Temperature-dependent interaction potential between NF$_3$ molecules and thermophysical properties of gaseous NF$_3$

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Abstract A temperature-dependent effective intermolecular interaction potential is applied to describe the interaction between two nitrogen fluoride (NF$_3$) molecules in gas phase. To this end, a spherically-symmetric ($n$-$6$) Lennard-Jones temperature-dependent potential (LJTDP) is used. The ($n$-$6$) LJTDP takes into account the influence of vibrational excitation of the molecules on the potential parameters, namely, the equilibrium distance $r_m$ and the potential well depth $\varepsilon$. The potential parameters at $T = 0$ K were obtained from the very small amount of existing thermophysical equilibrium and transport properties of low-density NF$_3$ gas. Fitting formulae are tabulated for a fast and reliable prediction of the thermophysical properties and potential parameters in the temperature range between 200 K and 1200 K. A comparison is also presented between our estimates for some thermophysical properties of the NF$_3$ gas with the available experimental and calculated data.

1. Introduction
Nitrogen trifluoride (NF$_3$) is a gas primarily used in the semiconductor industry. Its usage has increased during the last years as it is still not included in the list of gases controlled by the Kyoto protocol. Because of its high percentage conversion to fluorine, NF$_3$ is used as a substitute to other fluorinated species, such as perfluorocarbons and SF$_6$ for plasma etching and CVD chambers cleaning. However, there is a lack of sufficient thermophysical data on gaseous NF$_3$ over a large temperature range, which would allow for a reliable prediction of its thermophysical behavior. This is probably be the reason for the relatively poor knowledge of its intermolecular interaction energy as well.

Oghaz et al. [1] have determined an effective interaction potential function by inversion of the reduced viscosity collision integrals at zero density. In their later work [2], a new approach has been proposed to the estimation of viscosity in dilute and dense pure NF$_3$. They have also calculated the viscosity in the zero-density limit between 224 K and 349 K by using different potential energy functions, namely Lennard-Jones (12-6), Mie (14-7), Hartree-Fock-Dispersion and the Maitland-Smith extended [$n,m$] Lennard-Jones potential.

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The main goals of our study were:
i) to obtain an effective interaction potential energy function of two NF$_3$ molecules by using simultaneously the available equilibrium (second $pVT$-virial coefficient, $B$, and acoustic second virial coefficient, $\beta$) and transport properties (viscosity, $\eta$) of gaseous NF$_3$;

ii) to predict the temperature dependence of $B(T)$, $\eta(T)$ and $\rho D(T)$ in the large temperature interval between 200 K and 1200 K.

2. Theoretical background

The ($n$-$6$) LJTDP was introduced and discussed in full detail in our earlier work, see e.g. [3]. Briefly, the intermolecular interaction potential energy $U(r,T)$ is modelled as

$$U(r,T) = \frac{\varepsilon(T)}{n-6} \left[ 6 \left( \frac{r_m(T)}{r} \right)^6 - 9 \left( \frac{r_m(T)}{r} \right)^4 \right].$$  \hspace{1cm} (1)

Here $r$ and $T$ are the center-of-mass distance and temperature, respectively, $r_m(T)$ is the equilibrium distance, $\varepsilon(T)$, the potential energy well depth, and $n$, the repulsive parameter, the latter being independent of the temperature. The temperature dependence of $r_m(T)$ and $\varepsilon(T)$ is the result of a Boltzmann-type averaging over the occupation of the molecule’s higher vibrational levels. It is described by:

$$r_m(T) = r_m(T = 0 K) + \delta(T)$$  \hspace{1cm} (2)

and

$$\varepsilon(T) = \varepsilon(T = 0 K) \left( \frac{r_m(T = 0 K)}{r_m(T)} \right)^6,$$  \hspace{1cm} (3)

where $\delta$ is a temperature-independent fit parameter, whereas the function $f(T)$ indicates the influence of the vibrational excitation of the molecule on its geometrical radius. The function $f(T)$ can be calculated at any $T$ if the vibrational frequencies of the molecule are known.

