

Direct Determination of the Interaction Potentials of He-N₂, Ne-N₂ and Ar-N₂ from the Extended Principle of Corresponding States

E. K. Goharshadi¹

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The pair-potential energy functions for He-N₂, Ne-N₂, and Ar-N₂ have been determined from a direct inversion of the experimentally reduced viscosity collision integrals obtained from the corresponding-states correlation. The resulting potentials are in excellent agreement with the potentials independently obtained from molecular beam scattering measurements. The potentials have been used to predict the diffusion and viscosity coefficients for each system, and they are found to be in reasonable agreement with experimental values.

KEY WORDS: collision integrals; corresponding states; molecular beam; potential energy function; viscosity.

1. INTRODUCTION

The interaction forces in simple atom-molecule systems are of fundamental importance for a variety of physical and chemical processes. In the early 1970s, most information concerning intermolecular forces was inferred from studies of thermophysical properties [1]. In contrast to the theory, which was elegant, the general method of inferring molecular potentials from it was essentially very difficult [2]. 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 potentials resulting from this method do not appear to be unique.

The failure of the traditional fitting procedure described above to establish unique potentials has encouraged the search for more direct methods of determining the potential from transport-coefficient data. It has

¹ Department of Chemistry, Ferdowsi University, Masshad 91384, Iran.

been demonstrated that such inversion of transport-property data is practical [3] and that some insight into the reasons for its success has been gained.

The aim of the present paper is to present an application of the inversion procedure for the simplest case of an anisotropic interaction, namely, that of molecular nitrogen with He, Ne, and Ar.

The pair potential-energy functions for He-N₂, Ne-N₂, and Ar-N₂ were determined with the inversion method based on the experimental reduced viscosity collision integrals obtained from the corresponding-states correlation [4]. A comparison of the potentials with the previously determined potentials is included [5-7]. The resulting potentials are used to predict the diffusion and viscosity coefficients for each system, and they are found to be in good agreement with experimental values.

2. THE INVERSION PROCEDURE

In the Chapman-Enskog theory [8], the transport properties of a gas can be expressed in terms of a set of collision integrals, $\Omega^{(l,s)}(T)$, characterized by the values of l and s . For example, the viscosity is a function of $\Omega^{(2,2)}(T)$. These integrals are functions of the temperature, T , and they depend on the interaction potentials between the atoms or molecules in the gas.

It is more convenient to render the values of the integrals dimensionless by dividing them by their corresponding rigid-sphere values. A reduced collision integral which is a function only of the reduced temperature, $T^* = kT/\epsilon$, may be defined as

$$\Omega^{(l,s)*}(T^*) = \Omega^{(l,s)}(T) / \Pi \sigma^2 \quad (1)$$

where σ is the scaling parameter such that $V(\sigma) = 0$, and k is Boltzmann's constant. The reduced collision integrals can be expressed in the form of triple integrals. In this work, the triple integrals were calculated with a program based on that of O'Hara and Smith [9, 10].

The universal function $\Omega^{(2,2)*}$ can be used to determine the intermolecular potential by an "inversion procedure." The inversion method is similar to that described in a previous paper [11] for CH₄-CH₄, and the same principle of corresponding states was used [4]. It is capable of correlating equilibrium and transport properties of the noble gases, 11 polyatomic gases, and their multicomponent mixtures over a very wide temperature range with an accuracy comparable to that of the best measurements [12]. According to this law, the collision integral $\Omega^{(2,2)*}$ is defined as

$$1 \leq T^* \leq 10 \quad (2a)$$

$$\Omega^{(2,2)*} = \exp[0.4664 - 0.56991(\ln T^*) + 0.19591(\ln T^*)^2 - 0.03879(\ln T^*)^3 + 0.00259(\ln T^*)^4]$$

$$T^* \geq 10 \quad (2b)$$

$$\Omega^{(2,2)*} = (\rho^*)^2 \alpha^2 [1.04 + a_1(\ln T^*)^{-1} + a_2(\ln T^*)^{-2} + a_3(\ln T^*)^{-3} + a_4(\ln T^*)^{-4}]$$

All parameters have the same meaning as in Ref. 4.

