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Vapour liquid equilibria of the Lennard-Jones fluid from the NpT plus test particle method

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Using an improved version of the recently suggested NpT + test particle method, phase equilibria are determined for the Lennard-Jones fluid in the temperature range $T^* = 0{\cdot}70$ to $T^* = 1{\cdot}30$ in steps of $\Delta T^* = 0{\cdot}05$. For the final results, gas simulations are necessary only at the two highest temperatures; for $T^* = 1{\cdot}20$ and downwards the gas phase can be described with sufficient accuracy by the Haar–Shenker–Kohler equation. The resulting vapour pressures, bubble and dew densities can be correlated by the equations

$$\ln p_\sigma^* = 1{\cdot}2629T^* - 4{\cdot}8095/T^* - 0{\cdot}15115/T^{*4},$$

$$\rho'^* = \rho_c^* + 0{\cdot}477(T_c^* - T^*)^{1/3} + 0{\cdot}2124(T_c^* - T^*) - 0{\cdot}01151(T_c^* - T^*)^{3/2},$$

$$\rho''^* = \rho_c^* - 0{\cdot}477(T_c^* - T^*)^{1/3} + 0{\cdot}05333(T_c^* - T^*) + 0{\cdot}1261(T_c^* - T^*)^{3/2},$$

with the critical temperature and density being $T_c^* = 1{\cdot}310$ and $\rho_c^* = 0{\cdot}314$, respectively. Then a detailed comparison with other simulation results and perturbation theory results is given. Outstanding findings are that the present data are rather smooth, that they match quite well the early data of Hansen and Verlet (1969, *Phys. Rev.*, **184**, 151) and are much closer to perturbation theory than most previous results. Finally, using the vapour pressure equation and directly calculated volume changes and enthalpies of vaporization in combination with the Clausius–Clapeyron equation reveals excellent thermodynamic consistency in the present results.

1. Introduction

Recently, we suggested the NpT + test particle method for the determination of vapour liquid phase equilibria (VLE) by simulation [1]. The basic idea of that method is simply to determine the phase equilibrium from the intersection of the vapour and the liquid branches in the chemical potential versus pressure diagram. An improved version of this method has been used in the meantime for the determination of an effective pair potential for carbon dioxide, being of two-centre Lennard-Jones plus point quadrupole type [2]. Other existing methods for the determination of VLE by simulations are the constrained MC method of Hansen and Verlet [3], the calculation of an averaged chemical potential in combination with an equation of state for the liquid by Adams [4], the application of the grand canonical MC method by Adams [5], the calculation from an equation of state for the whole fluid region by Nicolas *et al.* [6], the Gibbs ensemble method [7–10] and a modification thereof [11] as well as the simulation of the liquid–vapour interface [12]. As all these methods were applied to the Lennard-Jones (LJ) system and as for most of these methods results are available only for the LJ system, we decided to apply the NpT + test particle method also to that system in order to facilitate comparison with the other methods.

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2. The method

We consider a pure fluid with a given intermolecular potential between the particles. The basic idea of the NpT + test particle method for the determination of the vapour liquid phase equilibria is to construct at a given temperature the liquid and the vapour branches in the μ,p (chemical potential versus pressure) plane and to find the point of intersection of these two branches.

Let us assume a prescribed temperature T, and start with the construction of the liquid branch in the μ,p plane. In general, one will have a rough idea about the vapour pressure p_σ of the fluid under consideration at the given temperature. The construction of the liquid branch isotherm starts from an arbitrarily chosen pressure p_0, which should be not too different from the still unknown vapour pressure p_σ; at low temperatures the pressure $p = 0$ can be taken as a good choice for p_0. Having fixed T and p_0, a molecular dynamics or Monte Carlo simulation has to be performed now in the NpT ensemble. In order to obtain from this simulation also the chemical potential, we apply Widom's test particle method [14], according to which

$$\mu/kT = -\ln\langle V\exp(-\beta\psi)\rangle/N, \tag{1}$$

where ψ denotes the potential energy of the test particle, V the instantaneous volume and the brackets ensemble averaging in the isobaric-isothermal ensemble. From this one simulation at T and p_0 we obtain the chemical potential μ the density ρ and also the isothermal compressibility β_T by

$$\beta_T = \frac{1}{kT}\frac{1}{\langle V\rangle}\{\langle V^2\rangle - \langle V\rangle^2\}. \tag{2}$$

For later purposes it is also important to compute the enthalpy h as well as its isothermal derivative with respect to the pressure

$$\left(\frac{\partial h}{\partial p}\right)_T = -\frac{1}{kT}\{\langle UV\rangle - \langle U\rangle\langle V\rangle\} - \frac{p}{kT}\{\langle V^2\rangle - \langle V\rangle^2\}. \tag{3}$$

The crucial point is now that from this one simulation we have obtained the chemical potential as a function of the pressure not only at p_0 but also in a certain surrounding of p_0 as the density and the isothermal compressibility yield just the first coefficients in the Taylor expansion

$$\mu = \mu_0 + \left(\frac{\partial\mu}{\partial p}\right)_0 (p - p_0) + \frac{1}{2}\left(\frac{\partial^2\mu}{\partial p^2}\right)_0 (p - p_0)^2 + \cdots, \tag{4}$$

with

$$\left(\frac{\partial\mu}{\partial p}\right) = v, \tag{5}$$

and

$$\left(\frac{\partial^2\mu}{\partial p^2}\right) = -\beta_T v, \tag{6}$$

where $v = \langle V\rangle$. We should note that the accuracy of this isotherm branch is not so much influenced by using only a second order Taylor expansion but rather by the accuracy of $\mu(p_0)$ achieved in the simulation.

