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Direct Determination of the Interaction Potentials of Ar–Xe, Kr–Xe, and Ar–Kr from the Extended Principle of Corresponding States

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Intermolecular pair-potential energy functions are given for all the unlike interactions of Ar, Kr, and Xe. The potentials are determined by direct inversion of experimental reduced viscosity collision integrals obtained from the corresponding-states correlation. The results are in good agreement with the potentials proposed by Ron Aziz.

Intermolecular forces are responsible for most of the physical and chemical properties of matter. Although the exact nature of these forces is very complicated, there are no conceptual difficulties.

The specific information about potential energy functions can be extracted by the inversion of thermophysical data. This technique largely eliminate the need for the unsatisfactory trial and error methods which have been used to obtain information about potential energy functions from thermophysical data.[1)]

In this work, a direct inversion of experimental reduced viscosity collision integrals obtained from the corresponding-states correlation is used to determine the Ar–Xe, Kr–Xe, and Ar–Kr interaction potentials. These potentials are in good agreement with the HFD-C potentials proposed by R. A. Aziz et al.[2,3)]

The inversion techniques employed here have previously been applied by Boushehri et al. and have been described in some detail.[4)]

Inversion Procedure

In the Chapman–Enskog theory[5)] of a dilute gas, the transport properties of the 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, 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 by their corresponding rigid sphere values. A reduced collsion integral which is only a function of the reduced temperature, $T^*=K_B T/\varepsilon$, may be defined as

$$\Omega^{(l,s)*}(T^*) = \Omega^{(T,\varepsilon,\sigma)}/\pi\sigma^2, \tag{1a}$$

where σ is the scaling parameter such that $U(\sigma)=0$ and $K_B T$ has its usual meaning. The reduced collision integrals can be expressed in the form of triple integrals. In this work, the triple integrals were calculated using a program based on that of O'Hara and Smith.[6,7)] Higher collision integrals can be generated by use of the relation

$$\Omega^{(l,s+1)*} = \Omega^{(l,s)*}[1+\frac{1}{s+2}\frac{\mathrm{d}ln\Omega^{(l,s)*}}{\mathrm{d}T^*}]. \tag{1b}$$

The universal function $\Omega^{(2,2)*}$ can be used to determine the intermolecular potential by an "**inversion procedure**". Our inversion methods were closely based on those of Clancy and her colleagues[8)] and were recently checked by Boushehri et al.[9,10)]

In this work we analyse the extended principle of corresponding states in terms of the unlike pair potentials. The collision integral $\Omega^{(2,2)*}$, which describes viscosity, is defined as[11)]

$$\begin{aligned} &0 \le T^* \le 1.2: \\ &\Omega^{(2,2)*} = 1.1943(C_6^*/T^*)^{1/3}[1+a_1(T^*)^{1/3} \\ &\quad + a_2(T^*)^{2/3} + a_3(T^*) + a_4(T^*)^{4/3} \\ &\quad + a_5(T^*)^{5/3} + a_6(T^*)^2], \end{aligned} \tag{2a}$$

$$\begin{aligned} &1.2 \le T^* \le 10: \\ &\Omega^{(2,2)*} = \exp[0.46641 - 0.56991(lnT^*) + 0.19591(lnT^*)^2 \\ &\quad - 0.03879(lnT^*)^3 + 0.00259(lnT^*)^4], \end{aligned} \tag{2b}$$

$$\begin{aligned} &T^* \ge 10: \\ &\Omega^{(2,2)*} = (\rho^*)^2\alpha^2[1.04 + a_1(lnT^*)^{-1} + a_2(lnT^*)^{-2} \\ &\quad + a_3(lnT^*)^{-3} + a_4(lnT^*)^{-4}]. \end{aligned} \tag{2c}$$

All parameters in these equations are the same as Ref. 11.

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 distance around a value r.[8)] It is always possible to make this idea exact by defining a function G_η such that

$$U(r) = G_\eta(T^*)\cdot T^*, \tag{3a}$$

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

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

where G_η is a temperature-dependent viscosity which changes about 0.72 at high temperature to −0.561 at low temperature but which is remarkably similar for a large number of reasonable potentials. Therefore, finding $U(r)$ from $\Omega^{(2,2)*}$ is straightforward when ε is equal to unity. Equations 2a, 2b, and 2c can be inverted by the above method to yield $U(r)/\varepsilon$ as a function of r/σ.

