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Taylor-Expansion Monte Carlo Simulations of Classical Fluids in the Canonical and Grand Canonical Ensemble

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In this article the Taylor-expansion method is introduced by which Monte Carlo (MC) simulations in the canonical ensemble can be speeded up significantly. Substantial gains in computational speed of 20–40% over conventional implementations of the MC technique are obtained over a wide range of densities in homogeneous bulk phases. The basic philosophy behind the Taylor-expansion method is a division of the neighborhood of each atom (or molecule) into three different spatial zones. Interactions between atoms belonging to each zone are treated at different levels of computational sophistication. For example, only interactions between atoms belonging to the primary zone immediately surrounding an atom are treated explicitly before and after displacement. The change in the configurational energy contribution from secondary-zone interactions is obtained from the first-order term of a Taylor expansion of the configurational energy in terms of the displacement vector **d**. Interactions with atoms in the tertiary zone adjacent to the secondary zone are neglected throughout. The Taylor-expansion method is not restricted to the canonical ensemble but may be employed to enhance computational efficiency of MC simulations in other ensembles as well. This is demonstrated for grand canonical ensemble MC simulations of an inhomogeneous fluid which can be performed essentially on a modern personal computer. © 1995 Academic Press, Inc.

1. INTRODUCTION

Basic problems in the (equilibrium) statistical–physical description of condensed matter concern the computation of macroscopic properties like internal energy U, pressure P, or magnetization M in terms of configurations of individual molecules [1–4]. Analytically this is a formidable task even if microscopically small representations of the system of interest are considered because the potential field acting on each molecule (due to interactions with others and, in general, external fields) is a complicated function of the spatial positions of all N molecules. Thus, additional simplifying and generally uncontrollable assumptions have to be introduced to compute any of the macroscopic quantities of interest [4].

However, with the advent of large scale computers some forty years ago the basic problem in statistical physics became tractable at least numerically by means of computer simulations. In a computer simulation the evolution of a microscopically small sample of the macroscopic system is determined by computing trajectories of each molecule for a microscopically small period of observation. An advantage of computer simulations is their treatment of the microscopic sample in essentially a first principles fashion; the only significant assumption concerns the choice of an interaction potential [5].

Due to the power of modern supercomputers (both *vector* and *parallel*) which can literally handle hundreds of millions of floating point operations (i.e., divisions, multiplications, etc.) per second, computer simulations are nowadays perceived as "a *third branch* complementary to the ... two traditional approaches" [6]: theory and experiment. In fact, computer simulations may be viewed as "virtual experiments" given the complexity of systems and physical phenomena currently investigated which range from, say, systems of geophysical importance [7] to interfacial phenomena [8].

A particular potent simulation technique is the so-called Monte Carlo (MC) [9] method by which properties of classical [10] and quantum systems [11] can be computed. However, this article is exclusively concerned with MC simulations of the former. A particular advantage of the MC method is its applicability to virtually any non-trivial statistical–physical ensemble (see Table I in [3, 12, 13]). The preference given to a specific ensemble is usually a matter of computational convenience. For example, diffusion-controlled processes may be studied under conditions where N molecules are confined to a fixed volume V at constant temperature T, thus suggesting the canonical ensemble. In inhomogeneous systems or investigations of phase equilibria, on the other hand, the grand canonical ensemble may be more appropriate in which (besides V and T) the chemical potential μ is a thermodynamic state variable.

In the context of many-particle systems (which are of concern here) the MC method generates numerically a sequence (i.e., a chain) of microstates (subject to constraints posed by the set of thermodynamic state variables) which (in the limit of sufficiently long chains) are distributed according to the probability density of the chosen ensemble. Generation of the chain is effected by a random walk in the (hyper)space of microstates known as Markov process. Based upon the theory of Markov processes [14] a new microstate n is realized at random from

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TABLE I

Technical Details of Canonical and Grand Canonical Ensemble Monte Carlo Simulations Employing the Taylor-Expansion Method

Ensemble for homogeneous bulk fluid	Canonical
Number of atoms	200
Starting configuration	random
Number of equilibration steps	1.5×10^5
Number of steps between subsequent averages	3N
Total number of MC steps	7.5×10^5–10^6
Radius of primary zone sphere r_1	$1.5\ \sigma$ (see Section II.3)
Thickness of secondary zone shell $\Delta r = r_2 - r_1$	$0.7\ \sigma$ (sphere, see text)
Radius of neighbor list r_N	$2.5\ \sigma$ (sphere, see text)
Potential cutoff (pressures and energies) r_c	$3.0\ \sigma$ (sphere, see text)
Ensemble for inhomogeneous fluid	Grand canonical
Starting configuration	random
Number of equlibration steps	3.5×10^5
Number of steps between subsequent averages	200
Total number of MC steps	4.0×10^6
Radius of primary zone sphere r_1	$1.8\ \sigma$
Thickness of secondary zone shell $\Delta r = r_2 - r_1$	$0.7\ \sigma$ (cylinder, see text)
Radius of neighbor list r_N	$2.7\ \sigma$ (cylinder, see text)
Potential cutoff (pressures and energies) r_c	$3.5\ \sigma$ (cylinder, see text)

its immediate predecessor m with a *relative* probability $\Pi = f_n/f_m$ where f_n and f_m are the *absolute* probability densities associated with m and n [10].

Several algorithms have been suggested in the past by which numerical realizations of Markov chains (henceforth referred to as *Markov chains* for simplicity) can be generated in MC simulations [10, 15, 16]. Presumably the most frequently employed algorithm in the context of classical (non-lattice) systems has been suggested in the seminal paper by Metropolis *et al.* [16]. Although the "classical" Metropolis algorithm was designed for the canonical ensemble, hybrid schemes for many other ensembles have been devised thereafter [12, 13, 17, 18].

As will be detailed below, the Metropolis algorithm (as well as other algorithms) involves in essence a computation of the *change* in configurational energy $\Delta\Phi_{mn} = \Phi_n - \Phi_m$ associated with the transition $m \rightarrow n$ which is the most time-consuming step in a MC simulation. It is the purpose of this article to describe a technique by which the computation of $\Delta\Phi_{mn}$ can be speeded up significantly. The heart of the new method is a division of the neighborhood of each atom or molecule into primary, secondary, and tertiary zones. The respective energy contributions $\Delta\Phi_{mn}^{(1)}$, $\Delta\Phi_{mn}^{(2)}$, and $\Delta\Phi_{mn}^{(3)}$ are treated at different levels of sophistication to achieve the desired savings of computer time.

Application of the new method to simulations in the canonical ensemble will be discussed subsequently in Section II. However, extension to other ensembles is straightforward. This is demonstrated in Section III for grand canonical ensemble MC simulations of an inhomogeneous model system currently employed in investigations of boundary lubrication phenomena [19]. It is shown in Section III that with the new MC method relevant research can be done essentially on a modern personal computer. However, the ideas outlined here are in no way restricted to this class of computers. In fact, vectorized and/or parallelized MC programs will equally benefit from the programming strategies discussed in this paper.

II. TAYLOR-EXPANSION MONTE CARLO SIMULATION IN THE CANONICAL ENSEMBLE

II.1. *The Concept of Conventional Monte Carlo Simulations*

In the canonical ensemble, where a thermodynamic state is uniquely determined by specifying N, V, and T [1–3] ensemble averages $\langle O \rangle_e$ can be expressed in the classical limit as

$$\begin{aligned}\langle O \rangle_e &= \frac{\int_{V^N} O(\mathbf{r}^N) \exp[-\beta\Phi(\mathbf{r}^N)]\, d\mathbf{r}^N}{\int_{V^N} \exp[-\beta\Phi(\mathbf{r}^N)]\, d\mathbf{r}^N} \\ &= \int_{V^N} O(\mathbf{r}^N) f(\mathbf{r}^N; N, V, T)\, d\mathbf{r}^N\end{aligned} \tag{1}$$

where $\beta = (k_B T)^{-1}$ (k_B Boltzmann's constant), $\mathbf{r}^N$ is an abbreviation for the set $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$ Φ is the configurational energy and $O(\mathbf{r}^N)$ is a microscopic representation of the macroscopic quantity of interest. For instance, if $O(\mathbf{r}^N) = \Phi(\mathbf{r}^N)$, $\langle O \rangle_e = U$ where U is the mean configurational energy. Equation (1) also defines the probability density (of microstates) in the canonical ensemble, $f(\mathbf{r}^N; N, V, T)$. Since the integrals in Eq. (1) are highly multidimensional even for a microscopically small system (and next to impossible to solve analytically without introducing additional assumptions) the MC method can be employed to solve Eq. (1) numerically. Therefore, Eq. (1) is discretized in configuration space as

$$\langle O \rangle_e = \lim_{M \to M_{\max}} \frac{\sum_{m=1}^{M} O(\mathbf{r}_m^N) \exp[-\beta\Phi(\mathbf{r}_m^N)]}{\sum_{m=1}^{M} \exp[-\beta\Phi(\mathbf{r}_m^N)]}. \tag{2}$$

