High dimensional geometry in statistical mechanics. A new microcanonical sampling method

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Abstract: The Hyper Volume Monte Carlo (HVMC) method recently proposed by Fernandes and Ramalho (1) is reviewed. The geometrical and statistical roots of the method, its application to simple and to molecular systems, as well as a comparison with results from Molecular Dynamics, are presented. The spontaneous magnetization curve for a 2-dimensional Ising model, obtained by HVMC, is also shown. Finally, some potential applications of the HVMC method are pointed out.

1. Introduction

The Monte Carlo method introduced by Metropolis et al. (2) to sample the canonical ensemble has been extended to other ensembles such as NpT (3,4) and μVT (4,5) 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:

$$f(N, V, E) = \delta[H(\Gamma) - E]\left(\int d\Gamma \, \delta[H(\Gamma) - E]\right)^{-1}$$

where δ is the Dirac delta function, H is the Hamiltonian and Γ is the phase-space vector. Such a mathematical form is not amenable to numerical work. Thus, its introduction in the usual Monte Carlo procedure is not so straightforward.
A short survey of the Monte Carlo methods to sample the microcanonical ensemble has been presented elsewhere (1). In this lecture, we review the Hyper Volume Monte Carlo (HVMC) method recently proposed by Fernandes and Ramalho (1), to perform microcanonical simulations by sampling the configurational and momenta spaces, and we present some applications of the method to simple (1) and to molecular (6) systems as well as a comparison with results obtained by Molecular Dynamics (MD). We also present the spontaneous magnetization curve for a 2-dimensional Ising model, obtained by HVMC, with the critical point in close agreement with Onsager's analytical solution (7). Finally, we refer to some potential applications of the HVMC method and we point out that it is the full nondeterministic counterpart of the isoenergetic MD method .

2. Geometry

The volume of a n-dimensional hypersphere is given (8) by:

$$V = A_n r^n$$

where A_n is a constant and r is the radius. In the particular case of a 3-dimensional sphere, $A_n = 4/3 \, \pi$ and $n = 3$.
The ratio of the volume of a spherical shell to the total volume of the hypersphere is:

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

If n is of the order 10^{23}, then $\Delta V / V \approx 1$ for values as small as $\Delta r / r \approx 10^{-23}$. Therefore, the total volume of a spherical shell approaches the total volume of the sphere when $n \to \infty$. In the appealing words of Callen (8): " In an imaginary world of high dimensionality there would be an automatic and perpetual potato famine, for the skin of the potato would occupy essentially its entire volume."

3. Statistical Mechanics

It is well-known that, in a microcanonical ensemble, the entropy, S, can be defined through different formulas (9, 10) such as:

$$S = k_B \ln \Omega(N, V, E)$$

$$S = k_B \ln \omega(N, V, E)$$

where k_B is the Boltzmann constant,

$$\Omega(N, V, E) = C \iint \Theta[E - H(R, P)] \, dR \, dP$$

is the phase-space volume and

$$\omega(N, V, E) = C \iint \delta[E - H(R, P)] \, dR \, dP$$

is the phase-space density.

$\Theta[x] = 1$ if $x > 0$ and zero otherwise, is the unit step function; $\delta[x] \neq 0$ if $x = 0$ and zero otherwise, is the Dirac δ-function and C is a constant.

The phase-space volume is the number of states under the hypersurface of energy E. The phase-space density is the density of sates between the hypersurfaces with energies E and E - Δ, with $\Delta \ll E$. In other words, the phase-space volume represents the " bulk of the potato" and the phase-space density represents the " skin of the potato"!.

The equivalence of the two definitions of entropy means that, in the thermodynamic limit, the number of states with energies between E and E - Δ is essentially equal to the number of states with energies less than E, and this result is essentially independent of Δ . This counter-intuitive, but enormously useful result has its roots in the geometry of the high-dimensional space, as we have seen before.

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, in alternative to combinatorial techniques, which are impracticable for complex systems.

Therefore, the phase-space volume:

$$\Omega(N, V, E) = C \iint \Theta[E - H(R, P)] \, dR \, dP$$

can be assumed as the microcanonical partition function. This is extremely useful, for the function $\Theta[x]$ is amenable to numerical work in contrast to the Dirac δ-function present in the phase-space density.

4. The HVMC method

The consideration of the phase-space volume, as the microcanonical partition function, allows us to set up the HVMC (Hyper Volume Monte Carlo) method to simulate the microcanonical ensemble by sampling the momenta and configurational spaces:

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

(ii) Generate a new state (**R'**,**P'**) by giving random displacements to the position and momentum of 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 $H(\mathbf{R'}, \mathbf{P'}) < E$ then
      accept the new state as a new element of the ensemble
else
      reject the new 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 has no random numbers involved in contrast to the usual Monte Carlo methods.

