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Direct Determination of the Intermolecular Potential of $Kr—N_2$, $Xe—N_2$ and $He—SF_6$ from the Extended Principle of Corresponding States

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A more direct semi-empirical inversion has been developed that obtains a non-parametric potential from experimental data. The method is iterative and coverage rapidly once a good choice has been made for the initial starting potential. To be specific, the aim of an inverse method is to obtain the potential by considering the experimental data as a functional, instead of fitting the data to a constrained potential for having a few parameters. The interaction potentials are estimated for the $Kr—N_2$, $Xe—N_2$ and $He—SF_6$ and comparisons of the potentials with the earlier values were made. The resulting potentials were used to predict the diffusion coefficient for Kr—Ne.

INTRODUCTION

Intermolecular forces are responsible for many of the bulk properties of matter in all its phases. For example, a realistic description of the relationship among pressure, volume and temperature of a gas must include the effects of attractive and replusive forces between molecules. Accurate knowledge of the pair potential energy function is essential for the understanding of various molecular processes and chemical reactions.[1] Molecular descriptions of condensed matter depend on having knowledge of the pairwise interactions as well as the many-body forces which govern the dynamics of discrete constituents. The determination of potential energy surfaces has come a long way[2–6] and generally can be pursued by two different approaches: one is to perform *ab initio* quantum chemistry calculations within the Born-Openheimer approximation, and the other is to perform inversion of experimental data. Important strides in these endeavours have been made, especially in the past decade[7–10], because of recent important advances on many fronts.

Nevertheless, the most cutting edge computational quantum chemistry approaches to produce high-accuracy *ab initio* potential energy surfaces are still limited to relatively small systems of a few atoms and can only be afforded to calculate potential energies at a finite number of discrete geometric, typically

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around the equilibrium position. Moreover, *ab initio* potential energy often does not possess the accuracy comparable to that needed to explain the modern laser spectroscopic data. On the other hand, existing numerical procedures applied for exclusively of a parameter fitting nature[11], except for some simple systems.

Inversion Method: The inversion method to be described allows for the simultaneous use of experimental data from measurements of several different properties.

In the present work we report an application of the inversion procedure for determining the Kr—N_2, Xe—N_2 and He—SF_6 interaction potentials and are compared with the previously determined potentials. For the Kr—Ne the diffusion coefficients are also predicted by resulting potentials.

RESULTS AND DISCUSSION

The exact reduced potential for systems of Kr—N_2, Xe—N_2 and He—SF_6 are calculated by direct inversion method on viscosity from extended principle of corresponding states. For this purpose O'Hara[12, 13] computer programmings are used and flow chart is illustrated in Figure 1.

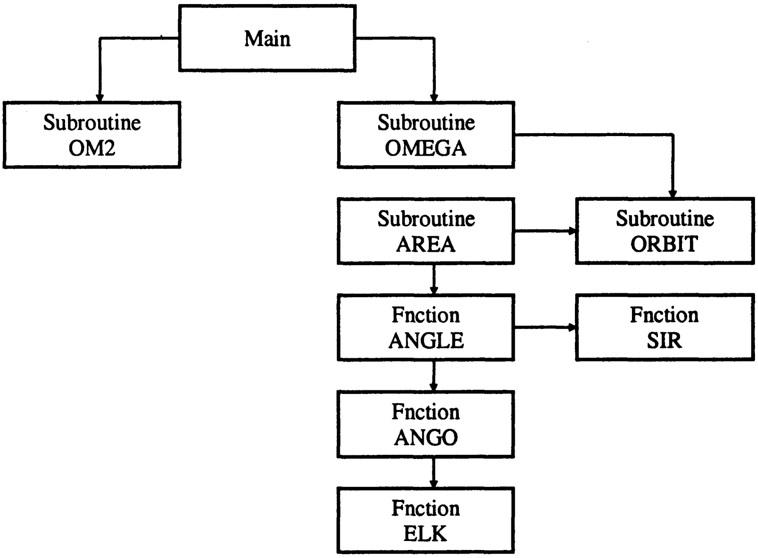

Fig. 1. Flow chart illustrating how the interatomic and inter- and intramolecular potential energy can be obtained, via *ab initio* calculations

The intermolecular potential energy, U and repulsion energy, V(r) are calculated from $U = 1/r$ and $V(r) = A/r^{12}$, respectively. A is a constant and obtained from $A = V/U^{12}$. The values and V(r) for systems of Kr—N_2, Xe—N_2 and He—SF_6 are listed in Table-1. The attraction energy, V(r) is obtained from $V(r) = -C/r^6$, where C is a constant and calcualted from $C = -V/U^6$.

