THE EXTENDED LAW OF CORRESPONDING - STATES AND THE INTERMOLECULAR POTENTIALS FOR Ar-Ar, Ar-Kr AND Kr-Kr

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Abstract

An inversion procedure is used to obtain from the extended principle of corresponding - states the pair interaction potentials for argon, krypton and its mixture over a temperature range from absolute zero to the onset of ionization. The experimentally-reduced viscosity collision integrals obtained from the corresponding - states correlation have been inverted directly to give the reduced-intermolecular potential energy curves corresponding to the collision integrals. These directly determined potentials are in good agreement with the potentials independently obtained from the molecular-beam scattering measurements, which were fitted by ESMSV for Ar-Ar and Kr-Kr and by SMSV for Ar-Kr.

Introduction

For dilute gases, the transport coefficients depend only on the binary interactions between molecules in the gas. The Chapman-Enskog solution of the Boltzmann equation for dilute monatomic gases relates the transport coefficients to a series of collision integrals $\Omega^{(1,s)}$ [1]. For example, the coefficient of shear viscosity, η, is primarily related to $\Omega^{(2,2)}$. It has become possible to determine the potential energy function accurately for the inert gases by simultaneously fitting a number of measured quantities [2-9].

A very precise extended principle of corresponding states has been formulated for the noble gases by Najafi *et al.* [10]. It has proved capable of correlating the low - density equilibrium and transport properties of the noble gases and of their mixtures, over a very wide temperature range, with an accuracy comparable to the best measurements. Direct inversion techniques

for the potential derived from gaseous transport coefficients have been developed that do not require any explicit assumption about the functional form of the potential [11-13].

In this paper, the problem of determining the potential energy functions of Ar-Ar, Ar-Kr and Kr-Kr from the extended principle of corresponding states with emphasis on the viscosity have been re-examined. We have found that the principle succeeds for the Ar and Ar-Kr mixture at both low and high temperatures, but for Kr there is a small deviation at intermediate and high temperatures.

Here we consider the experimental reduced viscosity collision integrals obtained from the corresponding - states correlation, and perform a direct inversion to determine the reduced potential energy curves corresponding to these collision integrals. These potential functions are compared with the Exponential - Spline - Morse - Spline - Van der Waals (ESMSV) for Ar-Ar and Kr-Kr and with the Spline - Morse - Spline - Van der Waals (SMSV) for Ar-Kr [14-15]. The potential is able to predict various

other transport properties such as A*, B*, C*, E* and F* as a function of the reduced temperature.

Method of Calculation

The rigorous kinetic - theory formula for the shear viscosity η of a dilute gas is

$$\eta = \frac{5}{16} \frac{(\pi M k_B T)^{1/2}}{\Omega^{(2,2)}} f_\eta \qquad (1)$$

where M is the molecular mass, k_B is Boltzmann's constant, and f_η and $\Omega^{(2,2)}$ depend on the temperature T and the intermolecular potential. The factor f_η is always very close to unity. The normalization of the collision integral $\Omega^{(2,2)}$ has been chosen so that it is equal to πd^2 for rigid spheres of diameter d.

The viscosity coefficients of the noble gases are correlated in the extended principle of corresponding states by the formula [10]

$$\Omega_{ext}^{(2,2)*} = 1.1943 \, (C_6^*/T^*)^{1/3}[1+a_1(T^*)^{1/3} + a_2(T^*)^{2/3}$$

$$a_3(T^*)+a_4(T^*)^{4/3}+a_5(T^*)^{5/3}+a_6(T^*)^2] \qquad 0 \le T^* \le 1.2 \quad (2a)$$