Equation (2) is still not immediately amenable to numerical evaluation because $f(\mathbf{r}^N; N, V, T)$ is an extremely narrow and sharply peaked function in configuration hyperspace [1–3]. However, if configurations $\mathbf{r}_m^N$ are generated with a probability given by $f(\mathbf{r}^N; N, V, T)$, that is according to their *importance*, Eq. (2) can be rewritten as

$$\langle O \rangle_e = \lim_{M \to M_{\max}} \frac{1}{M} {\sum_{m=1}^{M}}' O(\mathbf{r}_m^N), \tag{3}$$

where the prime on the summation sign refers to a chain of configurations generated according to their *absolute* probability of occurrence given by $f(\mathbf{r}^N;\, N,\, V,\, T)$. This prescription is known as *importance sampling* [5, 10]. Unfortunately, $f(\mathbf{r}^N;\, N,\, V,\, T)$ is unknown because of the unknown denominator in Eq. (1) and Eq. (3) cannot be solved without further ado. However, if the chain of configurations is generated by a Markov process it can be shown that only *relative* probabilities $f_n/f_m = \exp]-\beta\{\Phi(\mathbf{r}_n^N) - \Phi(\mathbf{r}_m^N)\}] = \exp[-\beta\ \Delta\Phi_{mn}]$ are required to generate a new configuration from the immediately preceding one so that in a sufficiently long chain a particular configuration occurs with the desired probability *proportional to* $f(\mathbf{r}^N;\, N,\, V,\, T)$ [5, 6, 10, 14]. Thus, a realization of the transition $m \rightarrow n$ depends only on the associated change in configurational energy $\Delta\Phi_{mn}$ which is immediately computationally accessible.

One numerical recipe by which a Markov chain of configurations can be generated is the Metropolis algorithm [5, 16]. Consider for simplicity an atomic system. Then the *conventional* implementation of the "classical" Metropolis algorithm proceeds by picking sequentially (or at random) one of the N atoms, say i and computing its configurational energy

$$\Phi(\mathbf{r}_{i,m}) = \sum_{j \neq i}^{N} \varphi(r_{ij,m}), \tag{4}$$

where φ is the (pairwise additive) interaction potential, $r_{ij,m} = |\mathbf{r}_{i,m} - \mathbf{r}_{j,m}|$ and $\mathbf{r}_{i,m}$ denotes the position of atom i in configuration m. Equation (4) applies to a homogeneous bulk phase but can be extended easily to inhomogeneous phases in the presence of external fields (see Section III.3). The atom is next displaced by a small amount via

$$\mathbf{r}_{i,n} = \mathbf{r}_{i,m} + d_r(\mathbf{1} - 2\boldsymbol{\xi}) = \mathbf{r}_{i,m} + \mathbf{d}, \tag{5}$$

where $\mathbf{1} = (1, 1, 1)$ and $\boldsymbol{\xi}$ is a vector whose three components are pseudo-random numbers distributed uniformly on the interval $[0, 1]$. Equation (5) defines the displacement vector $\mathbf{d}$. $|\mathbf{d}| \ll \sigma$ because d_r is usually a small fraction of the atomic "diameter" σ (see Table IV) to allow roughly 60–70% of all attempted displacements to be accepted according to the Metropolis criterion

$$\Pi_1 = \begin{cases} 1 \quad ; & \Delta\Phi_{mn} \leq 0 \\ \exp[-\beta\, \Delta\Phi_{mn}]; & \Delta\Phi_{mn} > 0 \end{cases} \tag{6}$$

where $\Phi(\mathbf{r}_{i,n})$ is computed via an expression analogous to Eq. (4) (replacing, however, $\mathbf{r}_{i,m}$ by $\mathbf{r}_{i,n}$). If the configurational energy is lowered by moving i, the displacement is immediately accepted; if $\Delta\Phi_{mn} > 0$ the transition $m \rightarrow n$ is accepted with the desired probability if $\exp[-\beta\ \Delta\Phi_{mn}] > \xi$ where ξ is another pseudo-random number (on the interval $[0, 1]$ [5, 10]).

The 60–70% acceptance rate which favors smaller displacements is not a general condition on MC simulations. This applies to both the conventional and the Taylor-expansion method to be introduced below (see Section II.3, Table IV). In fact, there is considerable freedom in the adjustment of acceptance rates (i.e., the choice of d_r). In general, results obtained in MC can be expected to be reliable if d_r is chosen such that roughly 30–80% of all displacement attempts succeed. If d_r is too large or too small, on the other hand, then the system may (in a given number of MC steps) evolve insufficiently in configuration space because too few or too many displacement attempts are accepted. Under these circumstances the distribution of microstates cannot be expected to comply with $f(\mathbf{r}^N;\, N,\, V,\, T)$ and $\langle O \rangle_e$ will be in error.

II.2. *Computation of the Change in Configurational Energy*

From a numerical perspective the computer time required by a MC simulation is determined by two factors, namely the value of $M_{\max}$ (usually of the order of 10^5–10^7) and the upper summation limit in Eq. (4). The precise value of $M_{\max}$ depends largely on the precision sought for the quantity of prime interest $\langle O \rangle_e$. Depending on the physical nature of $\langle O \rangle_e$ various techniques have been designed to minimize $M_{\max}$. However, none of these is of any concern here and the interested reader is referred to Chaps. 4 and 6 in [5].

On the contrary, this paper focusses on minimizing the number of terms to be computed explicitly in evaluating Eq. (4) before and after i is displaced. Assuming φ to be short-range (e.g., Lennard–Jones-type potentials which are still employed in the overwhelming number of MC simulations of classical fluids), three different interaction zones can be defined to achieve this goal. Φ can then be expressed accordingly as a sum of three terms, namely

$$\Phi = \Phi_1 + \Phi_2 + \Phi_3, \tag{7}$$

where the arguments $\mathbf{r}_{i,m}$ and $\mathbf{r}_{i,n}$ have been dropped temporarily. Φ_1 is the configurational energy resulting from interactions between atom i and N_1 neighboring atoms $j^{(1)}(i)$ both located in a primary zone immediately surrounding i. Similarly, Φ_2 refers to interactions between i and N_2 atoms $j^{(2)}(i)$ in a secondary zone adjacent to the primary zone and, last but not least, Φ_3 refers to interactions between i and the remaining $N_3 = N - N_1 - N_2$ atoms $j^{(3)}(i)$ in an outermost tertiary zone which ends at the (virtual) boundaries of the simulation cell if periodic boundary conditions are employed [5].

Savings of computer time depend on the size of the three zones (i.e., the values of N_1, N_2, and N_3) and different levels of sophistication with which the three terms on the r.h.s. of Eq. (7) can be treated. Due to the symmetry of homogeneous bulk phases (cf. Section III.3) it seems natural to associate with the primary zone a sphere of radius r_1 centered on $\mathbf{r}_{i,m}$. The secondary zone is taken to be a spherical shell of thickness $\Delta r = r_2 - r_1$. If r_2 is sufficiently large one may assume

$$\Delta\Phi_3 = \Phi_3(\mathbf{r}_{i,n}) - \Phi_3(\mathbf{r}_{i,m}) \cong 0 \tag{8}$$

because $|\mathbf{d}|$ is small compared with typical distances r_{ij} corresponding to the tertiary-zone interactions so that φ (which is small for sufficiently large r_{ij} anyway) depends only negligibly on the change $\mathbf{r}_{i,m} \rightarrow \mathbf{r}_{i,n}$ (see Eq. (5)). Thus, N_3 interactions between i and $j^{(3)}(i)$ are neglected entirely during the course of the simulation. In the secondary zone

$$\Delta\Phi_2 = \Phi_2(\mathbf{r}_{i,n}) - \Phi_2(\mathbf{r}_{i,m}) \approx 0 \tag{9}$$

is not negligible but still small enough to permit an expansion of $\Phi_2(\mathbf{r}_{i,n})$ in a Taylor series

$$\Phi_2(\mathbf{r}_{i,n}) = \Phi_2(\mathbf{r}_{i,m}) + \left(\frac{\partial\Phi_2}{\partial\mathbf{r}_{i,m}}\right) \cdot \mathbf{d} + \cdots . \tag{10}$$

truncated after the second term. Inserting Eq. (10) into Eq. (9) yields

$$\Delta\Phi_2 \approx \left(\frac{\partial\Phi_2}{\partial\mathbf{r}_{i,m}}\right) \cdot \mathbf{d}. \tag{11}$$

