

Hard spheres in the isobaric-isoenthalpic ensemble†

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We derive the rules for collisions between hard spheres in arbitrary dimensions in the isobaric-isoenthalpic ensemble. The static and time-dependent properties of the one-dimensional hard rod system are investigated in detail, both theoretically and numerically.

1. INTRODUCTION

Molecular dynamics (MD) simulation methods are an important tool in the study of the equilibrium and dynamical properties of materials. In a 'standard' MD simulation at constant volume and constant energy one solves the classical equations of motion of the interacting particles and obtains the properties one is interested in as time averages. Assuming ergodicity, these equal the corresponding microcanonical ensemble averages. This ensemble is however not always the best for comparison with experiments which are usually carried out at constant pressure and/or temperature. Various methods were therefore developed recently to perform MD simulations in other ensembles: cf. the works of Andersen [1], Woodcock [2], Evans and Morris [3], Nosé [4], Parrinello and Rahman [5].

This paper is concerned with Andersen's method for MD simulations in the isoenthalpic-isobaric (H, P, N) ensemble. In this scheme the volume of the system is a dynamical variable which changes in response to imbalances between the internal and external pressures. There have been many applications of this ensemble to a variety of systems with Lennard-Jones and other potentials, cf. [6, 7].

Until now, however, there have been (to our knowledge) no studies in this ensemble of systems with hard core interactions. To perform simulations of these systems it is first necessary to determine the collision dynamics which, as we shall see, are different from the usual elastic collision rules in the microcanonical ensemble. We do this here and we further test the efficiency of the (H, P, N) ensemble for hard core systems by studying the behaviour of hard rods in one-dimension, both numerically and theoretically.

At constant volume the hard rod system is essentially equivalent to hard points on a line and the thermodynamic as well as some dynamical properties can

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The shortest distance between a pair of particles measured along the torus is just the usual 'minimum image' value, $\min_{\mathbf{n}} \{V^{1/\nu}(\mathbf{q}_i - \mathbf{q}_j) + \mathbf{n}V^{1/\nu}\}$. The total kinetic energy of the system of N particles is then

$$\sum_{i=1}^N \frac{m}{2} \dot{\mathbf{R}}_i \cdot \dot{\mathbf{R}}_i = V^{2/\nu} \sum_{i=1}^N \frac{m}{2} \dot{\mathbf{q}}_i \cdot \dot{\mathbf{q}}_i + \frac{mN}{2(2\pi)^2 V^2} V^{2/\nu} \frac{\dot{V}^2}{V^2}. \quad (3)$$

The second term in the right-hand side of (3) depends only on the volume and can be absorbed in the driving term that one has to add by hand anyway. Note that, while this correction is small in three dimensions or more, it is non-negligible in one and two dimensions.

The hamiltonian corresponding to the Andersen lagrangian is

$$H_A(\mathbf{q}_i, \boldsymbol{\pi}_i, V, \Pi) = \frac{1}{V^{2/\nu}} \sum_{i=1}^N \frac{\pi_i^2}{2m} + \sum_{i<j} u(V^{1/\nu} |\mathbf{q}_i - \mathbf{q}_j|) + \frac{\Pi^2}{2M} + P_E V.$$

The (real) momenta \mathbf{p}_i are then related to the scaled momenta $\boldsymbol{\pi}_i$ by

$$\mathbf{p}_i = \frac{\boldsymbol{\pi}_i}{V^{1/\nu}}.$$

The hamiltonian and $\sum_{i=1}^N \boldsymbol{\pi}_i$ (but not $\sum_{i=1}^N \mathbf{p}_i$) are constants of the motion.

