Chemical potential of quadrupolar two-centre Lennard-Jones fluids by gradual insertion

Jadran Vrabec*, Matthias Kettler, Hans Hasse
Institut für Technische Thermodynamik und Thermische Verfahrenstechnik, Universität Stuttgart, D-70550 Stuttgart, Germany

Keywords: molecular simulation, Monte-Carlo, quadrupolar fluid, chemical potential, gradual insertion

Abstract

The gradual insertion method for direct calculation of the chemical potential by molecular simulation is applied in the NpT ensemble to different quadrupolar two-centre Lennard-Jones fluids at high density state points. The results agree well with Widom’s test particle insertion but show at very high densities significantly smaller statistical uncertainties. The gradual insertion method, which is coupled here with preferential sampling, extends the density range where reliable information on the chemical potential can be obtained. Application details are reported.

* author for correspondence, tel.: +49-711/685-6107, fax: +49-711/685-7657, email: vrabec@itt.uni-stuttgart.de
1 Introduction

All molecular simulation techniques for the calculation of the chemical potential which are accompanied with trial insertion (or deletion) of real or ghost particles become inaccurate and finally fail in the case of high densities, especially when applied to molecular fluids with strong interactions. This is the case for the conventional test particle insertion method by Widom [1] as well as for the Gibbs ensemble (GE) [2] and grand canonical Monte-Carlo ensemble (GC) [3], which demand insertion and deletion attempts of real particles.

Therefore, different Monte-Carlo techniques have been proposed to improve the efficiency of the calculation of the chemical potential. Recent developments are, e.g., the expanded ensemble methods [4,5], the particle deletion scheme [6], the augmented grand canonical ensemble [7], or the scaled particle Monte-Carlo method [8]. An overview is given by Kofke and Cummings [9].

In the present work, an expanded ensemble method is used. A first version was published by Vorontsov-Velyaminov et al. [4]. That method was applied for gradual insertion by Nezbeda and Kolafa [5], who additionally introduced preferential sampling. Related work with expanded ensemble methods is described e.g. in [10,11,12].

We use the gradual insertion method as proposed by Nezbeda and Kolafa [5] which is based on the following idea: instead of inserting or deleting a real particle, a fluctuating particle is introduced, that undergoes changes in a set of different discrete 'sizes' or states of coupling with all other particles. Additionally, the preferential sampling of the fluid in the vicinity of the fluctuating particle is introduced for a further increase of accuracy.

This method was applied to different ensembles (NVT [5], GC [5], GE [13], and NpT [14,15]) using different interaction potentials such as the hard sphere fluid [5], the square-well fluid [13], the spherical Lennard-Jones fluid [14,16], and to ternary mixtures of hard
spheres and hard heteronuclear diatomics \cite{17}.

In this work we apply the gradual insertion method for the first time to a polar intermolecular potential, the two-centre Lennard-Jones plus point quadrupole fluid. That potential allows to describe the thermodynamic properties of many real fluids, like carbon dioxide, ethyne, propyne, or carbon disulfide with good accuracy, as has been shown in a comprehensive study \cite{18,19}. The present study is performed in the NpT ensemble at high densities. The results are critically compared to test particle insertion. Details on the gradual insertion method, which is used here together with preferential sampling, are given.

\section{Method}

In the following we briefly summarize the gradual insertion method in a NVT ensemble, for more details see \cite{5}. The key element of the method is to introduce a ‘fluctuating particle’ which can appear at different states of coupling with all other particles. This set of states starts from a pointwise, completely interactionless or decoupled state, up to the fully coupled state, in which the fluctuating particle has the same properties as the other particles. Each of the partially coupled states is related to a NVT sub-ensemble with no physical meaning. These sub-ensembles can be depicted in a scheme as follows:

\begin{equation}
[N] \leftrightarrow [N + \psi_1] \leftrightarrow \cdots \leftrightarrow [N + \psi_{k-1}] \leftrightarrow [N + \psi_k],
\end{equation}

