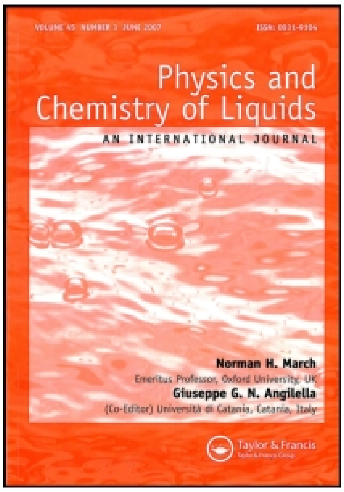

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Comparison of Various Potential Models for the Simulation of the Pressure of Liquid and Fluid N_2

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We have performed molecular dynamics (MD) calcuations with 256 particles to simulate the pressure of liquid and fluid nitrogen in the low and the high pressure regions. The pressure in MD calculations is extremely sensitive for the form of the potential employed and therefore this quantity is best suited to test intermolecular potentials. We have studied eight different potential models including a three-body potential. Of the potential functions considered, the existing purely effective Lennard-Jones (LJ) potentials—1-centre and 2-centres—do not suffice to give the experimental pressure for the whole pressure range. The 2-LJ-centres models derived from potential hypersurfaces calculated by "ab initio" methods produce slightly better results and led to an optimal model potential which reflects the experimental data within the statistical error of the MD. The 2-LJ centres model potential function we used for the fit cannot model the fine structure of the "ab initio" calculated hypersurface, but describes it in a balanced way when the higher energies are excluded systematically. We have achieved this by a certain weighting procedure.

1 INTRODUCTION

A detailed comparison of computer simulation results and experimental data requires sufficient and accurate measurements for the considered quantity of the liquid. In many cases, the existing experimental data do not allow such an extended investigation.

However, for liquid and fluid N_2, there is a wealth of very accurately measured properties, which permit comparisons with computer simulation results over a wide region of thermodynamic states.

The aim of the present study was to demonstrate the applicability of existing and new potential functions for the purpose of simulating real *pVT* data of nitrogen. Such an investigation seemed to be of large interest, since computer simulation calculations refer mostly only to few thermodynamic states in the low pressure range.

Furthermore, as the computation of the pressure by simulations is extremely sensitive to the employed potential function, such a test is best suited to indicate shortcomings of potential models.[1]

The N_2 molecule has a bond length of 1.102 Å[2] and a quadrupole moment of -1.52×10^{-26} e.s.u.[3] Both quantities are relatively small, and so a description of the interaction of these molecules is still possible on the basis of simple, spherically symmetric potential models.

We consider both types of potentials, pure effective pair potential functions and those deduced from energy hypersurfaces calculated by "ab initio" computations. Additionally we study a model which includes explicitly three-body interactions of the Axilrod–Teller type.

2 THE POTENTIALS

2.1 Basis aspects

Our investigation considers essentially model potentials of the Lennard-Jones (12-6) (LJ) type to guarantee simple and fast molecular dynamics (MD) calculations. It has been shown that even for potential models consisting of several sites a fast MD computation results when LJ functions are used for the centres.[4,5,6] An exclusion is presented by the potential which involves a triple-interaction term of the Axilrod--Teller form. MD computations with this potential require evaluation of three-body interactions, and thus the calculations are one or two orders of magnitude slower than ordinary MD based on pair forces. We shall however discuss these simulations in paragraph 2.3.

Of these LJ pair potentials we study two groups, which comprise the existing effective pair potentials and fit potentials for "genuine" pair-interaction-hypersurfaces calculated by "ab initio" methods. For the latter we exclusively used 2-centres LJ functions (2 LJC), whereas for the effective potentials, a spherically symmetric (1 LJC) one was also tested.