To understand the behaviour of the system when $N \rightarrow \infty$ it is useful to consider the following canonical transformation:

$$\begin{aligned} \tilde{\mathbf{q}}_i &= N^{1/\nu} \mathbf{q}_i, & v &= \frac{V}{N}, \\ \tilde{\boldsymbol{\pi}}_i &= N^{-1/\nu} \boldsymbol{\pi}_i, & \tilde{\Pi} &= \Pi N. \end{aligned}$$

This rescaling has the advantage that both v and $\tilde{\boldsymbol{\pi}}_i$ remain of order unity as $N \rightarrow \infty$. The hamiltonian now reads

$$\begin{aligned} H_A(\tilde{\mathbf{q}}_i, \tilde{\boldsymbol{\pi}}_i, v, \tilde{\Pi}) &= N \left\{ \frac{1}{v^{2/\nu}} \frac{1}{N} \sum_{i=1}^N \frac{\tilde{\pi}_i^2}{2m} \right. \\ &\quad \left. + \frac{1}{N} \sum_{i<j} u(v^{1/\nu} |\tilde{\mathbf{q}}_i - \tilde{\mathbf{q}}_j|) + \frac{\tilde{\Pi}^2}{2MN^3} + P_E v \right\} \quad (4) \end{aligned}$$

and relation (2 b) becomes

$$\mathbf{p}_i = \frac{\tilde{\boldsymbol{\pi}}_i}{v^{1/\nu}}. \quad (5)$$

Note that $\tilde{\Pi}^2/2MN^3 = \frac{1}{2}NM|\dot{v}|^2$. Therefore, as $N \rightarrow \infty$ with H_A/N held constant, we see that \dot{v} scales as $1/\sqrt{N}$, provided the potential u is stable (i.e. $\forall N$ and $\forall x_i \in \mathbb{R}^{\nu} : \sum_{1 \leq i < j \leq N} u(x_i - x_j) \geq -C^{\text{ste}}N$ for some $C^{\text{ste}} \geq 0$). On the other hand, the particle equations of motion are

$$\begin{aligned} \frac{d\tilde{\mathbf{q}}_i}{dt} &= \frac{\tilde{\boldsymbol{\pi}}_i}{mv^{2/\nu}}, \\ \frac{d\tilde{\boldsymbol{\pi}}_i}{dt} &= -v^{1/\nu} \sum_{j \neq i} \nabla u(v^{1/\nu} |\mathbf{q}_i - \mathbf{q}_j|). \end{aligned}$$

For short range potentials the equations of motion of the particles are independent of N . Thus we identify two time scales; one at which the particles interact and a second over which the volume changes, which is \sqrt{N} slower.

In the sequel, we will continue using the hamiltonian (4) but will drop the superscript tilde for convenience.

Assuming Andersen's ergodic-like hypothesis [1] leads us to the following appealing interpretation of the applied external pressure, P_E ([10]). Consider the equation determining the motion of the volume: take its time average and then replace the time average by a canonical average to yield

$$P_E = \frac{1}{\bar{v}\beta} - \frac{1}{\bar{v}} \frac{1}{N} \sum_{i < j} \langle (\mathbf{r}_i - \mathbf{r}_j) \cdot \nabla u(\mathbf{r}_i - \mathbf{r}_j) \rangle_{\text{can}} + \text{correction terms}, \quad (6)$$

where \bar{v} denotes the average volume per particle and β denotes the inverse temperature. As $N \rightarrow \infty$ the correction terms tend to zero and hence, in this limit, P_E is equal to the virial pressure (which is defined by the first two terms of the RHS of (6)).

3. THE HARD SPHERE GAS IN THE CONSTANT PRESSURE ENSEMBLE

For convenience, we first treat the case of hard spheres in 3 dimensions. In the absence of collisions, the equations of motion read

$$\dot{\mathbf{q}}_i(t) = \frac{\boldsymbol{\pi}_i(t)}{mv(t)^{2/3}}, \quad \dot{\boldsymbol{\pi}}_i(t) = 0, \quad (7a-b)$$

$$MN \frac{d^2 v}{dt^2}(t) = -P_E + \frac{2}{3v(t)^{5/3}} \frac{1}{N} \sum_{i=1}^N \frac{\boldsymbol{\pi}_i^2(t)}{2m}. \quad (7c)$$

