Hypervolumes in microcanonical Monte Carlo

Fernando M.S. Silva Fernandes a,*, J.P. Prates Ramalho b

a Department of Chemistry and CECUL, University of Lisboa,
Rua Ernesto de Vasconcelos, Bloco C1, Piso 5, 1700 Lisboa, Portugal
b Department of Chemistry, University of Évora, Rua Romão Ramalho, 59, 7000 Évora, Portugal

Received 20 February 1995; revised 9 May 1995
Hypervolumes in microcanonical Monte Carlo

Fernando M.S. Silva Fernandes a,*, J.P. Prates Ramalho b

a Department of Chemistry and CECUL, University of Lisboa, Rua Ernesto de Vasconcelos, Bloco C1, Piso 5, 1700 Lisboa, Portugal
b Department of Chemistry, University of Évora, Rua Romão Ramalho, 59, 7000 Évora, Portugal

Received 20 February 1995; revised 9 May 1995

Abstract

A Monte Carlo method to perform microcanonical simulations by sampling the configurational and momenta spaces is presented. The technique was inspired by the method of hypervolumes for calculating the entropy in a microcanonical ensemble. Although this method is strictly proven in the thermodynamic limit, the hypervolume Monte Carlo (HVMC) algorithm, presented in this article, works well with a relatively small number of particles. In contrast to other algorithms for microcanonical Monte Carlo simulations, the HVMC method does not involve previous integrations over the momenta space or demons. Therefore, it can be used with any form of Hamiltonian. Thermal and structural properties for the Lennard-Jones system obtained by NVE molecular dynamics are compared with results from the HVMC method. The agreement is excellent. Additionally, the method provides the speed distribution functions of the system which are, also, in excellent agreement with the results from molecular dynamics. A discussion of the HVMC method in the context of the statistical mechanical theory of the microcanonical ensemble is presented.

1. Introduction

The Monte Carlo method introduced by Metropolis et al. [1] to sample the canonical ensemble has been extended to other ensembles such as NPT [2,3] and $μVT$ [3,4] ensembles by a relatively straightforward introduction of the appropriate Boltzmann factors in the Metropolis algorithm. The constraint of constant total energy, $E$, in a microcanonical ensemble involves a $δ$-probability density function:

$$ f(N, V, E) = δ(H(Γ) - E) \times \left( \int dΓ δ(H(Γ) - E) \right)^{-1}, $$

where $δ$ is the Dirac delta function, $H$ is the Hamiltonian and $Γ ≡ (r_1, ..., r_{3N}, p_1, ..., p_{3N})$ is the $6N$-dimensional phase vector of a system with $N$ atoms. Such a mathematical form is not amenable to numerical work. Thus, its introduction in the usual Monte Carlo procedure is not so straightforward.

The first microcanonical sampling method was proposed by Bunker [5]. In general terms it is based on the following arguments [6]. A microcanonical ensemble sample consists of a finite set of coordinates and weights $\{Γ_i, w(Γ_i)\}$ such that for any dynamical property $A(Γ)$:

$$ ⟨A⟩_{N, E} = \int dΓ A(Γ) f(N, V, E) \approx \sum_{i=1}^{L} A(Γ_i) w(Γ_i). $$

* To whom correspondence should be addressed.
In generating the sample it is understood, of course, that a nonzero weighting function $w(I')$ must be found.

If the coordinate transformation

$$r_1, \ldots, r_{3N} \rightarrow r_1, \ldots, r_{3N-1}, E,$$  

(3)

with the Jacobian

$$J = \frac{\partial p_{3N}}{\partial E} = \frac{m_{3N}}{p_{3N}}, \quad p_{3N} \geq 0$$  

(4)

is made, Eq. (2) can be rewritten as

$$\langle A \rangle_E = \frac{\int d^3 r_1, \ldots, d^3 r_{3N-1} |p_{3N}|^{-1}}{2 \int d^3 r_1, \ldots, d^3 r_{3N-1}} \times \left[ A(r_1, \ldots, +|p_{3N}|) + A(r_1, \ldots, -|p_{3N}|) \right],$$  

(5)

where $r_1, \ldots, r_{3N-1}$ are restricted to values such that

$$e = H(I') - (p_{3N}^2/2m_{3N}) < E.$$  

(6)

Therefore $|p_{3N}|$ is determined by

$$|p_{3N}| = [2m_{3N}(E-e)]^{1/2}$$  

(7)

and Bunker's algorithm can be outlined as follows:

(i) Generate $L/2$ random values of $r_1, \ldots, r_{3N-1}$ satisfying (6).

