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Monte Carlo Grand Canonical Ensemble Calculation in a Gas–Liquid Transition Region for 12–6 Argon

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A Monte Carlo method for the grand canonical ensemble is described and used to study the gas–liquid transition of a 12–6 fluid at a reduced temperature of 1.15. In the region of the transition the gaseous and liquid phases are rarely accessible one from the other and points were found which lie on the metastable branches of a van der Waals loop. Transition parameters and the entropy of the liquid have been calculated and the results compared with previous Monte Carlo calculations and with experimental data for argon.

1. INTRODUCTION

Calculation of the thermodynamic properties of fluids using the Monte Carlo (MC) method is well established [1–5] and has led to valuable insights into the structure of real fluids. Most calculations of this type have used the canonical (N, V, T) ensemble and have shown that the properties of classical, real, monatomic fluids are well represented in the high density region by particles interacting with a Lennard–Jones (12–6) potential.

The work described here was carried out in connection with a larger scale MC study of fluids in an external potential field and describes the use of a grand canonical (μ, V, T) ensemble to study the gas–liquid transition region of a 12–6 fluid at reduced temperature $T^*(=kT/\epsilon)$ of 1.15.

This system was previously studied by Hansen and Verlet [6] using the canonical ensemble and 864 particles. In their computations the total volume was subdivived into a number of smaller volumes and upper and lower bounds were set on the number of particles in each subvolume in the MC chain. These bounds were chosen so as to obtain satisfactory convergence without modifying the thermodynamic properties in the single phase regions. The resulting pressure–volume curve showed a van der Waals loop and the Maxwell equal area construction was used to find the transition pressure.

An earlier study of this kind with 32 particles was made by Wood [1] but the results were insufficient to enable the transition pressure to be accurately located from a Maxwell construction.

Unlike the canonical ensemble the isothermal–isobaric (N, p, T) and grand canonical ensembles (μ, V, T) in general exhibit only one stable phase for a given set of parameters. For any $T \leqslant T_c$ there is only one value of pressure (in the isothermal–isobaric ensemble) or μ (in the grand canonical ensemble) for which two phases can be in equilibrium.

The isothermal–isobaric ensemble has been employed for a study of 12–6 argon in the gas–liquid transition region using 32 particles [7]. At a temperature close to the experimental critical temperature and a pressure of 0.9 of the vapour pressure, fluctuations between gas phase and liquid phase volumes were observed in the MC chain. However, at lower temperatures the phase obtained was strongly dependent on the initial configuration and volume to the extent that, in some cases, negative pressures were necessary in order to induce a transition to the gas phase from an initially liquidlike configuration.

The majority of calculations using the grand canonical ensemble [8–10] are more suited to particles constrained to move on a lattice than to continuous systems. An exception is the work of Norman and Filinov [11] which appears to have been overlooked in the western literature until now and which was brought to light only after these calculations were well advanced. A comparison of this work with the method described here is made in the discussion section (Sect. 5).

In Section 2 the equations of the grand canonical ensemble are written in a form suitable for the MC importance sampling method. Section 3 describes the sampling procedure and the results of the calculations are reported in Section 4.

2. GENERAL EQUATIONS

The given parameters in the grand canonical ensemble are temperature T, volume V and the set of chemical potentials

$$\boldsymbol{\mu} \equiv \{\mu_\alpha \,;\, 1 \leqslant \alpha \leqslant s\}$$

for the s species.

We wish to calculate the ensemble average $\langle f \rangle$ of a phase function $f_{\mathbf{N}}([\mathbf{N}])$, where

$$[\mathbf{N}] \equiv \{\mathbf{r}_1^{(1)}, \mathbf{r}_2^{(1)}, \ldots, \mathbf{r}_{N_1}^{(1)}, \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_{N_2}^{(2)}, \ldots, \mathbf{r}_{Ns}^{(s)}\}$$

is the configuration set corresponding to the composition set

$$\mathbf{N} \equiv \{N_1, N_2, \ldots, N_s\}.$$

$\mathbf{r}_i^{(\alpha)}$ is the coordinate of particle number i of species α and N_α is the number of particles of that species.

