A grand canonical simulation technique for dense and confined fluids with application to a Lennard-Jones fluid

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Grand canonical simulations, (specified chemical potential), are performed with a fixed number of particles by coupling variations in the system size to the instantaneous chemical potential determined by virtual test particle methods. This is a modified form of the pseudo-grand canonical method of Mehta and Kofke [Mol. Phys. 86, 139 (1995)]. For dense fluids the method has the advantage of allowing the chemical potential to be specified without inserting particles, and is particularly suited to confined fluids, allowing the geometry to be changed at constant chemical potential. For the test particle determination of the chemical potential a preferential cell sampling method is developed that improves the excluded volume map sampling of Dietrick et al. [J. Chem. Phys. 90, 2370 (1989)]. It is several orders of magnitude more efficient than crude Monte Carlo sampling, and 4–40 times more efficient than restricted umbrella sampling. The methods are tested on Lennard-Jones fluids, in the bulk at reduced densities up to 0.95, and confined between two planar walls. © 1997 American Institute of Physics. [S0021-9606(97)50329-1]

INTRODUCTION

The chemical potential is conjugate to the particle number and is used in open systems that are able to exchange particles with a reservoir. It is one of the specified variables of the grand canonical ensemble, the others being volume and temperature. Grand canonical Monte Carlo simulations for fluids have been used for a number of years, beginning with Norman and Filinov,1 and Adams.2,3 In these techniques real particles are inserted or removed from the fluid during the simulation in a Markov process with a probability dependent upon the specified chemical potential. The difficulty with this approach is that in dense fluids there is an exceedingly small probability of a molecular sized cavity appearing, and insertions become so rare that extremely long simulations are required for good statistics. Similarly at low temperatures the probability of a destruction event is greatly reduced. This situation can be ameliorated somewhat by searching for suitable cavities and biasing the insertion attempts,4 but it remains a formidable problem. Another difficulty with the technique is that the insertion or deletion of a particle is a local non-equilibrium event, and it takes some time for the fluid to relax. In consequence recently inserted particles are more likely to be the ones removed, and particles are also more likely to be inserted back into the cavity left by a recently removed particle.5 The discontinuity of the creation/destruction event makes the technique problematic for molecular dynamics simulations, necessitating a modification that uses equations of motion for a continuously variable coupling.6

Alternatively it is possible to perform canonical simulations (fixed number of particles, volume, and temperature), either Monte Carlo or molecular dynamics, and to estimate the chemical potential from the local field felt by a virtual test particle randomly inserted into the fluid. This method, due to Widom,7,8 also begins to fail at high densities since it is highly likely that a point selected at random will overlap the core region of a molecule of the fluid. In this case umbrella sampling techniques, such as those described by Shing and Gubbins,9,10 can be used to improve the statistics. The excluded volume map sampling method described by Dietrick et al.11 is also very efficient. Alternatively one can use a partially coupled particle, either real12–14 or virtual,15 which also improves the estimate of the chemical potential at higher densities. Widom’s expression can be used in Monte Carlo and in molecular dynamics simulations16,17 but in both techniques it only allows the chemical potential to be measured, not specified. This is a particularly severe limitation for studies of inhomogeneous or confined fluids when one usually wants to describe the properties of the fluid in equilibrium with a known bulk fluid.

This paper sets out a hybrid technique that combines the virtue of the grand canonical method in setting the chemical potential, with the advantage of the virtual particle test methods that avoids the perturbation of the fluid structure, since it uses neither creations, destructions, nor partially coupled solutes. The temperature and number of particles are fixed, and the density is determined during the course of the simulation by variations of the size of the container in response to whether the current estimate of the chemical potential is larger than or smaller than that specified. That is, the size of the system is changed by an amount

$$\Delta L = \alpha \left( 1 - \frac{e^{-\beta \mu_i}}{e^{-\beta \mu}} \right), \quad (1)$$