(ii) Use (7) to get $p_{3N} = [2m_{3N}(E-e)]^{1/2}$ and produce $L I'$-values with nonvanishing weight.

(iii) Set $w(I') = 1/L|p_{3N}|$.

(iv) Calculate averages using (2).

The above algorithm has been successfully applied by Bunker to generate sample ensembles for the internal degrees of freedom for triatomic molecules [5], but difficulties were found for larger molecules such as CH$_3$NC [7]. Apart from problems of computational efficiency, the Bunker procedure has a weighting function $|p_{3N}|^{-1}$ which is singular at any point on the $(6N-2)$-dimensional surface separating the accessible from the inaccessible part of phase space. Although this problem can be overcome for small molecules at the cost of numerical effort, that is not so for large molecules or simulations of condensed-matter systems.

Creutz [8] has introduced a different microcanonical ensemble Monte Carlo sampling. The method starts, for example, from a point in phase-space such that the potential energy $U(r^N) < E$. An extra degree of freedom, the so-called demon, with energy $E_D$, is introduced such that $E_D = E - U(r^N)$. A random walk is then set up in the configurational space, so that further states on the hypersurface of energy $E$ are generated. This is done in the following way. If a configuration is generated such that its potential energy, $U'$, is less than the potential energy of the previous configuration, $U$, the new configuration is accepted and the energy of the demon is increased by $\Delta = U - U'$. Otherwise, the move is only accepted if the demon has enough positive energy to give. The acceptance decision, therefore, has no random numbers involved.

The procedure is formally expressed by the following phase-space density:

$$\omega(N, V, E) = C \int \int \delta(U(r^N) + E_D - E) \, dr^N \, dE_D.$$  

(8)

Thus, the variable $E_D$ is analogous to the kinetic energy carried by the conjugate momenta, although the demon is not associated with any single degree of freedom in the original system.

The algorithm satisfies a restricted form of detailed balance. The energy of the demon will become exponentially distributed:

$$P(E_D) \propto \exp(-\beta E_D),$$  

(9)

for energies small compared with the total energy of the system and the inverse temperature can be calculated from the average value of the demon energy:

$$\beta = \frac{1}{T} \ln(1 + 4/\langle E_D \rangle).$$  

(10)

Creutz [8] has successfully applied the method to simulations with SU(2) lattice gauge theory on a $6^4$ site lattice. Some disadvantages of the approach have been, however, pointed out. First, finite-size effects on small systems are potentially more serious than in the canonical approach. Second, the specific heat can not be directly calculated from the fluctuations in the potential energy. On the other hand, it is noteworthy that the above procedure does not really simulate the microcanonical ensemble. What is kept almost constant is the total potential energy. The real microcanonical ensemble can, however, be simulated by introducing a demon for every quadratic term in the kinetic energy. The same rules as above are applied, randomly selecting a demon to pay or accept the potential energy.
formulated the full statistical mechanics of the microcanonical ensemble and they have shown that the usual thermodynamic functions can be directly worked out from the microcanonical sampling in configurational space. The temperature, for example, is given by
\[ T = \frac{2\langle E - U(R) \rangle}{3Nk_B}. \] (15)

Recently, Ray [13] has successfully applied the method of Severin et al. and the formulation of Pearson et al. to simulate a 500-particle fcc Lennard-Jones crystal at zero pressure.

The purpose of this article is to present a Monte Carlo algorithm to sample the microcanonical ensemble both in configurational and momenta spaces. It was inspired by the method of hypervolumes described by Callen [14] to calculate the entropy in a microcanonical ensemble. Thus, we shall designate the method as hypervolume Monte Carlo (HVMC). In the next section we discuss the statistical and geometrical roots of the method and the computational details. The results for a Lennard-Jones system are shown and discussed in Section 3. Finally, Section 4 contains the conclusions of this work.

2. The HVMC method and computational details

It is well-known that the entropy in a microcanonical ensemble can be defined through different basic equations all of them equivalent in the thermodynamic limit [12,15]. This apparent ambiguity in the definition of the entropy is one of the reasons pointed out by Pearson et al. [12] for the general tendency of abandoning the microcanonical ensemble in favor of the canonical, grand canonical and other formalisms.

