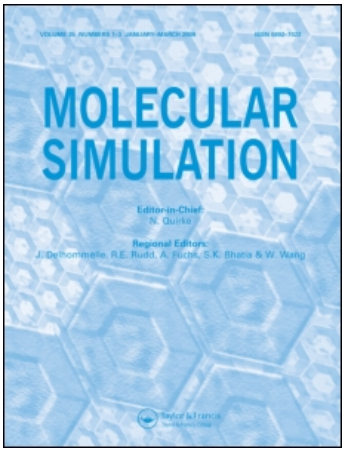

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ORTHOBARIC DENSITIES FROM SIMULATIONS OF THE LIQUID VAPOUR INTERFACE

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Molecular dynamics studies of the liquid vapour interface of a Lennard-Jones fluid performed on a CYBER 205 are reported for $kT/\varepsilon = 0.70$, 0.85, and 1.10. The main emphasis is on the orthobaric fluid densities: their dependence on different cut-off radii and long range corrections as well as their comparison with the coexisting densities from bulk fluid simulations. As previously reported bubble densities from bulk simulations differ by about 3 per cent at $kT/\varepsilon = 1.10$, phase equilibrium was redetermined there with the NpT + test particle method. Concerning the bubble densities from the interface simulations, increase of the cut-off radius and use of long range corrections shift them up rather close to the "bulk" values. The dew densities from the interface simulations which for the usual cut-off radius of 2.5σ are mostly too high by a factor of 3 are decreased dramatically by accounting for the long range part of the potential. For a cut-off radius of 5σ and long range corrections they agree with the "bulk" values within the accuracy of the latters which, however, is estimated to be only by about 20 per cent. Some characteristic density profiles are also shown.

KEY WORDS: Phase equilibrium, liquid-vapour interface.

1. INTRODUCTION

The final goal of the project in which the present studies are performed is an understanding of the evaporation and condensation at a free liquid surface. In a first paper, the dynamics of the molecules in the liquid vapour interface at equilibrium have already been investigated by molecular dynamics (MD) simulations [1]. Before proceeding to simulations for evaporation into vacuum by non-equilibrium molecular dynamics (NEMD) which follow recent work on liquid flow in pores [2], we wanted to get a deeper understanding of the accuracy of equilibrium simulations of the interface. A point of special concern are the coexisting densities of the liquid and the gas resulting from interface simulations. Especially the latter are important in determining the evaporation coefficient from NEMD but also in equilibrium studies of gas adsorption [3].

Results for coexisting liquid and gas densities of the Lennard-Jones (LJ) fluid taken from previous papers [4–11] and the present work are presented in Figures 1 and 2. We learn that the results based on bulk fluid simulations [4–7] are clearly separated from the results of the interface simulations [8–11] obtained with a cut-off radius of 2.5σ and without long range corrections. The reason for the difference is in the fact

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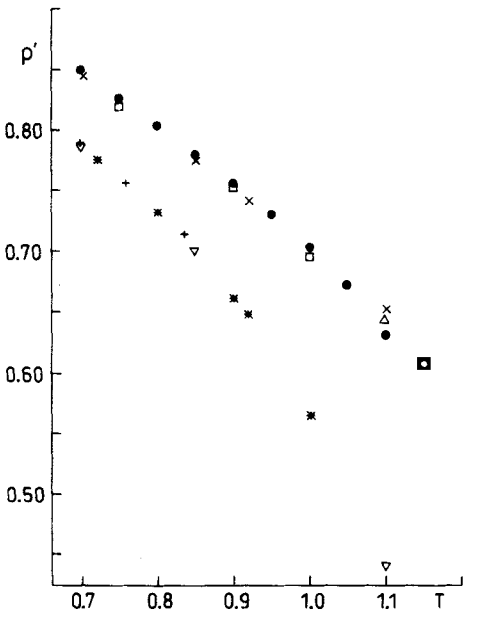

Figure 1 Bubble densities of the LJ fluid from bulk and interface simulations. Bulk simulation results: ● Adams [4], ○ Adams [5], × Nicolas *et al.* [6], □ Panagiotopoulos [7], △ NpT + test particle result from this work. Results from interface simulations all with a cut-off radius of 2.5σ and no long range correction: + Chapela *et al.* [8], * Nijmeijer *et al.* [11], ▽ this work.

