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Prediction of Thermodynamic Properties for Fluid Nitrogen with Molecular Dynamics Simulations

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Molecular dynamics simulation results in the isochoric–isothermal ensemble are reported for a two-center Lennard–Jones model of fluid nitrogen characterized by the fixed molecular elongation $L = l/\sigma = 0.3292$. New values of ε and σ were determined by fitting the vapor pressure and the saturated liquid density of the model to experimental data at 94.67 K. The required vapor–liquid equilibrium data of the model were taken from a study using the NpT + test particle method. The resulting values are $\varepsilon/k = 36.32013$ K (36.673 K) and $\sigma = 0.32973$ nm (0.33078 nm), with values in parentheses being those obtained previously from a Weeks Chandler–Andersen-type perturbation theory. Then pressures and internal energies were calculated by molecular simulations for 110 state points in the temperature range from 72 to 430 K and for densities up to 35 $\text{mol} \cdot \text{L}^{-1}$. Comparison of the predictions based on the new parameters with the empirical equation of state of Jacobsen et al. shows good to excellent agreement except in the near-critical region. Moreover, for almost all state points the new parameters yield an improvement over old ones from perturbation theory.

KEY WORDS: Lennard–Jones two-center potential model; molecular dynamics simulations; nitrogen; thermodynamic properties.

1. INTRODUCTION

In several recent papers, it was demonstrated that good to excellent predictions of the thermodynamic data of pure fluids and mixtures in the whole fluid region can be obtained by molecular simulations. Recent examples are

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methane [1, 2], ethane [3, 4], propane [5], oxygen [6, 7], carbon dioxide [8, 9], and R152a [10] as well as the mixtures methane + ethane [11] and carbon dioxide + ethane [12]. For nitrogen results for the solid state [13–19] and the shock wave region [20] are available.

A crucial point in this computer modeling of real substances is the determination of effective potentials. For that purpose, Singer and coworkers [21, 22] used zero-pressure liquid densities and internal energies which were obtained from simulations and fitted to extrapolated experimental data. An extension of this procedure uses saturated liquid densities and vapor pressures [23, 24] calculated by a WCA-type perturbation theory [25]. For linear two-center Lennard–Jones (2CLJ) molecules the essential idea is to fit the model parameters ε and σ to the experimental saturated liquid density and the vapor pressure at one temperature and to adjust the molecular elongation to the steepness of the vapor pressure curve. This method was also applied to *n*-center Lennard–Jones (nCLJ) potentials [26, 27] and Kihara potentials [28] and therefrom presently potential models are available for about 20 substances. Use of these potentials in simulations for methane [1], ethane [3, 4], propane [5], and oxygen [6] showed that the determination of the potential parameters via the vapor–liquid phase equilibria (VLE) is a successful route.

An alternative way to the VLE calculation by perturbation theory is the direct use of molecular simulations for which the NpT + test particle method [29] turned out to be appropriate [30–32]. Besides computational consistency, direct VLE simulations also overcome the present restriction of perturbation theory to nonpolar substances. This procedure has already been applied to carbon dioxide [9] and gave again good to excellent predictions of the thermodynamic properties.

The purpose of the present paper is a study on nitrogen. For this molecule, a 2CLJ potential has previously been determined from perturbation theory [23] having the parameters $\varepsilon/k = 36.673$ K, $\sigma = 3.3078$ Å, and $L = l/\sigma = 0.3292$. As for the 2CLJ fluid with elongation $L = 0.3292$ the vapor–liquid equilibrium has already been determined with the NpT + test particle method [33] we simply use these VLE data here and readjust the parameters ε and σ by fitting them to the experimental values of the saturated liquid density and of the vapor pressure at one temperature. Then, NVT molecular dynamics simulations—i.e., simulations at a given particle number N, Volume V, and temperature T—are performed for the 2CLJ-0.3292 fluid at 110 state points in the whole fluid region. The interesting item is to see, how well the thermodynamic data are predicted with the new model in comparison with the experimental equation of state (EOS) for nitrogen from Jacobsen et al. [34] and in comparison to the old parameters determined by perturbation theory. In some cases the predictions of the old potential model are also compared to the EOS of Jacobson et al. A second aim of this work is to create extensive data sets for the construction of a physically based equation of state for 2CLJ fluids.