In the microcanonical ensemble the entropy can be defined, for example, by the following equations:
\[ S = k_B \ln \Omega(N, V, E), \] (16)
\[ S = k_B \ln \omega(N, V, E), \] (17)
where \( k_B \) is the Boltzmann constant,
\[ \Omega(N, V, E) = C \int \int \Theta[E - H(P, R)] \, dP \, dR \] (18)
is the phase-space volume and
\[ \omega(N, V, E) = C \int \int \delta[E - H(P, R)] \, dP \, dR \] (19)

Schranz et al. [11] have outlined a microcanonical sampling procedure based on the method of Severin et al. and they have demonstrated its usefulness in applications to 1D linear chains and 3D molecules such as H2O, SiH2 and Si2H4.

Severin et al. [6] did not seem to have recognized the full statistical mechanics of the microcanonical ensemble and they have proposed a further sampling in momenta space, which it is not necessary, at all, in the above formulation. Indeed, Pearson et al. [12] have

change for every trial move. Applications and generalizations of the method can be found in Refs. [9, 10].

Severin et al. [6] have proposed an alternative method for sampling in the microcanonical ensemble. The basic idea is to exploit separability of the kinetic and potential energies. If the Hamiltonian has the form:
\[ H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(r_N) \] (11)
the phase-space density can be rewritten as
\[ \omega(N, V, E) = C \int \int \delta \left( \sum_{i=1}^{N} \frac{p_i^2}{2m_i} \right. \]
\[ - \left( E - U(r_N) \right) \] \[ dP^N \, dR^N. \] (12)

Integrating over the momenta coordinates:
\[ \omega(N, V, E) = C_{3N} \int \left[ E - U(r_N) \right]^{(3N-2)/2} \]
\[ \times \Theta \left[ E - U(r_N) \right] \, dR^N, \] (13)
where \( C_{3N} \) is a constant and \( \Theta(x) = 1, x > 0 \) and zero otherwise, is the unit step function.

Eq. (13) is numerically tractable and the usual Metropolis algorithm can be used to obtain a microcanonical sampling in configurational space. Thus, the transition probability from a configuration \( R \) to a configuration \( R' \) is
\[ \pi(R \to R') = \min \left( 1, \frac{\left[ E - U(R') \right]^{(3N-2)/2} \Theta \left[ E - U(R') \right]}{\left[ E - U(R) \right]^{(3N-2)/2} \Theta \left[ E - U(R) \right]} \right). \] (14)

Schranz et al. [11] have outlined a microcanonical sampling procedure based on the method of Severin et al. and they have demonstrated its usefulness in applications to 1D linear chains and 3D molecules such as H2O, SiH2 and Si2H4.

Severin et al. [6] did not seem to have recognized the full statistical mechanics of the microcanonical ensemble and they have proposed a further sampling in momenta space, which it is not necessary, at all, in the above formulation. Indeed, Pearson et al. [12] have
is the phase-space density.

The phase-space volume is the number of states enclosed by the hypersurface of energy $E$ and the phase-space density is the density of states between the hypersurfaces of energies $E$ and $E - \Delta$, with $\Delta \ll E$.

The equivalence of Eqs. (16) and (17) means that, in the thermodynamic limit, the number of states with energies between $E$ and $E - \Delta$ is essentially equal to the number of states with energies less than $E$, and this result is essentially independent of $\Delta$.

As Callen [14] explains, this strange, but enormously useful result, has its roots in the geometry of the high-dimensional phase-space. The ratio of the hypervolume of a spherical shell to the total volume of the hypersphere is:

$$\frac{\Delta V}{V} \approx n \frac{\Delta r}{r},$$

where $n$ is the dimension of the space and $r$ the radius of the hypersphere. Taking $n = 10^{23}$, $\Delta V/V \approx 0.1$ if $\Delta r/r \approx 10^{-24}$, becoming of the order of unity for values of $\Delta r/r$ as small as $\Delta r/r \approx 10^{-22}$. Quoting Callen [14]: "In an imaginary world of high dimensionality there would be an automatic and perpetual potato famine, for the skin of a potato would occupy essentially its entire volume!".

Thus, the calculation of the entropy in a microcanonical ensemble can be reduced to the evaluation of the hypervolume enclosed by the hypersurface of energy $E$, avoiding combinatorial techniques, which are impracticable for complex systems.

