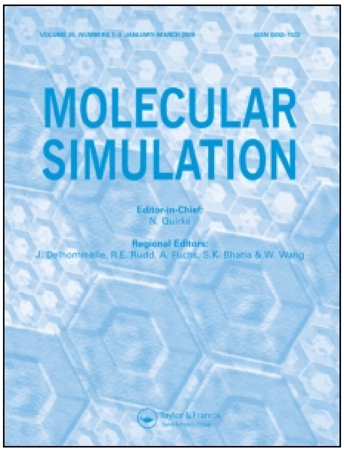

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Efficient Volume Changes in Constant-Pressure Monte Carlo Simulations

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EFFICIENT VOLUME CHANGES IN CONSTANT-PRESSURE MONTE CARLO SIMULATIONS

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A new method for calculating the energy change resulting from an affine deformation of the system in constant-pressure Monte Carlo simulations is presented. The energy changes accompanying particle displacements are calculated exactly, but those accompanying volume changes are approximated. The latter energy is estimated from a Taylor expansion whose coefficients depend on the energetics of the system in its predeformed state. This method does not require an assumption of conformal potentials and is as readily applied to molecular systems and mixtures as to simple monatomic fluids. The expansion employed is not self-truncating and two *ansatzen* for this purpose are considered. The results obtained using these methods are compared with those from constant-pressure simulations using exact, time-consuming summations of the pair interactions in the affinely deformed system. Because of the additional overhead required, the method is not especially efficient for ordinary NPT simulations. However, it is found to be an order of magnitude faster than conventional constant-pressure algorithms when frequent volume changes are required or when simulating phase transitions using the Gibbs-Duhem integration technique.

Keywords: Volume changes; NPT simulation; Gibbs-Duhem integration

1. INTRODUCTION

Constant-pressure Monte Carlo methods make up an increasingly large fraction of simulation studies on molecular systems. They have proven essential in the study of aqueous solutions, phase equilibrium and adsorption phenomena. With pressure fixed, the standard simulation methods require trial volume changes in which all the particles are moved in an affine fashion. In a typical implementation, one volume change is attempted after each cycle of displacements. If an exact enumeration of the energy is required, the computational cost of a single volume change is a significant fraction of the cost of an entire cycle of N particle moves. This is a serious impediment and contrasts markedly with constant-pressure molecular dynamics methods [1]. In these MD simulations, volume changes are explored simultaneously with particle displacements and the computational cost of including the volume dynamics is roughly comparable to adding a single particle to the system.

It is possible to utilize the properties of certain power-law potentials to eliminate the need for the explicit summation of the individual contributions to the energy when an attempted volume change occurs [2]. Although very useful, this trick becomes increasingly cumbersome for atomically detailed systems and for long chain molecules. Scaling is impossible for potentials with tabular or transcendental forms, such as the Morse potential, and for molecular systems with fixed bond lengths. For these more demanding situations, several strategies have been suggested.

The simplest device to avoid the extensive computations required is to defer volume changes to every fifth or more cycle of particle movements [3, 4]. Though this reduces the expense of the volume change on a *per-cycle* basis, it also retards the exploration of the volume fluctuations that are essential to the method. In some circumstances, considerably longer runs may be required to achieve suitably stable averages and the apparent savings would then be lost. Other strategies are possible [5–10]. Recently, Escobedo and dePablo have developed a method to generate volume fluctuations in isothermal-isobaric Monte Carlo simulations for flexible (or semi-flexible) chain molecules [11, 12]. The technique involves a one-dimensional fluctuation in contrast to the conventional symmetric change of the entire simulation box.

In certain applications, volume changes must be executed as frequently as particle displacements. Constant pressure simulations then become impossibly slow. One such application is the Gibbs-Duhem integration technique developed by Kofke [13, 14] for simulation of phase equilibria. The "osmotic" version of this method for fluid mixtures requires three types of moves chosen with equal probability: 1) N attempted particle displacements; 2) a single volume change attempt; 3) N attempted particle insertions or deletions. Near the critical point, the particle insertion/deletion step is often performed at constant density [15] and therefore requires an affine deformation for every insertion/deletion attempt. When the scaling trick cannot be used, this proves to be a severe bottleneck for large systems.

The energy evaluation scheme introduced here is based on a truncated Taylor expansion (TTE) of the instantaneous potential energy. It is restricted to continuous, n-fold differentiable potentials. For this very broad class of systems, the use of this expansion eliminates the need to perform an explicit summation of the particle energies when making a volume change. The TTE method for energy implementation can be trivially implemented and requires no new counting methods or bookkeeping.