where $\beta = 1/k_B T$ is the inverse temperature, $\mu$ is the specified chemical potential, $\mu_i$ is the chemical potential for configuration $i$, estimated from Widom’s equation, and $\alpha$ is the gain a positive constant of the order of $10^{-4} - 10^{-3}$. This feedback technique differs from so-called force balance Monte Carlo in which the fluctuations in system size are actually part of the ensemble.13
The idea of varying the density in grand canonical simulations by changing the volume and avoiding particle insertions and deletions has previously been considered by Mehta and Kofke. They formulate a pseudo grand ensemble in which trial volume changes are accepted with a probability dependent upon the chemical potential and the pressure, which must be known as a function of density. Although both functions can be estimated during the course of the simulation, (which information can be used to improve the estimate of the density at the specified chemical potential, thereby making some virtue out of a necessity), the computational demands are obviously compounded by the number of density nodes and the range of density fluctuations. Escobedo and de Pablo reduced the number of requisite nodes by using a Taylor expansion of the equation of state; they applied the pseudo-ensemble method to polymer chains. Camp and Allen applied the method of Mehta and Kofke to the coexistence of a Lennard-Jones fluid in the Gibbs ensemble and concluded that in this particular case the method was less efficient than conventional insertion methods. In contrast the present feed-back method has a fixed gain $\alpha$ and the change in volume is determined by the difference between the instantaneous and the specified chemical potential. In other words all of the computational effort is directed to the state point of interest, and one therefore expects that the feed-back method will be more efficient than the pseudo grand canonical formulation of Mehta and Kofke. However in common with that earlier method, the present method is a hybrid of a simulation and a numerical technique that enjoys its greatest advantage over conventional grand canonical simulations at high densities. Mehta and Kofke applied their method to hard-sphere fluids at reduced densities up to 0.92, and here we treat bulk Lennard-Jones fluids at reduced densities up to 0.95.

The feed-back method is suited for simulations of a bulk fluid, in which case it is the size of the central cell of the periodic system, which is used as the unit of length, that is varied. It is also suited for inhomogeneous fluids. For semi-infinite systems, such as a planar slit pore, or a cylindrical pore, it is the size of the periodically replicated central cell that is varied, (or it could be the separation or the radius). For a fully contained system it is the size of the container, (such as the radius of a spherical pore), that is varied, with the effect that the number of confined molecules ends up being the same as would be adsorbed in a container of the average size at the specified chemical potential. Although primarily designed for Monte Carlo simulations, the method also appears applicable to molecular dynamics, by varying the volume analogously to current isobaric methods, [e.g., replace the left side of Eq. (1) by $\bar{L}$].

The problem then is in two parts; first estimate the instantaneous chemical potential, and then vary the density in response. There have been a number of attempts to find an efficient solution to the former problem. As mentioned above crude Monte Carlo fails at high densities because of the overwhelming likelihood that a point selected at random will overlap the core region of one of the molecules. A big improvement is provided by the restricted umbrella sampling schemes developed by Shing and Gubbins, which in essence thoroughly explore a cavity once it has been found. Below a variant of these is used with some success. Two further schemes are also explored. An annealed, multistage sampling method uses Metropolis sampling at an elevated temperature. This turns out to be comparable to the restricted umbrella sampling method for most cases, but can be worse for certain configurations. Finally, a variant of the included volume map sampling method developed by Deitrick et al. is implemented. That method subdivides the system into thousands of small cells, and uses crude Monte Carlo sampling within those cells not wholly contained within the core region of a molecule. The refinement used here, called preferential cell sampling, uses more sampling points in those cavity cells that are not adjacent to a core cell. This preferential cell sampling is 4–40 times more efficient than the restricted umbrella sampling method for typical high density configurations.

The feed-back method is here tested for a Lennard-Jones fluid, both in the bulk and confined between two planar walls. For the bulk case the subcritical isotherm $T^* = 1$ is explored up to densities $\rho^* = 0.95$, and the results agree with those obtained from conventional methods. For the slit pore a fluid in equilibrium with a bulk $T^* = 1$, $\rho^* = 0.75$ is simulated for separations $h^* = 4–11$. The results agree with the conventional grand canonical Monte Carlo simulations of Bérard et al. This is a rather severe test because the liquid cavitates at small separations, and it is found that the present method is well able to follow the metastable branches.

I. METHOD

A. Estimation of the chemical potential

The chemical potential, which in essence measures the cost of adding one more particle to an $N$ particle system, may be divided into ideal and excess parts, $\mu = \mu^{id} + \mu^{ex}$. For a volume $V$ and temperature $T$ the ideal part is

$$\mu^{id} = k_B T \ln[\Lambda^3/(N+1)/V]. \quad (2)$$

Without loss of generality one can set $\Lambda = 1$, since the thermal wavelength provides an additive constant setting the arbitrary zero of the chemical potential. (Here and throughout all lengths are in terms of the Lennard-Jones diameter $\sigma$.) The excess chemical potential is the negative of the change in the excess Helmholtz free energies when an atom is added, which is related to the ratio of the configuration integrals.