The foregoing analysis allows us to take Eq. (18) to set up the following algorithm for sampling the microcanonical ensemble both in configurational and momenta space:

(i) Start from a configuration $R$ such that $U(R) < E$ and from a set of momenta $P$, for example, $P = 0$.

(ii) Generate a new state $(R', P')$ by giving random displacements to the position and momentum of a particle $i$, taken at random or sequentially.

(iii) Accept or reject the new state with probability:

$$\pi[(R, P) \rightarrow (R', P')] = \min \left(1, \frac{\Theta[E - H(R', P')]}{\Theta[E - H(R, P)]} \right),$$

that is to say, if $H(R', P') < E$ then accept the new state as a new element of the ensemble.

else reject the state and count the old one as a repeated element of the ensemble.

end if

(iv) Take averages of the dynamical properties over the generated ensemble.

Note that the acceptance decision (iii) has no random numbers involved.

We must point out a few details in our implementation of the above algorithm. First, each Monte Carlo cycle has two independent cycles: one over the positions and the other over the momenta. This allows independent adjustments of the maximum displacements of the positions and momenta in order to obtain a rate of acceptance of $\sim 50\%$. Second, it is essential to guarantee a zero total linear momentum. This can be done in different ways. We have chosen a very simple one: when a particle $i$ is given a random displacement of the momentum, a different particle is randomly chosen and given just the opposite displacement.

In order to check out the HVMC algorithm we have performed a series of simulations of the Lennard-Jones system by NVE molecular dynamics (MD) at different densities and temperatures ranging from solid to fluid states. The final values of the total energy were the inputs for the HVMC program at the same MD densities. The number dependence was analyzed by repeating the simulations with different number of particles, namely: 32, 108, 256, 500 and 864.

Cubic periodic boundary conditions were used with the minimum-image convention and a cut-off radius of 2.5 (except for the calculations with 32 particles where the cut-off radius was $\sim 1.7-1.9$). Reduced units were used throughout and long-range corrections were applied to the energy and pressure. The temperature and pressure in the HVMC program were calculated from the mean kinetic energy and virial theorem as in the MD program. For each thermodynamic state studied, both programs started from a fcc lattice and equilibration runs with 3000–5000 cycles were always followed by production runs with 3000–15000 cycles. In order to approach a pre-defined temperature, the usual periodic scaling of the velocities was applied in the MD equilibration runs. Both programs produced the typi-
3. Results and discussion

Table 1 presents the results, obtained by the MD and HVMC methods, for the total energy, potential energy, kinetic energy and pressure at different densities, temperatures and number of particles.

The comparisons between the radial distribution functions and speed distribution functions obtained by the MD and HVMC methods are shown in Figs. 1–4 only for some of the simulated thermodynamic states.

The agreement between the results from molecular dynamics and from the HVMC method is excellent for all the presented thermodynamic states and number of particles. The fluctuations of the potential and kinetic energies obtained by the HVMC method are equal, as they must be in a true microcanonical ensemble, and similar to the ones obtained by molecular dynamics. Therefore, the specific heats, not explicitly indicated in Table 1, are also similar in both methods.

The structure and speed distribution functions of the system, obtained by molecular dynamics, are totally reproduced by the HVMC method for all the thermodynamic states and number of particles studied in the present work.

The results do not appear to be significantly sensitive to the number of particles used in the present simulations.

Finally, the behavior of the total angular momentum has also been analyzed. It is well-known that the
Table 1
Reduced thermal properties of the Lennard-Jones system from MD and HVMC methods