that in the interface studies the real LJ fluid was not considered rather a fluid to be called LJ2.5 which is different from the LJ fluid through the neglect of the attractive part of the potential beyond 2.5σ. Neglecting part of the attractive energy lowers the critical temperature T_c and whilst Adams [5] estimated for the LJ system kT_c/ε to be 1.30, it was estimated for the LJ2.5 system by van Megen and Snook [12] to be 1.12. As a consequence of this lower critical temperature, the bubble densities of the LJ2.5 system are lower and the dew densities higher. The increase in the dew density is remarkable and from Figure 2 it is seen to be a factor of about 3 for the temperature intervall from $kT/\varepsilon = 0.70$ up to 1.10. It is obvious that such a strong increase in the dew density may have serious consequences on the interpretation of NEMD results for evaporation into vacuum but also for equilibrium adsorption results [3,13].

In constructing Figures 1 and 2 we have neglected the paper of Lee and Barker [14], as they used an external potential and the paper of Chapela *et al.* [15], as these Monte Carlo results are inconsistent with the other data. We also neglected one result of Nijmeijer *et al.* [11] and those of Reference [3] as the cut-off radii there are considerably larger than 2.5σ. In Reference [3] the resulting bubble and dew densities are already rather close to the bulk values, but a further discussion of these results may not be very conclusive as a non-spherical cut-off was used there for reasons intrinsic to the considered problem. In Reference [11] a system with 2048 particles with a cut-off of 7.33σ was used at $kT/\varepsilon = 0.92$. The resulting bubble density is 0.740 ± 0.002 compared to 0.7458 from Adams [4] and 0.7417 from Nicolas *et al.* [6] and the resulting dew density is 0.018 ± 0.001 compared to 0.01529 from Adams [4] and 0.01591 from Nicolas *et al.* [6].

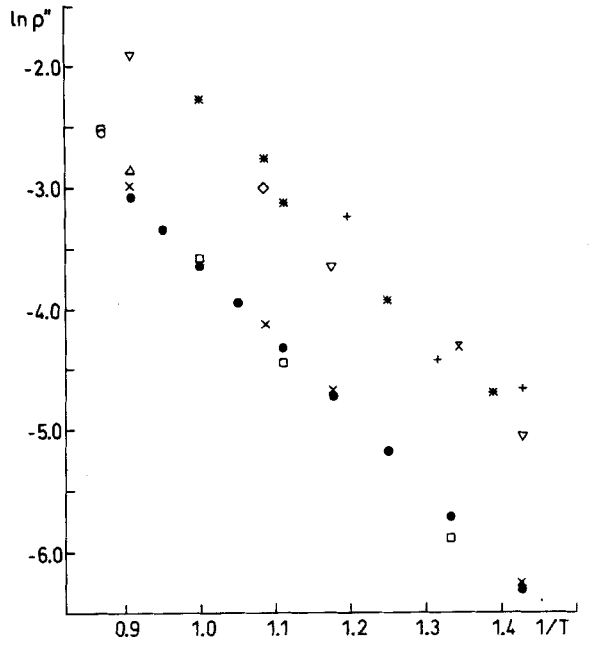

Figure 2 Dew densities of the LJ fluid from bulk and interface simulations in a ln ρ'' vs. $1/T$ representation. Bulk simulation results: ● Adams [4], ○ Adams [5], × Nicolas *et al.* [6], □ Panagiotopoulos [7], △ NpT + test particle result from this work. Results from interface simulations all with a cut-off radius of 2.5σ and no long range correction: + Chapela *et al.* [8], * Nijmeijer *et al.* [11], ▽ this work, ⧖ Rao and Levesque [9], ◇ Rao and Berne [10].

From the one simulation of Nijmeijer *et al.* [11] we learn that increasing the cut-off radius shifts the orthobaric densities from interface simulation towards the bulk values. One should, however, note that using that large cut-off radii requires also large particle numbers and consequently long computation times. Alternatively, we could think about an inhomogenous long range correction which was already suggested by Rowley *et al.* [16] and proved to be important for adsorption studies with a cut-off of 2.5σ. In this paper, we will combine both methods, increase of the cut-off radius and use of long range corrections in order to explore how well the orthobaric densities from interface simulations can be brought into agreement with those from bulk simulations. With respect to the long range corrections, we will again use two different types, one which models the density profile by a step function and a second one which uses a density profile consistent with the simulated one. Studies will be performed at $kT/\varepsilon = 0.70, 0.85$, and 1.10 which are representative for a low, a medium and a high temperature.