The direct inversion procedure for the viscosity is based on the idea that, at a given T^* , the value of $\Omega^{(2,2)*}$ is determined by the potential over only a small range of separation around a value r [13]. It is always possible to refine this idea by defining a function G_η such that

$$V(r) = G_\eta(T^*) T^* \quad (3a)$$

Table I. Dimensionless Collision Integrals $\Omega^{(l,s)*}$ and the Related Ratios for He-N₂

$\log T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	B^*	C^*
0.0	1.0510	1.2064	1.0888	0.9580
0.1	1.0199	1.1712	1.0993	0.9595
0.2	0.9874	1.1307	1.1071	0.9513
0.3	0.9535	1.0867	1.1144	0.9476
0.4	0.9186	1.0414	1.1131	0.9446
0.5	0.8833	0.9969	1.1130	0.9424
0.6	0.8484	0.9548	1.1122	0.9410
0.7	0.8142	0.9158	1.1114	0.9402
0.8	0.7812	0.8797	1.1110	0.9397
0.9	0.7406	0.8458	1.1108	0.9395
1.0	0.7185	0.8136	1.1108	0.9394
1.1	0.6890	0.7825	1.1107	0.9393
1.2	0.6607	0.7521	1.1103	0.9393
1.3	0.6336	0.7225	1.1092	0.9394
1.4	0.6077	0.6935	1.1073	0.9398
1.5	0.5830	0.6652	1.1039	0.9405
1.6	0.5598	0.6375	1.0978	0.9419
1.7	0.5382	0.6101	1.0875	0.9445
1.8	0.5187	0.5830	1.0728	0.9486
1.9	0.5016	0.5569	1.0552	0.9546
2.0	0.4873	0.5327	1.0371	0.9620

and $\Omega^{(2,2)*}$ is approximately defined by

$$\Omega^{(2,2)*} = (r/\sigma)^2 \quad (3b)$$

where G_η is known as the inversion function, which changes from about 0.72 at high temperatures to 0.561 at low temperatures. However, despite this temperature variation, G_η is remarkably similar for all reasonably realistic potential functions. Therefore, finding $V(r)$ is straightforward when ε is unity. Equations (2a) and (2b) can be inverted by the above method to yield $V(r)/\varepsilon$ as a function of r/σ . To do so, one inserts the value of G_η , given by Clancy et al. [13], into Eq. (3a) to obtain the potential energy (V/ε); the corresponding value of r/σ may be obtained from the collision integral calculated from Eqs. (2a) and (2b). This process may be repeated until convergence is obtained. At each step in the iteration process the percentage deviation of the $\Omega^{(2,2)*}$ calculated from the potential and its correlated values $\Omega^{(2,2)*}$ is determined. The convergence is usually obtained after only two iterations [14]. We have obtained accurate reduced potentials for He-N₂, Ne-N₂, and Ar-N₂ by this procedure.

Table II. Dimensionless Collision Integrals $\Omega^{(l,s)*}$ and the Related Ratios for Ne-N₂

$\log T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	B^*	C^*
0.0	1.4159	1.6274	1.2302	0.8570
0.1	1.2834	1.4538	1.0188	0.8598
0.2	1.1683	1.3080	1.1599	0.8692
0.3	1.0720	1.1900	1.1340	0.8821
0.4	1.0160	1.0967	1.1167	0.8757
0.5	0.9283	1.0235	1.1074	0.9087
0.6	0.8747	0.9657	1.1041	0.9189
0.7	0.8293	0.9187	1.1043	0.9264
0.8	0.7890	0.8790	1.1060	0.9314
0.9	0.7540	0.8438	1.1077	0.9345
1.0	0.7211	0.8112	1.1087	0.9364
1.1	0.6904	0.7803	1.1091	0.9376
1.2	0.6615	0.7504	1.1090	0.9384
1.3	0.6341	0.7213	1.1087	0.9390
1.4	0.6086	0.6928	1.1081	0.9394
1.5	0.5831	0.6651	1.1072	0.9399
1.6	0.5595	0.6385	1.1061	0.9405
1.7	0.5371	0.6131	1.1051	0.9410
1.8	0.5157	0.5890	1.1046	0.9416
1.9	0.4954	0.5661	1.1049	0.9420
2.0	0.4760	0.5443	1.1059	0.9421