In order to construct the gas branch of the isotherm, one can in principle proceed

as for the liquid branch. At lower temperatures, however, the dew densities are rather low and physically based equations of state (EOS) are available for that density region. As the use of these EOSs requires considerably less computer time than a simulation it is favourable to use an EOS to describe the gas. Moreover, a constant pressure simulation at these low densities requires (at least in MD) considerable experience. A low density EOS that can be used for all intermolecular potentials is the viral expansion truncated after the second virial coefficient B which can be obtained easily by direct integration over the Mayer f-function. From the basic equation for the residual Helmholtz energy a^{res} as a function of the density ρ

$$a^{\mathrm{res}}/RT = B\rho, \tag{7}$$

one immediately obtains

$$\frac{p}{\rho kT} = 1 + B\rho. \tag{8}$$

The relation $\mu = \mu(p)$ is obtained from equation (7) as

$$\mu/kT = \ln\rho + 2B\rho, \tag{9}$$

with ρ being given by inversion of equation (8) as

$$\rho = [(4Bp/kT + 1)^{1/2} - 1]/2B. \tag{10}$$

For nonpolar molecules, an interesting extension of the truncated virial expansion to higher densities is given by the Haar–Shenker–Kohler equation [13], sometimes also called perturbed virial expansion

$$a^{\mathrm{res}}/RT = B\rho + a_{\mathrm{H}}^{\mathrm{res}}/RT - B_{\mathrm{H}}\rho, \tag{11}$$

where $a_{\mathrm{H}}^{\mathrm{res}}$ denotes the free energy of appropriately chosen hard bodies and B_{H} the hard body second virial coefficient. The two above mentioned equations of state, the truncated virial expansion and the HSK equation, are more or less restricted to lower densities. For the purpose of calculating VLE, this means that at higher temperatures the dew density may be already outside the region of validity of these equations. Hence, for the higher temperatures one has to perform also a simulation on the gas side. Then, in decreasing the temperature one has to check by parallel use of the simulations and the EOS where the latter enters its region of validity and can replace the simulation.

So far, we have determined the liquid branch of $\mu(p)$ in the form of equation (4) by one simulation. The gas branch of $\mu(p)$ is obtained at the higher temperatures also in the form of equation (4) by one simulation; at the lower temperatures it is obtained from the truncated virial expansion in the form of equations (9) and (10) or the HSK analogue without a simulation. The intersection of these two isotherm branches then yields immediately the vapour pressure p_σ.

The next items of interest are the bubble density ρ' and the dew density ρ''. Let us denote the result from the liquid simulation at pressure p_0 by ρ_0 and β_{T0}, then we obtain in a straightforward way

$$\rho' = \rho_0 + (\beta_{T0}\rho_0)(p_\sigma - p_0). \tag{12}$$

If on the gas side a simulation had been performed the procedure for the determination of the dew density would be the same. Otherwise, the gas density belonging to p_σ has to be determined via the EOS. In that case, a certain caution is necessary if the

truncated virial expansion has been used. Generally, the relation $\mu(p)$ expressed by equations (9) and (10) is accurate still at pressures where the thermal equation of state, equation (8), has broken down already. This means that, eventually, for the determination of the vapour pressure a simulation for the gas may not be necessary, but it may become necessary for the determination of the dew density.

The final quantity of interest is the enthalpy of vaporization which requires the enthalpy on the dew and the bubble lines. The latter can be obtained from the enthalpy h_0 and its pressure derivative $(\partial h/\partial p)_0$ computed at the pressure p_0 as

$$h(p_\sigma) = h_0 + \left(\frac{\partial h}{\partial p}\right)_0 (p_\sigma - p_0). \tag{13}$$

The enthalpy on the dew line can be obtained by the same procedure if a simulation has been performed for the gas. Otherwise, appropriate thermodynamic manipulations with the EOS yield the desired result.

We should mention that the above described procedure is somewhat different from that used in the original publication [1]. Although it was pointed out that one simulation for each phase would be sufficient, we actually used two. The idea was that with two pairs of μ and $(\partial\mu/\mathrm{d}p)$ a higher accuracy could be achieved in determining the isotherm branch. Presently, we believe that the resulting gain in accuracy does not justify the effort of a second simulation and the subsequent regression procedure; a more detailed investigation of that question, however, would still be interesting. We also would like to remark that the dependence of the chemical potential on the test particle cut-off radius reported previously [1] does not exist, and was caused by an error in our programing of the long range correction of the test particle potential energy ψ [1*b*].