2. METHOD

2.1. Basic Equations

Since all intermolecular potentials in the system must be continuous and n-fold differentiable, the TTE method is inapplicable to any system in which there is a hard core or other discontinuity in the potential. Energy changes involved in particle displacements or in constant-volume insertions and deletions are calculated exactly. Those associated with volume changes are approximated. A typical volume deformation will take the system from volume V to a new volume $\xi^3 V$. Consequently, the positions of the N particles in the system changes from $(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ to $(\xi\mathbf{r}_1, \xi\mathbf{r}_2, \ldots \xi\mathbf{r}_N)$. Any property A that depends on the particle positions can be approximated as an n^{th}-order Taylor expansion about the original configuration:

$$A' \cong A + \sum_{j=1}^{n} \frac{v^j}{j!} \frac{d^j A}{d\xi^j}\bigg|_{\xi=1} \equiv A + \sum_{j=1}^{n} \frac{v^j}{j!} \delta^{[j]} A \tag{1}$$

where $v \equiv \xi - 1$, $A' \equiv A(\xi)$, $A \equiv A(\xi = 1)$ and $\delta^j A \equiv \dfrac{d^j A}{d\xi^j.}\bigg|_{\xi=1}$

The configurational energy is generally obtained in MC simulations from

$$U = U_{\text{core}} + U_{\text{tail}}, \tag{2}$$

where U_{core} represents an explicit and exact calculation over some subset of all the particles in the system, typically all interactions within some cutoff radius, r_c. The quantity U_{tail} is an estimate of all the interactions outside the core set, usually obtained in some mean field limit.

Our strategy is to apply the expansion in Equation (1) to the calculation of the core energy and its derivatives. When a volume change is attempted, the new estimate for U_{core} is approximated by

$$U'_{\text{core}} \cong U_{\text{core}} + \sum_{j=1}^{n} \frac{v^j}{j!} \delta^{[j]} U_{\text{core}} \tag{3}$$

which, for the change in energy, is just

$$\Delta U_{\text{core}} \cong \sum_{j=1}^{n} \frac{v^j}{j!} \delta^{[j]} U_{\text{core}} \tag{4}$$

The derivatives, $\delta^{[j]}U_{\text{core}}$, will themselves change upon deformation, and these changes are taken into account using the appropriate expansions. In general, the expansion for each derivative $\delta^{[j]}U_{\text{core}}$ will be truncated at successively lower orders in v:

$$\delta^{[j]}U'_{\text{core}} \cong \delta^{[j]}U_{\text{core}} + \sum_{i=j+1}^{n} \frac{v^{(i-j)}}{(i-j)!} \delta^{[i]}U_{\text{core}} \tag{5}$$

For a n^{th}-order correction, this process provides no correction for the final term in the expansion, $\delta^{[n]}U_{\text{core}}$. We replace the highest-order term with an average over some "recent" set of particle positions. Two explicit choices are examined in Section 2.5.

2.2. Pairwise Additive Forces

For a simple pairwise additive system U_{core} is commonly given by

$$U_{\text{core}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}) \quad \ni r_{ij} < r_c \tag{6}$$

and U_{tail} by the approximation

$$U_{\text{tail}} = 2\pi N\rho \int_{r}^{\infty} dr\, r^2 u(r) g(r) \cong 2\pi N\rho \int_{r_c}^{\infty} dr\, r^2 u(r) \tag{7}$$

The resulting TTE expressions for $\delta^{[m]}U_{\text{core}}$ are then easily obtained

$$\delta^{[m]}U_{\text{core}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left. \frac{d^m u(\xi r_{ij})}{d\xi^m} \right|_{\xi=1}$$

$$= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} r_{ij}^m \frac{d^m u(r_{ij})}{dr_{ij}^m} = \frac{1}{2} \sum_{i=1}^{N-1} \Phi_i^{[m]} \quad \ni r_{ij} < r_c \tag{8}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and

$$\Phi_i^{[m]} \equiv \sum_{\substack{j=1 \\ j \neq i}}^{N} r_{ij}^m \frac{d^m u(r_{ij})}{dr_{ij}} \quad \ni r_{ij} < r_c \tag{9}$$

The $\Phi_i^{[m]}$ can be calculated and updated with modest overhead whenever the energy change for a particle displacement is evaluated.

It is important to recognize that the expansion does not change the number of interactions in the approximate calculation of the core energy. Thus, if r_c is the truncation distance for the initial system, then $r_c' = \xi r_c$ is the requisite truncation distance for the affinely deformed system. A tail correction must be applied to the energies and the derivatives of the pre- and post-deformed systems, obtained by using these two values for r_c in Equation (7). Note that the derivatives required in the first term of the expansion, $\delta^{[1]}U_{\text{core}}$, are also required to estimate the core contribution to the fluctuating virial pressure and thus do not usually impose any additional overhead.

2.3. Many-Body Potentials

Extension to systems with intramolecular or multi-body interactions is trivial. The presence of pure orientation variables in the potential does not affect this analysis since these quantities are fixed parameters in the affine deformation. The presence of higher-body forces leads to somewhat more complex but nonetheless tractable equations. For instance, the expansion of a typical three-body contribution to the energy to the second order in v would yield

$$\begin{aligned}\sum_{i<j<k} u_3(\xi r_{ij}, \xi r_{ik}, \xi r_{jk}) &= \sum_{i<j<k} u_3(r_{ij}, r_{ik}, r_{jk}) \\ &+ v \sum_{i<j<k} \left[r_{ij}\frac{du_3}{dr_{ij}} + r_{ik}\frac{du_3}{dr_{ik}} + r_{jk}\frac{du_3}{dr_{jk}} \right] \\ &+ \frac{v^2}{2} \sum_{i<j<k} \left[r_{ij}^2 \frac{d^2u_3}{dr_{ij}^2} + r_{ik}^2 \frac{d^2u_3}{dr_{ik}^2} + r_{jk}^2 \frac{d^2u_3}{dr_{jk}^2} + r_{ij}r_{ik}\frac{d^2u_3}{dr_{ij}dr_{ik}} \right. \\ &\left. + r_{ik}r_{jk}\frac{d^2u_3}{dr_{ik}dr_{jk}} + r_{ij}r_{jk}\frac{d^2u_3}{dr_{ij}dr_{jk}} \right] + \cdots \end{aligned} \tag{10}$$

where r_{ij}, r_{ik} and r_{jk} are the three relevant interparticle separations.