As the long range tail of the LJ potential has that much influence on the orthobaric densities it may have also some influence on the resulting density profile in the interface, especially at higher temperatures. This problem will also be investigated in the present paper.

Before proceeding to these interface studies, we still want to recalculate the phase equilibrium for $kT/\varepsilon = 1.10$, as Figure 1 shows there a difference of 3 per cent between the results of Adams [4] and of Nicolas *et al.* [6]. Unfortunately, this

Table 1 Comparison of bubble densities ρ', dew densities ρ'', and vapour pressures p_σ for the LJ fluid from the bulk simulations of Adams [4], Nicolas *et al.* [6], and this work

Source	T	ρ'	ρ''	p_σ
Adams [4]	1.10	0.6319	0.0468	0.0413
Nicolas [6]	1.10	0.6518	0.0500	0.0435
This work	1.10	0.6442	0.0569	0.0472
Adams [4]	0.85	0.7798	0.00878	0.00701
Nicolas [6]	0.85	0.7752	0.00914	0.00728
Adams [4]	0.70	0.8494	0.00182	0.00125
Nicolas [6]	0.70	0.8460	0.00190	0.00131

temperature was not considered by Panagiotopoulos in his Gibbs ensemble calculations [7]. Here we will use the recently suggested NpT + test particle method [17].

In section 2 of this paper we present phase equilibrium data from bulk simulations of the LJ fluid at the three temperatures to be considered. In section 3 specific details of the interface simulations will be given together with the long range correction methods. The more general details of the simulations are postponed to the Appendix. Finally, in section 4 the results of the interface simulations will be presented and discussed.

In the following the reduced quantities $T^* = kT/\varepsilon$, $\rho^* = \rho\sigma^3$, and $p^* = p\sigma^3/\varepsilon$ will be used and the asterisk be omitted if no confusion can occur.

2. PHASE EQUILIBRIUM DATA FROM BULK SIMULATIONS

Let us start with an inspection of the phase equilibrium data for the Lennard-Jones fluid as they were given by Adams [4] and can be obtained from the equation of state of Nicolas [6]. For the three temperatures to be considered here, $T = 0.70, 0.85$, and 1.10 these data are compiled in Table 1. We note that the vapour pressures and dew densities agree at the lower temperatures by about 4 per cent whilst the agreement at the high temperature is only by about 6 per cent. Moreover, we see that whilst the bubble densities agree within 0.5 per cent at the lower temperatures, there is a discrepancy of more than 3 per cent at the high temperature. We therefore thought it to be interesting to recalculate the phase equilibrium there with the recently developed NpT + test particle method [17]. The results are contained in Table 1 and Figures 1 and 2.

Regarding Figure 1 we observe that the bubble density determined here is lying slightly above the straight line connecting Adams' [4, 5] bubble densities at $T = 1.05$ and 1.15 which is a satisfying result.

In addition, we learn from Table 1 that the vapour pressure and the dew density determined here are remarkably higher than the values of Adams [4] and Nicolas *et al.* [6]. To support our results, we mention two facts. The one is that a WCA-type perturbation theory [18] has already been observed [19] to yield higher vapour pressures than were obtained by Adams. Secondly, our vapour pressure is in quite good agreement with that of real methane [20] which can be well described by a LJ-interaction in the whole fluid region [21] using the parameters of Reference [19] or of McDonald and Singer [22]. A recalculation of the whole coexistence curve of the

LJ-fluid with the NpT + test particle method together with a more detailed discussion shall be given elsewhere [23].

For the following, we will assume as the reference orthobaric densities at $T = 1.10$ those determined here and at the lower temperatures the values given by Adams [4] keeping in mind that the dew densities may be inaccurate by about 20 per cent.

3. DETAILS OF THE INTERFACE SIMULATIONS

In order to obtain the liquid vapour interface, the following procedure was applied. The system of N particles was started from an ordered state in a rectangular box of dimension $L_x \times L_y \times L_z$ with $L_x = L_y$. A first run was made in that box with usual periodic boundary conditions and the minimum image conventions in all three dimensions in order to get a liquid state. Then the periodic boundary conditions were removed in the z-direction. At the same time the box was enlarged in the z-direction symmetrically from L_z to $3L_z$ with reflecting walls on both sides. The system was equilibrated now over a period of at least 20000 time steps resulting in a liquid slab in the center of the box in phase equilibrium with the gas on both sides.

