Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble

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A methodology is presented for Monte Carlo simulation of fluids in a new ensemble that can be used to obtain phase coexistence properties of multicomponent systems from a single computer experiment. The method is based on performing a simulation simultaneously in two distinct physical regions of generally different densities and compositions. Three types of perturbations are performed, a random displacement of molecules that ensures equilibrium within each region, an equal and opposite change in the volume of the two regions that results in equality of pressures, and random transfers of molecules that equalize the chemical potentials of each component in the two regions. The method is applied to the calculation of the liquid–gas coexistence envelope for the pure Lennard-Jones (6, 12) fluid for several reduced temperatures from the vicinity of the triple point to close to the critical point $(T^* = 0.75$ to $T^* = 1.30)$. Good overall agreement with previously available literature results is obtained, with some deviations at the extremes of this temperature range.

1. Introduction

The calculation of the phase equilibrium behaviour of fluids (pure components and mixtures) from fundamental information on the intermolecular interactions is of significant theoretical and practical value. Phase equilibrium properties form the basis for a large number of separations used by the process industries, and determine the behaviour of a wide range of physical systems. From a theoretical point of view, the problems of effective testing of theories of the liquid state and determining appropriate intermolecular potentials for representing real fluids can greatly benefit from knowledge of the phase equilibrium behaviour of model fluids. Such properties have inherently greater discriminatory power [1] than the simple thermodynamic or structural properties that have been commonly utilized in the past.

The canonical (NVT) ensemble Monte Carlo technique introduced by Metropolis *et al.* in 1953 [2] has been extensively used to study the equilibrium properties of fluids [3, 4]. Extensions of the technique to the constant pressure (NPT) ensemble [5, 6] and the grand canonical (μVT) ensemble [7–9] have significantly broadened the scope of the basic methodology. The μVT ensemble allows specification of the chemical potential and can thus be used to study the coexistence properties of fluids. Such applications have until now been limited

to single component systems [8, 9]. One of the reasons for this is that the number of simulations that need to be performed for the determination of a phase envelope increases dramatically with the number of components in a mixture. Recent developments based on the Widom potential-distribution theory [10] have also allowed the determination of the chemical potential from NVT Monte Carlo [11] or Molecular Dynamics [12, 13] simulations. These methods have been used to calculate vapour–liquid phase equilibria for binary systems [14, 15]. The calculations required are long, and some prior knowledge of the appropriate location of the phase equilibrium region is required.

The purpose of this work is to introduce a method for Monte Carlo simulation in a new ensemble, for which we propose the name 'Gibbs ensemble', that enables the direct calculation of the phase coexistence properties of pure components and mixtures from a single simulation, without need for determining or specifying the chemical potential. The validity of the method is demonstrated by the calculation of the coexistence properties of the pure Lennard-Jones (LJ) (6, 12) fluid. The LJ fluid was chosen because it is by far the best studied continuous potential ([16, 9] and references quoted therein), and gives a reasonable approximate representation of the properties of spherically symmetric, nonpolar real fluids.

In the following sections we first present the theoretical foundation for the proposed method, give some implementation details of the calculations and

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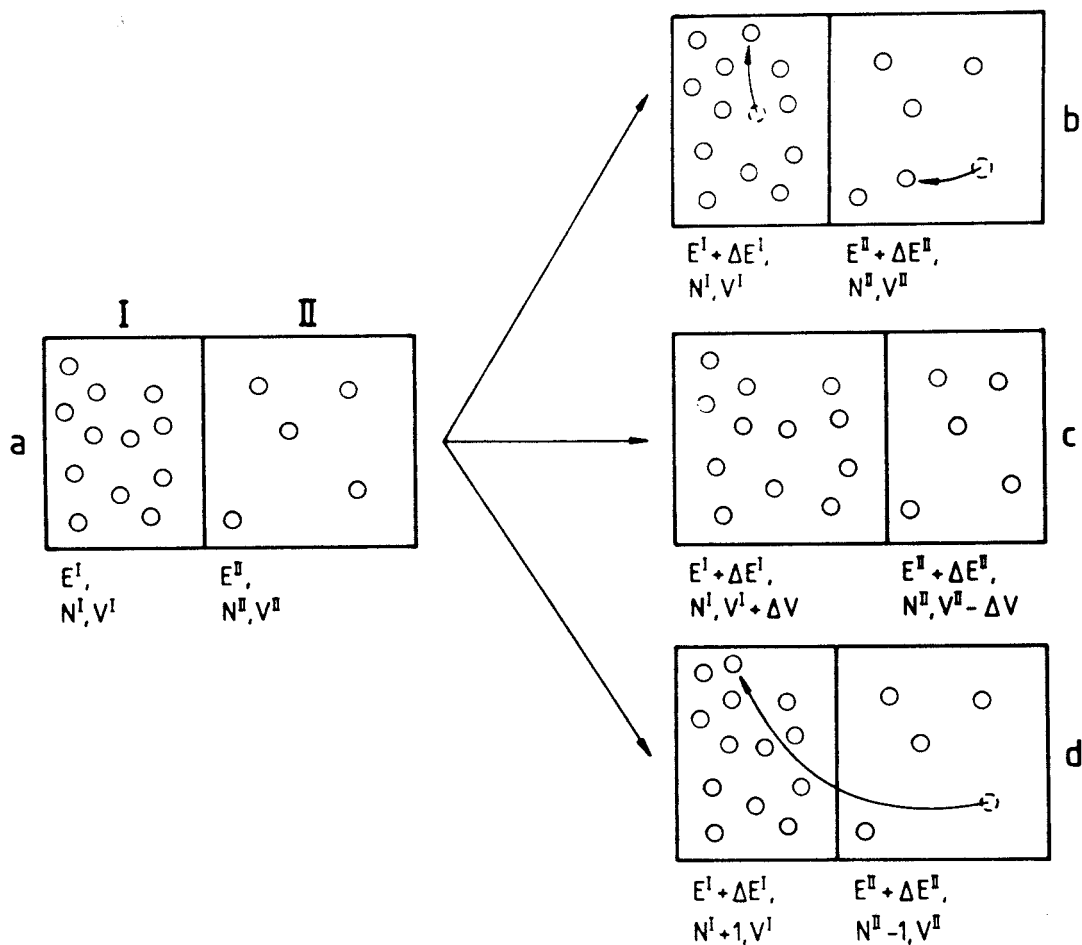
Figure 1. Schematic illustration of the possible steps for the proposed method.