2.4. Stiff and Rigid Molecules

It is often difficult or impossible to employ the scaling methods for volume changes when the system of interest involves molecular species. For a molecular model involving rigid bonds, the only possible affine deformation must translate the molecules as a whole, without internal distortion. Thus, separation between nonequivalent sites on two different molecules will not scale in proportion to the parameter ξ. If the bonds are allowed to vibrate and all interaction sites are centered on the atoms, then a simple scaling method *can* be used. However this will allow individual bonds to stretch. The maximum allowable deformation will be determined by the highest frequency molecular mode. This means that for realistically stiff vibrational models, each volume change will be extremely small and that an adequate exploration of the volume fluctuations will require very lengthy simulations. One can also use a molecule-based affine deformation for these stiff systems. During an affine deformation, the individual molecules are frozen in their most recent internal configuration. Just as in the rigid-molecule systems, the simple form of the scaling trick becomes inapplicable.

The TTE method can be applied to both rigid and stiff models of molecular systems. The basic equations, Equations (3)–(5), are unaffected but working expressions for the $\delta^{[j]}U_{\mathrm{core}}$ differ. Let $\mathbf{R}_i$ be the position of some fixed point (perhaps the center of mass) in molecule i and $\mathbf{r}_{i\alpha}$ be the absolute position of site α in molecule i. During a molecule-based affine deformation, $\mathbf{R}_i \rightarrow \xi\mathbf{R}_i$ but the quantity $\boldsymbol{l}_{i\alpha} \equiv \mathbf{r}_{i\alpha} - \mathbf{R}_i$ remains unchanged as do the vector relationships among the various $\boldsymbol{l}_{i\alpha}$. Any purely intramolecular contributions to the potential do not contribute to the energy change accompanying system deformations. Upon deformation,

$$\mathbf{r}'_{i\alpha j\gamma} = \xi\mathbf{R}_{ij} + (\boldsymbol{l}_{j\gamma} - \boldsymbol{l}_{i\alpha}) \tag{11}$$

Since the site–site separations, $r_{i\alpha j\gamma} \equiv |\mathbf{r}_{i\alpha} - \mathbf{r}_{j\gamma}|$ are not directly proportional to ξ, the required expressions will have a more complicated dependence than for simple atomic systems.

Defining,

$$\delta^{[n]} r_{i\alpha j\gamma} \equiv \left. \frac{d^n r_{i\alpha j\gamma}}{d\xi^n} \right|_{\xi=1}, \tag{12}$$

one obtains

$$\delta^{[1]}r_{i\alpha j\gamma}=\frac{\mathbf{R}_{ij}\cdot\mathbf{r}_{i\alpha j\gamma}}{r_{i\alpha j\gamma}}, \tag{13}$$

$$\delta^{[2]}r_{i\alpha j\gamma}=\frac{R_{ij}^2-[\delta^{[1]}r_{i\alpha j\gamma}]^2}{r_{i\alpha j\gamma}}, \tag{14}$$

and

$$\delta^{[3]}r_{i\alpha j\gamma}=-3\frac{\delta^{[1]}r_{i\alpha j\gamma}\,\delta^{[2]}r_{i\alpha j\gamma}}{r_{i\alpha j\gamma}}, \tag{15}$$

In simple atomic systems, with only a single site on each molecule, all derivatives beyond the first vanish. This is made evident by setting $r_{i\alpha j\gamma}=R_{ij}$ in Equations (13)–(15).

For a potential model whose intermolecular contribution is made up of simple site–site potentials on different molecules,

$$U=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{\alpha=1}^{n_i}\sum_{\gamma=1}^{n_j}u(r_{i\alpha j\gamma}), \tag{16}$$

where α designates one of the n_i sites on molecule i and γ designates one of the n_j sites on molecule j. For notational simplicity, we have suppressed any designation of the actual site species. It is to be understood that the function $u(r_{i\alpha j\gamma})$ changes, depending on the character of the sites α and γ and that only sites within appropriate cutoff distances are included in the sum.

