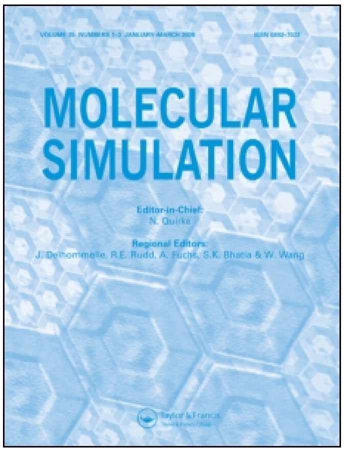

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# The Lennard-Jones Fluid Revisited: Computer Simulation Results

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# THE LENNARD-JONES FLUID REVISITED: COMPUTER SIMULATION RESULTS

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Pseudoexperimental data of high accuracy on the pressure and the internal energy of the Lennard-Jones fluid have been generated both by the Monte Carlo and molecular dynamics methods for five subcritical and three supercritical isotherms. Values of the chemical potential of the Lennard-Jones fluid computed by a new version of the gradual insertion particle method for two isotherms up to very high densities are also reported and discussed, and compared with existing data.

KEY WORDS: Monte Carlo simulation, molecular dynamics simulation, Lennard-Jones fluid, chemical potential, gradual insertion particle method.

## INTRODUCTION

In the course of our systematic research devoted to the development of equations of state for real fluids [1, 2] we have recently (for reasons stated in our previous communication [3]) embarked on a project aiming at developing an analytic theoretical equation of state for the Lennard-Jones (LJ) fluid whose accuracy should be as good as that of existing empirical, many parameter equations, such as those due to Nicolas *et al.* [4] and Sýs and Malijevský [5]. In order to develop such an equation of state one needs a base of pseudo-experimental data which (i) are dependable and sufficently accurate, (ii) cover with reasonable spacing the entire range of thermodynamic conditions of interest, and (iii) include preferably some other thermodynamic quantities than just the internal energy and pressure. These requirements prompted us to conduct a thorough literature search for the LJ fluid properties. Since the LJ fluid has been undoubtedly the most popular and most intensively studied realistic model of fluids over the last two decades, one would expect that its properties are known in all details with high accuracy. However, on the basis of

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our survey we had to conclude that, surprisingly, this is not completely true. In fact, we found that the above conditions are satisfied by none of the existing sets of pseudoexperimental data.

The early simulation data on the LJ fluid aimed at providing particular data bases which might have been used to check various theoretical, statistical-mechanical methods. However, the accuracy of these data meets by no means the contemporary standards. Later data were usually generated *ad hoc* for specific purposes, which efforts were largely unsystematic and brought data of not very high accuracy either. Relatively recent exceptions in attempting to treat the properties of the LJ fluid in a more or less systematic way represent the papers by Nicolas *et al.* [4], Sýs and Malijevský [5], Adachi *et al.* [6]. and Aim and Nezbeda [7].

Nicolas *et al.* [4] listed most of the data available by 1979, generated the pressure and internal energy data for 108 state points, and estimated parameters of the extended (32-constant) Benedict-Webb-Rubin equation of state, which has been considered as a standard for the LJ fluid ever since. Independently, Sýs and Malijevský [5] made thorough comparisons and assessment of literature data and presented another 21-parameter equation of state of the virial-expansion type. Adachi *et al.* [6] also listed some of the previous data, added data on pressure (unfortunately of not very high quality) for a number of state points and re-estimated parameters of the equation of state of the same functional form as Nicolas *et al.* In [7] an attempt was made to establish an evaluated data compilation for extensive comparisons with theory.

However, in neither of comprehensive collections [4] and [6] any uncertainties in the data are specified and in many cases not the original data but rather re-processed and/or rounded data are given. Moreover, we have not succeeded in tracing back several data points in the original papers at all. By careful re-examining the data sources we have found that in many cases the scatter of the data exceeds the uncertainty proclaimed by the authors and that it is not unusual that the discrepancy between two different data sources lies outside their combined errors [7]. The unsatisfactory overall situation may also be documented by the fact that even recently researchers developing equations of state preferred generating their own data [8] to relying upon data taken from the literature.

We should also point out that all the mentioned references give values of the internal energy and pressure only. Concerning other thermodynamic properties, a limited number of simulation data exists for the chemical potential, most of which are given for the reduced temperature $T^* = 1.2$ with considerable disagreement between various authors. Since the chemical potential is not a configurational property, to obtain it is quite a formidable task and investigations reporting it have therefore focussed on the methodology of simulations rather that on providing just data. Recently, two of us have proposed a modified version of the Widom insertion particle method [9] which allows one to get efficiently the chemical potential even at very high densities. (Let us recall here that Heinbuch and Fischer [10] claimed ". . . the test particle method seems to work up to the density $\varrho^* = 0.8$".) We have implemented this method for the LJ fluid (i) to clear up the discrepancies between the existing scattered data on the chemical potential for $T^* = 1.2$ and (ii) to generate the high-density data also for another isotherm.