After the equilibration period a production run was started which lasted over at least 18000 up to 75000 time steps. The local density was determined by counting the number of particles after each 10^{th} time step in 300 intervals in the z-direction and accumulating the numbers over the whole production run. Concerning the reflecting walls, one expects them to act rather similar as hard walls for which the sum rule $\rho = p/kT$ holds. In the actual calculation p should be the vapour pressure p_σ and as the dew density ρ'' is always greater than the ideal gas density corresponding to p_σ, the density profile has to drop down at the reflecting walls. Hence, the dew density was determined as the average density of the gas in both regions neglecting the strips close to the walls and approaching the liquid gas interfaces till a significant increase in the local density was observed. For the bubble densities, the counting was started at the center of the liquid slab and went outwards on both sides till the local density decreased.

Regarding the long range corrections, we must be aware that in an inhomogenous fluid an additional force is created by them. This has to be implemented into the molecular dynamics algorithm in a similar way as an external force. The easiest way to determine this additional force $\Delta\mathbf{F}$ is to calculate firstly the long range contribution Δu to the potential energy at a point $\mathbf{r}_1$ and then to differentiate, $\Delta\mathbf{F}(\mathbf{r}_1) = -\nabla_1(\Delta u(\mathbf{r}_1))$. To derive our working equation, let us start out with the expression for Δu

$$\Delta u(\mathbf{r}_1) = \int_{r_{12}>r_c} u(r_{12})\rho(\mathbf{r}_2)\, d\mathbf{r}_2, \tag{1}$$

where u is the intermolecular potential, r_c its cut-off radius in the simulation, and $\rho(\mathbf{r})$ the local density. For the special case of the LJ potential and planar geometry one obtains after straightforward calculations

$$\begin{aligned}\Delta u(z_1)/8\pi &= \int_{-\infty}^{-r_c} dz_{12}\rho(z_2)\,(z_{12}^{-10}/10 - z_{12}^{-4}/4) + \int_{-r_c}^{r_c} dz_{12}\rho(z_2)\,(r_c^{-10}/10 - r_c^{-4}/4) \\ &\quad + \int_{r_c}^{\infty} dz_{12}\rho(z_2)\,(z_{12}^{-10}/10 - z_{12}^{-4}/4),\end{aligned} \tag{2}$$

where $z_{12} = z_2 - z_1$, and the units used are ε for the energy, σ for all distances and σ^{-3} for the density. Differentiation then leads to the additional force contribution which in our case acts only in the z-direction

$$\Delta F_z(z_1)/8\pi = -\int_{-\infty}^{-r_c} dz_{12}\rho(z_2)\,(z_{12}^{-11} - z_{12}^{-5}) - \int_{r_c}^{\infty} dz_{12}\rho(z_2)\,(z_{12}^{-11} - z_{12}^{-5}), \quad (3)$$

and the unit for the force being ε/σ.

Equation (3) can now be implemented in two different ways into the simulations. One possibility is to take the local density $\rho(z)$ consistent with the resulting density profile which we call the LRC2 method. A simpler possibility for the liquid vapour interface simulations is to assume the density profile to be a step function with the discontinuity in the Gibbs dividing surface; we call that the LRC1 method. Let $z = l$ be the position of the discontinuity, then we have to distinguish three different cases depending on the position of z_1. A simple calculation yields

$$\Delta F_z(z_1)/8\pi = (\rho' - \rho'')[(l - z_1)^{-10}/10 - (l - z_1)^{-4}/4] \quad \textit{for } z_1 < l - r_c, \quad (4a)$$

$$= (\rho' - \rho'')[r_c^{-10}/10 - r_c^{-4}/4] \quad \textit{for} \quad (4b)$$

$$l - r_c < z_1 < l + r_c,$$

$$= (\rho' - \rho'')[(z_1 - l)^{-10}/10 - (z_1 - l)^{-4}/4] \quad \textit{for} \quad (4c)$$

$$z_1 > l + r_c.$$

In order to complete our terminology, we will denote a simulation in which no long range correction was made with LRC0.

4. RESULTS AND DISCUSSION

Results for the orthobaric densities at $T = 0.70$, 0.85 and 1.10 together with decisive simulation parameters are given in Table 2. Some characteristic density profiles are shown in Figures 3–6.

