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Computation of some thermodynamic properties of nitrogen using a new intermolecular potential from molecular dynamics simulation

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1. Introduction

It has been demonstrated that the excellent predictions of the thermodynamic data of pure fluids and mixtures can be obtained by molecular dynamics simulations. A crucial point in computer modeling of real substances is the determination of intermolecular interactions [1].

Since nitrogen is present in everyday life and many important technologies, the investigation of the nitrogen properties has been of great importance not only from basic scientific but also from technical point of view [2].

The purpose of the present paper is to determine an accurate nitrogen pair-potential energy function via the inversion of the reduced viscosity collision integrals. We have also computed the second virial coefficient of nitrogen using the obtained pair-potential at different temperatures and compared with experimental data. Some tranport properties of nitrogen such as viscosity, thermal conductivity, self-diffusion coefficient, and thermal diffusion factor have been also calculated using the obtained pair-potential at the wide ranges of temperature and density.

Finally, we have performed molecular dynamics simulation to obtain pressure, internal energy, and self-diffusion coefficient of nitrogen at different temperatures and densities using our calculated pair-potential and some other potentials. The molecular dynamics simulation has been also used to determine the equation of state for nitrogen in low and high pressure ranges.

2. Method

The pair- potential energy function has been obtained using the inversion of the reduced viscosity collision integrals.
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 [3].

3. Results and discussion

The reduced pair-potential energy function of nitrogen has been obtained using the inversion of the reduced viscosity collision integrals. A comparison between our calculated pair-potential with previously determined has been done. There is a good agreement between our calculated pair-potential and other literature potentials. The reason for a good accordance between our calculated potential and other potentials obtained using different methods such as the ab initio method and scattering experiment for nitrogen is based on the fact that our potential has been calculated using the inversion method. This method produces an isotropic pair potential energy that is a spherical averaged of the true potential multidimensional function over all possible relative orientations.

We have calculated the reduced second virial coefficient of nitrogen and compared with the corresponding literature data. The calculation of the second virial coefficient can be considered as a critical test for a potential [3]. The general agreement between the values of second virial coefficients calculated based on our resulting potential and the experimental and literature values confirm the validity of our potential.

We have calculated the viscosity, thermal conductivity, self diffusion coefficient, and thermal diffusion factor for nitrogen at different temperatures at atmospheric pressure. There are little deviations between our calculated properties and experimental data. It is plausible to say that this excellent accordance corresponds to the accuracy of our calculated potential for nitrogen.

We have performed MD simulation to obtain reduced pressure and internal energy of nitrogen using our calculated pair-potential and other potentials. At higher densities (ρ^*=0.1 and 1.0), the pressure values using our calculated potential show a better agreement with experimental data compared with other potentials.

We have also calculated the reduced heat capacity at constant volume, C_v^*, at different reduced temperatures using the simulated internal energies at constant reduced density. Our simulated values of C_v^* are nearly constant at different reduced temperatures which is expected for a classical MD simulation but at higher densities (ρ^*=0.1) our values decrease in spite of experimental data which increase at high temperatures which may be due to using the isotropic potential. Although our isotropic pair potential energy is a spherical averaged of the true potential multidimensional function but does not account explicity for rotational motion which decreases degree of freedom and so decreases C_v^* in the simulation.

The MD calculations have been used to determine the equation of state for nitrogen which may be used as a reference for nitrogen especially at high pressures. We calculated the reduced pressure of nitrogen for the reduced temperatures from 1 to 21 and reduced density from 0.001 to 2.7.

We have compared our calculated reduced self-diffusion coefficient for nitrogen at different temperatures and densities with the experimental data. The temperature dependence of our simulated values using different potentials is much less than those of experimental values.

4. Conclusions

We have determined the pair-potential energy function and reduced collision integrals of nitrogen via the inversion of reduced viscosity collision integrals and fitted with a HFD-like potential. This potential can reproduce the second virial coefficient, viscosity, thermal conductivity, self-diffusion coefficient, and thermal diffusion factor of nitrogen in a good accordance with experiment.

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