obtain a series of results for the coexistence curve of the LJ fluid at temperatures ranging from close to the triple point to almost the critical point of this system ($T^* = 0.75$ to $T^* = 1.30$; all units denoted with a * are reduced using the LJ potential parameters [15]). Finally, we suggest a range of additional applications for the proposed methodology.

2. Theory

The basic idea in our method is to attempt to simulate phase coexistence properties by following the evolution in phase space of a system composed of two distinct regions. The two regions have different (in general) densities and compositions and are at thermodynamic equilibrium both internally and with each other. The conceptually simplest way to develop the formalism is through thermodynamic arguments and fluctuation theory.

In figure 1(a), we show a system consisting of two regions labelled I and II. The system is considered under NVT conditions: it is assumed that the system

volume and the total number of molecules are constant and that an infinite medium of constant temperature completely surrounds the system. Note that the 'surface' separating the two regions in figure 1 is devoid of any physical significance and does not represent an interface. One may think of the two regions as large macroscopic volumes of coexisting vapour and liquid, with an interface that has a negligible effect on the total system properties. Since our attempt is to simulate the phase behaviour of the macroscopic (infinite) system, we would like to avoid introducing interfaces.

The first type of perturbations to be considered are conventional random displacements of molecules in either of regions I or II (or both), without a change in the volume or number of molecules in each region. First, we derive the criteria of acceptance of the new configuration based on a different argument than the one normally given [17]. Our starting point is the fluctuation equation by Landau and Lifshitz [18] that gives the probability $\mathscr{P}$ of a fluctuation in a closed system as

$$\mathscr{P} \propto \exp(\Delta S_t/k) = \exp(-\Delta E_{min}/kT), \qquad (1)$$

where ΔS_t is the change in entropy of the total system (which includes the infinite medium surrounding our NVT box) and ΔE_{min} is the minimum work required to carry out reversibly the change from the equilibrium condition of the system to the state of interest. T is the temperature of the medium and thus the equilibrium temperature of the NVT box. Now consider two such states, $\mathbf{x}$ and $\mathbf{x}'$ of the NVT box that deviate from the equilibrium state. Since the probability of occurrence of each state is given by (1), a sufficient condition [17] for a long sequence of such configurations to converge to the correct thermodynamic averages for the system is the detailed balance condition

$$\frac{\mathscr{P}(\mathbf{x} \to \mathbf{x}')}{\mathscr{P}(\mathbf{x}' \to \mathbf{x})} = \exp(-\Delta E_{min}/kT), \qquad (2)$$

where now ΔE_{min} is the minimum reversible work required to bring the system from state $\mathbf{x}$ to state $\mathbf{x}'$ and $\mathscr{P}(\mathbf{x} \to \mathbf{x}')$ is the probability of the transition. A convenient choice for the transition probability is then

$$\mathscr{P} = \min(1, \exp[-\Delta E_{min}/kT]). \qquad (3)$$

For the perturbation in the system resulting from the displacement of molecules as shown schematically in figure 1 (*b*), the difference in configurational energy

$$\Delta E_{min} = \Delta E^{I} + \Delta E^{II} \qquad (4)$$

is calculated, and the new configuration is accepted with the probability given by equation (3).