Thus the scaled momenta $\boldsymbol{\pi}_i$ are constant between collisions. The collision rules can be obtained by considering the following potential:

$$U_\varepsilon(r) = \frac{a-r}{\varepsilon} \theta(a-r).$$

$\theta(x)$ is the Heavyside function:

$$\left. \begin{aligned} \theta(x) &= 0, & \text{if } x < 0, \\ \theta(x) &= 1, & \text{if } x \geq 0. \end{aligned} \right\} \quad (8)$$

The hard sphere potential is recovered in the limit $\varepsilon \rightarrow 0$. Assume that particles 1 and 2 begin to interact at time t_1 , i.e.

$$\text{and } \left. \begin{aligned} |v(t_1)^{1/3}(\mathbf{q}_1 - \mathbf{q}_2)(t_1)| &= a \\ \frac{d}{dt} (v(t)^{1/3} |(\mathbf{q}_1 - \mathbf{q}_2)(t)|) \Big|_{t_1} &< 0. \end{aligned} \right\} \quad (9)$$

Assume moreover that no 2 other particles collide while these particles interact. (The probability for simultaneous collisions tends to zero in the limit $\varepsilon \rightarrow 0$).

It is easy to show that $\boldsymbol{\pi}_1 + \boldsymbol{\pi}_2$ is constant during the collision. Therefore it suffices to determine the change in $\boldsymbol{\pi}_1 - \boldsymbol{\pi}_2$. Put

$$q_{2x} - q_{1x} = r \sin \theta \cos \phi,$$

$$q_{2y} - q_{1y} = r \sin \theta \sin \phi,$$

$$q_{2z} - q_{1z} = r \cos \theta.$$

(Assume that $\theta(t_1) \neq 0$: if not, interchange the role of x and z variables.) In terms of these variables, the equations of motion during the collision are:

$$\frac{mv^{2/3}}{2} \frac{d^2 r}{dt^2} = \frac{v^{1/3}}{\varepsilon} + C_1(t), \tag{10 a}$$

$$MN^2 \frac{d^2 v}{dt^2} = \frac{1}{3\varepsilon} \frac{r}{v^{2/3}} + C_2(t), \tag{10 b}$$

$$\frac{d}{dt} \left(r^2 \frac{d\theta}{dt} \right) = 0, \quad \frac{d}{dt} \left(r^2 \sin^2 \theta \frac{d\phi}{dt} \right) = 0 \tag{10 c-d}$$

where the functions $C_1(t)$, $C_2(t)$ can be bounded by a constant independent of ε . Integrating equations (10 a-b) from t_1 up to $t \equiv t_1 + \varepsilon \bar{t}$, we find

$$r(t) = r(t_1) + \varepsilon \left\{ \dot{r}(t_1) \bar{t} + \frac{\bar{t}^2}{mv(t_1)^{1/3}} \right\} + O(\varepsilon^2), \tag{11 a}$$

$$v(t) = v(t_1) + \varepsilon \left\{ \dot{v}(t_1) \bar{t} + \frac{a \bar{t}^2}{6MN^2 v(t_1)} \right\} + O(\varepsilon^2). \tag{11 b}$$

Equations (11) hold as long as $v^{1/3}(t)r(t) \leq a$, i.e. as long as $\bar{t} \leq \bar{t}_c + O(\varepsilon)$, where

$$\bar{t}_c = \frac{-m \left\{ \dot{r}(t_1)v(t_1)^{1/3} + \frac{1}{3} \frac{a\dot{v}(t_1)}{v(t_1)} \right\}}{\left\{ 1 + \frac{ma^2}{18MN^2(v(t_1))^2} \right\}}. \tag{12}$$

Note that $\bar{t}_c > 0$ by assumption (9). Letting $\varepsilon \rightarrow 0$, we find that the positions of the particles do not change during the collision, and that the velocities are affected in the following way:

$$\left. \begin{aligned} \dot{r}' &= \dot{r} + \frac{2}{mv^{1/3}} \bar{t}_c, \\ \dot{v}' &= \dot{v} + \frac{a}{3MN^2 v} \bar{t}_c, \\ \theta' &= \theta, \quad \phi' = \phi. \end{aligned} \right\} \tag{13}$$