For the VLE calculation of the LJ fluid we decided to apply the HSK equation [13] on the gas side. Denoting the LJ potential by u with the usual parameters ε and σ we introduce a hard sphere diameter d by

$$d = \int_0^{2^{1/6}\sigma} [1 - \exp\{-\beta(u + \varepsilon)\}]\,\mathrm{d}r, \tag{14}$$

and a packing fraction η by

$$\eta = \frac{\pi}{6}\rho d^3. \tag{15}$$

Then the pressure, the chemical potential and the residual enthalpy are given by

$$\frac{p}{\rho kT} = 1 + B\rho + \frac{\eta^2(10 - 12\eta + 4\eta^2)}{(1-\eta)^3}, \tag{16}$$

$$\frac{\mu}{kT} = \ln\rho + 2B\rho + \frac{\eta^2(15 - 21\eta + 8\eta^2)}{(1-\eta)^3}, \tag{17}$$

$$\frac{h^{\mathrm{res}}}{RT} = \left(B - T\frac{\partial B}{\partial T}\right)\rho + \frac{(\eta^2 - T\partial\eta/\partial T)(10 - 12\eta + 4\eta^2)}{(1-\eta)^3}. \tag{18}$$

The region of validity of the HSK equation will be discussed in the next section by comparison with gas simulation results.

Two remarks are still necessary concerning the actual calculations. One is that if $\mu(p)$ was constructed by simulations, only the first derivative in the Taylor series expansion was included here. The second concerns the calculation of the enthalpy on

Table 1. Simulation raw data on the liquid side. The numbers in parentheses denote the uncertainties in the last digits.

T^*	p^*	ρ^*	β_T^*	u^{res*}	$\tilde{\mu}$
0·70	0·00	0·84257(18)	0·0847(55)	−6·0957(17)	−6·300(46)
0·75	0·00	0·82138(38)	0·0908(32)	−5·9069(33)	−5·694(28)
0·80	0·00	0·79887(39)	0·1125(75)	−5·7102(33)	−5·191(18)
0·85	0·00	0·77553(24)	0·117(11)	−5·5108(21)	−4·783(16)
0·90	0·01	0·75202(13)	0·154(16)	−5·3123(12)	−4·4338(90)
0·95	0·02	0·72833(26)	0·186(21)	−5·1157(21)	−4·108(18)
1·00	0·03	0·70179(37)	0·281(15)	−4·9018(25)	−3·8226(71)
1·05	0·03	0·67197(44)	0·369(39)	−4·6686(32)	−3·6115(96)
1·10	0·05	0·6414(12)	0·385(69)	−4·4331(84)	−3·391(13)
1·15	0·06	0·60557(64)	0·613(99)	−4·1693(34)	−3·2003(43)
1·20	0·08	0·5678(22)	1·05(12)	−3·897(14)	−3·0244(46)
1·25	0·10	0·5157(22)	2·32(48)	−3·541(14)	−2·8817(35)
1·30	0·12	0·4259(58)	13·6(40)	−2·965(36)	−2·7523(48)

the bubble line which, according to the general procedure described above, can be obtained from equation (13) with $(\partial h/\partial p)$ given by the fluctuation formula, equation (3). Alternatively, if simulation data are available on several isotherms lying close together, one can determine $(\partial h/\partial p)$ also via the thermodynamic relation

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p, \tag{19}$$

which was the procedure used here.

3. Simulation data and applicability of the HSK equation

The raw data necessary for the calculation of VLE were obtained by molecular dynamics simulations. Technical details including the method to determine the statistical uncertainties are described in the appendix.

In the following, the reduced quantities $T^* = kT/\varepsilon$, $p^* = p\sigma^3/\varepsilon$, $\rho^* = \rho\sigma^3$, $\beta_T^* = \beta_T\varepsilon/\sigma^3$ will be used. Moreover, the residual internal energy u^{res} is the average potential energy and $u^{res*} = u^{res}/N\varepsilon$. The residual enthalpy is defined as $h^{res} = u^{res} + pv - RT$, and $h^{res*} = h^{res}/N\varepsilon$. Finally, $\tilde{\mu}$ is the reduced density dependent part of the chemical potential, $\tilde{\mu} = \mu^{res}/kT + \ln \rho^*$.

Phase equilibria calculations were performed in the temperature range $T^* = 0{\cdot}70$ to 1·30 with temperature intervals $\Delta T^* = 0{\cdot}05$. The simulation raw data for all temperatures of the liquid are given in table 1. For the gas, simulations were performed in the temperature range $T^* = 1{\cdot}10$–1·30 with two independent runs at $T^* = 1{\cdot}20$; the results are given in table 2.

Table 2. Simulation raw data on the gas side.

