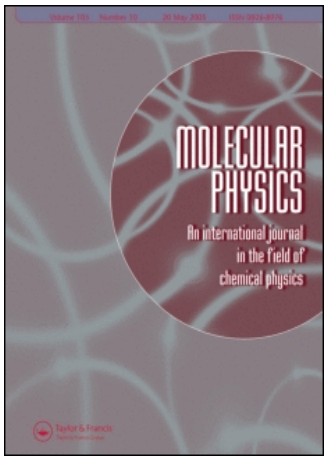

Molecular Physics
An International Journal in the Field of Chemical Physics
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713395160

A cavity-biased (**T, V, μ**) Monte Carlo method for the computer simulation of fluids

Mihaly Mezei [a]
[a] Department of Chemistry, Hunter College of the CUNY. New York, N.Y.. U.S.A.

Online Publication Date: 01 July 1980
To cite this Article: Mezei, Mihaly , (1980) 'A cavity-biased (**T, V, μ**) Monte Carlo method for the computer simulation of fluids ', Molecular Physics, 40:4, 901 - 906
To link to this article: DOI: 10.1080/00268978000101971
URL: http://dx.doi.org/10.1080/00268978000101971

MOLECULAR PHYSICS, 1980, VOL. 40, NO. 4, 901–906

A cavity-biased (T, V, μ) Monte Carlo method for the computer simulation of fluids†

by MIHALY MEZEI
Department of Chemistry, Hunter College of the CUNY,
New York, N.Y. 10021, U.S.A.

(*Received* 19 *November* 1979 ; *revision received* 15 *January* 1980)

A modified sampling technique is proposed for use in Monte Carlo calculations in the grand canonical ensemble. The new method, called the cavity-biased (T, V, μ) Monte Carlo procedure, attempts insertions of new particles into existing cavities in the system instead of at randomly selected points. Calculations on supercritical Lennard-Jones fluid showed an 8-fold increase in the efficiency of the insertion process using the new method. The highest density that can be successfully treated was raised by 35 per cent, making part of the liquid region of the Lennard-Jones fluid now accessible to theoretical study by this method.

1. INTRODUCTION

Monte Carlo simulation in the grand canonical (T, V, μ) ensemble has a significant advantage over simulation in the canonical (T, V, N) ensemble : the immediate availability of the free energy and its derivatives. Unfortunately, the simulation becomes less efficient with the increase of the density of the system, since the minimum variation in the density has to involve at least one full particle. The purpose of this paper is to present a simple biasing technique that significantly increases the efficiency of the importance sampling, thereby yielding a significant increase in the density limit of the method.

The (T, V, μ) simulation algorithm modified for cavity biasing is presented in § 2. Calculations on the Lennard-Jones (LJ) fluid based on this procedure are described in § 3. Numerical results and discussion on the comparison of the new sampling technique with a procedure previously proposed and considerations on the limiting density of the new method for the LJ fluid are presented in § 4.

2. THE DESCRIPTION OF THE METHOD

Monte Carlo simulations on the LJ fluid can be performed in the (T, V, μ) ensemble up to moderate densities by a direct generalization of the (T, V, N) ensemble Metropolis method described by Adams [1], based on earlier work by Norman and Filinov [2]. The grand canonical ensemble is characterized by the partition function

$$\Xi = \sum_{N=0}^{\infty} \exp(N\mu/kT) \int_V \exp(-U(\mathbf{r}^N)/kT)\, d\mathbf{r}^N/(\Lambda^{3N}N!), \qquad (1)$$

† This research was supported by NIH grant 1-ROH-NS12149-3.

0026-8976/80/4004 0901 $02·00

where N is the number of particles, $\mathbf{r}^N$ is the coordinate vector in the configuration space of N particles, V is the volume of the system, $U(\mathbf{r}^N)$ is the potential energy of the configuration $\mathbf{r}^N$, k is the Boltzmann factor, T is the absolute temperature and Λ is the usual kinetic factor: $\Lambda = h/(2\pi mkT)^{1/2}$ [3]. In this approach, the displacement of the particles according to the (T, V, N) prescription [4] is supplemented with an insertion attempt at a randomly selected point and with a deletion attempt of a randomly chosen particle. A random insertion attempt is accepted with probability

$$P_i^R = \min(1, V' \exp((\mu + U(\mathbf{r}^N) - U(\mathbf{r}^{N+1}))/kT)/(N+1)) \tag{2}$$

and a random deletion attempt is accepted with probability

$$P_d^R = \min(1, N \exp((-\mu + U(\mathbf{r}^N) - U(\mathbf{r}^{N-1}))/kT)/V') \tag{3}$$

where N is the number of particles before the insertion/deletion attempt, $V' = V/\Lambda^3$ [5]. The factors N and V' in equations (1 and 2) can be thought of as a correction factor for the asymmetry between the insertion and deletion attempts according to the general formalism of Hastings [6].