The term $\partial\Phi_2/\partial\mathbf{r}_{i,m}$ has a simple physical interpretation. From Eq. (4) it is immediately obvious that

$$\left(\frac{\partial\Phi_2}{\partial\mathbf{r}_{i,m}}\right) = \sum_{j=1}^{N_2} \frac{d\varphi}{dr_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}} = -\sum_{j=1}^{N_2} \mathbf{F}_{ij} = -\mathbf{F}_2(\mathbf{r}_{i,m}), \tag{12}$$

where $\mathbf{F}_2$ is the *total* force exerted on atom i in the *initial* configuration m by the N_2 atoms in the secondary zone. For the primary zone no simplifying assumption can be made because φ may depend strongly on $|\mathbf{d}|$. Thus,

$$\Delta\Phi_1 = \Phi_1(\mathbf{r}_{i,n}) - \Phi_1(\mathbf{r}_{i,m}) = \sum_{j\neq i}^{N_1} [\varphi(\mathbf{r}_{ij,n}) - \varphi(\mathbf{r}_{ij,m})] \tag{13}$$

needs to be evaluated in both configurations $\mathbf{r}_m^N$ and $\mathbf{r}_n^N$ but involves only a small number of N_1 terms if r_1 can be kept sufficiently small. Using Eqs. (8), (11), and (13) $\Delta\Phi_{mn}$ can then be written as

$$\Delta\Phi_{mn} = \Phi_1(\mathbf{r}_{i,n}) - \Phi_1(\mathbf{r}_{i,m}) - \mathbf{F}_2(\mathbf{r}_{i,m}) \cdot \mathbf{d}. \tag{14}$$

It is immediately obvious that Eq. (14) will lead to a considerable reduction of the computational effort compared with the standard textbook evaluation of $\Delta\Phi_{mn}$ [5]. As Allen and Tildesley point out "the change in potential energy is calculated by computing the energy of atom i with *all the other atoms before and after the move*" (see p. 119 in [5], italics by the author). From the discussion in Section II.1 it then follows that the computation of $\Delta\Phi_{mn}$ involves $2N$ terms (see Eq. (4) where (at constant density N/V) N depends linearly on V). On the contrary, Eq. (14) requires in principle an evaluation of $2N_1 + N_2 < N$ such terms: N_1 and N_2 contributions need to be computed *before* atom i is moved but only N_1 contributions need to be considered explicitly *after* atom i is displaced by $\mathbf{d}$.

It is noteworthy that in a brute force implementation of both methods N pair distances r_{ij} have to be computed before atom i is displaced. In the Taylor-expansion method this is required because the assignment of each atom j to primary, secondary or tertiary zone is based upon r_{ij}. Since r_2 is small it is sensible to reduce the number of pair distances beforehand by means of the standard neighbor list technique first suggested by Verlet [20]. Its application to MC is described in detail by Allen and Tildesley (see p. 147 in [5]). In principle, atom j is considered to be a neighbor of i if it is located within a cutoff solid (usually a sphere of radius $r_N > r_2$ in a homogeneous bulk phase) centered on i. Thus, i has $N_N(i)$ neighbors where $N > N_N(i) > N_1 + N_2$.

In the new Taylor-expansion MC computation of $\Delta\Phi_{mn}$ can finally be split into five elementary steps. *Before* atom i is displaced

- $N_N(i)$ pair distances $r_{ij,m}$ are computed (if size and shape of the cutoff solid are the same this number is identical to the one in the conventional method).
- Based upon $r_{ij,m}$ a distinction is made between primary zone interactions $r_{ij,m}^{(1)}$, secondary zone interaction $r_{ij,m}^{(2)}$ and tertiary zone interactions $r_{ij,m}^{(3)}$.
- $\Phi_1(\mathbf{r}_{i,m})$ and $\mathbf{F}_2(\mathbf{r}_{i,m})$ are computed via Eqs. (4) and (12).
- A neighbor list for the N_1 atoms belonging to the primary zone is constructed based upon the criterion $r_{ij,m}^{(1)} \leq r_1$. This list is a one-dimensional integer array which contains in consecutive storage locations N_1 addresses of neighboring atoms $j'(i)$.

After atom i is displaced according to Eq. (5)

- the previously constructed primary zone neighbor list is used to find the N_1 relevant atoms $j'(i)$ to recompute $r_{ij,n}^{(1)}$ and to obtain $\Phi_1(\mathbf{r}_{i,n})$ (Note that the conventional method would still have to recompute the much larger number of $N_N(i)$ pair distances $r_{ij,n}$).

While the primary zone neighbor list is reconstructed for each atom i at every MC step, the full neighbor list needs to be updated only in certain intervals. A diffusion criterion similar to the one proposed by Fincham and Ralston [21] is employed in the updating procedure. Whenever an atom diffuses a distance $\Delta \geq r_N - r_2$ away from its original position at the previous update its neighborhood is reidentified and its list entry reconstructed. It is then checked which atom $j(i)$ is a *new* neighbor of i and its respective neighborhood information is updated, too.

II.3. *Results for a Homogeneous Bulk Phase*

To demonstrate the correctness of the Taylor-expansion MC method in the canonical ensemble the mean configurational energy in a homogeneous bulk phase

TABLE II

Results of Taylor-Expansion (TE) and Conventional (Conv.) Canonical Ensemble Monte Carlo Simulations of Homogeneous Lennard–Jones (12, 6) Bulk Fluids at Various Thermodynamic States

			$-U^*/N$			P^*		
			This work			This work		
State	ρ^*	T^*	TE	Conv.	Ref. [24]	TE	Conv.	Ref. [24]
1	0.8	2.74	4.283 ± 0.016	4.270 ± 0.018	4.281	7.903 ± 0.073	7.900 ± 0.063	7.900
2	0.7	2.74	3.915 ± 0.015	3.907 ± 0.014	3.902	4.992 ± 0.046	5.048 ± 0.045	5.065
3	0.55	2.74	3.222 ± 0.016	3.202 ± 0.015	3.207	2.405 ± 0.022	2.440 ± 0.023	2.471
4	0.4	2.74	2.366 ± 0.018	2.360 ± 0.019	2.371	1.299 ± 0.016	1.314 ± 0.018	1.314
5	0.7	1.35	4.668 ± 0.018	4.661 ± 0.019	4.684	1.086 ± 0.018	1.122 ± 0.017	1.102
6	0.5	1.35	3.386 ± 0.019	3.392 ± 0.020	3.372	0.194 ± 0.013	0.180 ± 0.012	0.205
7	0.4	1.35	2.740 ± 0.021	2.757 ± 0.020	2.747	0.145 ± 0.013	0.159 ± 0.014	0.147

Note. Specified by density $\rho^* = \rho\sigma^3 = N_\sigma^3/V$ ($N = 200$) and temperature $T^* = k_B T/\varepsilon$ (k_B, Boltzmann's constant; N, number of atoms; V, volume). Configurational energy $U^* = U/\varepsilon$ and pressure $P^* = P\sigma^3/\varepsilon$ are given in reduced units (indicated by an asterisk) ε and σ see Section II.3. Error estimates are obtained in a series of independent runs for each state point (see text).

$$U = \left\langle \sum_{i=1}^{N_c-1} \sum_{j=i+1}^{N_c} \varphi(r_{ij}) \right\rangle + U_c = \langle \Phi \rangle \tag{15a}$$

and the compressibility factor (i.e. pressure P) [22]

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{3N} \left\langle \sum_{i=1}^{N_c-1} \sum_{j=i+1}^{N_c} r_{ij} \frac{d\varphi}{dr_{ij}} \right\rangle + \frac{\beta P_c}{\rho} \tag{15b}$$

are computed where

$$\varphi(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \tag{16}$$

is the Lennard–Jones (12, 6) potential. The well depth $\varepsilon k_B^{-1} = 120\ K$ and the atomic "diameter" $\sigma = 3.4 \times 10^{-10}\ m$ are chosen to model approximately (fluid) argon. Angular brackets indicate an average over the Markov chain. Since averages are taken after an initial equilibration period and subsequent averaging events are separated by relatively large intervals of a fixed number of MC steps (see Table I) no neighbor list is employed to evaluate Eqs. (15a, 15b). However, a potential cutoff criterion is employed so that only $N_c(N_c - 1)/2$ terms corresponding to $r_{ij} < r_c (r_c > r_N, N_c > N_N(i)$, r_c potential cutoff radius, see Table I) are computed explicitly. Thus, corrections U_c and P_c corresponding to the neglected range of interactions $r_c \leq r_{ij} \leq \infty$ have to be added at the end of the simulation which can be computed analytically under the assumption of a random distribution of atoms j around i for $r_{ij} \geq r_c$ (see Eqs. (4-1) in [23] for explicit expressions).