By inserting the value of G_η, given by Clancy and her colleagues,[8] in Eq. 3a the potential energy U/ε can be obtained and the corresponding value of r/σ may be obtained using the collision integral calculated from Eqs. 2a, 2b, and 2c. This process may be repeated until convergence is obtained. At each stage in the iteration process the per cent deviation of the $\Omega^{(2,2)*}$ (T^*) calculated from the potential and the correlated values $\Omega^{(2,2)*}$ (T^*) was determined. The iteration process ended when a minimum had occured in this quantity. Two iterations usually suffice.[4,12] The value of σ turns out to be equal to the value σ_0 such that $U(\sigma)_0)=0$, the precise values σ/σ_0 for Ar–Xe, Kr–Xe, and Ar–Kr are 0.9988, 0.9986, and 0.9987, respectively. The results obtained here cover the range from about the potential energy minimum inwards to a repulsion to about 100 times the well depth.

It should be mentioned that the second viral coefficient is more sensitive to the potential than the transport coefficients, since they are buried under one layer integration rather than three layers. Practical numerical procedures are available for finding $U(r)$ from the experimental second virial coefficient data. It can be shown that the width of the potential energy function may be defined in terms of the second virial coefficient at temperatures for which $T<\varepsilon/K_B$. Therefore, knowing the inner branch of the potential well from the viscosity, we can use this information in conjunction with the second virial coefficient data to determine the outer branch of the well uniquely. The equations used for this purpose are as follows:

$$U/\varepsilon = T^* - 1, \tag{4a}$$

and

$$r_R^3 - r_L^3 = -(B - b_0)N(T^*), \tag{4b}$$

where r_R and r_L are the coordinates of the outer and inner wall of the potential well, $b_0 = 2\pi N\sigma_0^3/3$, σ_0 is the collision diameter such that $U(\sigma_0)=0$ and $N(T^*)$ is given in Ref. 8. The second virial coefficient of pair noble gases is correlated in the extended principle of corresponding states by the formula[11]

$0 \le T^* \le 1.1$

$$\begin{aligned} B_0^* = {} & -(T^*)^{1/2}\varepsilon^{1/T^*}[1.18623 + 1.00824T^* \\ & + 4.25571(T^*)^2 - 18.6033(T^*)^3 + 20.4732(T^*)^4 \\ & - 8.71903(T^*)^5 + 1.14829(T^*)^6] \end{aligned} \tag{4c}$$

Thus the potential function is not obtained directly, but if the inner well wall is known, say from viscosity data inversion, the coordinates, r_R, of the outer well wall may be obtained.

Table 1. Dimensionless Collision Integrals $\Omega^{(l,s)^*} = \overline{\Omega}^{(l,s)}/\pi\sigma^2$ and the Related Ratios for Ar–Xe

$\log_{10} T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	B^*	C^*
−0.2	1.7520	1.9557	1.2591	0.8406
−0.1	1.5684	1.7510	1.2306	0.8401
0.0	1.4067	1.5648	1.1984	0.8461
0.1	1.2694	1.4046	1.1679	0.8572
0.2	1.1556	1.2728	1.1434	0.8713
0.3	1.0764	1.1674	1.1113	0.8750
0.4	0.9872	1.0844	1.1151	0.9000
0.5	0.9250	1.0188	1.1094	0.9114
0.6	0.8729	0.9658	1.1076	0.9202
0.7	0.8280	0.9211	1.1074	0.9267
0.8	0.7884	0.8817	1.1072	0.9311
0.9	0.7526	0.8457	1.1075	0.9342
1.0	0.6739	0.7765	1.0926	0.9543
1.1	0.6891	0.7801	1.1078	0.9377
1.2	0.6603	0.7494	1.1078	0.9388
1.3	0.6332	0.7198	1.1058	0.9397
1.4	0.6075	0.6906	1.1009	0.9409
1.5	0.5836	0.6616	1.0924	0.9429
1.6	0.5617	0.6326	1.0790	0.9466
1.7	0.5423	0.6041	1.0610	0.9519
1.8	0.5258	0.5772	1.0428	0.9591
1.9	0.5126	0.5532	1.0258	0.9672
2.0	0.5026	0.5331	1.0113	0.9755

Table 2. Dimensionless Collision Integrals $\Omega^{(l,s)^*} = \overline{\Omega}^{(l,s)}/\pi\sigma^2$ and the Related Ratios for Kr–Xe

