POTENTIAL OF BINARY INTERACTIONS AND THERMOPHYSICAL PROPERTIES OF CHLORINE IN A GAS PHASE

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Two models: (i) (n-6) Lennard-Jones (LJ) potential and a (ii) Lennard Jones Temperature-Dependent Potential (LJTDP) were used for the determination of the intermolecular interaction potential parameters (PP) and simultaneous approximation of the measured experimental thermophysical properties \((pVT)\) and acoustic second virial coefficients \(B\) and \(\beta\) and viscosity \(\eta\) for gaseous chlorine \((\text{Cl}_2)\). A comparison of the results shows slightly smaller deviations between measured and calculated data for LJTDP calculations compared to the \((n-6)\) LJ potential. This unessential priority of the LJTDP is compensated by the simplicity of \((n-6)\) LJ potential, which we recommend for calculations of different potential-dependent properties. We give tables with recommended data for of \(B\), \(\eta\), and self diffusion \(\rho D\), produced in the temperature range 200-900 K, which are convenient for inter- and extrapolations.

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1. Introduction

Chlorine is a gas with a huge importance in different branches of contemporary industry such as vinyl plastic chemistry, biochemistry, steel making, production of semiconductor devices, and as a source for disinfecting the drinking water. Despite of this there are not enough experimentally measured data for thermophysical properties.

The aim of our work is:

(i) to investigate interactions between two chlorine molecules using two models of intermolecular potentials (LJTDP and \((n-6)\) LJ potential);
(ii) to predict the potential parameters and create tables with reference data for the temperature dependencies of the thermophysical properties: \(B(T)\), \(\eta(T)\), and \(\rho D(T)\), calculated by means of a unique potential.

Previous researchers have compared their experimentally defined results of thermophysical properties of gaseous chlorine with the calculated ones obtained using simple spherically symmetric potentials. In 1986 a Two-Center LJ (2CLJ) potential was applied [1] to calculate \(B\), but the results were not satisfying. In 2002 Hurly [2] fitted \(\beta\) extracted from speed of sound measurements to a Hard-Core Square-Well (HCSW) and a Hard-Core Lennard-Jones (HCLJ) potential. In these calculations he also had to determine \(B\). With the second model the speed of sound was approximated with an accuracy of 0.2% and it was recommended as a more convenient. Although the temperature range of the measurements was rather narrow \((\Delta T = 260-440 \text{ K})\) Hurly used the same potential to calculate \(B\) at temperatures between 177 to 1770 K.

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2. Theoretical background

The calculations have been performed using two simple spherically symmetric potentials:

1. (n-6) Lennard Jones potential: 
   \[ U(r) = \frac{\varepsilon}{n-6} \left( \frac{r_m}{r} \right)^n - \frac{\varepsilon r_m^n}{r} \] 
   where \( \varepsilon \) is a potential well depth, \( r_m \) is an equilibrium distance and \( n \) is a repulsive parameter.

2. Lennard Jones temperature-dependent potential: 
   \[ U(r,T) = \frac{\varepsilon(T)}{n-6} \left( \frac{r_m}{r} \right)^n - \frac{\varepsilon r_m^n}{r} \] 
   where \( \varepsilon(T) \) is the equilibrium distance and \( n \) is a repulsive parameter.

In general, there is no difference between these two models except for the temperature dependence of the potential parameters \( \varepsilon \) and \( r_m \).

In the second model we consider the temperature dependence of the equilibrium distance 
\[ r_m(T) = r_m(0) + \delta(T) \] (\( \delta \) is the effective enlargement of molecular size at given temperature) and of the potential well depth 
\[ \varepsilon(T) = \varepsilon(0) \left( \frac{r_m(0)}{r_m(T)} \right)^n \] as a result from the vibrational excitation of the molecule.

The motivation for this choice was that although \( \text{Cl}_2 \) is not spherically symmetric it is a rather simple small two atomic molecule with one vibrational frequency (\( \nu=564.9 \text{ cm}^{-1} \)). Therefore, the average over all orientations of pair interactions can be approximated spherically. The existence of the essential population of the vibrationally excited molecules supports the second considered model [3].

Our preliminary experience with planar \( \text{BF}_3 \) molecule encourages us to try the LJTD [4] or (n-6) LJ potential models in this case.

3. Approximation of the existing experimental data by means of the LJTD or (n-6) LJ potential

The parameters of the interaction potential between two chlorine molecules at T=0 K: \( r_m(0) \), \( \varepsilon(0) \), \( n \) and \( \delta(0) \) are obtained by minimizing the sum \( F \) of squared deviations between \( M \) experimental (\( P_{\text{exp}} \)) and calculated (\( P_{\text{calc}} \)) values of the \( B \), \( \beta \) and \( \eta \), normalized to the accepted experimental error \( \alpha_{\text{exp}} \).

\[ F = \sum_{i=1}^{M} R_i^2 = \sum_{i=1}^{M} \left( \ln \left( \frac{P_{\text{calc},i}}{P_{\text{exp},i}} \right) + \alpha_{\text{exp},i} \right)^2 \]

The details of the procedure are given elsewhere [5].

