Articles

The Helium-Xenon Interaction Potential

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The He-Xe interaction potential has been determined using a direct inversion of the experimentally reduced-viscosity collision integrals obtained from the corresponding states correlation. The potential is in a good agreement with the previously determined potential. The potential predicts viscosity and diffusion coefficients and they are found to be in a good agreement with experiment.

Keywords : Collision integral, Corresponding states, Diffusion coefficient, Interaction potential, Viscosity coefficient.

Introduction

The forces between atoms or molecules are of interest to a scientist in a wide range of disciplines as these forces control the progress of molecular collisions and determine the bulk properties of matter.

Intermolecular forces have been determined by two fundamental approaches. Theoretical calculations are one approach to determine intermolecular forces. The other source of information on intermolecular forces is the experimental measurements of macroscopic and microscopic properties of matter which have functional dependences on the intermolecular potential energy function. Two procedures have been used for extracting the intermolecular potential energy function from the experimental data, fitting and inversion procedures. A potential model with a few adjustable parameters is assumed in fitting procedures. The parameters of the potential model are varied so as to obtain the optimum agreement between experiment and theory. The potentials from this method do not appear to be unique. The aim of an inversion method is to obtain the potential by considering the experimental data as a functional instead of fitting the data to a constrained potential form having a few parameters.[1,2]

Since helium and xenon mixtures have been proposed as good choice for working fluids in thermoacoustic refrigerators,[2] knowledge of interaction potential of He-Xe is necessary to calculate the transport properties. The purpose of this paper is to determine He-Xe interaction potential using a direct inversion of the experimentally reduced-viscosity collision integrals obtained from the corresponding states correlation.[4] The potential is in a good agreement with the previously determined potential.[5] The resulting potential has been used to predict viscosity and diffusion coefficients and they are found to be in a good agreement with experiment.

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Theory

The procedure is to utilize the extended principle of corresponding states[4] for the viscosity-collision integrals in terms of unlike potentials. The reduced collision integrals, $\Omega^{(2,2)*}$, which describes viscosity, according to this law is defined as:

$$0 \leq T^* \leq 1.2 \qquad (1a)$$

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

where

$$a_1 = 0.18$$
$$a_2 = 0.0$$
$$a_3 = -1.20407 - 0.195866(C_6^*)^{-1/3}$$
$$a_4 = -9.86374 + 20.2221(C_6^*)^{-1/3}$$
$$a_5 = 16.6295 - 3 1.3613(C_6^*)^{-1/3}$$
$$a_6 = -6.73805 + 12.6611(C_6^*)^{-1/3}$$

The dimensional parameter C_6^* characterizes the long range attractive tail of the potential.

$$1.2 \leq T^* \leq 10 \qquad (1b)$$

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

$$T^* \geq 10 \qquad (1c)$$

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

where

$$a_1 = 0.0$$
$$a_2 = -33.0838 + (\alpha_{10}\rho^*)^{-2}(20.0862 + (72.1059/\alpha_{10}) + (8.27648/\alpha_{10})^2)$$
$$a_3 = 101.571 - (\alpha_{10}\rho^*)^{-2}(56.4472 + (286.393/\alpha_{10}) + (17.761/\alpha_{10}^2))$$

$$a_4 = -87.7036 + (\alpha_{10}\rho^*)^{-2} (46.3130 + (277.146/\alpha_{10})$$
$$+ (19.0573/\alpha_{10})^2)$$

where ρ^* and V_o^* are high-temperature dimensionless scaling parameters. The values of ρ^*, V_o^*, and C_6^* are given in ref. 4. $\alpha_{10} = \ln(V_o^*/10)$ is the value of $\alpha = \ln V_o^* - \ln T^*$ at matching point of $T^* = 10$. T^* is reduced temperature, $T^* = kT/\varepsilon$, where ε is the potential well depth and k is Boltzmann's constant.