$\log_{10} T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	B^*	C^*
−0.2	1.7512	1.9517	1.2592	0.8413
−0.1	1.5683	1.7490	1.2311	0.8407
0.0	1.4071	1.5642	1.1989	0.8464
0.1	1.2699	1.4050	1.1686	0.8573
0.2	1.1561	1.2736	1.1437	0.8714
0.3	1.0632	1.1682	1.1266	0.8862
0.4	0.9876	1.0846	1.1136	0.9000
0.5	0.9256	1.0179	1.1057	0.9121
0.6	0.8741	0.9632	1.1002	0.9217
0.7	0.8304	0.9174	1.0979	0.9293
0.8	0.7924	0.8783	1.0988	0.9348
0.9	0.7584	0.8443	1.1020	0.9380
1.0	0.7271	0.8137	1.1062	0.9395
1.1	0.6974	0.7847	1.1091	0.9399
1.2	0.6691	0.7555	1.1075	0.9401
1.3	0.6421	0.7251	1.0955	0.9413
1.4	0.6171	0.6934	1.0847	0.9441
1.5	0.5947	0.6616	1.0664	0.9494
1.6	0.5756	0.6312	1.0469	0.9566
1.7	0.5602	0.6039	1.0141	0.9620
1.8	0.5484	0.5809	1.0138	0.9737
1.9	0.5401	0.5630	1.0039	0.9819
2.0	0.5346	0.5499	0.9966	0.9884

An accurate reduced potential is obtained for Ar–Xe, Kr–Xe, and Ar–Kr by performing an **INVERT** on the corresponding states viscosity, and this accurate potential can be used to obtain collision integrals and the following ratios of collision integrals which occur, in the formulas for the transport properties of Ar–Xe, Kr–Xe, and Ar–Kr.[13]

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

$$C^* = \Omega^{(1,2)*}/\Omega^{(1,1)}. \tag{5b}$$

Table 3. Dimensionless Collision Integrals $\Omega^{(l,s)*} = \overline{\Omega}^{(l,s)}/\pi\sigma^2$ and the Related Ratios for Ar–Kr

$\log_{10} T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	B^*	C^*
−0.2	1.7560	1.9627	1.2576	0.8380
−0.1	1.5697	1.7541	1.2286	0.8385
0.0	1.4068	1.5656	1.1963	0.8452
0.1	1.2689	1.4045	1.1664	0.8569
0.2	1.1551	1.2723	1.1421	0.8713
0.3	1.0623	1.1667	1.1247	0.8864
0.4	0.9869	1.0834	1.1136	0.9004
0.5	0.9251	1.0171	1.1059	0.9122
0.6	0.8737	0.9632	1.1021	0.9217
0.7	0.8298	0.9182	1.1005	0.9289
0.8	0.7915	0.8795	1.1017	0.9339
0.9	0.7570	0.8453	1.1045	0.9370
1.0	0.7252	0.8140	1.1078	0.9385
1.1	0.6952	0.7838	1.1087	0.9390
1.2	0.6666	0.7537	1.1059	0.9397
1.3	0.6397	0.7227	1.0968	0.9411
1.4	0.6148	0.6909	1.0825	0.9445
1.5	0.5927	0.6592	1.0648	0.9501
1.6	0.5740	0.6291	1.0451	0.9573
1.7	0.5589	0.6023	1.0274	0.9658
1.8	0.5475	0.5798	1.0122	0.9742
1.9	0.5394	0.5623	1.0022	0.9822
2.0	0.5341	0.5495	0.9964	0.9890

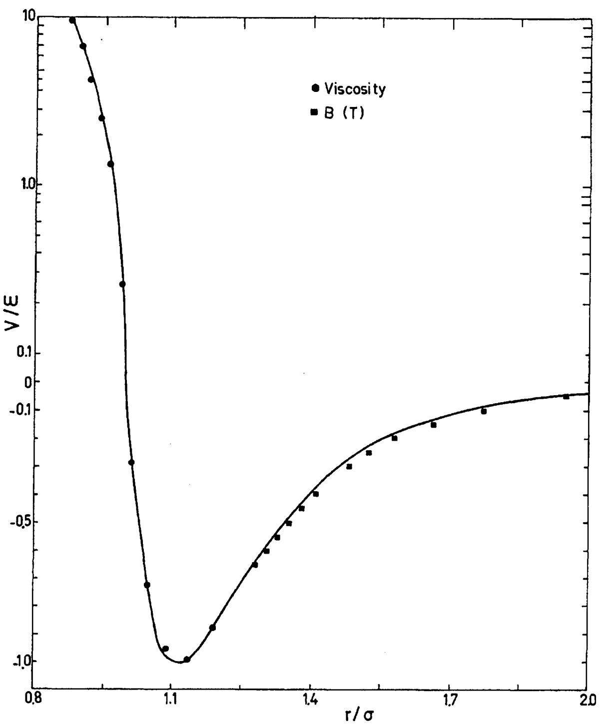

Fig. 1. Reduced pair potential obtained by **INVERT** of the corresponding-states viscosity for Ar–Xe (●) and results from the second virial coefficients (■). Shown for comparison is the Ron Aziz potential.[2]

