The role of the intermolecular potential in determination of equilibrium and dynamic properties of molecular nitrogen (N₂) properties: MD simulations

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Abstract. High precision approximation of the intermolecular potential is necessary for molecular dynamics (MD) simulations of the physical properties of molecular nitrogen (N₂). Recently, Quantum Mechanical (QM) high precision calculations (coupled-cluster singles-and-doubles with a perturbative triples corrections [CCSD(T)]) were used to determine N₂–N₂ intermolecular interaction. Using these data, the potential, covering all orientations of the pair of the nitrogen molecules, was obtained in the form invariant with respect of rotation of the reference system. The new N₂–N₂ potential remains in reasonably good agreement with the isotropically scaled potential function of van der Avoird et al, based on the results of Hartree–Fock calculations. Nitrogen equation of state, at pressures up to 30 GPa (300 kbar) and at temperatures from room temperature to 2000K, was obtained by MD simulations, employing the following potentials: the new CCSD(T) function, the nonscaled and scaled expression by van der Avoird et al., and four-atom interaction by Johnson et al. It was shown that the new potential gives considerably better agreement with the experimental data than in all other cases. MD simulations were also used to determine shear viscosity of nitrogen. It was shown that the influence on the potential variation on the MD obtained values of the viscosity is much stronger than on the equation of state, especially at higher densities. The results were compared with the experimentally measured values of the viscosity showing considerable difference between the date obtained from experiment and derived form MD simulations.

1. Introduction
Since nitrogen is ubiquitous in normal life and also, it is used in many important technologies, the investigation of its properties is a task of great importance. Both thermodynamic and dynamic properties of nitrogen were therefore studied in the past and they are intensively investigated at present. In particular, nitrogen-nitrogen (N₂ – N₂) intermolecular interaction potential was studied quite intensively. This was partially related to the fact that the intermolecular nitrogen-nitrogen
interaction is relatively weak and, in majority of instances, its energy is a tiny fraction of the total system energy, expressed as all electron energy, which is typical for quantum mechanical calculations. Therefore, extremely precise QM calculations are necessary for determination of the interaction potential at the precision level required for reliable simulation of its physical properties. For long time this task was simply too difficult and therefore, the semi-empirical methods, employing model potentials, were used [1]. These model potential functions include: the 6-12 Lennard Jones interaction with the added electrostatic quadrupole moments [2], de Boer atom-atom diatomic model [3], the Kihara core model [4] and Berne-Pechukas overlap potential [5]. Using these results and the analogy with hydrogen, Raich and Gillis constructed an anisotropic interaction of the pair of nitrogen molecules as sum of three terms: the electrostatic quadrupole-quadrupole interaction, long range dispersion terms and shape dependent repulsive overlap or valence contribution [1]. This approach was very fruitful in the following years as generalizations of Raich – Gillis formulation was later generally used to obtain fully anisotropic nitrogen molecular pair-potential [1].

Using the route devised by Raich and Gillis, Berns and van der Avoird employed Hartree-Fock calculations to obtain the short range part of the interaction potential [6]. The electrostatic long range part, expressed as series of multipole electrostatic interactions, was obtained from Hartree-Fock calculations by researchers belonging to the same group [7]. The dispersion terms were also put in the form of multipole series [7]. At approximately the same time, Bohm and Ahlrichs obtained very important result, showing that the pair-wise-interaction is a good approximation of the full nitrogen intermolecular potential [8].

A different route was used by Johnson et al. [9]. They treated the nitrogen molecule as a sum of the two atoms linked by the bond. In their formulation, the N$_2$-N$_2$ potential is a sum of four N-N potentials for the force acting between the atoms belonging to different molecules and the two additional terms describing the N-N intramolecular interactions. The intramolecular contribution term was parameterized using the N$_2$ molecule dissociation energy, the bond length and the vibration frequency. The interaction energy with the other molecule atoms was approximated using exponential-six function. The three different parameterizations of the exponential-six function were used: (i) by fitting to Hay’s configuration-interaction potential [10], (ii) by adjusting to Hugoniot data for N$_2$ [11], and from nonlinear fit to Pack’s electron gas calculations [10]. These three selections differ by about 20% in energy [9]. These formulations can account nitrogen interaction anisotropy, but their precision and validity, especially at high pressures, are hard to assess.