2. POTENTIAL MODEL AND SIMULATION METHODOLOGY

If we consider spherical molecules with continuous interaction potentials, the simplest, most frequently used potential in simulation studies is the Lennard–Jones (12/6) potential [35, 36]. In the case of nonspherical molecular fluids, however, the potential functions depend on both distance and mutual orientation of the particles. For nitrogen as a short linear molecule we use a site–site model. A pair of homonuclear molecules a, b will interact via a two-center Lennard–Jones (2CLJ) potential φ [37]

$$\varphi(\mathbf{r}, \omega_{\mathrm{a}}, \omega_{\mathrm{b}}) = \sum_{i} \sum_{j} \varphi^{\mathrm{SS}}(r_{ij}) = \sum_{i} \sum_{j} 4\varepsilon \left\{ \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right\} \tag{1}$$

where $\mathbf{r}$ is the distance between the centers of two molecules and ω_a and ω_b are the respective molecular orientations. i and j denote interaction sites on molecule a or b, respectively. r_{ij} is the site–site distance. As model parameters of the 2CLJ potential we have the Lennard–Jones interaction parameters ε and σ together with the molecular elongation $L = l/\sigma$. For nitrogen we use $l = 0.3292\sigma$ [23].

Our simulations were performed in a NVT ensemble using a predictor–corrector algorithm of fifth order [38]. Rotational motions are treated by the method of quaternions using a fourth-order predictor–corrector algorithm [39, 40]. All simulation runs were performed with 256 particles. We have used the minimum image convention, periodic boundary conditions, and a cutoff radius of $r_{\mathrm{c}} = 2.5 + L$. The long-range corrections were made by a method due to Neumann [41] and Lustig [42]. The temperature was kept constant by momentum scaling. For the integration the timestep Δt was chosen to be $\Delta t = 0.002$ in units of $\sigma \sqrt{m/\varepsilon}$.

The simulation was started either from a particle system arranged in a f.c.c. lattice or from a previous configuration followed by an equilibration period of 5000 timesteps. The length of the production period varied between 25,000 and 45,000 timesteps. The number of production steps is given together with the simulation results in Table I. The quantities directly obtained from the simulations are the pressure and the residual part of the internal energy. The uncertainties of the results were calculated according to the method of Fincham et al. [43].

Table I. Results of Residual Internal Energy, Pressure, and Their Uncertainties from MD Simulations for Nitrogen as a 2CLJ Fluid ($T^* = kT/\varepsilon$, $\rho^* = \rho\sigma^3$, $p^* = p\sigma^3/\varepsilon$, $u^{res*} = u^{res}/N\varepsilon$)

T^*	ρ^*	u^*	Δu^*	p^*	Δp^*	Prod. steps
11.826	0.0725	−1.375	0.004	0.908	0.0009	45,000
	0.1070	−2.027	0.007	1.389	0.0017	45,000
	0.1784	−3.374	0.006	2.560	0.0043	45,000
	0.2498	−4.710	0.005	4.044	0.0076	45,000
	0.2780	−5.222	0.008	4.787	0.0132	25,000
	0.3022	−5.643	0.007	5.501	0.0129	25,000
	0.3384	−6.291	0.010	6.775	0.0211	25,000
	0.3568	−6.609	0.006	7.460	0.0129	45,000
	0.3868	−7.092	0.009	8.828	0.0194	25,000
	0.3925	−7.190	0.006	9.103	0.0168	45,000
	0.4231	−7.669	0.007	10.747	0.0232	25,000
	0.4593	−8.190	0.006	13.094	0.0177	45,000
	0.5077	−8.769	0.011	17.003	0.0327	25,000
	0.5352	−9.026	0.009	19.801	0.0277	45,000
	0.5560	−9.185	0.010	22.156	0.0367	25,000
	0.6406	−9.384	0.016	35.089	0.0615	25,000
	0.6779	−9.183	0.011	42.891	0.0405	45,000
	0.7011	−8.973	0.017	48.388	0.0645	25,000
	0.7494	−8.173	0.010	62.450	0.0412	45,000
9.855	0.0725	−1.466	0.006	0.737	0.0010	45,000
	0.1070	−2.138	0.006	1.119	0.0017	45,000
	0.1784	−3.582	0.006	2.010	0.0038	45,000
	0.2498	−4.977	0.007	3.169	0.0067	45,000
	0.2780	−5.544	0.005	3.736	0.0072	25,000
	0.3020	−6.009	0.005	4.302	0.0095	25,000
	0.3384	−6.708	0.005	5.266	0.0076	25,000
	0.3568	−7.041	0.007	5.855	0.0146	45,000
	0.3868	−7.604	0.007	6.898	0.0149	25,000
	0.3925	−7.694	0.006	7.133	0.0139	45,000
	0.4231	−8.248	0.005	8.470	0.0121	25,000
	0.4593	−8.837	0.007	10.389	0.0195	45,000
	0.5077	−9.560	0.010	13.660	0.0341	25,000
	0.5352	−9.895	0.007	16.026	0.0226	45,000
	0.5560	−10.127	0.009	18.061	0.0345	25,000
	0.6406	−10.662	0.011	29.215	0.0377	25,000
	0.6779	−10.619	0.010	36.122	0.0394	45,000
	0.7011	−10.496	0.015	41.132	0.0607	25,000
	0.7494	−9.947	0.008	53.731	0.0350	45,000