The equations for the $\delta^{[j]}U_{\text{core}}$ then become

$$\delta^{[1]}U_{\text{core}}=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{\alpha=1}^{n_i}\sum_{\gamma=1}^{n_j}\frac{du(r_{i\alpha j\gamma})}{dr_{i\alpha j\gamma}}\delta^{[1]}r_{i\alpha j\gamma} \tag{17}$$

$$\delta^{[2]}U_{\text{core}}=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{\alpha=1}^{n_i}\sum_{\gamma=1}^{n_j}\frac{d^2u(r_{i\alpha j\gamma})}{dr_{i\alpha j\gamma}^2}[\delta^{[1]}r_{i\alpha j\gamma}]^2+\frac{du(r_{i\alpha j\gamma})}{dr_{i\alpha j\gamma}}\delta^{[2]}r_{i\alpha j\gamma} \tag{18}$$

$$\delta^{[3]}U_{\text{core}}=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\sum_{\alpha=1}^{n_i}\sum_{\gamma=1}^{n_j}\frac{d^3u(r_{i\alpha j\gamma})}{dr_{i\alpha j\gamma}^3}[\delta^{[1]}r_{i\alpha j\gamma}]^3$$

$$+3\frac{d^2u(r_{i\alpha j\gamma})}{dr^2_{i\alpha j\gamma}}\delta^{[1]}r_{i\alpha j\gamma}\delta^{[2]}r_{i\alpha j\gamma}+\frac{du(r_{i\alpha j\gamma})}{dr_{i\alpha j\gamma}}\delta^{[3]}r_{i\alpha j\gamma} \tag{19}$$

Though these expressions are slightly more complicated than those presented above for a simple atomic system, they are readily incorporated into the algorithm. When the $l_{i\alpha} = 0$, they become formally equivalent to the expressions presented earlier. Any purely internal interactions do not enter into the equations for volume changes using this molecule based affine deformation. These include bond stretches, bond bends and any other multibody intramolecular terms. Multibody intermolecular potentials can be included by an appropriate extension of Equation (11).

2.5. Truncation and Closure

For the highest-order term in the expansion, Equation (5) provides no correction for $\delta^{[n]}U_{\text{core}}$. Absent any other mechanism for estimating it, this term would remain unchanged in any affine deformation. As might be anticipated, the TTE will fail completely without some better estimate for the fluctuations in $\delta^{[n]}U_{\text{core}}$. This quantity is assumed to be small, and its instantaneous variations are assumed to have little effect on the calculation of lower-order $\delta^{[j]}U_{\text{core}}$ for reasonably long Monte Carlo sequences. Therefore, the exact quantity is replaced with a representative average. Two possible closures are considered below.

Lagging Average

A "lagging average" (LA) is defined as the thermal average value of $\delta^{[n]}U_{\text{core}}$ over some prior number of attempted particle displacements. For simple pairwise additive systems, this quantity is obtained by calculating $\Phi_i^{(n)}$ in Equation (8) each time a particle move is attempted. The instantaneous value of $\delta^{[n]}U_{\text{core}}$ is then approximated by

$$\delta^{[n]}U_{\text{core}} \cong \left\langle \delta^{[n]}U_{\text{core}} \right\rangle_{\text{LA}} \equiv \frac{N}{2t} \sum_{s=1}^{t} \Phi_i^{(n)}(s) \tag{20}$$

where i is the identity of the particle selected in the s^{th}-attempted move in the averaging sequence, t is the number of attempted displacements chosen for averaging, and $\Phi_i^{(n)}(s)$ is the value of $\Phi_i^{(n)}$ when the particle i is chosen for displacement at move s. The quantity $\Phi_i^{(n)}(s)$ is calculated using the particle positions at the end of the displacement move. The individual $\Phi_i^{(n)}(s)$ employed in Equation (20) differ from the exact $\Phi_i^{(n)}$ because they are acquired during the displacement of the individual particles. The particle positions at the time of the calculation thus differ slightly from the actual positions at the time of the attempted volume change. In general, not all particles will have been selected during the averaging period and some particles will have been selected more than once.

The averaging period, t, must be large enough to obtain a good statistical sampling of the full set of $\Phi_i^{(n)}$, but not so large as to include contributions from highly dated particle positions. During the testing of this approximation, a volume change was attempted at the end of N attempted particle displacements. The average was carried over that single cycle (i.e. $t = N$). With this choice, the average does not span any volume changes, probably a desirable circumstance. For simulations with a very large number of particles, a stable estimate may be achieved with less than a full cycle of attempted particle displacements.

Last Move Approximation

An alternative method is the "last move approximation" (LMA). It mimics the exact calculation indicated in Equation (5). Instead of taking a thermal average over a statistically representative set of particles (those chosen in the last t moves), the last available $\Phi_i^{(n)}$ for all N particles are averaged:

$$\delta^{[n]}U_{\text{core}} = \left\langle \delta^{[n]}U_{\text{core}} \right\rangle_{\text{LMA}} \equiv \frac{1}{2}\sum_{i=1}^{N} \Phi_i^{(n)}(s_i) \tag{21}$$

where s_i labels the Markov step in which the particle i was last considered for movement.

In general, there will be no way to guarantee that all particles will have been displaced since the last volume change. Thus, the LMA can contain contributions from several earlier system volumes. One way to avoid heavily dated contributions in the estimate of Equation (21) is to consider particles sequentially, rather than at random when attempting particle movements. This ensures each of the $\Phi_i^{(n)}$ are updated in every cycle of particle displacements but can lead to problems associated with microscopic reversibility. Strict adherence to microscopic reversibility in Monte Carlo calculations has often been ignored since it is a sufficient but not necessary condition for obtaining an equilibrium distribution. However, coupling sequential selection with Equation (21) does give rise to additional concerns. The contributions to $\delta^{[n]}U_{\text{core}}$ from low index particles $(1, 2, ,3, \ldots)$ will always be consistently more dated than high index particles $(N, N-1, N-2, \ldots)$. This is probably of little consequence in a homogeneous simple fluid in which all the particles are highly mobile. However, simulations of solids, polymers and interfaces often maintain a restricted spatial relationship among the particles throughout the course of the run. As a result, particular portions of the simulation cell may contribute consistently dated information to Equation (21). A simple solution to this problem is to make a sequential selection of the particle to be moved from an array of length N in which all the particles appear in random order and are periodically re-shuffled. Each particle would then be moved in every cycle, but not in any fixed sequence.