2.2 The parameters of the LJ potentials

Three effective pair potentials known from the literature were studied: a 1 LJC potential determined by McDonald *et al.*[7] and two 2 LJC potentials introduced by Cheung *et al.*[8,9] One of the latter was optimized in connection with a point quadrupole moment.[9] Additionally we determined a three-body potential which involves an 1 LJC term and an Axilrod-Teller term. Details are given in the next paragraph. All these potential parameters are summarized in the first part of Table I.

For the determination of the four fit potential functions we used data of the potential hypersurface N_2-N_2 calculated by Böhm *et al.*[10] and Berns *et al.*[11] As the data of Ref. 10 seemed to be more consistent and more exhaustive for the relevant configurations of the molecules, we based our fits primarily on these numbers. Due to the relatively complicated structure of the hypersurface[10] we did not expect a good fit by our chosen 3 parameter fit function. Using all the energy data of Ref. 10, we were actually not able to obtain a reasonable fit. Leaving out the values of higher energy (≥ 1000 K), we got a modest fit. However, it was useless for a reproduction of experimental pressures by MD. So we excluded the higher energies of the potential hypersurface systematically by a refined weighting procedure. All the "ab initio" values were artificially weighted according to a Boltzmann factor of which the exponent was normalized by liquid like temperatures of N_2. A description of this procedure can be found in the Appendix. This weighting method led to a fairly good fit, and additionally the generated 2 LJC function gave MD pressures in reasonable agreement with experiment. We exploited four different data sets for this procedure: (i) all the data for all the configurations of the molecules of the work of Böhm *et al.*[10]; (ii) all the values of Ref. 10 excluding those for the (0, 0, 0)-configuration (end to end); (iii) data produced by the best fit given by Ref. 10; (iv) all the data for all the configurations of the N_2 molecules of the work of Berns *et al.*[11] It should be noted that the best fit given by Ref. 10 accounts already for experimental data of the second virial coefficient.

The fits obtained by means of these four data sets have nearly the same quality, and we show for example a comparison of the original data and the fit function for the data set (i) in Figure 1-1a. These Figures demonstrate clearly the characteristics of the present 3-parameter fit: while the (0, 90, 0)-configuration (T-shaped) is well reflected by the fit, the (90, 90, 90)-configuration (crossed) is underestimated and the (90, 90, 0)-configuration (parallel) overestimated. An improvement of the fit should be possible when a further parameter is introduced into the model which takes account of these configuration-dependent differences.

We have summarized the 2 LJC potential parameters obtained by our fit procedure together with the "normalizing" temperature of the employed Boltzmann factor in Table I. Note that the site-site separation, d, of the 2 LJC fit function was always prescribed to give