Table I. *(Continued)*

T^*	ρ^*	u^*	Δu^*	p^*	Δp^*	Prod. steps
7.884	0.0725	−1.557	0.006	0.571	0.0009	45,000
	0.1070	−2.293	0.002	0.849	0.0017	45,000
	0.1784	−3.781	0.004	1.493	0.0022	45,000
	0.2498	−5.276	0.004	2.293	0.0048	45,000
	0.2780	−5.880	0.005	2.671	0.0069	25,000
	0.3022	−6.386	0.009	3.064	0.0105	25,000
	0.3384	−7.116	0.003	3.776	0.0085	25,000
	0.3568	−7.502	0.003	4.190	0.0057	45,000
	0.3868	−8.122	0.005	4.950	0.0115	25,000
	0.3925	−8.229	0.005	5.109	0.0139	45,000
	0.4231	−8.849	0.006	6.105	0.0122	25,000
	0.4593	−9.534	0.005	7.586	0.0160	45,000
	0.5077	−10.392	0.010	10.163	0.0347	25,000
	0.5352	−10.818	0.007	12.046	0.0241	45,000
	0.5560	−11.131	0.006	13.673	0.0204	25,000
	0.6406	−11.980	0.013	23.146	0.0537	25,000
	0.6779	−12.122	0.011	29.036	0.0414	45,000
	0.7011	−12.137	0.013	33.323	0.0542	25,000
	0.7494	−11.852	0.009	44.420	0.0376	45,000
5.913	0.0725	−1.691	0.008	0.398	0.0008	45,000
	0.1070	−2.464	0.008	0.576	0.0015	45,000
	0.1784	−4.064	0.008	0.946	0.0029	45,000
	0.2498	−5.624	0.007	1.387	0.0059	45,000
	0.2780	−6.254	0.006	1.604	0.0055	25,000
	0.3022	−6.799	0.005	1.813	0.0062	25,000
	0.3384	−7.615	0.005	2.204	0.0059	25,000
	0.3568	−8.018	0.006	2.455	0.0074	45,000
	0.3868	−8.680	0.004	2.911	0.0093	25,000
	0.3925	−8.813	0.006	3.050	0.0132	45,000
	0.4231	−9.489	0.004	3.652	0.0115	25,000
	0.4593	−10.266	0.005	4.652	0.0137	45,000
	0.5077	−11.276	0.006	6.448	0.0198	25,000
	0.5352	−11.820	0.005	7.769	0.0199	45,000
	0.5560	−12.194	0.005	9.034	0.0197	25,000
	0.6406	−13.458	0.007	16.363	0.0299	25,000
	0.6779	−13.795	0.007	21.222	0.0304	45,000
	0.7011	−13.894	0.010	24.960	0.0439	25,000
	0.7494	−13.934	0.009	34.256	0.0370	45,000

Table I. *(Continued)*

T^*	ρ^*	u^*	Δu^*	p^*	Δp^*	Prod. steps
3.942	0.0725	−1.972	0.012	0.222	0.0006	45,000
	0.1070	−2.850	0.012	0.291	0.0011	45,000
	0.1784	−4.553	0.011	0.385	0.0023	45,000
	0.2498	−6.267	0.017	0.447	0.0044	45,000
	0.2780	−6.859	0.012	0.474	0.0045	25,000
	0.3022	−7.411	0.010	0.512	0.0064	25,000
	0.3384	−8.259	0.011	0.594	0.0067	25,000
	0.3568	−8.676	0.007	0.659	0.0081	45,000
	0.3868	−9.389	0.008	0.777	0.0088	25,000
	0.3925	−9.483	0.008	0.815	0.0105	45,000
	0.4231	−10.252	0.007	1.060	0.0116	25,000
	0.4593	−11.105	0.004	1.468	0.0137	45,000
	0.5077	−12.253	0.007	2.400	0.0199	25,000
	0.5352	−12.902	0.005	3.139	0.0193	45,000
	0.5560	−13.370	0.006	3.926	0.0219	25,000
	0.6406	−15.055	0.008	8.978	0.0307	25,000
	0.6779	−15.661	0.006	12.433	0.0232	45,000
	0.7011	−15.923	0.007	15.295	0.0323	25,000
	0.7494	−16.282	0.005	22.769	0.0230	45,000
3.1536	0.4593	−11.500	0.006	0.158	0.0095	45,000
	0.5077	−12.688	0.006	0.674	0.0170	25,000
	0.5352	−13.375	0.003	1.169	0.0124	45,000
	0.5560	−13.884	0.006	1.675	0.0212	25,000
	0.6406	−15.794	0.007	5.565	0.0338	25,000
	0.7011	−16.827	0.008	10.968	0.0371	25,000
	0.7494	−17.340	0.005	17.585	0.0220	45,000
2.7594	0.5352	−13.629	0.003	0.111	0.0116	45,000
	0.5560	−14.151	0.006	0.527	0.0236	25,000
	0.6406	−16.171	0.006	3.797	0.0253	25,000
	0.7011	−17.302	0.008	8.676	0.0367	25,000
	0.7494	−17.907	0.007	14.804	0.0298	25,000
2.3652	0.6406	−16.570	0.005	1.916	0.0290	25,000
	0.7011	−17.803	0.007	6.269	0.0310	25,000
	0.7494	−18.509	0.006	11.839	0.0264	25,000
1.971	0.7011	−18.343	0.004	3.638	0.0247	25,000
	0.7494	−19.146	0.006	8.680	0.0274	25,000
1.5768	0.7011	−18.918	0.005	0.824	0.0232	25,000
	0.7494	−19.811	0.006	5.372	0.0289	25,000