Let us start with discussing the results at the highest temperature, $T = 1.10$. For run 13, characterized by $r_c = 2.5$ and LRC0, which means that we consider the LJ2.5 fluid, we see from Figure 3, that one does not obtain a well defined liquid slab but rather a Gaussian density profile. Extracting nevertheless rough values for the orthobaric densities one gets $\rho' = 0.441$ and $\rho'' = 0.149$ contained in Table 2. These values indicate that we are rather close to the critical temperature of the LJ2.5 fluid and give strong support to the estimate of van Megen and Snook [12] that the critical temperature of that fluid is 1.12. Including now in run 15 the long range correction LRC2 creates a sharper defined liquid slab as can be seen from Figure 3. The bubble density is increased now by about 30 per cent and the dew density decreased by the factor of 2. By comparing the results of runs 14 and 15 in Table 2 we also note that the effect of both long corrections LRC1 and LRC2 is nearly the same. A certain difference can be seen in the dew densities but it is not clear to us whether this is specifically due to the LRC or is within the accuracy of the simulations. The fact that LRC1 and LRC2 act rather similarly can be understood from Equations (4 a–c) which show that in LRC1 the correction force is rather smooth in spite of the assumed step function in the density.

Table 2 Orthobaric densities ρ' and ρ'' from the interface simulations of the LJ fluid at three different temperatures together with decisive simulation parameters. N is the number of particles, r_c the cut-off radius, TS the number of time steps in equilibrium, L_x and $3L_z$ give the size of the simulation box. LRC denotes the type of long range correction, where 0 means that no correction was made.

Run	N	r_c	TS	L_x	$3L_z$	LRC	ρ'	ρ''
$T = 0.70$								
1	864	2.5	60000	10.04	30.12	0	0.7857	0.00627
2	864	2.5	60000	10.04	30.12	1	0.8172	0.00374
3	864	4.5	30000	10.04	30.12	0	0.8339	0.00312
4	1372	4.5	25000	10.24	46.05	2	0.8378	0.00208
5	1372	5.0	25000	10.24	46.05	2	0.8403	0.00213
$T = 0.85$								
6	864	2.5	25000	10.27	30.81	0	0.7019	0.0256
7	864	2.5	61000	10.27	30.81	1	0.7448	0.0165
8	864	4.5	53000	10.27	30.81	0	0.7631	0.0134
9	864	4.5	55000	10.27	30.81	0	0.7642	0.0129
10	864	4.5	18000	10.27	30.81	1	0.7676	0.00767
11	1372	5.0	25000	10.47	47.10	2	0.7714	0.00918
12	1372	5.0	23000	10.47	47.10	2	0.7717	0.00861
$T = 1.10$								
13	864	2.5	25000	10.60	31.80	0	0.441	0.149
14	864	2.5	75000	10.60	31.80	1	0.570	0.0799
15	864	2.5	20000	10.60	31.80	2	0.565	0.0711
16	864	4.5	23000	10.60	31.80	0	0.6039	0.0683
17	864	4.5	47000	10.60	31.80	1	0.6107	0.0622
18	864	4.0	50000	9.26	41.67	2	0.6296	0.0518
19	1372	5.0	25000	10.80	48.60	2	0.6270	0.0572

Increasing the cut-off radius r_c to 4.5 and neglecting the long range correction (run 16) changes again the orthobaric densities dramatically compared to $r_c = 2.5$ without long range correction (run 13). The orthobaric densities are now even closer to the bulk values than in runs 14 and 15 where long range corrections were used for $r_c = 2.5$. Adding for $r_c = 4.5$ the long range correction LRC1 which was made in run 17 changes still the orthobaric densities but the effect is much weaker for this larger value of r_c than for $r_c = 2.5$.