3. RESULTS

Though the ideas presented here are intended for application to somewhat complex systems, we test the TTE simulation method on a simple Lennard-Jones (12–6) fluid. This has the advantage that extensive results are already available. We report here a series of NPT simulations of the Lennard-Jones system with $P^* = 1.02$, $T^* = 1.00$, which produces an average $\rho^* = 0.8$ (in the usual reduced units). A spherical cutoff was made at half the box length with standard end correction. No neighbor list, cell lists, or other time saving methods were introduced. The scaling trick was not used so that timing comparisons would be valid for situations in which the scaling trick cannot be employed. In our test implementation, the two closure schemes, LA and LMA, were found to be very comparable for the tested systems. For coding convenience, the LA was subsequently used throughout the test calculations reported here.

3.1. Stability

In order for the TTE energy change approximation to be applicable, the truncated expansion must be accurate. Simulations of 108 particles were conducted using the exact trajectory to propogate the Markov chain. The individual terms of the expansion were calculated and updated exactly at each Monte Carlo move. This provides for a direct assessment of the convergence of the series. After equilibration, a total of 2×10^7 traditional NPT configurations (N attempted displacement and one attempted volume change) were sampled. The exact energy and its Taylor expansion estimate were both averaged. Figure 1 shows the r.m.s difference between the exact and approximate configurational energies as a function of the acceptance fraction for volume change moves. This latter quantity is adjusted in the usual way and determines $\langle v^2 \rangle^{1/2}$ for the run. At this thermodynamic state, a volume-change acceptance fraction of 0.605 corresponds to $\langle v^2 \rangle^{1/2} = 0.00575$, while an acceptance fraction of 0.343 corresponds to $\langle v^2 \rangle^{1/2} =$

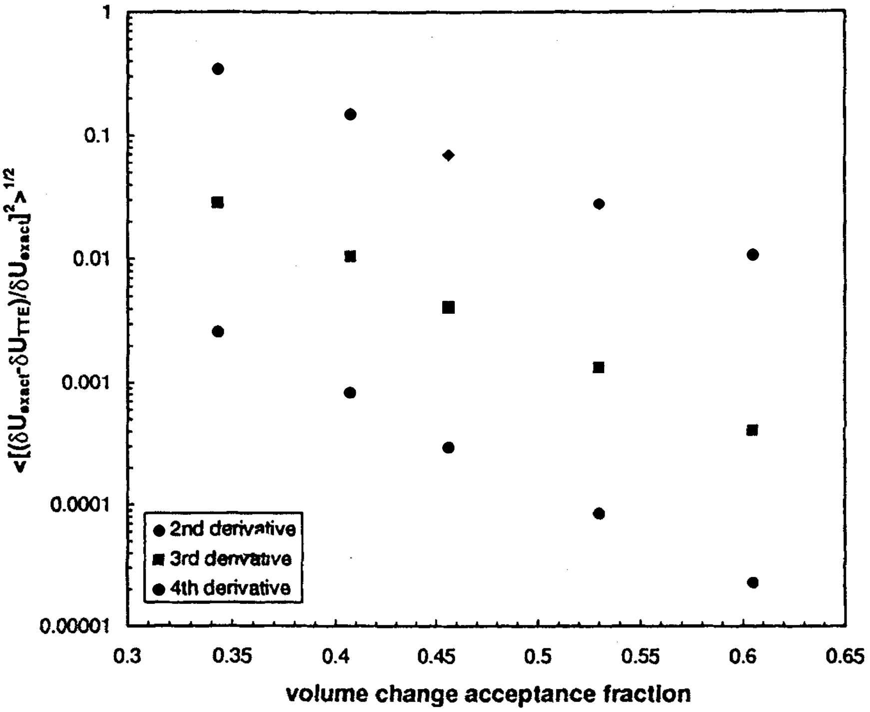

FIGURE 1 The r.m.s differences between the exact energy change, δU_{exact} and the TTE approximated energy change, $\delta U_{\text{approximate}}$, for a pure LJ fluid at $P^* = 1.02$, $T^* = 1.00$ and $\rho^* = 0.8$. TTE series are truncated at the indicated order. The highest order term is calculated exactly in the simulations reported in this figure. The LA and LMA were not used.

0.0122. As expected, the accuracy of the truncated series increases by about an order of magnitude for each additional term included in the series. In addition, the expansion truncated at any level becomes more accurate as the acceptance fraction increases.