In the following, reduced quantities $L = l/\sigma$, $T^* = kT/\varepsilon$, $\rho^* = \rho\sigma^3$, and $p^* = p\sigma^3/\varepsilon$ are used. Moreover, the residual internal energy u^{res} is the average potential energy and $u^{\mathrm{res}*} = u^{\mathrm{res}}/N\varepsilon$.

3. PREDICTION OF THERMODYNAMIC PROPERTIES

The selection of the state points for the simulations was to cover nearly the whole fluid region (Fig. 1). The results for the pressures and the residual internal energies, together with their statistical uncertainties, are given in Table I in reduced units. For a comparison of the simulation results with an accurate equation of state [34], one has to apply the Lennard–Jones potential parameters ε and σ. So far, these parameters were

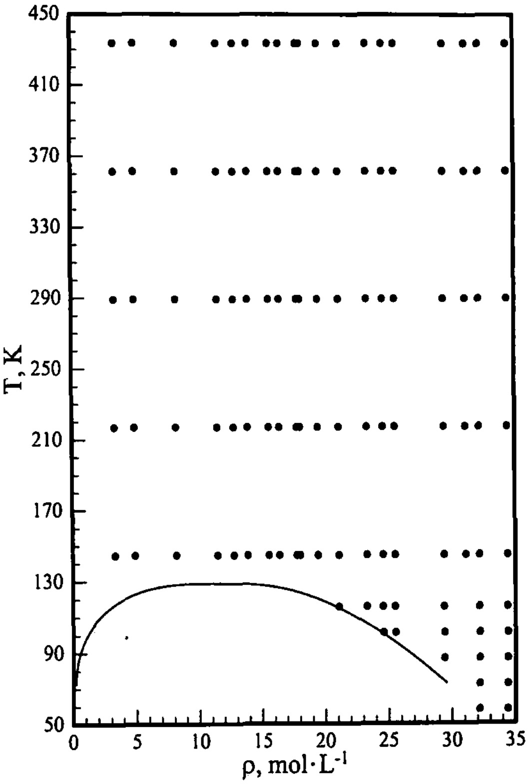

Fig. 1. The T–ρ projection of the MD simulation points reported in this work and the recently determined vapor–liquid equilibria of the two center Lennard–Jones fluid ($L = 0.3292$) referring to the new parameters ε and σ.

determined with a WCA-type perturbation theory by fitting the experimental vapor–liquid coexistence curve. The resulting values were $\varepsilon/k = 36.673$ K and $\sigma = 0.33078$ nm [23].

Recently, we determined the vapor–liquid equilibria of a two-center Lennard–Jones fluid with the elongation $L = 0.3292$ by MD simulations [33] (Fig. 1). To determine the vapor–liquid equilibria we applied the NpT + test particle method [30] to 2CLJ fluids of various elongations. The phase equilibria for nitrogen were calculated in the temperature range $T^* = 2.30$ to $T^* = 3.40$ with 12 state points on the liquid and 5 state points on the vapor branch by MD simulations. In order to determine the remaining state points on the gas branch we used the Haar–Shenker–Kohler equation [44], which is an accurate equation of state for low densities. The results for the vapor pressure p_σ^*, the bubble density ρ'^*, and the dew density ρ''^* were correlated by the equations

