.8579
c_D	−11.086
Parameters in Eq. 41	
a_λ (mW/mK)	0.483088
b_λ (mW/mK^2)	0.108657
c_λ (mW/mK^3)	−2.65E − 5

The calculated interaction viscosity, η_{12}, of the Ar–F_2 system was correlated with the following function:

$$\ln(\eta_{12}/\eta_0) = a_\eta \ln(T/T_0) + b_\eta/T + c_\eta/T^2 + d_\eta, \tag{39}$$

where $\eta_0 = 1$ μPas and $T_0 = 1$ K. Parameters in the above equation were allowed to vary for this system using the nonlinear least-square method. The above parameters are listed in Table 5.

It must be mentioned that, unfortunately, we experienced a lack of experimental data of dilute gas transport properties for the Ar–F_2 system to compare with our results and demonstrate

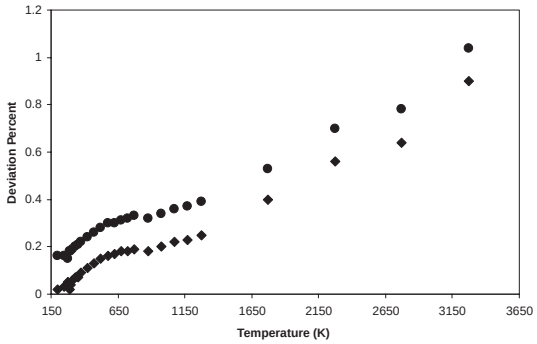

Fig. 3. The deviation of the calculated viscosities for an equimolar mixture of the Ar–F_2 system from the ones calculated from Richenberg's[23] (●) and Davidson's[24] (◆) methods. Deviation percent $= 100(\eta_{exp} - \eta_{cal})/\eta_{exp}$.

their extent of accuracies. Therefore, in the present study, we have confined ourselves to comparing our works with other methods given in literature. Figure 3 illustrates a deviation plots of the calculated mixture viscosity coefficients of the Ar–F_2 system, obtained from our inverted potential energy, and those obtained from Richenberg's[23] and Davidson's[24] methods. Absolute average deviation (AAD) of the viscosities from Richenberg's and Davidson's methods were found to be 0.2 and 0.34, respectively, which shows the desirable harmony of the present work with two other methods in a broad temperature range. It is worth mentioning that Poling et al.[25] have recommended Richenberg's method as the most consistently accurate method among the other methods cited in their book.

Figure 4 compares the calculated viscosities of a pure F_2 system with those given in the literature.[21,26,27] The calculated viscosities show acceptable agreement with the literature data.

Binary diffusion coefficients of gases are of special interest, for they can give information on forces between unlike molecules. Conversely, by the formulas of kinetic theory, knowledge of fundamental intermolecular forces can lead to gaseous diffusion coefficients. The binary diffusion coefficient of the Ar–F_2 system, D_{12}, was calculated from the inverted potential energy through its corresponding kinetic expressions 19, 20, and 21. The predicted values of this property were correlated with the following equation:

$$\ln(PD_{12}/P_0D_0) = a_D \ln(T/T_0) + b_D/T + c_D, \qquad (40)$$

where P is the pressure in atm and D_{12} is the binary diffusion coefficient in cm^2/s. Further, $P_0 = 1$ atm and $D_0 = 1\,cm^2/s$ and constants a_D, b_D, and c_D, are given in Table 5. The values of an equimolar mixture of this property at different temperatures have been given in Table 3 for the Ar–F_2 system. Diffusion coefficients of a pure F_2 system, in the temperature range $200\,K < T < 3273.15\,K$, obtained from the inverted potential energy of fluorine and using Eqs. 2, 5, 8, and 10, are listed in Table 4. Due to the lack of experimental values for mass and binary diffusion coefficients, we could not analyze the accuracies of our results concerning this property. Also, Table 4 contains the isotopic thermal diffusion factor, α_0, for fluorine fluid.

The thermal diffusion factor, α_T, which is the most sensitive transport coefficient to the details of the intermolecular potential and the most difficult to measure with a high degree of accuracy, was calculated for the Ar–F_2 system using the inverted pair potential energy and relations 22, 23, 24, and 25. Table 3 represents the values of the thermal diffusion factor of the Ar–F_2 dilute gas mixture in the aforementioned temperature range. It should be added that the thermal diffusion factor describes how a gas mixture can be separated under the influence of a temperature gradient. As the values of this property increase, separation of the gas mixture becomes easier. In the case of the Ar–F_2 mixture, because the mass ratio of the components is close to unity, the values of α_T are relatively low, and therefore separation of the components of this mixture can be a difficult task.