$$\mu^{ex} = F^{ex}_{N+1} - F^{ex}_N = -k_B T \ln Z^{ex}_{N+1}/Z^{ex}_N$$

$$= -k_B T \ln \frac{\int d\mathbf{r}_{N+1} e^{-\beta U_{N+1}} V}{\int d\mathbf{r}_N e^{-\beta U_N}} \quad (3)$$

$$= -k_B T \ln \left\{ \frac{1}{V} \int d\mathbf{r} e^{-\beta u(\mathbf{r}, r_N)} \right\}_N.$$  

This is Widom’s expression for the chemical potential. Here, $u(\mathbf{r}, r_N)$ is the potential energy between a test atom at
and the $N$ atoms of the system; the full potential for the 
$(N+1)$-atom system is $U_{N+1}=U_N+u(r_{N+1},r^N)$. The 
ensemble average is over the $N$ atoms of the system; these do 
not feel in any way the test atom, for which reason it is called 
a virtual particle.

1. Crude Monte Carlo quadrature

The several practical methods for evaluating this expression 
basically amount to evaluating the integral that is the 
average periodically during the simulation. One can choose 
several fixed points in the simulation cell and during the 
course of the simulation sample the local potential at these 
points. Alternatively one can sample at random points in the 
system, which is called crude Monte Carlo quadrature. For a 
large enough system the spatial average is equivalent to the 
ensemble average itself, and one need perform the quadrature 
only periodically during the simulation. In view of this the 
instantaneous excess chemical potential of the $i$th 
configuration is defined via

$$e^{-\beta \mu^e_i} = \frac{1}{V} \int e^{-\beta u(r_i^N)} \, dr,$$

and one has $\beta \mu^e_i = -\ln(e^{-\beta \mu^e_i})_N$. Note that because one 
averages over many configurations, and because for a sample 
of finite size the instantaneous excess chemical potential 
fluctuates from configuration to configuration, a relatively 
imprecise evaluation of each quadrature is permissible.

The simplest evaluation of the instantaneous excess chemical potential is by crude Monte Carlo quadrature. That is, one generates $M$ random points in the simulation cell and takes $\exp(\beta \mu_i^e) = M^{-1} \sum \exp(-\beta u(r_i, r^N))$. This method is useful at low to moderate densities, but it becomes impractical at higher densities because there is such a low probability of hitting the few cavities in the fluids which dominate the integrand; the random points almost all fall within the core region of one or other of the real atoms.

2. Umbrella sampling

Shing and Gubbins\textsuperscript{10} suggested that a restricted umbrella sampling technique be used at higher densities. Here, the system is divided into core regions and cavity regions by using a step function

$$W(u) = \begin{cases} 
1, & u \leq w \\
0, & u > w. 
\end{cases}$$

The threshold energy is typically $w = 200 k_B T$. Note that the system is not necessarily bicontinuous. Shing and Gubbins\textsuperscript{10} used this weighting function to estimate the virtual energy distribution in the cavity region, and then they combined this with the real energy distribution to obtain an estimate of the chemical potential. One can also use this weighting function directly. Since the integrand for the instantaneous excess chemical potential is essentially zero in the core region, one has

$$e^{-\beta \mu_i^e} = \frac{1}{V} \int e^{-\beta u(r_i^N)} W(u(r_i^N)) \, dr$$

$$= \frac{\int e^{-\beta u(r_i^N)} W(u(r_i^N)) \, dr}{\int W(u(r_i^N)) \, dr} \int W(u(r_i^N)) \, dr$$

$$= \langle e^{-\beta u(r_i^N)} \rangle_w W(u(r_i^N)).$$

The first term is an average of the test particle potential over the cavities in the fluid. It can be evaluated by the standard Metropolis algorithm: One chooses points at random in the simulation cell until one finds a cavity, and then one generates a Markov chain such that all trial steps that remain in the cavity region are accepted, and all trial steps into the core region are rejected, while a simple average of the Boltzmann factor is taken over the chain. The second average above is the fraction of the system volume that is occupied by cavities. It can be evaluated by crude Monte Carlo quadrature (it equals the fraction of randomly generated points that lie in a cavity), and typically can be obtained with acceptable precision from the attempts to find a cavity for the first average.

