Chemical potential by gradual insertion of a particle in Monte Carlo simulation

K. K. Mon and Robert B. Griffiths

Physics Department, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
and Center for the Joining of Materials, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

The chemical potential of a fluid can be determined in a Monte Carlo simulation by gradually turning on or off the interaction of one particle with the other particles. This method, which can be employed at densities where a direct use of the Widom formula is impractical, has been tested on a two-dimensional fluid of particles with a Lennard-Jones pair interaction.

I. INTRODUCTION

In this paper we study a method for determining the chemical potential in a fluid using Monte Carlo simulation through the *gradual* insertion of a new particle or deletion of a particle already present. The basic idea of slowly turning on or off the interaction between one particle and the rest has been used previously by Squire and Hoover,[1] and Mruzik *et al.*[2] in a slightly different context. As applied to chemical potentials it is in effect a variation of the umbrella sampling method used by Shing and Gubbins,[3] and should be useful at high densities where poor statistics render a direct use of the Widom[4] and the de Oliveira[5] and Shing[3] formulas impractical. An application of the basic formulas of Sec. II to a two-dimensional Lennard-Jones fluid is given in Sec. III, followed in Sec. IV by a discussion of advantages and disadvantages of this approach.

II. FORMULAS FOR CHEMICAL POTENTIAL

Let U_N be the potential energy of a set of N identical particles located at the points $r_1, r_2, \ldots, r_N$, and let

$$\Psi(r_1, \ldots, r_{N+1}) = U_{N+1}(r_1, \ldots, r_{N+1})$$
$$- U_N(r_1, \ldots, r_N) \qquad (2.1)$$

be the increment in potential energy upon adding an additional particle at the position r_{N+1}. If U_N is given by a pair potential Φ,

$$U_N = \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j<i}}^{N} \Phi(|r_i - r_j|) , \qquad (2.2)$$

then

$$\Psi = \sum_{i=1}^{N} \Phi(|r_{N+1} - r_i|) . \qquad (2.3)$$

Let μ be the chemical potential of the fluid minus that of an ideal gas at the same density and temperature. Then whether or not (2.2) holds it can be shown that[4,5,3]

$$e^{-\beta\mu} = \langle e^{-\beta\Psi} \rangle_N , \qquad (2.4)$$

$$e^{\beta\mu} = \langle e^{\beta\Psi} \rangle_{N+1} , \qquad (2.5)$$

where $\beta = 1/k_B T$ and the ensemble averages $\langle \ \rangle$ are defined later in (2.8). Note that (2.4) refers to an ensemble of N atoms in which the $N+1$ atom is inserted "at random," whereas in (2.5), the $N+1$ atom, which is in effect being deleted, has its position correlated with those of the other atoms through the potential energy U_{N+1}.

Both formulas (2.4) and (2.5) can be used to calculate μ by Monte Carlo simulation at low densities, but both fail at higher densities in fluids of strongly repulsive molecules (hard spheres, Lennard-Jones, etc.) because the average of $\exp(-\beta\Psi)$ for (2.4) or $\exp(\beta\Psi)$ for (2.5) is much larger than the most probable value in the ensemble in question, and hence the simulation provides poor statistics for estimating the average. This effect was discussed by Shing and Gubbins,[3] who also proposed strategies for getting around the difficulty.

Our procedure of gradual insertion or deletion depends on introducing a set of "weakened" increments Ψ_λ, $0 \leq \lambda \leq 1$, with

$$\Psi_0 = 0, \quad \Psi_1 = \Psi . \qquad (2.6)$$

In particular in the case of pair interactions one can introduce a "weakened" Φ_λ, with $\Phi_0 = 0$ and $\Phi_1 = \Phi$, and let

$$\Psi_\lambda = \sum_{i=1}^{N} \Phi_\lambda(|r_{N+1} - r_i|) . \qquad (2.7)$$

We let $\langle \ \rangle_{N+\lambda}$ be an average with respect to an ensemble in which the $N+1$ particle interacts with the remainder through the weakened potential:

$$\langle O \rangle_{N+\lambda} = \int dr_1 \cdots dr_{N+1} O e^{-\beta(U_N + \Psi_\lambda)} /$$
$$\int dr_1 \cdots dr_{N+1} e^{-\beta(U_N + \Psi_\lambda)} , \qquad (2.8)$$

where O is any function of $r_1, \ldots, r_{N+1}$. Note that $\lambda = 0$ and $\lambda = 1$ correspond to ensembles of N and $N+1$ particles, respectively.