Employing earlier results, van der Avoird, Wormer and Jensen (AWJ) formulated full potential, including electrostatic, dispersion and overlap terms in the form invariant with respect to rotation of the coordinate system [12]. The dispersion interaction was expressed using Tang and Toennis damping function [13]. By comparing their own results and those of Bohm and Ahlrichs, AWJ found that the Hartree-Fock approximation significantly underestimates the overlap energy. Therefore they introduced isotropic scaling factors for the slope of the interaction potential and the exponents of damping function of Tang and Toennis. They have also found that this adjusted potential better recovers several nitrogen properties, such as: lattice parameters for α - nitrogen at very low pressure (p = 0), the sublimation (or cohesion) energy, isothermal compressibility of α - nitrogen at pressure and temperature close to zero, phonon frequencies obtained from the infrared, Raman and neutron scattering experiments [14]. Despite the above successes, the magnitude of the two arbitrarily introduced scaling factors, close to 1.5, and the fact that these factors were rotationally invariant, poses serious question whether the AWJ potential is close to the exact one, both in the radial and the angular dependence. The obtained results suggest also that the high pressure phase γ is not well described if the angular dependence is not correct. Similarly, the results more sensitive to the anisotropy of the potential, like scattering measurements or Raman line-widths, indicate that the AWJ potential seriously underestimates the anisotropy of nitrogen potential [15].

Recently, Stallcop and Partridge have performed ab initio calculations for the pair of two rigid N$_2$ molecules in coupled-cluster singles and doubles approach with perturbation account of the triple excitations, usually denoted as CCSD(T) approach [16]. They obtained several versions of nitrogen
intermolecular potentials, depending on the basis sets used. The potential was again adjusted to recover the measured value of the second virial coefficient B(T). Thus the basic flaw of AWJ approach was not removed. The results published by Stallcop and Partridge are not complete and cannot be used independently for the simulations of the properties of nitrogen. Therefore, a high precision CCSD(T) calculations were necessary to derive the interaction energy for large number of different configurations of the pair of N$_2$ molecules. These results were obtained and recently used to determine the intermolecular potential in the system rotation invariant form [17].

For the pressures below 30 GPa, at room or higher temperatures, nitrogen is supercritical fluid, inert chemically. At extremely high pressures nitrogen looses its very stable molecular structure. In fact, the results of shock wave compression experiments show that, at about 33 GPa and 6000K, nitrogen undergoes continuous molecular to non-molecular transition [18]. The problems related to the transition to atomic form are outside the scope of this work, and will not be discussed here.

The results presented below were obtained using molecular dynamic (MD) modeling of the nitrogen in the molecular form. Several potential were used: the one proposed by Johnson et al. [9], the scaled and non-scaled potential of van der Avoird et al. [12], and the recently derived CCSD(T) based function [18]. The two basic physical properties: the equation of state and the shear viscosity will be considered. The results will be critically compared with the existing experimental data. The conclusions regarding the form of the nitrogen potential will be drawn.

2. Different approximations of the N$_2$-N$_2$ intermolecular potential

Molecular nitrogen (N$_2$) bonding energy, equal to 937.6 kJ/mole (9.72 eV/molecule), is the highest of all diatomic molecules [17]. This is due to the existence of triple chemical bond between N atoms which creates the region of high electronic density between the two nitrogen atoms. Therefore, either special model potential could be used, or very precise QM calculations are necessary to recover the nitrogen intermolecular interaction with high precision.

An example of fairly successful implementation of model function is the potential proposed by Johnson et al. which combines the separate atom-atom interaction of the atoms belonging to the different molecules with the bond energy describing the intramolecular interactions [9]. The three different versions of the potential were proposed by these authors. The bond energy was the same in all three versions. It was selected to be of the Morse form:

$$\phi_{\text{bond}}(r) = D_e \left(1 - \exp\left(-\xi\left(\frac{r}{r_e} - 1\right)\right)\right)$$  (1)

where $D_e$ is the classical dissociation energy, $r_e$ is the equilibrium interatomic distance, and $\xi$, related to the cubic anharmonicity of the potential $\alpha$ by the following relation: $\xi = (2/3)\alpha$, is given by:

$$\xi = \left(\frac{m\omega^2 r_e^3}{4D_e}\right)^{1/2}$$  (2)

The following values were used: $D_e = 114\ 950$ K = $158.7057 \times 10^{-20}$ J, $\hbar\omega_e = 3393.5$ K = $4.6852 \times 10^{-20}$ J, $r_e = 1.097\ 685$ Å, $m = 14.0067$ amu and $\xi = 951\ 86$. The first quoted numbers are those originally used by Johnson et al. [9] (the energy was expressed in temperature units), the second ones are their equivalents in standard units, used in the simulations presented here.