The average $\langle f\rangle$ is given by [12a].

$$\langle f\rangle = \frac{\sum_{\mathbf{N}=0}\int d[\mathbf{N}]\, f_{\mathbf{N}}([\mathbf{N}])\, g_{\mathbf{N}}([\mathbf{N}])}{\sum_{\mathbf{N}=0}\int d[\mathbf{N}]\, g_{\mathbf{N}}([\mathbf{N}])}\,. \tag{2.1}$$

The weighting function for the grand canonical ensemble is given by

$$g_{\mathbf{N}}([\mathbf{N}]) = \mathbf{Z}^{\mathbf{N}} \exp\{-\beta U_{\mathbf{N}}([\mathbf{N}])\}/\mathbf{N}\,!, \tag{2.2a}$$

$$\mathbf{Z}^{\mathbf{N}} = \prod_{\alpha=1}^{s} Z_\alpha^{N_\alpha}, \qquad \mathbf{N}! = \prod_{\alpha=1}^{s} N_\alpha\,!\,, \tag{2.2b}$$

and for monatomic molecules,

$$Z_\alpha = (2\pi\hbar^2\beta/m)^{-3/2}\exp(\beta\mu), \qquad \beta = 1/kT, \tag{2.2c}$$

$U_{\mathbf{N}}[\mathbf{N}]$ is the potential energy of the configuration $[\mathbf{N}]$.

We next introduce a maximum composition set **M** such that the summations over N in (2.1) can, with negligible error, be restricted to subsets of **M**. For a one component system **M** would be the maximum number of particles which could be packed into V given a sensible hard core cut off. In the multicomponent case **M** would be the union of the maximum composition sets M_α, $1 \leqslant \alpha \leqslant s$.

We define an occupation set $\mathbf{n}^{(\alpha)}$ for each species α containing M_α elements of which N_α are unity and the remainder are zero, thus

$$\mathbf{n}^{(\alpha)} \equiv \{n_1^{(\alpha)}, n_2^{(\alpha)},\ldots, n_{M_\alpha}^{(\alpha)}\}, \tag{2.3a}$$

$$n_i^{(\alpha)} = 0 \quad \text{or} \quad 1, \qquad N_\alpha = \sum_{i=1}^{M_\alpha} n_i^{(\alpha)}. \tag{2.3b}$$

The integrals of Eq. (2.1) may now be considered as functions of $\mathbf{n} \equiv \{\mathbf{n}^{(\alpha)}, 1 \leqslant \alpha \leqslant s\}$ and the maximum configuration set $[\mathbf{M}]$. When $n_i^{(\alpha)}$ is zero the integral is independent of the coordinate $\mathbf{r}_i^{(\alpha)}$ and the ith particle is designated as a "fictitious particle." The system thus contains N_α real particles and $M_\alpha - N_\alpha$ fictitious particles of component α and the total number of particles (real plus fictitious) is a fixed number M,

$$M = \sum_{\alpha=1}^{s} M_\alpha\,. \tag{2.4}$$

The sums and integrals of Eq. (2.1) may now be replaced by sums over all occupation sets n and integrals over the configuration set $[\mathbf{M}]$, e.g.,

$$\sum_{\mathrm{NCM}} \int d[\mathbf{N}]\, g_{\mathbf{N}} = \sum_{\mathrm{NCM}} \prod_{\alpha=1}^{s} \left\{\frac{V^{(N_\alpha - M_\alpha)}(M_\alpha - N_\alpha)!\, N_\alpha\,!}{M_\alpha\,!}\right\} \int d[\mathbf{M}]\, g_{\mathbf{N}}\,. \tag{2.5}$$

The factor $V^{N_\alpha - M_\alpha}$ appears because integration over each fictitious coordinate in Eq. (2.1) gives a factor V while the reciprocal of the combinatorial factor in Eq. (2.5) is the number of possible occupation sets **n** for a given composition set **N**.