where $[N+\psi_j]$ denotes a sub-ensemble with $N$ regular particles and one fluctuating particle in the state $j$, with $j = 0, \ldots, k$. The interaction energy of the fluctuating particle with the remaining particles is denoted by $\psi_j$, in the fully coupled state by $\psi_k$, and in the fully decoupled state it is $\psi_0 = 0$. Note that $[N + \psi_k]$ equals $[N + 1]$. The arrows describe the
transitions between neighbouring states. Finally, $w_j$ denotes the weight of the state $j$.

Additionally to the standard Monte-Carlo moves in a NVT ensemble, trial translation and trial rotation, the trial change of fluctuating particle state is necessary. The probability of accepting a change of the fluctuating particle from state $i$ to state $j$ is given by

$$P_{\text{acc}}(i \rightarrow j) = \min \left( 1, \frac{w_j \cdot \Pi(j \rightarrow i)}{w_i \cdot \Pi(i \rightarrow j)} \cdot \exp \{ -\beta (\psi_j - \psi_i) \} \right),$$

where $\Pi(j \rightarrow i)$ and $\Pi(i \rightarrow j)$ denote a priori transition probabilities of the respective changes and $\beta$ is the Boltzmann factor.

The chemical potential in the NVT ensemble is obtained from

$$\mu = \mu^{id}(T) + kT \cdot \ln \frac{N}{V} + kT \cdot \ln \left( \frac{w_k}{w_0} \cdot \frac{\text{Prob}[N]}{\text{Prob}[N+1]} \right),$$

where $\text{Prob}[N]$ and $\text{Prob}[N+1]$ are the probabilities to observe an ensemble with $N$ and $N+1$ particles, respectively. The parenthesis $<>$ denote the ensemble average. Furthermore, $\mu^{id}(T)$ is the temperature dependent ideal part of the chemical potential. If the fluctuating particle is in the fully decoupled state, an insertion attempt into a random new position follows. When the fluctuating particle reaches the fully coupled state another particle is chosen randomly, to be treated as the fluctuating one.

Improvement of efficiency often can be obtained by using the preferential sampling method, see e. g. Allen and Tildesley [3]. The idea is to sample particles preferentially in the vicinity of the fluctuating particle. Therefore, a function $f(r)$ is introduced, denoting the probability of an attempt to move a host particle in a distance $r$ from the fluctuating particle.

The following steps are necessary to keep the microreversibility condition [5]:

(i) random choice of a host particle,

(ii) acceptance of this choice with the probability $f(r_{\text{old}})$,
(iii) random choice of a new position and orientation of the host particle,
(iv) acceptance of this choice with the probability \( \min(1, f(r_{\text{new}})/f(r_{\text{old}})) \),
(v) the new configuration is accepted with the probability \( \min(1, \exp\{-\beta(U_{\text{new}} - U_{\text{old}})\}) \),

where \( U \) denotes the configurational energy.

In order to extend the gradual insertion method to the NpT ensemble the volume fluctuation step has to be considered additionally. To set the pressure \( p \), a volume change from \( V_{\text{old}} \) to \( V_{\text{new}} \) is accepted with the probability \[ P_{\text{acc}}(V_{\text{old}} \rightarrow V_{\text{new}}) = \min\left(1, \left(\frac{V_{\text{new}}}{V_{\text{old}}}\right)^N \cdot \exp\{-\beta(p(V_{\text{new}} - V_{\text{old}}) + U_{\text{new}} - U_{\text{old}})\}\right). \tag{4} \]

This step was applied at random position within the Markov chain, independent from the state of the fluctuating particle. Similar to the NVT ensemble, only configurations with a fully coupled fluctuating particle contribute to the Monte-Carlo sampling of physical properties.

