Journal of Statistical Physics, Vol. 39, Nos. 1/2, 1985

Molecular Dynamical Simulation of the Canonical Ensemble

Ernesto Bonomi[1]

Received November 28, 1984; revised June 11, 1984, December 13, 1984

We apply a technique to simulate the canonical ensemble, mixing molecular dynamics and Monte Carlo techniques, in which particles suffer virtual hard shocks. In the limit of infinite time the system approaches a Boltzmann distribution. A good approximation to the Boltzmann distribution is achieved in computationally accessible time for some model systems including the one-dimensional jellium.

KEY WORDS: Metropolis algorithm; Brownian dynamics; molecular dynamics; computer simulation.

1. INTRODUCTION

Statistical mechanics deals with complex systems in equilibrium with the surrounding environment including the many interacting particles of which matter is built.

To surmont the difficulties of this problem, the computer simulation has become an important experimental tool.

Frequently, simulations use adaptations of the Metropolis algorithm.(1)

This procedure simulates the evolution of a system in contact with a heat bath at temperature T as it is observed at random times (canonical ensemble), generating a Markovian process which leads to a unique stationary probability density proportional to the Boltzmann weight:

$$\rho(x) \sim \exp[-\beta H(x)] \tag{1}$$

$$\beta = \frac{1}{KT} \tag{2}$$

---

[1] Centre de Physique Théorique de l'École Polytechnique, Plateau de Palaiseau—91128 Palaiseau—Cedex—France.

$H(x)$ is the energy associated to the internal configuration x and K the Boltzmann constant.

A second method commonly used is molecular dynamics.(2,3)

This procedure consists of solving numerically the equations of motion for a dynamical evolution which conserves the total energy E. (microcanonical dynamics). In this way, the system explores the set of admissible configurations x under the constraint $H(x) = E$ and, according to the ergodic theorem, direct measurements allow the evaluation of the expectation value of any dynamical observable.

For instance, the temperature T, which does not appear in this method as a control parameter, is determined through the equipartition theorem by measuring the average kinetic energy.

If the number of particles were macroscopically large, it would be expected that the molecular chaos generated by the microcanonical dynamics describe at statistical equilibrium, the same physical reality as the canonical ensemble.

Unfortunately, at low energy, trapping of the phase-space trajectory can occur especially if the number of particles is not very large, as is often the case.

The idea is consequently to "reshuffle" the system, i.e., to introduce from time to time or in a continuous way random forces which in a certain sense play the role of the very large number of particles which should be introduced in the dynamics. A first alternative molecular dynamics, or Brownian dynamics(4,5) consists in taking explicitly into account friction and a random Gaussian force, which together represent the surrounding environment.

Standard arguments concerning the Markovian nature of the process relate the Langevin equations of motion governing Brownian dynamics and the Fokker–Planck equation, whose stationary solution is precisely (1).

The temperature T is unambiguously defined by a fluctuation-dissipation relation involving the damping constant and the diffusion constant.

However, in place of the continuous action of friction, we might prefer a discrete process in which particles are subject to only a random force. It seems worthwhile to combine the pure dynamic evolution where interesting collective motion can take place, with a discretized "reshuffling" whose main purpose is to untrap the phase-space trajectory. Such a procedure has been proposed by Hans C. Anderson.(6) The present paper uses a similar technique (developed unaware of Ref. 6). It concretizes this idea simulating the canonical ensemble by a molecular dynamics in which, from time to time, particles suffer hard shocks with "virtual particles" that can be called the heat bath.

In our method, time intervals are taken proportional to the Boltzmann weight (1), in which one substitutes for the temperature KT a new parameter θ (when $\theta \to \infty$ time intervals become constant). At the end of each interval, the molecular dynamics is stopped and re-initiated by replacing the velocity components of a given number of particles, by random numbers, distributed according to the normal law at temperature σ. Notice that neither θ nor σ are the equilibrium temperature of the system that we want to simulate. In fact, the temperature T is related to θ and σ, $(KT)^{-1} = \sigma^{-1} + \theta^{-1}$, and it appears as the control parameter of the simulation.