As an example, for the nominal chemical potential $\mu = 0$, which at $T^* = 1$ corresponds to a density of $\rho \sigma^3 = 0.9$, blocks of 200–500 independent chains were used to evaluate $\langle e^{-\beta u} \rangle_w$ once every 40 cycles (20,000 configurations, being 40 attempted moves for each of the 512 atoms). Both long (100 steps) and short (20 steps) chains were tried, for a total number of evaluations of 4–50 million. At high densities it seemed wise to use a large number of short chains because the cavities become isolated, trapping each chain; the statistics for a single chain are not representative of the quadrature. Note that these numbers are about an order of magnitude greater than those used by Shing and Gubbins,\textsuperscript{10} who reported using a single chain of 100–200 steps after every 200 or so configurations, for a total of about 1.5 million evaluations, ($T^* = 1.2, \rho \sigma^3 = 0.85$). The present choices are arguably conservative, since it is probably unnecessary to evaluate the instantaneous excess chemical potential with greater precision than the fluctuation between configurations.

The restricted umbrella sampling concentrates on the important cavities of the fluid and was found to be about four times more efficient than the simplest approach described in the preceding section. At the highest densities only 2%–5% of the fluid is occupied by cavities, and these should obviously be sampled most thoroughly since they give the dominant contribution to the instantaneous chemical potential. Its worth mentioning that another method described by Shing and Gubbins\textsuperscript{10} was explored, namely one involving the ratio of virtual and real particle energy distributions. This method did not appear to offer significant improvement, as Powles et al.\textsuperscript{17} also concluded.

3. Annealed sampling

The difficulty with the restricted umbrella sampling method outlined above is that at very high densities the cavities become isolated. One needs many chains with few steps, since each chain samples essentially a single cavity. Random
sampling, as in crude Monte Carlo, is required to find a cavity to start each chain. At the highest densities with cavity fractions around 4%, the cost of this initiation step can be substantial and the method loses its advantage over crude Monte Carlo. Attempting to jump out of a cavity by using large steps with a low acceptance rate within the chain would similarly vitiate the method.

One way to alleviate the problems caused by isolated cavities is partially to decouple the virtual particle from the real particles, effectively carrying out the sampling at an artificially elevated temperature. That is, Widom’s expression can be written in the form

\[ e^{-\beta \mu_i^{ex}} = \frac{1}{V} \int e^{-\beta u(r, r_i^N)} d\mathbf{r} \]

\[ = \frac{\int e^{-\beta u(r, r_i^N)} e^{-\beta \lambda u(r, r_i^N)} d\mathbf{r} \int e^{-\beta \lambda u(r, r_i^N)} d\mathbf{r}}{\int d\mathbf{r}} \]

\[ = \langle e^{-\beta \lambda u(r, r_i^N)} \rangle_{\lambda} \langle e^{-\beta \lambda u(r, r_i^N)} \rangle, \quad (7) \]

where the conjugate of the coupling parameter is \( \tilde{\lambda} = 1 - \lambda \).

This process can obviously be continued for further stages,

\[ e^{-\beta \mu_i^{ex}} = \langle e^{-\beta \lambda u(r, r_i^N)} \rangle \prod_{j=1}^{n} \langle e^{-\beta \lambda_j u(r, r_i^N)} \rangle, \quad (8) \]

but in practice this appears unnecessary. After one stage the final unweighted ensemble average can be accurately evaluated with relative ease, and there is no advantage in using intermediate stages. Like the restricted umbrella sampling technique discussed above, this method avoids sampling the inner cores of the real particles. For suitably low values of the coupling \( \lambda \), it has the additional virtues of allowing the virtual particle to visit many cavities by traversing the lowered saddle between the real particles, and of the Markov chain preferentially sampling the valley floor.

This method was tested on a Lennard-Jones fluid at \( T^* = 1 \) and \( \rho^* = 0.9 \). In a typical test a single stage with \( \lambda = 0.005 \) was used, corresponding to an effective temperature of 200. The weighted ensemble average was carried out using 10 independent chains of 1000 steps. The unweighted average was evaluated using crude Monte Carlo quadrature with 500 random points. It would have been possible to fix the value of the coupling constant by monitoring the diffusion of the chains through the system, but this was not done. For particular configurations, those with large values of \( \exp(-\beta \mu_i) \), the method yielded comparable precision to the restricted umbrella sampling technique discussed above with about four times fewer evaluations, but more generally it appeared slightly less efficient. The reasons for this are not fully understood, but it is possible that the high temperature flattens the valley floor to such an extent that the chain spends most of its time on the sides of the mountains.