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>p</th>
<th>E</th>
<th>T</th>
<th>U</th>
<th>K</th>
<th>P</th>
<th>Cy/10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD</td>
<td>32</td>
<td>0.88</td>
<td>-6.737(008)</td>
<td>0.303(028)</td>
<td>-7.191(045)</td>
<td>0.454(043)</td>
<td>-4.359(220)</td>
<td>10</td>
</tr>
<tr>
<td>HVMC</td>
<td>32</td>
<td>0.88</td>
<td>-6.747(009)</td>
<td>0.305(030)</td>
<td>-7.205(045)</td>
<td>0.458(045)</td>
<td>-4.401(230)</td>
<td>15</td>
</tr>
<tr>
<td>MD</td>
<td>108</td>
<td>0.88</td>
<td>-6.739(002)</td>
<td>0.288(015)</td>
<td>-7.172(022)</td>
<td>0.433(023)</td>
<td>-4.387(114)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>108</td>
<td>0.88</td>
<td>-6.742(003)</td>
<td>0.284(015)</td>
<td>-7.168(023)</td>
<td>0.426(023)</td>
<td>-4.364(122)</td>
<td>3</td>
</tr>
<tr>
<td>MD</td>
<td>256</td>
<td>0.88</td>
<td>-6.699(002)</td>
<td>0.302(011)</td>
<td>-7.153(016)</td>
<td>0.453(017)</td>
<td>-4.274(085)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>256</td>
<td>0.88</td>
<td>-6.700(001)</td>
<td>0.298(008)</td>
<td>-7.147(012)</td>
<td>0.446(012)</td>
<td>-4.234(069)</td>
<td>3</td>
</tr>
<tr>
<td>MD</td>
<td>500</td>
<td>0.88</td>
<td>-6.714(001)</td>
<td>0.296(007)</td>
<td>-7.158(011)</td>
<td>0.445(011)</td>
<td>-4.308(055)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>500</td>
<td>0.88</td>
<td>-6.714(001)</td>
<td>0.297(007)</td>
<td>-7.160(011)</td>
<td>0.446(011)</td>
<td>-4.310(061)</td>
<td>3</td>
</tr>
<tr>
<td>MD</td>
<td>864</td>
<td>0.88</td>
<td>-6.646(001)</td>
<td>0.316(007)</td>
<td>-7.120(010)</td>
<td>0.474(010)</td>
<td>-4.030(064)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>864</td>
<td>0.88</td>
<td>-6.646(000)</td>
<td>0.314(006)</td>
<td>-7.118(010)</td>
<td>0.472(010)</td>
<td>-4.052(051)</td>
<td>3</td>
</tr>
<tr>
<td>MD</td>
<td>32</td>
<td>0.88</td>
<td>-3.573(028)</td>
<td>1.352(130)</td>
<td>-5.600(192)</td>
<td>2.028(196)</td>
<td>4.709(817)</td>
<td>10</td>
</tr>
<tr>
<td>HVMC</td>
<td>32</td>
<td>0.88</td>
<td>-3.616(042)</td>
<td>1.339(132)</td>
<td>-5.624(197)</td>
<td>2.008(198)</td>
<td>4.590(840)</td>
<td>15</td>
</tr>
<tr>
<td>MD</td>
<td>108</td>
<td>0.88</td>
<td>-3.722(002)</td>
<td>1.298(067)</td>
<td>-5.669(101)</td>
<td>1.947(101)</td>
<td>4.362(431)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>108</td>
<td>0.88</td>
<td>-3.734(012)</td>
<td>1.286(067)</td>
<td>-5.663(100)</td>
<td>1.929(100)</td>
<td>4.380(432)</td>
<td>10</td>
</tr>
<tr>
<td>MD</td>
<td>256</td>
<td>0.88</td>
<td>-3.694(001)</td>
<td>1.302(045)</td>
<td>-5.648(068)</td>
<td>1.954(068)</td>
<td>4.504(301)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>256</td>
<td>0.88</td>
<td>-3.699(005)</td>
<td>1.315(043)</td>
<td>-5.671(065)</td>
<td>1.972(065)</td>
<td>4.392(288)</td>
<td>3</td>
</tr>
<tr>
<td>MD</td>
<td>32</td>
<td>0.60</td>
<td>0.500(016)</td>
<td>2.634(170)</td>
<td>-3.452(254)</td>
<td>3.952(256)</td>
<td>2.988(810)</td>
<td>10</td>
</tr>
<tr>
<td>HVMC</td>
<td>32</td>
<td>0.60</td>
<td>0.417(081)</td>
<td>2.607(168)</td>
<td>-3.494(243)</td>
<td>3.911(251)</td>
<td>2.829(768)</td>
<td>15</td>
</tr>
<tr>
<td>MD</td>
<td>108</td>
<td>0.60</td>
<td>0.168(002)</td>
<td>2.478(085)</td>
<td>-3.549(128)</td>
<td>3.717(128)</td>
<td>2.693(406)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>108</td>
<td>0.60</td>
<td>0.145(023)</td>
<td>2.477(087)</td>
<td>-3.571(129)</td>
<td>3.716(130)</td>
<td>2.603(411)</td>
<td>10</td>
</tr>
<tr>
<td>MD</td>
<td>256</td>
<td>0.60</td>
<td>0.134(002)</td>
<td>2.464(056)</td>
<td>-3.561(085)</td>
<td>3.695(085)</td>
<td>2.684(268)</td>
<td>3</td>
</tr>
<tr>
<td>HVMC</td>
<td>256</td>
<td>0.60</td>
<td>0.125(009)</td>
<td>2.445(054)</td>
<td>-3.543(081)</td>
<td>3.668(081)</td>
<td>2.695(265)</td>
<td>10</td>
</tr>
</tbody>
</table>