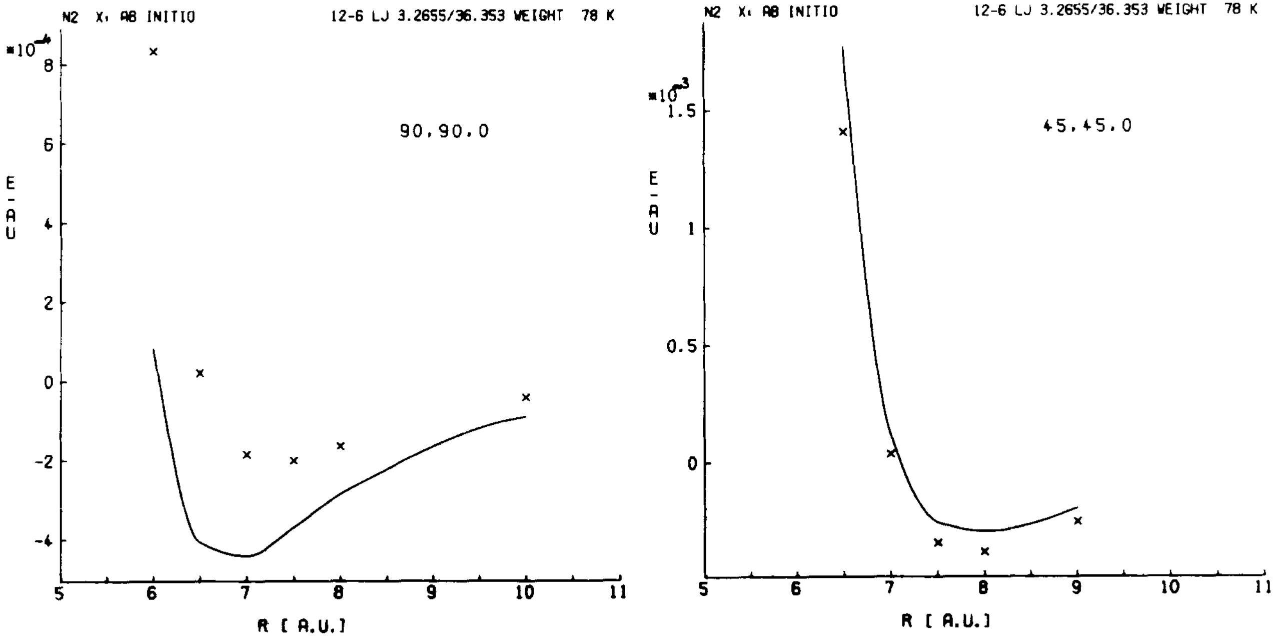

FIGURE 1 Comparison of energy data for N_2–N_2 calculated by 'ab initio' methods and obtained by a 2 LJC fit function (FIT 1). The configuration considered is indicated by the angle-triplet: φ, ψ.

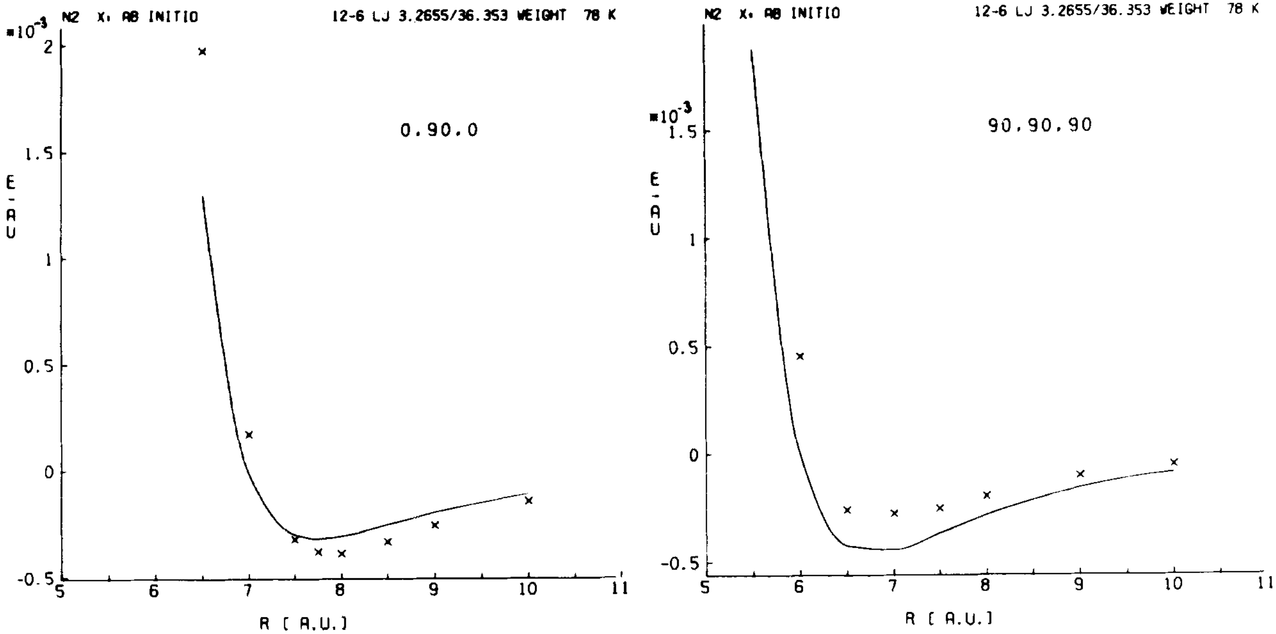

FIGURE 1a As in Figure 1, but other configurations.