The interaction of the atoms belonging to different molecules was cast in the exp-6 form:

$$\phi_{\text{atom}}(r) = \frac{\epsilon}{\alpha - 6} \left\{6 \exp\left[-\alpha\left(\frac{r}{r_0} - 1\right)\right] - \alpha\left(\frac{r}{r_0}\right)^6\right\}$$  (3)
The three versions of the potential differ by the selection of the values of the parameters: ε, r₀, and α. In our simulations, we used the third version presented by Johnson et al., i.e. the one obtained from Pack electron-gas calculations [10], as it recovers the experimental data better than the two others. In this version, the following parameter values were adopted: ε = 26.5 K = 36.587 *10⁻²³ J, r₀ = 3.877 Å and α = 12.896. The relaxed bond length, i.e. the distance between the N atoms, used to fit the above parameters, was selected to be: r'e = 1.17397 Å [9].

The other choice that avoids the use of the model potential containing the parameters, adjusted to the experimental results, is to resort to ab initio total energy calculations in order to derive the interaction potential. This entails application of sophisticated computational scheme, capable to account the electron-electron correlations with sufficiently high precision. The N₂-N₂ system is, in fact, the closed shell system, composed of the two nitrogen molecules, weakly interacting at majority of typical distances. The total system energy of the system is close to 7 keV, which is six orders of magnitude larger than typical N₂-N₂ interaction energy, which may be estimated using the interaction energy at the minimum of the potential, about 1.6* 10⁻²² J (10 meV or equivalently 80 cm⁻¹). The comparison of these data indicates that extremely high precision calculations are necessary for correct description of the potential at various distances.

The above requirements essentially exclude Hartree-Fock self consistent field (SCF) approximation, characterized by large numerical errors [19,20]. As it turned out, the SCF results could be used providing that appropriate scaling is used. This route was used by van der Avoird et al. (AWJ) [12]. They used the SCF potential and the molecule orientation independent scaling factors to readjust the potential to the experimental data. In order to verify the validity of the procedure, the two versions of AWJ potential, i.e. scaled and nonscaled, were used in our simulations.

By its nature, the SCF single determinant wavefunctions do not account Coulomb interactions completely. These interactions determine the correlations of the opposite spin electrons [20]. A natural extension of SCF approach is to use either configuration interaction (CI) [21,22] or coupled cluster (CC) [23-25] schemes which account electron-electron correlations by the use of series excitation operators, modifying single determinant SCF wavefunctions. In the case when sufficiently high excitation are included, these two methods are characterized by high numerical precision, necessary for proper determination of nitrogen intermolecular potential.

An important advantage of CC over CI is that the CC method is size consistent, i.e. in the case of non-interacting molecules, the total CC wavefunction may be written as a product of wavefunctions of separate molecules at any truncation of the series. This is not valid for CI approximation; therefore we are convinced that, for our purposes, the CC method is better suited, especially at larger distances between nitrogen molecules.

We used Gaussian commercial package in Rev 03 [26], in coupled-cluster singles-and-doubles with a perturbative triples corrections [CCSD(T)] approximation, which, at present, is a standard choice for high precision QM calculations. According to the investigations of a single N₂ molecule by Kowalski and Piecuch [27], and by Ruden et al. [28], the contribution of higher order terms is about 18.8 cm⁻¹ and 0.03 pm for the harmonic oscillator frequency and the equilibrium distance, respectively [28]. While the energy error seems to be large, as compared to the intermolecular interaction energy, it was obtained on top of the triple bond N₂ binding energy, equal to 9.72 eV/molecule. The numerical errors scale with the binding energy; therefore we expect that the error for the intermolecular interaction energy is at least one order of magnitude smaller, which is sufficient for reliable determination of the N₂ interaction potential.

The QM results were obtained using aug-cc-pVQZ basis set, for the total number of 315 different configurations of the pair of N₂ molecules. These configurations, marked as points in the four dimensional space in R, θₐ, φₐ, and θᵦ coordinates, create 3 x 6 x 5 x 6 mesh, which is sufficient for determination of the full anisotropic potential. The total number of points was 540 but, due to the symmetry, their number could be reduced to 315, which was used in the approximation procedure by
Berns and van der Avoird [6]. We used identical scheme, so that the number of points is smaller than that in the procedure used by AWJ [12] for determination of the short range overlap interaction.