It is clear that if only this type of perturbation were to be considered, the simulation in each of the two regions separately would sample the NVT ensemble in each region. The simplest way of performing such a step would be to attempt to change the configuration of a single region at a time. It is easy to show that in this case, the presence of two independent regions does not affect the calculated properties in each region, with the exception of a trival effect on convergence rates from the fact that only a portion of the attempted moves are relevant for each region. This would however also be true if attempted moves were made simultaneously in the two regions.

We now consider a different type of perturbation, in which the volumes of the two regions are changed so as to keep the total system volume constant. In figure 1(*c*), we consider a perturbation in volume of region I, with a corresponding equal and opposite change in the volume of region II. The new configurations in each region would be obtained by scaling the positions of the particles to the new volume, a procedure familiar from NPT ensemble simulations. If ΔE^{I} and E^{II} are the resulting changes in configurational energy of the two regions, the total reversible work required to bring about this change is

$$\Delta E_{min} = \Delta E^{I} + \Delta E^{II} - N^{I}kT \ln \frac{V^{I} + \Delta V}{V^{I}}$$

$$- N^{II}kT \ln \frac{V^{II} - \Delta V}{V^{II}}. \qquad (5)$$

The last two terms in equation (5) result from the ideal gas contribution to the change in system entropy. Since the two regions are to be kept at constant temperature, the surrounding medium must provide a heat input equal to $-T \Delta S^{IG}$ (where ^{IG} denotes the ideal-gas contribution). The total system is under NVT conditions and thus the probability of acceptance of the configuration with the changed volume is again simply given by equation (3).

The same formalism provides a simple and intuitive way to derive the acceptance criteria for the NPT ensemble simulation [6]. If region II is much larger than region I and if its properties are not affected by the small volume change (that is, if region II is effectively infinite) then the acceptance criterion implied by (3) is

$$\mathscr{P} = \min\left(1, \exp\left[-\left(\Delta E^{I} - N^{I}kT \ln \frac{V^{I} + \Delta V}{V^{I}}\right.\right.\right.$$

$$\left.\left.\left. + P\Delta V\right)\middle/ kT\right]\right) \quad (6)$$

so that the simulation for region I is in effect an NPT simulation (provided that the number of molecules in region I is kept constant). In deriving equation (6) from equation (5), the $P\Delta V$ term results from the thermodynamic relationship for the pressure of region II, $P = -(\partial E^{II}/\partial V)_{T,N}$, exactly valid at the limit of an infinite region II.

Clearly, if this type of perturbation is considered in addition to the displacement steps (that ensure equilibration within each region), the equilibrium configuration of the total system would be one in which the pressure in both regions would be identical. This pressure (contrary to the case for an NPT ensemble simulation) is not specified externally. The system adjusts itself to locate the appropriate value for the pressure.

In a similar manner, we now consider in figure 1(*d*) a perturbation in regions I and II which consists of the movement of a single molecule from region II to region I. The transfer of a molecule from one region to the other does not take place through an interfacial region: in a simulation, one would select a molecule at random from one region to disappear and appear at a

random point in the other region. The appropriate change in energy would be

$$\Delta E_{min} = \Delta E^{I} + \Delta E^{II} + N^{I}kT \ln \frac{N^{I}+1}{N^{I}}$$

$$+ N^{II}kT \ln \frac{N^{II}-1}{N^{II}} + kT \ln \frac{V^{II}}{N^{II}-1}$$

$$- kT \ln \frac{V^{I}}{N^{I}+1}. \tag{7}$$

As previously, the acceptance criterion for the new configuration is then given by equation (3). In this case the formalism reduces to the criterion for an μVT ensemble simulation [8] in region I, if region II is infinite. If no change in the volume of system I is attempted, under these conditions the simulation in region I samples the grand canonical (μVT) ensemble. The chemical potential μ that appears in the μVT ensemble acceptance criterion would arise in this case as an explicit parameter from the thermodynamic expression $\mu = (\partial E^{II}/\partial N^{II})_{T,V}$, exact at the limit of an infinite region II. Equation (7) is written for a single component system for simplicity, but can be easily extended to a multicomponent system.

In the proposed simulation method, the two regions are thus coupled in a way that implicitly (that is, without specifying a value for the chemical potential) assures that the chemical potential of all components in the two regions would be identical.

In essence then, we are proposing a simulation method that combines elements of the NVT, NPT and μVT ensembles in a way that, at least in principle, results in two regions in internal equilibrium that obey the following conditions

$$\left.\begin{array}{l} P^{I} = P^{II}, \\[2mm] \mu_i^{I} = \mu_i^{II}, \text{ for all species present}, \end{array}\right\} \tag{8}$$

where P is the pressure and μ_i the chemical potential of species i.

The set of equations (8) are necessary and sufficient conditions for phase equilibrium between the two regions I and II, as originally derived by J. W. Gibbs more than 100 years ago [19]. It is for this reason that we propose the name 'Gibbs ensemble' for a simulation on the lines described above, with the purpose of obtaining the properties of coexisting phases. Each of the two regions taken separately samples the 'generalized ensemble' introduced by Hill [20], in which a system is at mechanical, thermal and material contact with its surroundings. We prefer, however, to use the term 'Gibbs ensemble' over the less specific 'generalized ensemble'.

