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.

Theory

The procedure is to utilize the extended principle of corresponding states4 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:

\[
0 \leq T^* \leq 1.2 \quad (1a)
\]

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

where

\[
\begin{align*}
a_1 &= 0.18 \\
a_2 &= 0.0 \\
a_3 &= -1.20407 - 0.195866 (C_6^*)^{-1/3} \\
a_4 &= -9.86374 + 20.2221(C_6^*)^{-1/3} \\
a_5 &= 16.6295 - 3.13613 (C_6^*)^{-1/3} \\
a_6 &= -6.73805 + 12.6611(C_6^*)^{-1/3}
\end{align*}
\]

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

\[
1.2 \leq T^* \leq 10 \quad (1b)
\]

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

\[
T^* \geq 10 \quad (1c)
\]

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

where

\[
\begin{align*}
a_1 &= 0.0 \\
a_2 &= -33.0838 + (\alpha_0^0 \rho^0)^{-2} (20.0862 + (72.1059/\alpha_0^0) + (8.27648/\alpha_0^0)^2) \\
a_3 &= 101.571 - (\alpha_0^0 \rho^0)^{-2} (56.4472 + (286.393/\alpha_0^0) + (17.761/\alpha_0^0)^2)
\end{align*}
\]

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\[ a_4 = -87.7036 + (\alpha_{10} \rho^*)^2 \left( 46.3130 + \frac{277.146}{\alpha_{10}} + \frac{19.0573}{\alpha_{10}}^2 \right) \]

where \( \rho^* \) and \( V_0^* \) are high-temperature dimensionless scaling parameters. The values of \( \rho^* \), \( V_0^* \), and \( C_6^* \) are given in ref. 4. \( \alpha_{10} = \ln \left( V_0^* /10 \right) \) is the value of \( \alpha = \ln V_0^* - \ln T^* \) at matching point of \( T^* = 10 \). \( T^* \) is reduced temperature, \( T^* = kT/\varepsilon \), where \( \varepsilon \) 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 \( G_\eta \) such that

\[ V^*(r) = \frac{V(r)}{\varepsilon} = T^* G_\eta(T^*) \]

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:

\[ \frac{V}{\varepsilon} = T^* - 1 \quad (4a) \]

and

\[ r^*_R - r^*_L = -(B - b_0) N(T^*) \quad (4b) \]

where \( r_R \) and \( r_L \) are the coordinates of the outer and inner wall of the potential well, \( b_0 = 2\pi N_A \sigma^3 /3 \), \( \sigma \) 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\(^4\)

\[ 0 \leq T^* \leq 1.1 \]

\[ B^* = -(T^*)^{1/2} \rho^* \left( 1.18623 + 1.00824 T^* + 4.25571(T^*)^2 - 18.6033(T^*)^3 + 20.4732(T^*)^4 - 8.71903(T^*)^5 + 1.14829(T^*)^6 \right) \]

Thus, the outer wall wall \( r_R \), can be obtained from the inner 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

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

\[ C^* = \frac{\Omega^{(1,2)}/\Omega^{(1,1)}}{\Omega^{(1,1)}} \quad (5b) \]

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.\(^7\)
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 2. Viscosity coefficients of He-Xe mixtures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>xHe</th>
<th>ηmix (µPa s)</th>
<th>ηmix (exp) (µPa s)</th>
<th>Dev (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>0.2677</td>
<td>24.27</td>
<td>24.17</td>
<td>0.41</td>
</tr>
<tr>
<td>0.5316</td>
<td>25.48</td>
<td>25.44</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>0.8687</td>
<td>25.46</td>
<td>25.50</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>373.15</td>
<td>0.2677</td>
<td>29.84</td>
<td>29.86</td>
<td>0.07</td>
</tr>
<tr>
<td>0.5316</td>
<td>30.95</td>
<td>30.97</td>
<td>-0.06</td>
<td></td>
</tr>
<tr>
<td>0.8687</td>
<td>30.06</td>
<td>30.09</td>
<td>-1.00</td>
<td></td>
</tr>
<tr>
<td>483.15</td>
<td>0.2677</td>
<td>37.49</td>
<td>37.50</td>
<td>-0.02</td>
</tr>
<tr>
<td>0.5316</td>
<td>38.44</td>
<td>38.50</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>0.8687</td>
<td>36.41</td>
<td>36.41</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>568.15</td>
<td>0.2677</td>
<td>43.01</td>
<td>43.02</td>
<td>0.08</td>
</tr>
<tr>
<td>0.5316</td>
<td>43.85</td>
<td>43.90</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>0.8687</td>
<td>41.04</td>
<td>40.87</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>698.15</td>
<td>0.2677</td>
<td>50.81</td>
<td>50.93</td>
<td>0.24</td>
</tr>
<tr>
<td>0.5316</td>
<td>51.53</td>
<td>50.97</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>0.8687</td>
<td>47.71</td>
<td>47.46</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>778.15</td>
<td>0.2677</td>
<td>55.18</td>
<td>55.21</td>
<td>-0.04</td>
</tr>
<tr>
<td>0.5316</td>
<td>55.87</td>
<td>55.84</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>0.8687</td>
<td>51.60</td>
<td>51.35</td>
<td>0.49</td>
<td></td>
</tr>
</tbody>
</table>

*ref. 10.*

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.

Table 3. Diffusion coefficients of He-Xe

<table>
<thead>
<tr>
<th>T (K)</th>
<th>D12 (10^{-4} m^2 s^{-1})</th>
<th>D12 (exp) (10^{-4} m^2 s^{-1})</th>
<th>Dev (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>220.0</td>
<td>0.3224</td>
<td>0.3214</td>
<td>0.31</td>
</tr>
<tr>
<td>240.0</td>
<td>0.3740</td>
<td>0.3726</td>
<td>0.37</td>
</tr>
<tr>
<td>260.0</td>
<td>0.4283</td>
<td>0.4260</td>
<td>0.54</td>
</tr>
<tr>
<td>273.3</td>
<td>0.4661</td>
<td>0.4630</td>
<td>0.67</td>
</tr>
<tr>
<td>280.0</td>
<td>0.4857</td>
<td>0.4832</td>
<td>0.51</td>
</tr>
<tr>
<td>300.0</td>
<td>0.5461</td>
<td>0.5422</td>
<td>0.72</td>
</tr>
<tr>
<td>315.0</td>
<td>0.5930</td>
<td>0.5910</td>
<td>0.34</td>
</tr>
<tr>
<td>320.0</td>
<td>0.6090</td>
<td>0.6048</td>
<td>0.69</td>
</tr>
<tr>
<td>340.0</td>
<td>0.6748</td>
<td>0.6690</td>
<td>0.87</td>
</tr>
<tr>
<td>360.0</td>
<td>0.7434</td>
<td>0.7363</td>
<td>0.96</td>
</tr>
<tr>
<td>380.0</td>
<td>0.8146</td>
<td>0.8053</td>
<td>1.15</td>
</tr>
<tr>
<td>400.0</td>
<td>0.8882</td>
<td>0.8771</td>
<td>1.27</td>
</tr>
</tbody>
</table>

*ref. 5.* "ref. 11."

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 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.

Conclusion

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.

References