We suggest a modification of the insertion process which allows for insertion only at points where a cavity of suitable radius R_c exists. In this case the acceptance probabilities P_i^R and P_d^R will be modified: V will be replaced by the volume of the subspace that is formed by the union of all points that are centres of a cavity of radius greater than or equal to R_c. Accordingly, the insertion and deletion attempts will be accepted with the respective probabilities

$$P_i^{CB} = \min(1, V' P_c^N \exp((\mu + U(\mathbf{r}^N) - U(\mathbf{r}^{N+1}))/kT)/(N+1)) \tag{4}$$

$$P_d^{CB} = \min(1, N \exp((-\mu + U(\mathbf{r}^N) - U(\mathbf{r}^{N-1}))/kT)/(V' P_c^{N-1})) \tag{5}$$

where P_c^N is the probability of finding a cavity of radius R_c or larger, provided the system consists of N particles. This procedure will henceforth be referred to as the ' cavity-biased (T, V, μ) Monte Carlo method '.

The realization of the proposed sampling thus requires the computation of P_c^N and the finding of a point that is the centre of a cavity of radius R_c or larger. By generating a number of uniformly distributed test points, and finding the fraction of them that are in a suitable cavity, one obtains both a Monte Carlo estimate for P_c^N and also a definite point where a new particle can be inserted. As the simulation proceeds, the estimate of P_c^N will necessarily improve.

There is a possibility, however, that none of the generated points are found to be in a suitable cavity. This will affect the calculation in two ways. First, one will have to execute a simple random insertion and accept it with probability P_i^R and, secondly, the acceptance probabilities of the deletion step must be modified to maintain microscopic reversibility. Since a random insertion occurs with probability $(1-P_c^N)^{N_t}$, where N_t is the number of test points generated, it follows that the deletion acceptance will have to be chosen as P_d^{CB} with probability $(1-(1-P_c^N)^{N_t}$ and as P_d^R with probability $(1-P_c^N)^{N_t}$. To justify this process, consider two ensembles, sampled by the random procedure (2) and (3) and the cavity-biased procedure (4) and (5). The insertion step samples the first ensemble with probability $(1-P_c^N)^{N_t}$ and the second ensemble with probability $1-(1-P_c^N)^{N_t}$. If these probabilities are used to select the ensemble that is to be sampled by a deletion step, then both ensembles will be sampled

correctly and can be considered as a single ensemble, since the distributions generated by (2) and (3) should be identical to the distributions generated by (4) and (5).

It should also be noted that the mixing of the two samplings can be eliminated by continuing the search for a cavity at each insertion step until one is found. This possibility, however, was not explored in the present study.

Based on all of the above considerations the proposed algorithm for the (T, V, μ) Monte Carlo simulations consists of the following steps :

(1) Initialize N, $\mathbf{r}^N$.

(2) Perform a particle displacement according to the canonical ensemble Metropolis method.

(3) Perform an insertion/deletion step as follows :

(3.1) With probability 1/2 go to step 3.3.

(3.2) Insertion :

Generate N_t points.
Find the number of points that are in a cavity.
Update the estimate of P_c^N.
If no point was found to be in a cavity, go to step 3.2.2.

(3.2.1) Cavity-biased insertion :

Insert one particle at one of the points which was found to be in a cavity.
Accept the insertion with probability P_i^{CB}.
Go to step 4.

(3.2.2) Random insertion :

Insert a particle at a randomly selected point.
Accept the insertion with probability P_i^R.
Go to step 4.

(3.3) Deletion :

Choose a particle randomly.
With probability $(1-P_c^{N-1})^{N_t}$ go to step 3.3.2.

(3.3.1) Cavity-biased deletion :

Delete the chosen particle with probability P_d^{CB}.
(Note, that in case $N-1$ was not sampled yet in the calculation, P_c^{N-1} is to be obtained by extrapolating from P_c^N, P_c^{N+1}, . . ., or is to be set equal to P_c^N if N is the only value sampled. In the calculations reported here, linear extrapolation was used.)
Go to step 4.

(3.3.2) Random deletion :

Delete the chosen particle with probability P_d^R.

(4) Accumulate ensemble averages.

(5) Repeat from step 2 until acceptable convergence limits have been reached.

The cavity radius R_c should have a value higher than the hard core of the particles. Its most efficient choice can be determined by short trial runs. It was found that as the density of the system is increased the most efficient choice of R_c is to be slightly decreased.

The choice of N_t can similarly be determined by short trial runs. Clearly, one would like to have a substantial number of successful insertions into cavities, thus $(1-P_c^N)^{N_t}$ should not be close to zero. On the other hand, increasing N_t increases the computational work. However, the significance of the extra work is decreasing with the increase in the complexity of the intermolecular potential, since the relative effort spent on searching for a cavity is decreasing.