$$\ln p_\sigma^* = 5.05777 - 22.81996/T^* + 19.358/T^{*4} \tag{2}$$

$$\begin{aligned}\rho'^* = \rho_c^* &+ 0.256875(T_c^* - T^*)^{1/3} \\ &+ 0.0598274(T_c^* - T^*) + 0.00196816(T_c^* - T^*)^{3/2}\end{aligned} \tag{3}$$

$$\begin{aligned}\rho''^* = \rho_c^* &- 0.256875(T_c^* - T^*)^{1/3} - 0.0182637(T_c^* - T^*) \\ &+ 0.04391910(T_c^* - T^*)^{3/2}\end{aligned} \tag{4}$$

with $T_c^* = 3.5436$ and $\rho_c^* = 0.24524$.

To determine new values of the parameters ε and σ, the bubble density and the vapor pressure from the correlations, Eqs. (2) and (3), were fitted at a medium temperature to experimental values. The temperature for the fit was choosen to be the half between the critical and the triple point of nitrogen $T_{\mathrm{Fit}} = 94.67$ K. The corresponding experimental values for the vapor pressure and the bubble density are taken from the Jacobsen equation of state for nitrogen [34]. The parameters resulting from this procedure are $\varepsilon/k = 36.32013$ K and $\sigma = 0.32973$ nm, while the previous parameters were $\varepsilon/k = 36.673$ K and $\sigma = 0.33078$ nm [23]. The new parameters are now used in a comparison of the simulated results with those of the equation of state. For that, one has to rescale the results of Table I with the new Lennard–Jones parameters into real units. Table II shows the results for the simulated residual internal energies and pressures in real units in comparison with results from the Jacobsen equation of state [34]. We observe, in general, good to excellent agreement between the simulation-predicted data and those from the equation of state. Another point is the question whether the new parameters ε and σ yield better

Table II. Comparison of Residual Internal Energies and Pressures from MD Simulations with Results from the Jacobsen Equation of State [34] for Nitrogen with $\varepsilon/k = 36.32013$ K and $\sigma = 0.32973$ nm

T (K)	ρ (mol·L^{-1})	$u^{\mathrm{res}}_{\mathrm{EOS}}$ (J·mol^{-1})	$u^{\mathrm{res}}_{\mathrm{MD}}$ (J·mol^{-1})	Δu (%)	p_{EOS} (MPa)	p_{MD} (MPa)	Δp^{a} (%)
429.52	3.359	−417.3	−415.2	0.5	12.65	12.72	−0.41
	4.958	−613.5	−612.2	0.2	19.34	19.42	−0.39
	8.264	−1014.0	−1018.9	−0.5	35.41	35.81	−0.89
	11.569	−1403.7	−1422.4	−1.3	56.21	56.57	−0.42
	12.877	−1553.2	−1577.0	−1.5	66.33	66.95	−0.58
	13.997	−1678.4	−1704.2	−1.5	76.10	76.95	−0.66
	15.677	−1859.8	−1899.8	−2.2	93.04	94.76	−0.99
	16.527	−1948.0	−1995.8	−2.4	102.85	104.35	−0.74
	17.916	−2085.6	−2141.6	−2.7	120.99	123.49	−0.98
	18.180	−2110.7	−2171.3	−2.9	124.78	127.34	−0.96
	19.596	−2238.8	−2315.9	−3.4	147.12	150.33	−0.95
	21.276	−2373.6	−2473.2	−4.2	178.80	183.16	−0.97
	23.515	−2516.6	−2648.2	−5.2	231.82	237.84	−0.94
	24.791	−2575.0	−2725.5	−5.8	268.69	276.98	−1.06
	25.755	−2605.9	−2773.6	−6.4	300.25	309.92	−1.07
	29.674	−2587.7	−2833.8	−9.5	468.91	490.82	−1.37
	31.402	−2489.5	−2773.1	−11.4	568.20	599.96	−1.58
	32.473	−2395.2	−2709.6	−13.1	638.91	676.86	−1.64
	34.713	−2103.5	−2468.0	−17.3	812.29	873.55	−1.99
357.93	3.359	−445.2	−442.7	0.6	10.30	10.30	−0.01
	4.958	−653.6	−645.6	1.2	15.56	15.65	−0.28
	8.264	−1079.0	−1081.7	−0.2	28.10	28.11	−0.04
	11.569	−1496.5	−1502.9	−0.4	44.15	44.33	−0.27
	12.877	−1658.8	−1674.1	−0.9	52.00	52.26	−0.31
	13.997	−1796.0	−1814.7	−1.0	59.62	60.17	−0.54
	15.677	−1997.4	−2025.7	−1.4	72.94	73.66	−0.52
	16.527	−2097.0	−2126.2	−1.4	80.73	81.91	−0.73
	17.916	−2254.8	−2296.2	−1.8	95.27	96.48	−0.59
	18.180	−2284.1	−2323.5	−1.7	98.32	99.77	−0.67
	19.596	−2435.8	−2409.7	−2.2	116.49	118.48	−0.72
	21.276	−2602.2	−2668.7	−2.5	142.63	145.33	−0.73
	23.515	−2793.9	−2886.8	−3.3	187.17	191.08	−0.73
	24.791	−2883.6	−2988.1	−3.6	218.61	224.18	−0.83
	25.755	−2939.8	−3058.1	−4.0	245.78	252.63	−0.88
	29.674	−3040.4	−3219.6	−5.9	393.90	408.66	−1.04
	31.402	−3002.2	−3206.7	−6.8	482.81	505.28	−1.24
	32.473	−2947.1	−3169.5	−7.5	546.71	575.36	−1.37
	34.713	−2741.4	−3003.6	−9.6	705.14	751.59	−1.65