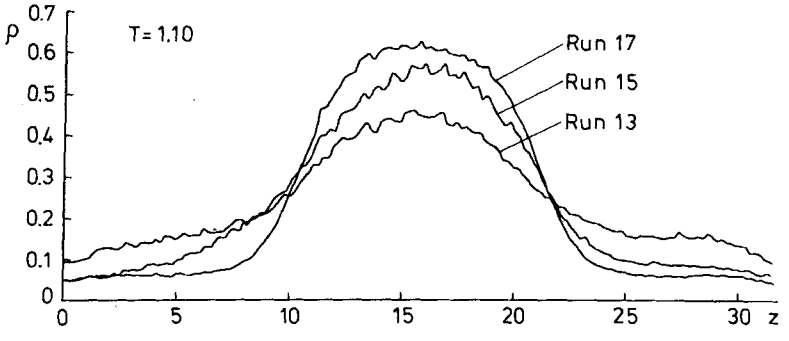

Figure 3 Density profiles of the liquid vapour interface at $T = 1.10$ from three simulations showing the effect of the cut-off radius and the long range correction. Run 13: $r_c = 2.5$, no LRC; run 15: $r_c = 2.5$, LRC2; run 17: $r_c = 4.5$, LRC1.

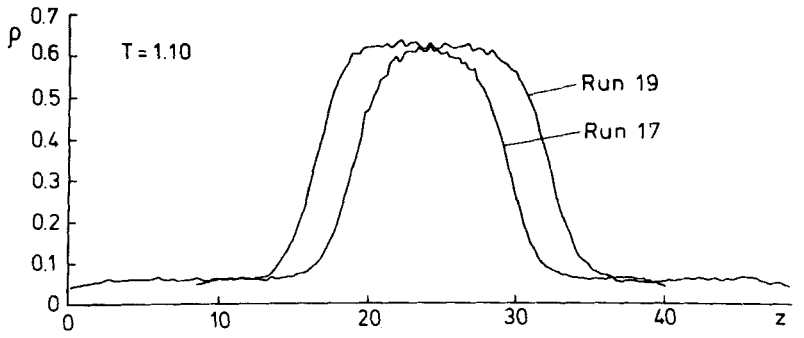

Figure 4 Density profiles of the liquid vapour interface at T = 1.10 from two simulations, showing the effect of the cut-off radius and the box length. Run 17: $r_c = 4.5$, $3L_z = 31.80$; run 19: $r_c = 5.0$, $3L_z = 48.60$.

Looking on the density profile of run 17 in Figure 3 one gets the feeling that the limiting values of the density have not yet been reached on both ends of the liquid vapour interface. Hence, the simulation box was made larger in the z-direction in runs 18 and 19. The profile of run 19 which is compared in Figure 4 with the profile of run 17 seems to have reached now "horizontal" values in the liquid and the gas. The bubble densities of runs 18 and 19 agree also reasonably well but we must state that they are still lower by about 2.5 per cent than the bulk value. It is somewhat surprising that the dew densities from runs 18 and 19 differ by nearly 10 per cent. Presently we do not have another explanation for that discrepancy than that it may be within the accuracy of the simulations. Comparing these dew densities with the bulk values we note that the result from run 19 is rather close to the NpT + test particle method and even the value of run 18 is higher than the results of Adams [4] and Nicolas [6] given in Table 1.

For $T = 0.85$ much of what has been stated above can be repeated keeping in mind that simulation becomes simpler at lower temperatures as the LJ2.5 system is further away from its critical point and the broadness of the liquid vapour interface becomes smaller with decreasing temperature. Of interest here is a comparison between runs

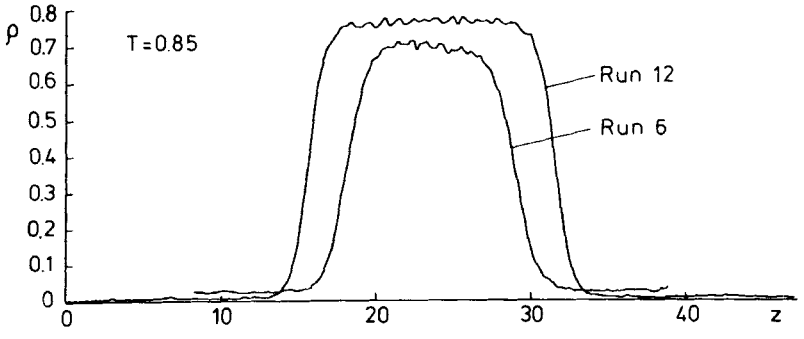

Figure 5 Density profiles of the liquid vapour interface at $T = 0.85$ from two simulations. Run 6: $r_c = 2.5$, no LRC, $3L_z = 30.81$; run 12: $r_c = 5.0$, LRC2, $3L_z = 47.10$.