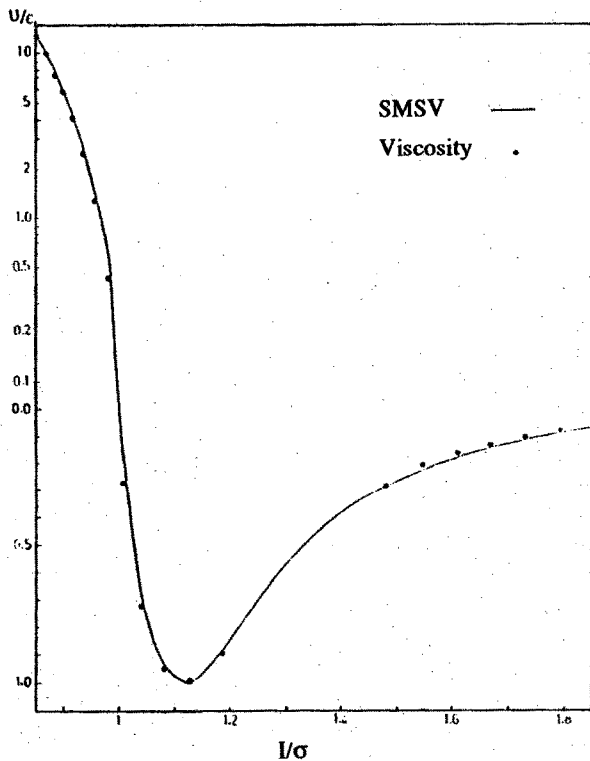$$\Omega_{ext}^{(2/2)*} = \exp[0.46641 - 0.56991(\ln T^*) + 0.19591(\ln T^*)^2$$

$$-0.03879(\ln T^*)^3 + 0.00259(\ln T^*)^4] \quad 1.2 \le T^* \le 10 \quad (2b)$$

$$\Omega_{ext}^{(2,2)*} = (\rho^*)^2 \alpha^2[1.04 + a_1(\ln T^*)^{-1} + a_2(\ln T^*)^{-2}$$

$$a_3(\ln T^*)^{-3} + a_4(\ln T^*)^{-4}] \qquad T^* \ge 10 \qquad (2c)$$

where $\Omega^{(2,2)*} = \Omega^{(2,2)}/\pi\sigma^2$, σ is a distance scaling parameter and the other quantities have the same meaning as in reference 10. The convenient reduced temperature is defined as

$$T^* = k_B T/\varepsilon, \qquad (3)$$

Figure 1. Reduced pair potentials obtained by INVERT of the corresponding - states viscosity for the argon ( ) and krypton ( ) gases
Shown for comparison is a typical curve fitted by ESMSV (ref. (14)). Note that the scale changes from linear to logarithmic at U/ε = 0.1.
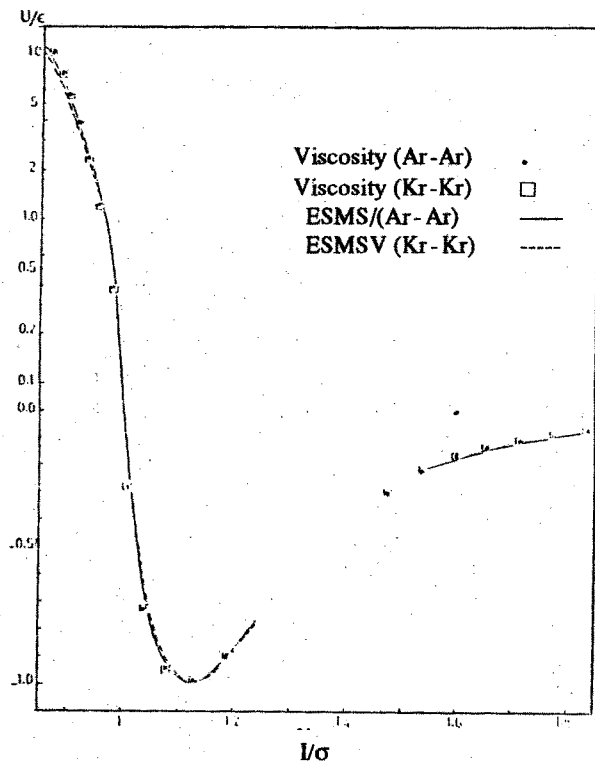
Figure 2. Reduced pair potential obtained by INVERT of the corresponding - states viscosity for the Ar-Kr gas mixture ( ). Shown for comparison is a typical curve fitted by SMSV (ref. 15). Note that the scale changes from linear to logarithmic at U/ε = 0.1.

Table I. Dimensionless collision integrals $\Omega^{(1,s)*} = \Omega^{(1,s)}/\pi\sigma^2$ and their ratios $A^* = \Omega^{(2,2)*}/\Omega^{(1,1)*}$, $B^* = [5\Omega^{(1,2)*} - 4\Omega^{(1,3)*}]/\Omega^{(1,1)*}$ $C^* = \Omega^{(1,2)*}/\Omega^{(1,1)*}$, $E^* = \Omega^{(2,3)*}/\Omega^{(2,2)*}$ and $F^* = \Omega^{(3,3)*}/\Omega^{(1,1)*}$ as a function of the reduced temperature T^*. These values were calculated with an accuracy of 0.1% from the reduced potential obtained by direct inversion of the corresponding - states viscosity for Ar, Kr and Ar-Kr.