TABLE-1
THE INTERMOLECULAR POTENTIAL ENERGY, U = 1/r AND REPULSION ENERGY, $V(r) = A/r^{12}$, FOR Kr—N_2, Xe—N_2 AND He—SF_6

r	U	$V^a(r)$ Kr—N_2	$V^b(r)$ Xe—N_2	$V^c(r)$ He—SF_6
1.58	0.6329	17.4029	17.4701	18.8123
1.56	0.6410	20.2773	20.3556	21.9196
1.55	0.6452	21.9041	21.9887	23.6781
1.53	0.6536	25.5982	25.6970	276713
1.52	0.6579	27.6938	27.8007	29.9367
1.50	0.6667	32.4647	32.5900	35.0939
1.49	0.6711	35.1780	35.3138	38.0270
1.47	0.6803	41.3712	41.5309	44.7218
1.46	0.6849	44.9026	45.0760	48.5392
1.44	0.6944	52.9854	53.1899	57.2766
1.43	0.6993	57.6068	57.8291	62.2723

[a]At $T^* = 20$, $V = 14.4$, $U = 0.6234$, $A = V/U^{12} = 4212.1704$
[a]At $T^* = 20$, $V = 14.4$, $U = 0.6228$, $A = V/U^{12} = 4228.4310$
[a]At $T^* = 20$, $V = 14.4$, $U = 0.6190$, $A = V/U^{12} = 4553.3100$

The values of attraction for three studied systems are shown in Table-2.

TABLE-2
THE INTERMOLECULAR POTENTIAL ENERGY, U = 1/r AND ATTRACTION ENERGY, $V(r) = -C/r^6$, FOR Kr—N_2, Xe—N_2 AND He—SF_6

r	U	$V^a(r)$
∞	0.0000	0.0000
8	0.1250	-5.2020×10^{-4}
5.5	0.1818	-4.9267×10^{-3}
3.8	0.2632	-4.5334×10^{-2}
3.5	0.2857	-7.4165×10^{-2}
3.1	0.3226	–0.1537
2.75	0.3636	–0.3153

[a]At $T^* = 1$, $V = -0.7390$, $U = 0.4191$, $C = -V/U^6 = 136.3761$

The relative percentage deviation, RPD, for collision integrals, $\Omega^{(2,2)*}$ is calculated from

$$\text{RPD} = \frac{\Omega^{(2,2)*}_{\text{calc.}} - \Omega^{(2,2)*}_{\text{cs.}}}{\Omega^{(2,2)*}_{\text{cs.}}} \times 100 \qquad (1)$$

where $\Omega^{(2,2)*}_{\text{calc.}}$ and $\Omega^{(2,2)*}_{\text{cs.}}$ are calculated reduced viscosity collision integrals from potential and those obtained from extended corresponding states. The reduced viscosity collision integrals, $\Omega^{(2,2)*}$ at $T^* \geq 10$ are obtained from the following equation[14]:

$$\Omega^{(2,2)*} = (\rho^*)^2\alpha^2[1.04 + \alpha_1(\mathrm{In}T^*)^{-1} + \alpha_2(\mathrm{In}T^*)^{-2} + \alpha_3(\mathrm{In}T^*)^{-3} + \alpha_4(\mathrm{In}T^*)^{-4}] \quad (2)$$

The RPD values of $\Omega^{(2,2)*}$ at T^* from 1 to 20 for three systems of Kr—N_2, Xe—N_2 and He—SF_6 are listed in Table-3.

The intermolecular potential energies which directly obtained from viscosity corresponding states are more reliable rather than other properties. Calculated potential energies for Kr—N_2 give good agreement with those obtained by McCourt *et al.*[15] and compared graphically and shown in Fig. 2. For He—SF_6 the obtained results are compared with reported values by Taylor *et al.*[16] (Fig. 3). In literature there is no values reported for Xe—N_2; hence, only potentials by inversion method are shown graphically in Figure 4.

The difussion coefficents, $D/m^2\ s^{-1}$ by inversion method are calculated for Kr—Ne from the following equation:

$$D = \frac{3}{16} \cdot \frac{(2\pi kT/\mu)^{1/2}}{\pi\sigma^2 P\Omega^{(2,2)*}} \quad (3)$$

where k, μ, σ, P and $\Omega^{(1,1)*}$ are Boltzman constant, active mass, collision diameter, pressure and reduced diffusion collision integrals, respectively.

