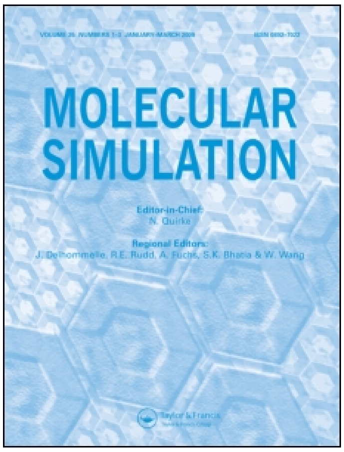

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Direct Evaluation of Vapour-Liquid Equilibria by Molecular Dynamics using Gibbs-Duhem Integration

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DIRECT EVALUATION OF VAPOUR-LIQUID EQUILIBRIA BY MOLECULAR DYNAMICS USING GIBBS-DUHEM INTEGRATION

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An application of the Gibbs-Duhem integration [D. A. Kofke, *J. Chem. Phys.*, **98**, 4149 (1993)] for the direct evaluation of vapour-liquid equilibria by molecular dynamics is presented. The Gibbs-Duhem integration combines the best elements of the Gibbs ensemble Monte Carlo technique and thermodynamic integration. Given conditions of coexistence at one coexistence point, simultaneous but independent NPT molecular dynamics simulations of each phase are carried out in succession along saturation lines. In each simulation, the saturated pressure is adjusted to satisfy the Clapeyron equation. The Clapeyron equation is a first-order nonlinear differential equation that prescribes how the pressure must change with the temperature to maintain coexistence. The Clapeyron equation is solved by the predictor-corrector method. Running averages of enthalpy and density of each phase are used to evaluate the right-hand side of the Clapeyron equation. The Gibbs-Duhem integration method is applied to a two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence point was taken from published data or was determined *via* the Widom test particle insertion method. Implementation of the Gibbs-Duhem integration with a thermodynamic model for the vapour phase is also presented.

KEY WORDS: Vapour-liquid equilibria, molecular dynamics, Gibbs-Duhem integration.

1 INTRODUCTION

Prediction of vapour-liquid equilibria (VLE) by molecular dynamics (MD) simulations is tedious and time-consuming work. Two approaches are typically used. The first approach involves calculations of PVT data along isotherms and subsequent applications of the Maxwell equal area rule [1]. The second approach combines MD with the Widom test particle insertion method when searching for conditions of coexistence (equality of the pressure, temperature and chemical potential) [2]. Both approaches require carrying out MD simulations at state points that are not laid on the saturation curves.

The Gibbs ensemble Monte Carlo (GEMC) technique [3] greatly simplifies the search and evaluation of coexistence conditions. It enables one with a single simulation to locate and evaluate the coexistence condition for a given system at a given temperature. The GEMC relies on particle insertions, and problems inherent in the particle insertion method occur at high densities [4]. The GEMC also fails when dealing with systems modelled by complex intermolecular potentials unless special biasing procedures are employed.

Recently, Kofke [5] has proposed a new method for the direct evaluation of phase coexistence by molecular simulations: the Gibbs-Duhem integration. He applied it to the Lennard-Jones fluid. The Gibbs-Duhem integration combines the best elements of the GEMC technique and thermodynamic integration. The method entails simultaneous NPT simulations of each phase (like the GEMC method). The mechanism for equating the chemical potential is the Clapeyron equation. Hence, in contrast to the GEMC method, no particle insertion is necessary. Starting at a state point for which the two phases are known to be in equilibrium, the Gibbs-Duhem integration method can be used to trace out the phase diagram directly and efficiently.

In this study, we applied the Gibbs-Duhem integration method to the molecular fluid: the two-centre Lennard-Jones (2CLJ) fluid of elongation of 0.505. We chose the 2CLJ fluid of elongation 0.505 because its VLE has been recently determined from the NPT plus test particle method [6], and thus, it can serve for comparison with the results obtained from the Gibbs-Duhem integration method. Moreover, Saager *et al.* [7] have used the 2CLJ fluid of elongation 0.505 in the construction of the physically based equation of state. This application also prompted us to calculate the VLE for this fluid. In contrast to Kofke [5] who utilized the NPT Monte Carlo (MC) method, we carried out the NPT simulations by the NPT MD method. The MD method has advantages over the MC method in that dynamical properties can be assessed. The next section presents the Clapeyron equation and its numerical solution by predictor-corrector methods. Section 3 gives the 2CLJ potential and simulation details. Section 4 presents results of the Gibbs-Duhem integration for (a) the starting coexistence condition given by Kriebel *et al.* data [6], (b) the starting coexistence condition predicted *via* the Widom test particle insertion method, and (c) the use of thermodynamic model for the vapour phase. Finally, we given conclusions in Section 5.