TABLE I

Parameters characterizing the potential functions used in this work

Name	σ/Å	d/Å	$\frac{\varepsilon}{k}\Big/K$	$Q\cdot 10^{26}$/esu	$c_r\cdot 10^{11}$/erg Å^9	Comments
1 LJC	3.636	—	101.6	—	—	Ref. 7
1 LJC + TR	3.634	—	12.5	—	4.19	this work
2 LJC	3.310	1.090	37.3	—	—	Ref. 8
2 LJC + Q	3.314	1.101	35.3	1.52	—	Ref. 9
FIT 1	3.2655	1.094	36.2717	—	—	Ref. 10 for fit; temperature for the Boltzmann factor (TBF): 78 K
FIT 2	3.2932	1.094	33.1076	—	—	Ref. 10 for fit but without (0, 0, 0) configuration. TBF: 150 K
FIT 2A	3.2932	1.094	36.5	—	—	from FIT 2 but ε from FIT 1
FIT 3	3.3091	1.094	37.8806	—	—	Ref. 10 for fit but using the data of the 'best fit' given in Ref. 10; TBF: 78 K
FIT 4	3.2008	1.094	43.2034	—	—	Ref. 11 for fit; TBF: 78 K

approximately the bond length of the N_2 molecule. So the 2 LJC model function consists practically only of two free parameters!

2.3 The three-body potential function

To investigate the effect of three-body terms, we tried a potential of the following form:

$$u_t = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \frac{c_t}{r_{12}^3 r_{23}^3 r_{13}^3}\left(1 + \frac{3}{8}\frac{F_1 F_2 F_3}{r_{12}^2 r_{23}^2 r_{13}^2}\right),$$

where the first term of the right hand side is the common LJ potential and the second term represents the triple dipole potential energy of three spherically symmetric neutral molecules.[12,13] The separations r_{12}, r_{23}, r_{13} denote the sides of the triangle formed by the interacting three atoms. F_1, F_2 and F_3 are given by the sum of the squares of these separations:

$$F_1 = -r_{12}^2 + r_{23}^2 + r_{13}^2;\ F_2 = r_{12}^2 + r_{23}^2 - r_{13}^2;\ F_3 = r_{12}^2 - r_{23}^2 + r_{13}^2.$$

And the constant c_t characterizes the strength of the interactions. Evaluation of the forces necessary for MD simulations requires consideration of $N\cdot(N-1)\cdot(N-2)/6$ triplets of atoms additionally to the $N\cdot(N-1)/2$ pairs normally taken into account. We should however not give the details of these computations here, as they can be found in Ref. 14. The pressure was calculated by the virial expression[13] which is explicitly presented in the Appendix. By many pilot MD runs we adjusted the potential parameters σ, ε and c_t to reproduce the experimental pressure for the low and the high pressure region. The finally obtained numbers are listed in Table I. We note that the ε-parameters of the u_t-potential is somewhat larger than that of the 1 LJC potential given by Ref. 7. This is however reasonable considering the fact that the triplet interaction term enhances the potential energy of a system of liquid structure.[14]

3 THE MD CALCULATIONS

For the 1 LJC and the 2 LJC potentials, we performed conventional MD in the NVEp-ensemble using the method derived by Singer *et al.*[15] for linear molecules. Fully vectorized Fortran programmes were used,[16] and thus the execution time on the Cyber 205 was small for 108 and 256 molecules. Some technical details of these computations are presented in Table II.