We are aware of the fact that by producing "just another" set of pseudoexperimental data for the LJ fluid we may seemingly contribute to certain overworking of the field but for the purpose of our ultimate goal the data satisfying the above requirements are a prerequisite. In our simulations care was thus taken of all methodological aspects of the simulation methods and in this respect the present paper may be viewed as an LJ analogue to the well known paper of Erpenbeck and Wood [11] on hard spheres. We believe that our assessment of the quality of the existing data for the properties of Lennard-Jonesium justifies the present paper. Its aim is to produce a benchmark set of accurate thermodynamic data (including dependable estimates of uncertainties) which may be used both to critically evaluate the previuous data and to develop equations of state.

We present accurate simulation results, obtained by both the Monte Carlo (MC) and molecular dynamics (MD) methods, for the pressure and internal energy based on seven isotherms in the range $T^* \in \langle 0.72, 4.85\rangle$ and the MC results for the density dependence of the chemical potential on two isotherms, $T^* = 1.2$ and 1.45. While the simulations of the former two properties both by the MC and MD methods are now more or less routine computations, the simulation of the chemical potential still represents an interesting piece of theoretical of methodological work. In fact, the highest density for which the chemical potential is given has previously been considered too high for simulations.

## 2. CHEMICAL POTENTIAL FROM MC SIMULATIONS

Direct evaluation of non-configuratioal quantities, such as the Helmholtz free energy or chemical potential, poses severe difficulties. Several methods have been deveLOped to cope with this problem (for a review see e.g. [12, 13]) but they all share a common shortcoming: their efficiency rapidly deteriorates with increasing density. Nezbeda and Kolafa [9] devised a scheme, a modified insertion particle method, which allows one to use the Widom insertion method [14] even at very high densities. The method consists of two steps: (i) the insertion of a pointwise particle and (ii) a gradual growth of the inserted particle. In paper [9] three different implementations of step (ii) for the fluid of hard spheres were considered. The method (denoted as method B in [9]) in which only a single simulation in an NVT ensemble with the inserted particle with fluctuating size is performed, turns out to be the most efficient one. For this reason we have implemented this method also for the Lennard-Jonesium.

Let us consider a conventional canonical ensemble of $N$ particles to which an additional particle is added. The original $N$ particles interact via a pair-wise potential $u$, $u = u(\{\phi\})$, where $\{\phi\}$ denotes a set of potential parameters, and the additional particle interacts with the remaining particles via the potential $u(\{\phi'\})$. Let us further assume that the values of the parameters $\{\phi'\}$ fluctuate taking on values from a discrete set $\{\phi_i\}$, $i = 1, \ldots, k$, where $\{\phi_k\} = \{\phi\}$. The system may thus undergo the transitions:

$$\underset{1}{[N]} \longleftrightarrow \underset{w_1}{[N+\{\phi_1\}]} \longleftrightarrow \underset{w_2}{[N+\{\phi_2\}]} \longleftrightarrow \ \ldots \ \longleftrightarrow \underset{w_k}{[N+\{\phi_k\}]} \equiv [N+1], \quad (1)$$

where the brackets denote appropriate sub-ensembles (consisting of $N$ or $N+1$ particles) and $w_i$ are weights assigned to the respective ensembles. The transition $[N] \rightarrow [N \times \{\phi_1\}]$ means the creation of an additional particle at a random position and the inverse transition describes an annihilation of such a particle. Chain (1) of transitions thus represents the gradual insertion of a test particle, i.e. a gradual transition from the $N$-particle system to the $(N+1)$-particle system.

According to general theoretical relationships [9], the probability of accepting the change of potential parameters by one position (either to the left or to the right) in chain (1) is given by [9]

$$P_{\mathrm{acc}}(\mathrm{old} \rightarrow \mathrm{new}) = \min\{1, F(\mathrm{old} \rightarrow \mathrm{new}) \exp -\beta(U_{\mathrm{new}} - U_{\mathrm{old}})]\}, \tag{2}$$

where

$$F(\mathrm{old} \rightarrow \mathrm{new}) = \{P(\mathrm{new} \rightarrow \mathrm{old})\, w_{\mathrm{new}}\}/\{P(\mathrm{old} \rightarrow \mathrm{new})\, w_{\mathrm{old}}\}, \tag{3}$$

$U_{\mathrm{old}}$ and $U_{\mathrm{new}}$ are the total potential energies of the old and new configurations, respectively, and $P(\mathrm{new} \rightarrow \mathrm{old})$ and $P(\mathrm{old} \rightarrow \mathrm{new})$ are *a priori* trial probabilities of the respective transitions (for details see the original paper [9]). The residual chemical potential is then obtained from the relationship

$$\beta\mu_{\mathrm{res}} = \beta(\mu - \mu_{\mathrm{id}}) = \ln\{w_k\ \mathrm{Prob}[N]/\mathrm{Prob}[N+1]\}, \tag{4}$$

where $\mu_{\mathrm{id}}$ is the chemical potential of the ideal gas at the same temperature and density as the system under consideration and $\beta = 1/(kT)$, where $k$ is the Boltzmann constant and $T$ is the absolute temperature. Prob$[N]$ denotes the probability of observing a sub-ensemble with exactly $N$ original particles in chain (1) and $w_k$ is the weight of the sub-ensemble $[N+1]$ with exactly $N+1$ identical original particles.