Density ($\rho$), total energy ($E$), temperature ($T$), potential energy ($U$), kinetic energy ($K$) and pressure ($P$); $N$ is the number of particles and Cy the number of cycles in production runs. The numbers in parentheses are the r.m.s. (standard deviations over the entire production runs), so 0.303(028) means 0.303±0.028.

symmetry of the space imposed by the usual periodic boundary conditions does not conserve the total angular momentum [3]. The typical behavior in our MD microcanonical simulations has been the rapid fluctuation of the total angular momentum which may reach, at equilibrium, values of the order $10^2$ in reduced units ($10^{-24}$ g cm$^2$ s$^{-1}$). A similar behavior has also been observed in our HVMC simulations. Lantelme et al. [16] have reported fluctuations of the same order of magnitude in a MD microcanonical simulation of molten NaCl.

It is possible to generate a microcanonical ensemble with zero total angular momentum by taking a frame of reference which follows the bulk rotation and cancels the angular momentum. Although we have not tried that in the present study, Lantelme et al. [16] have pointed out that the required changes in velocities are very small and, on average, represent 0.3% of the magnitude of the mean velocity. Moreover, they have also mentioned that with this procedure the internal energy has remained constant, as without the constraint, the time reversal motion has been observed and properties like the self-diffusion coefficients did not seem to be sufficiently influenced.
4. Final remarks

The overall agreement of our HVMC results with the results from molecular dynamics is excellent. Although the equivalence between the phase-space density and phase-space volume is strictly proven in the thermodynamic limit, our results show that the equivalence is valid, to a good extent, with a relatively small number of particles.

It would be useful to show how small the number of particles has to become before the method becomes inaccurate. In this sense, we have in progress a systematic study involving clusters of atoms and molecular systems and the results will be reported in a future communication. However, we should mention, as a very preliminary result, that we have equilibrated, by NVE molecular dynamics, a micro-cluster of 8 ions of KCl, at 9.9 K, obtaining a total energy of $-620.240 \pm 0.003 \text{ KJ mol}^{-1}$. The values obtained by HVMC were, respectively, 9.3 K and $-620.261 \pm 0.021 \text{ KJ mol}^{-1}$, based on runs with 40000 cycles. Although the agreement is apparently very good, it is necessary to consider more thermodynamic states and to carry out a thorough analysis before any sound conclusion can be drawn.

The HVMC method is the full nondeterministic counterpart of the NVE molecular dynamics method. Their equivalence in the present study is a further demonstration that deterministic chaos may be generated by the coupled Newton's equations of motion for many-body systems. Note that the HVMC method does not involve the integration of motion equations. Ordered and chaotic motions in dynamical systems is a complex question not completely settled down. Since the pioneering work by Fermi, Pasta and Ulam [17] it has been recognized that the transition from ordered to chaotic motions in many-body systems is directly related to nonlinearities and energy thresholds, number of degrees of freedom and time scales [18]. The chaotic behavior observed in the present study is presumably due to a combination of those factors.

As the HVMC method does not require previous integrations over the momenta space, it can be used with any form of Hamiltonian. In the majority of cases of practical interest in condensed-matter simulations, the Hamiltonian can be put in the form (11) and the integration over momenta can be carried out analytically. In those cases, the sampling over momenta is not required, but this does not mean that such a sampling should never be used in Monte Carlo simulations. In the study of flexible molecules with constraints, for example, the sampling over momenta may be advantageous [19]. Other potentially important applications of microcanonical Monte Carlo were pointed out by Creutz [8] and Ray [13] such as the simulation of the Ising model under the influence of a magnetic field, the study of solid-solid structural phase transformations, cases where the force calculation is complicated (e.g., 3, 4 and higher-body forces or in density-functional molecular dynamics approaches) and simulated annealing.

Acknowledgements

The Computing Services at Faculty of Sciences, University of Lisboa, are gratefully acknowledged for the allocation of computational resources.

References