T^*	p^*	ρ^*	β_T^*	u^{res*}	$\tilde{\mu}$
1·10	0·05	0·06179(16)	23·2(24)	−0·5422(15)	−3·3252(14)
1·15	0·06	0·07366(44)	30·7(22)	−0·640(11)	−3·1989(24)
1·20	0·08	0·10715(45)	25·5(15)	−0·9002(64)	−3·0085(10)
1·20	0·08	0·10694(15)	25·2(17)	−0·8978(30)	−3·0094(14)
1·25	0·10	0·1463(18)	31·8(42)	−1·184(19)	−2·8712(24)
1·30	0·12	0·1929(21)	24·2(89)	−1·509(18)	−2·7531(15)

Table 3. Comparison of chemical potentials from simulations and the HSK equation.

T^*	p^*	$\tilde{\mu}_{sim}$	$\tilde{\mu}_{HSK}$	Δ/Δ_{simgas}	Δ/Δ_{simliq}
1·10	0·05	−3·325 2(14)	−3·320 3	3·5	0·38
1·15	0·06	−3·198 9(24)	−3·197 6	0·5	0·30
1·20	0·08	−3·008 5(10)	−3·005 6	2·9	0·63
1·20	0·08	−3·009 4(14)	−3·005 6	2·7	0·83
1·25	0·10	−2·871 2(24)	−2·863 5	3·2	2·2
1·30	0·12	−2·753 1(15)	−2·747 3	3·9	1·2

Columns 3 and 4 contain the gas phase results, their difference being Δ. Moreover, Δ_{simgas} is the simulation uncertainty for $\tilde{\mu}$ on the gas side whereas Δ_{simliq} denotes that uncertainty on the liquid side.

Table 4. Comparison of gas densities from simulations and the HSK equation.

T^*	p^*	ρ^*_{sim}	ρ^*_{HSK}	$\Delta/\%$
1·10	0·05	0·061 79(16)	0·061 97	0·3
1·15	0·06	0·073 66(44)	0·073 19	−0·6
1·20	0·08	0·107 15(45)	0·106 14	−0·9
1·20	0·08	0·106 94(15)	0·106 14	−0·7
1·25	0·10	0·146 3(18)	0·144 5	−1·2
1·30	0·12	0·192 9(21)	0·179 4	−7·0

The crucial point is to determine the temperature up to which the HSK equation can be used to describe the gas. In order to answer this question, we compare in table 3 the chemical potential from the HSK equation with simulation results and, in table 4, the density. First, we learn from table 3 that the $\tilde{\mu}$ values from HSK agree for all temperatures except for $T^* = 1{\cdot}25$ with the simulated values within the first three digits, which is remarkable. For the further discussion we use the statistical uncertainties of the chemical potential Δ_{simgas} on the gas side and Δ_{simliq} on the liquid side as well as the difference $\Delta = \tilde{\mu}_{HSK} - \tilde{\mu}_{simgas}$. The essential idea is now that the HSK equation can be used for $\mu(p)$ as long as Δ is either smaller than Δ_{simgas} or Δ_{simliq}, which is the case up to $T^* = 1{\cdot}20$. For the densities, the difference $\rho^*_{HSK} - \rho^*_{sim}$ is given in table 4 as a percentage, and we learn that it remains below 1% also up to $T^* = 1{\cdot}20$. This again is a remarkable accuracy in that temperature and pressure range where the p, ρ-isotherms become already rather flat. Hence, we decided to use the HSK equation for the gas up to $T^* = 1{\cdot}20$ and the simulation data only at $T^* = 1{\cdot}25$ and $1{\cdot}30$.

4. Phase equilibria results and discussion

The phase equilibria were calculated according to the method described above in the temperature range $T^* = 0{\cdot}70$–$1{\cdot}30$ with $\Delta T^* = 0.05$. The data for the liquid phase were taken from table 1. For the gas phase, the HSK equation was used up to $T^* = 1{\cdot}20$, and for the higher temperatures the simulation data from table 2 were used. The results are compiled in table 5 together with uncertainty values calculated from the error propagation law; no statistical uncertainties were assumed for the HSK values.

Having obtained the vapour pressures p_σ, the bubble densities ρ' and the dew densities ρ'' at each temperature independently of the results at other temperatures, it seemed interesting to correlate the coexistence properties by equations. On that

Table 5. Vapour liquid phase equilibria.