## 3. COMPUTATIONAL DETAILS

We performed simulations on the system of particles interacting via a pair-wise LJ potential $u_{\mathrm{LJ}}$ given by

$$u_{\mathrm{LJ}}(r) = 4\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^6], \tag{5}$$

where $\sigma$ and $\varepsilon$ are the potential parameters, $\{\phi\} = \{\sigma, \varepsilon\}$; $\sigma$ scales distances and $\varepsilon$ measures the strength of the interaction. Throughout the paper we use dimensionless quantities, namely the reduced temperature $T^*$, reduced number density $\varrho^*$, reduced pressure $P^*$, and reduced residual internal energy $U^*$, defined as follows

$$T^* = 1/(\beta\varepsilon), \quad \varrho^* = N\sigma^3/V, \quad P^* = \mathrm{P}\sigma^3/\varepsilon, \quad U^* = U/(N\varepsilon), \tag{6}$$

where $P$, $V$, and $N$ denote the pressure, volume and number of particles in the system, respectively.

We performed two independant sets of MC simulations, one conventional (hereafter denoted as MC1) with $N$ identical particles to obtain the internal energy and pressure, and the other (hereafter denoted as MC$\mu$) with $N+1$ particles to get the chemical potential. To complete the MC1 simulations and to check their accuracy, we also used the MD method at some state points to get the former thermodynamic properties.

### *3.1. Monte Carlo simulation*

For the MC1 simulation we used the standard Metropolis algorithm with cubic periodic boundary conditions. The *LJ* potential was truncated at the atom-atom separation $r_{\text{cutoff}}$, for which the value $r_c=4$, $(r_c=r_{\text{cutoff}}/\sigma)$, was adopted in most cases. The potential used for sampling in the liquid and dense fluid range was shifted to obtain a continuous function,

$$\begin{aligned} u_{\mathrm{MC}}(r) &= u_{\mathrm{LJ}}(r)-u_{\mathrm{LJ}}(r_c), \quad r<r_c, \\ &= 0 \qquad\qquad\qquad\quad , \quad r>\mathrm{r_c}. \end{aligned} \tag{7}$$

To evaluate the potential energy for all pairs, however, the original function $u_{\mathrm{LJ}}(r)$ was summed up for $r<r_c$. The cut-off corrections were computed using the usual assumption that the fluid is homogenous for $r>r_c$ and that the average density in the $r_c$-sphere is the same as the bulk density, which is good approximation for dense systems. The equation of state was obtained from the virial of forces [15]. Specifically, for the chemical potential the cut-off correction is, assuming potential (7), given by

$$\mu_{\text{cor}}=\frac{32N\pi\varepsilon}{3V}\left[\frac{2\sigma^9}{3r_c^9}-\frac{\sigma^3}{r_c^3}\right] \tag{8}$$

In one MC1 step a randomly chosen particle attempted a displacement with the probability distribution uniform in a spherical shell formed by spheres of diameters $r_d$ and $r_d/2$ (in other words, small displacements were disallowed by definition). To achieve high efficiency (and fast convergence), the diameter $r_d$ was set so that the acceptance ratio was about 0.25 [16]. After discarding the initial nonequilibrium configurations, typically 3 to 7 million one-step configurations were generated for each state point; however, for the isotherm close to the critical point we generated about 40 million configurations. The sample contained 512 molecules which ensured that the systematic errors were less than the statistical uncertainties [17]. The statistical errors of the averages were estimated by the method proposed in [18,19], i.e. by the summation of the autocorrelation coefficients $c_t$ up to infinity. In extrapolating to long lags $t$ the "hydrodynamic tail" was assumed to behave as $c_t \sim t^{-3/2}$ [20].

The MC1 simulations were performed on several computers; it took up to 50 hours to get the result for one thermodynamic state on a Soviet made EC-1045 machine (equivalent to IBM/370 system). Some data at the vicinity of the critical point were obtained on a Silicon Graphics computer on which about thirty hours were needed to generate 40 million configurations for one state point.

The MC$\mu$ simulation differs from the MC1 simulation by an additional trial move in which a change of the potential parameters of the "marked" (inserted) particle is attempted. Whether the attempted move was a particle displacement or a change of the potential parameters of the marked particle was determined randomly with the probability of 75 per cent assigned to the former move.

To implement the method outlined in Section 2, one has to specify the set of parameters $\{\phi_i\}$, the weights $w_i$, and the transition probabilities $P$.

For determining $\sigma_i$ parameters we followed the guidelines given in [9] and set

$$\sigma_i = (i/k)^{1/2}\,\sigma, \quad i = 1, \ldots, k \tag{9}$$

with $k = 6$. We further considered as reasonable to let $\varepsilon_i$ increase with increasing $\sigma_i$ and used a simple linear ansatz:

$$\varepsilon_i = (i/k)\,\varepsilon. \tag{10}$$

To make the simulation efficient, the weights $w_i$ should yield such probabilities Prob$[N]$ that the condition Prob$[N] \cong$ Prob$[N+1]$ be satisfied. To find such $w_i$, one may use a rough estimate of $\mu$ if this is available (e.g. from an equation of state) or to begin with an arbitrary value of $w_k$ and adjust it then during the initial course of the simulation. Further, to simplify conditions (2) and (3), we set $F(\text{old} \rightarrow \text{new}) = 1$. Finally, making use of the equality $P[N] \rightarrow P[N + \{\phi_1\}] = 1$ and assuming a constant transition probability,