3. Results and discussion

The potential parameters at $T = 0$ K were obtained by minimizing the sum $F$ (equation 4) of the squared deviations between the experimental and calculated thermophysical properties, normalized to their relative experimental errors $a_{exp}$. Here $M$ is the number of experimental data points.

$$F = \sum_{\beta = 1}^{M_{\beta}} \frac{\ln \left( \frac{B_{\exp}}{B_{\calc}} \right)^2}{a_{\exp,\beta}} + \sum_{\beta = 1}^{M_{\beta}} \frac{\ln \left( \frac{\beta_{\exp}}{\beta_{\calc}} \right)^2}{a_{\exp,\beta}} + \sum_{\eta = 1}^{M_{\eta}} \frac{\ln \left( \frac{\eta_{\exp}}{\eta_{\calc}} \right)^2}{a_{\exp,\eta}}$$  \hspace{1cm} (4)

The available experimental data for the thermophysical properties of NF$_3$ are very scarce. In the case of the second $pVT$-virial coefficient $B$, we used the data of Lemmon and McLinden [4]. The accepted $a_{exp}$ of these data is in the range between 2 % and 5 %. For the second acoustic virial coefficient $\beta$, only the experimental results of Hurly [5] are available in the literature. Although measured in the small temperature range between 200 K and 425 K, these measurements have a large impact on the resulting potential parameters due to their high relative accuracy (error about 0.2 −1 %). Hurly’s experimental data for the viscosity [5, 6] are also substituted into our minimization procedure. Their accuracy is in the range between 0.7 % and 3 %. Our survey of the literature showed that no experimental data are available for the self-diffusion coefficients of NF$_3$. 


The minimization procedure was carried out with all available data. The results obtained for the potential parameters of the \((n-6)\) LJTDP at \(T = 0\) K are: \(\frac{\varepsilon}{k_B} = (273.89 \pm 3.44)\) K, \(r_m = (4.254 \pm 0.014) \times 10^{-10}\) m, \(n = 24.13 \pm 0.62\) and \(\delta = (0.0045 \pm 0.0001) \times 10^{-10}\) m with a root-mean-square deviation of \(\text{RMS} = \sqrt{\frac{\sum (P_{\text{exp}} - P_{\text{calc}})^2}{M}} = 0.786\) \(a_{\text{exp}}\). The quality of our \((n-6)\) LJTDP can be seen in figure 1.

In this figure, the calculated thermophysical properties \(P_{\text{calc}}\) are compared to the experimentally obtained input data \(P_{\text{exp}}\). It can be seen that the relative deviations \((P_{\text{exp}} - P_{\text{calc}})/a_{\text{exp}}\) lie mostly in the range between \(\pm 1\cdot a_{\text{exp}}\). This means that the \((n-6)\) LJTDP is able to reproduce the experimental data within their error limits. Additionally, the data points shown in figure 1 are distributed more or less symmetrically towards the zero line defined by our calculated data.

In figures 2-4, our results obtained with the \((n-6)\) LJTDP are compared to other correlations which are given in the literature. We also included the self-diffusion coefficient \(\rho D\) in this comparison.

In figure 2, our calculations of the second \(pVT\)-virial coefficient, \(B\), are compared to the correlations of Tsonopoulos [7]. The maximum deviation is \(-4.07\) cm\(^3\)/mol. This small deviation shows that both models do coincide well within their error bars. A comparison of the viscosities obtained from different models is shown in figure 3. It can be seen that the relative deviation between our calculations and the results of other authors are mostly in the range between \(\pm 3\) %.

**Figure 1.** Relative deviations between the \((n-6)\) LJTDP solution (zero line) and the experimental input data of NF\(_3\).

**Figure 2.** Absolute deviations \(\Delta B = B_{\text{Ref.7}} - B_{\text{LJTDP}}\) of the second \(pVT\)-virial coefficients between the results of [7] and the values obtained in this work.

**Figure 3.** Relative deviations \(\Delta \eta/\eta = 100(\eta_{\text{Ref.12}} - \eta_{\text{LJTDP}})/\eta_{\text{LJTDP}}\) of the viscosity calculated in [2] (various potential energy functions) and [10]-[12] and the values obtained in this work.
In figure 4, the relative deviations between the binary self-diffusion coefficient $\rho D$ of Liley [12] and our results are shown. In table 1, we present our recommended values for the potential parameters $r_m$ and $\varepsilon$ as well as for the thermophysical properties $B$, $\eta$, and $\rho D$.