2 THE CLAPEYRON EQUATION

The Gibbs-Duhem equation for pure substance [8] can be written as

$$d(\beta\mu) = h d\beta + \beta v dp, \tag{1}$$

where μ is the chemical potential, h the molar enthalpy, v the molar volume, p the pressure, and $\beta = 1/k_B T$, with k_B the Boltzmann constant and T the absolute temperature. By writing Eq. (1) for two coexisting phases, liquid (l) and vapour (v), and, by equating the right-hand sides, the Clapeyron equation results in

$$\left(\frac{d\log p}{d\beta}\right)_\sigma = -\frac{\Delta h}{\beta p \Delta v} = f(\beta, p). \tag{2}$$

In Eq. (2), $\Delta h = h_v - h_l$ is the difference in molar enthalpies of the coexisting phases, and $\Delta v = v_v - v_l$ the difference in molar volumes of the coexisting phases; the subscript σ indicates that the derivative is taken along the saturation line. Eq. (2) is a first-order nonlinear differential equation that prescribes how the pressure must change with the temperature for two phases to remain in coexistence.

Given an initial condition, i.e., the pressure, temperature and $f(\beta, p)$ at one coexistence point, Eq. (2) can be solved numerically by a predictor-corrector method. We successfully applied the Adams predictor-corrector [5, 9]

$$\mathrm{P}\ \ y_{i+1} = y_i + \frac{\Delta\beta}{24}(55f_i - 59f_{i-1} + 37f_{i-2} - 9f_{i-3}) \tag{3}$$

$$\mathrm{C}\ \ y_{i+1} = y_i + \frac{\Delta\beta}{24}(9f_{i+1} + 19f_i - 5f_{i-1} + f_{i-2}) \tag{4}$$

to calculate the pressure. In Eqs. (3) and (4), y stands for $\log p$, f for $f(\beta,p)$, P for the predictor, C for the corrector, and $\Delta\beta$ is the step in the β. The Adams algorithm requires four prior simulations. We performed the start-up as follows: The pressure at the first simulation point was predicted by the trapezoid predictor-corrector

$$\mathrm{P}\ \ y_1 = y_0 + \Delta\beta f_0 \tag{5}$$

$$\mathrm{C}\ \ y_1 = y_0 + \frac{\Delta\beta}{2}(f_1 + f_0). \tag{6}$$

Then, the midpoint predictor-corrector

$$\mathrm{P}\ \ y_2 = y_0 + 2\Delta\beta f_1 \tag{7}$$

$$\mathrm{C}\ \ y_2 = y_0 + \frac{\Delta\beta}{3}(f_2 + 4f_1 + f_0) \tag{8}$$

was used to determine the pressure at the second point. Finally, the midpoint predictor

$$y_3 = y_1 + 2\Delta\beta f_2 \tag{9}$$

with the Adams corrector

$$y_3 = y_2 + \frac{\Delta\beta}{24}(9f_3 + 19f_2 - 5f_1 + f_0) \tag{10}$$

was used to compute the pressure at the third point. The quantities needed to evaluate the right-hand side of the Clapeyron equation were obtained from simultaneous but independent NPT MD simulations of the liquid and vapour phase.

3 SIMULATION METHOD

3.1 Intermolecular potential

We applied the Gibbs-Duhem integration method to the 2CLJ fluid. The pair potential for the 2CLJ fluid is

$$u_{2CLJ}(r,\omega_i,\omega_j)=\sum_{a=1}^{2}\sum_{b=1}^{2}4\varepsilon\left[\left(\frac{\sigma}{r_{ab}}\right)^{12}-\left(\frac{\sigma}{r_{ab}}\right)^{6}\right]. \tag{11}$$

In Eq. (11), r_{ab} is the distance between atom a of molecule i and atom b of molecule j, ε and σ are the Lennard-Jones energy and size parameters, and ω is the orientation of molecules. In the following, we used the Lennard-Jones reduced units: $L^*=l/\sigma, r^*=r/\sigma, t^*=t/(\sigma\sqrt{(m/\varepsilon)}), T^*=k_B T/\varepsilon, \rho^*=\rho\sigma^3, p^*=p\sigma^3/\varepsilon, u^*=u/N\varepsilon$, $h^*=h/N\varepsilon, \mu^*=\mu/\varepsilon$, and $B^*=B/\sigma^3$.