The above algorithm is straightforwardly implemented, although there are some technicalities to be taken into account. We are not going into them, for they are fully described in the original article by Fernandes and Ramalho (1).

In the following section we present and discuss some applications of the HVMC method.

5. Applications and Discussion

5.1. Simple Systems

The Lennard-Jones (LJ) system is a standard model for testing theories and computer simulation methods. As such, we have carried out extensive calculations on that system, examining the dependence on the number of particles and eventual ergodic problems. To this end, we have performed, by MD-NVE, a series of calculations ranging from solid to fluid states with different number of particles. The final values of the total energy were the inputs for the HVMC program at the same MD densities. The complete set of results can be seen in the original article by Fernandes and Ramalho (1). Here, we only present a few ones.

TABLE 1. Reduced thermal properties of the Lennard-Jones system from MD and HVMC methods: density (ρ), total energy (E), temperature (T), potential energy (U) and kinetic energy (K); N is the number of particles. The numbers in parentheses are the r.m.s. (standard deviations over the entire production runs) of the last digit(s), so 0.303(028) means 0.303 ± 0.028.

	N	ρ	E	T	U	K
MD	32	0.88	-6.737(008)	0.303(028)	-7.191(045)	0.454(043)
HVMC	32	0.88	-6.747(009)	0.305(030)	-7.205(045)	0.458(045)
MD	864	0.88	-6.646(001)	0.316(007)	-7.120(010)	0.474(010)
HVMC	864	0.88	-6.646(000)	0.314(006)	-7.118(010)	0.472(010)
MD	32	0.60	0.500(016)	2.634(170)	-3.452(254)	3.952(256)
HVMC	32	0.60	0.417(081)	2.607(168)	-3.494(243)	3.911(251)
MD	256	0.60	0.134(002)	2.464(056)	-3.561(085)	3.695(085)
HVMC	256	0.60	0.125(009)	2.445(054)	-3.543(081)	3.668(081)

The agreement between the results from MD and from HVMC methods is excellent for all the 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 MD. Therefore, the specific heats, not explicitly indicated in Table 1, are also similar in both methods.

The following figures show the radial and speed distribution functions obtained by MD and HVMC methods.
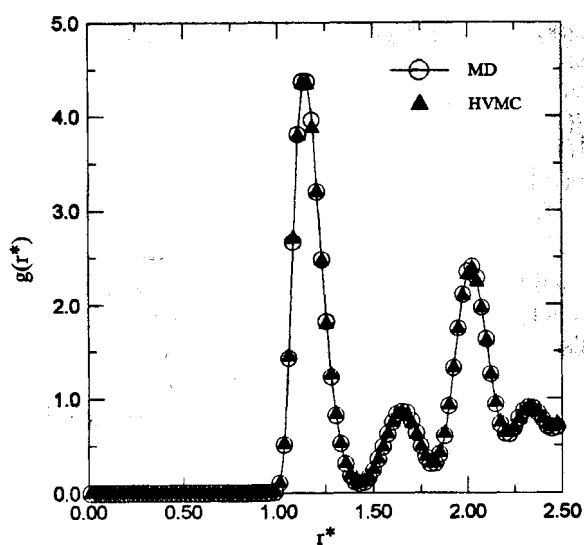

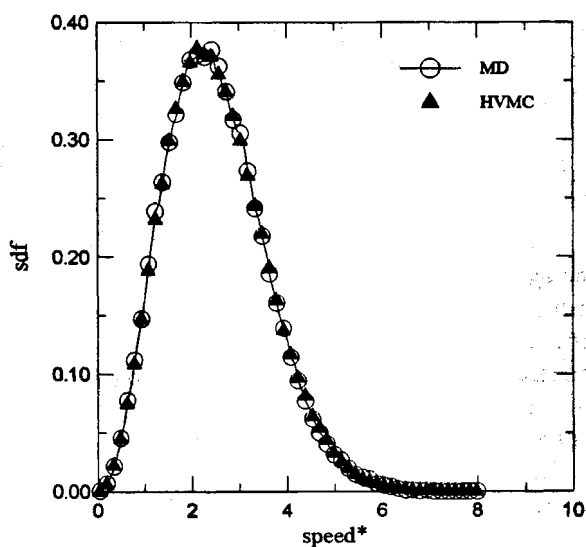Fig. 1 Radial distribution functions of the LJ system (N=108, ρ = 0.88, T≈0.3).

Fig. 2 Speed distribution functions of the LJ system (N=256, ρ = 0.6, T≈2.4).

The structure of the system, obtained by MD, is totally reproduced by HVMC as well as the speed distribution function. Note that an interesting characteristic of the HVMC method is the possibility of obtaining velocity distribution functions. This is in contrast to the usual Monte Carlo methods where no sampling over the momenta space is performed.