$\text{Log}T^*_{10}$	$\Omega^{(2,2)*}$	A^*	B^*	C^*	E^*	F^*
-1	4/042	1/043	1/134	0/829	0/877	0/900
-0/9	3/639	1/048	1/150	0/852	0/893	0/920
-0/8	3/316	1/053	1/166	0/867	0/905	0/931
-0/7	3/053	1/06	1/190	0/874	0/914	0/935
-0/6	2/830	1/071	1/223	0/874	0/920	0/933
-0/5	2/628	1/088	1/256	0/867	0/917	0/929
-0/4	2/424	1/104	1/277	0/855	0/906	0/923
-0/3	2/211	1/117	1/279	0/845	0/892	0/919
-0/2	1/991	1/123	1/263	0/838	0/880	0/916
-0/1	1/777	1/122	1/235	0/837	0/874	0/915
0/0	1/583	1/116	1/202	0/842	0/875	0/918
0/1	1/416	1/109	1/172	0/853	0/883	0/925
0/2	1/279	1/103	1/146	0/868	0/896	0/935
0/3	1/170	1/100	1/127	0/883	0/909	0/946
0/4	1/083	1/098	1/113	0/897	0/922	0/958
0/5	1/015	1/099	1/105	0/910	0/934	0/970
0/6	0/959	1/101	1/099	0/920	0/942	0/981
0/7	0/912	1/103	1/096	0/928	0/949	0/989
0/8	0/873	1/107	1/095	0/935	0/954	0/996
0/9	0/839	1/111	1/097	0/939	0/959	1/001
1/0	0/810	1/117	1/103	0/941	0/962	1/004
1/1	0/783	1/125	1/111	1/940	0/964	1/007
1/2	0/757	1/134	1/117	0/939	0/962	1/011
1/3	0/730	1/14	1/115	0/938	0/956	1/018
1/4	0/699	1/139	1/103	0/938	0/949	1/024
1/5	0/665	1/130	1/084	0/941	0/944	1/028
1/6	0/631	1/114	1/061	0/948	0/942	1/030
1/7	0/600	1/094	1/038	0/957	0/946	1/028
1/8	0/573	1/072	1/019	0/966	0/953	1/025
1/9	0/551	1/052	1/006	0/976	0/963	1/021
2/0	0/535	1/036	0/997	0/984	0/973	1/017

where ε is the depth of the potential energy well. Equations (2a) - (2c) can be inverted by the method described in the following paragraph to yield U/ε as a function of r/σ. The evaluation of the triple integral is made by using the Gatland version of the computer program developed by O' Hara and Smith [16].

The inversion procedure of Smith and co - workers [2-5] for the viscosity is based on the idea that at a given T^* the value of $\Omega_{ext}^{(2,2)}$ is determined by the potential over only a small range of separation distances around a value of $\bar{r}$. That is

$$\Omega_{ext}^{(2,2)} = \pi \bar{r}^2 \qquad (4)$$

and

$$U_n(\bar{r}) = U_n(\bar{\Omega}_n^{(2,2)}(T^*)). \qquad (5)$$

The initial value of potential function, $U_o(\bar{\Omega}_o^{(2,2)}(T))$ was chosen according to the Lennard - Jones (12,6) model, where the values of $\Omega_0^{(2,2)}$ are given by Viehland et al. [17]. The corresponding value of r may be repeated to obtain an improved U(r). The present results converged after three iterations.

Results

We have obtained an accurate reduced potential energy function for argon, krypton and its mixture by INVERT of the corresponding - states viscosity with no additional information. The results obtained after three iterations are illustrated in Figures 1 and 2, showing that the derived potentials are in agreement with the potentials proposed by Lee for Ar-Ar and Aziz for Ar-Kr. These accurate potentials allow the kinetic - theory collision integrals, which are needed to calculate other transport properties, to be obtained more accurately than is possible by the extended corresponding - states analysis of such properties, because viscosity measurements are much more

accurate than are measurements of the other properties. Table I contains such results. The method described in this work enables us to determine an accurate potential energy function for the molecules purely from the viscosity data, without additional information.

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