3.2 *Simulation details*

We carried out the NPT MD simulations using the Andersen algorithm [4]. The temperature was kept constant by the isokinetic scaling of translational and angular velocities after every timestep. The equations of translational motion were solved by the Gear predictor-corrector algorithm of the fifth order. The rotational motion was treated by the method of quaternions and it was solved by the Gear predictor-corrector algorithm of the fourth order[4]. The minimum image convention, periodic boundary conditions and cut-off radius equal to the half-box length were used. Long-range corrections of the internal energy and pressure were included [4]. For the integration, the timestep $\Delta t^*=0.002$ was chosen. The membrane mass M^* was set to $5\cdot10^{-4}$ for the liquid and $1\cdot10^{-6}$ for the vapour [6]. All simulation runs were performed with 256 molecules.

We performed the Widom test particle insertion method in the NVT ensemble to calculate the chemical potential needed .for the determination of the initial coexistence point. The calculation of the chemical potential was carried out with 500 real and 500 test molecules. After every timestep, the test molecules were inserted randomly with the same cut-off radius as the real molecules. Equilibration periods consisted of 5000 timesteps, and production runs took 30000 timesteps. The reliability of the MD code was checked to reproduce some published data in the NPT ensemble (the density, enthalpy and chemical potential) [6] and in the NVT ensemble (the pressure and internal energy) [7].

We proceeded with the Gibbs-Duhem integration method as follows: Starting from fcc lattices, we performed the NVT MD simulations of the liquid and vapour phases at the initial coexistence point. Following simulations continued in the NPT ensemble. At each temperature, the simulations of the liquid and vapour phases were performed simultaneously but independently. The temperature was increased and the predictor pressure was calculated according to Eq. (5). Afterwards, the liquid and vapour structures were allowed to relax 3000 timesteps. At the end of relaxation period, all accumulators were set to zero. The subsequent production run of the liquid and vapour phases was divided into eight timeblocks. The first timeblock consisted of 3000 timesteps and the following timeblocks contained 1000 timesteps each. After each timeblock was completed, the computed running averages of liquid and vapour enthalpies, and liquid and vapour densities, were used to evaluate the right-hand side of the Clapeyron equation, and thus, to calculate the corrector pressure according to Eq. (6). Then, the temperature was again increased and the process was repeated. The predictor and corrector pressures were evaluated according to appropriate equations: Eqs. (3, 4 and 7–10). The reciprocal temperature $1/T^*$ was increased in constant steps $\Delta\beta$ of 0.006 or 0.009.

The Gibbs-Duhem integration had to be halted near the critical point because the liquid phase 'vapourized', i.e., the liquid density took on a vapour-like value after about 3000 timesteps. Such an event is unavoidable in the NPT MD simulation if the critical point is approached.

4 RESULTS AND DISCUSSION

We carried out the Gibbs-Duhem integration between temperatures T^* 1.85 and 2.8. The Clapeyron equation can be rewritten in the Lennard-Jones units as

$$\left(\frac{d\log p^*}{d(1/T^*)}\right)_\sigma = -\frac{T^*}{p^*}\frac{h_v^* - h_l^*}{1/\rho_v^* - 1/\rho_l^*}, \tag{12}$$

where ρ_v^* and ρ_l^* are the vapour and liquid number densities.

4.1 The starting coexistence condition given by Kriebel et al. data

Kriebel *et al.* [6] determined the VLE of the 2CLJ fluids by the NPT plus test particle method. We took their coexistence point at $T^* = 1.85$ as the initial condition for the Gibbs-Duhem integration. Figure 1 shows a comparison of the