As the volume fluctuates in the NpT ensemble, Eq. (3) has to be modified to calculate the chemical potential

\[
\mu = \mu^{id}(T) + kT \cdot \ln \left( \frac{N \cdot \frac{w_k}{w_0} \cdot \frac{\text{Prob}[N]}{\text{Prob}[N+1]}}{V} \right). \tag{5}
\]

Up to our knowledge, no formal derivation of Eq. (5) has been given in the literature so far. It is not within the scope of this work to close that gap. We will limit ourselves to show that the results from Eq. (5) are in agreement with Widom’s method, cf. section 4.

3 Investigated model and technical details

In the present investigation we consider the two-centre Lennard-Jones plus pointquadru-pole fluid (2CLJQ). It is composed of two identical Lennard-Jones sites a distance \( L \)
apart plus an ideal point quadrupole of moment $Q$ placed in the geometric centre of the molecule [20]. The charges of the quadrupole are arranged along the molecular axis in the symmetric sequence $+, -, -, +$ or, having the same energetic effect in pure fluids, $-, +, +, -$. A detailed description of this fluid is given in [21].

The Lennard-Jones parameters $\sigma$ and $\epsilon$ of the 2CLJQ pair potential were used for the reduction of the thermodynamic properties and the model parameters $L$ and $Q$: temperature $T^* = kT/\epsilon$, pressure $p^* = p\sigma^3/\epsilon$, density $\rho^* = \rho\sigma^3$, configurational energy $u^* = u/\epsilon$, elongation $L^* = L/\sigma$, squared quadrupolar moment $Q^{*2} = Q^2 / (\epsilon\sigma^5)$.

For the simulation runs $N = 512$ particles were used, the cut-off radius was set to $4\sigma$, applying periodic boundary conditions and the minimum image convention. The long range corrections for the two-centre Lennard-Jones potential [22] were considered, in the case of quadrupolar interactions no long range corrections have to be made. The number of loops, defined below, was 50 000. The maximum values of translation distance, rotation angle, and volume change were adjusted to yield acceptance rates of roughly 0.5. Statistical uncertainties were calculated by conventional block averaging [23].

The number of states of the fluctuating particle was chosen to $k = 6$. For the fluctuating particle in the state $j$ we set $\sigma_j/\sigma = (1/2 + \sqrt{j}/24)$, $\epsilon_j/\epsilon = j/k$, $L_j/L = 1$, and $Q^{*2}_j/Q^2 = j/k$. The diameter of the hard sphere, shielding the quadrupolar interaction site, was set to $0.4\sigma$, except for the fully decoupled state $j = 0$, where it is zero. The shielding does not allow quadrupolar interaction sites to approach closer to each other than $0.4\sigma$.

Finally, the weights $w_j$ had to be chosen. Starting from unity for all states, they were adjusted during an equilibration period in order to achieve a roughly equal distribution in the occurrence of all states.

One Monte-Carlo loop is defined here as $N$ trial translations, $2/3 \cdot N$ trial rotations, and 1
trial volume change, which are the regular NpT moves. The additional gradual insertion moves within a loop are: $M_C \cdot N$ attempts to change the state of the fluctuating particle, $M_F \cdot N$ attempts to translate the fluctuating particle, $2/3 \cdot M_F \cdot N$ attempts to rotate the fluctuating particle, $M_P \cdot N$ attempts to find a host particle for preferential translation, and $2/3 \cdot M_P \cdot N$ attempts to find a host particle for preferential rotation. Here, $M_C$, $M_F$, and $M_P$ are the parameters of the gradual insertion method.