\bar{t}_c is given by (12) and primes denote quantities after the collision. Relations (13) are easily transformed into relations for the original \mathbf{q}_i , $\boldsymbol{\pi}_i$. We give the result in arbitrary dimension v . Let

$$\bar{t}_c = \frac{- \left\{ \frac{(\boldsymbol{\pi}_2 - \boldsymbol{\pi}_1) \cdot (\mathbf{q}_2 - \mathbf{q}_1)}{a} + \frac{1}{v} \frac{a\dot{v}}{v} \right\}}{\left\{ 1 + \frac{ma^2}{2v^2 MN^2 v^2} \right\}}. \tag{14}$$

Then

$$\boldsymbol{\pi}'_2 - \boldsymbol{\pi}_2 = \frac{\bar{t}_c v^{2/v} (\mathbf{q}_2 - \mathbf{q}_1)}{a} = -(\boldsymbol{\pi}'_1 - \boldsymbol{\pi}_1) \tag{15 a}$$

$$\dot{v}' - \dot{v} = \frac{\bar{t}_c a}{vMN^2 v}. \tag{15 b}$$

In each collision, the value of \dot{v} therefore *increases* by a factor $1/N^2$, while the kinetic energy of the particles decreases or increases depending on whether the volume was expanding or contracting at the time of the collision.

Now, in the absence of collisions, \dot{v} changes typically by an amount $\sim 1/\sqrt{N}$ in a time period of order \sqrt{N} (see (7c)). During this time span, there will be on the average $\sim N^{3/2}$ collisions, each increasing \dot{v} by a factor $1/N^2$. Thus one sees that the effect of collisions on v is non-negligible.

It should be noted that the collision equations (15) remain valid when a soft potential is added to the hard core. We see from (15) that, as $a \rightarrow 0$, so does $\dot{v}' - \dot{v}$ and the change in kinetic energy. This is unimportant for $\nu > 1$, where $a \rightarrow 0$ implies the same for the frequency of collisions. (One recovers the ideal gas result in this case; see Appendix for a discussion of the ideal gas in the (HPN) ensemble.) In dimensions $\nu = 1$, we can however distinguish between the hard point ($a = 0$) and the ideal gas case. In the next section, we discuss some results for the (HPN)-MD simulations for hard rods in one dimension.

4. THE (HPN)-MD METHOD FOR HARD RODS IN ONE DIMENSION

It is well known that in the usual ensembles, the hard point gas ($a = 0$) and the hard rod case ($a \neq 0$) are completely equivalent. Any quantity obtained for the hard point gas can be transformed into the corresponding quantity for the hard rod gas by replacing the density ρ by $\rho/(1 - \rho a)$. In a constant pressure ensemble, these two systems are not equivalent. When $a = 0$, the collision rules reduce to

$$\pi'_1 = \pi_2, \quad \pi'_2 = \pi_1, \quad \dot{v}' = \dot{v}. \quad (16a)$$

It follows that

$$K \equiv \frac{1}{N} \sum_{i=1}^N \frac{\pi_i^2}{2m}$$

is a constant of the motion and that the volume per particle v satisfies

$$MN \frac{d^2v}{dt^2} = -P_E + \frac{2K}{v^3}. \quad (16b)$$

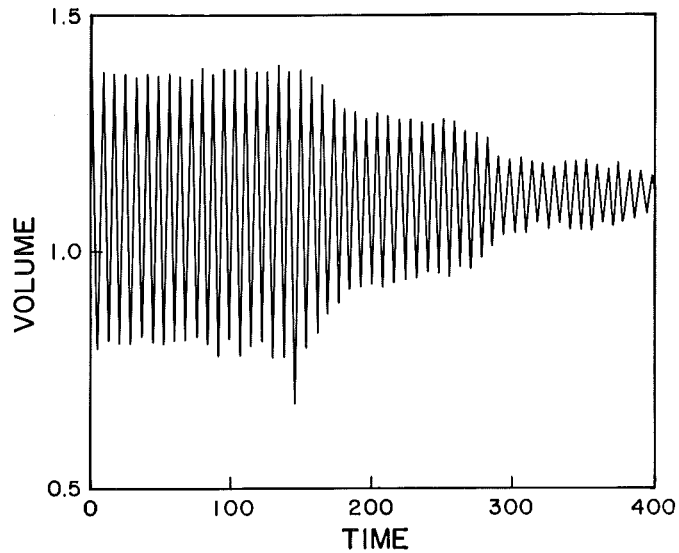
Equation (16b) has a stationary solution v_0 satisfying: $P_E v_0 = 2K/v_0^2$ which in terms of the real momenta p_i reads