Table III. Dimensionless Collision Integrals $\Omega^{(l,s)*}$ and the Related Ratios for Ar-N₂

$\log T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	B^*	C^*
0.0	1.3893	1.5719	1.2173	0.8623
0.1	1.2644	1.4163	1.1835	0.8662
0.2	1.1562	1.2841	1.1543	0.8754
0.3	1.0652	1.1765	1.1327	0.8874
0.4	0.9897	1.0910	1.1193	0.8999
0.5	0.9271	1.0232	1.1122	0.9107
0.6	0.8744	0.9687	1.1096	0.9192
0.7	0.8289	0.9232	1.1094	0.9256
0.8	0.7886	0.8833	1.1098	0.9300
0.9	0.7522	0.8467	1.1098	0.9330
1.0	0.7187	0.8123	1.1095	0.9351
1.1	0.6876	0.7795	1.1094	0.9334
1.2	0.6584	0.7483	1.1095	0.9376
1.3	0.6307	0.7185	1.1097	0.9383
1.4	0.6045	0.6898	1.1092	0.9388
1.5	0.5796	0.6620	1.1077	0.9393
1.6	0.5559	0.6350	1.1054	0.9401
1.7	0.5335	0.6091	1.1032	0.9410
1.8	0.5124	0.5845	1.1087	0.9420
1.9	0.4924	0.5615	1.1022	0.9428
2.0	0.4734	0.5401	1.1040	0.9431

These accurate potentials can be used to obtain collision integrals and the following ratios of collision integrals which occur in the transport properties of these systems.

$$B^* = (5\Omega^{(1,2)*} - 4\Omega^{(1,3)*})/\Omega^{(1,1)*} \quad (4a)$$

$$C^* = \Omega^{(1,2)*}/\Omega^{(1,1)*} \quad (4b)$$

The most commonly used collision integrals and their ratios for He-N₂, Ne-N₂, and Ar-N₂ are given in Tables I, II, and III, respectively.

3. RESULTS

The intermolecular pair potentials for He-N₂, Ne-N₂, and Ar-N₂ have been determined from a direct inversion of the experimentally reduced viscosity collision integrals obtained from the corresponding-states correlation. Comparisons of the present potentials with the previously determined

potentials are shown in Figs. 1–3. As these figures show, there is good agreement in each case between the calculated and the experimental potentials.

The temperature dependence of the transport coefficients may provide a critical test of the accuracy of the potentials. Theoretical expressions for the transport coefficients of binary mixtures can be found in standard treatises [15].

The calculated viscosity coefficients of these systems as a function of the mixture concentration together with the percentage deviation with the corresponding experimental values are shown in Tables IV to VI. The necessary collision integrals of the pure components He, Ne, Ar, and N₂ for calculating η_{mix} are taken from their inversion potentials [16–18]. For He–N₂ mixtures, the experimental η_{mix} values in the temperature range 298.15 to 563.15 K are taken from Kestin et al. [19]. The viscosity coefficients for the Ne–N₂ mixtures are available in the temperature range 298 to 573 K [20]. Hellemans et al. [21] measured the viscosity coefficients of Ar–N₂ mixtures.

The temperature dependence of the diffusion coefficients of the three systems have also been calculated. The results are shown in Tables VII–IX.