For the three-body potential, we calculated separately the pair- and triplet forces and then carried out the usual MD simulation. Neighbour

TABLE II

Technical details of the MD-computations

Number of molecules:	256
Time step:	0.5-1.0 ($\times 10^{-14}$ s)
Number of equilibration time steps:	400-800
Number of production time steps:	2000-4000
Cut off radius:	3.25 σ
Cut off radius for neighbour lists:	3.60 σ
Long range corrections:	with $g(r > r_c) = 1$, only for pair interactions

lists were held both for pair- and triplet interactions.[14] Computational times on the Cyber 205 are compared in Table III. It is seen that the time is increased by a factor of 25 when triplet forces of the Axilrod-Teller form are included. However, the vectorization of the MD programme for three-body interactions could not be optimized so well as the programmes for the pair-interactions. This should be born in mind, when the comparison is made. In some cases we performed computations with constraints[4,5] rather than using Singers method.[15] Agreement between the results of both methods was always achieved with slight advantages of the Singer method with regard to the computational time (see Table III).

The pressure was calculated by the virial, and long range corrections were done only for the Lennard-Jones potential functions.[1,15] The errors for the MD pressure values have been estimated in terms of about 5 different runs for a state of low and high pressure. We found an uncertainty of about ±30 bar for the low pressure states and 3-6 per cent for states of intermediate and high pressures.

4 THERMODYNAMIC STATES

For N_2 there exist extensive and accurate experimental material summarized in the IUPAC report by S. Angus *et al.*[17] We based our

TABLE III

Computation times for the vector computer CYBER 205 (per 100 intergration steps)

1 LJC	1.6 s
2 LJC (Singer[15])	6.2 s
2 LJC (constraints[4])	6.4 s
2 LJC + Q	11.8 s
1 LJC + TR	258.0 s

comparisons on these data which are accurate within 1 per cent as far as the pressure values we are interested in are concerned.

We have chosen two liquid like densities and temperatures below and far above the critical temperature of N_2 which amounts to 126.2 K. Inclusion of supercritical states ensured that the low and high pressure range could be studied at the same density. Although 8 different states have been investigated. These states are listed in connection with the results discussed below.

5 RESULTS

5.1 Comparison of experimental and MD pressures obtained with effective potentials

Table IV shows the MD pressures for the three effective LJ potentials taken from the literature and the present three-body potential. The third column of this table gives the experimental values. Both the temperature and pressure values of the MD simulations are mean values of at least two runs. Runs which did not end up in a temperature given in the table to within ± 1 K were discarded.

A comparison of the experimental and MD pressures listed in Table IV indicates that agreement is reached for the smaller density of 0.7003 gcm^{-3}. For the states of higher density, none of the investigated potentials leads to the experimental pressures, particularly not for the higher pressures according to higher temperatures. The 2 LJC + Q model gives good pressures for the low pressure range, but fails to describe the high pressure range. So the 2 LJC potential has to be

TABLE IV

Comparison of calculated and measured pressures of N_2 (effective potentials, see Table I for shortenings)

		Experiment	1 LJC	1 LJC + TR	2 LJC	2 LJC + Q
ρ/gcm^{-3}	T/K	p/bar	p/bar	p/bar	p/bar	p/bar
0.7003	100	27	30	−60	10	40
0.7003	150	523	540	450	540	550
0.7003	250	1406	1420	1340	1440	1500
0.7003	400	2537	2540	2530	2650	2730
0.8684	70	193	310	250	190	225
0.8684	100	800	910	870	870	890
0.8684	150	1709	1800	1800	1820	1850
0.8684	250	3238	3320	3400	3450	3510