$$P_E v_0 = \frac{2}{N} \sum_{i=1}^N \frac{p_i^2}{2m}.$$

This is simply the equation of state of the hard point gas [8]. Any other initial value of v , v_{in} , leads however to a periodically oscillating volume.

When $a \neq 0$, the situation is different. In this case there is no stationary solution for v , but, with a suitably chosen v_{in} , oscillations are small. Other v_{in} s lead to large fluctuations which however damp out at large times (figure). We now quantify the above remarks. It is convenient to introduce the two time scales t and $\tau = t/\sqrt{N}$. Define

$$\bar{v}(\tau) = v(t) \quad \text{and} \quad \bar{K}(\tau) = \frac{1}{N} \sum_{i=1}^N \frac{\pi_i^2}{2m}(t).$$



Typical evolution of the volume per particle when the hard core diameter is different from zero and either the initial volume per particle does not satisfy the equation of state or $\dot{v}(0) \neq 0$. The actual parameters used in this simulation are: $N = 50$, $a = 0.2$, $v(0) = 1.2$, $\dot{v}(0) = 0.2$, $P_E = 1$, $M = 0.1$ and $m = 1$. The initial velocities of the particles are gaussianly distributed with

$$\sum_{i=1}^N \pi_i = 0 \quad \text{and} \quad \frac{1}{2m} \sum_{i=1}^N \pi_i^2 = 0.4.$$

Over the time interval shown, each particle has collided about 200 times (the units are arbitrary but self-consistent).

Equations (7) and (15) can be combined into equations valid for all times. For instance, the equation for \bar{v} can be written as

$$\begin{aligned} \frac{Md^2\bar{v}(\tau)}{d\tau^2} = & -P_E + \frac{2}{(\bar{v}(\tau))^3} K(\tau) + \frac{a\bar{c}_N(\tau)}{(\bar{v}(\tau))^3 Nm} \sum_{1 \leq i < j \leq N} \\ & \times \left\{ (\pi_i - \pi_j)(t) + \frac{ma}{\sqrt{N}} \frac{d\bar{v}(\tau)}{d\tau} (-1)^{\alpha_{ij}} \right\}^2 \delta(a - \bar{v}(\tau) |q_i(t) - q_j(t)|) \end{aligned}$$

with

$$\alpha_{ij} = 0 \quad \text{if} \quad (q_i - q_j)(t) > 0,$$

$$\alpha_{ij} = 1 \quad \text{if} \quad (q_i - q_j)(t) < 0,$$

and

$$\bar{c}_N(\tau) = 1 \left/ \left(1 + \frac{ma^2}{2MN^2(\bar{v}(\tau))^2} \right) \right.$$

It is useful to average these equations over all possible initial configurations in the set A_N where $A_N = \{(q_1, \dots, q_N) \in \mathbb{R}^N \mid q_i \in [0, N] \text{ and } \min_{i \neq j} \{|q_i - q_j|\},$