Finally, the results do not appear to be significantly sensitive to the number of particles used in the simulations [32-864] and the excellent agreement between the results obtained from MD and HVMC suggests that ergodic problems are absent, at least for the present simulations.

5.2 Molecular Systems

Liquid methyl chloride, in a series of thermodynamic states, has been simulated by MD and HVMC methods.

The model consists of a CH_3 pseudoatom and of a chlorine atom separated by the experimental bond length (1.781 Å). The interaction between two CH_3Cl molecules A and B is described by

$$U_{AB} = \sum_{i \in A} \sum_{j \in B} \varepsilon_{ij} \left[(\sigma_{ij} / r_{ij})^{12} - (\sigma_{ij} / r_{ij})^6 \right] + q_i q_j / r_{ij}$$

with parameters referred to by Freitas et al. (11).

Cubic periodic boundary conditions with 108 molecules have been used. Equilibration runs with 10000 cycles have always been followed by production runs with 20000 cycles. In TABLE 2 we present some thermal properties obtained by MD-NpT and MC-NVT (11) and by HVMC (6).

TABLE 2. Thermal properties of liquid CH_3Cl from MD-NpT, MC-NVT and HVMC methods: density (ρ), potential energy (U), kinetic energy (K), total energy (E), temperature (T), pressure (p). The numbers in parentheses have the same meaning as in Table 1. The subindices trans and rot mean, respectively, translational and rotational.

		ρ / gcm^{-3}			
		1.07	1.04	1.01	0.98
U / kJmol^{-1}	MD	-24.57(34)	-23.66(36)	-22.85(38)	-21.74(46)
	MC	———	-23.76(22)	-22.89(23)	———
	HVMC	-24.65(16)	-23.71(17)	-22.88(18)	-21.81(20)
K / kJmol^{-1}	MD	3.65	4.17	4.60	5.21
	HVMC	3.71(16)	4.21(17)	4.61(18)	5.26(20)
K_{trans} / kJmol^{-1}	MD	2.19	2.49	2.74	3.11
	HVMC	2.23(14)	2.53(16)	2.76(17)	3.13(20)
K_{rot} / kJmol^{-1}	MD	1.47(14)	1.68(16)	1.86(18)	2.10(20)
	HVMC	1.48(12)	1.67(14)	1.85(16)	2.13(18)
E / kJmol^{-1}	MD	-20.92(34)	-19.49(39)	-18.25(41)	-16.53(51)
	HVMC	-20.93(01)	-19.51(01)	-18.27(02)	-16.55(02)
T / K	MD	176(7)	201(8)	221(9)	251(10)
	HVMC	179(7)	202(8)	222(9)	253(9)
T_{trans} / K	MD	175.4	200	220	249.39
	HVMC	179(11)	203(13)	221(14)	251(16)
T_{rot} / K	MD	177(17)	202(19)	224(22)	252(25)
	HVMC	178(15)	201(17)	223(19)	257(22)
p / MPa	MD	0(37)	0(39)	0(39)	0(39)
	MC	———	26(28)	26(29)	———
	HVMC	24(20)	23(23)	29(24)	31(24)

The agreement between the results obtained by HVMC and by MD is excellent. The fluctuations of the kinetic and potential energies are equal, as they must be in a true microcanonical ensemble. The agreement between the translational and rotational temperatures is also excellent and it reflects a correct equipartition of energy among the different degrees of freedom of the model: 3 translational and 2 rotational.

The structure of the system has been analysed through different site-site distribution functions (6) and in Figure 3 we show the CH_3-CH_3 distribution functions. In Figure 4, the speed distributions functions, at 200 K, are also displayed.

The structure of the system, obtained by MD, is totally reproduced by HVMC as well as the speed distribution function. Finally, we have checked out that the most probable molecular speeds obtained by HVMC are in accordance with the ones theoretically predicted, which is a further demonstration of a correct equipartition of energy.
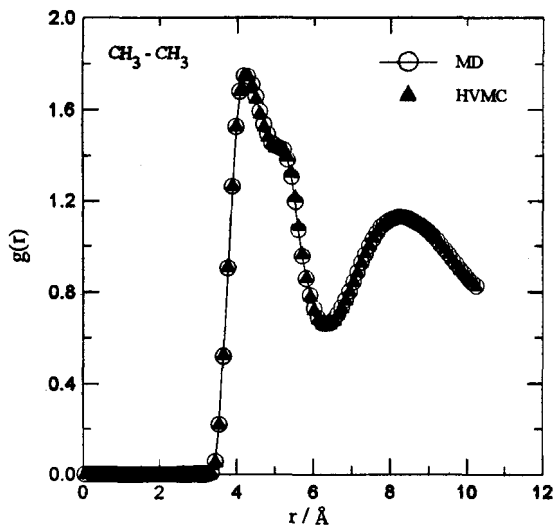
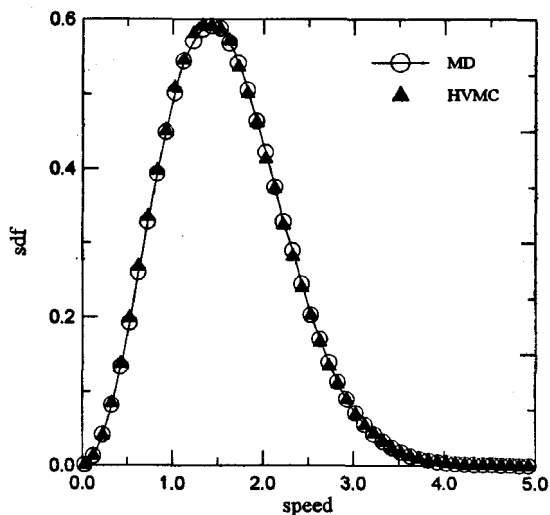Fig. 3 Site-site radial distribution functions of liquid CH_3Cl (N=108, T≈200K, p≈0).