The transport and equilibrium properties of \( \text{Cl}_2 \) have been scarcely measured. Despite of its industrial importance only very few experimental input data are available. The set of existing experimental data is listed in Table 1. All 53 experimental values of \( B \) (5 works), \( \beta \) (1 work) and \( \eta \) (4 works) have been included in the simultaneous approximation in order to define the parameters of the used intermolecular potentials. Amongst them there are very precise measurements of the speed of sound in low-pressure [2]. The first experimental data for \( \text{Cl}_2 \) (\( B \)) have been determined from Pier in 1908 [6] and the last ones (\( \beta \)) from Hurly in 2002 [2]. Naturally, the last more sophisticated experiments and the new computational technique add more reliability to the results of modeling.
4. Results and discussion

The potential parameters of the "best" solution of the ill-posed problem determine the most convenient potential of the selected type. The "best" solution for the \((n-6)\) LJ model was defined by 3 parameters: \(\varepsilon k_B = 506.7 \pm 4.1\) K, \(r_m = 4.248 \pm 0.009 \times 10^{-10}\) m, and \(n = 26.34 \pm 0.80\), and \(\delta = 0.0088 \pm 0.0003 \times 10^{-10}\) m with \(RMS = 1.473\) [3].

A comparison of the results shows slightly smaller deviations measured and calculated data for LJTDP calculations compared with the \((n-6)\) LJ potential. This essential priority of the LJTDP is compensated by the simplicity of \((n-6)\) LJ potential, which we recommend for calculations.

The deviations between measured and calculated data by means of LJTDP \(B, \beta, \eta\) normalized to the experimental errors, \(a_{\exp}\), are shown on Fig. 1. It is transparent that the experimental points are situated symmetrically towards the calculated ones (zero line). Within one experimental error are about 75% (39 points) of all data. Unfortunately, the number of the experimental data (\(M=53\)) is not large enough to apply the Gauss distribution for further statistical analysis. The standard deviation (0.894) is nearly twice smaller than our \(RMS\).

![Fig. 1. Deviations between experimental and calculated with the both of potentials values of \(B, \beta, \eta\) of \(\text{Cl}_2\).](image-url)
We recommend Table 2 of reference data for the thermophysical properties $B$, $\eta$ and $\rho D$.

Table 2. Thermophysical properties for gaseous chlorine obtained by means of the LJJDTP and $(n-6)$ LJ potential.

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>$-B$ (LJ), cm$^3$/mol</th>
<th>$-B$ (LJJDTP), cm$^3$/mol</th>
<th>$\eta$ (LJ), $\mu$Pa.s</th>
<th>$\eta$ (LJJDTP), $\mu$Pa.s</th>
<th>$\rho D$ (LJ), $10^3$, g/m.s</th>
<th>$\rho D$ (LJJDTP), $10^3$, g/m.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>405.894</td>
<td>405.621</td>
<td>11.802</td>
<td>11.764</td>
<td>15.402</td>
<td>15.373</td>
</tr>
<tr>
<td>300</td>
<td>281.235</td>
<td>281.484</td>
<td>13.849</td>
<td>13.823</td>
<td>18.102</td>
<td>18.090</td>
</tr>
<tr>
<td>350</td>
<td>207.452</td>
<td>207.790</td>
<td>15.887</td>
<td>15.875</td>
<td>20.752</td>
<td>20.758</td>
</tr>
<tr>
<td>400</td>
<td>158.925</td>
<td>159.222</td>
<td>17.911</td>
<td>17.915</td>
<td>23.349</td>
<td>23.379</td>
</tr>
<tr>
<td>550</td>
<td>79.639</td>
<td>79.673</td>
<td>23.795</td>
<td>23.844</td>
<td>30.763</td>
<td>30.853</td>
</tr>
<tr>
<td>600</td>
<td>64.077</td>
<td>64.028</td>
<td>25.681</td>
<td>25.738</td>
<td>33.120</td>
<td>33.229</td>
</tr>
<tr>
<td>650</td>
<td>51.434</td>
<td>51.308</td>
<td>27.510</td>
<td>27.575</td>
<td>35.401</td>
<td>35.518</td>
</tr>
<tr>
<td>700</td>
<td>40.965</td>
<td>40.768</td>
<td>29.289</td>
<td>29.366</td>
<td>37.608</td>
<td>37.736</td>
</tr>
<tr>
<td>800</td>
<td>24.654</td>
<td>24.331</td>
<td>32.740</td>
<td>32.831</td>
<td>41.864</td>
<td>42.019</td>
</tr>
<tr>
<td>850</td>
<td>18.183</td>
<td>17.804</td>
<td>34.396</td>
<td>34.483</td>
<td>43.913</td>
<td>44.078</td>
</tr>
<tr>
<td>900</td>
<td>12.549</td>
<td>12.120</td>
<td>36.001</td>
<td>36.089</td>
<td>45.910</td>
<td>46.085</td>
</tr>
</tbody>
</table>

In Figs. 2 and 3 our calculations for $B$ and $\eta$ (full lines) are compared with the reference values recommended by the National Institute of Standards and Technology, USA (symbols). In both cases very good coincidence can be seen.

![Temperature dependence of $B$.](image1)

![Temperature dependence of $\eta$.](image2)

**Fig. 2.** Temperature dependence of $B$.  
**Fig. 3.** Temperature dependence of $\eta$.

### 5. Conclusion

The calculations of the thermophysical properties of chlorine were successfully performed by two spherically-symmetric potentials. Our LJJDTP gives slightly better RMS but we recommend using the $(n-6)$ LJP for the sake of simplicity.

Algorithms for calculation the temperature dependencies $\eta(T)$, $\rho D(T)$ and $B(T)$ are:

$$
\eta(T) = 0.5805 + 0.04670828 \times (T/K) - 8.05020 \times 10^{-6} \times (T/K)^2, \mu\text{Pa.s}
$$

$$
\rho D(T) = 1.10827 + 0.0600390 \times (T/K) - 1.106849 \times 10^{-5} \times (T/K)^2, 10^3 \text{g/m.s}
$$

$$
B(T) = 78.630 - 82454.6/(T/K) + 2784176/(T/K)^2 - 3.133953 \times 10^{3}/(T/K)^3, \text{cm}^3/\text{mol}
$$
References