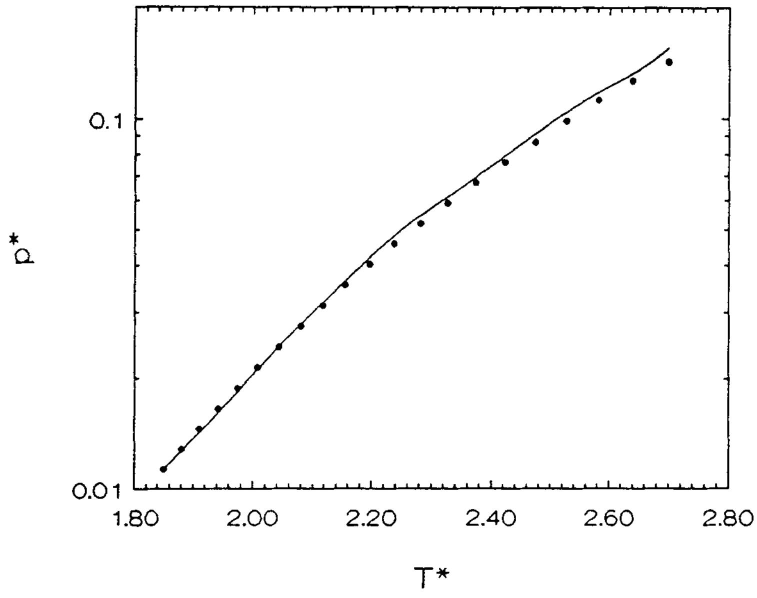

Figure 1 Vapor-liquid coexistence pressure p^* as a function of temperature T^* for the two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence condition given by Kriebel *et al.* data [6]. (– : Kriebel *et al.* [6]; •: the Gibbs-Duhem integration).

vapour-liquid coexistence pressure given by Kriebel *et al.* data with that calculated by the Gibbs-Duhem integration. The Gibbs-Duhem results agree very well with the Kriebel *et al.* results. The Gibbs-Duhem pressure is higher at low temperatures, and it is lower at high temperatures in comparison with the Kriebel *et al.* values. Figure 2 displays the coexistence envelope of the 2CLJ fluid of elongation 0.505 for the Gibbs-Duhem integration method and the NPT plus test particle method. The overall accord between both methods is more than satisfactory. However, at high temperatures both vapour and liquid densities are slightly lower in the case of the Gibbs-Duhem integration method. It is worthwhile to note that the test of the thermodynamic consistency of the Kriebel *et al.* VLE data by the Clapeyron equation [6] revealed differences between the right-hand and left-hand sides of the Clapeyron equation equal to about 13%. Those differences can cause discrepancies between our results and those of Kriebel *et al.*

We estimated the critical temperature $T_C{}^*$ and density $\rho_C{}^*$ from a least-squares fit of the law of rectilinear diameter

$$\frac{\rho_l^* + \rho_v^*}{2} = \rho_C^* + C_1(T^* - T_C^*) \qquad (13)$$

and the critical scaling relation

$$\rho_l^* - \rho_v^* = C_2(T_C^* - T^*)^{0.32}. \qquad (14)$$

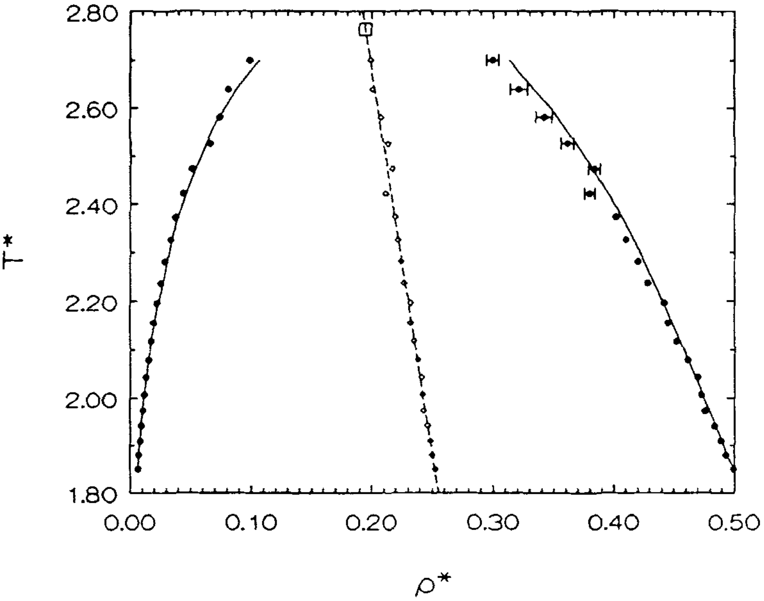

Figure 2 Coexistence envelope for the two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence condition given by Kriebel *et al.* data [6]. (— : Kriebel *et al.* [6]; ●: the Gibbs-Duhem integration). Error bars are included only if large than the plot marks. The diamonds describe the law of rectilinear diameter, and the critical point estimated from the Gibbs-Duhem integration data is indicated by the square.

The fit of Eq. (13) was performed over the entire temperature range, and the result is shown in Figure 2. Eq. (14) was fit for $T^* \geqslant 2.4$. The least-squares fit gives the fitting parameters $C_1 = -6.268 \cdot 10^{-2}$ and $C_2 = 0.475$, and the critical parameters $T_C^* = 2.764$ and $\rho_C^* = 0.195$. The analysis is not particularly sensitive to the location of the temperature cut-off for the fit of Eq. (14). The use of the cut-off $T^* \geqslant 2.5$ or $T^* \geqslant 2.3$ produces small differences in T_C^* and ρ_C^*. Our critical parameters can be compared with those of Kriebel *et al.*: $T_C^* = 2.800$ and $\rho_C^* = 0.206$.