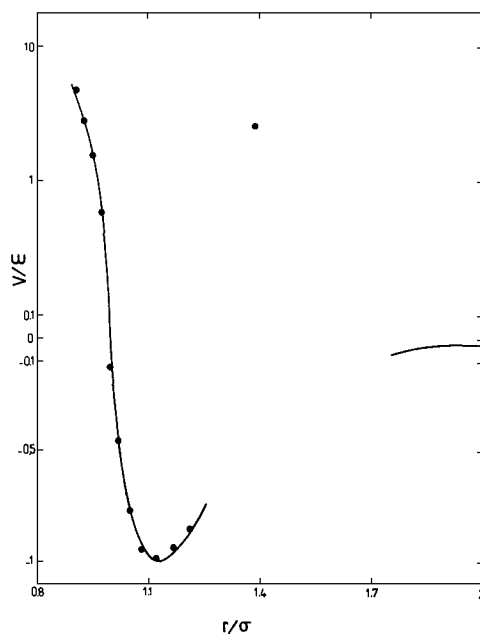


Fig. 1. Reduced pair potential obtained by inversion of the corresponding states for He–N₂ (·). The curve follows the molecular beam-scattering data [5].

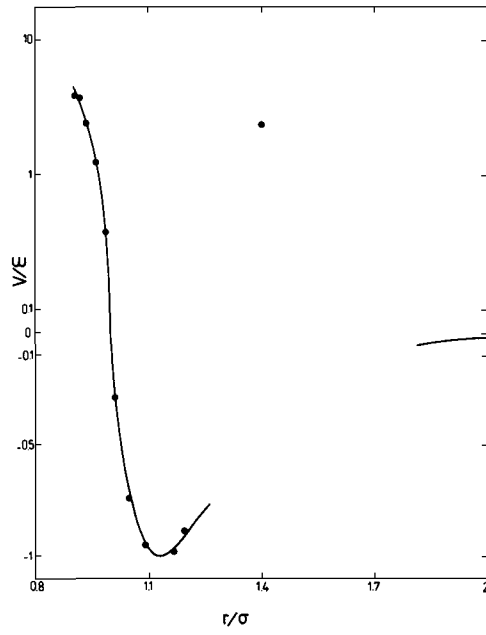


Fig. 2. Same as Fig. 1 for Ne-N₂ [6].

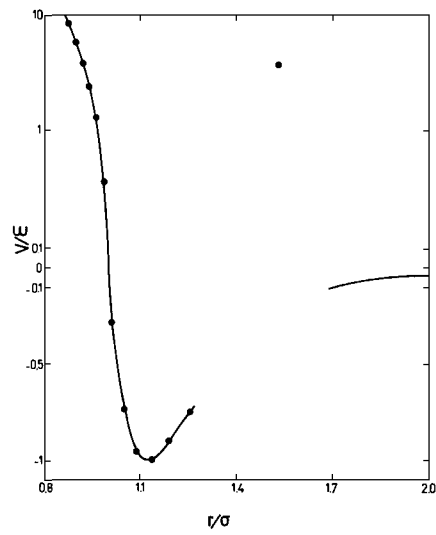


Fig. 3. Same as Fig. 1 for Ar-N₂ [7].

Table IV. Viscosity Coefficients of He-N₂ Mixtures

T (K)	x_{He}	η_{mix} (μP)	Dev. (%)
298.15	0.1911	181.9	0.60
	0.3633	187.2	0.27
	0.5746	194.0	0.05
	0.7545	198.8	0.05
	0.8399	199.9	0.34
	0.9277	199.3	0.50
373.15	0.1911	214.9	0.97
	0.3633	220.5	0.63
	0.5746	227.5	0.26
	0.7545	232.1	0.30
	0.8399	233.0	0.34
	0.9277	231.8	0.81
463.15	0.1911	250.3	1.14
	0.3633	256.5	0.66
	0.5746	264.2	0.34
	0.7545	269.4	0.22
	0.8399	270.4	0.37
	0.9277	269.2	0.81
563.15	0.1911	286.6	1.04
	0.3633	293.5	0.54
	0.5746	302.4	0.20
	0.7545	308.5	0.00
	0.8399	309.9	0.29
	0.9271	309.1	0.39