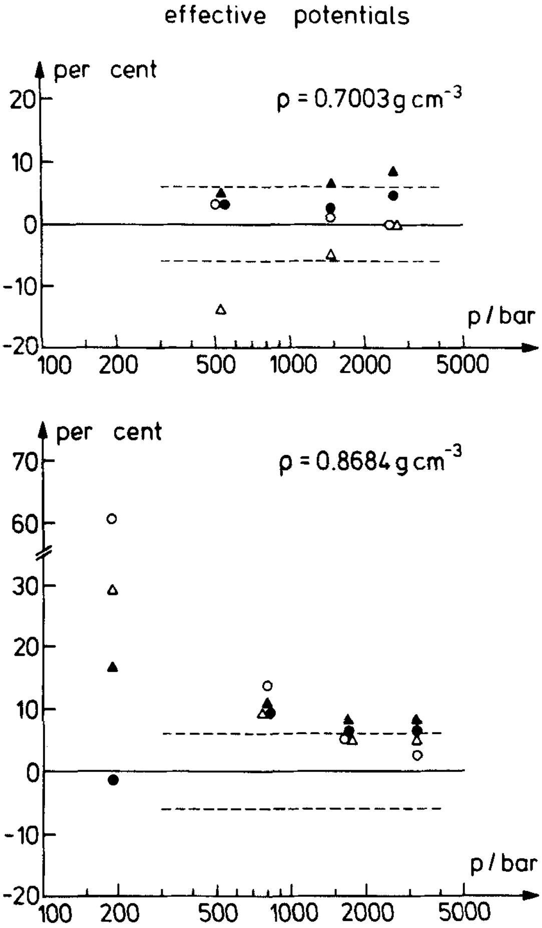

FIGURE 2 Percental deviation of the MD pressure from the experimental pressure, $(p_{MD} - p_{EXP}) \times 100/p_{EXP}$, plotted against the absolute value of the experimental pressure. The MD pressures are based on effective pair- and triplet potentials. A logarithmic scale is used for the x-axis. Error bars are indicated by broken lines. ○: 1LJC; △: 1 LJC + TR; ●: 2 LJC; ▲: 2 LJC + Q.

preferred giving reasonable values for states of low and high pressure. The three-body potential improves the MD pressure calculated with the 1 LJC potential only in the range of intermediate pressures at high density, but fails on the other hand to model the low pressure region.

To illustrate the differences between the MD results and the experimental data, plots of the percental deviation are presented in Figure 2. The data of very low pressure are suppressed to avoid unreasonably large numbers. It is seen from these plots that the LJ potentials generally produce too large pressures indicating a too steep repulsive branch of these potentials.

5.2 Comparison of experimental and MD pressures obtained with fit potentials for "ab initio" data

Table V shows the MD pressures calculated for four fitted 2 LJC potentials and the experimental data. The table contains only MD results for 2 LJC potentials which have been fitted to the "ab initio" hypersurface calculated by Böhm *et al.*[10] The fit function obtained by the data of Berns *et al.*[11] (see Table I, second part) gave much too small values and these were omitted in the Table V. At a density of 0.7003 gcm^{-3} and a temperature of 150 K, the MD pressure based on this latter potential is, for example, 360 bar smaller than the experimental one.

We see however from the Table that experimental and MD values agree better than in the case of the purely effective potentials. Particularly the third potential (FIT 2A) reproduces the experimental data within the error of our computation. We illustrate this by deviation curves plotted in Figure 3. These plots show that also for the high density the departures of the MD pressures from experiment are small and in the range of the statistical error. Apparently a fit to the "genuine" hypersurface leads to a potential function which has a much wider range of validity compared with purely effective potentials which are often built only for small thermodynamic ranges.