4 Results and discussion

In Fig. 1 running averages of the chemical potential for the 2CLJQ fluid ($L^* = 0.8, Q^{*2} = 4$) in the liquid phase at $T/T_c \approx 0.55$ are shown as a function of Monte-Carlo loops, or respectively, molecular dynamics time steps. The technical details of the molecular dynamics simulations are given in [21]. The Monte-Carlo loops, as defined here, and the molecular dynamics time steps should be roughly comparable in the sense that both result in a new configuration of the entire system. The better convergence of gradual insertion at this high density state point can clearly be seen. The large steps in the Widom curves are typical when this method is applied to very dense fluids. They are due to the bad statistics, which comes from the small number of test particles which contribute significantly to the average.

In Table 1, a comparison is given between simulation data from the present work and results from Widom’s method [1] taken from [21]. Six different 2CLJQ fluids are investigated in the liquid state close to the bubble line at two temperatures ($T/T_c \approx 0.55$ and $T/T_c \approx 0.8$, respectively). The first finding is, that the results of both methods agree within their statistical uncertainties, which is a numerical proof of Eq. (5). Regarding, secondly, the statistical uncertainties for all 2CLJQ fluids at the higher temperatures ($T/T_c \approx 0.8$), where intermediate liquid densities are found, both methods yield results
with approximately the same statistics. But for $T/T_c \approx 0.55$, where the densities are roughly 20% higher, the uncertainties of Widom's method increase by a factor of 10 to 15. On the other hand, the uncertainties of the gradual insertion increase only by a factor of about 2 to up to 4. So, at state points with high densities ($T/T_c \approx 0.55$) gradual insertion yields results that have considerably better statistics. For the 2CLJQ fluid with the highest elongation and highest quadrupole ($L^* = 0.8, Q^{*2} = 4$), at the low temperature, Widom's method is close to failure (the uncertainty in absolute numbers is almost $\pm 1$). Gradual insertion gives a decent result with $\pm 0.02$. In such very dense and strongly interacting fluids, the accuracy of Widom's method can not be improved significantly by using more test particles or by increasing the length of the simulation run.

In order to compare the computational effort, we performed Monte-Carlo simulations in the NpT ensemble on a conventional workstation applying both methods and keeping all other parameters, such as number of particles or cut-off radius constant. It turns out, that the simulation run with gradual insertion ($M_C=10$, $M_F=10$, $M_P=50$) needs 19.7 CPU h and the run with Widom's method (2 000 test particles after each loop) needs 3.7 CPU h. Therein, regular NpT configuration generation consumes 1.6 CPU h. So the computational effort for gradual insertion is an order of magnitude higher. For a comparison with the same CPU time spent for both methods, it would have been possible to increase the number of configurations or the number of test particles in Widoms method by a factor of 10. Increasing the number of test particles would have lead to no improvements, as their number is already very high. Increasing the number of configurations by a factor of 10 would have lead to a reduction of the statistical uncertainties by about a factor of 3 at best.

For the 2CLJQ fluid ($L^* = 0.8, Q^{*2} = 4$) at the lower temperature ($T/T_c \approx 0.55$) a study of the influence of the free parameters of the gradual insertion method on the chemical
potential is given in Table 2. The reference point is $M_C=10$, $M_F=10$, and $M_P=50$. These parameters were altered up and down by a factor of 2.5. The increase of the number of attempts to change the state of the fluctuating particle from $M_C=4$ to $M_C=10$ yields lower uncertainties, whereas upon further increase to $M_C=25$ no benefit was observed. The variation of the number of attempts to translate or rotate the fluctuating particle ($M_F$) seems to have no influence on the uncertainty in the investigated range of that parameter. The number of attempts to find a host particle for preferential translation or rotation ($M_P$) has the clearest influence on the uncertainty. Note that an increase above $M_P\approx 100$ is not recommended. For instance, at $M_P=125$ we have a relation of 125 preferential translation moves to one ordinary translation move. This extreme ratio leads to the slight deviation shown in the last line of Table 2.

5 Conclusion

This investigation shows that NpT simulations with gradual insertion combined with preferential sampling can yield results for the chemical potential of realistic strongly interacting molecular fluids at high densities with clearly improved statistics. It can be applied at state points where conventional test particle insertion breaks down.