Several thermodynamic states previously investigated by Hansen and Verlet [24] are considered in Table II for comparison. Regardless of temperature and density the excess internal energies computed by Taylor-expansion MC are in excellent agreement with Hansen and Verlet's results and data obtained here by the conventional method which are also included in Table II. Error estimates are obtained in a series of ten independent runs per thermodynamic state each starting from a random configuration but with a different seed for the pseudo-random number generator. Deviations between the three sets of results are smaller than 1% and no particular systematic tendency can be detected: For example, U/N for states 1, 2, 3, and 6 is slightly larger than the corresponding value from [24], while a slightly smaller value is observed for states 4, 5, and 7.

The corresponding pressures computed by the Taylor-expansion method deviate by less than 3% from the results of [24] as far as states 1–5 are concerned. P usually provides a more crucial test of accuracy in computer simulations. It is well known that P is generally more sensitive to numerical "inadequacies" (viz. coding errors, insufficient averaging etc.) and that accurate estimates are much harder to obtain (see Sect. 3-1 in [22]). A maximum deviation of 3% is yet to be expected under the conditions listed in Table I. However, a somewhat larger discrepancy of 5% (Taylor-expansion method) and 12% (conventional method) is observed for state 6. This is not surprising because P is very close to zero for these states. From Eqs. (15b) and (16) it is apparent that $P^* \approx 0$ (see Table II for a definition of reduced units indicated henceforth by *) is obtained if all atoms are separated by $r_{ij} \approx r_{\min}$ where $r^*_{\min} = r_{\min}/\sigma = 2^{1/6}$ is the interatomic separation where $\varphi(r_{ij})$ assumes its minimum and $d\varphi/dr_{ij}$ changes sign. Due to thermal fluctuations $P^* \approx 0$ results from summing (rather large) positive and negative terms $d\varphi/dr_{ij}$ which nearly cancel. Clearly, these conditions are numerically unfavourable and a much larger error for P at state 6 is inevitable. This is reflected by the statistical error associated with P: it turns out to be less than

TABLE III

The Dependence of Configurational Energy U^* and Pressure P^* on Primary (r_1) and Secondary Zone Potential cutoff (r_2) (in Units of σ) Employed in the Taylor-Expansion Monte Carlo Method at State Point 1 (See Table II)

r_1^*	r_2^*	$-U^*/N$	P^*
1.5	2.2	4.280	7.874
1.5	2.4	4.277	7.882
1.5	2.6	4.273	7.909
1.5	2.8	4.284	7.832
1.5	2.9	4.276	7.885
2.2	2.9	4.276	7.887

2% for states 1–5 and amounts to 7–9% for states 6 and 7 respectively. In view of this the almost perfect agreement between Hansen and Verlet's result for P and the one obtained here at state point 7 must be regarded somewhat fortuitous. If, on the other hand, P is reasonably large (states 1–5) partial cancellation of positive and negative terms is not a problem and the obtained numbers are much more reliable. The reader should note that the numerical problems just discussed are not characteristic of the MC method in general (conventional vs Taylor-expansion) but rather caused by the form of $\varphi(r_{ij})$. They are, therefore, expected to affect Hansen and Verlet's results the same way. In the absence of error estimates for the results of [24] it cannot be decided whether the slight deviations from them in Table II are significant. It is, however, emphasized that results obtained by the Taylor-expansion method and the conventional one in the present paper agree within mutual error bars regardless of the thermodynamic state considered.

While this agreement already indicates the correctness of the Taylor-expansion method, additional tests seem worthwhile. For instance, the relatively small value of r_2 (see Table I) may give rise to errors. At $r_2^* = 2.2$ $\varphi(r_{ij})$ has decayed only to 3.5% of its minimum value. Reliability of the Taylor-expansion results presented in Table II is therefore investigated by varying r_2 over the range $2.2 \leq r_2^* \leq 2.9$. Note that at $r_2^* = 2.9$ $\varphi(r_{ij})$ has decayed by roughly a factor of five compared with $r_2^* = 2.2$. Hence interactions between any pair of atoms separated by $r_{ij}^* \geq 2.9$ are truly negligible. However, the results compiled in Table III indicate that, in fact, the Taylor-expansion method yields already reliable results at the smaller cutoff $r_2^* = 2.2$ (based on error estimates in Table II for state 1). This observation is independent of the thermodynamic state considered.

Another possible source of error is associated with the present choice of $r_1^* = 1.5$. The value of r_1 obviously determines the contribution from interactions between atom i and its secondary-zone neighbors to $\Delta\Phi_{mn}$ in Eq. (14). The smaller r_1 the larger the possible error associated with truncating the Taylor expansion in Eq. (10) after the linear term. The influence of r_1 is therefore investigated for a representative case by enlarging its value from 1.5 to 2.2 while maintaining $r_2^* = 2.9$. Note that $\varphi(r_1^* = 1.5)/\varphi(r_1^* = 2.2) \cong 0.1$. The entry in Table III shows no evidence of a dependence of the Taylor-expansion results on r_1.

Similar to r_1 the value of d_r determines the accuracy of the approximation Eq. (10) because the magnitude of $\mathbf{F}_2 \cdot \mathbf{d}$ is controlled by it. To test the influence of d_r, results obtained by the Taylor-expansion method are compared with those from the conventional method in Table IV. Also listed are the respective acceptance rates. At state point 1 the acceptance rate determined for the Taylor-expansion simulation begins to differ from that characteristic of the conventional method for $d_r^* > 0.19$, whereas a somewhat larger value of 0.24 is determined for the lower-density state 4. Thus, the Taylor-expansion method can be expected to break down if d_r exceeds the values given above. Note that at state point 1 the acceptance rate at the breakdown threshold is already quite small so that the corresponding d_r is not very likely to be employed in an actual simulation for the reasons given at the end of Section II.1. It seems also noteworthy that even at the breakdown threshold the U/N and P obtained by the two methods still agree within error bars. Thus, truncation errors introduced by Eq. (10) are apparently rather small even if d_r is varied over a fairly wide range.

This is, perhaps, less surprising than it first seems if one keeps in mind that $\mathbf{F}_2$ in Eq. (12) reflects the local curvature of the configurational energy *hypersurface*. Although the force acting on the moved atom i due to any *one* of the remaining $(N_2 - 1)$ secondary atoms j may be substantial, $\mathbf{F}_2$ is the *resultant* of all $(N_2 - 1)$ such pairwise interactions. The total force on the moved atom due to secondary atoms is sufficiently small that the secondary contribution to the configurational energy shift can be reliably represented by a Taylor series truncated after the linear term. In other words, the predominant microstates are those for which the secondary atoms are so disposed spatially that the net force they exert on the moved atom is sufficiently small to render the Taylor series representation reliable. This is a key element of the new method.

The insensitivity of the Taylor-expansion method to variations of d_r within reasonable limits also indicates that the configurational energy hypersurface must be rather smooth which is expected for a system at thermodynamic equilibrium. This may also be concluded from the distribution of configurational energy $P(\Phi)$ which is a narrow gaussian provided configurational energy fluctuations are sufficiently small [1]. $P(\Phi)$ also reflects the distribution of microstates in configuration space. Thus, a comparison of $P(\Phi)$ computed by the Taylor-expansion method (under conditions listed in Table I) with the one obtained in a conventional MC simulation provides a further consistency test. The agreement between the two distributions in Fig. 1 reveals that the limiting distribution of microstates in configuration space generated by the Taylor-expansion method agrees with the one generated by the conventional method and therefore with $f(\mathbf{r}^N; N, V, T)$ (see Eq. (1)). Hence, in view of the various comparisons presented in this section it is concluded

TABLE IV

The Dependence of the Configurational Energy U^* and the Pressure P^* on the Size of the Displacement Parameter d_r (see Eq. (5))

		Acceptance ratio		$-U^*/N$		P^*	
State	d_r^*	TE	Conv.	TE	Conv.	TE	Conv.
1	0.071	0.703	0.701	4.287	4.288	7.845	7.937
1	0.076	0.683	0.687	4.278	4.267	7.885	7.896
1	0.088	0.640	0.638	4.286	4.288	7.854	7.847
1	0.126	0.511	0.516	4.273	4.270	7.920	7.922
1	0.189	0.349	0.354	4.300	4.278	7.804	7.918
1	0.252	0.238	0.246	4.345	4.282	7.600	7.845
4	0.079	0.854	0.853	2.373	2.374	1.308	1.301
4	0.099	0.821	0.824	2.371	2.369	1.287	1.297
4	0.119	0.781	0.791	2.366	2.358	1.286	1.305
4	0.159	0.724	0.721	2.382	2.367	1.291	1.329
4	0.198	0.661	0.669	2.386	2.378	1.278	1.298
4	0.238	0.604	0.618	2.393	2.378	1.274	1.298

Note. The results are obtained in Taylor-expansion (TE) and conventional (Conv.) canonical ensemble Monte Carlo simulations for a homogeneous Lennard–Jones (12, 6) bulk fluid. Two thermodynamic states specified in Table II are considered.

that the Taylor-expansion method yields reliable results under the conditions listed in Table I.