Figure 1 explores the absolute convergence of the Taylor expansion, but does not include any effects arising from the introduction of the LA or LMA closure. To assess the impact of the closures, we performed a series of parallel NPT simulations, starting from the same initial configuration and using the same random number sequence. In one simulation, an exact enumeration of the energy was used and, in the other, the TTE was employed using the LA closure. One volume change was attempted for each pass of N attempted displacements. Figure 2 shows the results of one such study. In each case, application of the TTE to some initial condition eventually leads to a divergence of the TTE energy from that calculated using the exact

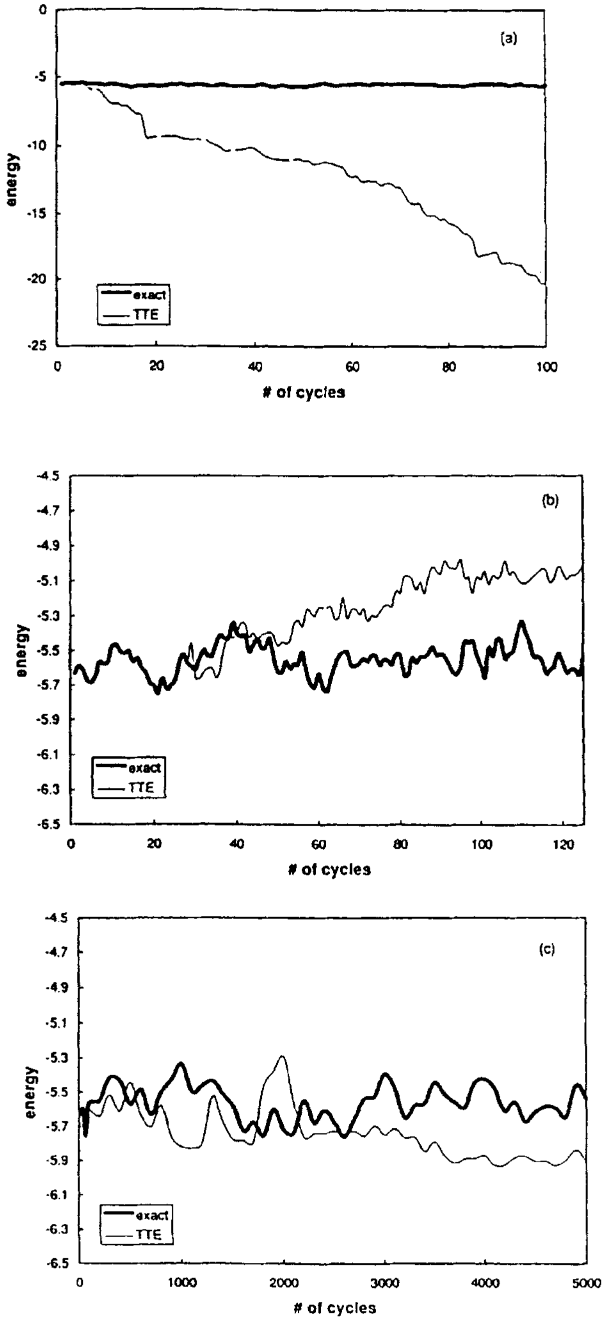

FIGURE 2 Propagation of truncation error, computed by applying the TTE method to a pure LJ fluid. Reduced configurational energy is plotted for a TTE series truncated using LA at: (a) 1st derivative; (b) 2nd derivative; (c) 3rd derivative. Simulation system parameters are identical to those in Figure 1.

Monte Carlo path. This manner in which this happens can be described as follows. First, the two trajectories remain in exact concordance for some period of time. Then, the configurational energies oscillate about one another for an additional period. Finally, the energy of the TTE simulation departs dramatically from that calculated in the exact simulation. The duration of each region lengthens with the inclusion of additional terms in the expansion. However, all orders of TTE eventually produce an energy that diverges from the exact result. Clearly a straightforward application of the TTE does not produce a viable simulation method.

A few simple tests clarify the extent of the problem. Simulations were again performed using both an exact enumeration of the energy and the TTE truncated at various orders and closed with the LA approximation. The allowed volume changes were determined using the exact energy change, but a hypothetical acceptance or rejection was also calculated using the TTE energy. A trajectory mismatch is defined as a Monte Carlo event in which the approximate calculation accepts a volume change and the exact calculation rejects it (or *vice versa*). Table I shows the average number of attempted volume changes at which the mismatch is first observed. In these calculations, one volume change was attempted following N attempted particle displacements and the average volume change acceptance was 51%. As expected, the higher the order of the expansion the longer the exact and approximate trajectories coincide. The results in Table I and Figure 2 suggest that the TTE algorithm becomes unstable because of an accumulation of trajectory mismatches. For a first-order truncation, we find that nearly every attempted volume change is incorrectly predicted. As the order of truncation is increased, the trajectory errors occur after increasingly larger number of cycles.

3.2. Updating

If we make an exact recalculation of the energy and the $\delta^{[n]}U_{\text{core}}$ after s attempted displacements, we find that the catastrophic behaviour shown in

TABLE I Trajectory mismatch

TTE n^{th}-derivative	*Mean number of attempted volume changes to mismatch*
1st	1.0
2nd	21.3
3rd	64.7
4th	75.4

Figure 2 disappears. Each such recalculation is computationally costly. Fortunately, the results in Table I show that for truncations at second order or higher, an appropriate value of s may be taken large enough to prove efficient while maintaining system stability. This resetting of the energy terms is similar to the *ad hoc* rescaling of velocities sometimes performed in traditional molecular dynamics simulations when potential truncation causes an increase in temperature [16]. Both types of adjustments are intended to correct for "trajectory errors" introduced by the approximations made.