$$P[N + \{\phi_i\}] \rightarrow P[N + \{\phi_{i+1}\}] = P = \text{const} \tag{11}$$

for all other $i$, we arrive at a relationship between the weights of the subensembles in the form

$$w_i = [(1 - P)/P]\, w_{i+l}, \quad w_0 = 1. \tag{12}$$

The transition probability $P$ is then given explicitly by

$$P = 1/(1 + w_k^{-1/k}). \tag{13}$$

Equations (9), (10), and (12) define completely the additional move of the MC$\mu$ simulations.

To estimate errors in the chemical potential values, we used a kind of block averages [21]. For that purpose the behaviour of the fluctuations (measured by the standard deviation) was studied in terms of length of subruns into which the total chain was divided, A series of such standard deviations was generated by a successive doubling of the length of subsets with the total length of the chain kept fixed. When the length of subruns is doubled and the standard deviation remains (nearly) constant, then this deviation provides a rough estimate of the error.

The system in which only one particle differs from the remaining particles is a typical system which calls for the use of the preferential sampling [15]. As an attempt to improve the efficiency of the MC$\mu$ simulations we therefore also used the preferential sampling for some systems whenever the scaled particle was smaller than the other particles; its environment was sampled according to the function $f(r)$, similar to that used in the previous simulations on hard spheres [9]:

$$\begin{aligned} f(r) &= 1 \qquad\quad , \text{ for } r<\sigma_{is}, \\ f(r) &= (\sigma_{is}/r)^4, \text{ for } r>\sigma_{is}, \end{aligned} \tag{14}$$

where $\sigma_{is} = (\sigma + \sigma_i)/2$.

This means that the trial moves of ordinary (i.e. unscaled) particles proceeded as follows:

(i) Choose an unscaled particle $m$ at random;
(ii) Calculate its distance $r$ from the scaled particle;
(iii) Attempt a trial move of particle m with the probability $\min[r_{\text{rand}}, f(r)]$, where $r_{\text{rand}}$ is a random number from the interval $(0, 1\rangle$;
(iv) If particle $m$ does attempt a move, the move is accepted with the probability $\min\{1, f(r_{\text{new}}) \exp[-\beta(U(r) - U(r_{\text{new}}))]/f(r)\}$, where $r_{\text{new}}$ is the new distance of particle $m$ from the scaled particle.

The MC$\mu$ simulations were performed on a PC-AT 80486/33 and it took about six hours to generate 1 million configurations for the system of 1000 particles. The total number of one-step configurations generated in one simulation varied from 20 to 50 million which means that up to 300 hours were needed to get the result for one state point.

### 3.2. Molecular dynamics simulation

For the MD simulation we used the Nose canonical ensemble [22]. The equations of motion read as

$$\dot{r}_i = p_i/m_i, \tag{15}$$

$$\dot{p}_i = f_i - p_i p_s/Q, \tag{16}$$

$$\dot{s} = s\, p_s/Q, \tag{17}$$

$$\dot{p}_s = \sum_{i=1}^{N} p_i^2/m_i - (3N-3)\, kT \tag{18}$$

where $r_i$, $p_i$, $f_i$, and $m_i$ denote the position, momentum, force, and mass of particle $i$, respectively, the time derivatives are marked by dots, $s$ and $p_s$ are additional variables, and $Q = (3N-3)\, kT\tau^2$, where $\tau$ is a constant with the dimension of time. These expressions were obtained from equations (2.4) through (2.9) of [22] by the time transformation, equation (2.25) of [22], ensuring that the time averages are equivelant to the canonical ones (provided that the system is ergodic).

The simulation potential was given by

$$\begin{aligned} u_{\mathrm{MD}}(r) &= u_{\mathrm{LJ}}(r) - \Delta u &&, \quad r < r_{c_1}, \\ &= (r^2 - r_{c_2}^2)^3 \, [A + (r^2 - r_{c_2}^2)\, B], && \quad r_{c_1} < r < r_{c_2}, \\ &= 0 &&, \quad r > r_{c_2}, \end{aligned} \tag{19}$$

where constants $A$, $B$, and $\Delta u$ were set so that the potential and its first and second derivatives were continuous; $r_{c_1}$ was typically set to the value of 4.5, whereas $r_{c_2} = r_{c_1} + 0.25$. Analogously as above, $u_{\mathrm{MD}} + \Delta u$ for $r < r_{c_2}$ was used to evaluate the internal energy and virial pressure while the integration of $u_{\mathrm{LJ}}(r) - \mathrm{u}_{\mathrm{MD}}(r)$ (which is zero for $r < r_{c_1}$) gave the cut-off corrections.