T^*	p_σ^*	ρ'^*	ρ''^*	h'^{res*}	h''^{res*}	$\tilde{\mu}_\sigma$
0·70	0·00131(6)	0·84266(18)	0·00193(10)	−6·7947(17)	−0·0367(19)	−6·298(46)
0·75	0·00264(7)	0·82158(38)	0·00363(10)	−6·6550(33)	−0·0651(18)	−5·690(28)
0·80	0·00470(9)	0·79929(39)	0·00617(12)	−6·5070(33)	−0·1052(21)	−5·184(18)
0·85	0·00769(13)	0·77623(25)	0·00970(22)	−6·3560(21)	−0·1580(36)	−4·772(16)
0·90	0·01168(12)	0·75221(13)	0·01426(16)	−6·1981(12)	−0·2228(25)	−4·4313(92)
0·95	0·01741(37)	0·72798(27)	0·02081(51)	−6·0393(21)	−0·3128(77)	−4·112(19)
1·00	0·02505(22)	0·70081(38)	0·02964(32)	−5·8601(25)	−0·4295(47)	−3·8296(74)
1·05	0·03384(43)	0·67292(46)	0·03974(65)	−5.6736(32)	−0·5562(92)	−3·606(10)
1·10	0·04511(83)	0·6401(12)	0·0533(14)	−5·4528(84)	−0·721(19)	−3·398(14)
1·15	0·05974(41)	0·60547(66)	0·07267(79)	−5·2200(34)	−0·950(11)	−3·2007(49)
1·20	0·07718(66)	0·5661(22)	0·0987(16)	−4·948(14)	−1·243(21)	−3·0285(56)
1·25	0·0973(11)	0·5125(26)	0·1339(67)	−4·568(25)	−1·631(43)	−2·8858(50)
1·30	0·1204(23)	0·428(15)	0·195(11)	−3·989(66)	−2·206(71)	−2·7517(88)

basis a good comparison can also be made with other simulation data and with perturbation theory results. Moreover, a vapour pressure correlation can also be used to check the thermodynamic consistency of the data.

In order to measure the quality of a correlation equation for a quantity X it is usual in empirical thermodynamics to use the standard deviation $D(X)$ defined as

$$D(X) = \left\{ \frac{1}{n} \sum_{i=1}^{n} \left[\frac{(X_{i,\mathrm{exp}} - X_{i,\mathrm{eq}})}{\Delta X_i} \right]^2 \right\}^{1/2}, \tag{20}$$

where $X_{i,\mathrm{exp}}$ denotes the measured value, $X_{i,\mathrm{eq}}$ the value from the correlation equation and ΔX_i the experimental uncertainty. It seems useful to apply the same concept also to simulation results with ΔX_i being the simulation uncertainty. The value $D = 1$ then means that, on the average, all quantities are represented by the correlation equation within their simulation uncertainty.

Let us start with the vapour pressure equation. The most simple ansatz one may think of is $\ln p_\sigma = a + b/T$ and a least squares procedure yields

$$\ln p_\sigma^* = 3{\cdot}0634 - 6{\cdot}7557/T^*, \tag{21}$$

with $D(p_\sigma) = 0{\cdot}88$. This equation is used now for a comparison of the present with previous simulation results as shown in figure 1. Included are results from Hansen and Verlet [3], Adams [4, 5], Gibbs ensemble results [7–10] and vapour pressures calculated from the Nicolas *et al.* equation of state [6]. Results from a modification of the Gibbs ensemble [11] were not included as they would be partly outside the figure. Considering our own results we recollect that equation (21) yields a standard deviation of only 0·88, and one can easily verify that the equation represents all data nearly within their simulation uncertainty. Nevertheless, the deviation of the directly calculated results from the correlation shows a systematic sinusoidal behaviour.

Looking now at the vapour pressures of Nicolas *et al.* [6], we observe that they are quite smooth and show a similar sinusoidal behaviour but are about 5% lower than our values. Similar observations hold for the low temperature Adams values [4] which, however, are even lower than those of Nicolas *et al.* The smooth behaviour of both data sets is not so surprising as they were obtained via equations of state by which the raw simulation data have already been smoothed. Such a presmoothing did not occur with our results, which were obtained directly from the simulations and independently of each other. The reoccurrence of the sinusoidal behaviour indicates

Figure 1. Comparison of the present with previous simulation data for the vapour pressure on the basis of the correlation $\ln p_\sigma^* = 3{\cdot}0634 - 6{\cdot}7577/T^*$. The symbols denote: ●, this work; +, Hansen and Verlet [3]; ○, Adams [4, 5]; ×, Nicolas *et al.* [6]; ▽, Panagiotopoulos [7]; △, Panagiotopoulos *et al.* [8]; ◇, Smit *et al.* [9, 10]. For $T^* = 1{\cdot}15$, the Hansen and Verlet value coincides with the present result within the graphical representation.

that it could have some physical background, a point which will be discussed later in more detail. There remains now the question why the Nicolas *et al.* and the low-temperature Adams results are considerably lower than ours. With respect to the Nicolas *et al.* results, we recall that in the construction of their equation of state they prescribed the critical quantities as $T_c^* = 1{\cdot}35$, $p_c^* = 0{\cdot}142$, and $\rho_c^* = 0{\cdot}35$ which, in our opinion, are all considerably too high. Adams [5] obtained $T_c^* = 1{\cdot}30$, $p_c^* = 0{\cdot}13$, and $\rho_c^* = 0{\cdot}33$, whereas this work yields $T_c^* = 1{\cdot}31$, $p_c^* = 0{\cdot}126$, and $\rho_c^* = 0{\cdot}314$, as will be seen later. As it is known from empirical thermodynamics that one prescribed point on the coexistence curve strongly influences the whole curve, one could think of comparing p/p_c as function of T/T_c. In that case the Nicolas *et al.* vapour pressures would be even higher by about 3% than ours. Hence, we believe that the rather low vapour pressures of Nicolas *et al.* are simply a consequence of their not completely justified assumptions on the critical quantities. The situation is rather different with Adams low-temperature results, who used a free energy expression composed of an equation of state for the liquid by McDonald and Singer [15] and a constant c fixing the absolute free energy value. The quantity c was determined by several grand canonical Monte Carlo simulations and subsequent averaging of the results. Closer inspection of the original data shows that for $T^* = 1{\cdot}15$ Adams gives in his low-temperature paper [4] the pair of values $\rho^* = 0{\cdot}66277$ and $\mu^{res}/N\varepsilon = -2{\cdot}981$ ($\mu^{res} = \mu - kT \ln \rho$), whereas in his high temperature paper [5] he obtained $\rho^* = 0{\cdot}663$ and $\mu^{res}/N\varepsilon = -2{\cdot}867$. This corresponds to a difference in $\tilde{\mu}$ of 0·10 which would raise his low-temperature vapour pressure by 10%; the published values