![Graph showing relative deviations $\Delta \rho D/\rho D$ versus temperature.]  

**Figure 4.** Relative deviations $\Delta \rho D/\rho D = 100(\rho D_{\text{Liley}} - \rho D_{\text{LJTDP}})/\rho D_{\text{LJTDP}}$ of the binary self-diffusion coefficient between the results calculated in Ref. [12] and the values obtained in this work.

**Table 1**. Recommended data for NF$_3$.

| $T$, K | $r_m$, $10^{-10}$ m | $\sigma_{k_B}$, K | $B$, cm$^3$/mol | $\eta$, $\mu$Pa·s | $\rho D$, $10^3$·g/(m·s) |
|-------|---------------------|-----------------|-----------------|----------------|-------------------|
| 200   | 4.259855            | 271.63          | -197.72         | 12.22          | 16.00             |
| 250   | 4.264275            | 269.95          | -125.50         | 14.99          | 19.55             |
| 300   | 4.269267            | 268.06          | -83.38          | 17.68          | 22.93             |
| 350   | 4.274497            | 266.10          | -55.85          | 20.25          | 26.15             |
| 400   | 4.279821            | 264.12          | -36.47          | 22.70          | 29.18             |
| 450   | 4.28513             | 262.16          | -22.11          | 25.02          | 32.08             |
| 500   | 4.290367            | 260.25          | -11.05          | 27.22          | 34.84             |
| 550   | 4.295491            | 258.39          | -2.27           | 29.31          | 37.44             |
| 600   | 4.300466            | 256.60          | 4.85            | 31.30          | 39.92             |
| 650   | 4.305244            | 254.90          | 10.74           | 33.19          | 42.30             |
| 700   | 4.309771            | 253.30          | 15.68           | 35.00          | 44.59             |
| 750   | 4.313991            | 251.81          | 19.87           | 36.74          | 46.79             |
| 800   | 4.317862            | 250.46          | 23.46           | 38.41          | 48.91             |
| 850   | 4.32136             | 249.25          | 26.57           | 40.02          | 50.97             |
| 900   | 4.324483            | 248.17          | 29.27           | 41.58          | 52.96             |
| 950   | 4.327245            | 247.22          | 31.63           | 43.10          | 54.88             |
| 1000  | 4.329675            | 246.39          | 33.72           | 44.57          | 56.76             |
| 1050  | 4.331804            | 245.66          | 35.56           | 46.00          | 58.59             |
| 1100  | 4.333671            | 245.03          | 37.21           | 47.40          | 60.37             |
| 1150  | 4.335303            | 244.48          | 38.68           | 48.77          | 62.11             |
| 1200  | 4.336738            | 243.99          | 40.01           | 50.10          | 63.81             |

*The parameters and properties given in the table are fitted by the following formulae: $r_m(T)(10^{-10}m)=4.254+0.17062\cdot\exp(-902.14/T)+2.76691\cdot10^{-5}T^2-2.13554\cdot10^{-8}T^3$, $B(T)(cm^3/mmol)=70.63-33411.7/T-3.43064\cdot10^6/T^2-1.23330\cdot10^8/T^3$, $\eta(T)(\mu Pa\cdot s)=-0.66622+0.0709095T-3.50206\cdot10^{-5}T^2+9.33423\cdot10^{-9}T^3$, $\rho D(T)(10^3\cdot g/(m\cdot s))=-0.013169+0.088446T-4.35150\cdot10^{-5}T^2+1.18078\cdot10^{-8}T^3$, with $T^*=T/K$. 
4. Conclusions
The \((n-6)\) LJTDP proposed is capable of reproducing different thermophysical equilibrium and transport properties of low-density gaseous \(\text{NF}_3\). The values recommended of the potential parameters, second virial coefficient \(B\), viscosity \(\eta\) and self-diffusion coefficient \(\rho D\) allow for a reliable interpolation of different properties in the temperature-range between 200 K and 1200 K; they can be used for further calculation necessary in some engineering and scientific projects.

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