4.2 *The starting coexistence condition predicted via the Widom test particle insertion method*

We determined the initial condition of the Gibbs-Duhem integration at $T^* = 1.85$ by (a) applying the Widom test particle insertion method on the liquid side, and (b) using the simple truncated virial equation of state [11]

$$\frac{p^*}{\rho^* T^*} = 1 + B^* \rho^* \tag{15}$$

on the vapour side. In Eq. (15), B^* is the second virial coefficient. The B^* was calculated by a non-product algorithm [12] and $B^* = -11.183$ at $T^* = 1.85$. From the simple truncated virial equation of state, the chemical potential in the vapour μ_v^* and vapour density ρ_v^* can be expressed as

$$\frac{\mu_v^*}{T^*} = \log \rho_v^* + 2B^* \rho_v^* \tag{16}$$

$$\rho_v^* = \frac{\sqrt{4B^* p^*/T^* + 1} - 1}{2B^*}. \tag{17}$$

We carried out the NVT MD simulations with the test particle insertions at $T^* = 1.85$ for densities 0.48, 0.49, 0.50, 0.51 and 0.52. The computed chemical potential and pressure were fitted to polynomials of the third order as displayed in Figure 3. The initial coexistence point for the Gibbs-Duhem integration was determined from the condition of the equality of the pressure and chemical potential in both phases. The resulting coexistence point at $T^* = 1.85$ is $p^* = 1.00 \cdot 10^{-2}$, $\rho_v^* = 0.58 \cdot 10^{-2}$, and $\rho_l^* = 0.499$. The obtained vapour-liquid coexistence pressure and vapour density are about 12% lower than the Kriebel *et al.* coexistence point $p^* = 1.13 \cdot 10^{-2}, \rho_v^* = 0.66 \cdot 10^{-2}$, and $\rho_l^* = 0.499$. Figure 4 and 5 compare the vapour-liquid coexistence pressure and the coexistence envelope for the 2CLJ fluid of elongation 0.505. As one can expect, the Gibbs-Duham pressure p^* and vapour density ρ_v^* are consistently lower than the Kriebel *et al.* values, and the discrepancies increase with temperature. This is due to lower initial values of p^* and ρ_v^* in comparison with the Kriebel *et al.* values. The fit of our data to Eqs. (13) and (14) gives the fitting parameters $C_1 = -7.156 \cdot 10^{-2}$ and $C_2 = 0.512$, and the critical parameters $T_C{}^* = 2.752$ and $\rho_C{}^* = 0.189$.

4.3 *A thermodynamic model for vapour phase*

The Gibbs-Duhem integration can be easily modified to incorporate a thermodynamic description of the vapour phase. Such a situation may occur either

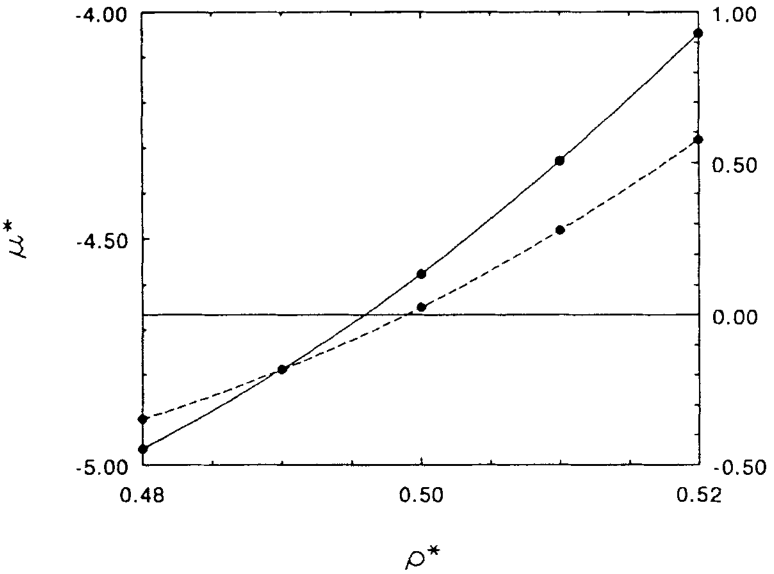

Figure 3 Chemical potential μ^*(–) and pressure p^* (– – –) computed from the NVT MD simulations with the test particle insertions as a function of density ρ^* (lines: the fit to polynomials of the third order; •: computed values).