The $N_2-N_2$ potential is expressed in the standard form, i.e. in the form of interaction of the two nitrogen molecules, denoted as (A) and (B):

$$V(\mathbf{R}, \hat{r}_A, \hat{r}_B) = \sum_{L_A, L_B, L} v^{L_A, L_B, L}(R)A^{L_A, L_B, L}(\mathbf{R}, \hat{r}_A, \hat{r}_B)$$

where $\mathbf{R} = (R, \hat{R}) = (R, \Theta, \Phi)$ is the vector pointing from the center of molecule A to the center of molecule B, $\hat{r}_A = (\theta_A, \phi_A)$ and $\hat{r}_B = (\theta_B, \phi_B)$ are the unit vectors, describing the orientation of the molecules A and B respectively, and $\hat{R} = (\Theta, \Phi)$ is the unit vector, describing the orientation of the vector $\mathbf{R}$. The angular dependence of the potential was described using the set of the spherical harmonics:

$$A^{L_A, L_B, L}(\mathbf{R}, \hat{r}_A, \hat{r}_B) = \sum_{M_A, M_B, M} \left( \begin{array}{ccc} L_A & L_B & L \\ M_A & M_B & M \end{array} \right) Y_{L_A M_A}(\hat{r}_A)Y_{L_B M_B}(\hat{r}_B)Y_{L M} (\hat{R})$$

where $Y_{lm} (\hat{r})$ denote the spherical harmonics and the symbol in bracket is Wigner 3-j coefficient. This form of the potential function assures invariance of the energy with respect to the rotation of the system as a whole. The dependence on the intermolecular distance $R$ was expressed using $v$ coefficients, i.e. the sum of the electrostatic, overlap and dispersion contributions:

$$v^{L_A, L_B, L} = v_{\text{elec}}^{L_A, L_B, L}(R) + v_{\text{overlap}}^{L_A, L_B, L}(R) + v_{\text{disp}}^{L_A, L_B, L}(R)$$

The electrostatic part is expressed in multipole series, as:

$$v_{\text{elec}}^{L_A, L_B, L}(R) = \delta_{L_A + L_B, L} C^{L_A, L_B}_{L} R^{-L_A - L_B - L}$$

where $\delta_{L_A + L_B, L}$ is Kronecker delta and $C^{L_A, L_B}_{L}$ are the coefficients, listed in the Table 1. Since we limited the number of the points as in the procedure used in Ref 6 [6], the coefficients for the $(L_A, L_B, L)$ equal to (6,4,10) and (6,6,12) were set equal to zero.

**Table 1. Coefficients - electrostatic and dispersion interaction**

| $L_A, L_B, L$ | $C^{L_A, L_B}_{L}$ (kJ mol$^{-1}$ nm$^{L_A+L_B+L}$) | $C_{\text{elec}}^{L_A, L_B, L}$ (kJ mol$^{-1}$ nm$^6$) | $C_{\text{overlap}}^{L_A, L_B, L}$ (kJ mol$^{-1}$ nm$^8$) | $C_{\text{disp}}^{L_A, L_B, L}$ (kJ mol$^{-1}$ nm$^{10}$) |
|-------------|---------------------------------|-----------------|-----------------|-----------------|
| 0, 0, 0     | 0                               | 4,119 $\cdot$ 10$^{-3}$ | 3,795 $\cdot$ 10$^{-4}$ | 3,491 $\cdot$ 10$^{-5}$ |
| 2, 0, 2     | 0                               | 2,165 $\cdot$ 10$^{-4}$ | 9,780 $\cdot$ 10$^{-5}$ | 1,380 $\cdot$ 10$^{-5}$ |
| 2, 2, 0     | 0                               | 5,454 $\cdot$ 10$^{-6}$ | 1,458 $\cdot$ 10$^{-5}$ | 3,150 $\cdot$ 10$^{-5}$ |
| 2, 2, 2     | 0                               | 6,518 $\cdot$ 10$^{-6}$ | $-$2,179 $\cdot$ 10$^{-6}$ | $-$8,662 $\cdot$ 10$^{-7}$ |
| 2, 2, 4     | 1,624 $\cdot$ 10$^{-3}$         | 5,247 $\cdot$ 10$^{-5}$ | 1,133 $\cdot$ 10$^{-5}$ | 5,778 $\cdot$ 10$^{-6}$ |
| 4, 2, 6     | 6,771 $\cdot$ 10$^{-5}$         | 0                | 0                | 0                |
| 4, 4, 8     | 5,411 $\cdot$ 10$^{-6}$         | 0                | 0                | 0                |
| 6, 2, 8     | 8,024 $\cdot$ 10$^{-7}$         | 0                | 0                | 0                |
Similarly, these terms vanish for London dispersion interaction, defined as:

\[
\nu_{\text{disp}}^{1-L_n} L_1 \cdots L_n (R) = - \sum_{n=6,8,10} f_n \nu_{\text{disp}}^{1-L_n} L_1 \cdots L_n (R) C_n^{1-L_n} L_1 \cdots L_n R^{-n}
\]  