Let us choose a finite set of values

$$0 = \lambda_0 < \lambda_1 < \cdots < \lambda_M = 1 \qquad (2.9)$$

for λ and define

$$\Delta\Psi_j = \Psi_{\lambda_{j+1}} - \Psi_{\lambda_j} . \qquad (2.10)$$

Then in analogy with (2.4) and (2.5), we define $\Delta\mu_j$ as

$$e^{-\beta\Delta\mu_j} = \langle e^{-\beta\Delta\Psi_j} \rangle_{N+\lambda_j} = 1/\langle e^{\beta\Delta\Psi_j} \rangle_{N+\lambda_{j+1}} , \quad (2.11)$$

whence it follows that

$$\mu = \sum_{j=0}^{M-1} \Delta\mu_j . \quad (2.12)$$

That is to say, the total chemical potential is a sum of increments, each amounting to a relatively small change (2.10) in the potential energy of interaction of the $N+1$ particle with the remainder. Note that (2.12) is exact, whatever the choice of M. Letting λ vary continuously, one obtains the formula

$$\mu = \int_0^1 \langle d\Psi_\lambda/d\lambda \rangle_{N+\lambda} d\lambda \quad (2.13)$$

by expanding the exponentials in (2.11) to lowest order and replacing the sum in (2.12) by an integral. Equation (2.13), of which a special case is in Hill's book,[6] has the simple intuitive interpretation that the chemical potential is the work required to reversibly insert an additional particle. Analogous expressions are found in Refs. 1 and 2.

Instead of, or in addition to using the averages in (2.11), one can, following Shing and Gubbins,[3] introduce probability densities

$$f_j(x) = \langle \delta(x - \Delta\Psi_j) \rangle_{N+\lambda_j} , \quad (2.14)$$

$$g_j(x) = \langle \delta(x - \Delta\Psi_j) \rangle_{N+\lambda_{j+1}} \quad (2.15)$$

for $x = \Delta\Psi_j$ in the ensembles which precede and follow this partial insertion; here δ denotes the Dirac delta function. They are related by

$$g_j(x) = e^{\beta\Delta\mu_j} f_j(x) e^{-\beta x} \quad (2.16)$$

which means that

$$e^{\beta\Delta\mu_j} = g_j(\Delta\Psi_j) e^{\beta\Delta\Psi_j} / f_j(\Delta\Psi_j) , \quad (2.17)$$

independent of $\Delta\Psi_j$. The right-hand side of (2.17) can be evaluated for various values of $\Delta\Psi_j$ to obtain estimates for $\Delta\mu_j$. The utility of this approach has been pointed out by Shing and Gubbins in the case in which a particle is inserted in a single step [$M=1$ in (2.9)], and it has the same advantages in the case of partial insertions.

The preceding formulas are easily generalized to the case in which $J > 1$ particles are simultaneously added to or deleted from the fluid. For example, when $J=2$, (2.1) is replaced by

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_{N+2}) = U_{N+2}(\mathbf{r}_1, \ldots, \mathbf{r}_{N+2})$$

$$- U_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) \quad (2.18)$$

and (2.4) by

$$e^{-2\beta\mu} = \langle e^{-\beta\Psi} \rangle_N , \quad (2.19)$$

etc. Note that Ψ includes a contribution from the interaction of the J particles among themselves.

We have assumed up until now that the ensemble averages $\langle \; \rangle$ refer to a constant volume as well as a constant temperature ensemble. But they are equally valid for a *constant pressure* ensemble, and some of the simulations discussed below in Sec. III refer to such an ensemble. To

be sure, in a system of finite size one expects formulas such as (2.4) to give results which deviate somewhat from the values in the thermodynamic ($N \to \infty$) limit. There is no reason to expect that these "finite size corrections" will be more severe in a constant pressure than in a constant volume ensemble, and the former may actually be preferable, in particular if two or more particles are added or deleted simultaneously.

III. APPLICATION TO A TWO-DIMENSIONAL FLUID

We have studied various ways of implementing the gradual insertion and/or deletion formulas of Sec. II in a Monte Carlo simulation of a two-dimensional fluid of particles interacting through a Lennard-Jones 6-12 pair potential

$$\Phi(r) = \epsilon[(\sigma/r)^{12} - (\sigma/r)^6] . \quad (3.1)$$

The potential is cut off at $r = 2\sigma$ and the energy is corrected for the tail in the standard way by assuming the pair correlation $g(r)$ is 1 for $r > 2\sigma$. We have used a reduced temperature $T^* = 1$ (i.e., $\epsilon = k_B T$) and two reduced densities (particles per unit area, with the latter in units of σ^2), $\rho^* = 0.48$ and 0.75.