The equations of motion were solved by the Hamming method [23] or the four-value Gear method [15], of which the latter was found slightly more efficient. The correlation time of energy exchange with the Nose thermostat was set to $\tau = 0.1 t_u$, where $t_u = \sigma(m/\varepsilon^{1/2})$ is the dimensionless time unit. The time steps were set so that the change of total Hamiltonian (i.e. increase in case of the Hamming method and decrease in case of the Gear method) within a typical correlation time (about $0.1 t_u$) was less than $10^{-4}$; typical values were about $(0.002 \div 0.0025) t_u$ per one evaluation of forces (we recall that the forces are evaluated twice within one step of the Hamming method). The time autocorrelation function of pressure and energy used to estimate the errors was fitted to damped oscillations (correspondingly to the oscillatory nature of the Nose dynamics) and the hydrodynamic tail.

## 4. RESULTS AND DISCUSSION

### *4.1. Pressure and internal energy*

As already mentioned in the proceeding sections, our emphasis is placed on accuracy and reliabilty rather than on producing large amounts of data. This is why we have implemented the two independant molecular simulation techniques and at some state points employed both of them in order to make a cross-check. The effect of the number of particles in the system on the simulation results has also been examined.

The generated pressure and internal energy data covering the ranges in the reduced temperature and reduced density ⟨0.72, 4.85⟩ and ⟨0,04, 1.0⟩, respectively, are summarized in Table 1, arranged whenever possible by isotherms. We present data for five subcritical temperatures, of which the highest ($T^* = 1.3$) is close to the critical point, and for three supercritical temperatures. As usual, the numbers in parentheses designate the estimated uncertainties related to the last digits in the given simulated quantities.

The MD method is apparently not suited for simulations at gaseous densities. The gas consists of many clusters and the transfer of an atom from one cluster to another is too slow. Since the relevant time correlation functions could not have been reasonably fitted, the uncertainty estimates are in this case more or less extrapolations and hence they can be adopted only with reservation.

**Table 1** Molecular simulation results on pressure and internal energy of the Lennard-Jones fluid; the reduced quanties $T^*$, $\varrho^*$, $P^*$, and $U^*$ are defined by equation (6).

| $T^*$ | $\varrho^*$ | $P^*$ | $U^*$ | method[a] | $N$ | cfg/tim[b] |
|---|---|---|---|---|---|---|
| 0.72 | 0.8484 | 0.206 (13) | −6.1124 (25) | MC | 512 | 5.5 |
| 0.72 | 0.8839 | 0.880 (13) | −6.3208 (25) | MC | 512 | 6.0 |
| 0.72 | 0.9158 | 1.692 (19) | −6.4855 (36) | MC | 512 | 6.9 |
| 0.8049 (15) | 0.8645 | 1.062 (11) | −6.1006 (23) | MD | 256 | $t = 44.6$ |
| 0.81 | 0.801 | 0.065 (10) | −5.7158 (17) | MC | 512 | 5.6 |
| 0.81 | 0.835 | 0.525 (9) | −5.9334 (21) | MC | 512 | 5.5 |
| 0.81 | 0.8645 | 1.066 (16) | −6.1072 (30) | MC | 256 | 2.8 |
| 0.81 | 0.8645 | 1.056 (24) | −6.1092 (44) | MC | 360 | 5.5 |
| 0.81 | 0.8645 | 1.088 (18) | −6.1041 (35) | MC | 512 | 4.9 |
| 0.81 | 0.8645 | 1.0961 (15) | −6.10221 (28) | NMD | 800 | $t = 2500$ |
| 0.81 | 0.9 | 1.939 (18) | −6.2892 (32) | MC | 512 | 5.0 |
| 0.81 | 0.95 | 3.568 (30) | −6.500 (6) | MC | 512 | 7.5 |
| 0.811252 | 0.8645 | 1.1026 (11) | −6.10083 (20) | MD | 864 | $t = 2800$ |
| 0.8116 (15) | 0.8 | 0.029 (17) | −5.711 (3) | MD | 256 | $t = 24.6$ |
| 1.05 | 0.7 | 0.1796 (15) | −4.85668 (40) | NMD | 600 | $t = 1296$ |
| 1.05 | 0.9 | 3.6013 (29) | −5.99805 (55) | NMD | 800 | $t = 1125$ |
| 1.2 | 0.04 | 0.04090 (2) | −0.3326 (10) | NMD | 128 | $t = 26000$ |
| 1.2 | 0.04 | 0.040851 (10) | −0.33534 (14) | MCp | 1024 | |
| 1.2 | 0.08 | 0.06849 (6) | −0.6657 (11) | NMD | 216 | $t = 17000$ |
| 1.2 | 0.08 | 0.068286 (36) | −0.67232 (32) | MCp | 1024 | |
| 1.2 | 0.7 | 0.6627 (32) | −4.7606 (8) | NMD | 600 | $t = 405$ |
| 1.2 | 0.8 | 1.9542 (12) | −5.36337 (24) | NMD | 686 | $t = 2952$ |
| 1.2 | 0.85 | 3.0476 (50) | −5.6203 (9) | NMD | 750 | $t = 364$ |
| 1.2 | 0.9 | 4.5628 (43) | −5.82875 (84) | NMD | 800 | $t = 378$ |
| 1.3 | 0.2 | 0.1214 (8) | −1.5402 (35) | MC | 512 | 2.9 |
| 1.3 | 0.2 | 0.1216 (4) | −1.5472 (30) | MCp | 512 | |
| 1.3 | 0.25 | 0.1243 (12) | −1.8785 (38) | MC | 512 | 3.7 |
| 1.3 | 0.28 | 0.1225 (13) | −2.0250 (20) | MC | 128 | 5.2 |
| 1.3 | 0.28 | 0.1196 (12) | −2.0598 (27) | MC | 256 | 5.6 |
| 1.3 | 0.28 | 0.1220 (12) | −2.0767 (23) | MC | 512 | 7.0 |
| 1.3 | 0.4 | 0.1117 (27) | −2.7907 (51) | MC | 256 | 5.1 |
| 1.3 | 0.4 | 0.1135 (24) | −2.8085 (57) | MC | 512 | 5.4 |
| 1.3 | 0.45 | 0.1194 (30) | −3.1056 (32) | MC | 512 | 5.1 |
| 1.3 | 0.5 | 0.1441 (35) | −3.4092 (30) | MC | 512 | 5.4 |
| 1.3 | 0.6 | 0.344 (6) | −4.0503 (16) | MC | 512 | 5.6 |
| 1.45 | 0.3 | 0.1993 (21) | −2.1015 (26) | MC | 512 | 2.7 |
| 1.45 | 0.3 | 0.1999 (7) | −2.1034 (18) | MCp | 512 | |
| 1.45 | 0.4 | 0.2347 (33) | −2.7220 (35) | MC | 512 | 3.2 |
| 1.45 | 0.5 | 0.343 (5) | −3.3418 (26) | MC | 512 | 4.0 |
| 1.45 | 0.7 | 1.431 (8) | −4.6098 (17) | MC | 512 | 6.3 |
| 1.45 | 0.95 | 8.326 (24) | −5.677 (5) | MC | 512 | 7.0 |
| 2.74 | 0.3 | 0.8663 (23) | −1.7896 (15) | MC | 512 | 3.1 |
| 2.74 | 0.55 | 2.499 (7) | −3.2032 (21) | MC | 512 | 3.9 |
| 2.74 | 0.8 | 7.992 (17) | −4.254 (4) | MC | 512 | 5.0 |
| 2.74 | 1.0 | 19.997 (36) | −4.224 (8) | MC | 512 | 4.5 |
| 2.775 (5) | 0.8 | 8.15 (3) | −4.223 (6) | MD | 256 | $t = 15.4$ |
| 4.85 | 0.2 | 1.127 (3) | −1.021 (3) | MC | 512 | 1.1 |
| 4.85 | 0.4 | 2.979 (17) | −1.975 (7) | MC | 512 | 0.7 |
| 4.85 | 0.6 | 6.683 (17) | −2.746 (5) | MC | 512 | 2.1 |
| 4.85 | 0.8 | 14.704 (37) | −3.023 (9) | MC | 512 | 2.1 |
| 4.85 | 1.0 | 31.32 (6) | −2.325 (12) | MC | 512 | 2.5 |