II.4. *CPU-Times*

Under conditions specified in Table I CPU-times for the new Taylor-expansion MC method are compared with those for the conventional method in Table V. Both methods employ a neighbor list technique briefly decribed in Section II.2. Table V reveals that the CPU-time is largely determined by density but only slightly affected by temperature. This is evident from Table V if one compares the ratio $(t_{\text{conv}} - t_{\text{TE}})/t_{\text{TE}}$ for state points 1 (0.366) and 4 (0.235) for which the density ratio is 2 whereas the corresponding ratio of temperatures is 1. The corresponding values for states 2 (0.368) and 5 (0.359) are much closer. Here the densities are the same but the temperature ratio is now 2.03.

The variations in absolute CPU-times reflect different numbers of atoms involved in each step of the computation. In the conventional method $2N_N$ pair distances r_{ij} have to be computed (*before* and *after* atom i is displaced). This is followed by an evaluation of $2N_2$ contributions to the configurational energies Φ_m and Φ_n. In the Taylor-expansion method one needs to compute only N_N pair distances r_{ij} *before* atom i is moved. With these N_1 terms contributing to Φ_1 and N_2 terms contributing to

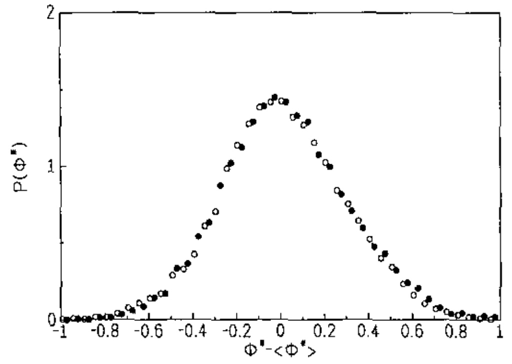

FIG. 1. The distribution of configurational energy $P(\Phi)$ as a function of the deviation of Φ from its ensemble average $\langle\Phi\rangle$ for thermodynamic state 1 (see Table II) obtained by Taylor-expansion (●) ($\langle\Phi^*\rangle = -4.287$) and conventional (○) ($\langle\Phi^*\rangle = -4.288$) canonical ensemble Monte Carlo simulations.

TABLE V

Comparison between CPU-Times per MC Step Obtained by the Taylor-Expansion (t_{TE}) and the Conventional Technique (t_{conv}) in the Canonical Ensemble (See Text)

State	$t_{\text{TE}}/10^{-3}$ s	$t_{\text{conv}}/10^{-3}$ s	$(t_{\text{conv}} - t_{\text{TE}})/t_{\text{TE}}$
1	2.644	3.611	0.366
2	2.443	3.343	0.368
3	2.287	2.961	0.295
4	2.075	2.563	0.235
5	2.409	3.273	0.359

Note. The CPU-times per Monte Carlo step are measured on a personal computer (COMPAQ ProLinea 4/50) consisting of an INTEL-486 (50 MHz) processor with mathematical coprocessor. For comparison only interactions $r_{ij} < r_2$ (see Table I) are included in the conventional technique. Thermodynamic states see Table II.

TABLE VI

The Average Number of Atoms Belonging to Primary ($\bar{N}_1$) and Secondary ($\bar{N}_2$) Zones (See Table I)

State	$\bar{N}_1$	$\bar{N}_2$	$\bar{N}_N$	d_r^*
1	10.98	24.04	51.67	0.069
2	9.60	20.67	45.19	0.072
3	7.45	15.95	35.37	0.114
4	5.31	11.63	25.60	0.127
5	9.80	20.52	45.32	0.066
6	7.03	14.36	32.32	0.103
7	5.63	11.52	25.93	0.127

Note. $\bar{N}_N$ is the average number of atoms in the neighbor list up to a radius r_N around a reference atom (see Table I). $d_r^* = d_r/\sigma$ is the maximum displacement of an atom during an MC step. See Table II for a definition of thermodynamic states.

$\mathbf{F}_2$ are evaluated. *After* atom i is displaced only N_1 pair distances contributing to Φ_1 have to be recomputed where the relevant atoms are identified via the primary zone neighbor list set up before. However, regardless of the particular thermodynamic state Table V shows that the Taylor-expansion method clearly surpasses the conventional MC method in terms of computational efficiency.

However, it seems surprising that the ratio $[2(N_N + N_1 + N_2)]/(N_N + 2N_1 + N_2)$ which reflects the relative computational effort required by both methods (and which should be proportional *in principle* to the ratio $(t_{\text{conv}} - t_{\text{TE}})/t_{\text{TE}}$ in Table V) is roughly constant as density changes (see Table VI) whereas $(t_{\text{conv}} - t_{\text{TE}})/t_{\text{TE}}$ varies between 0.235 (state 4) and 0.366 (state 1). However, a careful analysis reveals that the variation of the CPU-time ratio is caused by an increasing frequency of neighbor list updates as density decreases. Thus, the fraction of the total CPU-time consumed by the updates (which is the same for both methods) also increases as ρ becomes smaller thereby diminishing the "true" gain by the Taylor-expansion method somewhat. However, from a practical perspective it seems more sensible to compare both methods under operating conditions one would encounter in practice rather than presenting an analogue of the usual next-to-meaningless benchmark tests (which are always carried out under unrealistically ideal conditions) generally favored by the computer industry.

III. TAYLOR-EXPANSION MONTE CARLO SIMULATION IN THE GRAND CANONICAL ENSEMBLE

III.1. *General Remarks*

Diffusive steps which are the only event by which Markov chains are generated in the canonical ensemble are part of modified versions of the "classical" Metropolis algorithm applied to various other ensembles. The Taylor-expansion method described in Section II can therefore be employed in MC simulations for different ensembles as well. This will be demonstrated below for the grand canonical ensemble where a remarkable increase in computational efficiency can be achieved if the Taylor-expansion method is used.

In the grand canonical ensemble a thermodynamic state is uniquely specified by $\{\mu, V, T\}$ = const. [1–3]. Following standard textbook analyses [1–3] one can show that the analogue of Eq. (1) is given by (classical limit!)

$$\langle O \rangle_e = \frac{\sum_{N=0}^{\infty} (\Lambda^{-3N}/N!) \exp(\beta\mu N) \int_{V^N} O(\mathbf{r}^N) \exp[-\beta\Phi(\mathbf{r}^N)]\, d\mathbf{r}^N}{\sum_{N=0}^{\infty} (\Lambda^{-3N}/N!) \exp(\beta\mu N) \int_{V^N} \exp[-\beta\Phi(\mathbf{r}^N)]\, d\mathbf{r}^N} = \sum_{n=0}^{\infty} \int_{V^N} O(\mathbf{r}^N) f(\mathbf{r}^N; \mu, V, T)\, d\mathbf{r}^N \tag{17}$$

which defines the probability density $f(\mathbf{r}^{N(\mu)}; \mu, V, T)$ in the grand canonical ensemble. $\Lambda = (h^2/2\pi\beta m)^{1/2}$ (h Planck's constant, m atomic mass) is the thermal de Broglie wavelength.

A Markov chain of configurations is generated by a modified version of the "classical" Metropolis algorithm. The modified Metropolis algorithm proceeds as a pair of two steps where again the realization of each step depends only on the ratio f_l/f_k for old (k) and new trial configuration (l). In the first, purely diffusive step N is kept fixed and an atom is displaced according to Eq. (5). Since N = const. during the transition $k \to l$ it can easily be verified from Eq. (17) that the probability Π_1 is again given by Eq. (6) as in the canonical ensemble. In the second step the number of atoms is changed according to $\Delta N = N_l - N_k = \pm 1$. If $\Delta N = +1$ an atom enters the simulation cell at a randomly chosen position $\mathbf{r}_{i,l} = \xi V$ from a virtual reservoir of matter; if $\Delta N = -1$ an already existing atom is removed to that reservoir. The change in N is accepted (or rejected) on the basis of the *modified* Metropolis criterion

$$\Pi_2 = \begin{cases} 1 \quad ; & r_\pm > 0 \\ f_l/f_k = \exp(r_\pm); & r_\pm \leq 0, \end{cases} \tag{18}$$

where the argument of the pseudo-Boltzmann factor is given by

$$r_+ = B - \ln N_l - \beta\Phi_l(\mathbf{r}_{i,l}) \tag{19a}$$

for addition ($\Delta N = +1$) and by

$$r_- = -B + \ln N_k + \beta\Phi_k(\mathbf{r}_{i,k}) \tag{19b}$$

for removal ($\Delta N = -1$). The constant B is given by

$$B = \beta\mu - \ln(\Lambda^3/V) \tag{20}$$

in the notation of Adams [25]. If $r_\pm \leq 0$ addition or removal of an atom is accepted with the desired probability if $\exp(r_\pm) > \xi$ where ξ is a pseudo-random number distributed uniformly on the interval [0, 1]; if $\exp(r_\pm) < \xi$ the addition (removal) is finally rejected.