Equations (2.5) and (2.1) give, after some simplification

$$\langle f \rangle = \frac{\sum_{\mathbf{n}} \int d[\mathbf{M}]\, f(\mathbf{n}, [\mathbf{M}])\, h(\mathbf{n}, [\mathbf{M}])}{\sum_{\mathbf{n}} \int d[\mathbf{M}]\, h(\mathbf{n}, [\mathbf{M}])}, \tag{2.6}$$

$$h(\mathbf{n}, [\mathbf{M}]) = \prod_{\alpha=1}^{s} (Z_\alpha V)^{N_\alpha} (M_\alpha - N_\alpha)! \exp(-\beta U_{\mathbf{M}}(\mathbf{n}, [\mathbf{M}])). \tag{2.7}$$

Now let the configuration space be divided into a number of equal volume elements $\Delta\mathbf{x}$ each with configuration $\mathbf{x}$ at the centre. Then

$$\lim_{\Delta\mathbf{x}\to 0} \sum \Delta\mathbf{x} = \int d[\mathbf{M}], \tag{2.8}$$

and (6) becomes

$$\langle f \rangle = \sum_{\mathbf{n},\mathbf{x}} f(\mathbf{n}, \mathbf{x})\, u(\mathbf{n}, \mathbf{x}), \tag{2.9}$$

$$u(\mathbf{n}, \mathbf{x}) = h(\mathbf{n}, \mathbf{x}) \Big/ \sum h(\mathbf{n}, \mathbf{x}). \tag{2.10}$$

Equation (9) is the form of $\langle f \rangle$ required for MC sampling.

3. MONTE CARLO SAMPLING

3.1. *General Method*

The sum over states given by Eq. (2.9) is sampled by a Markov chain $y(t)$; $t = 1, 2, \ldots, \mathcal{N}$ where $y \equiv \{\mathbf{n}, \mathbf{x}\}$. A state in the Markov chain is generated from the previous one in the usual way using the probability $u(y)$ defined by Eq. (2.10). Thus a trial state y' is accepted as the next state if $u(y') \geqslant u(y)$; when $u(y') < u(y)$ the next state is y' (or y) dependent on whether $u(y')/u(y)$ is $\geqslant \xi$ (or $< \xi$) a random number distributed uniformly in the range 0 to 1.

When the state y' is chosen in the neighbourhood of y in such a way as to satisfy ergodic requirements [1] then the average $\bar{f}$ over the Markov chain converges to $\langle f \rangle$,

$$\bar{f} = \frac{1}{\mathcal{N}} \sum_{t=1}^{\mathcal{N}} f(y(t)), \qquad \lim_{\mathcal{N}\to\infty} \bar{f} = \langle f \rangle. \tag{3.1}$$

For the one component system investigated here the trial state for the particle i with coordinate $\mathbf{r}_i = (x_i, y_i, z_i)$ and occupation number n_i is generated cyclically as

$$\begin{aligned} x_i' &= x_i + (2\xi_1 - 1)\,\delta \quad \text{etc.} \\ n_i' &= n_i\,; \qquad \xi_4 \leqslant 1/2, \\ n_i' &= 1 - n_i\,; \qquad \xi_4 > 1/2, \end{aligned} \tag{3.2}$$

where δ is a step lenth parameter and ξ_j's are random numbers uniformly distributed in the range 0 to 1.

The next state can be generated in one of four possible ways depending on the values of n_i and ξ_4 :

(i) $n_i = 0$, $\xi_4 \leqslant 1/2$. A fictitious particle is moved, the next state is always y'.

(ii) $n_i = 1$, $\xi_4 \leqslant 1/2$. A real particle is moved, the MC test is the same as that for the canonical ensemble.