Acknowledgements

We gratefully acknowledge financial support by Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 412, University of Stuttgart.
References

[1] B. Widom, J. Chem. Phys. 39 (1963) 2808.

[2] A. Z. Panagiotopoulos, Mol. Phys. 61 (1987) 813.

[3] M. P. Allen and D. J. Tildesley, Computer simulations of liquids, Clarendon Press, Oxford, 1987.

[4] S. V. Shevkunov, A. A. Martinovski, and P. N. Vorontsov-Velyaminov, High Temp. Phys. (USSR) 26 (1988) 246.

[5] I. Nezbeda and J. Kolafa, Mol. Simul. 5 (1991) 391.

[6] G. C. Boulougouris, I. G. Economou and D. N. Theodrou, Mol. Phys. 96 (1999) 905.

[7] R. D. Kaminski, J. Chem. Phys. 101 (1994) 4986.

[8] M. Barosova, A. Malievski, S. Labik, W. R. Smith, Mol. Phys. 87 (1996) 423.

[9] D. A. Kofke, P. T. Cummings, Mol. Phys. 92 (1997) 973.

[10] A. P. Lyubartsev, A. A. Martinovski, S. V. Shevkunov, and P. N. Vorontsov-Velyaminov, J. Chem. Phys. 96 (1992) 1776.

[11] A. P. Lyubartsev, A. Laaksonen, and P. N. Vorontsov-Velyaminov, Mol. Simul. 18 (1996) 43.

[12] P. Attard, J. Chem. Phys. 98 (1993) 2225.

[13] M. Strnad and I. Nezbeda, Mol. Simul. 22 (1999) 193.

[14] H. L. Vörtler, Verhandl. der Dt. Phys. Ges. 17A (1993) 965.

[15] H. L. Vörtler, Habilitationsschrift, Universität Leipzig, 2001.

[16] J. Kolafa, H. L. Vörtler, K. Aim and I. Nezbeda, Mol. Simul. 115 (1993) 305.

[17] M. Strnad and I. Nezbeda, Mol. Phys. 85 (1995) 91.

[18] J. Vrabec, J. Stoll, and H. Hasse, J. Phys. Chem. B 105 (2001) 12126.

[19] J. Stoll, J. Vrabec, and H. Hasse, AIChE J., submitted (2001).

[20] C. G. Gray and K. E. Gubbins, Theory of molecular fluids, Volume 1: Fundamentals, Clarendon Press, Oxford, 1984, p. 76.

[21] J. Stoll, J. Vrabec, H. Hasse, and J. Fischer, Fluid Phase Equilibria 179 (2001) 339.
[22] R. Lustig, Mol. Phys. 65 (1988) 175.

[23] D. Fincham, N. Quirke, and D. J. Tildesley, J. Chem. Phys. 84 (1986) 4535.
Table 1
Density, configurational energy, and chemical potential for different 2CLJQ fluids close to their bubble lines at $T/T_c \approx 0.55$ (upper blocks) and $T/T_c \approx 0.8$ (lower blocks). Method A: gradual insertion with the parameters $M_C = 10$, $M_F = 10$, and $M_P = 50$; Method B: Widom’s test particle method [21]. The numbers in paranthesis denote the uncertainty in the last digits.