III.2. *Efficient Addition and Removal of Atoms*

The ratio of diffusive and addition (removal) steps is largely arbitrary. The only requirement is an equal probability of addition and removal *attempts* [26]. Thus, one can draw a random number ξ and try to remove an existing atom if $\xi < 0.5$ and add one if $\xi > 0.5$. If an atom is to be removed the choice of a particular one is arbitrary. In fact, one may select the one involved in the immediately preceding diffusive step. This will be demonstrated below in Section III.3. Depending on its outcome Φ_k in Eq. (19b) can be expressed as

$$\Phi_k = \Phi_m = \Phi_1(\mathbf{r}_{i,m}) + \Phi_2(\mathbf{r}_{i,m}) + \Phi_c; \qquad \text{unsuccessful displacement} \quad (21a)$$

$$\Phi_k = \Phi_n = \Phi_1(\mathbf{r}_{i,n}) + \Phi_2(\mathbf{r}_{i,m}) - \mathbf{F}_2(\mathbf{r}_{i,m}) \cdot \mathbf{d} + \Phi_c; \qquad \text{successful displacement} \quad (21b)$$

where Φ_c is a correction due to the finite potential cutoff r_2 and the change in density $\Delta\rho = -1/V$ associated with the removal attempt. Explicit analytical expressions for Φ_c and different cutoff solids are given in the Appendix of [27]. Using Eqs. (21) is convenient because the terms on the right hand side are already known from the attempted preceding displacement of i in the Taylor-expansion formalism except for

$$\Phi_2(\mathbf{r}_{i,m}) = \sum_{i \neq j}^{N_2} \varphi(r_{ij,m}) \qquad (21c)$$

However, only N_2 interactions have to be considered in addition to the already available information Φ_1, $\mathbf{F}_2$ and $\mathbf{d}$. Equation (21c) can be evaluated alongside with Φ_1 and $\mathbf{F}_2$ if the decision whether an addition or a removal attempt *is to follow* the displacement step is made *before* atom i is moved. Contrary to standard practice [26] where $N_1 + N_2$ interactions of a randomly selected atom (regardless of the one just moved) have to be computed (in addition to $N_N(i)$ distances r_{ij} if a neighbor list is employed) only N_2 such terms are required here. From Table VI it follows that $\overline{N}_2/(\overline{N}_1 + \overline{N}_2 + \overline{N}_N) \approx 0.3$ under the present conditions (see Table I). Thus, roughly the same CPU-time reduction can be expected for the removal step if Eqs. (21) are used.

Unfortunately, no similar scheme is possible if an atom is added because it has not been in the simulation cell, yet. Thus, its "history" prior to the addition attempt is unknown. As a consequence Φ_1, Φ_2, $\mathbf{F}_2$, and $\mathbf{d}$ are not available from a preceding diffusive step involving that atom. However, in a dense fluid a considerable amount of computer time can be saved by taking into consideration the ultimate failure of most addition attempts (ca. 90–98% depending on thermodynamic conditions). Due to a lack of sufficient space addition attempts will frequently put the new atom i "on top" of an already existing one j. The resulting Φ_l will then be positive and may be so large that it outweighs B and $\ln N_l$ in Eq. (19a) to such an extent that even the comparison of $\exp(r_+)(r_+ \ll 0)$ with ξ will not effect the final decision to reject the addition attempt.

Φ_l is computed in a loop running over r_{ij}. Thus, one may encounter r_{ij}'s early in the loop for which the corresponding $\varphi(r_{ij})$'s are too large so that none of the remaining, yet to be evaluated terms $\varphi(r_{ij})$ can eventually reduce Φ_l enough. Thus, $B - \ln N_l$ cannot compete with $-\beta\Phi_l$ which renders an addition attempt likely to be successful. In this case it would be wasteful (and presumably is in most MC programs) to continue the summation of $\varphi(r_{ij})$ until the loop concludes. On the contrary, it would be much more economic if a decision could be made at each step in the loop whether or not an addition attempt is eventually doomed to fail (and, therefore, whether or not the loop should continue). Such a decision is, in fact, possible on the basis of the *accumulated* configurational energy

$$\Phi_l(N') = \sum_{i \neq j}^{N'} \varphi(r_{ij}) + \Phi_c; \qquad N' = 1, \ldots, N, \qquad (22a)$$

where N' is the index of the innermost loop in an actual MC program. Based upon $\Phi_l(N')$ a quantity

$$r_+(N') = B - \ln N_l - \beta[\Phi_l(N') - \varepsilon(N' - N)]; \qquad N' = 1, \ldots, N \qquad (22b)$$

can be defined which in the limit $N = N'$ (i.e., when the loop concludes) goes over to r_+ in Eq. (19a). The fourth term on the r.h.s. of Eq. (22b) *assumes* the remaining (yet to be computed) r_{ij}'s to equal $r_{\min}$ which would be energetically most favourable because $\varphi(r_{\min}) = -\varepsilon$. Any addition attempt is certain to fail eventually if at any step in the loop $r_+(N')$ falls short of some threshold. The threshold value is largely arbitrary but should be small enough to ensure that an addition attempt is very unlikely even if the Metropolis criterion (comparison between $\exp(r_+)$ and ξ) would be applied. For all practical purposes -20 is found to be a reasonably small value for the threshold. Thus, in the actual MC program accumulation of $\Phi_l(N')$ is terminated before the full loop concludes if $r_+(N') < -20$ which is the case in, say roughly 60–80% of all attempted additions in a dense fluid depending on its thermodynamic state.

III.3. *Results*

To demonstrate the correctness of the MC procedure in the grand canonical ensemble described in the previous section, simulations are performed for an inhomogeneous fluid. The system consists of a molecularly thin monatomic film between two plane-parallel molecularly smooth rigid surfaces (i.e., walls) separated by a distance $s_z = |z^{(1)} - z^{(2)}|$ where $z^{(1)}$ and $z^{(2)}$ represent positions of lower and upper wall respectively. As before (see Section II.3) interactions between film atoms are described by the Lennard–Jones potential given in Eq. (16). However, since the walls represent an external field expressions for the configurational energy have to be modified according to

$$\Phi = \sum_{i \neq j}^{N} \varphi(r_{ij}) + \sum_{k=1}^{2} \psi^{(k)}(z_i) = \Phi_{\mathrm{FF}} + \Phi_{\mathrm{FW}} \tag{23a}$$

where the film–wall potential is given by [27]

$$\psi^{(k)}(z_i) = 2\pi\varepsilon d_s \left[\frac{2}{5}\left(\frac{\sigma}{z_i - z^{(k)}}\right)^{10} - \left(\frac{\sigma}{z_i - z^{(k)}}\right)^{4}\right]. \tag{23b}$$

In Eq. (23b) $d_s = N_s\sigma^2/s^2 = 0.7827$ ($s^* = 7.9925$, side length of the square simulation cell in the x, y plane) is the surface density and z_i is the z-coordinate of a film atom. ε and σ are taken identical for film–film and film–wall interactions for which the values given in Section II.3 are employed.

Quantities computed are the mean configurational energy

$$U = U_{\mathrm{FF}} + U_{\mathrm{FW}} \tag{24a}$$

where the first term on the r.h.s. is identical with U in Eq. (15a) and

$$U_{\mathrm{FW}} = \left\langle \sum_{k=1}^{2} \sum_{i=1}^{N} \psi^{(k)}(z_i) \right\rangle. \tag{24b}$$

Because of the cylindrical symmetry of the film (on account of the presence of the walls) a cutoff cylinder instead of a sphere is used here. Thus, U_c (see Eq. (15a)) is of a different form which can be found in the Appendix of [27] (Eq. (A6)). In addition, the normal component P_{N} of the pressure tensor **P** is computed. P_{N} may be written as

$$P_{\mathrm{N}} = P_{\mathrm{N,FF}} + P_{\mathrm{N,FW}} \tag{25}$$

The film–film contribution is computed by analogy with Eq. (15b) as

$$\frac{\beta P_{\mathrm{N,FF}}}{\rho} = 1 - \frac{\beta}{\langle N \rangle} \left\langle \sum_{i=1}^{N_c - 1} \sum_{j=i+1}^{N_c} \frac{z_{ij}}{r_{ij}} \frac{d\varphi}{dr_{ij}} \right\rangle + \frac{\beta P_{\mathrm{N,c}}^{\mathrm{FF}}}{\rho} \tag{26a}$$

where $\langle N \rangle$ is the average number of film atoms and $\rho = \langle N \rangle / V$. An explicit expression for $P_{\mathrm{N,c}}^{\mathrm{FF}}$ is given in the Appendix of [28]. Similarly,

$$\frac{\beta P_{\mathrm{N,FW}}}{\rho} = -\frac{\beta}{\langle N \rangle} \left\langle \sum_{k=1}^{2} \sum_{i=1}^{N} (z_i - z^{(k)}) \frac{d\psi^{(k)}}{dz_i} \right\rangle. \tag{26b}$$

The MC calculations proceed in a slightly different manner here because a cutoff cylinder of infinite height centered on z_i is employed. Thus, in the Taylor-expansion method r_2 (see Section II.2) is taken to be the radius of a cylindrical shell in the x, y plane. r_1, on the other hand, is still the radius of a sphere inscribed into the cylinder where $\Delta r^* = r_2^* - r_1^* = 0.5$ as before in the bulk phase (see Table I). The correction Φ_c in Eqs. (21a), (21b), and (22b) is also computed for the cutoff cylinder and an explicit expression is given in Eq. (A7) of [27].