(iii) $n_i = 0$, $\xi_4 > 1/2$. A fictitious particle is both moved and changed to a real particle. Here,

$$u(y')/(u(y) = ZV \exp(-\beta\, \Delta U)/(M - N).$$

(iv) $n_i = 1$, $\xi_4 > 1/2$. A real particle is moved and changed to a fictitious particle. Here,

$$u(y')/u(y) = (M - N + 1) \exp(-\beta\, \Delta U)/ZV.$$

In the cases (ii), (iii), and (iv) the change in the total potential energy is the same as that for the ith particle and is stored in a table of pairwise interactions. Only the nonzero energies of the real particles need to be stored and this is done by indexing each particle with a "store pointer," P_i . P_i is zero for fictitious particles and has a unique integer value in the range $0 < P_i \leqslant N_s$, ($N_s > N$) for each real particle. Here N_s is an upper limit whose value is discussed below. The pairwise interactions between real particles are then stored in $N_s(N_s - 1)/2$ locations indexed by P_i in an upper triangular array. When a new particle (i) is created its pairwise interactions with the other real particles are calculated. If the trial is successful P_i is given a nonzero value which is used as an index for inserting the new interactions into the pair-interaction array. When a particle (j) is destroyed P_j is set equal to zero and its previous value becomes available for a future successful creation trial.

A trap incorporated in each creation trial ensures that $N \leqslant N_s$. When this condition is violated the programme is halted, the P_i and r_i before the trial are stored and the programme restarted with a larger value of N_s. This procedure ensures that the minimum amount of store is used for a calculation.

Calculations were coded in Fortran for the University of London CDC 6600 computer and approximately 10,000 steps per minute could be generated at the liquid densities used in this work.

3.2. *The Transition Region*

General considerations [12b] show that for calculations based on the grand canonical ensemble the probability $P(N)$ of observing N particles in the system is bimodal in the region of a phase transition; the area under each peak being proportional to the number of systems in the corresponding phase in a representative ensemble. As the size of the system increases the range of activity (temperature and volume being constant) over which the two peaks have comparable areas decreases. The locus of the maxima in $P(N)$ is associated with those metastable regions of the van der Waals loop, in the corresponding canonical ensemble, where the gradient of the pressure p versus density ρ curve is positive. The unstable region ($\partial p/\partial\rho < 0$) of the van der Waals loop is associated with the minimum of $P(N)$.

If one of the maxima in $P(N)$ is inaccessible from a state corresponding to the other maximum then the $p - \rho$ curve calculated from the grand canonical ensemble will include the metastable regions of the loop but will not include the unstable region. In the next section we show that this is the case with the MC sampling method described above. In the liquid–vapour transition region the two peaks in $P(N)$ are relatively inaccessible from each other.

4. RESULTS FOR 12–6 ARGON

In the Lennard–Jones pair potential

$$\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}], \tag{4.1}$$

the parameters ϵ and σ were those appropriate for Ar ($\epsilon/k = 119.8\text{K}$, $\sigma = 0.3405$ nm) and were used as units of energy and length, respectively; the mass of the argon atom was 6.690×10^{-26} kg. The pair potential was cut off at a value of r equal to half the length L of the cubic periodic cell and the minimum image method [1] was used to calculate the total potential energy and pair-virials. Corrections to the potential energy for the long range interaction ($r > L/2$) were calculated by integration over a uniform particle density [13]. The maximum number of particles M was 864 and L was chosen so that 864 spheres of diameter 0.8 could be packed into the cell in a *fcc* array.

No systematic study of the effect of step length or convergence has been made, but test calculations indicate that convergence is not very sensitive to small changes in the step length. The acceptance of trial states of type (i) is unaffected by step length and at equilibrium the number of accepted trial states of type (iii) and (iv) are equal. As the step length is increased the overall acceptance of trial states drops and the rates of accepted trial states of type (ii) to type (iv) decreases. A step length of ~0.06 was used which led to about 50 % and 45 % acceptance of all trial states and trial states of type (ii) plus type (iv), respectively. The ratio of accepted trial states of type (ii) to type (iv) was about 8.