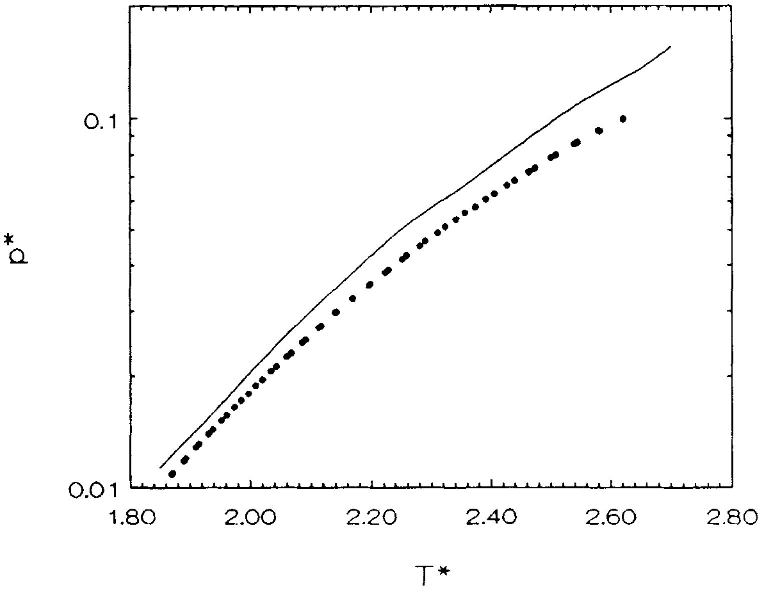

Figure 4 Vapour-liquid coexistence pressure p^* as a function of temperature T^* for the two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence condition predicted *via* the Widom test particle insertion method. (– : Kriebel *et al.* [6]; •: the Gibbs-Duhem integration).

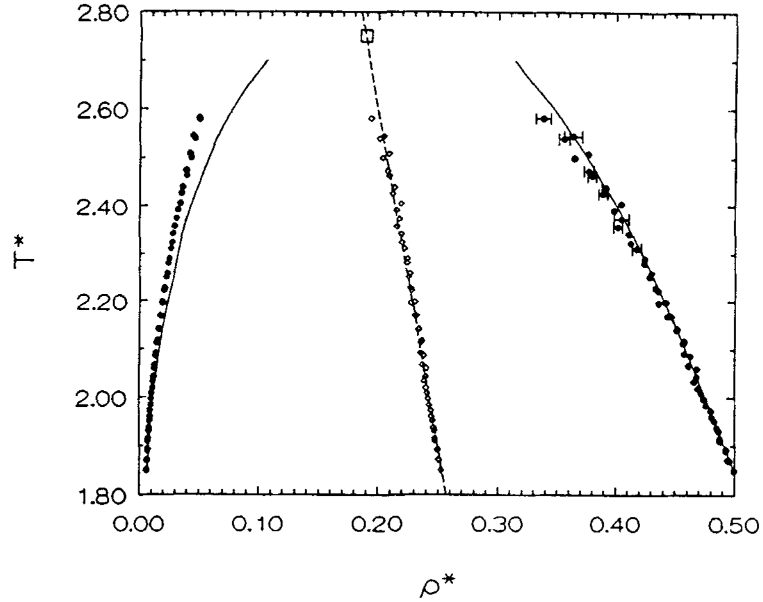

Figure 5 Coexistence envelope for the two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence condition predicted *via* the Widom test particle insertion method. Error bars are included only if larger than the plot marks. (— : Kriebel *et al.* [6]; •: the Gibbs-Duhem integration). The diamonds describe the law of rectilinear diameter, and the critical point estimated from the Gibbs-Duhem integration data indicated by the square.

when extensive experimental or simulation data are available and a suitable thermodynamic model has been found, or when a potential model successfully describes the liquid phase, but it fails to describe the vapour phase [13]. We implemented the simple truncated virial equation of state (Eq. (15)), but the idea can be readily extended to a more complicated thermodynamic model. The simple truncated virial equation of state is valid for low densities. The second virial coefficient B^* was calculated by the non-product algorithm [12] and it is presented in Figure 6. The calculated values of B^* were fitted to the equation [14]

$$B^*(T^*) = a_1\left\{1 - a_2\left[\exp\left(\frac{a_3}{T^*}\right) - 1\right]\right\}. \tag{18}$$

The fitting parameters are $a_1 = 2.6729, a_2 = 3.5672$, and $a_3 = 1.6601$.