### 4. Preferential cell sampling

The problem with the above methods is that they do not really incorporate enough information about the fluid structure in the initial search for a cavity. By locating and avoiding the core regions of the atoms one can greatly increase in efficiency of the search. This is the essence of the excluded volume map sampling method developed by Deitrick et al.\(^{11} \)

The system is subdivided into small cells, typically a tenth of a core diameter in edge length. For each atom one finds the cell containing its center, and all of the surrounding cells that lie entirely within the core exclusion region of the atom. This divides the fluid into core cells and cavity cells, (which may partially contain core regions), and one avoids searching the core cells. Since a typical high density configuration with a cavity fraction of 3% has 75%–85% core cells, one immediately improves the sampling efficiency by a factor of 4–5 by not sampling the core cells.

One can go further and group the cavity cells into boundary cells, which have one or more neighbouring cells belonging to the core, and inner cavity cells. Typically there may be 30–60 times as many boundary cells as inner cavity cells. It is also typical at high densities that the inner cavity cells contribute 30–100 (or in one case 10\(^5 \)) times as much per cell to the instantaneous chemical potential. Hence one should search these inner cavity cells more thoroughly. It was found that a reasonable recipe was to use 60\(^3 \) cells, (size 0.14\( \sigma \), giving typically 40 000 cavity cells), and to generate one point at random in each of the boundary cells, and ten random points in each of the inner cavity cells. Using more cells certainly improved the precision and also the efficiency, (since the fraction of core cells increases toward the continuum limit of 97%) but given the constraint of using at least one point per cell, the present recipe gave acceptable precision in reasonable computer time. (In fact this recipe gives more precision for each quadrature than is really necessary; in some cases only a fraction of the boundary cells were searched.) Further sub-groupings can be made, but configurations with one or more inner cavity cells were comparatively rare unless very small cells were used.

In detail, the exponential of the negative of the instantaneous chemical potential is the spatial average of the Boltzmann factor. Hence one sums the Boltzmann factor of the sampled cells and divides by the total number of cells, since they all have the same volume. The value of the Boltzmann factor of a sampled cell equals the sum of the sampled values of the cell divided by the number of samples per cell of that type, which may be less than one for a boundary cell.

Comparison was made between this preferential cell sampling method and the restricted umbrella sampling method described above for several high density configurations, (\( \rho^* = 0.9, T^* = 1.0 \)). The cell method achieved comparable precision using a factor of 4–40 less computer time. (A similar conclusion was drawn by Deitrick et al.\(^{11} \)) The reasons for this lie in the efficiency of constructing the cell occupancy table, and in the saving obtained by searching only those regions where a cavity could possibly be. It should be mentioned that the method could be further im-

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proved by using a spatially based neighbor table in evaluating the instantaneous chemical potential. (An atom-based neighbor table was used in the restricted umbrella sampling method.)

Estimating the chemical potential can significantly add to the computer time of a simulation. It was found that preferential cell sampling (60° cells of size 0.14σ, sampling each boundary cell once and each inner cavity cell ten times, giving a standard deviation of 0.15 for the instantaneous chemical potential at high densities), once every 40 moves per atom increased the computer time by a factor of 2.5. Sampling every eighth boundary cell once and each inner cavity cell five times increased the computer time by a factor of 1.3 while giving a standard deviation of about 0.2. Considering the fact that the fluctuations in the instantaneous chemical potential between configurations were found to be considerably greater than the latter, sampling an even lower fraction of the boundary cells would be worthwhile.

B. Adjustment of the density

Having determined the instantaneous chemical potential, the size of the system is adjusted according to Eq. (1). The density can also be varied directly, \( \rho' = \rho - \alpha (1 - e^{-\beta \mu_i}/e^{-\beta \mu}) \), with the new system size being \( L' = (N/\rho')^{1/3} \). At higher densities there may be a small advantage to doing the adjustment this way, but for a small enough gain the two methods are equivalent. Since the ideal chemical potential varies during the course of the simulation its instantaneous value should be included,

\[
e^{-\beta \mu_i} = \frac{V_i}{\Lambda^3 (N + 1)} e^{-\beta \mu_i^{ex}}.
\]

The expression given in Eq. (1) was found to be more stable than the otherwise tempting linearised version. In particular, let \( L_i \) be the size after configuration \( i \), and suppose one has taken \( M \) snapshots for the average. Then from Eq. (1) the average change in size is

\[
\langle \Delta L \rangle = (L_M - L_0)/M = \alpha (1 - (e^{-\beta \mu_i})/e^{-\beta \mu}.
\]

Clearly if the average chemical potential equals the specified chemical potential, than there will not have been a net change in system size. If the average chemical potential is larger than that specified, then the average step is positive, and the system will have increased in size, (i.e., decreased in density), during the course of the simulation, and vice versa. Systems started from previous runs at different chemical potentials or at different separations were found to equilibrate considerably greater than the latter, sampling an even lower fraction of the boundary cells would be worthwhile.

