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Direct Measurement of the Intermolecular Potentials of CH_4–Xe, CH_4–Kr, CH_4–Ar, and CH_4–Ne from the Extended Principle of Corresponding States

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An inversion procedure is used to obtain from the extended principle of corresponding states the interaction potentials over a range of reduced temperature extending from 1 to the onset of ionization. These directly measured potentials for CH_4–Xe, CH_4–Kr, CH_4–Ar, and CH_4–Ne agree excellently with the potentials independently known from the crossed molecular-beam technique.

A very precise extended principle of corresponding states has been formulated for the noble gases and eleven polyatomic gases at low density.[1,2] It has been proved that it is capable of correlating equilibrium and transport properties of the noble gases, eleven polyatomic gases, and their multicomponent mixtures, over a very wide temperature range, with an accuracy comparable to the best measurements.[3] This principle seeks the maximum use of theory and experiment that can be obtained without assumptions about the functional form of the pair interaction potential.

Direct inversion techniques for the calculation of potentials from data on transport and second virial coefficients have been developed that do not require any explicit assumption to be made about the functional form of the potential.[4—11] Although the mathematical bases for some of these inversion techniques are not fully understood, there seems to be no doubt about their success for the noble gas potentials and similar simple interactions.[12]

In this paper, we consider the experimental reduced viscosity collision integral obtained from the corresponding states correlation and perform a direct inversion to calculate the reduced potential energy curve corresponding to this collision integral.[11] Comparison of these results with the potentials independently known from the crossed molecular-beam techniques is interesting.[13]

Interaction Potential from Viscosities

The direct inversion procedure for the viscosity is based on the idea that at a given T the values of $\Omega^{(2,2)*}$ have been chosen so that they are equal to πd^2 for rigid spheres of diameter d. $\Omega^{(2,2)*}$ is determined by the potential over only a small range of separation distance around a value r_0.[4,11] For a given potential it is always possible to make this idea exact by defining a function G such that

$$\Omega^{(2,2)*} = \pi r_0^2 \tag{1}$$

and

$$V(r_0) = GT^*, \tag{2}$$

where $T^* = K_B T/\varepsilon$ and ε is (say) the depth of the potential energy well. G depends almost entirely on the single variable T^* defined above, and is only weakly dependent on other features of the potential.[4] A finding $V(r)$ from $\Omega^{(2,2)*}$ is straightforward when ε is equal to unity. A reasonable potential model is chosen to start the interaction, from which trial values of $V(r_0)$ are calculated, and so on until convergence is obtained and the $\Omega^{(2,2)*}$ calculated from the potential agrees with the correlation values within some predecided limit over the available temperature range. An initial estimate of $G(T^*)$ is calculated from (Table 1) of Ref. 9. Convergence is usually obtained after only two iterations.[14] The results would be entirely within the accuracy of the experimental values.

The viscosities are correlated in the extended principle of corresponding states by the formula given in the Appendix.[3]

These correlation collision integrals can be generalized to unlike molecules. The interaction collision integrals $\Omega_{ij}^{(2,2)*}$ for $i{\neq}j$ correspond to a hypothetical single substance the molecules of which interact according to a pairwise $i-j$ potential. For $i{=}j$, the collision integrals are those for the corresponding pure substance i. The potential strength is characterized by an average potential-minimum well depth ε, and the potential range by an average potential-minimum position r_m. We have adopted the fairly elaborate combination rules developed by Bzowski et al.[15] for use in a correlation scheme for the properties of low-density gas mixtures.[3]

Equations A1—A3, given in the Appendix, can be inverted by the method described in the preceding paragraph to yield V/ε as a function r/σ. The value of σ turns out to be nearly, but not quite, equal to the value σ_0 such that $V(\sigma_0){=}0$. The precise values are $\sigma_0/\sigma{=}0.997$ for CH_4–Xe, 0.998 for CH_4–Kr, 0.998 for CH_4–Ar, and 0.998 for CH_4–Ne. The results cover the ranges from about the potential energy minimum inward to a repulsion energy to 100 times the well depth. The well regions and the lower part of repulsive walls are shown in Figs. 1, 2, 3, and 4, where we have used σ_0 as the scaling parameter. These accurate potentials can be used to obtain kinetic-theory collision integrals needed to calculate transport properties other than viscosity. A typical result for the most commonly needed collision integrals and their ratios is given in Table 1. Properties of an equimolar mixture of methane and argon (CH_4–Ar) is given in Table 2. The techniques represent a direct advance on the traditional methods of force-fitting data to potential functions of primitive forms. The results obtained in this way for CH_4–Xe,