The type of simulation described above should theoretically result in the correct values for the coexistence properties of a system at a given temperature, avoiding unstable states. If, for example, in a pure component system the initial conditions are chosen so that the density is in the unstable region (where $\partial P/\partial V > 0$) the system should rearrange itself to result in two stable phases (with $\partial P/\partial V < 0$). An initial state in a metastable region, however, would be thermodynamically stable, and we cannot expect to be able to observe a phase split during a simulation of reasonable length, unless random fluctuations bring one of the regions past the stability limit.

The equilibrium density of each region is uniquely determined by the condition of phase equilibrium and the temperature. This, by simple mass balance, results in a specified average number of molecules in each region. The extent of each region, however, is only well defined in a two-phase region.

In the previous discussion, we did not specify the size of each region, but implicitly assumed it was macroscopic. In a simulation of finite length, we can only have a microscopic number of molecules of each species in each region. The solution to this is to consider each region as composed of a large number of identical subcells with a microscopic number of molecules and apply conventional periodic boundary conditions.

3. Computational aspects

In the implementation of the theory described above, several choices need to be made concerning the computational method. We have used the following procedures for the calculations.

Initial conditions. The choice of initial densities and number of molecules in each region affects the equilibrium values of the number of molecules in the way described in the previous section. In a simulation with a limited number of molecules (of the order of 10^2–10^3) one needs to select an initial state that, after equilibration, would have a large enough number of molecules in each subcell to ensure appropriate sampling of the equilibrium properties of that phase. In the case of the pure LJ fluid the phase diagram is reasonably well known from previous investigations and we were able to select initial conditions that would always result in a sufficient number of molecules in each region, as shown in the next section. The initial conditions were intentionally chosen to deviate from the previously obtained equilibrium values for the gas and liquid densities, so as to verify that the results are not influenced by these initial conditions. In a case where no information is available on the phase behaviour of a fluid, a small number of short exploratory calculations would give the approxi-

mate densities (and compositions, in the case of a multi-component system) of the coexisting phases.

The initial configuration in each cell was a face-centred cubic lattice appropriate for the initial density in each region. The initial number of molecules was allowed to be different from the number that would completely fill such a lattice ($4K^3$, where K is an integer). In this case, a lattice with the next highest number of sites was selected and the molecules placed at random positions in the lattice, thus leaving potentially empty spaces (the lattice spacing would have to be decreased in this case to result in the desired actual density). The initial lattice was observed to 'melt' in a matter of a few tens of thousands of configurations even at the lowest temperature and highest liquid density investigated ($T^* = 0.75, \rho^* \approx 0.8$).

Displacement steps. It was decided to perform a number of random displacements of the molecules of each phase before attempting to change the volume or number of molecules in each region. Every molecule in turn in each region was moved by adding a random value from a uniform distribution to the molecular coordinates. The maximum displacement was adjusted so as to give, if possible, an average acceptance ratio of the attempted moves equal to 50 per cent. The average value of the energy and pressure and the (constant) value of the density over the displacement steps were recorded.

Volume change steps. At the end of the displacement period, a single volume change attempt was performed. The interval ΔV was again chosen from a uniform distribution of sizes $[-\alpha V_{\min} \leqslant \Delta V \leqslant \alpha V_{\min}]$, where $V_{\min}$ is the minimum value of the volumes of the two regions, and the factor α was adjusted to give an acceptance ratio for the volume changes equal on the average to 50 per cent. The calculation of the energy and pressure after the volume change steps was performed by utilizing the scaling properties of the LJ potential, as described in [6]. A long range correction, as described below, was taken into account in calculating the energy change of the two regions for use in equations (3) and (5).

Particle interchange steps. First, it was decided at random and with equal probabilities which of the two regions would be the receiving end for the particle interchange. The other region would then be the supplying end. Then, a test position was chosen at random in the receiving region, and the distances from the molecules of this region were calculated. As a time-saving measure, if the minimum distance was lower than a cutoff value, r_{cutoff} (selected so as to give $\exp(-E_{\text{cutoff}}/kT) = 10^{-15}$), the attempted move was immediately rejected. If no significant overlap was found, the test particle energy, including long-range corrections, was calculated and a random molecule from the supplying region was selected

to be interchanged into the trial position. The new configuration was accepted with a probability given by equations (3) and (7).

It was observed that at higher reduced temperatures, where the probability of accepting an interchange is relatively high, erroneous results (with average pressures higher than the ones corresponding to equilibrium NVT calculations) resulted for the liquid side if a large number of attempts was performed at a single instance. This can be explained from the fact that after a large change of the average number of molecules in one region, some equilibration is necessary. The problem was alleviated by selecting the number of attempted interchanges for a given run so as to result, on the average, to a small percentage (maximum 1–3 per cent) of the number of molecules in each cell being interchanged at any given instance. Another possible solution to this problem, namely adjusting the number of attempted interchanges or terminating the attempt after a given number of successful interchanges, would bias the sequence of configurations and should not be performed.