Figure 2. Deviation plot of our directly calculated vapour pressure from the correlation equation $\ln p_\sigma^* = 1{\cdot}2639\ T^* - 4{\cdot}8095/T^* - 0{\cdot}15115/T^{*4}$. Note the different scale in comparison with figure 1.

[4] are too low by 8% in comparison with our data. In this connection it is remarkable that his vapour pressures suddenly jump above ours at $T^* = 1{\cdot}15$, where he changes from the low temperature [4] to the high temperature [5] vapour line. An additional indication that the chemical potential obtained by Adams from the equation of state is too low is given by a comparison at the state point $T^* = 1{\cdot}20$, $\rho^* = 0{\cdot}70$. His equation of state yields there $\mu^{\text{res}}/kT = -1{\cdot}99$, whereas the most reliable simulation values from different authors yield $-1{\cdot}92 \pm 0{\cdot}02$, as shown in the appendix.

We want to consider now the vapour pressures which were calculated directly by simulations without using an equation of state. Looking first at the results of the pioneering work of Hansen and Verlet [3], we note that at $T^* = 1{\cdot}15$ our results coincide with theirs within the graphical representation in figure 1. At $T^* = 0{\cdot}75$ their vapour pressure is lower by about 5% than our value, but we should remember that only our uncertainty there amounts to about 3%. Hence, we conclude that the agreement of the present with those more than 20-year-old results is quite satisfying. As far as the Gibbs ensemble results [7–10] are concerned, not much can be said about them except that they are strongly scattered.

Let us return now to the correlation equation for our vapour pressure results. As it seems that the sinusoidal deviation of the directly simulated vapour pressures from correlation equation (21) may have some physical reason, it is rewarding to look for a better correlation. That was found to be

$$\ln p_\sigma^* = 1{\cdot}2629\ T^* - \frac{4{\cdot}8095}{T^*} - \frac{0{\cdot}15115}{T^{*4}}, \tag{22}$$

with $D(p_\sigma) = 0{\cdot}61$. A deviation plot of the simulation data from this correlation given in figure 2 reveals the better performance of equation (22) in comparison with equation (21). It may be interesting now to look on the derivatives $\mathrm{d}[\ln(p/p_c)]/\mathrm{d}(T_c/T)$ from equations (21) and (22) and from some real substance equations displayed in figure 3. Without overemphasizing the point, we get from inspection of figure 3 the impression that equation (22) is not merely a better fit to the simulated vapour pressures but also contains somewhat more physics than equation (21).

Next, we consider equations for the dew density ρ'' and the bubble density ρ'. Regarding the functional form, we decided to start from a Guggenheim-type expression

Figure 3. The derivatives d ln (p/p_c)/d(T_c/T) from the LJ vapour pressure equation: – – –, equation (21); ——, equation (22); and from equations of real substances: ○, Ne [16]; +, Ar [16]; and x, CH_4 [17].

$\rho_c \pm c_1(T_c - T)^{1/3}$ and to extend that somewhat to get a good overall representation of our simulation results. Such a procedure gave

$$\rho''^* = \rho_c^* - 0{\cdot}477\,(T_c^* - T^*)^{1/3} + 0{\cdot}05333\,(T_c^* - T^*) + 0{\cdot}1261\,(T_c^* - T^*)^{3/2}, \tag{23}$$

with deviation $D(\rho''^*) = 1{\cdot}2$ and

$$\rho'^* = \rho_c^* + 0{\cdot}477\,(T_c^* - T^*)^{1/3} + 0{\cdot}2124\,(T_c^* - T^*) - 0{\cdot}01151\,(T_c^* - T^*)^{3/2}, \tag{24}$$

with deviation $D(\rho'^*) = 1{\cdot}1$. The critical temperature and density obtained via these correlations are $T_c^* = 1{\cdot}310$ and $\rho_c^* = 0{\cdot}314$. These equations are taken again as a basis for comparison of the present with previous simulation results displayed in figures 4 and 5.