The results in Table VII indicate excellent agreement between the present method and results obtained earlier [27] by the conventional method. As before for the bulk phase the deviations between various contributions to the mean configurational energy are smaller than 1%. Particularly noteworthy is the good agreement between the normal pressure contributions $P_{\mathrm{N,FF}}$ and $P_{\mathrm{N,FW}}$ from both methods. This is significant because P_{N} changes sign and varies more strongly with the thermodynamic state compared with U. However, agreement is somewhat less satisfactory for states where P_{N} is a sum of comparably large numbers of opposite sign (state 5). The same comments made earlier in Section II.3 concerning partial cancellation in sums of comparably large positive and negative numbers apply here too if $P_{\mathrm{N,FF}} \approxeq -P_{\mathrm{N,FW}}$. Thus, on the whole Table VII illustrates the correctness of the modified grand canonical ensemble method described in Section III.2.

This may be further demonstrated by considering distributions of configurational energy P(Φ) and the number of atoms $P(N)$ determined by the present method and the one described in [25, 27], which is distinct from the former in that the conventional method (see Section II.1) is applied to the diffusive substep and that atoms subjected to removal attempts are picked at random. By analogy with the canonical ensemble (see Section II.3) $P(\Phi)$ and $P(N)$ reflect the distribution of microstates in configuration space according to $f(\mathbf{r}^{N(\mu)}; \mu, V, T)$ (see Eq. (17)). As can be seen in Fig. 2 $P(\Phi)$ and $P(N)$ obtained by the two grand canonical ensemble MC implementations are in excellent agreement with each other. Similar agreement is found for the other thermodynamic state. The adequacy of the more efficient scheme is thus further substantiated.

However, one might suspect that a subtle unphysical correlation is introduced by the present algorithm if the atom subject to a prior displacement attempt is subjected immediately to a removal attempt, even though the outcome of the removal attempt is not directly determined by the outcome of the displacement attempt. Clearly, if the atom to be removed is picked at random [25, 27] there will be a certain (average) number of MC steps between removal and the preceding displacement attempt. Thus, the environment of an atom selected later for removal may have changed in the meantime because of successful displacement, removal or addition of neighboring atoms,

TABLE VII

Grand Canonical Ensemble Monte Carlo Simulations of an Inhomogeneous Fluid (See Text)

		$\langle N\rangle$		$-U^*_{FF}/\langle N\rangle$		$-U^*_{FW}/\langle N\rangle$		P^*_N		$P^*_{N,FF}$		$P^*_{N,FW}$		
s^*_z	$-\mu^*$	This work	Ref. [27][a]	This work	Ref. [27]	This work	Ref. [27][b]	This work	Ref. [27]	This work	Ref. [27]	This work	Ref. [27]	$t/10^{-3}$ s
2.15	9.23	50.4	50	2.141	2.109	5.076	5.074	−0.759	−0.76	0.419	0.42	−1.178	−1.18	1.320
2.20	9.26	50.3	50	2.103	2.101	4.860	4.860	−1.106	−1.11	0.425	0.42	−1.531	−1.53	1.325
2.30	9.30	50.6	51	2.128	2.117	4.390	4.408	−1.111	−1.20	0.459	0.46	−1.570	−1.65	1.344
2.40	9.34	51.8	52	2.149	2.145	3.967	3.974	−0.714	−0.73	0.536	0.54	−1.250	−1.26	1.381
2.50	9.39	54.4	54	2.209	2.196	3.598	3.600	0.179	0.20	0.716	0.73	−0.551	−0.53	1.457
2.60	9.42	62.2	62	2.454	2.421	3.265	3.278	2.145	2.04	1.287	1.26	0.858	0.79	1.657
2.70	9.46	79.8	80	3.113	3.106	3.017	3.002	5.650	5.70	2.459	2.48	3.191	3.22	2.105
2.80	9.49	91.5	92	3.548	3.555	3.003	3.004	5.164	5.25	2.382	2.42	2.782	2.84	2.416
3.00	9.56	98.1	99	3.685	3.703	2.914	2.920	1.286	1.30	1.097	1.11	0.189	0.19	2.618

Note. Thermodynamic states are specified in terms of $s^* = 7.9925$; s^*_z, μ^*, and $T^* = 1.00$. Results obtained by the method described in Section III.2 are compared with those obtained by the conventional method (see text) in [27]. For a definition of reduced units of energies (columns 2, 4, 5) and pressures (columns 6, 7, 8) see Table II. The CPU-times per Monte Carlo step (column 9) are measured on a personal computer (COMPAQ ProLinea 4/50) consisting of a 50 MHz INTEL-486 processor with mathematical coprocessor.

[a] Rounded to the nearest integer.

[b] Because of a coding error in an earlier MC program results presented in Table VII of [27] are too small by a factor of 2. This error did, however, not affect the Markov chain generation in [27].

whereas this is prevented by the scheme proposed in Section III.2. To test the latter for spurious correlations between displacement and removal, one may compute the fraction of atoms removed successfully after they had been moved successfully (x_s) and unsuccessfully ($x_u = 1 - x_s$) in a preceding displacement attempt (Note that the fraction of atoms involved in an unsuccessful removal attempt following successful displacement equals the acceptance rate of the diffusive substep). These numbers are compared with those obtained within the scheme where atoms are picked at random [25, 27]. If atoms are picked at random any deviation of x_s from 0.5 reflects physically significant correlations between removal and displacement attempts whereas significant deviations of x_s between the scheme proposed in Section III.2 and the one employed in [25, 27] would cast doubt on the validity of the former. For the two representative states considered in Fig. 2 $x_s = 0.462$ ($s^*_z = 2.20$, $\mu^* = -9.26$), 0.441 ($s^*_z = 2.95$, $\mu^* = -9.50$) are obtained by the scheme proposed in Section III.2 while the corresponding figures obtained by picking atoms at random are 0.475 and 0.439 respectively which are still close to 0.5 and deviate only insignificantly. Perhaps more striking are the values $x_s = 0.695$ (present scheme), 0.701 (random selection, [25, 27]) determined for the thermodynamic state $\mu^* = -16.90$, $s^*_z = 4.5$, $s^* = 7.9925$, $T^* = 1.60$ which suggests that, depending on the state, physically significant correlations between displacement and removal indeed exist, regardless of methodology. The latter state exhibits considerable density fluctuations, as reflected by an acceptance rate of about 11% for removal or addition of atoms, which is quite high. This should perhaps not be surprising, however, because the thermodynamic state of the bulk fluid at the same temperature and chemical potential is sufficiently close to the critical point; one would therefore expect the confined fluid to exhibit features of the near-critical regime of thermodynamic states also [29]. In any case, the agreement between the values of x_s reported renders unlikely the possibility of spurious correlations introduced by the grand canonical ensemble MC scheme proposed in Section III.2. This notion is corroborated by the plots shown in Fig. 2.

Its usefulness is underlined by the CPU-times per MC step listed in column 9 of Table VII. As it turns out between 1.5 and 3.0 h of CPU-time on a modern personal computer are required to study a complex system which is still of great relevance to actual research involving molecularly thin confined films [19]. These times are obtained by using a neighbor list as before (see Section II). In addition a technique described by Allen and Tildesley (p. 129 in [5]) is employed to handle the varying length of the neighbor list on account of addition and removal of atoms.