$|q_i - q_j \pm N| \geq [a/\bar{v}(0)]$. Studying these averaged equations around $t = \tau = 0$, one finds (denoting the average by $\langle \cdot \rangle_{\text{av}}$)

$$\left. \frac{Md^2 \langle \bar{v}(\tau) \rangle_{\text{av}}}{d\tau^2} \right|_{\tau=0} = -P_E + \frac{2\bar{K}(0)}{\bar{v}(0)^2(\bar{v}(0) - a)} - \frac{a\pi_{cm}^2}{\bar{v}(0)^3(\bar{v}(0) - a)m} + O\left(\frac{1}{\sqrt{N}}\right) \quad (17a)$$

$$\left. \frac{d \langle \bar{K}(\tau) \rangle_{\text{av}}}{d\tau} \right|_{\tau=0} = \frac{+2a\left(\frac{\pi_{cm}^2}{2m} - \bar{K}(0)\right) \frac{d\bar{v}(0)}{d\tau}}{\bar{v}(0)(\bar{v}(0) - a)} + O\left(\frac{1}{\sqrt{N}}\right) \quad (17b)$$

where

$$\pi_{cm} = \frac{1}{N} \sum_{i=1}^N \pi_i.$$

One also verifies that

$$\frac{d^2}{d\tau^2} (\langle \bar{v}^2(\tau) \rangle_{\text{av}} - \langle \bar{v}(\tau) \rangle_{\text{av}}^2)_{\tau=0} = O\left(\frac{1}{N}\right), \quad (18a)$$

$$\frac{d}{d\tau} (\langle \bar{K}^2(\tau) \rangle_{\text{av}} - \langle \bar{K}(\tau) \rangle_{\text{av}}^2)_{\tau=0} = O\left(\frac{1}{N}\right). \quad (18b)$$

Equations (17a)–(18b) imply that for the volume \bar{v} to be satisfactory in the limit $N \rightarrow \infty$, it has to satisfy the equation

$$P_E = \frac{2\bar{K}}{\bar{v}^2(\bar{v} - a)} - \frac{a\pi_{cm}^2}{\bar{v}^3(\bar{v} - a)m}.$$

When the momenta $p_i = \pi_i/\bar{v}$ have a maxwellian distribution at temperature T , we recover the equation of state for hard rods [8]

$$P_E(\bar{v} - a) = kT. \quad (19)$$

With \bar{v}_{in} satisfying (19), one sees only small fluctuations in the volume at finite N . For other choices of \bar{v}_{in} , one sees larger fluctuations which persist over long times, but eventually decrease (see the figure). We believe that this damping of the oscillations only occurs after times which are large compared to \sqrt{N} . Indeed, suppose that equations (17)–(18) actually hold for all times and suppose that we could take the limit $N \rightarrow \infty$. The volume \bar{v} would then satisfy (assuming that $\lim_{N \rightarrow \infty} \pi_{cm} = 0$)

$$\frac{Md^2 \bar{v}(\tau)}{d\tau^2} = -P_E + \frac{2\bar{K}(\tau)}{(\bar{v}(\tau))^2(\bar{v}(\tau) - a)}. \quad (20)$$

The conservation of the hamiltonian yields

$$\frac{M}{2} \left(\frac{d\bar{v}(\tau)}{d\tau} \right)^2 + P_E \bar{v}(\tau) + \frac{\bar{K}(\tau)}{(\bar{v}(\tau))^2} = C_1. \quad (21)$$

Combining (20)–(21), one obtains the following equation for

$$\left. \begin{aligned} \bar{v}_a(\tau) &= \bar{v}(\tau) - a, \\ \frac{M}{2} \frac{d^2(\bar{v}_a(\tau))^2}{d\tau^2} &= 2(C_1 - P_E a) - 3P_E \bar{v}_a(\tau). \end{aligned} \right\} \quad (22)$$

The solutions of (22) are periodically oscillating functions. We conclude that there is no damping at timescales of order \sqrt{N} .

4.1. Velocity correlation functions

We have studied the velocity-velocity autocorrelation function for the hard rod system in the (HPN)-ensemble. For a system of 50 particles and volume oscillations of order 10 per cent, we find agreement with the usual microcanonical results [9], (up to statistical precision), at least for small times. Accurate results for the long time tail are difficult to obtain numerically. For this reason it is hard to obtain a reliable estimate of the diffusion constant and we have not attempted to calculate this quantity in the (HPN)-ensemble.