The interaction energies calculated during the particle interchange steps are precisely the test and real particle energies and can be used (although we did not implement this step in our simulations) for the determination of the chemical potential of the two regions without any increase in the computational time required.

Long-range corrections. For the number of molecules we have been using in the simulations, the minimum edge length, L, of each periodic cell is always greater than 5_σ, and normally in the vicinity of $6–8_\sigma$ for the liquid regions. The normal practice in previous simulations, truncating the LJ potential at a distance equal to $L/2$, half the box edge length, was not followed in this work. All interactions between the molecules in a cell and their minimum-image neighbours were included in the energy calculation. The minimum image neighbours can be at distances ranging from 0 (in practice, the minimum distance of approach cannot be less than $\sim 0.8_\sigma$) to $(\sqrt{3}/2)L$. The ideas underlying this treatment of the interactions stem from a recent work by Theodorou and Suter [21] that demonstrated that it is possible to obtain structural information for a simulated system with periodic boundary conditions for distance up to the maximum $(\sqrt{3}/2)L$. They provide equations that describe how the radial distribution function $g(r)$ should be corrected for distances between $L/2$ and $(\sqrt{3}/2)L$ (equation (13) in [21]). In essence, by allowing the calculations to proceed for distances between $L/2$ and $(\sqrt{3}/2)L$, one does not take into account a fraction of possible interacting pairs (in addition to the minimum-image pairs), that smoothly changes from 0 for $r = L/2$ to 1 at $(\sqrt{3}/2)L$. The advantage from this treatment is that it

Table 1.   Details of the simulations performed.

T^*	N	Initial conditions					$M_{eq}/10^6$	$M_t/10^6$	f_I	Average values	
		N^I	N^{II}	$\rho^{*,I}$	$\rho^{*,II}$					N^I	N^{II}
1.30	500	250	250	0.35	0.35		0.5	1.3†	20	49.7	450.3
1.30	300	150	150	0.25	0.25		0.3	1.2†	10	70.5	229.5
1.25	500	250	250	0.30	0.30		0.5	1.5	10	67.0	433.0
1.25	300	150	150	0.20	0.20		0.5	2.0	10	85.5	214.5
1.15	300	150	150	0.20	0.20		0.5	1.5	50	73.1	226.9
1.15	500	250	250	0.20	0.20		0.5	3.0‡	50	113.2	386.8
1.00	500	150	350	0.06	0.60		0.5	1.9	150	64.0	436.0
1.00	300	150	150	0.06	0.60		0.6	1.9	100	60.4	239.6
0.90	300	150	150	0.03	0.60		0.6	1.9	400	55.0	245.0
0.75	500	50	400	0.001	0.60		1.5§	3.5	2000	129.4	370.6
0.75	300	100	200	0.005	0.60		0.9§	2.3	2000	53.7	246.3

† Run failed at this number of configurations because one region became empty; see text.

‡ The density in the two regions showed long-period oscillations.

§ An equilibration period of 100 000 steps with no particle interchange was performed initially to allow for 'melting' of the lattice for the dense phase.

effectively increases the range of the potential that is explicitly taken into account, and thus decreases (by about 50 per cent) the long-distance corrections, without increasing the computation time required. The long distance corrections were calculated by integrating the potential in two parts, from $L/2$ to $(\sqrt{3}/2)L$ using the expression mentioned above for the corrected radial distribution function, and from $(\sqrt{3}/2)L$ to $+\infty$ by using $g(r) = 1$.

One possible complication that may arise in a Gibbs ensemble simulation (but also for any ensemble such as NPT or μVT that entail different types of steps) is the effect on the calculated system properties of potential interactions between the various types of steps taken. A simple verification of the absence of such interactions is to perform an NVT calculation (by not allowing any changes in volume or number of molecules of each region) at the set of average conditions obtained from a Gibbs ensemble run, and compare the corresponding results for the energy and pressure. We performed such checks for all runs presented in the following section. For the set of simulation parameters reported in table 1, no significant difference was found between Gibbs-ensemble calculations and NVT calculations at the same conditions.

The calculations were performed on a fast vector processor (CRAY 1S) using automatic vectorization. All internal loops were made vectorizable. The time required for the calculations depends on the total number of molecules and the number of attempted interchanges, but is typically less than 5 CPU minutes for 10^6 configurations generated with $N = 500$ molecules.

4.   Results and discussion

In table 1, we present a summary of the simulations performed for the calculation of the coexistence properties of the pure LJ fluid. The table gives details for the simulations performed at each temperature, including information about the initial conditions, the number of configurations M_{eq} that were performed in order to equilibrate the state of the systems (M_{eq} initial configurations were discarded for each run) and the total number M_t of configurations generated. Note that the number of interchange attempts, f_I, was determined from preliminary runs (not included in the table) so as to obey the limitations discussed in the previous section. A rapidly increasing number of attempted interchanges was necessary at lower reduced temperatures where the probability of successful interchange is small. In most cases, the final (equilibrium) number averages and densities in each region were significantly different from their initial values.