[a] MC = Monte Carlo, MCp = Monte Carlo with only truncated (i.e. not shifted) potential, MD = microanonical molecular dynamics, NMD = Nose canonical molecular dynamics.

[b] for the MC method: (number of configurations) × $10^{-6}$; for the MD method: the MD time $t$.

In the low-density MC1 simulations the use of only truncated potential (i.e. without shifting) was considered as more appropriate. The effect of this change is marginal as can be observed from the pairs of data given for the state points of $T^* = 1.3$, $\varrho^* = 0.2$ and $T^* = 1.45$, $\varrho^* = 0.3$.

The results for the state points of $T^* = 0.81$, $\varrho^* = 0.8645$ and $T^* = 1.3$, $\varrho^* = 0.28$ again document the well known (but still often not respected) fact that the simulation data obtained for a number of particles in the system lower than about 500 may easily be loaded with systematic errors exceeding by far the estimates of uncertainties. Indeed, this fact casts certain doubt on any literature data generated for smaller systems. On the other hand, any agreement between data from different sources based on a system with less than about 500 particles may be considered rather a fortuitous coincidence. This is also the reason why we do not present here any extensive comparisons with previous data. Comprehensive assessment and detailed evaluation of the entire body of data on the LJ fluid will be a subject of another communication [24].

For illustrative purposes we mention only a few items of the literature data from the most interesting to us regions of thermodynamic conditions.

Some of our results for isotherms $T^* = 0.72$ and 0.81 (see Table 1) may directly be compared with the values obtained for the corresponding state points by McDonald and Singer [25] by the MC simulation on a system of 108 particles. Although the authors presented an analysis of possible sources of errors in their data, they did not specify any explicit uncertainty estimates. Based on what has been stated in reference [25], our guess of uncertainties in the reported values of $P^*$ was 0.04 [7]. It turns out, however, that only the data points at the lowest densities (i.e. $\varrho^* = 0.8484$ at $T^* = 0.72$ and $\varrho^* = 0.801$ at $T^* = 0.81$) agree with our new data (see Table 1) within the combined uncertainty estimates. At all other densities the pressure data given in [25] are far too low: $P^* = 1.482$ at $T^* = 0.72$ and $\varrho^* = 0.9158$; $P^* = 1.000$ at $T^* = 0.81$ and $\varrho^* = 0.8645$. Regarding the internal energy data, a rule of thumb says that the simulated internal energies should be about four times more precise than the pressure obtained within the same run, which would lead to uncertainties in $U^*$ of reference [25] about 0.01. Nevertheless, all the internal energy values presented in [25] for the two considered isotherms are lower (i.e. larger negative numbers) by at least 0.02 than those given in Table 1. It should be noted that the simulation data of McDonald and Singer [25] have generally been accepted for years as reliable.