It may appear fruitful to include many higher order terms in the expansion, but the expense of maintaining the additional $\delta^{[j]}U_{\text{core}}$ must also be considered and a profitable balance found. This is especially critical for molecular systems since the required expressions are more complex. For the Lennard-Jones system under study, the 3rd-order expansion appears optimal.

3.3. Accuracy

Figures 3–5 compare the density, pressure and configurational energy calculated from an exact Monte Carlo simulation and from the approximate TTE simulations for a range of acceptance fractions. All simulations were initiated from the same random number seed and from identical configurations. Results are shown for TTE simulations truncated at the second, third and fourth derivatives. The LA closure was employed, with updates every 20 cycles of particle displacements. In each run, the system was equilibrated for 2×10^6 configurations, followed by a run of 20×10^6 production configurations. All approximated trajectories give results that fall well within the uncertainty of the exact trajectory. We note that second through fourth-order schemes all appear to be about equally valid. This is understandable because a 20 cycle update frequency is within the mean interval to mismatch for all TTE truncations of order two and above. If a larger interval is used, the second-order result begins to show some statistically significant deviations from the exact calculation. Note, however, that very little is gained in increasing the interval, since updating once every 20 cycles adds only a few percent to the computational load.

3.4. Computational Savings

The cost of maintaining the overhead of the approximation in the displacement steps must be small compared to the gain made during an affine deformation if the algorithm is to be viable. Table II compares the execution times for various moves that contribute to the exact and approximated

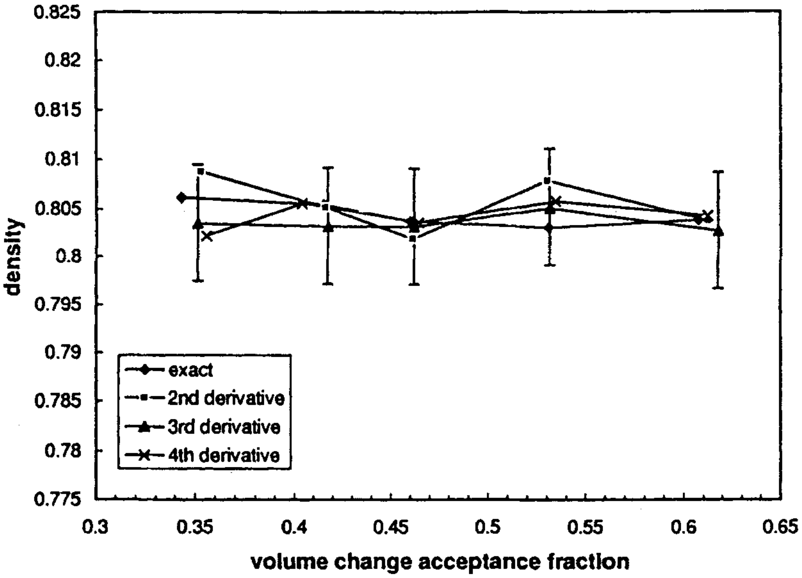

FIGURE 3 Comparison of the reduced densities calculated using the exact and TTE trajectories. LA truncation was used with an exact update every 20 particle displacement cycles for all the approximated trajectories. Standard deviation error bars are shown for the exact simulations. Simulation system parameters are same as in Figure 1.

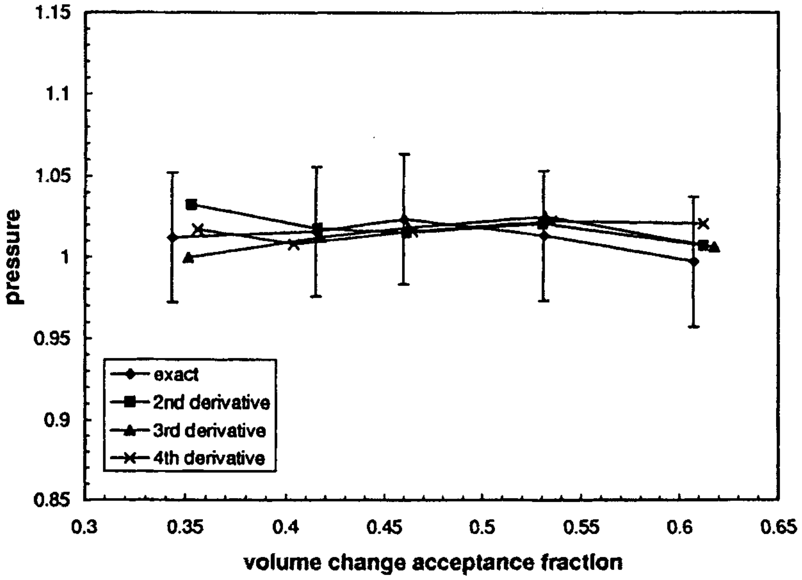

FIGURE 4 Comparison of reduced pressures calculated using the exact and the TTE trajectories. See Figure 3 for details.