TABLE V

Comparison of calculated and measured pressures of N_2 (fit-potentials, see Table I for shortenings)

		Experiment	FIT 1	FIT 2	FIT 2A	FIT 3
ρ/gcm^{-3}	T/K	p/bar	p/bar	p/bar	p/bar	p/bar
0.7003	100	27	5	120	20	0
0.7003	150	523	530	605	535	520
0.7003	250	1406	1380	1490	1420	1470
0.7003	400	2537	2530	2660	2600	2670
0.8684	70	193	85	280	160	165
0.8684	100	800	690	890	810	840
0.8684	150	1709	1630	1805	1740	1810
0.8684	250	3238	3090	3350	3310	3470

6 DISCUSSION AND CONCLUSIONS

We have investigated various potential functions to examine their usefulness of reproducing the experimental pressure of liquid and fluid N_2 by MD calculations. The pressure of a MD system is an extremely sensitive quantity concerning the form of the inserted potential. So calculation of the pressure by MD is a severe test for the underlying

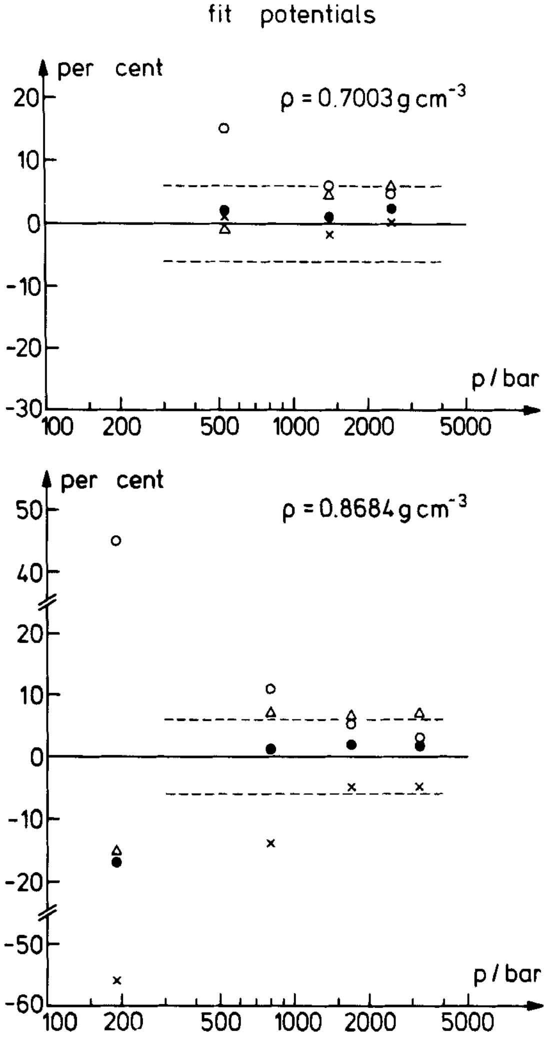

FIGURE 3 As in Figure 2, but for the fit potentials. × : FIT 1; ○: FIT 2; ●: FIT 2A; △: FIT 3.

potential function. In particular, the low pressure range of the system probes the attractive part of the potential, while the high pressure range probes the repulsive part. Both ranges have been considered herein, and one of the main results is that most of the existing effective pair potentials for N_2 cannot account for the fluid high pressure region.

Further interesting findings are the following:

i) a simplified three-body potential of the Axilrod–Teller form is not suited to model the N_2 pressure in the liquid range.

ii) the "ab initio" calculated energy surface of N_2–N_2 is too complicated as to be modelled by a 2 LJC function.

iii) leaving out the higher energies of the surface a modest fit to the surface can be obtained by a 2 LJC function.

iv) such a fit shows large deficiencies for configurations, where the centres of mass of the molecules are nearest.

v) the "best" 2 LJC function determined in this work reflects the experimental pressure to within 5 per cent for the whole range of thermodynamic states considered.

Böhm *et al.*[10] have also given a fit to their potential hypersurface by a 2 LJC potential plus a quadrupole energy function. Their fit is better than ours, at least for two relevant molecule configurations. However, the MD pressure calculated for a liquid state is an order of magnitude too high. This indicates that care must be taken, when the pure pair potential hypersurface is fitted by 2LJC potential functions. We believe, however, that the pressure calculated by Ref. 10 is not accurately corrected for the long range part of the potential.