Adams [26] reported data for four temperatures of the range $T^* \in \langle 1.15, 1.35 \rangle$ within and nearby the vapour-liquid coexistence region of the LJ fluid, simulated by the grand canonical MC method. Considering the important isotherm $T^* = 1.30$, although the single pressure values may agree somewhere on the verge of combined possible uncertainties (not given in [26]), our more accurate results indicate that the isotherm still exhibits a clearly subcritical shape. This gives support to the critical temperature being higher then $T_c^* = 1.30$, the value adopted by Adams [26]. However, it has to be borne in mind that this statement relates to the size of the system studied as it is well known (see Hansen and Verlet [27] and Smith *et al.* [28]) that it is the finite size of the system which crucially affects the resulting $T_c^*$ estimate. The critical region and the determination of the "true" critical temperature of the LJ fluid still deserves a more detailed study.

### 4.2. *Chemical potential*

As it has already been mentioned earlier, there were three main goals of the MC$\mu$ simulations:

(1) to demonstrate that the new version of the insertion particle method, outlined in Section 2, is able to produce the chemical potential not only for

**Table 2** The residual chemical potential of the Lennard-Jones fluid at the reduced temperature $T^* = 1.2$.

| $\varrho^*$ | $N$ | $\beta\mu_{res}$ simulated<br>this work[b] | <br>this work[c] | <br>ref. [29] | <br>ref. [28] | <br>ref. [10] | <br>ref. [27] | calcd.[a]<br>ref. [4] |
|---|---|---|---|---|---|---|---|---|
| 0.7 | 64 | −1.992 (5) | | | | | | −1.987 |
| | 108 | | | −1.833 | −1.889 | −1.93 | −2.01 | |
| | 125 | −1.945 (50) | −1.975 (5) | | | | | |
| | 200 | | | −1.902 | | | | |
| | 216 | −1.958 (70) | | | | | | |
| | 256 | | | | −1.908 | −1.98 | | |
| | 500 | | | −1.898 | −1.940 | −1.91 | | |
| | 512 | −1.957 (80) | | | | | | |
| 0.8 | 64 | −0.655 (80) | | | | | | −0.692 |
| | 108 | | | −0.521 | −0.51 | | −0.68 | |
| | 125 | −0.736 (90) | | | | | | |
| | 200 | | | −0.596 | | | | |
| | 216 | −0.637 (100) | | | | | | |
| | 256 | | | | −0.56 | | | |
| | 500 | | | −0.594 | −0.58 | | | |
| | 512 | −0.689 (100)[d] | | | | | | |
| | 1000 | −0.608 (120)[d] | | | | | | |
| 0.85 | 64 | 0.414 (130) | 0.392 (80)[e] | | | | | 0.345 |
| | 108 | | | 0.548 | | | 0.33 | |
| | 125 | 0.400 (150) | | | | | | |
| | 200 | | | 0.536 | | | | |
| | 216 | 0.471 (160) | 0.427 (160) | | | | | |
| | 500 | | | 0.418 | | 0.40 | | |
| | 512 | 0.384 (90)[f] | | | | | | |
| | 1000 | 0.431 (150)[f] | 0.359 (180)[f] | | | | | |
| 0.9 | 1088 | | | 1.98 | | | | 1.723 |
| | 125 | 1.856 (150) | | | | | | |
| | 216 | 1.736 (150) | | | | | | |
| | 500 | | | 1.86 | | | | |
| | 512 | 1.862 (100) | | | | | | |
| | 1000 | 1.839 (100)[e] | 1.822 (180)[g]<br>1.931 (130)[g] | | | | | |

[a] calculated from equation (3) of ref. [4].
[b] normal sampling.
[c] preferential sampling.
[d] 33 million configurations.
[e] 42 million configurations.
[f] 50 million configurations.
[g] two independent runs with 50 million configurations.
Unmarked values are results of simulation runs with 25 million configurations.

dense hard body fluids but also for very dense realistic fluids where other methods fail;

(2) to assess discrepancies in existing data;

(3) to produce new data on a supercritical isotherm up to very high density.

To reach these goals, we carried out (i) a number of simulations for $T^* = 1.2$ at four densities using for each density also a different number of particles ranging from 64 up to 1000, and (ii) simulations with 1000 particles for $T^* = 1.45$ at three densities, with the highest one being $\varrho^* = 0.95$. The results are summarized in Tables 2 and 3. For comparison we also show in Table 2 the existing data obtained by other simulation methods and in both tables then the values calculated from Nicolas *et al.* [4] equation of state.