(8)

where Tang and Toennis damping function is:

\[
f_n^{1-L_n} L_1 \cdots L_n (R) = 1 - \sum_{k=0}^{n} a_k^{1-L_n} L_1 \cdots L_n \cdot R^k \cdot \exp \left(- \alpha^{1-L_n} L_1 \cdots L_n \cdot R - \beta^{1-L_n} L_1 \cdots L_n \cdot R^2 \right)
\]  

(9)

\[
a_k = \sum_{i=k/2}^{k} \frac{\alpha^{2i-k} \beta^{k-i}}{(2i-k)! (k-i)!}
\]  

(10)

The coefficients are listed in Table 2. The sum runs over all integer \(i\) values (in the case when \(k\) is odd, the initial \(i\) value is the integer resulting from division of \(k\) by 2). The short range or overlap interaction is given by:

\[
\nu_{\text{overlap}}^{1-L_n} L_1 \cdots L_n (R) = F^{1-L_n} L_1 \cdots L_n \exp \left(- \alpha^{1-L_n} L_1 \cdots L_n \cdot R - \beta^{1-L_n} L_1 \cdots L_n \cdot R^2 \right)
\]  

(11)

where the coefficients were obtained by the use of CCSD(T) results.

| \(L_{\lambda_1 L_{\alpha_1}}\) | \(L_{\lambda_2 L_{\alpha_2}}\) | \(L_{\lambda_3 L_{\alpha_3}}\) \(F^{L_{\lambda_1 L_{\alpha_1}}}\) (kJ mol\(^{-1}\)) | \(\alpha^{L_{\lambda_1 L_{\alpha_1}}}\) (nm\(^{2}\)) | \(\beta^{L_{\lambda_1 L_{\alpha_1}}}\) (nm\(^{2}\)) |
|---|---|---|---|---|
| 0, 0, 0 | 2.8478 \times 10^{4} | 1.1064 \times 10^{1} | 3.6899 \times 10^{1} |
| 2, 0, 2 | 9.0024 \times 10^{1} | 8.8428 | 3.8176 \times 10^{1} |
| 2, 2, 0 | 1.0841 \times 10^{2} | -2.9439 | 5.1960 \times 10^{1} |
| 2, 2, 2 | -4.0285 \times 10^{1} | 1.0930 | 4.7670 \times 10^{1} |
| 2, 2, 4 | 6.5419 \times 10^{1} | 9.4469 | 3.9388 \times 10^{1} |
| 4, 0, 4 | 1.6028 \times 10^{1} | 8.9254 | 3.8277 \times 10^{1} |
| 4, 2, 2 | 9.3398 \times 10^{1} | -1.5597 \times 10^{1} | 6.5891 \times 10^{1} |
| 4, 2, 4 | -4.1600 \times 10^{1} | -6.7843 \times 10^{1} | 4.9233 \times 10^{1} |
| 4, 2, 6 | 2.7633 \times 10^{1} | 1.2160 \times 10^{1} | 3.7111 \times 10^{1} |
| 4, 4, 0 | -5.6779 \times 10^{0} | -8.2570 \times 10^{1} | 1.4890 \times 10^{2} |
| 4, 4, 2 | -1.5435 \times 10^{0} | -9.1007 \times 10^{1} | 1.5929 \times 10^{2} |
| 4, 4, 4 | 5.5700 \times 10^{1} | -3.0125 \times 10^{1} | 8.3531 \times 10^{1} |
| 4, 4, 6 | -6.1088 | -2.0943 | 5.1267 \times 10^{1} |
| 4, 4, 8 | 2.1840 \times 10^{1} | 1.5694 \times 10^{1} | 3.5594 \times 10^{1} |
| 6, 0, 6 | 7.4753 \times 10^{1} | 1.7922 \times 10^{1} | 2.6677 \times 10^{1} |
| 6, 2, 4 | 2.5770 \times 10^{2} | -1.7763 \times 10^{1} | 6.6740 \times 10^{1} |
| 6, 2, 6 | -1.8191 \times 10^{1} | 8.6153 | 3.6955 \times 10^{1} |
| 6, 2, 8 | 3.0364 \times 10^{3} | 2.3517 \times 10^{1} | 2.3421 \times 10^{1} |

* For \(R > 14\alpha_0\), \(\beta\) for negative values are replaced by zero.