C. Simulation details

A sub-critical Lennard-Jones fluid in the bulk and confined between planar hard-walls was studied. The Metropolis algorithm was used, and periodic boundary conditions with the minimum image convention were employed. A potential cut-off of 2.5σ was used; in the bulk this was spherical, and for the confined fluid it was cylindrical. A tail correction that assumed the average density beyond the cut-off, (uniform or inhomogeneous, \( ^2 \) respectively), was included. The core region for the evaluation of the instantaneous chemical potential was set at \( w = 200k_B T \). Simulations were carried out with up to 512 atoms, and of the order of 10 million configurations (attempted moves) were generated. A move was attempted for each atom in a cycle with an acceptance rate of 20%–50%. Every four cycles ensemble averages for the pressure and density profiles were taken. Every 40 cycles the instantaneous chemical potential was evaluated, and the system size was adjusted. Little attempt was made to optimise this choice, and the trade-off between the frequency of such evaluations and the precision of each evaluation was not explored in detail. The error in the chemical potential, (as measured by the departure of the average from the specified value, or by the estimated standard error), was generally less than 0.1\( k_B T \) at moderate densities, and the estimated standard error of the density was generally less than 0.002.

II. RESULTS

A. Bulk fluid

Table I summarizes the results that were obtained for the sub-critical isotherm \( T^* = 1.0 \). The specified chemical potential ranged from \(-4\) to \( 2 \), corresponding to a density range of \( 0.68 \) to \( 0.95 \). Evidently the data in the table demonstrate that the feed-back method is capable of maintaining the specified chemical potential. At moderate densities the average chemical potential was within 0.1\( k_B T \) of the specified one, with a similar statistical error. At the highest densities the error was somewhat larger.

In Fig. 1 the data are compared with data from the parameterisation of the Lennard-Jones equation of state given by Nicholas et al. \( ^23 \) It can be seen that the present feed-back method agrees quite well with that parameterisation, which confirms the validity of the approach. At the highest chemical potential using a potential cut-off of 2.5σ causes a systematic underestimation of the density, as can be seen from the results that use a cut-off of 3.5σ. Figure 2 shows a similar comparison for the pressure, which is generally a more sensitive thermodynamic property. Again there is good agreement with the known results. One concludes that the feed-back method correctly mimics an open system with specified chemical potential, and that it is a viable approach for dense bulk fluids.
TABLE I. Data for a bulk Lennard-Jones fluid at a temperature $T^*=1.0$. Here, $N$ is the number of atoms and $M$ is the millions of configurations generated.