The number of real particles $\langle N\rangle$, energy $\langle U\rangle$ and pressure $\langle p\rangle$ were calculated by averaging N, $U_N([N])$ and the pair-virial

$$\sum_{i>j=1}^{N} r_{ij}\frac{d\phi(r_{ij})}{dr_{ij}}$$

over the MC chain after discarding at least the first 400,000 states (except where otherwise stated). The results are shown in Table I for $T^* = 1.15$ and values of the activity Z spanning the gas–liquid transition. Entropies have been calculated using the thermodynamic relation

$$TS = 1.5kT + \langle U\rangle - \mu\langle N\rangle + \langle p\rangle V,$$

all the quantities on the right hand side being given parameters or calculated averages for each run.

TABLE 1

Results of MC runs at $T^* = 1.15$. The reduced activity Z and reduced pressure $\langle p\rangle$ are in units of $1/\sigma^3$ and ϵ/σ^3 respectively. The column headed states gives the total length of the MC chain and the number of states used to calculate the averages

Run number	$Z/10^{-2}$	Initial Condition	States/41,472		$\langle N\rangle$	$\langle p\rangle.10^2$	$\langle U\rangle/\langle N\rangle$	$S/\langle N\rangle k$
			Total	Average				
1	4.203	Liquid $N = 182$	44	22	22.5	5.85	0.628	12.88
2	4.413	Liquid $N = 182$	60	18(a)	175	−4.89	3.89	9.22
				28(b)	25.2	6.48	0.688	12.27
3A	4.623	Gas $N = 39$	50	40	29.4	6.82	0.820	12.05
3B	4.623	Liquid $N = 190$	71	41	181	0.202	4.01	9.15
3C	4.623	Random $N = 86$	54	28	28.4	—	0.809	—
3D	4.623	Liquid $N = 181$	72	41	183	4.15	4.04	9.18
4	4.833	Random $N = 86$	75	28(c)	33.8	7.06	0.944	12.33
				33(d)	185	−0.017	4.07	9.05
5A	4.938	Gas $N = 39$	86	14(e)	36.8	7.18	1.01	12.23
				42(f)	186	5.86	4.10	9.09
5B	4.938	Liquid $N = 189$	74	64	187	4.59	4.12	9.05
5C	4.938	Liquid $N = 199$	70	60	185	6.00	4.07	9.12
6	5.043	Gas $N = 39$	72	58	190	7.33	4.17	9.02
7	5.254	Liquid $N = 199$	70	39	196	13.3	4.32	8.93

Averages are taken over the partial sums numbered (a) 11–28, (b) 33–60, (c) 13–40, (d) 43–75, (e) 5–18, (f) 45–86.

The number of real particles and nature of the initial conditions for each run are indicated in Table I. "Liquid" and "Gas" refer to a corresponding initial state with a fluidlike configuration of real particles. "Random" means that the initial condition was a *fcc* array of real and fictitious particles with 1 % of real particles, chosen at random, and the remainder fictitious. The sampling errors, estimated from the partial averages taken every 41,472 states were of the order of 0.7 % and 1.4 % for $\langle N \rangle$ and $\langle U \rangle$, respectively, at liquid densities and 2 % and 6 % at the gas densities. The sampling error on $\langle p \rangle$ was of the order 0.025 and 0.004 at the liquid and gas densities.

The runs numbered 2, 4, and 5*A* each showed two sections. The initial condition and first section (partial sums 11–28) of run 2 correspond to liquid densities and the second section (partial sums 33–60) to a gas density. The runs 4 and 5*A* had the initial conditions "Random" and "Gas," respectively, and the first sections correspond to gas densities followed by a jump to liquid densities after apparent convergence. The runs 5*B* and 5*C*, at the same activity as run 5*A*, with different "Liquid" initial conditions showed only one section.