Fig. 4 Speed distribution functions of liquid CH_3Cl (N=108, T≈200K, p≈0).

5.3 Ising Model

The 1/2 Ising model (7,9,12), without applied magnetic field, has been simulated in two dimensions by HVMC (6). The Hamiltonian of the system is:

$$H = -J\sum_{<ij>} s_i\, s_j$$

where J is the interaction constant, taken equal to 1 in the present work, and s = ± 1 is the spin variable. The summation is extended to the nearest neighbours.

A 100 x 100 spin lattice has been considered and equilibration runs with 10000 cycles have always been followed by equilibration runs with the same number of cycles.

The potential energy/spin has been varied between 0 and -2 (the later value is the ground state of the 2-dimensional model). The magnetization of the system is defined as:

$$M = < \sum_i s_i\ /\ n^\circ\, spins >$$

The existence of a continuous phase transition in this 2-dimensional model was analytically demonstrated by Onsager (7) a long time ago. Our results, displayed in Figure 5, show the spontaneous magnetization of the system, characterized by a critical point in the range [-1.4, -1.1] of the potential energy/spin. This is in agreement with the prediction of Onsager. The simulation of the 2-dimensional Ising model has been performed before by other methods (12). The purpose of the present calculations is to check out the ability of the HVMC method to detect the critical point of the model.
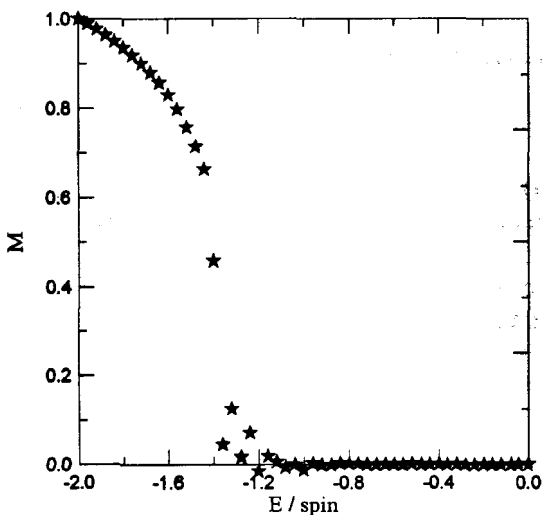
Fig. 5 Magnetization versus potential energy/spin.

6. Final Remarks

The HVMC method is theoretically correct and of simple computational implementation. It only needs some straightforward alterations in the code of a NVT Monte Carlo program.

The overall agreement of our HVMC results with the results from MD and the analytical results of Onsager 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.

How small the number of particles has to become before the method becomes inaccurate?. We have in progress a systematic study involving clusters of atoms and molecules and the results will be reported in a future communication. However, we should mention, as a very preliminary result, that we have equilibrated, by MD-NVE, a microcluster of 8 ions of KCl at 9.9 K, obtaining a total energy of -620.240 $\pm$ 0.003 kJ mol^{-1}. The values obtained by HVMC were, respectively, 9.3 K and -620.261 $\pm$ 0.021 kJ mol^{-1}. Although the agreement is apparently very good, it is necessary, of course, 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 isoenergetic Molecular Dynamics method. Their equivalence, in the present simulations, is a further demonstration that deterministic chaos may be generated by the coupled Newton's equations of motion. Note that the HVMC method does not involve the integration of motion equations.

As the HVMC method does not require previous integrations over the momenta space it can be used with any form of Hamiltonian. Some potentially important applications of the microcanonical Monte Carlo have been pointed out by Frenkel (13), Creutz (14) and Ray (15) such as: the study of flexible molecules with constraints, the simulation of the Ising model under the influence of a magnetic field, the study of solid $\rightarrow$ solid 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.

Acknowledgement

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