Table V. Viscosity Coefficients of Ne-N₂ Mixtures

T (K)	x_{Ne}	η_{mix} (μP)	Dev. (%)
298	0.0	177.0	0.61
	0.2	196.0	0.76
	0.4	218.2	0.81
	0.6	244.6	0.77
	0.8	276.2	0.75
	1.0	314.9	0.60
373	0.0	209.1	0.99
	0.2	230.9	1.03
	0.4	256.4	1.00
	0.6	286.6	1.00
	0.8	322.9	1.10
	1.0	367.4	0.97
473	0.0	247.7	1.20
	0.2	272.4	1.30
	0.4	301.5	1.40
	0.6	336.2	1.50
	0.8	378.4	1.43
	1.0	430.7	1.32

Table VI. Viscosity Coefficients of Ar-N₂ Mixtures

T (K)	x_{N_2}	η_{mix} (μP)	Dev. (%)
298.15	0.2073	215.0	-0.92
	0.4160	206.2	-0.63
	0.6011	197.0	-0.75
	0.7811	188.1	-0.48
367.15	0.2073	257.2	-0.46
	0.4160	245.1	-0.49
	0.6011	233.3	-0.68
	0.7811	222.5	-0.36
467.15	0.2073	308.7	-0.96
	0.4160	294.8	-0.37
	0.6011	280.2	-0.53
	0.7811	266.4	-0.22
673.15	0.2073	402.3	-0.30
	0.4160	381.0	-0.37
	0.6011	361.4	-0.30
	0.7811	341.0	-0.47
767.15	0.2073	439.2	-0.41
	0.4160	415.5	-0.53
	0.6011	394.8	-0.35
	0.7811	374.1	-0.19

Table VII. Diffusion Coefficients of the He-N₂ System

T (K)	D_{12} ($\text{cm}^2 \cdot \text{s}^{-1}$)	Dev. (%)
195.10	0.346	-0.61
205.20	0.377	-0.53
218.07	0.417	-0.48
234.22	0.471	-0.64
255.50	0.544	-0.37
280.00	0.635	-0.95
290.00	0.674	-1.05
300.00	0.714	-1.12
310.00	0.754	-1.07
320.00	0.795	-1.02
337.90	0.871	-0.93
356.07	0.952	-1.06
373.09	1.031	-1.28
385.49	1.088	-1.40
400.21	1.158	-1.22

Table VIII. Diffusion Coefficients for the Ne-N₂ System

<i>T</i> (K)	<i>D</i> ₁₂ (cm ² ·s ⁻¹)	Dev. (%)
212.24	0.1815	-0.94
255.44	0.2499	-0.97
280.00	0.2926	-0.58
300.00	0.3292	-0.27
320.00	0.3678	-0.08
352.51	0.4325	-0.91
373.15	0.4745	1.76
398.28	0.5279	-0.28
445.34	0.6454	0.80
473.15	0.7149	2.20
673.15	1.2989	1.00
873.15	2.0132	0.63

Experimental values of diffusion coefficients of He-N₂, Ne-N₂, and Ar-N₂ have been reported in Refs. 22, 23, and 7, respectively.

4. CONCLUDING REMARKS

The present potentials for He-N₂, Ne-N₂, and Ar-N₂ provide a good overall account of the experimental properties considering their stated uncertainty in measurement. Thus the present work not only has generated potential functions for these systems, but also demonstrates the validity of the inversion procedure for anisotropic systems. Furthermore, it has taken

Table IX. Diffusion Coefficients of the Ar-N₂ System

<i>T</i> (K)	<i>D</i> ₁₂ (cm ² ·s ⁻¹)	Dev. (%)
252.7	0.1441	-0.35
300.0	0.1971	0.75
356.1	0.2673	0.11
373.2	0.2910	1.02
400.2	0.3284	0.18
473.2	0.4412	1.08
573.2	0.6136	1.35
673.2	0.8097	1.14
773.2	1.0273	0.84

us a step closer to the ultimate goal of predicting anisotropic potentials without too much effort and with considerable confidence.

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