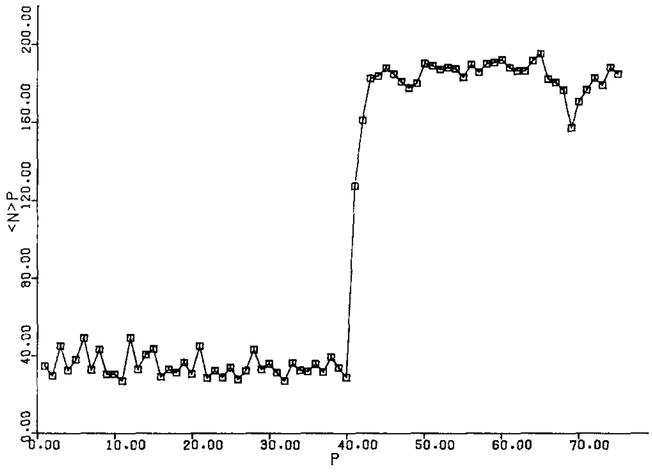

FIG. 1. The Monte Carlo run 4. $\langle N \rangle_p$ is the *p*th partial average, containing 41,472 states, of the number of real particles.

The partial averages and averaged histograms of the number of real particles for run 4 are shown in Figs. 1 and 2. The averaged histograms of the number of real particles is an estimate of the probability $P(N)$ and it can be seen from Fig. 2 that for each section of the run $P(N)$ has, apart from statistical fluctuation, only one maximum.

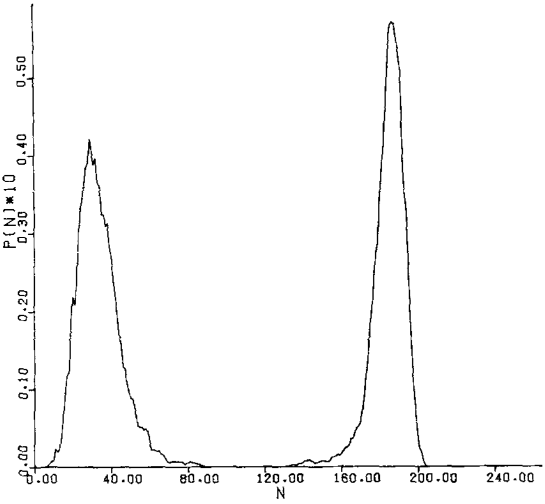

FIG. 2. Histogram of the number of real particles in the Monte Carlo run 4. The peak at low (high) N is from the partial averages numbers 13–40 (43–75) of the Monte Carlo chain.

The runs 3*A* and 3*B* start from the initial conditions "Gas" and "Liquid," respectively, and have the same value of the activity. They converge to corresponding gas and liquid phases and no jumps between the phases were observed. The additional runs 3*C* and 3*D* at the same activity with initial conditions "Random" and "Liquid" of length 54 and 72 partial sums converge to gas and liquid phases, respectively, and did not show any jumps between phases.

Liquid configurations at activities below that of run 2 or gas configurations at activities higher than run 5*A* could not be maintained.

Figures 3 and 4 show plots of the pressure and activity against density, respectively. The region in which the MC points indicate that the density is two valued correspond to the metastable regions of the van der Waals loop. Also shown are curves fitted to the points in the van der Waals loop calculated for the restricted canonical ensemble by Hansen and Verlet [6].

Figure 5 shows a plot of pressure versus activity for values taken from Table 1 for the gas and liquid branches of the pressure–density curve. The gas–liquid transition activity obtained from the intersection in Fig. 5 is $5.03.10^{-2}$. Despite the scatter of the points on the liquid branch the transition can be estimated to within ±.001 and since the gas branch pressures are more precise than those on the liquid branch the transition pressure can be estimated to within ±.005, which is approximately five times smaller than the sampling errors of the liquid branch pressures.

The pressure, density and latent heat $\mathscr{L}$ for the transition are compared with experimental values for *Ar* [14] and the values calculated by Hansen and Verlet [6]

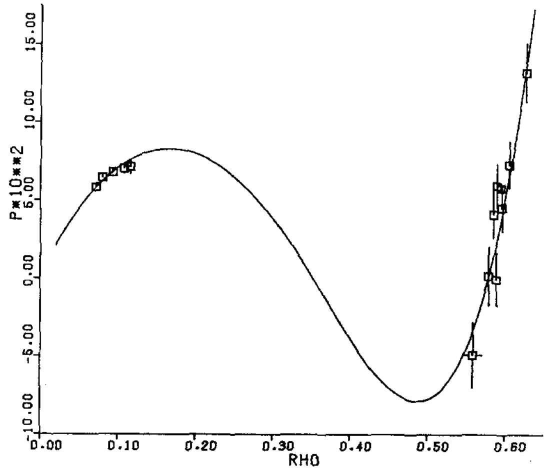

FIG. 3. Pressure versus density at $T^* = 1.15$. The bars on the points represent the estimated sampling errors. The solid curve is the van der Waals loop of the restricted canonical ensemble [6].