<table>
<thead>
<tr>
<th>$\beta \mu$</th>
<th>$\langle \beta \mu \rangle$</th>
<th>$\langle \rho \sigma^3 \rangle$</th>
<th>$\langle \beta \rho \sigma^3 \rangle$</th>
<th>$\langle U/N \epsilon \rangle$</th>
<th>$N$</th>
<th>$M$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-4$</td>
<td>$-4.012 \pm 0.007$</td>
<td>$0.676 \pm 0.003$</td>
<td>$-0.12 \pm 0.01$</td>
<td>$-4.73 \pm 0.02$</td>
<td>512</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>$-3.29$</td>
<td>$-3.30 \pm 0.03$</td>
<td>$0.757 \pm 0.002$</td>
<td>$0.44 \pm 0.03$</td>
<td>$-5.28 \pm 0.02$</td>
<td>512</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>$-2$</td>
<td>$-2.00 \pm 0.07$</td>
<td>$0.827 \pm 0.001$</td>
<td>$1.43 \pm 0.03$</td>
<td>$-5.70 \pm 0.007$</td>
<td>512</td>
<td>10</td>
<td>0.01</td>
</tr>
<tr>
<td>$-1$</td>
<td>$-1.09 \pm 0.12$</td>
<td>$0.864 \pm 0.003$</td>
<td>$2.26 \pm 0.08$</td>
<td>$-5.90 \pm 0.02$</td>
<td>512</td>
<td>10</td>
<td>0.005</td>
</tr>
<tr>
<td>0</td>
<td>$0.00 \pm 0.09$</td>
<td>$0.899 \pm 0.002$</td>
<td>$3.22 \pm 0.07$</td>
<td>$-6.05 \pm 0.009$</td>
<td>512</td>
<td>20</td>
<td>0.0005</td>
</tr>
<tr>
<td>0.5</td>
<td>$0.51 \pm 0.16$</td>
<td>$0.913 \pm 0.004$</td>
<td>$3.7 \pm 0.1$</td>
<td>$-6.11 \pm 0.01$</td>
<td>512</td>
<td>15</td>
<td>0.001</td>
</tr>
<tr>
<td>1</td>
<td>$1.03 \pm 0.07$</td>
<td>$0.9119 \pm 0.0007$</td>
<td>$3.63 \pm 0.02$</td>
<td>$-6.11 \pm 0.004$</td>
<td>512</td>
<td>31</td>
<td>0.0002</td>
</tr>
<tr>
<td>1$^a$</td>
<td>$1.05 \pm 0.14$</td>
<td>$0.921 \pm 0.002$</td>
<td>$3.99 \pm 0.07$</td>
<td>$-6.14 \pm 0.008$</td>
<td>512</td>
<td>31</td>
<td>0.0002</td>
</tr>
<tr>
<td>2</td>
<td>$2.04 \pm 0.22$</td>
<td>$0.944 \pm 0.003$</td>
<td>$4.9 \pm 0.1$</td>
<td>$-6.22 \pm 0.01$</td>
<td>512</td>
<td>51</td>
<td>0.0002</td>
</tr>
<tr>
<td>2$^a$</td>
<td>$1.94 \pm 0.20$</td>
<td>$0.950 \pm 0.002$</td>
<td>$5.12 \pm 0.09$</td>
<td>$-6.22 \pm 0.007$</td>
<td>512</td>
<td>31</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

$^a$Cut-off $= 3.5 \sigma$.

B. Confined fluid

Table II gives results for a Lennard-Jones fluid confined to a slit pore, for $T^*=1.0$ and $\beta \mu = -3.29$. The separation $h$ between the hard walls is the width of the region available to the centers of the atoms. The density of the bulk subcritical liquid in equilibrium with the confined fluid is 0.76. Previously this particular liquid had been used in conventional grand canonical Monte Carlo to explore separation-induced cavitation.$^{21}$ It is evident from the table that the present feed-back simulation technique and conventional grand canonical Monte Carlo,$^{21}$ mainly because of the flexibility that the gain offers. The present results indicate that the liquid spinodal lies between $h = 4.0 \sigma$ and $h = 3.9 \sigma$, which is consistent with the results of Bérard et al.$^{21}$

The average density $\bar{\rho} = \langle N/h L^2 \rangle$ of the confined fluid is shown in Fig. 3, where comparison is made between the present feed-back technique and conventional grand canonical Monte Carlo.$^{21}$ There is good agreement between the two, which again confirms the validity of the present method. On the gas branch the agreement is excellent, but on the liquid branch at larger separations there appears a small systematic difference between the two, which is consistent with the slight difference in the respective bulk densities (0.76 versus 0.75$^{21}$.) The origin of the discrepancy probably lies in the different values used for the potential cut-off in the bulk;
the present calculations used 2.5σ, whereas Bérard et al. used a value of 4.5σ.

Also shown in Fig. 3 are small and large separation asymptotes. The average density is formally

$$\bar{\rho}(h) = \frac{1}{h} \int_{-h/2}^{h/2} \rho(x; h) \, dx,$$

which for the simulation is just $\bar{\rho}(h) = \langle N/hL^2 \rangle$. Asymptotically one expects

$$\bar{\rho}(h) \sim \rho + \frac{2\Gamma_0}{h} - C(h^{-4}), \quad h \to \infty,$$

where the adsorption excess per unit area for an isolated wall is

$$\Gamma_0 = \int_0^\infty [\rho_0(x) - \rho] \, dx.$$

[The relation between the density profiles is $\rho_0(x) = \lim_{h \to 0} \rho(x - h/2; h)$, $x > 0$.] The asymptotic formula allows the present simulation of the confined fluid to be used to estimate the adsorption excess of a Lennard-Jones fluid at a hard-wall. Using the simulated bulk density $\rho = 0.757\sigma^{-3}$, a fit to the large-separation simulation data in Fig. 3 gave $\Gamma_0 = -0.34\sigma^{-2}$.