\((\alpha_0 = 5.291 \times 10^{-11} \text{ m} \text{ i.e. } R > 0.7406 \text{ nm})\)
The comparison of the Johnson, the non-scaled and the scaled AWJ potentials, and also the present fully ab initio derived potential, is presented in Fig. 1. Both radial and angular dependence of these potentials is shown. Generally, the new potential is much closer to the scaled AWJ function. This confirms the general validity of AWJ scaling. It has to be pointed out that the uniform angle independent scaling is oversimplified, as shown by the various relation of the scaled and new potential for different orientation of the molecules. The angular dependence is more important for the determination of the dynamic properties of nitrogen, like viscosity, thermal conductivity, etc. The angularly averaged values are more relevant for the determination of pressure, i.e. for the equation of state.

![Graph showing potentials comparison](image1)

**Figure 1.** Comparison of the Johnson et al. [9], nonscaled AWJ, scaled AWJ [12], and fully ab initio derived potential: upper row – radial dependence, lower row – angular dependence

3. **Equation of state**

Nitrogen equation of state was simulated by MD procedure, using a box, which has periodic boundary conditions (PBC) imposed at all walls. The pressure – temperature data, for 300K and 1200K, are shown in Fig. 2. Presently developed, scaled and nonscaled AWJ and Johnson potentials were used. For comparison, we have plotted the experimental data collected and critically assessed by Jacobsen et al. [29]. These results, presented in Fig. 2 prove that the best agreement with the experimental data is for the case of the new potential. For lower temperatures, i.e. for 300K - 1200K range, the best MD results recover the experimental data of Jacobsen et al. with the precision better than 1%. For the highest temperature, used in our simulations, i.e. for T = 2000K, the error is about 2.5%. The increase of the error is due to the fact that rigid rotor approximation is less precise at very high temperatures when the nitrogen molecules are excited to higher vibrational states.

We can also compare the present data with the previously reported results [30] where, using AWJ potential, we obtained the agreement of 4% and 7% at high and low temperatures, respectively. In the
present work we obtained definitely better agreement than the previously reported, which we attribute to the new interaction potential. This confirms that the new nitrogen-nitrogen intermolecular interaction potential definitely better reflects the magnitude of the real interaction. The increase of the error at high temperatures is related to deviation from rigid rotor approximation. Unfortunately, the determination of the interaction potential without rigid rotor approximation is definitely beyond our present numerical capabilities.

For higher pressures, i.e. above 1GPa, the only data regarding nitrogen equation of state were those obtained by Johnson et al. [9]. We have used their potential in our MD simulations to compare with the results obtained using other potentials. The data obtained using Johnson potential are in better agreement that nonscaled AWJ potential, but they are definitely worse that those obtained using both scaled AWJ and newly developed potentials.

Table 3. Coefficients $c_i$ for the new equation of state of nitrogen (Eq. 12a-c).