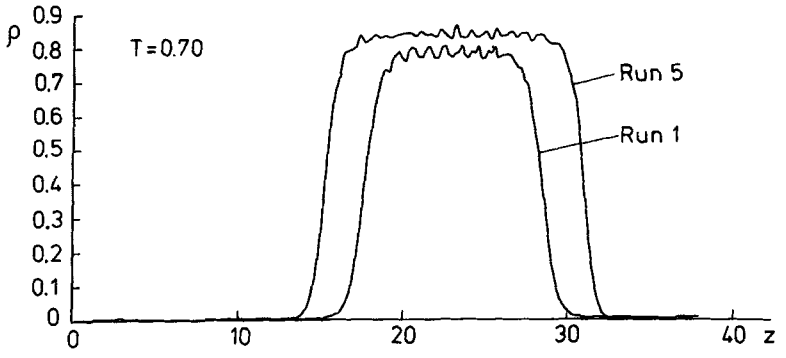

Figure 6 Density profiles of the liquid vapour interface at $T = 0.70$ from two simulations. Run 1: $r_c = 2.5$, no LRC, $3L_z = 30.12$; run 5: $r_c = 5.0$, LRC2, $3L_z = 46.05$.

8 and 9 and runs 11 and 12 which pairs were made under the same conditions and allow conclusions about the reproducibility of the results. We learn that the bubble densities agree nearly within 0.1 per cent in both cases but we also see that the dew densities from runs 11 and 12 differ by 6.6 per cent. Concerning the resulting values for the orthobaric densities we note that the bubble density from runs 11 and 12 with $r_c = 5.0$ and LRC2 is again lower than the bulk value, now by about 1 per cent, and that the dew densities agree within their scattering with the bulk values of Adams and Nicolas given in Table 1. The density profiles from run 6 with $r_c = 2.5$, no long range correction and a box length of 30.81 and from run 12 with $r_c = 5.0$, LRC2 and a box length of 47.10 are shown in Figure 5. This picture is rather similar to that given by Nijmeijer *et al.* [11] for $T = 0.92$ and shows besides the difference in the limiting liquid and gas densities also that the slope of the interface profiles is still somewhat different.

Let us finally come to lowest temperature $T = 0.70$. Compared to the higher temperatures the effect of correcting for the cut-off is smaller here for the bubble density and the density profiles are shown in Figure 6. The change in the dew densities between runs 1 and 5, however, is again a factor of 3 and the resulting dew density is higher by 13 per cent than the values of Adams and Nicolas given in Table 1. We also note that the slopes of the density profiles of runs 1 and 5 are still slightly different.

Summarizing we come to the conclusion that increasing the cut-off radius in the simulation and including long range corrections shift the orthobaric densities from the interface simulations close to the bulk values. The interface bubble densities however remain always somewhat lower than the bulk values: by 2.5 per cent at $T = 1.10$ and by 1 per cent at the lower temperatures. This result agrees with the findings of Nijmeijer *et al.* [11] and needs still some explanation. The interface dew densities decrease by a factor of 3 by accounting for the long range part of the potential but remain uncertain by about 10 per cent. Taking this inaccuracy into account they agree with the existing bulk dew densities within the accuracy of the latters which, however, is estimated to be only by about 20 per cent. For calculations of the surface tensions, which were not performed here, it may be still of interest that the cut-off radius has also an effect on the slope of the density profile in the interface.

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APPENDIX: METHODOLOGY OF THE SIMULATIONS

This Appendix yields details of the basic molecular dynamics algorithm used both in the bulk and the interface simulations. The algorithm follows closely the primer of Haile [24] using a fifth order predictor-corrector algorithm [25]. The program was vectorized following suggestions of Vogelsang *et al.* [26] using the CYBER 200 FORTRAN language and ran on the CYBER 205 machine at Ruhr-Universität Bochum.

The Hamiltonian of the used particles consisted of LJ potentials with a cut-off radius $r_{c,R}$ which was taken as 2.5 if not stated differently. Periodic boundary conditions together with the minimum image condition were employed in the bulk simulations in all three and in the interface simulations in the two transversal dimensions. The long range corrections were performed in the bulk simulations as usual, i.e. they had to be taken into account in the NpT runs after each time step. The long range corrections of the interface simulations are described in the main text. The time step was $\Delta t = 0.005\,\sigma\sqrt{m/\varepsilon}$ and the temperature was kept constant by momentum scaling i.e. using an isokinetic ensemble.