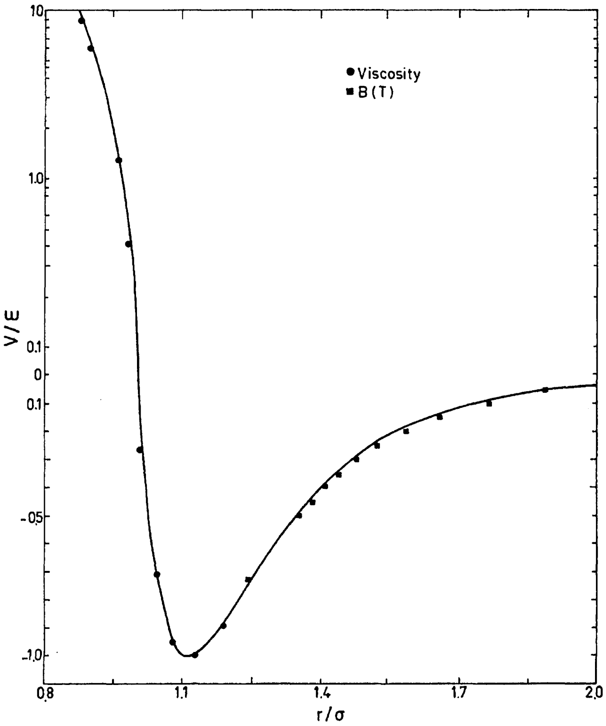

Fig. 2. Same as Fig. 1, for Kr–Xe. Shown for comparison is the Aziz potential.[2]

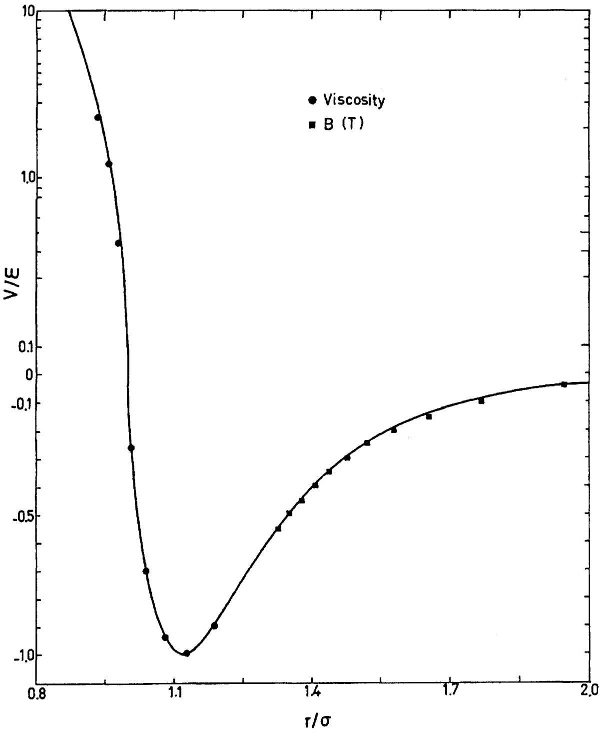

Fig. 3. Same as Fig. 1, for Ar–Kr. Shown for comparison is the Ron Aziz potential.[3]

These collision integrals and the related ratios for Ar–Xe, Kr–Xe, and Ar–Kr are given in Tables 1, 2, and 3, respectively. The accuracy of these values is better than 0.1%.

Results and Discussion

The intermolecular pair-potentials for all the unlike interactions among Ar, Kr, and Xe has been obtained from the corresponding states viscosity. At long range only the well-width of potential obtained from second virial coefficient data is available. This has been used in conjunction with the inner coordinates of the well obtain in the viscosity inversion to give the potential energy in the separation range. The results obtained in this way for Ar–Xe, Kr–Xe, and Ar–Kr are in reasonable agreement with the **HFD-C** potentials proposed by R. A. Aziz et al.[2,3] and it can support the reliability of Boushehri's inversion method.[4] Figures 1, 2, and 3 show such results for Ar–Xe, Kr–Xe, and Ar–Kr, respectively.

An important advantage of our method is that, by determining as much of the potential energy function as possible directly from the viscosity data, the need for lengthy multiparameter fitting procedures is largely removed.

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