A typical plot of the evolution of density of each region for the length of a simulation is presented in figure 2 for the $N = 500$ run at $T^* = 1.00$. As can be observed, the initial densities change very rapidly (over a few tens of thousands of configurations generated) from their initial values, and subsequently fluctuate around a mean value, assumed to be the equilibrium value. 0.5×10^6 configurations for this run were rejected to ensure that the results are not influenced by the initial conditions. Some long-period oscillations in the number of molecules in each region are evident, but we feel that a reasonably good estimate of the number of molecules in each region can be obtained over the length of the
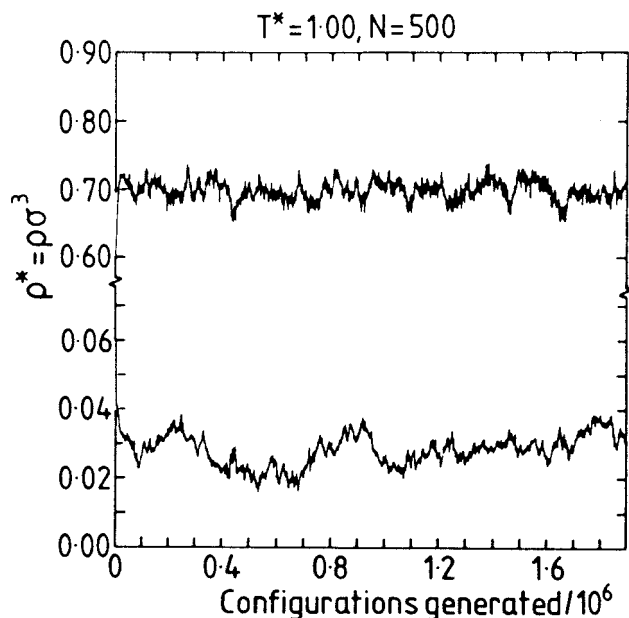
Figure 2. Density in each of the two regions versus configuration number for the run at $T^* = 1.00, N = 500$.

Figure 3. Density in each of the two regions versus configuration number for the run at $T^* = 1.15, N = 300$.

simulation run. The average properties of the two regions were found to be stable (with small random fluctuations) after the initial equilibrium period. Similar results for the stability of the average properties calculated in each region were obtained for the other simulation runs, except as noted below. Longer equilibration times were required for the lowest temperature ($T^* = 0.75$), as shown in table 1, but the average densities in each region were constant after the equilibration period. The slow convergence at the low temperatures is due to the high density of the liquid that results in low probability of successful interchanges.

In figure 3, a case is presented where the initial conditions in the two regions were identical, and correspond to a point of material instability ($T^* = 1.15, \rho^* = 0.20$). As expected, the system evolves away from the unstable region and forms two distinct phases apparently stable over the length of the simulation. Since the two regions are indistinguishable at the initial conditions of the run, which of the two regions will become the gas and which the liquid phase is decided by random fluctuations.

As the critical point is approached (previously estimated at $T^* = 1.35$ [16]), the fluctuations in number density of the two coexisting phases increase and it becomes more difficult to obtain a stable long simulation. For the runs at $T^* = 1.25$, some drifting of the average values of the densities in the two regions was observed even after 2×10^6 configurations, and thus the calculated results (table 2) have high estimated uncertainties. In addition, for $T^* = 1.30$, the two simulations
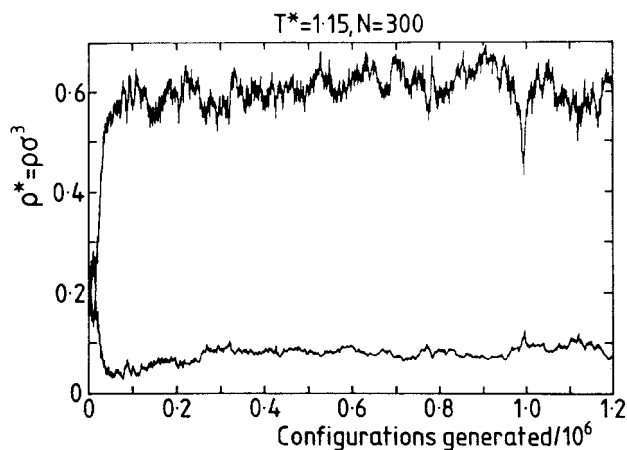
failed after the number of configurations indicated in table 1, because one of the two regions was left with no molecules. That this is possible, was indicated in the previous section; close to the point of phase homogeneity, the numbers of molecules in each region are not well defined. It was felt, however, that stable phases were observed over a large enough number of configurations to permit calculation of their average properties (with correspondingly large estimated uncertainties).