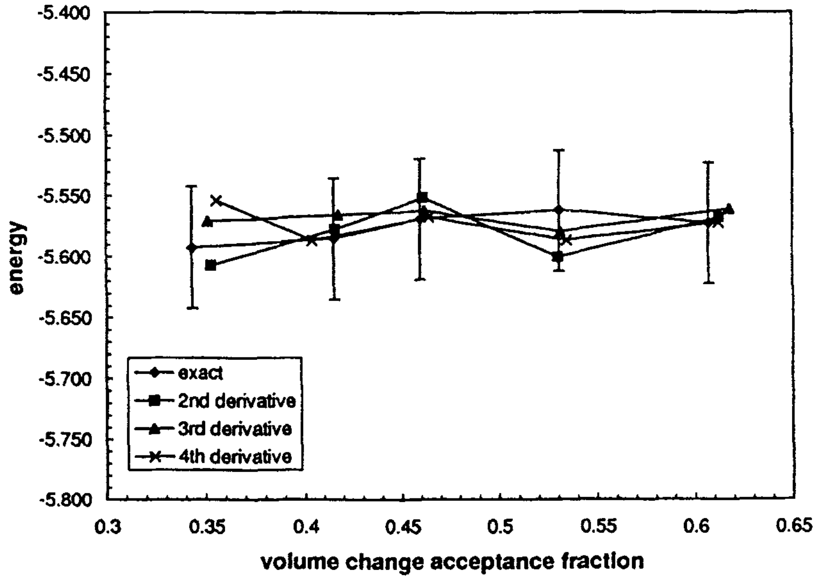

FIGURE 5 Comparison of reduced configurational energies calculated using the exact and the TTE trajectories. See Figure 3 for details.

trajectories. A series of simulations were conducted using 108 and 512 particles on a Sun Sparc 10 (model 30). The scaling trick was not used in the exact simulations in order to mimic a situation in which it would be inapplicable. Three types of moves were performed; particle displacements, volume changes and the insertion or deletion of a particle at constant density. The calculation of an energy change for constant density insertions and deletions is carried out in two steps. First the energy change for a constant volume insertion or deletion is calculated exactly. Then, a density-preserving volume change is carried out using the TTE equations. The sum of the two terms is the net energy change used in accepting or rejecting the event [15]. Table II shows the advantages and disadvantages introduced for each type of move. Using the TTE, moves requiring affine deformations (straight volume changes or insertions and deletions at constant density) execute about 50 times faster than the exact calculations. However, the price of maintaining and updating the $\delta^{[j]}U_{\text{core}}$ causes ordinary particle displacements to execute more slowly. Whether this cost is greater than the savings gained in the affine deformations depends on the relative frequency of the various Monte Carlo events.

TABLE II Simulation times for exact and TTE trajectories

			Exact Trajectory		*TTE Trajectory*	
# of particles	*Type of Move*	*# of attempts*	*CPU [sec]*	*attempts/ sec*	*CPU [sec]*	*attempts/ sec*
108	displacement	10,000	9.0	1111.1	14.2	704.2
512	displacement	10,000	49.4	202.4	127.3	78.6
108	volume	10,000	241.8	41.4	5.2	1,923
512	volume	10,000	5,478	1.8	92.1	108.6
108	insert/delete*	10,000	253.7	39.4	6.1	1,639
512	insert/delete*	10,000	5,588	1.8	93.4	107.1

* Insertion or deletion of a particle at constant density.

TABLE III Efficiency of truncated taylor expansion

Type of Cycles [*# of cycles*]	*# of particles*	*CPU [sec]* *Exact*	*CPU [sec]* *TTE*	*TTE efficiency*
conventional	$N = 108$	3,641	4,617	1.3 × slower
NPT*	$N = 512$	92,556	195,696	2.1 × slower
[3×10^4]				
Gibbs-Duhem	$N = 108$	954	73.0	13.1 × faster
integration	$N = 512$	95,843	3,768	25.4 × faster
[1×10^3]				

* One attempted volume change per N attempted particle moves.

Table III compares this mix in two extreme cases. The first is a conventional NPT simulation, with each cycle consisting of N attempted displacements followed by a single attempted volume change. The second is a Gibbs-Duhem simulation that also includes N attempted insertions or deletions at constant density. The table shows that the additional overhead of the TTE algorithm causes it to execute more slowly that an ordinary NPT algorithm, even with explicit enumeration of the energy changes at attempted volume changes. However, when volume changes are frequent, as in the Gibbs-Duhem or other schemes for simulating phase equilibria, the advantages of the TTE scheme become apparant.

4. CONCLUSIONS

A time saving method for affine deformations in constant-pressure Monte Carlo simulations has been introduced. The method involves a Taylor expansion of the current energy and the expansion coefficients simply depend on the energetics of the pre-deformed state. The approximation is applicable to any continuous, *n*-fold differentiable intermolecular potential. For molecular systems, two kinds of volume changes can be undertaken. One based on an affine deformation of the positions of all atoms in the molecule or one based on an affine deformation of the molecular centers. This allows very stiff or even rigid degrees of freedom to be removed from consideration when attempting volume changes

Two suitable closures of the TTE series were considered. Others are possible. Tests on a simple Lennard-Jones system reveal that the approximation algorithm is stable and accurate when infrequent exact updating of the expansion coefficients is included. Timing comparisons suggest that this algorithm is not exceptionally efficient for an ordinary NPT simulation because of the overhead involved in maintaining series terms. However, the proposed method appears very effective when affine deformations occur with frequency comparable to particle displacements. These include several popular methods for simulating phase equilibria.

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