We started the Gibbs-Duhem integration from the initial condition given *via* the Widom test particle insertion method. The vapour density ρ_v^* was obtained from Eq. (17) and the difference in the enthalpies $h_v^* - h_l^*$ was expressed according to [15] by

$$h_v^* - h_l^* = -u_l^* + p^*\left(\frac{1}{\rho_v^*} - \frac{1}{\rho_l^*}\right) + \rho_v^* T^*\left(T^*\frac{dB^*}{dT^*} - B^*\right). \tag{19}$$

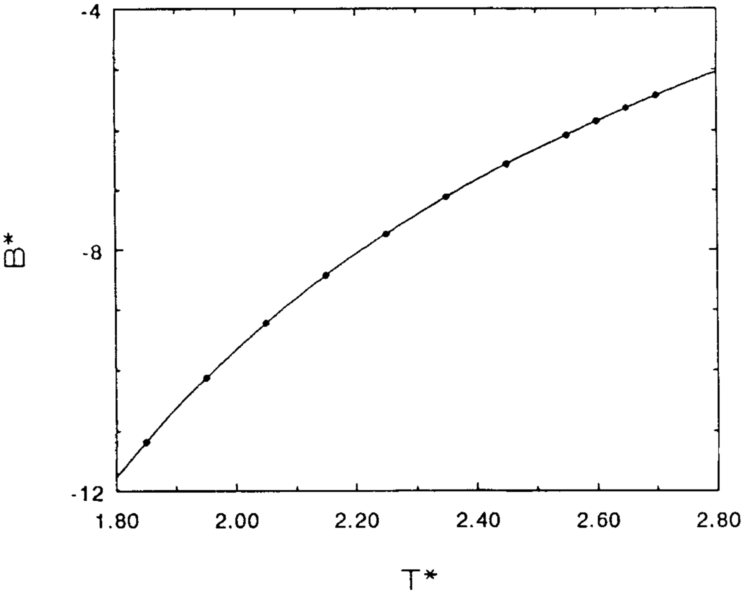

Figure 6 Second virial coefficient B^* as a function of temperature T^* (— : the fit to Eq. (18); ●: calculated values).

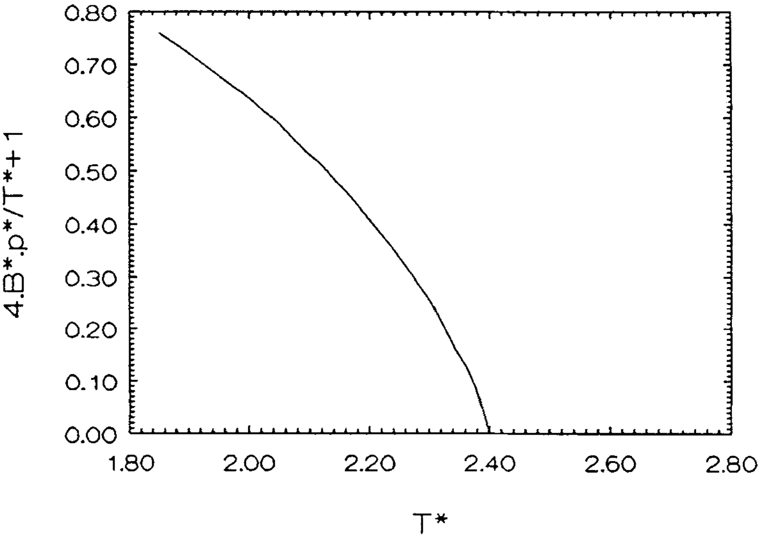

Figure 7 Region of validity the simple truncated virial equation of state. The simple truncated virial equation of state is valid until $4B^*p^*/T^* + 1$ (Eq. (17)) is positive.