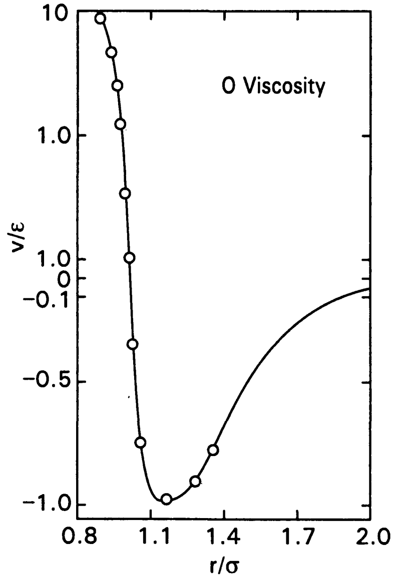

Fig. 2. The intramolecular potential energy for Kr-N_2 : (O) from viscosity corresponding states and solid curve from McCourt[15]

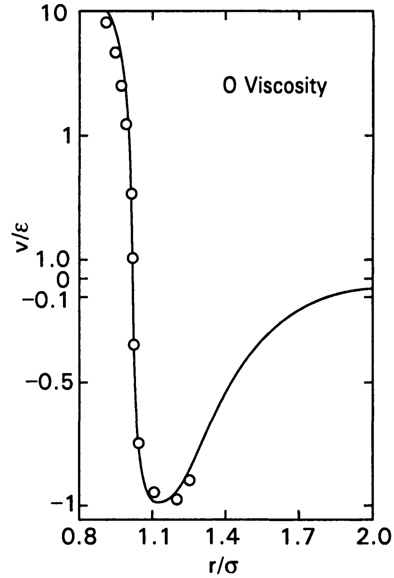

Fig. 3. The intramolecular potential energy for He-SF_6 (O) from viscosity corresponding states and solid curve from Taylor[16]

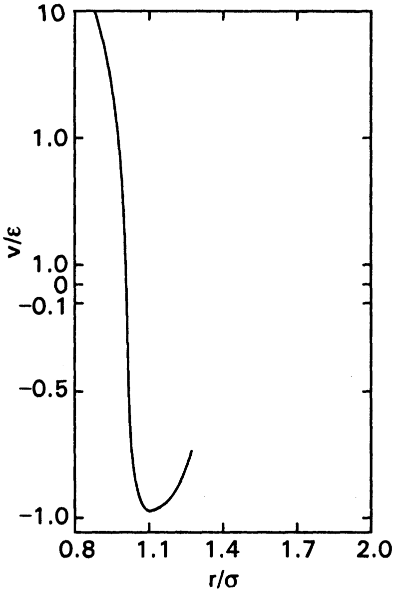

Fig. 4. The intramolecular potential energy for Xe-N_6 from viscosity corresponding states

TABLE-3

CALCULATED VALUES OF REDUCED VISCOSITY COLLISION INTEGRALS, RPD ($\Omega^{(2,2)*}$) FROM EQ. (1) FOR THE Kr—N_2, Xe—N_2 AND He—SF_6

T*	RPD ($\Omega^{(2,2)*}$)	RPD ($\Omega^{(2,2)*}$)	RPD ($\Omega^{(2,2)*}$)
	Kr—N_2	Xe—N_2	He—SF_6
1.00000	−1.20	−1.20	−1.37
1.25893	0.01	0.01	−0.09
1.58489	0.38	0.38	0.31
1.99526	0.43	0.43	0.35
2.51189	0.43	0.42	0.32
3.16228	0.49	0.47	0.32
3.98107	0.57	0.55	0.40
5.01187	0.61	0.61	0.51
6.30957	0.55	0.56	0.59
7.94328	0.31	0.35	0.58
10.00000	0.13	−0.07	0.41
12.58925	0.74	−0.67	0.01
15.84893	−1.30	−1.24	0.71
19.95262	−1.70	−1.68	−1.72

TABLE-4
VALUES OF DIFFUSION COEFFICIENTS, D/m^2 s^{-1} CALCULATED FROM EQ. (3) AND EXPERIMENTAL VALUES OBTAINED FROM REF. 15 ALONG THE RELATIVE PERCENTAGE DEVIATION, RPD^a FOR Kr—N$_2$

T/K	$D^a_{calc.}/10^{-4}$ m^2 s^1	$D^a_{expt.}/10^{-4}$ m^2 s^1	RPD^b
212.28	0.0814	0.0850	4.235
235.42	0.0990	0.1020	2.941
255.72	0.1155	0.1182	2.284
276.44	0.1340	0.1356	1.180
398.15	0.1536	0.1530	–0.392
299.16	0.1546	0.1580	2.152
300.00	0.1554	0.1595	2.570
320.00	0.1748	0.1794	2.564
329.53	0.1845	0.1851	0.324
352.36	0.2090	0.2083	–0.336
373.15	0.2312	0.2340	1.197
420.34	0.2862	0.2870	0.279
473.15	0.3529	0.3570	1.148
573.15	0.4944	0.4980	0.723
673.15	0.6533	0.6570	0.563
773.15	0.8286	0.8330	0.528

^{a}P = 1 atm, RPD = $[(D_{expt.} - D_{calc.})/D_{expt.}] \times 100$

The values of diffusion coefficients along with their relative percentge deviation, RPD, are listed in Table-4. As results show that deviation is about 5% hence, inversion method is good enough for determination of diffusion coefficient.

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