[a] The relative difference in the density is referring to the difference between the simulated pressure and the pressure of the equation of state.

Table II. *(Continued)*

T (K)	ρ (mol·L^{-1})	$u^{\text{res}}_{\text{EOS}}$ (J·mol^{-1})	$u^{\text{res}}_{\text{MD}}$ (J·mol^{-1})	Δu (%)	p_{EOS} (MPa)	p_{MD} (MPa)	Δp^{a} (%)
286.35	3.359	−479.9	−470.2	2.0	7.94	7.98	−0.58
	4.958	−702.3	−692.5	1.4	11.82	11.88	−0.51
	8.264	−1154.2	−1141.7	1.1	20.68	20.88	−0.81
	11.569	−1599.1	−1593.3	0.4	31.85	32.08	−0.50
	12.877	−1773.7	−1775.5	−0.1	37.34	37.36	−0.04
	13.997	−1922.3	−1928.3	−0.3	42.70	42.85	−0.22
	15.677	−2143.3	−2148.9	−0.3	52.21	52.82	−0.62
	16.527	−2253.8	−2265.3	−0.5	57.85	58.61	−0.65
	17.916	−2431.7	−2452.5	−0.8	68.54	69.24	−0.46
	18.180	−2465.0	−2484.9	−0.8	70.81	71.47	−0.41
	19.596	−2640.5	−2672.1	−1.2	84.48	85.39	−0.43
	21.276	−2839.2	−2879.1	−1.4	104.56	106.11	−0.53
	23.515	−3081.5	−3138.3	−1.8	139.84	142.16	−0.54
	24.791	−3203.9	−3266.9	−2.0	165.29	168.51	−0.59
	25.755	−3287.0	−3361.5	−2.3	187.59	191.26	−0.57
	29.674	−3513.9	−3617.6	−2.9	312.76	323.77	−0.90
	31.402	−3539.5	−3660.5	−3.4	390.06	406.15	−1.02
	32.473	−3526.1	−3665.1	−3.9	446.37	466.12	−1.07
	34.713	−3411.1	−3579.1	−4.9	588.19	621.36	−1.31
214.76	3.359	−530.9	−510.5	3.8	5.54	5.56	−0.47
	4.958	−772.7	−743.9	3.7	7.98	8.05	−0.94
	8.264	−1256.5	−1227.2	2.3	13.12	13.23	−0.78
	11.569	−1727.9	−1698.2	1.7	19.26	19.40	−0.55
	12.877	−1913.3	−1888.4	1.3	22.28	22.43	−0.46
	13.997	−2071.82	−2053.0	0.9	25.28	25.37	−0.20
	15.677	−2309.5	−2299.6	0.4	30.75	30.83	−0.13
	16.527	−2429.8	−2421.2	0.3	34.09	34.34	−0.35
	17.916	−2625.7	−2621.3	0.2	40.61	40.72	−0.12
	18.180	−2662.9	−2661.4	0.0	42.02	42.66	−0.63
	19.596	−2860.8	−2865.5	−0.2	50.76	51.08	−0.23
	21.276	−3091.2	−3100.2	−0.3	64.20	65.08	−0.45
	23.515	−3384.9	−3405.2	−0.6	89.01	90.19	−0.38
	24.791	−3541.6	−3569.3	−0.8	107.68	108.67	−0.25
	25.755	−3652.8	−3682.5	−0.8	124.44	126.36	−0.40
	29.674	−4014.7	−4064.0	−1.2	223.38	228.89	−0.56
	31.402	−4109.1	−4165.8	−1.8	287.40	296.85	−0.71
	32.473	−4140.4	−4195.8	−1.3	335.08	349.14	−0.89
	34.713	−4122.1	−4207.8	−2.0	458.33	479.18	−0.93

[a] The relative difference in the density is referring to the difference between the simulated pressure and the pressure of the equation of state.