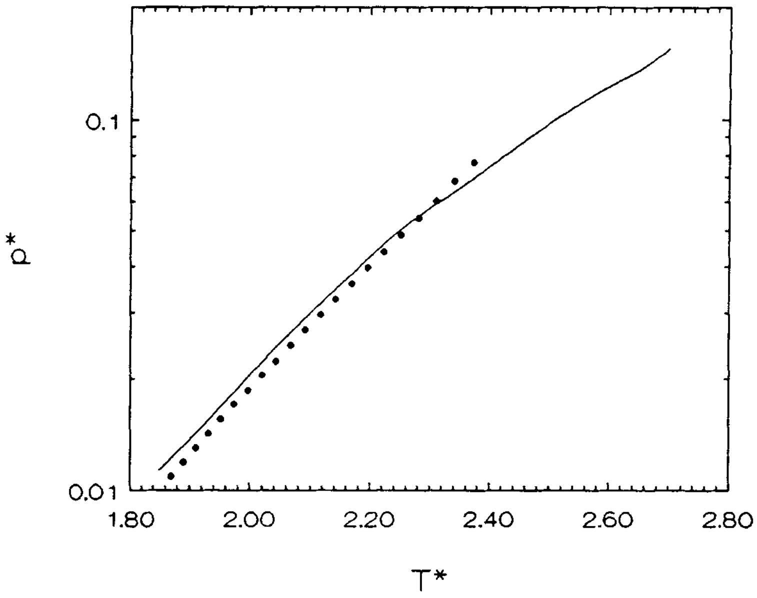

Figure 8 Vapour-liquid coexistence pressure p^* as a function of temperature T^* for the two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence condition predicted *via* the Widom test particle insertion method. (— : Kriebel *et al.* [6], •: the Gibbs-Duhem integration with the thermodynamic model for the vapour phase).

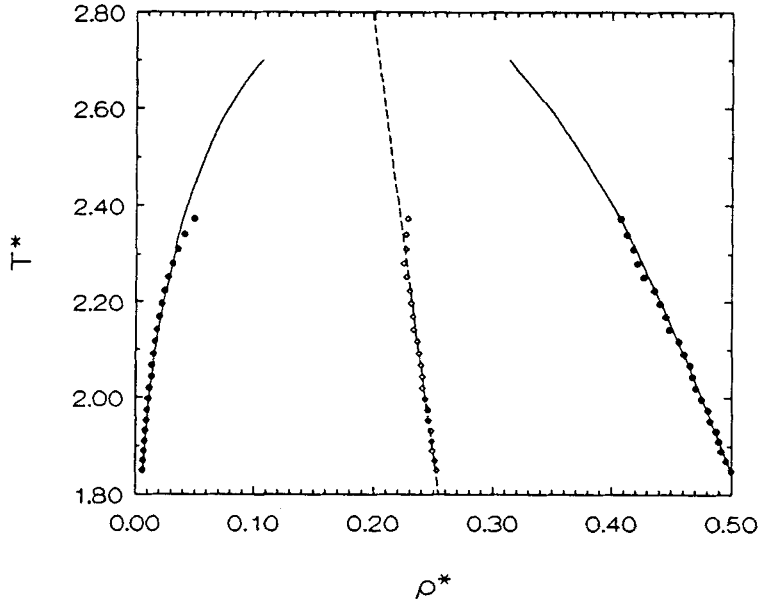

Figure 9 Coexistence envelope for the two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence condition predicted *via* the Widom test particle insertion method. (— : Kriebel *et al.* [6]; •: the Gibbs-Duhem integration with the thermodynamic model for the vapour phase). Error bars are included only if larger than the plot marks. The diamonds describe the law of rectilinear diameter.

In Eq. (19), u_l^* is the potential energy of the liquid. The Gibbs-Duhem integration had to be halted near the temperature 2.4 because the root-square in Eq. (17) is not longer defined, as is shown in Figure 7.

Figure 8 and 9 present the results of the Gibbs-Duhem integration. One can see that the pressure increase for the Gibbs-Duhem integration is steeper than for the NPT plus test particle method (Figure 8); nevertheless, accord between the two methods is very good. The coexistence envelope for the Gibbs-Duhem integration agrees very well with the Kriebel *et al.* data (Figure 9). Only the last two vapour values in Figure 9 are influenced by the loss of validity the simple truncated virial equation of state.

5 CONCLUSIONS

We directly evaluated the vapour-liquid equilibria by MD simulations using the Gibbs-Duhem integration method [5]. The Gibbs-Duhem integration method, like the GEMC method, performed simultaneous but independent simulations of each 'phase. However, in contrast to the GEMC, the Gibbs-Duhem integration method does not require the particle insertion. The Gibbs-Duhem integration method was applied to the 2CLJ fluid of elongation 0.505. The necessary initial coexistence point for initation of the Gibbs-Duhem integration was taken from (a) Kriebel *et al.* data [6], and (b) was determined *via* the Widom test particle insertion method. In case (a), the agreement between the Gibbs-Duhem and Kriebel *et al.* VLE data is very good. In case (b), the agreement is less satisfactory because the initial pressure and vapour density determined *via* the Widom test particle insertion method is lower. We also showed how the Gibbs-Duhem integration method can be easily modified to incorporate a thermodynamic description of the vapour phase, e.g., the simple truncated virial equation of state.

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