3. Calculations

The proposed cavity-biased Monte Carlo method was tested on the LJ fluid since the limits of the original method were well established there. The formalism of Adams [1] was used, where the system is characterized by the usual reduced temperature T^*, the reduced volume V^* and a parameter B related to the excess chemical potential μ' as

$$B=\mu'/kT+\ln\langle N\rangle \tag{6}$$

where $\langle N\rangle$ is the (T, V, μ) ensemble average of the number of particles. The long range corrections due to the simultaneous insertion or deletion of the particles were included using the assumption that the density is constant outside the cut-off radius of the potential. The cut-off radius was chosen to be the radius of the inscribed sphere of the simple cubic unit cell. For the Metropolis step uniform cubic displacement was used, with the stepsize adjusted to obtain near 50 per cent acceptance ratio (a common, but not necessarily optimal practice).

The basic result of the calculations is reflected in the value obtained for $\langle N\rangle$ and related quantities. The efficiency of the insertion/deletion process can be assessed by considering the acceptance ratio of the insertion/deletion steps, the range of N that was sampled and the computational effort spent.

4. Results and discussion

The results for the LJ fluid are collected in the table. It can be seen that for $T^*=2{\cdot}0$, where the original method breaks down at relative density $\rho^*=0{\cdot}65$ [1] with an acceptance ratio of 2·2 per cent for the insertion/deletion step, the cavity-biased insertion yields 38 per cent acceptance ratio with only double the amount of computer time. The results of the two calculations agree with each other within their error limits but differ from the results of Adams on the same system by 2 per cent (Adams' calculation gave $\langle N\rangle=160$). This difference can probably be attributed to the deficiency noticed by Adams in the random number generator used. (In the present work, different random number generators were used to obtain the results for the two methods.)

For the consideration of the increase in computer time it has to be pointed out that the extra computational effort associated with the cavity-biased insertion is independent of the system ; thus the time considerations become less important

Results for the supercritical ($T^*=2{\cdot}0$) LJ fluid.

Method	Ratio (per cent)	N-range	B	N_t	ρ^*	$\langle N\rangle$	Length	Time
RAN	2·2	144–183	5·0		0·65	$164{\cdot}1\pm1{\cdot}1$	500 K	0·10
C.B.	38	146–182	5·0	75	0·65	$163{\cdot}7\pm0{\cdot}3$	400 K	0·20
C.B.	6·1	95–111	7·0	100	0·82	102	50 K	0·22
C.B.	1·1	103–116	8·5	70	0·89	111	50 K	0·17
C.B.	2·2	103–116	8·5	150	0·88	108	25 K	0·25

The length of the run is in the unit of 1000 composite (displacement + insertion/deletion) steps. The time is given in seconds/1000 steps/N, on the Amdahl 470/V6 computer. $\langle N\rangle$ is the average number of particles obtained. B, ρ^*, and N_t are defined in the text.

with an increase in the complexity of the system. Furthermore, for larger systems considerable savings can be achieved by dividing the volume into smaller regions and keeping track of the content of each subsegment, since the extra work involved in the cavity-biased insertion this way is independent of the system size and quite small. The calculations reported in this paper, however, have not employed this device.

In order to determine the density where the new method breaks down, several smaller calculations were performed. These calculations were much shorter than the first two discussed above since it was found that the acceptance ratios are very well defined over a short segment of the run. The results show that the acceptance ratio drops to 2·2 per cent at $\rho^*=0{\cdot}88$. The increase in the computer time is by a factor of 2·5 but the gain in the density limit is 35 per cent, a significant increase.

5. Conclusions

Results on the supercritical ($T^*=2{\cdot}0$) LJ fluid showed an 8-fold increase in the efficiency of the insertion/deletion steps and the limiting density was found to extend into the liquid density region at the cost of increasing the computational efforts with a factor of 2·5. The cavity-biased (T, V, μ) Monte Carlo method is thus found to be superior to the original grand canonical ensemble Monte Carlo method developed by Norman and Filinov and Adams [1, 2].

The density limit found on the supercritical LJ fluid shows that the application of the method to liquids still presents considerable difficulties (for liquid water at room temperature $T^*=0{\cdot}1$ and $\rho^*=0{\cdot}9$), but they should be within the range of the method if the length of the run is considerably increased. Since the computation of the free energy of a liquid in general requires several Monte Carlo runs [7, 8], this proposition still can be a competitive one. Work is currently under way in this direction.

The author is grateful to Professor David L. Beveridge for constant encouragement and valuable discussions on the subject.

References

[1] Adams, D. J., 1975, *Molec. Phys.*, **29,** 311.
[2] Norman, G. E., and Filinov, V. S., 1969, *High Temp. USSR*, **7,** 216.
[3] Valleau, J. P., and Torrie, G. M., 1977, *Statistical Mechanics*, Part A, edited by Bruce J. Berne (Plenum Publishing Corp.).
[4] Metropolis, N. A., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H., and Teller, E., 1953, *J. chem. Phys.*, **21,** 1087.
[5] Barker, J. A., and Henderson, D., 1976, *Rev. mod. Phys.*, **48,** 587.
[6] Hastings, W. K., 1970, *Biometrika*, **57,** 97.
[7] Mezei, M., Swaminathan, S., and Beveridge, D. L., 1978, *J. Am. chem. Soc.*, **100,** 3255.
[8] Torrie, G. M., and Valleau, J. P., 1977, *J. comput. Phys.*, **23,** 187.