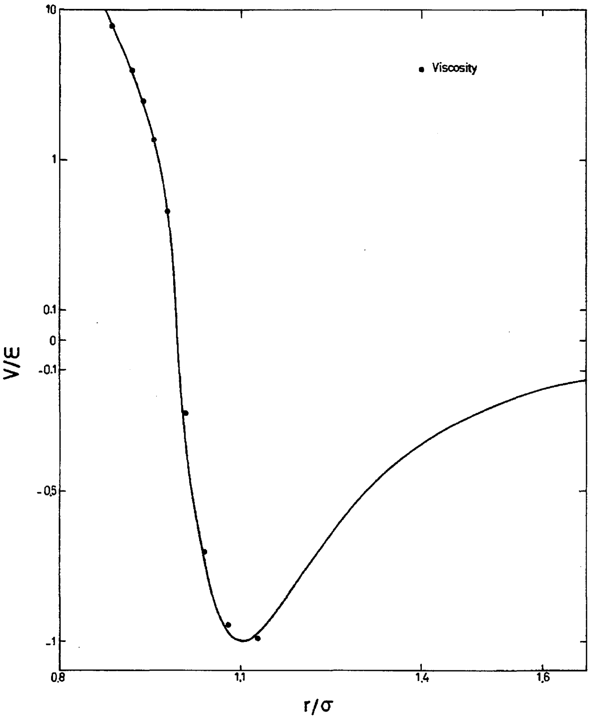

Fig. 1. Intermolecular potential for CH_4–Xe. (●), our potential, the solid curve follows the molecular-beam scattering data.[13]

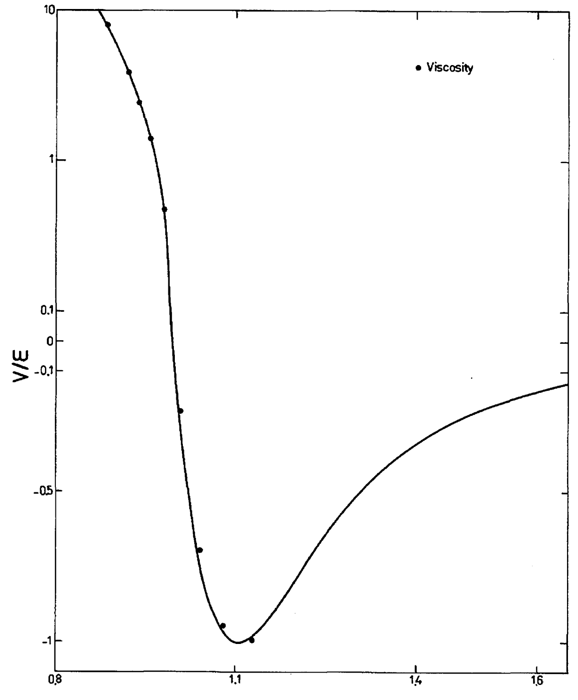

Fig. 2. Same as Fig. 1, for CH_4–Kr.

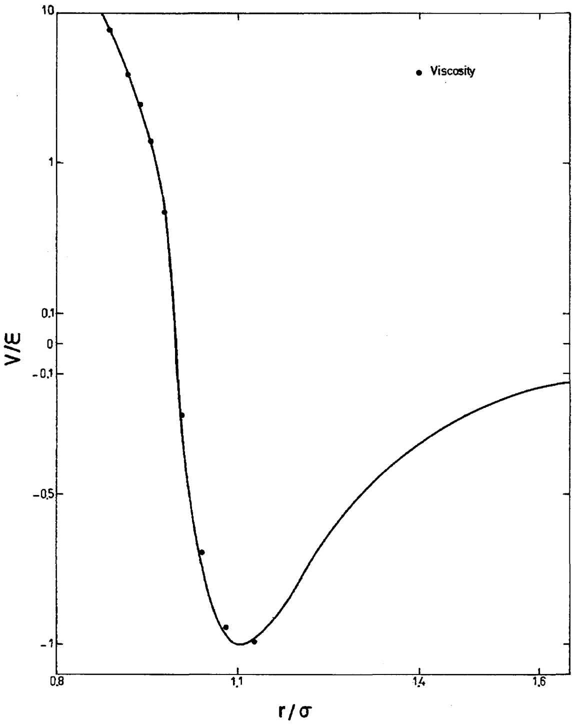

Fig. 3. Same as Fig. 1, for CH_4–Ar.