Table II. *(Continued)*

T (K)	ρ ($\mathrm{mol \cdot L^{-1}}$)	$u^{\mathrm{res}}_{\mathrm{EOS}}$ ($\mathrm{J \cdot mol^{-1}}$)	$u^{\mathrm{res}}_{\mathrm{MD}}$ ($\mathrm{J \cdot mol^{-1}}$)	Δu (%)	p_{EOS} (MPa)	p_{MD} (MPa)	Δp^{a} (%)
143.17	3.359	−637.8	−595.5	6.6	3.06	3.10	−1.76
	4.958	−923.3	−860.7	6.8	4.00	4.06	−2.52
	8.264	−1470.8	−1374.9	6.5	5.32	5.38	−1.97
	11.569	−1965.5	−1892.4	3.7	6.40	6.25	3.77
	12.877	−2152.5	−2071.2	3.8	6.92	6.63	5.44
	13.997	−2311.6	−2238.0	3.2	7.48	7.16	4.30
	15.677	−2551.3	−2494.0	2.2	8.67	8.31	2.73
	16.527	−2674.1	−2619.9	2.0	9.52	9.21	1.72
	17.916	−2877.4	−2835.1	1.5	11.45	10.87	2.02
	18.180	−2916.5	−2863.8	1.8	11.91	11.40	1.62
	19.596	−3128.6	−3096.0	1.0	15.06	14.82	0.47
	21.276	−3384.3	−3353.6	0.9	20.80	20.54	0.30
	23.515	−3725.9	−3700.3	0.7	33.43	33.57	−0.08
	24.791	−3916.7	−3896.0	0.5	44.11	43.91	0.08
	25.755	−4056.8	−4037.4	0.5	54.31	54.92	−0.20
	29.674	−4562.1	−4546.3	0.3	122.00	125.58	−0.49
	31.402	−4731.5	−4729.2	0.0	170.27	173.92	−0.36
	32.473	−4812.0	−4808.5	0.1	207.84	213.95	−0.49
	34.713	−4898.9	−4916.7	−0.4	309.99	318.50	−0.45
114.54	21.276	−3533.5	−3472.7	1.7	2.66	2.21	1.21
	23.515	−3885.9	−3831.5	1.4	9.47	9.43	0.04
	24.791	−4089.9	−4038.9	1.2	16.40	16.35	0.037
	25.755	−4241.9	−4192.7	1.2	23.54	23.42	0.056
	29.674	−4807.6	−4769.6	0.8	76.56	77.84	−0.22
	32.473	−5111.6	−5081.5	0.6	150.31	153.42	−0.28
	34.713	−5245.9	−5236.2	0.2	242.99	245.98	−0.17
100.22	24.791	−4183.9	−4115.8	1.6	1.94	1.55	0.33
	25.755	−4341.2	−4273.4	1.6	7.35	7.37	−0.01
	29.674	−4940.5	−4883.4	1.1	52.39	53.11	−0.14
	32.473	−5274.0	−5224.9	0.9	119.48	121.36	−0.18
	34.713	−5434.9	−5407.6	0.5	207.04	207.08	−0.00
85.90	29.674	−5080.9	−5003.8	1.5	26.88	26.80	0.02
	32.473	−5448.6	−5376.1	1.3	86.82	87.70	−0.09
	34.713	−5640.9	−5589.3	0.9	168.76	165.61	0.20
71.59	32.473	−5637.9	−5539.3	1.7	51.46	50.88	0.07
	34.713	−5873.2	−5781.8	1.6	126.99	121.42	0.38

[a] The relative difference in the density is referring to the difference between the simulated pressure and the pressure of the equation of state.

results than the previous [23] values. Using the data from Table I, we produced a similar Table II with the old parameters and found that for almost all state points better results are obtained with the new parameters. As an example of improved accuracy, Fig. 2 shows the relative difference in the density referring to the difference in the pressure from the simulation and the equation of state as obtained with the old and the new LJ