This shuffling procedure operates in such a way as to avoid the continuous action of any friction, allowing the system to reach a statistical equilibrium, whose probability density is a good estimate of 1), in the limit of the available running time.

Let us point out that if the random forces are very frequent, the state of the system at two different times will be totally uncorrelated. In this limit we deal practically with a pure Monte Carlo method where the different states are randomly sampled (practically, we reintroduce a "virtual trajectory" through a Markof chain).

Our procedure is more general than the one of Ref. 6 quoted above since we introduce, through the external parameters θ and σ, two competitive processes. The possibility that at low temperature and high density the system may be trapped requires the existence of fast particles with respect to the thermal velocity; these particles can be generated by taking σ slightly greater then β^{-1}. The necessity to keep constant the temperature T implies also a modification of the time-interval between the artificial collisions. Computer experiments show that it is convenient for mixing efficiently the phase-space trajectory, to disturb simultaneously more than one particle. This operation is, of course, possible in our procedure. It allows, for example, to simulate the one-dimensional jellium for a fixed value of the coupling constant in reasonable computational time.

As a final comment, let us mention the recent work of Shūichi Nosé(7): He presents a molecular dynamics method at constant temperature in which, by introduction of an additional degree of freedom, the total energy of the physical system is allowed to fluctuate. This method is purely dynamical.

2. CANONICAL ENSEMBLE SIMULATION

We consider a classical system containing N confined identical particles of mass $m = 1$ inside a box with impermeable sides.

To simulate the interaction of the system with a heat bath at temperature T, we assume that particles suffer hard shocks with virtual particles, whose velocities and positions are randomly defined.

For each interacting particle, the equations of motion are written in the following way:

$$\begin{cases} \dot{v}_i = -\dfrac{\partial H}{\partial q_i} + \Delta v_i(t) \displaystyle\sum_{\alpha=-\infty}^{\infty} \delta(t-t_\alpha) \\ \dot{q}_i = v_i \end{cases} \tag{3}$$

where H is the Hamiltonian of the system. We refer to the time t_α as *hits*. At each hit, the particle coordinate is unchanged:

$$q_i(t_\alpha+0) = q_i(t_\alpha-0) \tag{4}$$

but the particle velocity component receives an increment:

$$v_i(t_\alpha+0) - v_i(t_\alpha-0) = \Delta v_i(t_\alpha) \tag{5}$$

Between two hits particles move in a microcanonical way, conserving the total energy (Figure 5):

$$\begin{aligned} E_\alpha &= H(\mathbf{v}_1, \ldots, \mathbf{v}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N) \\ &= \sum_{i=1}^{N} \frac{\mathbf{v}_i^2}{2} + \phi(\mathbf{q}_1, \ldots, \mathbf{q}_N) \end{aligned} \tag{6}$$

In this collision process, each component of the new velocity $v_i(t_\alpha+0)$ is assumed to be a random Gaussian variable

$$v_i(t_\alpha+0) \sim \mathcal{N}(0, \sqrt{\sigma}) \tag{7}$$

and the time interval between two hits $|I_\alpha| = t_{\alpha+1} - t_\alpha$, is taken proportional to the Boltzmann factor:

$$|I_\alpha| = C \exp\left(\frac{E_\alpha}{\theta}\right) \tag{8}$$

The flow induced by the above procedure is expected to converge to a statistical steady state, in which configurations of the phase space are correctly displayed according to (1). Moreover, the temperature T should be connected to the variance σ of the gaussian noise (7) and to the constant θ appearing in (8) by the following expression:

$$\beta = \frac{1}{\sigma} + \frac{1}{\theta} \tag{9}$$

A heuristic proof of these statement is given in the next section. From this last expression, we can extract two extreme cases of the thermalization process.