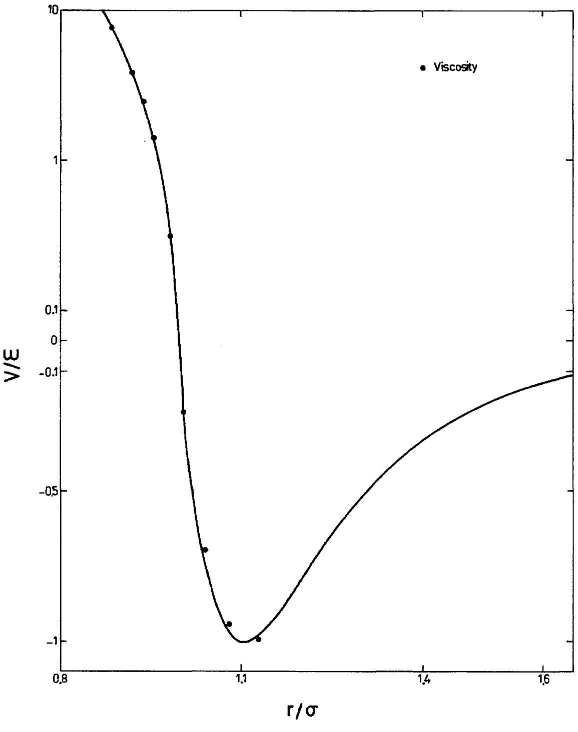

Fig. 4. Same as Fig. 1, for CH_4–Ne.

Table 1. Dimensionless Collision Integrals and thr Related Ratios for CH_4–Ar[a)]

$\log_{10} T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	A^*	B^*	C^*
0.0	1.394	1.555	1.115	1.193	0.8486
0.1	1.261	1.399	1.109	1.167	0.8596
0.2	1.149	1.270	1.105	1.144	0.8738
0.3	1.058	1.165	1.101	1.126	0.8882
0.4	0.9841	1.073	1.090	1.113	0.9013
0.5	0.9231	1.015	1.100	1.105	0.9130
0.6	0.8722	0.9613	1.102	1.101	0.9224
0.7	0.8288	0.9167	1.106	1.100	0.9294
0.8	0.7908	0.8787	1.111	1.101	0.9342
0.9	0.7565	0.8450	1.117	1.104	0.9375
1.0	0.7250	0.8139	1.123	1.105	0.9390
1.1	0.6953	0.7843	1.128	1.107	0.9400
1.2	0.6672	0.7554	1.132	1.107	0.9402
1.3	0.6403	0.7269	1.135	1.107	0.9405
1.4	0.6146	0.6985	1.137	1.103	0.9411
1.5	0.5904	0.6700	1.135	1.096	0.9426
1.6	0.5679	0.6412	1.129	1.084	0.9456
1.7	0.5478	0.6125	1.118	1.067	0.9502
1.8	0.5304	0.5851	1.103	1.049	0.9570
1.9	0.5162	0.5601	1.085	1.032	0.9649
2.0	0.5053	0.5387	1.066	1.016	0.9731

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

CH_4–Kr, CH_4–Ar, and CH_4–Ne are in reasonable agreement with the potentials proposed by Liuti et al.[13)] and it can support the relability of Boushehri's inversion method. Our estimated accuracies are about 1% for viscosity, 5% for diffusion, and 25% for thermal diffusion. Collision integrals needed to write say the viscosity of the CH_4–Ne, CH_4–Kr, and CH_4–Xe are distributed on request.

Conclusions

The interaction potentials directly measured from the corresponding-states viscosity allow the kinetic-theory collision integrals needed to calculate other transport properties to be obtained with more accuracy than is possible by a corresponding-states analysis of such properties, primarily because viscosity measurements are much accurate than are measurements of the other properties. Table 1 contains such results. It should be noted that many polyatomic gases obey the same corresponding-states relations as do the noble gases.[2)] Comparison can be made with a potential found by crossed molecular-beam techniques and are shown in Figs. 1, 2, 3, and 4. We repeat, this result has a practical significance: Calculations of other properties are considerably eased by introducing Table 1, e.g. Table 2. In this work, the triple integrals are evaluated by using the Gatland version of a computer program developed by O'Hara and Smith with an accuracy of 0.1%.[16)]

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Table 2. Properties of an Equimolar Mixture of Methane and Argon (CH_4–Ar)[a)]