| $i$ | $c_1$   | $p_{x1}$ | $p_{y1}$ | $i$ | $c_1$   | $p_{x1}$ | $p_{y1}$ |
|-----|----------|-----------|-----------|-----|----------|-----------|-----------|
| 1   | 1.3923·10^4 | 0         | 0         | 36  | 1.2249·10^4 | 4         | 4         |
| 2   | 4.1643·10^4 | 1         | 0         | 37  | 3.4797·10^3 | 6         | 4         |
| 3   | 1.0143·10^4 | 0         | 1         | 38  | -1.7816·10^4 | 7         | 4         |
| 4   | 5.6175·10^4 | 2         | 0         | 39  | 5.9612·10^3 | 5         | 6         |
| 5   | 2.1570·10^4 | 1         | 1         | 40  | -1.3060·10^3 | 7         | 6         |
| 6   | -5.9437·10^2 | 0         | 2         | 41  | 5.0350·10^3 | 3         | 4         |
| 7   | 4.3124·10^4 | 3         | 0         | 42  | 1.3381·10^4 | 2         | 5         |
| 8   | 1.3886·10^4 | 2         | 1         | 43  | 9.5754·10^2 | 5         | 3         |
| 9   | -2.6985·10^3 | 1         | 2         | 44  | -2.6779·10^4 | 6         | 3         |
| 10  | 1.6797·10^4 | 4         | 0         | 45  | -3.9784·10^4 | 4         | 5         |
| 11  | -3.7499·10^3 | 3         | 1         | 46  | -3.1512·10^3 | 2         | 7         |
| 12  | -5.6862·10^3 | 2         | 2         | 47  | 2.8167·10^3 | 8         | 3         |
| 13  | -1.6845·10^2 | 5         | 0         | 48  | 3.3869·10^4 | 6         | 5         |
| 14  | 3.4035·10^3 | 1         | 3         | 49  | -1.1001·10^4 | 6         | 6         |
| 15  | -8.7323·10^3 | 4         | 1         | 50  | -4.9037·10^3 | 2         | 3         |
| 16  | -5.1870·10^3 | 0         | 4         | 51  | 2.6733·10^4 | 4         | 3         |
| 17  | -1.0624·10^3 | 3         | 2         | 52  | 1.7940·10^3 | 9         | 1         |
| 18  | -3.9074·10^3 | 6         | 0         | 53  | -1.3852·10^4 | 5         | 5         |
| 19  | 1.7163·10^3 | 5         | 1         | 54  | 1.7599·10^3 | 3         | 7         |
| 20  | -1.2353·10^4 | 1         | 4         | 55  | -5.0971·10^3 | 9         | 3         |
| 21  | 4.9783·10^3 | 6         | 1         | 56  | 6.8713·10^3 | 9         | 4         |
| 22  | -7.4409·10^2 | 5         | 2         | 57  | 7.3557·10^2 | 10        | 4         |
| 23  | 4.0763·10^3 | 0         | 6         | 58  | -1.4906·10^2 | 1         | 5         |
| 24  | -3.0792·10^4 | 3         | 5         | 59  | 9.2570·10^3 | 7         | 2         |
| 25  | -4.2914·10^3 | 7         | 3         | 60  | -6.7223·10^2 | 10        | 5         |
| 26  | 2.1791·10^3 | 0         | 3         | 61  | -1.0674·10^2 | 8         | 1         |
| 27  | -1.6429·10^3 | 0         | 5         | 62  | -3.8851·10^3 | 9         | 2         |
| 28  | -7.5549·10^2 | 2         | 6         | 63  | -1.2313·10^4 | 8         | 4         |
| 29  | 2.0842·10^4 | 7         | 5         | 64  | 8.4419·10^3 | 8         | 6         |
| 30  | -1.6747·10^3 | 4         | 2         | 65  | 9.9384·10^2 | 8         | 0         |
| 31  | -1.6268·10^3 | 7         | 0         | 66  | 3.4963·10^2 | 9         | 0         |
| 32  | 1.2804·10^4 | 3         | 3         | 67  | 1.3813·10^3 | 10        | 2         |
| 33  | -1.4132·10^3 | 7         | 1         | 68  | -8.7471·10^2 | 10        | 3         |
| 34  | 2.4826·10^3 | 6         | 2         | 69  | -4.9918·10^3 | 10        | 0         |
| 35  | 8.5344·10^3 | 1         | 6         |     |           |           |           |
The equation of state was constructed in the form of scaled function of the density and the temperature [30], as:

\[
P(x, y) = \sum_{i=1}^{69} c_i x^{p_i} y^{q_i}
\]

(12a)

where:

\[
x = 1 + \frac{2(\rho - 1.899)}{1.899 - 0.0003528}
\]

(12b)

\[
y = 1 + \frac{(T - 2000)}{1000}
\]

(12c)

In this equation pressure is expressed in bars, density in g/cm\(^3\) and temperature in Kelvins. The coefficients \(c_i\), obtained by adjusting these functions to the CCSD(T) numerical data, are listed in Table 3.

In Figure 2, a comparison of the equation of state obtained from MD simulations for different nitrogen interaction potentials and the experimental data by Jacobsen et al. [29], is shown.

Comparison of the MD results and the experimental data confirms that the radial dependence of the interaction potential is well recovered by our CCSD(T) calculations, and also that the previous versions of the potential describe the radial dependence with reasonably good precision. An important results, with respect to the angular dependence of the potential, could be derived from the comparison of the experimental and MD data on the nitrogen viscosity, especially at higher densities. This will be discussed in the next Section.