In the opposite extreme of small separations a confined liquid must behave as an ideal gas, since the two-dimensional density must vanish if the three-dimensional average density is to remain finite, $\bar{\rho}^{(2)} = \hbar\bar{\rho}(h) \to 0$. Consequently one has the formally exact limiting result

$$\bar{\rho}(h) \to \Lambda^{-3} e^{\beta \mu}, \quad h \to 0.$$
provides additional confirmation of the validity of the feedback technique. The limiting result also shows that the confined liquid has to cavitate at small separations in order to give an average density equal to the fugacity.

The density profiles shown in Fig. 4 are as one would expect, with a marked depletion of fluid in the neighborhood of the walls. In fact at large separations this depletion is approximately independent of separation (as it must be to fit the large separation asymptote in Fig. 3), and it would be hard to distinguish the profiles if they were superimposed by measuring the distance from one wall. Approaching the spinodal separation the negative adsorption excess is particularly noticeable, not only near the walls but also in the center of the cell. This central decrement remains measurable even at the largest separations, where it can be seen that the density is still noticeably less than the bulk density. This shows that it is essential to use a grand canonical technique (either conventional or the present feedback method), in order to describe an inhomogeneous fluid in equilibrium with a bulk fluid. It is a common but dubious practice to take the density in the center of the pore to be that of the bulk fluid it is supposed to be in equilibrium with. A guide to the statistical errors is provided by the departure of the profiles from perfect symmetry. The kink evident at the ends of some of the large separation profiles is likely an artefact of the rather short potential cut-off \( 2.5 \sigma \) that was used.

Figure 5 shows the net pressure as a function of separation. This was taken to be the total pressure at a given separation less the total pressure at a large separation, in the present case \( h = 7 \sigma \) \( (\beta p(h) \sigma^3 = 0.47) \), and in the case of Ref. 21, \( h = 9 \sigma \) \( (\beta p(h) \sigma^3 = 0.42) \). Ideally the pressure to be subtracted would be the simulated bulk pressure, but due to the different potential truncations used (spherical in the bulk, cylindrical between the walls), there is a systematic difference between the two. In this context the simulations of Bérrard et al.\(^{21}\) are superior to the present ones since they used in this case a cylindrical cut-off of \( 5 \sigma \) compared to the present \( 2.5 \sigma \). The large separation data in Table II tend to a total pressure of 0.55, which is significantly larger than the simulated bulk pressure of 0.44. Using a cut-off of \( 3.5 \sigma \) reduces the total pressure at \( h = 10 \sigma \) to 0.47, which confirms that it is the potential truncation that is the main source of the discrepancy. Despite the systematic errors in the total pressure, for the net pressure there is good agreement between the present feedback simulations and the conventional grand canonical simulations,\(^{21}\) and both show a steeply increasing attraction as the spinodal separation is approached.

**CONCLUSION**

This paper has been concerned with two problems: how to estimate efficiently the chemical potential, and how to obtain the density corresponding to a specified chemical potential. For the former it was concluded that crude Monte Carlo quadrature was useful at low densities, umbrella sampling at moderate densities, and preferential cell sampling at the highest densities. Preferential cell sampling is a modified form of the excluded volume map sampling given by Dejnick et al.\(^{11}\) and it was found typically to increase the computer time of the underlying canonical simulation by a factor of 1.3–2.5. The lower figure was for sampling every eighth boundary cell, and sampling each inner cavity cell five times; even fewer samples would be reasonable, since the precision in the average chemical potential is currently dominated by the fluctuations between configurations.

The problem of obtaining the density was solved by coupling the system size to the chemical potential, which differs from conventional grand canonical Monte Carlo, which couples the particle number to the chemical potential. The idea of avoiding particle insertions by changing the system size originally occurred to Mehta and Kofke.\(^{18}\) Unlike the
original implementation, the present feedback method does not require the equation of state to be simultaneously simulated, but works by increasing or decreasing the system size depending whether the instantaneous chemical potential is greater or less than the specified chemical potential. The method was here tested in Monte Carlo simulations; it should also be useful in the molecular dynamics technique. It was concluded that the method was applicable to both bulk and confined fluids, and that it could handle the liquid-gas transition and metastability. Using feed-back to couple non-conjugate thermodynamic variables could presumably find wider application than is explored here.