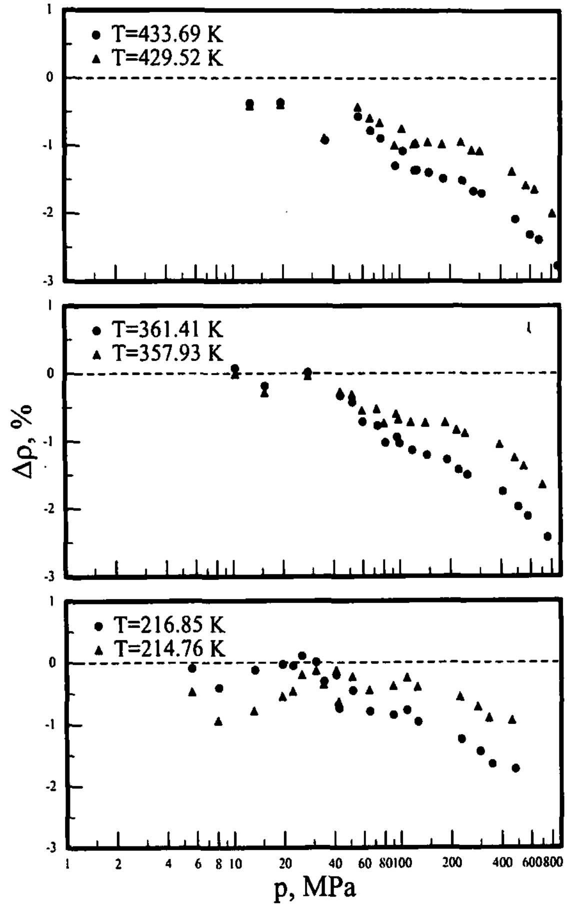

Fig. 2. Comparison of pressures from MD simulations with results from the equation of state of Jacobsen et al. [34] for nitrogen calculated with the old (●) and the new (▲) Lennard–Jones parameters at selected isotherms. The deviations for the pressuress are given as the relative difference in the density referring to the difference between the simulated pressure and the pressure of the equation of state.

parameters for three isotherms. The internal energies predicted with the new LJ parameters are in general also more accurate than determined by the old ones, except in the critical region and at very low temperatures, where a small increase in the deviations has to be noted.

The phase equilibrium data from MD simulations are also compared with experimental data by using the new and the old LJ parameters. The percentage deviations in the vapor pressures and the bubble and the dew densities are shown in Fig. 3. As had to be expected, the agreement is better with the new parameters. The accurate predictions for the saturated liquid density at the lower temperatures are very satisfying. On the other hand,

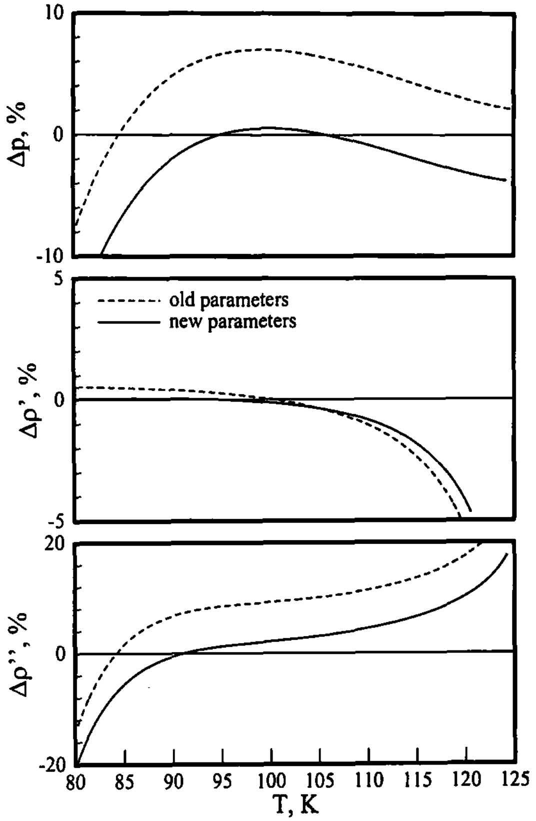

Fig. 3. Deviations of phase equilibria data obtained by MD simulations with the old (-----) and the new (——) Lennard-Jones parameters referring to the experimental equation of state of Jacobsen et al. [34] for nitrogen.

we observe there strong deviations in the vapor pressure which can be attributed to problems in the determination of the chemical potential via the NpT + test particle method at the liquid branch.

4. SUMMARY

We have calculated the thermodynamic properties of fluid nitrogen from an effective pair potential with two adjustable parameters. The determination of new Lennard–Jones parameters ε and σ results in good to excellent predictions of pressures and internal energies over the whole fluid range. Only in the critical region, do we have a significant deviation of pressures and internal energies between simulated and experimental values. This may be due to the fact, that the critical temperature of the 2CLJ fluid ($L = 0.3292$) $T_c^* = 3.5436$ compared with the critical temperature of nitrogen $T_{cN_2}^* = 3.4745$ is too high. A comparison of the new with the old LJ parameters shows in general a better prediction behavior of the new parameters.

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