| $T^*$ | $p^*$ | $\rho^*$ | $u^*$ | $\mu/kT$ | Method |
|-------|-------|----------|-------|----------|--------|
| $L^* = 0.4, Q^{*2} = 0$ |       |          |       |          |        |
| 1.7875 | 0.5960 (3) | -15.524 (8) | -6.31 (2) | A |
|       | 0.5952 (2) | -15.504 (6) | -6.34 (6) | B |
| 2.6 | 0.4747 (8) | -11.80 (2) | -3.867 (4) | A |
|       | 0.4718 (6) | -11.74 (1) | -3.882 (7) | B |
| $L^* = 0.4, Q^{*2} = 4$ |       |          |       |          |        |
| 2.09 | 0.6566 (3) | -23.58 (1) | -7.05 (3) | A |
|       | 0.6562 (2) | -23.57 (1) | -6.8 (5) | B |
| 3.04 | 0.5180 (8) | -16.70 (3) | -3.95 (1) | A |
|       | 0.5154 (4) | -16.61 (2) | -3.98 (1) | B |
| $L^* = 0.6, Q^{*2} = 0$ |       |          |       |          |        |
| 1.4025 | 0.5008 (2) | -12.706 (6) | -6.59 (1) | A |
|       | 0.5001 (2) | -12.689 (5) | -6.57 (7) | B |
| 2.04 | 0.3947 (7) | -9.51 (2) | -4.03 (1) | A |
|       | 0.3931 (4) | -9.47 (1) | -4.058 (8) | B |
| $L^* = 0.6, Q^{*2} = 4$ |       |          |       |          |        |
| 1.628 | 0.5521 (2) | -19.06 (1) | -7.31 (3) | A |
|       | 0.5513 (2) | -19.03 (1) | -7.6 (4) | B |
| 2.368 | 0.4310 (7) | -13.33 (2) | -4.16 (1) | A |
|       | 0.4298 (5) | -13.29 (2) | -4.16 (1) | B |
| $T^*$ | $p^*$ | $\rho^*$ | $u^*$ | $\mu/kT$ | Method |
|------|------|---------|------|----------|--------|
| $L^* = 0.8, Q^{*2} = 0$ | | | | | |
| 1.177 | 0 | 0.4389 (2) | -11.124 (4) | -6.82 (1) | A |
| | | 0.4384 (1) | -11.109 (4) | -6.7 (1) | B |
| 1.712 | 0.03 | 0.3421 (6) | -8.19 (1) | -4.161 (8) | A |
| | | 0.3398 (5) | -8.14 (1) | -4.192 (8) | B |
| $L^* = 0.8, Q^{*2} = 4$ | | | | | |
| 1.342 | 0 | 0.4963 (2) | -17.31 (1) | -7.91 (2) | A |
| | | 0.4955 (2) | -17.276 (8) | -8.3 (8) | B |
| 1.952 | 0.03 | 0.3932 (4) | -12.36 (1) | -4.495 (8) | A |
| | | 0.3928 (4) | -12.35 (1) | -4.51 (2) | B |
Table 2
Influence of the gradual insertion parameters on the chemical potential of the 2CLJQ fluid $(L^* = 0.8, Q^*^2 = 4)$ at $T^* = 1.342, p^* = 0$. The numbers in parenthesis denote the uncertainty in the last digits.

| $M_C$ | $M_F$ | $M_P$ | $\mu/kT$  |
|-------|-------|-------|-----------|
| 10    | 10    | 50    | -7.97 (2) |
| 4     | 10    | 50    | -8.00 (5) |
| 25    | 10    | 50    | -8.04 (3) |
| 10    | 4     | 50    | -8.00 (4) |
| 10    | 25    | 50    | -7.99 (4) |
| 10    | 10    | 20    | -7.97 (6) |
| 10    | 10    | 125   | -7.94 (1) |
Running averages of the chemical potential over Monte-Carlo loops, or respectively, molecular dynamics time steps of independent simulation runs for the 2CLJQ fluid ($L^* = 0.6, Q^* = 4$) at $T^* = 1.628, p^* = 0$ using $N = 512$ particles and a cut-off radius $r_c = 4 \sigma$. Thick line: Monte-Carlo simulation using gradual insertion with the parameters $M_C=10, M_F=10$, and $M_P=50$. Thin lines: Three different molecular dynamics simulation runs using Widom's method with 2 000 test particles at each time step. Dashed lines: straight horizontal guide to the eye.
Fig. 1.