The remarkable feature of the inversion procedure for viscosity is that it identifies a point on the experimental $\Omega^{(2,2)}$ versus temperature curve with a single point on $V(r)$ function. It is always possible to make this idea exact by defining a function G_η such that

$$V^*(r) = V(r)/\varepsilon = T^* \cdot G_\eta(T^*) \tag{2}$$

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 universal among a whole class of potential functions possessing repulsive and attractive branches joined by a single minimum. Equations (1a) to (1c) 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.*[6] into Eq. (2) to obtain the potential energy $V(r)/\varepsilon$; the corresponding value of r/σ may be obtained from the collision integral calculated from eqs. (1a), (1b), and (1c) by the equation

$$(r/\sigma) = (\Omega^{(2,2)*})^{1/2} \tag{3}$$

This process may be repeated until convergence is obtained. At each step in the iteration process the percent deviation of the $\Omega^{(2,2)*}$ calculated from the potential and its correlated value was determined. The convergence is usually obtained after only two or three iterations.

It can be shown that the width of the potential energy function may be defined in terms of the second virial coefficient at temperatures from which $T < \varepsilon/k$.[6] 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:

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

and

$$r^3_R - r^3_L = -(B - b_O) N(T^*) \tag{4b}$$

where r_R and r_L are the coordinates of the outer and inner wall of the potential well, $b_o = 2\pi N_A \sigma^3/3$, σ is the collision diameter such that $V(\sigma) = 0$ and $N(T^*)$ is given in ref. 6. The second virial coefficient of pair noble gases is correlated in the extended principle of corresponding states by the formula[4]

$$0 \leq T^* \leq 1.1 \tag{4c}$$

$$B^*_o = -(T^*)^{1/2} \varepsilon^{1/T^*} (1.18623 + 1.00824 T^* + 4.25571(T^*)^2$$
$$-18.6033 (T^*)^3 + 20.4732(T^*)^4 - 8.71903 (T^*)^5$$
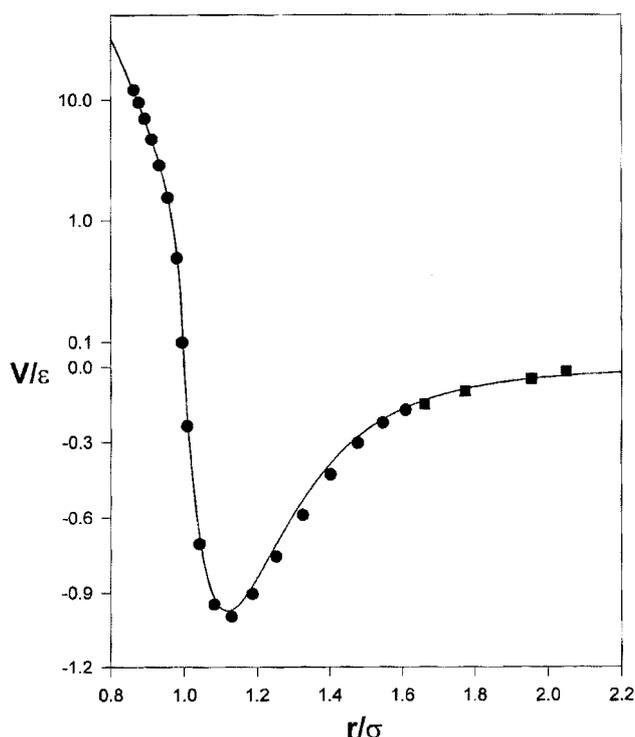$$+ 1.14829 (T^*)^6)$$

Figure 1. Reduced pair potential obtained by inersion method for He-Xe (●) and results from the second virial coefficients (■). The solid curve is Keil *et al.* potential.[5]

Thus, the outer well wall r_R, can be obtained from the inner well wall using viscosity data, Eqs. (4b), and (4c).

Results

The interaction potential of He -Xe has been determined from a direct inversion of the experimentally reduced viscosity collision integrals obtained from the corresponding states correlation. 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 obtained from the viscosity inversion to give the potential energy in the separation range. Figure 1 shows the present potential with the previously determined potential.

The combination of collision integrals occur frequently enough in the expression for the transport coefficients of pure gases and mixtures of gases to make it worth while giving them special symbols. They are

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

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

The most commonly used collision integrals and their ratios of He-Xe is given in Table 1.