As it follows from equation (4), the chemical potential is given by the probabilities of observing the systems with $[N]$ and $[N+1]$ particles. To reach the $[N+1]$ state, the scaled particle must ultimately grow into the "normal" particle, but this change is more and more difficult to take place with increasing density. Although we began experiencing certain problems already for $\varrho^* = 0.9$, we ran into real problems for $\varrho^* = 0.95$ in the simulations without using the preferential sampling: the probability that the scaled particle will swell into the full size particle was practically zero. It turns out that this problem can be easily overcome by using the preferential sampling, in which case the observance of the $[N+1]$ state was comparable with that at lower densities without using the preferential sampling. At lower densities the results obtained with and without the preferential sampling and the efficiency of the respective simulations were practically the same.

It is evident that the chemical potential is, by its nature, subject to large fluctuations. Furthermore, the residual chemical potential is given by the difference of two large terms and at certain thermodynamic conditions it changes sign. At these conditions the estimated and actual values may differ considerably. In the light of these facts the results for $\varrho^* = 0.7$ and 0.9 are very good: they are subject to about 5 and 10 per cent errors, respectively; the uncertainty is evidently larger for $\varrho^* = 0.8$ and 0.85. For comparison we recall that Shing and Gubbins [29] did not touch the problem of errors in their data at all and Fischer and coworkers [10] somehow estimated the uncertainty in their data at lower and medium densities to be several per cent. A more reliable estimate of errors was

**Table 3** The residual chemical potential of the Lennard-Jones fluid at the reduced temperature $T^* = 1.45$.

| $\varrho^*$ | $\beta\mu_{\text{res}}$ this work[a] | $\beta\mu_{\text{res}}$ calculated[b] |
|---|---|---|
| 0.5 | −1.469 (70)[c] | −1.557 |
| 0.7 | −0.615 (70)[d] | −0.696 |
| 0.95 | 4.64 (20)[e] | 4.625 |

[a] Monte Carlo with $N = 1000$ and preferential sampling.
[b] calculated from equation (3) of ref. [4].
[c] 20 million configurations.
[d] 25 million configurations.
[e] 50 million configurations.

made by Smit and Frenkel [30] whose data for $\varrho^* = 0.8$ exhibit much larger uncertainty than ours. Finally, concerning the last set of data by Deitrick *et al.* [31], the claimed errors are unrealistically small to be taken seriously.

We estimated the errors in our data by the method outlined in subsection 3.1. When plotting the average values of the chemical potential along the chain (i.e. $\mu$ averaged over subruns), an interesting phenomenon was observed at the two highest densities considered, $\varrho^* = 0.9$ at $T^* = 1.2$, and $\varrho^* = 0.95$ at $T^* = 1.45$. At these densities the chemical potential showed the behaviour corresponding rather to a metastable phase: $\mu$ was fluctuating about two distinct different levels with relatively rare jumps from one level to another. Since the crystallization at these temperatures takes place at higher densities than those used in the simulations, at the moment we do not have any rational explanation for such observations.

To study the $N$-dependence of the chemical potential, for each density we performed several simulations using different number of particles in the basic cell. Smit and Frenkel [30] developed a theoretical model for the $N$-dependence and their simulations at lower densities confirmed the validity of the model. However, as it can be seen from Table 2, we may hardly draw any conclusion on the $N$-dependence of the chemical potential at higher densities and the same seems to apply also to the data by Deitrick *et al.* [31].

It is seen from Table 2 that for $\varrho^* = 0.7$, 0.8 and 0.9 all the data agree within their estimated combined experimental errors. Only for $\varrho^* = 0.85$ the value of 0.33 given by Shing and Gubbins [29] seems to be slightly off.

In Table 3 we show fresh new data for the isotherm $T^* = 1.45$. In these simulations we did not use any *a priori* knowledge of the chemical potential (e.g. for obtaining the weight $w_k$) and so the comparison of the chemical potential from the simulations with that obtained from the empirical Nicolas *et al.* [4] equation of state provides a fair test of the correctness of the simulation. In addition to this test, in all the MC$\mu$ simulations we also calculated the pressure from the configurations with $N$ and $N+1$ identical particles. In no case the difference between the pressures obtained in MC1 and MC$\mu$ simulations exceeded 0.5 per cent.

## 5. CONCLUSIONS

In the present paper we report (i) data on the pressure and internal energy of the Lennard-Jones fluid for eight isotherms of the reduced temperature range $T^* \in \langle 0.72, 4.85 \rangle$ simulated by both the Monte Carlo and molecular dynamics methods and (ii) data on the chemical potential of the Lennard-Jones fluid for two isotherms of $T^* = 1.2$ and 1.45 simulated by the Monte Carlo method. Placing the primary emphasis on accuracy of the generated data, great care was taken with all methodological aspects of the computer simulations. While our requirement to produce data of the highest accuracy is obvious, the choice of the thermodynamic conditions is relatively arbitrary, dictated only by the need to cover the state space suffiently to allow an evaluation of existing data and to establish a benchmark set for equation of state development. We have foccussed on the vicinity of the triple point where the existing data were subject to the largest errors and on the region around the critical point.

A new version of the insertion particle method was implemented for the Lennard-Jones fluid and proved to be useful for generating the chemical potential data in the very dense fluid region. The study revealed the necessity of using the preferential sampling at the highest densities considered.

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