The results obtained for the coexistence properties of the pure LJ fluid and comparisons with available literature direct calculations are summarized in table 2. The table gives the average density, pressure and energy for each region, as obtained from the simulations (excluding the initial equilibrium period). The estimated errors for the various properties are shown in parentheses: the numbers indicate the standard deviation in units of the last decimal digit of the corresponding quantity. The estimated errors were obtained by averaging over blocks of 0.15 to 0.25×10^6 configurations, a procedure that has been commonly followed in the past.

For the second temperature listed in table 2, $T^* = 1.25$, there are significant deviations between our calculated results and the only set of previously available data by Adams [9]. Adams does not give the estimated errors for the coexistence densities, but the intersection procedure he employed for the calculations is liable to large errors at the vicinity of a critical point. At conditions so close to the critical point it is expected that any method that uses a small number of molecules would give results dependent on the system size, and the equilibrium would be very slow (critical slowing-down). The results at this temperature, and also at $T^* = 1.30$, the temperature closest to the critical point, verify both expectations in terms of the slow drifting in the properties of the two regions observed during the simulations

Table 2.   Results for the coexistence properties of the pure LJ (6, 12) fluid and comparison with literature.

Source	T^*	N	ρ_G^*	P_G^*	E_G^*	ρ_L^*	P_L^*	E_L^*
This work	1.30	500	0.24 (2)	0.125 (7)	−1.74 (13)	0.45 (3)	0.114 (7)	−3.10 (12)
This work	1.30	300	0.17 (1)	0.119 (5)	−1.30 (8)	0.47 (3)	0.121 (17)	−3.22 (19)
Adams [9]	1.30		0.22 (2)	0.127		0.43 (2)		
This work	1.25	500	0.123 (14)	0.091 (9)	−0.95 (14)	0.505 (23)	0.091 (14)	−3.47 (15)
This work	1.25	300	0.110 (17)	0.089 (9)	−0.88 (4)	0.533 (40)	0.105 (32)	−3.66 (24)
Adams [9]	1.25		0.19	0.111	−1.54	0.544		−3.73
This work	1.15	500	0.076 (7)	0.061 (7)	−0.657 (12)	0.606 (12)	0.062 (11)	−4.17 (8)
This work	1.15	300	0.082 (5)	0.064 (4)	−0.706 (4)	0.610 (2)	0.081 (16)	−4.20 (10)
Hansen and Verlet [3]	1.15		0.073	0.0597		0.606		
Adams [9]	1.15		0.077	0.0630	−0.673	0.609		−4.20
This work	1.00	500	0.0281 (32)	0.0239 (23)	−0.255 (31)	0.698 (3)	0.007 (15)	−4.87 (3)
This work	1.00	300	0.0271 (37)	0.0233 (27)	−0.249 (33)	0.695 (5)	−0.006 (18)	−4.86 (5)
Adams [8]	1.00		0.0261	0.0227	−0.237	0.703		−4.91
This work	0.90	300	0.0115 (14)	0.0096 (11)	−0.113 (14)	0.753 (14)	0.002 (32)	−5.32 (3)
Adams [8]	0.90		0.0131	0.0108	−0.126	0.756		−5.35
This work	0.75	500	0.0028 (2)	0.0019 (2)	−0.030 (2)	0.820 (6)	0.004 (20)	−5.90 (5)
This work	0.75	300	0.0027 (4)	0.0019 (3)	−0.030 (4)	0.820 (5)	0.009 (22)	−5.90 (5)
Hansen and Verlet [3]	0.75		0.0035	0.0025		0.825		
Adams [8]	0.75		0.0033	0.0024	−0.038	0.826		−5.96

and an apparent effect of system size. As expected, the system with the smallest number of molecules appears to have the highest critical temperature [9]. The differences however are not large, and this suggests that the $N = 500$ results may be close to the infinite system properties.

In figure 4, we plot the coexistence curve for the pure LJ fluid as obtained from our simulations and compare graphically the results from the available literature sources. The line corresponding to the law of rectilinear diameters [22] is also shown in figure 4. The points from our simulations follow a straight line to within their respective accuracy. The $T^* = 1.25$ results from Adams [9] deviate significantly from the line, and are probably suspect. The critical temperature from the plot for the $N = 500$ system appears to be slightly below the accepted [16] value of 1.35. An extrapolation of the line of rectilinear diameters to the critical region gives an estimate of the critical density as $\rho_c = 0.31 \pm 0.02$, again below the previously accepted value of 0.35.

At the intermediate range of temperatures ($T^* = 1.15$ to $T^* = 0.90$), the results are in satisfactory agreement with those of previous investigations. The agreement is within our estimated error limits. There is little dependence on system size for the results at $T^* = 1.15$, 1.00 or 0.75. The deviations among the different sets of results for the gas phase density appear to be random. Some systematic deviations for the liquid phase density are possible, but the differences are small (our results are

on the average lower by 0.5 per cent). The uncertainties in the energy and pressure of the two phases result almost entirely from fluctuations in density observed during the Gibbs ensemble simulations. If no attempts to interchange or move molecules are made (NVT ensemble operation), then the computer program that we are using gives the energy and pressure at a given density in close agreement with literature values [16].