The temperature dependence of the transport coefficients may provide a critical test of the accuracy of the potential. Theoretical expressions for the transport coefficients of binary mixtures can be founding standard treatises.[7]

Table 1. Dimensionless collision integrals $\Omega^{(l,s)*}$ and the related ratios for He-Xe

$\log_{10} T^*$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	B^*	C^*
-0.2	1.7640	1.9697	1.2597	0.8380
-0.1	1.5766	1.7601	1.2305	0.8380
0.0	1.4123	1.5707	1.1908	0.8445
0.1	1.2732	1.4087	1.1677	0.8561
0.2	1.1584	1.2758	1.1431	0.8705
0.3	1.0648	1.1697	1.1254	0.8856
0.4	0.9887	1.0861	1.1145	0.8995
0.5	0.9263	1.0199	1.1091	0.9112
0.6	0.8740	0.9666	1.1076	0.9202
0.7	0.8290	0.9220	1.1081	0.9266
0.8	0.7893	0.8830	1.1094	0.9308
0.9	0.7532	0.8474	1.1104	0.9336
1.0	0.7198	0.8137	1.1108	0.9353
1.1	0.6886	0.7813	1.1104	0.9365
1.2	0.6593	0.7497	1.1086	0.9375
1.3	0.6317	0.7187	1.1042	0.9388
1.4	0.6060	0.6880	1.0960	0.9409
1.5	0.5824	0.6575	1.0830	0.9444
1.6	0.5614	0.6274	1.0663	0.9497
1.7	0.5435	0.5989	1.0478	0.9567
1.8	0.5289	0.5731	1.0301	0.9648
1.9	0.5177	0.5512	1.0151	0.9733
2.0	0.5097	0.5001	1.0038	0.9812

Table 2. Viscosity coefficients of He-Xe mixtures

T (K)	x_{He}	η_{mix} (μPa s)	$\eta_{mix}{}^a$ (exp)	Dev (%)
298.15	0.2677	24.27	24.17	0.41
	0.5316	25.48	25.44	0.16
	0.8687	25.46	25.50	-0.16
373.15	0.2677	29.84	29.86	-0.07
	0.5316	30.95	30.97	-0.06
	0.8687	30.06	30.09	-1.00
483.15	0.2677	37.49	37.60	-0.29
	0.5316	38.44	38.59	-0.39
	0.8687	36.41	36.41	0.00
568.15	0.2677	43.01	42.95	0.14
	0.5316	43.85	43.52	0.76
	0.8687	41.04	40.87	0.41
698.15	0.2677	50.81	50.73	0.16
	0.5316	51.53	50.97	1.10
	0.8687	47.71	47.46	0.53
778.15	0.2677	55.18	55.21	-0.05
	0.5316	55.87	55.84	0.05
	0.8687	51.60	51.35	0.49

^{a}ref. 10.

The calculated viscosity coefficient of He-Xe as a function of temperature and the mixture concentration together with their corresponding experimental values is shown in Table 2.

Table 3. Diffusion coefficients of He-Xe

T (K)	D_{12} (10^{-4} m^{2}s^{-1})	D_{12} (exp)	Dev (%)
220.0	0.3224	0.3214^a	0.31
240.0	0.3740	0.3726^a	0.37
260.0	0.4283	0.4260^a	0.54
273.3	0.4661	0.4630^b	0.67
280.0	0.4857	0.4832^a	0.51
300.0	0.5461	0.5422^a	0.72
315.0	0.5930	0.5910^b	0.34
320.0	0.6090	0.6048^a	0.69
340.0	0.6748	0.6690^a	0.87
360.0	0.7434	0.7363^a	0.96
380.0	0.8146	0.8053^a	1.15
400.0	0.8882	0.8771^a	1.27

^{a}ref. 5. ^{b}ref. 11.

The necessary collision integrals of the pure components He and Xe are taken from their inversion potentials.[8,9]

Table 3 contains the temperature dependence of the diffusion coefficient of He-Xe.

Conclusion

The present potential for He-Xe provides a good overall account of the experimental properties of He-Xe considering their stated uncertainty in measurements. Thus the inversion procedure used in this work provides a l technique for the direct determination of intermolecular pair potential energy functions. An important advantage of inversion method is that, the need for lengthy multiparameter fitting procedure is largely removed.

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