IV. DISCUSSION AND CONCLUSIONS

In this article an efficient new recipe for Monte Carlo simulations is presented. In these simulations a sequence of configurations may be generated by the Metropolis algorithm the heart of which are random displacements of atoms or molecules. Displacements are accepted (or rejected) on the basis of the associated change in configurational energy. Efficiency of the new method is achieved by treating interactions between atoms at different levels of computational sophistication. For a short-range potential three levels associated with different (spatial) zones can be defined. Interactions between a reference atom i and its N_1 neighbors $j^{(1)}(i)$ located in a primary zone immediately surrounding i are explicitly evaluated *before* and *after* i is displaced. The change in configurational energy due to interactions between i and N_2 neighbors $j^{(2)}(i)$ belonging to the adjacent secondary zone are included by a Taylor expansion of the relevant contribution to the configurational energy in terms of the small displacement $\mathbf{d}$ of i. Thus, these N_2 contributions are computed only once *before* i is moved from its old position $\mathbf{r}_i$ to $\mathbf{r}_i + \mathbf{d}$. Interactions between i and neighbors $j^{(3)}(i)$

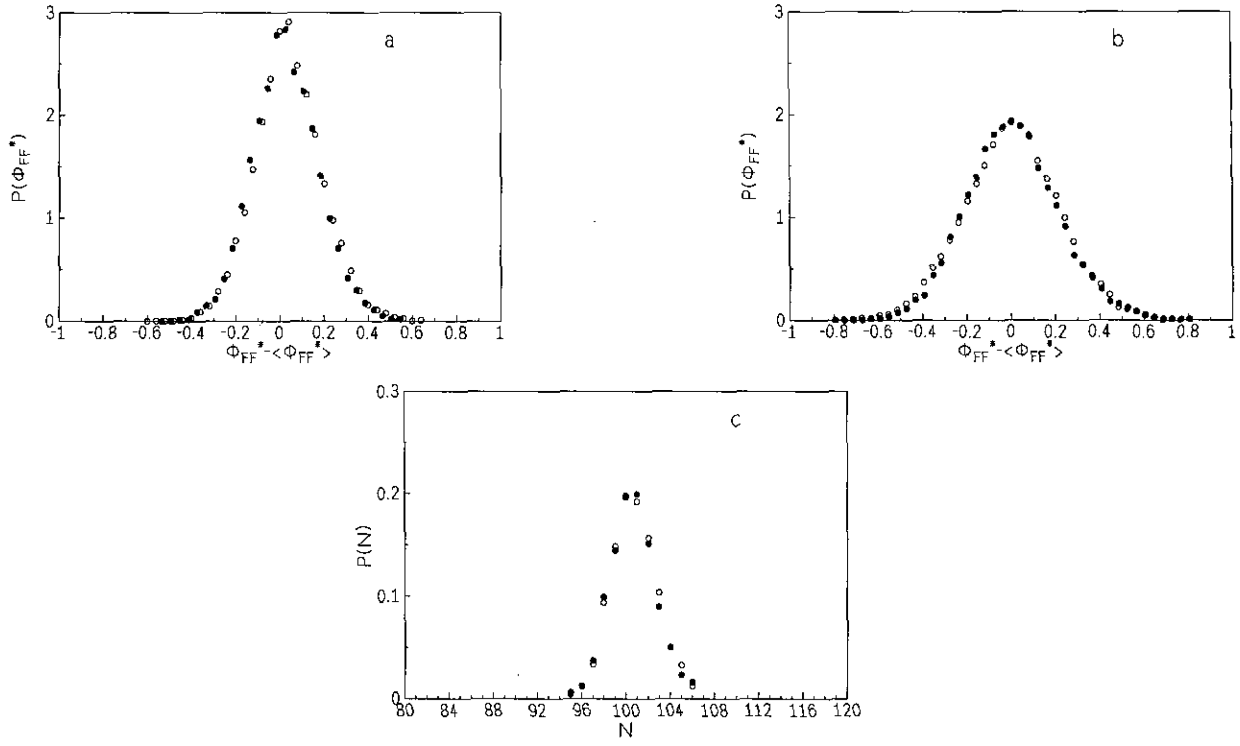

FIG. 2. (a) The distribution of the film–film contribution to the configurational energy $P(\Phi_{FF})$ as a function of the deviation of Φ_{FF} from its ensemble average $\langle\Phi_{FF}\rangle$ (see Eq. (23a)) at $s^* = 11.3031$, $s_\zeta^* = 2.20$, $T^* = 1.00$, $\mu^* = -9.26$ (see Tables I, VII). The curves are obtained by Taylor-expansion Monte Carlo in the grand canonical ensemble (see Section III.2) (○) ($\langle\Phi_{FF}^*\rangle = -2.103$) and the implementation described in [25, 27] (●) ($\langle\Phi_{FF}^*\rangle = -2.101$) in which atoms are subjected to removal attempts randomly rather than sequentially (see text). (b) The same as (a) but $s^* = 7.9925$, $s_\zeta^* = 2.95$, $T^* = 1.00$, $\mu^* = -9.50$; Taylor-expansion Monte Carlo (○) ($\langle\Phi_{FF}^*\rangle = -3.701$), implementation described in [25, 27] (●) ($\langle\Phi_{FF}^*\rangle = -3.695$). Note the much broader distribution due to less severe confinement of the film. (c) The distribution of the number of atoms $P(N)$ accomodated by the film. The curves shown pertain to the thermodynamic state defined in (b). The corresponding curves for the thermodynamic state in (a) fall essentially on top of the present ones and are therefore not shown.

located in a tertiary zone surrounding the secondary one are completely ignored because for sufficiently small $|\mathbf{d}|$ the associated change in configurational energy is negligible. Measurements reveal that, depending on density, standard textbook implementations of the Metropolis algorithm require between 20–40% more CPU-time than the Taylor-expansion method.

The Taylor-expansion method is similar in spirit to the multiple time-step method in molecular dynamics (MD) simulations [30] of fluids with short-range interactions. An analogous division into primary and secondary zones is made and only forces between atoms belonging to the primary zone are calculated at every time-step. Secondary forces are updated only in intervals of a certain number of MD steps. In the meantime the change of secondary forces is estimated by employing a Taylor-expansion *ansatz*. This expansion includes up to third-order derivatives of the secondary forces and is found to provide a reasonably accurate description of their time evolution [30].

The multiple time-step MD technique differs in two significant aspects from the Taylor-expansion MC method presented here. First, forces in multiple time-step MD are expanded in *time* whereas in Taylor-expansion MC the energy field acting on an atom is expanded in terms of that atom's *displacement* **d**. Second, the multiple time-step technique yields much larger savings of computer time (typically a factor of 3–5 [30]) compared with the Taylor-expansion method (see Table V). This seems to be caused by at least two effects. In the multiple time-step method time derivatives of the forces can be expressed in terms of spatial derivatives of the interaction potential and time derivatives of atomic positions both of which are readily available in MD [30]. For example, the first-order derivative of the potential (i.e., the force) must be calculated anyway and higher-order derivatives can be obtained from it by simple multiplications. Forces are also required for the N_2 atoms of the secondary zone in Taylor-expansion MC. However, forces are not part of the conventional Metropolis algorithm. The relative effort in computing a vector quantity like $\mathbf{F}_2$ may to some extent counterbalance the gain from avoiding a double calculation of the scalar Φ up to r_2. More importantly, however, computation of the force matrix in MD involves arithmetic operations of the order of N^2 whereas in MC the computation of Φ requires operations of N. Thus, if the explicit computation of a large fraction of interactions can be neglected in MD for a number of time-steps the net gain has to be expected to grow quadratically, too. In Taylor-expansion MC, on the other hand, CPU-time savings are expected to grow only linearly and are predominantly achieved during the displacement step, that is they are effective only in 50% of the total number of MC steps (counting separately the computation of the configurational energy *before* and *after* atom i is displaced).

Nevertheless, Taylor-expansion MC is shown to be an efficient and useful new method in the simulation of classical condensed phases. This is exemplified in the article by employing the Taylor-expansion method in grand canonical ensemble MC simulations of inhomogeneous films. It is then possible to run a simulation on a modern personal computer within only a few hours even for systems which have previously been simulated exclusively on a vector computer. However, this will only be true if sufficiently ''simple'' model systems are considered. Fortunately, the Taylor-expansion technique is not restricted to scalar processors but has recently been incorporated into a fully vectorized MC program optimized for a CRAY YMP/832 [19]. The measured CPU-times on the CRAY are smaller by roughly a factor of 10–20 compared with the ones reported in Table V. Parallelization of the method should also be straightforward. It should also be noted that the Taylor-expansion method can be applied to MC simulations in virtually any statistical-physical ensemble because a diffusive step (as in the canonical ensemble) is always involved.

Finally, the Taylor-expansion method should also be applicable to molecular fluids where φ will be implicitly or explicitly angle-dependent to take into account the orientation dependence of the intermolecular interactions. Application to site–site potentials (which are implicitly angle-dependent) should be straightforward and no modifications of the method as described here are expected. For explicitly angle-dependent models dependence of Φ on, say polar and azimuthal angles may require more (and, perhaps, higher-order) terms in the Taylor expansion. In this case usefulness of the method remains to be shown.

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