T	η	D(1.013 bar)	α_T
K or °C	μPa s	10^{-4} m^2 s^{-1}	
200 K	11.99	0.1012	0.0556
250	14.45	0.1544	0.0785
300	17.24	0.2164	0.0977
0 °C	15.88	0.1818	0.0886
20	16.89	0.2072	0.0955
40	17.87	0.2339	0.1017
60	18.83	0.2618	0.1075
80	19.79	0.2907	0.1128
100	20.70	0.3211	0.1174
150	22.83	0.4020	0.1274
200	24.80	0.4897	0.1354
250	26.72	0.5840	0.1417
300	28.57	0.6846	0.1468
350	30.35	0.7915	0.1508
400	32.05	0.9042	0.1540
450	33.71	1.0224	0.1566
500	35.31	1.1464	0.1587
600	38.37	1.4104	0.1617
700	41.31	1.6957	0.1639
800	44.13	2.0010	0.1654
900	46.84	2.3264	0.1663
1000	49.49	2.6707	0.1667
1500	61.74	4.6632	0.1666
2000	72.95	7.0776	0.1656
2500	83.44	9.8830	0.1649
3000	93.42	13.0541	0.1645

a) η=Viscosity, D=Diffusion, and α_T=Thermal Diffusion.

Appendix: Collision Integrals

$\Omega^{(2,2)*}$, CH_4

$1 \le T^* \le 10$

$$\Omega^{(2,2)*} = \exp[0.46641 - 0.56991(\ln T^*) + 0.19591(\ln T^*)^2 - 0.03879(\ln T^*)^3 + 0.00259(\ln T^*)^4]. \qquad \text{(A1)}$$

$T^* \ge 10$

$$\Omega^{(2,2)*} = (\rho^*)^2(\alpha)^2[1.04 + a_1(\ln T^*)^{-1} + a_2(\ln T^*)^{-2} + a_3(\ln T^*)^{-3} + a_4(\ln T^*)^{-4}], \qquad \text{(A2)}$$

where ρ^*, α, and a's are the same as given in Ref. 3. $\Omega^{(2,2)*}$, noble gases

$T^* \le 1.2$

$$\Omega^{(2,2)*} = 1.1943(C_6^*/T^*)^{1/3}[1 + a_1(T^*)^{1/3} + a_2(T^*)^{2/3} + a_3(T^*) + a_4(T^*)^{4/3} + a_5(T^*)^{5/3} + a_6(T^*)^2]. \qquad \text{(A3)}$$

$1.2 \le T^* \le 10$

$$\Omega^{(2,2)*} = \text{same as Eq. A1}.$$

$$T^* \geq 10$$
$$\Omega^{(2,2)*} = \text{same as Eq. A2}.$$

All terms appeared in the above Eq. A3 are the same as those of Ref. 3.

References

1) B. Najafi, E. A. Mason, and J. Kestin, *Physica A (Amsterdam)*, **119A**, 387 (1983).

2) A. Boushehri, J. Bzowski, J. Kestin, and E. A. Mason, *J. Phys. Chem. Ref. Data*, **16**, 445 (1987).

3) J. Bzowski, J. Kestin, E. A. Mason, and F. J. Uribe, *J. Phys. Chem. Ref. Data*, **19**, 1179 (1990).

4) D. W. Gough, G. C. Maitland, and E. B. Smith, *Mol. Phys.*, **24**, 151 (1972).

5) G. C. Maitland and E. B. Smith, *Mol. Phys.*, **24**, 1185 (1972).

6) D. W. Gough, E. B. Smith, and G. C. Maitland, *Mol. Phys.*, **25**, 1433 (1973).

7) G. C. Maitland, *Mol. Phys.*, **26**, 513 (1973).

8) D. W. Gough, E. B. Smith, and G. C. Maitland, *Mol. Phys.*, **27**, 867 (1974).

9) D. W. Gough, G. P. Matthews, E. B. Smith, and G. C. Maitland, *Mol. Phys.*, **29**, 1759 (1975).

10) P. Clancy, D. W. Gough, C. P. Matthews, E. B. Smith, and G. C. Maitland, *Mol. Phys.*, **30**, 1397 (1975).

11) A. Boushehri, L. A. Viehland, and E. A. Mason, *Chem. Phys.*, **28**, 313 (1977).

12) G. C. Maitland, E. A. Mason, L. A. Viehland, and W. A. Wakeham, *Mol. Phys.*, **36**, 797 (1978).

13) G. Liuti, F. Pirani, U. Buck, and B. Schmidt, *Chem. Phys.*, **126**, 1 (1988).

14) A. Boushehri, *Physica A (Amsterdam)*, **97A**, 206 (1979).

15) J. Bzowski, E. A. Mason, and J. Kestin, *Int. J. Thermophys.*, **9**, 131 (1988).

16) H. O'Hara and F. J. Smith, *J. Comput. Phys.*, **5**, 328 (1970); *Comput. Phys. Commun.*, **2**, 47 (1971).