When σ tends to infinity, the Gaussian density tends to a uniform density over the whole real axis, and $\beta = 1/\theta$. This situation is illustrated in Figure 1: for different values of θ, the phase-space trajectory of one particle moving in an external field $\phi(q)$ is simulated. The potential $\phi(q) = \gamma q^2(q^2 - 1)^2$, $\gamma = 27/4$, has three minima equal to zero at $q = -1, 0, 1$ and the energy gap to pass between then is equal to one. Of course, the implementation of this procedure for large σ gives rise at each hit to the delicate numerical calculation of $\exp(-E_\alpha/\theta)$ slowing down considerably the simulation and leading to possible underflow messages. For these two

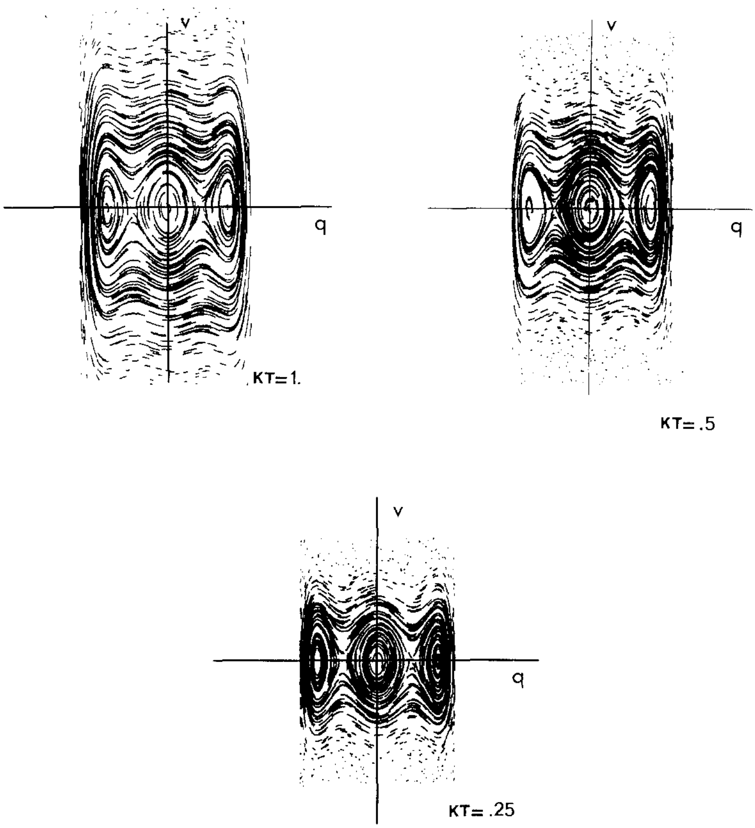

Fig. 1. Computer simulation of the trajectory in phase space of a particle moving in an externed field $\phi(q) = \gamma q^2(q^2 - 1)^2$ $\gamma = 27/4$ and suffering hard shocks with virtual particles: $\sigma = \infty$.

reasons, to perform the computer simulation we consider only a uniform distribution in the interval $[-4\sqrt{\theta}; 4\sqrt{\theta}]$ for the possible new velocity. Of course, so doing we neglect the very large energies, but in that case the time-intervals considered would be extremely short and their contribution totally negligible. Consequently, σ can be really considered infinite and, from (9), $\theta = KT$.

Table I shows for some thermodynamical quantities (mean square velocity, average energy, average potential energy, specific heat) the comparison between the exact value derived from the definition of the canonical ensemble, and the numerical values obtained as time average by simulation: the agreement is remarkable (see also Figure 2).

These numerical difficulties disappear when, for a fixed value of σ, θ tends to infinity. In this situation, time intervals become constant and the inverse temperature is given by $\beta = 1/\sigma$.

To illustrate this case, one dimensional jellium has been investigated. In this system we consider a set of N particles of charge $-e$, immersed in a neutralizing background of positive charge with density $\rho = (N+s)/L$, confined in a box $[0, L]$. s is called the excess of charge. In Ref. 8 it is shown that this system, in the canonical ensemble, is in a crystalline state for all values of the coupling constant $\lambda = (2e^2/\rho KT)^{1/2}$. This is proven by showing that the one-particle density function $n(q)$ in the thermodynamic limit is a