As was pointed out earlier, thermal conductivity, λ, can not be predicted through the Chapman–Enskog scheme. In this respect, we employed Eqs. 26, 27, 28, 29, 30, and 31, which are based on the Ross et al.[9] version of the kinetic theory, to predict thermal conductivity coefficients over the nearly wide range of temperatures. The calculated thermal conductivity of an equimolar dilute gas mixture of the Ar–F_2 system has been presented with the following simple function:

$$\lambda = a_\lambda + b_\lambda T + c_\lambda T^2, \qquad (41)$$

where the above parameters are given in Table 5. It is of importance to mention that we set C_{rot}/R equal to 1 for the linear molecule F_2 and C_{vib} the vibrational part of the heat capacity of the diatomic molecule F_2. Necessary for calculating thermal conductivity, was determined using the statistical mechanical approach:

$$\frac{C_{vib}}{R} = \sum_{j=1}^{k} \left(\frac{\Theta_{vj}}{T}\right)^2 \frac{\exp(\Theta_{vj}/T)}{[\exp(\Theta_{vj}/T)]^2}. \qquad (42)$$

Here, the symbol Θ_{vj} identifies the characteristic vibrational temperature for the vibrational degree of freedom j.[28] Table 3 also includes numerical values of the thermal conductivity of an equimolar Ar–F_2 gas mixture. In the case of the thermal conductivity of Ar–F_2, we suffered from a lack of experimental values to compare with our results.

The major benefit of the present study is that in addition to the prediction of viscosity with an acceptable accuracy, our inverted pair potential energy is capable of providing other transport properties such as thermal conductivity, binary diffusion coefficients, and thermal diffusion factors. Another advantage of the inversion procedure is that the values of one property that are known accurately can be used to predict other properties that are known by experiment, but less accurately. Viscosity is usually measured with substantially greater accuracy than diffusion coefficients and thermal diffusion factors. Starting with $u(r)$, we have been able to use the accuracy of the viscosity to improve that of, for instance, diffusion coefficients.

Concluding Remarks

The present paper has described corresponding states viscosity analysis by use of the inversion method, which yielded unique effective and isotropic pair potential energies for F_2 and Ar–F_2 systems. Therefore, the inversion procedure is of considerable importance to obtain non-parametric interaction potential energy and transport properties. This method provides an opportunity to assess the accuracy of a proposed model's potential energy by direct comparison with experi-

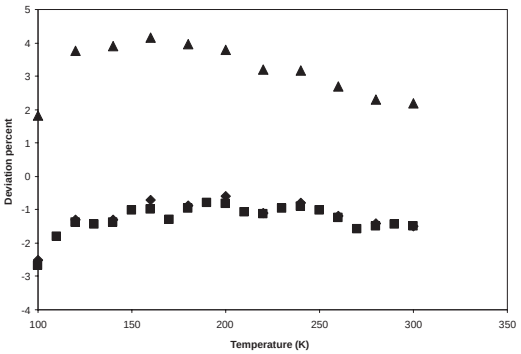

Fig. 4. The deviation of the calculated viscosities for the pure F_2 system from the ones given in Refs. 21 (◆), 26 (■), and 27 (▲). Deviation percent = $100(\eta_{exp} - \eta_{cal})/\eta_{exp}$.

mental data. Furthermore, this scheme relieves us of the variation of the parameters of a selected multi-parameter analytic equation for the pair potential function to optimize the fit to a wide range of thermophysical data of a material, and guarantees a unique potential energy.

Owing to the difficulties associated with the experimental determination of all relevant transport properties of fluids and fluid mixtures within a wide range of temperatures, few experimental data exist. In these circumstances, there is a need to search for calculation procedures to supplement the available experimental data. Any such calculation procedure should have a firm statistical–mechanical foundation. Such a foundation exists for low-density pure gases and gaseous mixtures in the form of the formulae resulting from the Ross et al. solution of Wang Chang–Uhlenbeck for thermal conductivity and the Chapman–Enskog solution of the Boltzmann equation for the remaining transport properties.

In short, we conclude by pointing out that the inversion procedure is on the one hand a powerful method for generating potential energies from the law of corresponding states of viscosity and on the other a valuable supplement for obtaining transport properties, especially at either high or low temperatures where direct measurements may be practically impossible.

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