Considering first the representation of our own results by the equations, we notice from figures 4 and 5 that they are quite well correlated except, perhaps, at $T^* = 1{\cdot}30$.

Figure 4. Comparison of the present with the previous simulation data for the dew density on the basis of the correlation, equation (23). Symbols as in figure 1.

Figure 5. Comparison of the present with previous simulation data for the bubble density on the basis of the correlation, equation (24). Symbols as in figure 1. Note that the scale is different for the higher temperatures.

The deviations there are not simply due to some scattering but reflect the discrepancy between finite size simulation results and the Guggenheim $(T - T_c)^{1/3}$ assumption, which we believe to be a reasonable description for an infinite system close to the critical temperature. Inspecting now the deviations of our directly calculated dew densities from the correlation equation in figure 4, we see a reasonable correspondence with the vapour pressure results in figure 1. Moreover, we note from figure 5 the very good representation of the bubble densities by the equation.

Looking now at figure 4 for the dew densities of the other authors [3–10] we get very much the same picture as obtained already from the vapour pressures. Interesting again is the very small deviation of the Hansen and Verlet results [3] from ours.

We proceed now to the comparison of the bubble densities with results of other authors, as shown in figure 5. We note that at the low temperatures the bubble densities are not very much influenced by the vapour pressure but rather reflect the accuracy of the liquid zero pressure density. The low temperature results of Adams [4] rely practically on the pvT data of McDonald and Singer [15], the pressures in which were already found by Nicolas *et al.* [6] to be too low at a given density. This fully explains why Adams' bubble densities are larger than ours by 0·5%. The Nicolas *et al.* results [6] agree at low temperatures reasonably well with ours, but drift off at the higher temperatures in order to reach the prescribed critical density $\rho_c^* = 0{\cdot}35$. Again, the good agreement between Hansen and Verlet data [3] and ours is interesting. A confirmation of our bubble densities is also given by the Gibbs ensemble results [7–10], especially by the first published ones [7].

Having given above correlation equations for the vapour pressure, the dew and the bubble density, it may in addition be of some interest to give also correlations for the chemical potential at phase equilibrium and for the enthalpy of vaporization. These were obtained as

$$\tilde{\mu}_\sigma = -\frac{1{\cdot}3084}{T^{*2}} - \frac{2{\cdot}5215}{T^*} - 0{\cdot}0077787\, T^{*6}, \tag{25}$$

with $D(\tilde{\mu}_\sigma) = 0{\cdot}65$ and

$$\Delta h_v^* = 6{\cdot}4925\,(T_c^* - T^*)^{1/3} + 2{\cdot}9644\,(T_c^* - T^*)^{2/3} - 1{\cdot}8502\,(T_c^* - T^*)^{3/2}, \tag{26}$$

with $D(\Delta h_v^*) = 0{\cdot}98$.

It remains now to check the phase equilibrium data with respect to their thermodynamic consistency by using the Clausius–Clapeyron equation in the form

$$\frac{\partial \ln p_\sigma^*}{\partial(1/T^*)} = -\frac{T^*}{p_\sigma^*}\frac{\Delta h_v^*}{\Delta v^*}, \tag{27}$$

with $\Delta v^* = 1/\rho''^* - 1/\rho'^*$. Obviously, one has to insert one of the vapour pressure equations (21) or (22) into the LHS. For the term of the RHS we decided to use the directly calculated values from table 5; its uncertainty was calculated by the error propagation law. The results presented in table 6 show that with both vapour pressure equations the equality required by equation (27) is fulfilled within the uncertainties of the terms on the RHS. Moreover, it is remarkable that the directly calculated term on the RHS again reproduces the maximum at medium temperatures shown by equation (22).

Finally, we give in table 7 a comparison of the present simulation results with those obtained from a WCA-type perturbation theory [18]. A previous comparison

Table 6. Consistency test of the phase equilibrium data on the basis of Clausius–Clapeyron equation.

T^*	$-\frac{T^*}{p_\sigma^*}\left(\frac{\Delta h_v^*}{\Delta v^*}\right)$	$\frac{\partial \ln p_\sigma^*}{\partial(1/T^*)}$ (Eqn (21))	$\frac{\partial \ln p_\sigma^*}{\partial(1/T^*)}$ (Eqn (22))
0·70	−6·99(48)	−6·756	−7·191
0·75	−6·83(26)	−6·756	−6·953
0·80	−6·78(19)	−6·756	−6·799
0·85	−6·73(19)	−6·756	−6·706
0·90	−6·69(10)	−6·756	−6·662
0·95	−6·69(22)	−6·756	−6·654
1·00	−6·71(10)	−6·756	−6·677
1·05	−6·71(14)	−6·756	−6·724
1·10	−6·71(23)	−6·756	−6·792
1·15	−6·79(10)	−6·756	−6·877
1·20	−6·89(15)	−6·756	−6·978
1.25	−6·84(48)	−6·756	−7·092
1·30	−6·90(80)	−6·756	−7·219

The term $-(T^*/p_\sigma^*)(\Delta h_v^*/\Delta v^*)$ together with its uncertainty was calculated from the values in table 5. The derivatives $\partial \ln p_\sigma^*/\partial(1/T^*)$ were formed by using either equation (21) or (22).