Table I. Comparison between the Canonical Ensemble Average and the Simulation Time-Average: $\phi(q) = \gamma q^2(q^2-1)^2$, $\gamma = 27/4$

kT	$\langle v^2 \rangle$	$\langle E \rangle_{\mathrm{CAN}}$	$\langle E \rangle$	$\langle POT \rangle_{\mathrm{CAN}}$	$\langle POT \rangle$	c_{CAN}	c
0.10	0.099	0.108	0.108	0.058	0.058	0.976	0.980
0.15	0.149	0.152	0.151	0.077	0.076	0.802	0.795
0.20	0.199	0.190	0.189	0.090	0.089	0.712	0.706
0.25	0.249	0.224	0.223	0.099	0.098	0.663	0.656
0.30	0.300	0.256	0.257	0.106	0.107	0.636	0.636
0.40	0.398	0.319	0.318	0.119	0.119	0.609	0.605
0.60	0.597	0.438	0.438	0.138	0.140	0.593	0.587
0.80	0.795	0.557	0.553	0.157	0.155	0.590	0.582
1.0	0.994	0.675	0.671	0.175	0.174	0.591	0.591
1.2	1.190	0.793	0.785	0.193	0.190	0.592	0.581
1.4	1.400	0.911	0.911	0.212	0.211	0.594	0.595
1.6	1.594	1.030	1.027	0.230	0.230	0.595	0.597
1.8	1.792	1.150	1.146	0.250	0.250	0.597	0.596
2.0	1.985	1.269	1.263	0.269	0.270	0.599	0.603

$\langle \cdot \rangle$ indicates simulation results.

$\langle \cdot \rangle_{\mathrm{CAN}}$ indicates canonical ensemble theoretical results.