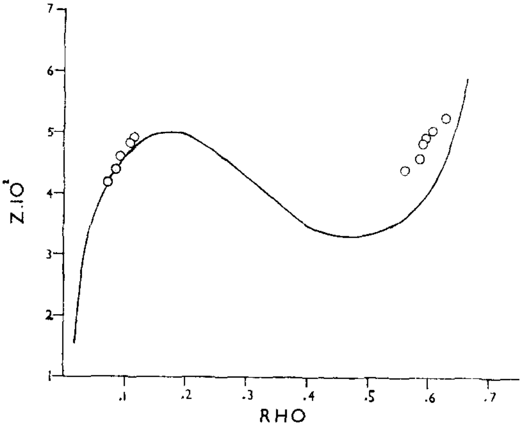

FIG. 4. Activity versus density at $T^* = 1.15$. The solid curve is the van der Waals loop of the restricted canonical ensemble [6].

in Table II. The entropy of the liquid at the transition point is shown in Table II together with the experimental value [15]. The magnitude of the corresponding configurational part of the free energy is 18% below the value calculated by Hansen and Verlet by integration of the equation of state for the restricted canonical ensemble.

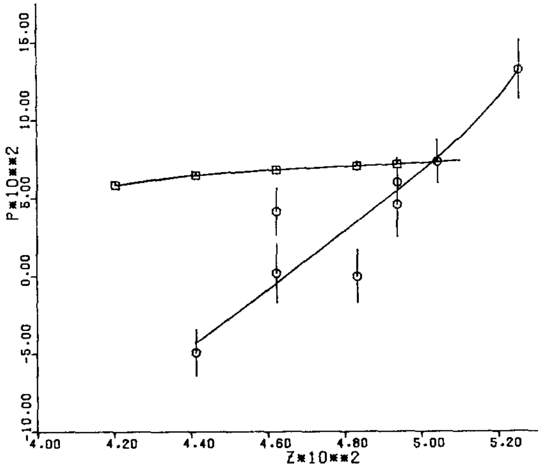

FIG. 5. Pressure versus activity at $T^* = 1.15$. The squares (circles) correspond to the gas (liquid) phase. The bars on the points represent the estimated sampling errors.

TABLE II

Liquid-gas transition data at $T^* = 1.15$. p, ρ_g and $\mathscr{L}$ are the transition pressure, gas density, liquid density and latent heat of evaporation in reduced units. S_l is the entropy of the liquid at the transition point.

	$p.10^2$	ρ_g	ρ_l	$\mathscr{L}$	S_l/NK
This work	7.29	0.124	0.605	3.56	9.04
Restricted Canonical Ensemble [6]	5.97	0.073	0.606	4.34	—
Experimental Values for Ar [14, 15].	6.64	0.093	0.579	3.73	9.42

5. DISCUSSION

The grand canonical MC method described in this work when applied to the gas–liquid transition region for 12–6 argon yields points corresponding to the metastable regions of the van der Waals loop; the liquid phase being virtually inaccessible from the gas phase and vice versa. For example, in run 4 one jump was observed in the 3×10^6 states of the MC chain. There are two possible causes for this infrequency of jumps between phases.

(i) The range of activities in which the two peaks of $P(N)$ have comparable areas may be very narrow for the size of system considered.