Pressures of the gas and liquid regions obtained from the simulations generally agree to within their corresponding standard deviations, thus verifying that the simulations reach equilibrium for the pressure. The standard errors for the pressure on the gas region are, as expected, significantly lower than the corresponding values for the liquid and can thus be more usefully identified as the equilibrium vapour pressure at the corresponding temperature.

A difference of 30 per cent for the gas phase density was obtained at $T^* = 0.75$ between our results and the two available literature estimates. Runs with different initial conditions and number of molecules in each region ($N = 300$ and $N = 500$) gave virtually identical results. The calculated values of Adams [8] are from an extrapolation of the equation of McDonald and Singer [4] over a large range of reduced temperatures (from $T^* = 1.00$ to $T^* = 0.75$), and the estimated error is not reported. The results from Hansen and Verlet [3] were obtained by integrating the pressure-density relationship
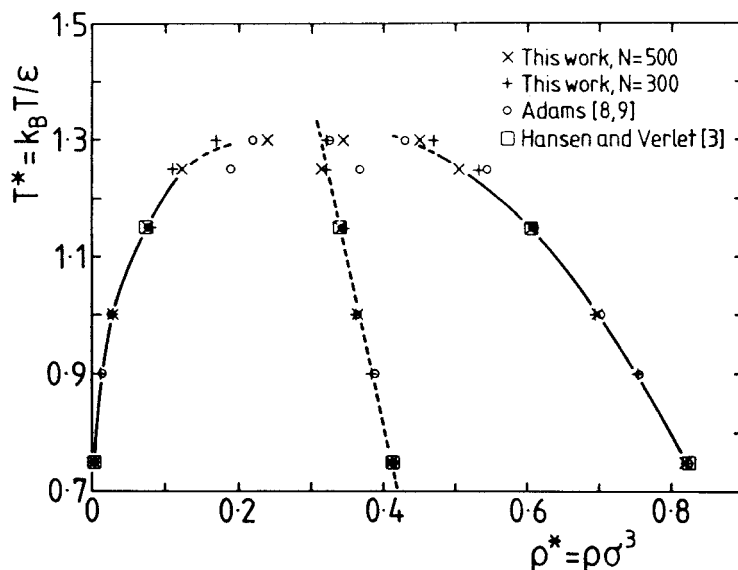
Figure 4. Liquid-vapour phase coexistence curve (————) and line of rectilinear diameters (– – – – – –) for the pure LJ (6, 12) fluid. (×) this work, $N = 500$; (+) this work, $N = 300$; (◯) Adams [8, 9]; (☐) Hansen and Verlet [3]. The continuous line is drawn through the $N = 500$ results for visual clarity.

through the unstable region (by constraining density fluctuations) and this procedure may introduce some systematic error. Even if we accept that the deviation is entirely due to error resulting from our proposed method, the prediction of the coexistence curve at a temperature close to the triple point from a single simulation may still be an attractive alternative to the long thermodynamic integration through the unstable region. For comparison, if one were to obtain similar results from a chemical potential calculation, one would need to calculate the chemical potential to within ± 0.2 reduced units (this being the difference in chemical potential between $\rho^* = 0.0027$ and $\rho^* = 0.0035$ at $T^* = 0.75$) for a liquid density of $\rho^* = 0.82$. This appears not to be possible with the conventional test particle method without full umbrella sampling [23].

In summary, we have demonstrated that the proposed method for the calculation of phase coexistence properties of fluids gives results in reasonable agreement with literature values for the properties of the pure LJ fluid. The method was applied for reduced temperatures from close to the triple point to the vicinity of the critical point and shown to give consistent results throughout this range.

The proposed method has significant advantages in terms of speed and simplicity over currently available techniques even for the simple case of one-component systems. A possible area of the application of the technique that needs to be considered is the calculation of coexistence curves for multicomponent systems. The

principle of the method may prove valid for direct calculation of equilibria between fluid phases (liquid–gas, liquid–liquid or fluid–fluid) in a system with an arbitrary number of components. In such a system, the currently available techniques are clearly impractical due to the very large number of simulations required and the uncertainties associated with the calculation of the chemical potential for dense phases. The proposed technique has the potential of accomplishing the same task in a single simulation. The application of the technique to multicomponent systems will be the subject of future work in this area.

Note added in proof.—After this work was completed, Panagiotopoulos *et al.* [24] obtained a different derivation of the acceptance criteria for the volume change and particle interchange steps. The interchange criterion given in [24] differs from equation (7) by a factor of order $O(1/N)$, resulting from the use of Stirling's approximation for the ideal-gas entropy expression in this work. For the set of conditions given in table 1, the two interchange criteria give

virtually identical results. However, if the number of molecules of a species in one region is small, the interchange criterion given in [24] should be substituted for equation (7).

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