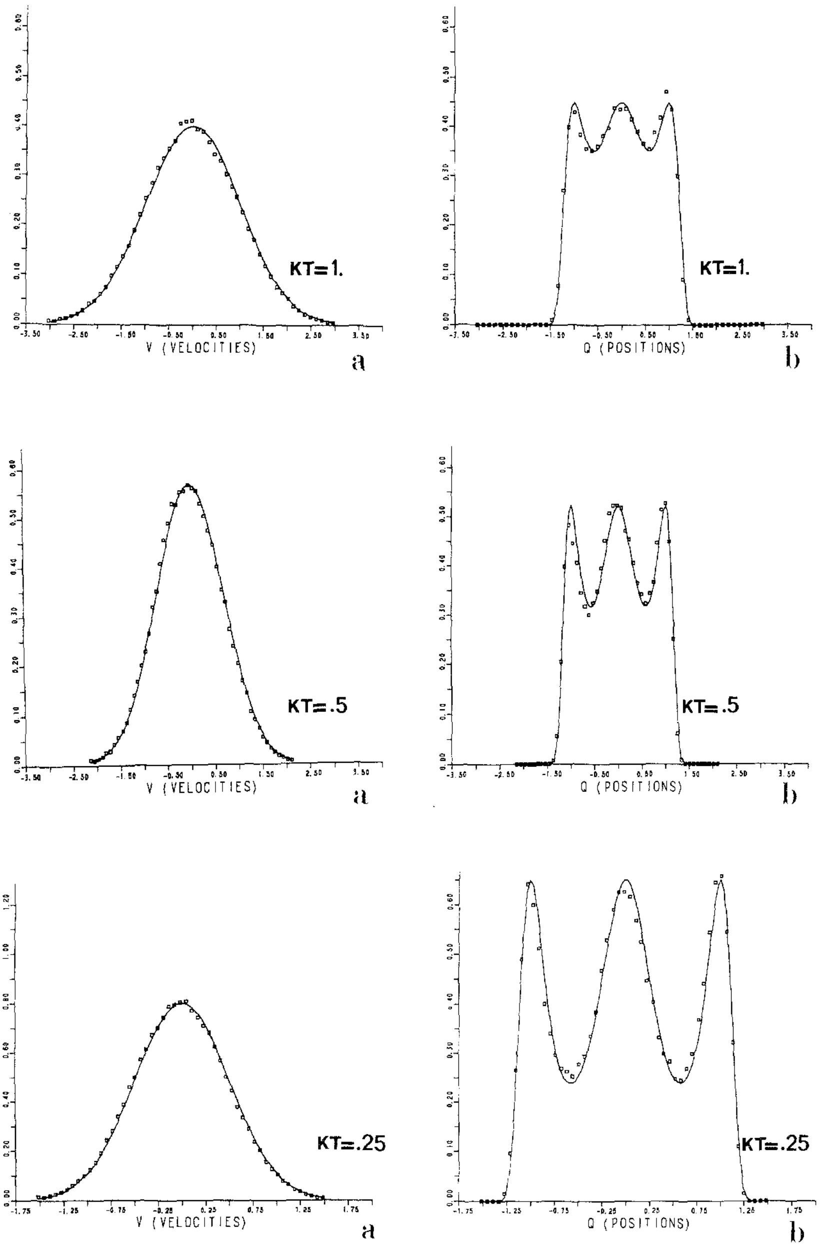

Fig. 2. The particle moves in the external field $\phi(q)=\gamma q^2(q^2-1)^2$, $\gamma=27/4$, $\sigma=\infty$: ☐, computer simulation;—exact result. (a) Velocity distribution; (b) spatial density.

periodic function of the coordinate q. In Ref. 9 an exact expression for $n(q)$ is calculated when the thermodynamic limit is realized by sending only one wall to infinity. This expression for $n(q)$ allows, for any value of s, a display of the state of the system near the fixed boundary. It has been shown$^{(10)}$ that we can identify one-dimensional jellium with a set of identical linear oscillators each bound to a fixed center of atraction coupled by hard elastic collisions (this point of view is strictly equivalent to the concept of crossing). A microcanonical computer code of this system is described in Ref. 10 and surprisingly, in these simulations no periodic structure appears on $n(q)$ for $\lambda \simeq 1$.

It was indicated in this reference that a larger coupling constant should consequently be used. This is what has been done in Figure 3a, where it is evident that the microcanonical dynamics exhibits a poor ergodic behavior owing to the absence of energetic particles (belonging to the tail of the velocity Gaussian distribution). It is precisely the action of those particles which efficiently mix the phase space.

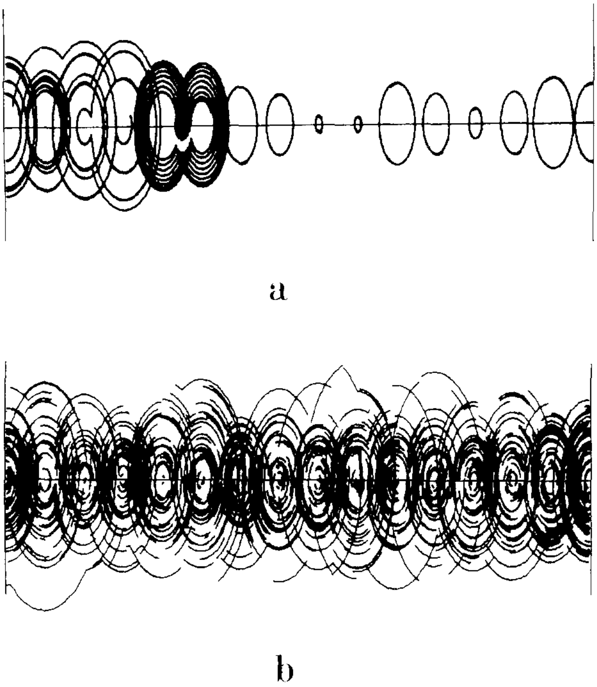

Fig. 3. Computer simulations of one-dimensional jellium with 16 particles λ is a coupling constant and $s = -1$ the excess of charge.$^{(5)}$ Position is plotted horizontally and velocity vertically. (a) Microcanonical dynamics; (b) microcanonical dynamics, particles suffer virtual shocks: $\theta = \infty$, $\lambda = 1$.