Our first attempt was based on the use of

$$\Phi_\lambda = \lambda\Phi \quad (3.2)$$

in (2.7), with λ increased in a quasicontinuous manner by equal amounts for each Monte Carlo pass, using (2.13), approximated by a sum, to evaluate μ. This worked very badly in a dense fluid, presumably because when λ is small the rapid increase with λ of the effective radius of the repulsive part of Φ_λ, the r at which

$$\lambda\epsilon(\sigma/r)^{12} = k_B T , \quad (3.3)$$

makes the insertion irreversible. Another way of viewing the problem is that (3.2) leads to a $d\Psi_\lambda/d\lambda$ which diverges as the new particle approaches a particle already present in the fluid, and hence bad sampling statistics for (2.13).

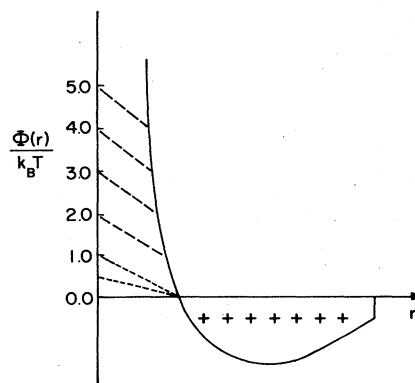These difficulties at small λ were reported in Refs. 1

FIG. 1. Insertion of a particle using approach II. The solid curve is the pair potential (schematic), while the broken lines represent successive stages of the weakened potential Φ_λ (see text).

TABLE I. Simulation results at lower density. Asterisk denotes the attractive part of the potential added in the early stages. (See text.)

$N+1$	Ensemble	P^*	ρ^*	Method[a]	Number of stages	μ
$15+1$	NPT	0.525	0.45±0.03	I, A, ins.	5	−0.139±0.12
$15+1$	NPT	0.525	0.45±0.03	I, B	2	−0.09 ±0.12
$15+1$	NPT	0.525	0.45±0.03	II*, A, ins.	5	−0.212±0.16
$15+1$	NPT	0.525	0.45±0.03	II, C, ins.	101	−0.014±0.05
$35+1$	NPT	0.525	0.47±0.02	I, A, ins.	6	−0.075±0.13
$35+1$	NPT	0.525	0.47±0.02	I, B	3	−0.19 ±0.25
$35+1$	NPT	0.525	0.47±0.02	I, B	2	−0.18 ±0.3
$15+1$	NVT	0.51	0.465	I, A, ins.	3	−0.23 ±0.1
$15+1$	NVT	0.51	0.465	I, B	3	−0.206±0.1
$35+1$	NVT	0.52	0.477	I, A, ins.	4	−0.199±0.2
	b	0.525	0.48			−0.1468
	b	0.5033	0.47			−0.1714

[a]Method. I and II refer to the two sequences for inserting (ins.) or deleting (del.) a particle and A, B, C to the different methods of calculating the chemical potential indicated in the text.
[b]Thermodynamic integration using the results of Ref. 7.

and 2, which also give strategies for dealing with the problem. We ourselves used two somewhat different approaches. The first, designated I, consists of "growing" the new particle by successive increments of both σ and ϵ. For example, the sequence $(\epsilon_\lambda, \sigma_\lambda)$ given by (0,0), $(10^{-5}, 0.2)$, (0.4,1.), (0.6,1.), and (1,1), expressed as fractions of the (full strength) ϵ and σ in (3.1), was employed successfully at the higher density (see the last simulation result in Table I). A certain amount of experimentation was necessary to determine appropriate ϵ_λ and σ_λ values.

An alternative approach, hereafter designated by II, consists of replacing the divergent repulsive part of the pair potential by a finite approximation, Fig. 1, which rises in steps. For small λ, Φ_λ has the form indicated by the successive dotted lines and is zero for $r > \sigma$. Once $\Phi_\lambda(0)$ reaches $k_B T$, further increments lead to the "tree stump" shape indicated by the dashed lines. This continues until Φ_λ is identical to Φ for those $r < \sigma$ at which the

latter is less than, say $8k_B T$, at which point further increases have negligible effect. The negative part of Φ for $r > \sigma$ is turned on at the same time as $\Phi_\lambda(0)$ increases from 6 to $7k_B T$, although the precise moment is not crucial; the third line in Table I was obtained with the negative part turned on while $\Phi_\lambda(0)$ increased from 1 to $2k_B T$. In the case of quasicontinuous insertion of the particle (100 or more steps), Φ_λ is gradually lowered for $\sigma < r < 2$ in the manner suggested by the line of plusses in Fig. 1, at the same time as $\Phi_\lambda(0)$ is increasing from 6 to $7k_B T$. A variant of this approach in which the positive part of Φ_λ has a flat top—the dotted and dashed lines in Fig. 1 are horizontal rather than slanted—did not work quite as well, as the system tended to stay in a metastable configuration.

We employed three methods for evaluating μ corresponding to Eqs. (2.11), (2.17), and (2.13), respectively, and hereafter denoted as simple ensemble average (A), ra-

TABLE II. Simulation results at higher density.