4. Viscosity

MD simulations of the nitrogen viscosity were carried out using two different approaches. In the first case, the equilibrium molecular dynamic (EMD) procedure is based on Green-Kubo relation for the velocity-velocity correlation functions. In this approach the equilibrium time-lag correlation functions should be obtained. The box shape of the simulated volume with the periodic boundary conditions imposed at all walls, was used in MD procedure. These simulations provide precise and reliable data. Unfortunately, they require massive computations, and were not widely used in our simulations.

The EMD approach is based on Green – Kubo formula for the shear viscosity [31]:
\[
\eta = \lim_{t \to \infty} \left( \frac{V}{kT} \right) \int_0^t \langle \sigma_{xy} (s) \sigma_{xy} (0) \rangle ds \quad (13)
\]

where the symbol \(<…>\) denotes average in the phase space and the stress shear tensor \(\sigma_{xy}\) is expressed by standard definition, as:

\[
\sigma_{xy} = \left( \frac{1}{V} \right) \sum_i \left( m_i v_{ix} v_{iy} + f_{ix} y_i \right) \quad (14)
\]

In the above formula \(f_{ix}\) denotes x component of the force, acting on i-th molecule where the index (i) runs over all molecules in the system.

In the second approach nonequilibrium molecular dynamics (NEMD) is used. This scheme is based on the application of thermodynamic force which drives the system out of equilibrium to the stationary regime. In this approach a linear relation between the thermodynamic force and the response of the system is assumed. As a rule, the coefficient in this relation plays a role of generalized susceptibility. Thus a precise determination of the force and the estimate of the response of the system is crucial. Generally, this is a difficult task, and therefore NEMD derived values are burdened by larger errors [31].

A typical implementation of the NEMD method enforces the simple planar Couette flow, in which the tangential shear stress and the velocity gradient are evaluated. The ratio of these two quantities gives the shear viscosity. In our simulations we impose the velocity gradient by adding and subtracting the specified velocity (or momentum) of the molecules crossing the upper and lower surface, respectively. In both, parallel to the flow directions, periodic boundary conditions are imposed. The stress component is evaluated from the momentum transfer in the unit time, for the unit area. The velocity gradient is obtained by division of the velocity difference at the opposite surfaces by the distance between them.

![Graph](image)

**Figure 3.** Comparison of the shear velocity obtained from MD simulations using two different potentials and the experimental data by Lemmon and Jacobsen [32].

The MD data on shear viscosity were obtained for the two cases: Johnson et al. [9] and new CCSD(T) derived potentials [18]. These MD data and also the nitrogen viscosity derived from the critical review of experimental data by Lemmon and Jacobsen [33] are presented in Fig. 3. The comparison of these data indicates that the viscosity obtained in the kinetic regime, i.e. for low densities, where the interaction could be well approximated by instantaneous collision events, recovers the experimental data for all investigated potentials. This indicates that the MD simulation procedure is basically valid. However, for higher densities, the MD values are about 30% lower than the
experimental data. There exists some differences between two used potential, but in general the change related to the selected potential is relatively small. Slightly better agreement is obtained for our ab initio derived potential. Thus these data are not satisfactory and they indicate that the treatment of the nitrogen intermolecular interaction is not adequate and needs further investigations.

5. Summary
The results that were reported in this paper can be summarized as follows:
- nitrogen intermolecular potential was obtained using results of high precision CCSD(T) calculations
- equation of state of nitrogen at pressures up to 30 GPa was obtained by MD simulations
- the results of MD simulations of the nitrogen equation of state are generally in good agreement with the experimental data for all used potentials: Johnson et al. [9], nonscaled and scaled AWJ [12] and our newly developed ab initio derived potential [18]. This confirms that the radial dependence of the nitrogen potential is properly described.
- The best agreement with the experimental data for the equation of state is obtained for new CCSD(T) potential, while the scaled AWJ and Johnson potential give slightly inferior results and the nonscaled AWJ potential is characterized by the largest deviation from the experimental data.
- nitrogen viscosity experimental data are well recovered in kinetic regime for all considered potentials
- for higher densities the MD results are in considerable disagreement with the experimental data for all potentials
- further studies of the nitrogen intermolecular potential anisotropy and its role in the transport properties of nitrogen is necessary.

Acknowledgement
The results presented in this paper has been supported by Poland’s Ministry of Science and Higher Education grants no R003601 and N202 042 32/1171. The calculations were made using computing facilities of Interdisciplinary Centre for Mathematical and Computational Modelling of Warsaw University (ICM UW).

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