An expensive way to improve the statistics is of course to deal with a greater number of particles. On the other hand, using the procedure just described above ($\theta \to \infty$, $KT = \sigma$) in which time intervals between two hits are kept constant, the thermalization process is accelerated by the introduction of the "artificial" shocks as shown in Fig. 3b: each impinging particle is reemited with a new random Gaussian velocity and, globally, this shuffing process prevents the trapping of the phase-space trajectory. Figure 4 illustrates the comparison between the exact statistical behavior of the system in the canonical formalism and the computer simulation: $\lambda = 1$

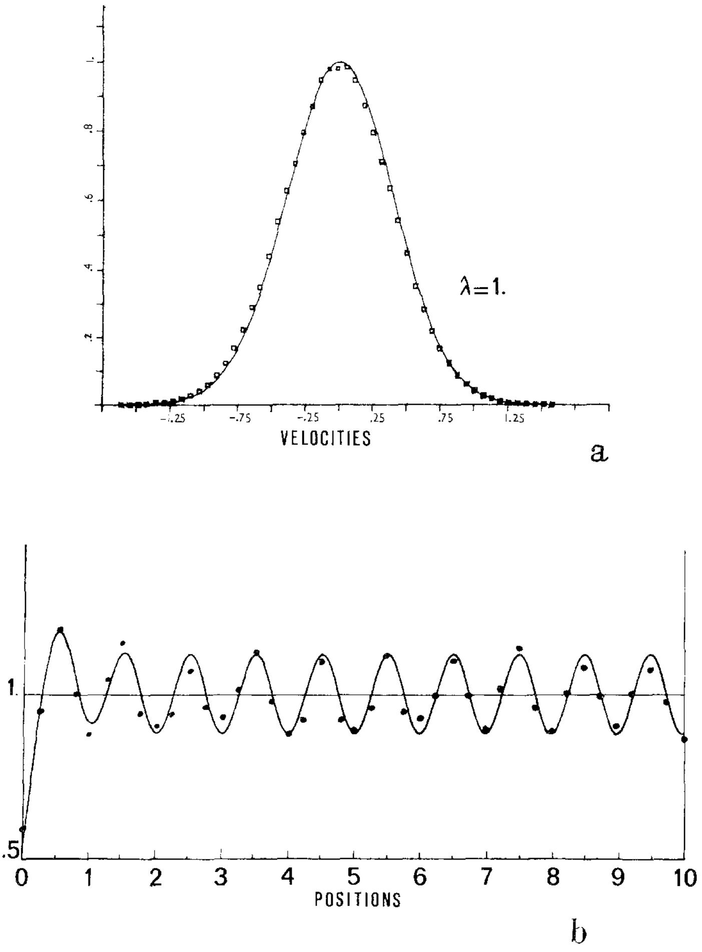

Fig. 4. One-dimensional jellium, 20 particles, $\lambda = 1$, $s = 0$: □, Computer simulation;—, exact result. (a) Velocity distribution; (b) one-particle density function.

and $s=0$. The crystalline state predicted in Ref. 8 and the boundary effect calculated in Ref. 9 (solid line) are confirmed. Notice that this last procedure is nothing else but the generalization of the procedure used in Ref. 9 to study the same problem.

3. THE PHASE PROCESS

Let x be a point in the Γ-phase space

$$x=(v,q)=(\mathbf{v}_1,\ldots,\mathbf{v}_N,\mathbf{q}_1,\ldots,\mathbf{q}_N)$$

Let a canonical trajectory in Γ be defined by

$$x_t=T_t x, \qquad x\in\Gamma \tag{10}$$

where T_t represents the group of transformations governing the dynamics. Let $\rho_n(x)\,dx$ be the probability to find, just after the nth hit, the system inside a volume element dx located at $x\in\Gamma$; then

$$\rho_n(x)=\int_\Gamma dy\rho_{n-1}(y)\,\mathscr{P}(x\mid y) \tag{11}$$

where $\mathscr{P}(x\mid y)$ is the probability density to have a transition from $y=(\bar v,\bar q)$ to $x=(v,q)$. See Fig. 5.