5. REMARKS

(1) One interesting question is the following. Assume that the initial momenta are chosen randomly according to the probability law $\frac{1}{2}\{\delta(\pi_i - c) + \delta(\pi_i + c)\} d\pi_i$. Is there a limiting stationary distribution and is it maxwellian? Clearly in the case of hard points the initial distribution does not change (see (16 a)). The case $a \neq 0$ is less obvious and we will present only a partial answer. For $c = 1$, $a = 0.2$ and the density $\rho = 1$, we verified that the distribution changes only very slowly. In fact, the following argument shows that for times of the order $N^{1-\delta}$ ($\delta > 0$), no significant spread in the distribution is seen and only for times of the order N can one expect the spread to become important. Follow, instead of a particle, a pulse through the system. In each collision the momentum of a pulse changes by an amount

$$\frac{am}{\sqrt{N}} \frac{d\bar{v}}{d\tau} \left(+O\left(\frac{1}{N^2}\right) \right), \quad \text{i.e. by an amount } \sim \frac{1}{\sqrt{N}}. \quad (23)$$

On the other hand, if $N_c(t)$ denotes the number of collisions encountered by a pulse during the time interval $[0, t]$, one can show that

$$\{\langle N_c(t)^2 \rangle - \langle N_c(t) \rangle^2\} \sim t \quad (24)$$

for t large (but not so large that the pulse will have travelled a macroscopic distance in the box). The average here is over the initial position of the particles. (23) implies that the momentum of the pulse will oscillate with the same period as the volume. On the other hand, deviations between the momentum of two pulses travelling in the same direction can be bounded using (23) by the difference in the number of collisions encountered by the two pulses multiplied by a C^{ste}/\sqrt{N} . By (24) this product will be of the order $N^{-\delta/2}$ for the time periods of the order $N^{1-\delta}$, proving the statement.

(2) In the microcanonical ensemble it is particularly easy to perform hard sphere MD simulations. The trajectories can be calculated to machine precision and the use of collision tables greatly reduces the computational effort [11]. However in the (HPN) ensemble there is no simple analytic formula for the times between collisions. In addition one cannot use a collision list since after each collision the time evolution of the volume changes. The time to all future collisions is then modified in a non-simple way. The simulation of hard spheres in the

(HPN) ensemble is therefore of the same complexity as the simulation of systems with hard cores plus soft potentials in the (NVE)-ensemble.

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APPENDIX

(HPN)-MD method for the ideal gas

It is easily verified that, for the ideal gas,

$$K \equiv \frac{1}{N} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}$$

is a constant of the motion. The volume satisfies the following equation:

$$NM \frac{d^2 v(t)}{dt^2} = \left\{ \frac{2K}{v(v(t))^{1+2/v}} - P_E \right\}. \quad (\text{A } 1)$$

For each value of K , there exists a stationary solution for the volume, satisfying

$$P_E v = \frac{2}{v} \frac{K}{v^{2/v}},$$

which in terms of the real momenta \mathbf{p}_i reads

$$P_E v = \frac{2}{v} \frac{1}{N} \sum \frac{\mathbf{p}_i^2}{2m}. \quad (\text{A } 2)$$

This is exactly the ideal gas law. If another starting value for v is chosen, then the volume will oscillate with a period proportional to $\sqrt{(MN)}$. In this case a discrepancy will be observed between the internal pressure P_{INT} and the external pressure P_E . Indeed, denoting the time average by $\langle \cdot \rangle_{\text{time}}$, we find

$$P_E = \frac{2}{v} K \left\langle \frac{1}{v(t)^{1+2/v}} \right\rangle_{\text{time}}, \quad (\text{A } 3 \text{ a})$$

while, using the virial, we find

$$P_{\text{INT}} = \frac{2}{v} K \left\langle \frac{1}{v(t)} \right\rangle_{\text{time}} \left\langle \frac{1}{v(t)^{2/v}} \right\rangle_{\text{time}}. \quad (\text{A } 3 \text{ b})$$

One easily verifies that (A 3 a) differs from (A 3 b) for small oscillations, and this discrepancy will even hold in the thermodynamic limit.

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