(ii) The MC sampling method may be inadequate for sampling both phases. The second factor may apply in this work because the number of real particles in the system is only changed by one at a time. Thus to get from a liquid phase to a gas phase state even when the areas of the two peaks in $P(N)$ are comparable, the system has to pass through states with very low values of $P(N)$. An ideal sampling method would give frequent jumps between the two phases when the areas of the two peaks in $P(N)$ were comparable or would unambiguously, regardless of initial conditon converge on one phase.

Two methods were investigated in an attempt to overcome these difficulties. In the first the number of particles created or destroyed in a single step was greatly increased. In the second two Markov chains, corresponding to gas and liquid, respectively, were run in parallel in such a way that one chain represented the actual system at each step and jumps between the chains were determined by importance sampling. Neither of these methods was successful in giving the frequent jumps between the phases required for a good estimate of a bimodal $P(N)$ or in unambiguously converging on one phase.

Despite these limitations in the grand canonical MC method the transition pressure is easily obtained from the metastable regions by equating the pressure calculated from the virial and the activities of the gas and liquid at the transition point. The value of transition pressure obtained is 10 % above the value for experimental argon at $T^* = 1.15$. The corresponding latent heat of evaporation and entropy of the liquid are 5 % and 4 % below the experimental value. This agreement with experimental argon is satisfactory and in keeping with the agreement between real and 12–6 argon previously observed in the single-phase region [2, 16].

An important feature of the method described here is that the recreation of particles becomes easier the lower the density because the probability of unfavourable interactions is reduced, and this is similar in effect to increasing the step length. Adequate sampling of the gas configuration space is therefore possible. The results confirm that the method can be operated at both gas and liquid densities without changing the step length. Norman and Filinov, using 30–40 particles at $T^* = 1.0$, found results [11] similar to those reported here but did not note any metastable regions of the van der Waals loop and did not calculate pressures from the pair-virial. Their method differs from the present one in by-passing the use of fictitious coordinates by choosing as the state parameters an ordered set of coordinates for the particles in the system. Details of the sampling procedure, which is a hybrid of the symmetric and asymmetric methods [1], are given in the original paper. Test calculations with their method have shown that metastable states do occur for the size of system used in this work and that these results have about the same estimated sampling error per unit of computing time as the present work but that the storage requirement is lower.

The metastable states found in the (N, p, T) ensemble Monte Carlo calculation [7] at $T^* = 1.0$ may be attributed to the metastable regions of the van der Waals loop in a similar fashion to this work, with the probability $P(V)$ of observing the value V taking the place of $P(N)$. However since the unstable region of the van der Waals loop can never be realized from an (N, p, T) calculation [12b] a Maxwell equal area construction can not be made to determine the transition pressure. At $T^* = 1.24$ jumps between the two phases for the (N, p, T) calculation are more frequent than in the present work (about once every 6.10^4 states). This may be due either to the higher temperature and smaller system used (32 particles) in the (N, p, T) work or to an inherent superiority for sampling both phases. At $T^* = 1.24$ this method showed repeated jumps between the phases when the pressure was 10% below the experimental value.

The results of Hansen and Verlet for the restricted canonical ensemble at $T^* = 1.15$ predict a transition pressure ~10% below the experimental value and 19% below the value reported here. The latent heat of evaporation is 22% above the grand canonical ensemble value. Restrictions of the density fluctuations in the canonical ensemble would be expected to favour the liquidlike phase over the gas phase in the two phase region and may account for this discrepancy.

A possible source of error in our method lies in the small average number of particles sampled for the gas phase, which may create finite system effects. That this is unlikely to be the case is strongly supported by the $z - \rho$ plot (Fig. 4), which shows good agreement on the gas density side with the results of Hansen and Verlet, but poor agreement on the liquid density side.

The cell size will also be important close to the transition point. When the cell is small there may be a significant correlation between particles in adjacent cells and a consequential modification of the transition parameters might be expected.

The MC grand canonical method offers several advantages over the canonical and (N, p, T) ensembles in the transition region. Further investigation of MC chains showing jumps between the gas and liquid phases and the effect of cell size would be desirable and the study of systems close to the critical point may even be possible with this method.

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