Considering that at each hit the particle coordinates are unchanged but each component of the new velocities are random Gaussian numbers, $\mathscr{P}(x/y)$ can be explicity written

$$\begin{aligned}\mathscr{P}(x\mid y)&=c(\sigma)\,e^{-K(v)/\sigma}\,\delta(q-q_t)\\ q_t&=q(\bar v,\bar q,t), \qquad t=|I_{n-1}|\end{aligned} \tag{12}$$

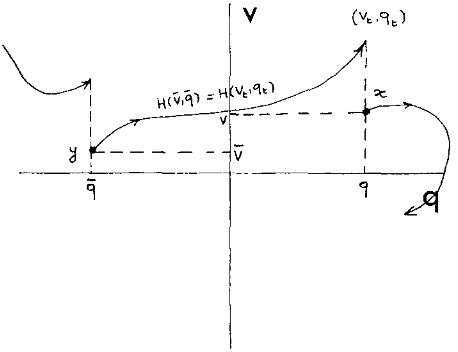

Fig. 5. Phase process.

where $K(v)=(1/2)\sum_{i=1}^{N} v_i^2$ and $c(\sigma)$ is a normalization constant. Introducing (12) in (11), we obtain

$$\rho_n(x) \sim e^{-K(v)/\sigma} \int_{T} dy\, \rho_{n-1}(y)\, \delta(q-q_t) \tag{13}$$

where $t=t[H(y)]$.

Obviously, we can always write

$$\int_{\Gamma} dy\, \rho_{n-1}(y)\, \delta(q-q_t) = \int dE \int_{\Gamma} dy\, \rho_{n-1}(y)\, \delta(q-q_t)\, \delta(E-H(y)) \tag{14}$$

Since the only trajectories considered in the inside integral are such that $H(y)=E$, the t that appears in q_t is just a single number. As the dynamics conserves the total energy, then

$$H(y)=H(y_t) \tag{15}$$

and, consequently, it follows from the Liouville's theorem that

$$dy=dy_t \tag{16}$$

Assuming $\rho_{n-1}(y) \sim e^{-H(y)/\sigma}$, using (14), (15), and (16), the chain equation (13) gives

$$\begin{aligned} \rho_n(x) &\sim e^{-K(v)/\sigma} \int_{\Gamma} dy_t\, e^{-H(y_t)/\sigma}\, \delta(q-q_t) \times \int dE\, \delta(E-H(y_t)) \\ \rho_n(x) &\sim e^{-H(x)/\sigma} \end{aligned} \tag{17}$$

Equation (17) implies that the Boltzmann factor (1) is a stationary solution of (13).

In the following, we shall suppose that it is the only stationary solution. Let $f(x)$ be a state function defined for all $x \in \Gamma$ and let $\langle f \rangle(t)$ be its expectation measured at time $t \in [0, \infty[$. Assume that as $t \to \infty$ the process described above approaches its statistical steady state, then

$$\lim_{t \to \infty} \langle f \rangle(t) = \langle f \rangle$$

where

$$\langle f \rangle = \lim_{M \to \infty} \frac{\sum_{n=0}^{M} \int_{I_n} f(x_t)\, dt}{\sum_{n=0}^{M} |I_n|} \tag{18}$$

x_t, $t \in [t_n, t_{n+1}[$, is the trajectory defined by (10), which starts from the configuration $x_n \in \Gamma$ resulting from the nth virtual shock.

This implies that each integral is a function only of the initial configurations x_n:

$$F(x_n) = \int_{I_n} f(x_t)\,dt \tag{19}$$

Expression (20) becomes

$$\langle f \rangle = \frac{\sum_{n=0}^{\infty} F(x_n)}{\sum_{n=0}^{\infty} |I_n|}$$

So that, assuming the ergodicity of the process,

$$\langle f \rangle = \frac{\int_\Gamma dx\, \rho(x)\, F(x)}{\int_\Gamma dx\, \rho(x)\, |I(x)|} = \frac{N}{D} \tag{20}$$

According to (8) and (17), we have

$$|I(x)| \sim e^{-H(x)/\theta}$$

$$\rho(x) \sim e^{-H(x)/\sigma}$$

From the definition (19) of $F(x)$, we find

$$N = \int_\Gamma dx\, \rho(x) \int_{I(x)} f(T_t x)\, dt$$

and rescaling the time gives

$$N = \int_0^1 d\tau \int_\Gamma dx\, \rho(x)\, |I(x)|\, f(x_\tau)$$

where

$$x_\tau = T_{\tau |I(x)|}\, x$$

Since the energy and volumes of the phase space are conserved during the time interval $I(x)$, then (14)–(16) allow us to write

$$N = \int_\Gamma dx_\tau\, \rho(x_\tau)\, |I(x_\tau)|\, f(x_\tau) \cdot \int_0^1 d\tau$$