[18] made with the data of Adams [4] showed a considerable discrepancy in the vapour pressures of about 15%. As the present vapour pressures are about 9% higher than those of Adams, the discrepancy is reduced now to about 5%. Also, the bubble densities are now in slightly better agreement. This proves that perturbation theory is considerably more accurate than was thought for a long time. It also explains the big success in the prediction of real substance thermodynamic data by simulations [19, 20] which used effective pair potentials determined with the help of perturbation theory.

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Appendix

The NpT molecular dynamics simulations were performed using the algorithm of Andersen [A1]. The number of real particles was 1372 throughout, the time step was 0·005 in the usual units. The starting configuration was a f.c.c. lattice, the equilibration period went over 5 000 time steps with the first 1 000 time steps in NVT. The production run went over 55 000 time steps with the exception of $T^* = 0{\cdot}70$ with

Table 7. Comparison of vapour pressures and bubble densities from simulations and perturbation theory PT [18].

	p_σ^*		ρ'^*	
T^*	Sim (Eqn (22))	PT	Sim (Eqn (24))	PT
0·7290	$2{\cdot}005 \times 10^{-3}$	$2{\cdot}104 \times 10^{-3}$	0·8303	0·8278
0·8748	$9{\cdot}551 \times 10^{-3}$	$9{\cdot}904 \times 10^{-3}$	0·7646	0·7675
1·0206	$2{\cdot}836 \times 10^{-2}$	$2{\cdot}990 \times 10^{-2}$	0·6892	0·7019

Figure A1. Estimation of the statistical uncertainty from the running average for the example of the chemical potential $\tilde{\mu}$ at $T^* = 0{\cdot}75$ and $p^* = 0$.

100 000 time steps and $T^* = 0{\cdot}75$ with 75 000 time steps. The real particle cut-off radius was taken as large as possible within the fluctuating elementary cell cube, the smallest value being $5{\cdot}7\sigma$ for $T^* = 0{\cdot}70$; in addition, the usual long range corrections were included. The membrane mass M was 5×10^{-4} for the liquid and 1×10^{-6} for the gas. After each time step, 1 000 test particles were inserted at random with a cut-off radius being nearly equal to the real particle cut-off radius; correct long range corrections for the test particle energy were made. All calculations were performed with vectorized codes on a Cyber 205.

The determination of all statistical uncertainties was made from the fluctuation of the running average in the second half of the production. As an example, the running average and the estimation of the uncertainty are shown in figure A1 for the chemical potential $\tilde{\mu}$ at $T^* = 0{\cdot}75$ and $p^* = 0$. This method is perhaps not so sophisticated as that suggested by Fincham *et al.* [A2]. It can, however, be argued that the uncertainty determined in that way is roughly equal to twice the invariance of an assumed Gaussian distribution divided by the square root of the number of time steps.

To be on the safe side, we made some counterchecks of NpT and NVT simulations. First, we considered the state point $T^* = 1{\cdot}0$, $p^* = 0{\cdot}03$, for which the NpT simulation gave, according to table 1, $\rho^* = 0{\cdot}70179(37)$, $\tilde{\mu} = -3{\cdot}823(7)$ and $u^{res*} = -4{\cdot}9018(25)$. Starting now from the density obtained, an NVT run (500 particles, 500 test particles, 50 000 production time steps) gave $p^* = 0{\cdot}028\,8(48)$, $\tilde{\mu} = -3{\cdot}841(16)$ and $u^{res*} = -4{\cdot}898\,3(17)$. In addition, we considered the state point $T^* = 1{\cdot}2$, $\rho^* = 0{\cdot}7$, for which chemical potentials are available from different authors. Our NVT run (500 particles, 500 test particles, 50 000 production time steps) gave $p^* = 0{\cdot}666(8)$,

$\tilde{\mu} = -2{\cdot}287(13)$ and $u^{res*} = -4{\cdot}758\,1(14)$. Starting then an NpT run with the same number of particles, test particles and time steps at $p^* = 0{\cdot}666$ resulted in $\rho^* = 0{\cdot}699\,2(6)$, $\tilde{\mu} = -2{\cdot}278(12)$ and $u^{res*} = -4{\cdot}752\,8(48)$. These two examples demonstrate the very good consistency between the NpT and NVT simulations. Comparing now the residual chemical potentials $\mu^{res}/kT = \tilde{\mu} - \ln \rho^*$ for the second state point with the results of other sources, we have here $-1{\cdot}92$ (NpT) and $-1{\cdot}93$ (NVT), whereas we obtained previously $-1{\cdot}90$ (500 particles) [A3] and $-1{\cdot}91$ (500 particles, proper long range correction) [A4]. The result of Deitrick *et al.* is $-1{\cdot}90$ (200 and 500 particles) [A5], and Smit and Frenkel obtained $-1{\cdot}91$ (256 particles) and $-1{\cdot}94$ (500 particles) [A6].

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