We plan to improve our two parameter LJ fit potential by a third parameter allowing for a slight modification of the parameter depending on the pair configuration of the molecules. This requires, however, a considerable change of our present MD programme version[20] and a precise knowledge of the relevant pair configurations in liquid N_2.

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Appendix

1 THE FIT PROCEDURE

For our fit we used a 2-centres LJ pair potential model function of the form:

$$u_{ij} = 4\varepsilon \sum_{a=1}^{2} \sum_{a'=1}^{2} \left[\left(\frac{\sigma}{|\mathbf{r}_{ia} - \mathbf{r}_{ja'}|} \right)^{12} - \left(\frac{\sigma}{|\mathbf{r}_{ia} - \mathbf{r}_{ja'}|} \right)^{6} \right]$$

where i, j refer to the molecules and a, a' to the LJ centres. $|\mathbf{r}_{i1} - \mathbf{r}_{i2}|$ denotes the separation of the centres of a molecule i. To determine ε, σ and $d = |\mathbf{r}_{i1} - \mathbf{r}_{i2}|$ we employed a multiparameter fit procedure in terms of a FORTRAN programme CURFIT. This subroutine combines a gradient search with an analytical solution of a linearized fit function.[18] The validity of the fit was measured by χ^2:

$$\chi^2 = \frac{1}{f} \sum_i \left[\frac{1}{\sigma_i^2} (y_i - y(x_i))^2 \right],$$

where $1/\sigma_i^2$ denotes the weight of a data point y_i, $y(x_i)$ is a point obtained by an arbitrary analytical function and f represents the number of degrees of freedom. σ_i was set equal to the inverse Boltzmann factor:

$$\sigma_i = \exp\left[\frac{y_i}{kT} \right],$$

k being the Boltzmann constant and T the boiling temperature of N_2 (see Table I). This choice of σ_i made a balanced fit possible and strongly favoured small and negative energies. χ^2 was always smaller than 10^{-6}.

2 THE VIRIAL FOR THE AXILROD–TELLER TERM OF THE THREE-BODY POTENTIAL

Our three-body potential, u_t, consists of a two-body term which is a LJ potential and a three-body term which has the Axilrod–Teller form:

$$u_t = u_{\mathrm{LJ}}(r_{lm}) + u_{\mathrm{AT}}(r_{ij}, r_{jk}, r_{ik}),$$

where the r_{lm} denote the pair separations of the particles. u_{AT} is given by the expression

$$u_{\mathrm{AT}}(r_{ij}, r_{jk}, r_{ik}) = \frac{c_t}{r_{ij}^3 r_{jk}^3 r_{ik}^2}\left(1 + \frac{3}{8}\frac{F_1 F_2 F_3}{r_{ij}^2 r_{jk}^2 r_{ik}^2}\right)$$

where $F_1 = -r_{ij}^2 + r_{jk}^2 + r_{ik}^2$; $F_2 = r_{ij}^2 + r_{jk}^2 - r_{ik}^2$ and $F_3 = r_{ij}^2 - r_{jk}^2 + r_{ik}^2$. The r_{ij}, r_{jk} and r_{ik} denote the three separations of an arbitrary triplet of atoms.

The MD pressure is calculated by the virial equation. For the three-body term we have:[13,19]

$$\frac{pV}{NkT} = -\frac{1}{3\,NkT}\sum_{i<j<k}^{N}\left[r_{ij}\frac{\partial}{\partial r_{ij}} + r_{jk}\frac{\partial}{\partial r_{jk}} + r_{ik}\frac{\partial}{\partial r_{ik}}\right]u_{\mathrm{AT}}(r_{ij}, r_{jk}, r_{ik})$$

where p denotes the pressure of the system, V the volume, T the temperature and k the Boltzmann constant. N is the number of particles. The derivatives are readily obtained.

The summation over the particle coordinates can be carried out simultaneously when the forces are evaluated. The long-range correction for this term has been avoided, as the cut-off radius amounted to 3.25 σ.