Finally,

$$\langle f \rangle = \frac{\int_\Gamma dx\, \rho(x)\, |I(x)|\, f(x)}{\int_\Gamma dx\, \rho(x)\, |I(x)|} = \frac{\int_\Gamma dx\, \exp[-(1/\sigma + 1/\theta)\, H(x)]\, f(x)}{\int_\Gamma dx\, \exp[-(1/\sigma + 1/\theta)\, H(x)]} \tag{21}$$

Expression (17) and (21) prove that the process which is generated introducing virtual shocks in the microcanonical dynamics displays correctly configurations of the phase space according to the Boltzmann factor (1), where the inverse temperature β is given by expression (9).

Notice that the procedure can be modified by disturbing at each hit only a limited set $J = \{j_1, j_2, \dots, j_M\}$ of particles. This extension of the procedure allows us to write the transition probability (12) in the following way:

$$\mathscr{P}(x \mid y) = c(\sigma) \exp\left(-\frac{1}{2\sigma} \sum_{j \in J} \mathbf{V}_j^2\right) \delta(q - \bar{q}_t) \prod_{j \notin J} \delta(\mathbf{v}_j - \bar{\mathbf{v}}_j(t)) \qquad (22)$$

where $\mathbf{v}_j(t) = \mathbf{v}_j(\bar{v}, \bar{q}, t)$.

Introducing (22) in (11), it is easly seen that (17) still holds, for any set J of M particles, $1 \leqslant M \leqslant N$.

4. CONCLUSION

The object of this work was to exhibit an algorithm in which particles suffer "virtual collisions." After a relaxation time, configurations of phase space are visited according to the Boltzmann probability density.

Although the thermodynamical state functions are computed as time-average quantities, we do not claim any contribution to the ergodic problem since the canonical ensemble was forced upon the system. Nevertheless, it is interesting to be able to introduce the canonical ensemble and, more precisely, the temperature through two external parameters The first one is the "temperature σ" of the Gaussian velocity distribution, the second one being the "temperature θ" associated to the time intervals.

These parameters are connected to the inverse temperature β and control the randomness effort which is necessary to allow the escape of the system from trapped situations while keeping eventually the molecular dynamics undisturbed during time intervals which may be chosen arbitrarily long.

ACKNOWLEDGMENT

The author would like to express a gratitude to Joel Feldman and Marc Roy Feix for helpful discussions.

REFERENCES

1. N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, and E. Teller, Equations of state calculations by fast computing machines, *J. Chem. Phys.* **27**:1087–1092 (1953).

2. B. J. Alder and T. E. Wainwright, Studies in molecular Dynamics. I. General method, *J. Chem. Phys.* **31**:459–466 (1959).
3. L. Verlet, Computer experiments in classical fluids. I. Thermodynamical properties of Lennard-Jones molecules, *Phys. Rev.* **159**:98 (1967).
4. T. Schneider and E. Stoll, Molecular-dynamics study at a three-dimensional are-component model for distortive phase transitions, *Phys. Rev. B* **17**:1302–1322 (1978).
5. P. Turq, F. Lantelme, and H. L. Friedman, Brownian dynamics: Its application to ionic solutions, *J. Chem. Phys.* **7**:3039–3044 (1977).
6. H. C. Andersen, Molecular dynamics simulations at constant pressure and for temperature, *J. Chem. Phys.* **72**:2384–2393 (1980).
7. Shüichi Nosé, A molecular dynamics method for simulations in the canonical ensemble, *Mol. Phys.* **52**:255–268 (1984).
8. H. Kunz, The one-dimensional classical electron gas, *Ann. Phys.* (N.Y.) **85**:303–335 (1974).
9. E. Bonomi, E. Jamin, M. Navet, and M. R. Feix, Wall effects in one-dimensional hellium, *Phys. Lett.* **70A**:199–201 (1979).
10. M. R. Feix, M. Navet, and E. Bonomi, Computer experiments in one-dimensional plasma, in *Proceedings of the NATO Advanced Institute of Strongly Coupled Plasmas* (Plenum Press, Nex York, 1977).