$N+1$	Ensemble	P^*	ρ^*	Method[a]	Number of stages	μ
$35+1$	NPT	2.388	0.75±0.005	I, A, ins.	3	2.77±0.7
$15+1$	NVT	2.8	0.775	II, A, ins.	6	2.37±0.3
$15+1$	NVT	2.8	0.775	II, A, del.	6	2.41±0.17
$15+1$	NVT	2.8	0.775	II, C, ins.	130	2.6 ±0.1
$15+1$	NVT	2.8	0.775	II, C, del.	180	2.48±0.25
$35+1$	NVT	2.5	0.76	I, B	3	2.0 ±0.4
$35+1$	NVT	2.5	0.76	I, A, ins.	3	2.27±0.7
	b	2.388	0.75			2.27
	b	2.57	0.76			2.5
	b	2.87	0.775			2.88

[a]As in Table I.
[b]Thermodynamic integration (as in Table I).

tio of distributions of $\Delta\psi$ (B), and continuous insertion (C). Both constant area ("volume") and constant pressure ensembles, denoted NVT and NPT, were employed with two different numbers of particles: $15 + 1$ and $35 + 1$. For insertions using a small number of steps, on the order of 12000 passes after reaching equilibrium were used for averaging for each stage. In the case of quasicontinuous insertions or deletions, employing 100 or more stages, we used 600 passes per stage and did not wait for the system to reach equilibrium after a small increment (or decrement) in the potential before beginning averaging.

The results for the two densities are given in Tables I and II. Here ρ^* denotes the average density in our NPT ensemble, and $N + \frac{1}{2}$ divided by the area for the NVT ensemble. The pressure in appropriate dimensionless units is P^*; for the NVT ensemble it is the mean of the values for N and $N + 1$ particles. The number of stages is the integer M in (2.9), so that a direct use of (2.4) or (2.5) corresponds to a 1 stage insertion or deletion. In the ratio method (B) we actually carried out a simulation for $M + 1$ stages including the "pure" N and $N + 1$ particle systems. The error estimates for method (A) were obtained from standard block averages (5 to 10 blocks) and those for (B) by comparison of the ratios obtained for different values of $\Delta\Psi_j$. For (C) the error estimates were obtained by repeating the procedure four or five times and comparing the results. In methods (A) and (C) one uses a different sequence of steps to obtain μ depending on whether the particle is inserted or deleted, so we have noted which was the case for the examples in Tables I and II.

Generally speaking, the results obtained by different methods of gradual insertion are consistent with one another within the (rough) error estimates and also consistent with values obtained from thermodynamic integration of the isotherm of Barker et al.[7] as indicated at the bottom of each table.

IV. CONCLUSION

The results in Sec. III indicate that the gradual insertion and/or deletion procedure can actually be made to work in a high-density situation in which the direct use of formulas (2.4) and (2.5) is impractical. To be sure, the actual series of intermediate steps must be chosen with some care and "experimentation," as seems to be true of the alternative umbrella sampling method of Shing and Gubbins.[3] We believe that the method of inserting a particle with a weakened potential has some advantage in provid-

ing physical insight about the intermediate ("biased") probability distributions which are sampled. However, there remains a practical question about whether gradual insertion/deletion is actually more economical in computer time than alternative techniques, and it is at this point that we should note some disadvantages of the method.

First, as noted by Shing and Gubbins, there are practical advantages to methods in which one only has to simulate a homogeneous fluid of identical particles, in which "test particles" if present have no influence on the motion of other particles, as one can be collecting other interesting statistical data on the fluid (pressure, energy, etc.) using the same configurations employed for determining the chemical potential. This advantage disappears as soon as one goes to umbrella sampling, of which gradual insertion and/or deletion is a particular form.

In addition, the fact that one particle differs from the rest and that one is evaluating averages associated with this unique particle means that a longer run (total number of passes) is needed to obtain good statistics than if one were calculating some average in which all the particles entered in a symmetrical way. One way of improving the efficiency is to gradually insert several particles rather than just one. However, such a procedure must be used with caution, since there may be important effects from particles with weakened potentials colliding with each other and then drifting apart. Whereas such effects are of course included in principle in the ensemble averages and thus part of the "right answer," one can well imagine them giving rise to serious fluctuations in practice.

One can, to be sure, treat all of the particles as identical provided all of the interactions are simultaneously turned on or off at the same rate. Such a procedure is effectively another way of obtaining the chemical potential by "thermodynamic integration," analogous to starting with a low density gas and integrating

$$d\mu = \rho^{-1}dp$$

along an isotherm. What this suggests is that the gradual insertion or deletion of a single particle may well be cost effective in computer time only in situations in which thermodynamic integration is impractical.

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