# Molecular dynamics of one-dimensional hard rods*

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(Received 4 August 1972)

The validity of computer experiments is tested by comparisons between exact one-dimensional hard-rod calculations and molecular dynamics experiments with 1000 hard rods. The computer results are shown to agree with exact values of the pressure, pair-correlation function, velocity autocorrelation function, and the diffusion coefficient.

## INTRODUCTION

While the basic formalism of statistical mechanics has been extended to many areas, the number of problems which can be solved exactly, remains small. Yet, a number of seemingly intractable problems of the three-dimensional world become amenable to analysis when recast in one dimension.[1] One-dimensional investigations can be used as a testing ground for approximations.

The development of computers has provided an alternative method for attacking the $N$-body problem. Starting with an interaction potential and an initial configuration, Newton's equations of motion are integrated to generate a trajectory in phase space. Equilibrium and time correlation functions are then determined by time-averaging properties over this trajectory. Computer experiments are done on finite systems, albeit with periodic boundary conditions. Moreover, the averaging is done over finite times, rather than the infinite times required by statistical mechanics. In this paper we investigate these limitations by comparing computer experiments on a one-dimensional system of hard rods with the exact analytical solution of this system.

## COMPARISON OF "THEORY" AND "EXPERIMENT"

The hard rod (HR) potential has the form

$$U(x) = \infty \quad x < 1$$
$$= 0 \quad x > 1 \ , \tag{1}$$

where the positions are measured in units of the hard rod length $\sigma$. The equations of motion for a finite system consisting of $N = 1000$ rods are solved by the method described in Appendix A. The number density of the one-dimensional fluid is 0.935 in reduced units or 0.2746 Å$^{-1}$.

In this section we examine a number of properties in order to test the reliability of the machine calculations.

One of the important properties of a liquid is its pair correlation function $g(R)$. This function can be obtained exactly for a periodic one-dimensional system of hard rods in the length $L$. The derivation of $g(R)$ is given in Appendix B. It is found that

$$g(R) = 0 \ , \qquad R < \sigma \ ,$$
$$g(R) = l \sum_{N_1=0}^{N-2} \frac{[R-(N_1+1)\sigma]^{N_1}\{1-[R-(N_1+1)\sigma]/N(l-\sigma)\}^{N-N_1-2}(N-1)!}{N_1!(N-N_1-2)!(l-\sigma)^{N_1+1}N^{N_1+1}} \ , \quad R \geq \sigma \ , \tag{2}$$

where $l = L/N$, $\sigma$ is the hard rod diameter, and the summation is carried out up to terms for which $R - (N_1 + 1)\sigma > 0$. $g(R)$ has been determined on the computer for $N = 1000$ from the HR trajectory data by a direct counting method. To compute $g(R)$, we count the number of rods in the interval $\Delta R$ at a distance $\pm R$ from the reference rod. $g(R)$ was averaged over 600 time origins of data as well as 1000 particles. The $\Delta R$ spacing was taken as $0.01\sigma$. A comparison between the machine calculation and Eq. (2) for the same mesh size is displayed in Fig. 1. The agreement is excellent.

Equation (2) gives the value of $g(R)$ at contact $g(\sigma)$,

$$g(\sigma) = \frac{(1 - 1/N)}{(1 - N\sigma/L)} \ . \tag{3}$$

For our conditions, this expression gives $g(\sigma) = 15.37$ but for a spacing of $\Delta R = 0.01\sigma$ the machine results gave $g(\sigma) = 13.18$. Since $g(R)$ is very narrow around $1\sigma$ (see Fig. 1) it is necessary to recompute $g(R)$ with a fine mesh in order to determine $g(\sigma)$. If this is not done it is possible that a higher value of $g(R)$ would be overlooked if it fell between mesh points. $g(R)$ was recomputed for $\Delta R = 0.0001\sigma$; $g(\sigma)$ was then found to be 15.08 demonstrating the difficulty in the determination of accurate values of the contact pair correlation function.

The pressure equation of state for a hard rod system is

$$PL/NkT = 1 + ng(\sigma)\sigma \ , \tag{4}$$

where $n = N/L$. From Eq. (4), the machine $g(\sigma)$(15.08), and our thermodynamic conditions (see Appendix A), we find that $P_g = 5.045 \times 10^{-6}$ dyn. This should be compared to the exact pressure $P_e = 5.136 \times 10^{-6}$ dyn and the collision pressure $P_c = 5.176 \times 10^{-6}$ dyn (see Appendix B). The $g(\sigma)$ from Eq. (3)(15.37) gives $P_g = 5.136 \times 10^{-6}$ dyn. All of these numbers are consistent within machine error.

The dynamics of HR systems has been studied by several investigators. Jepsen[2] was able to obtain a closed expression for the diffusion coefficient, $D$, if the initial velocity distribution was Maxwellian. Another interest-

  

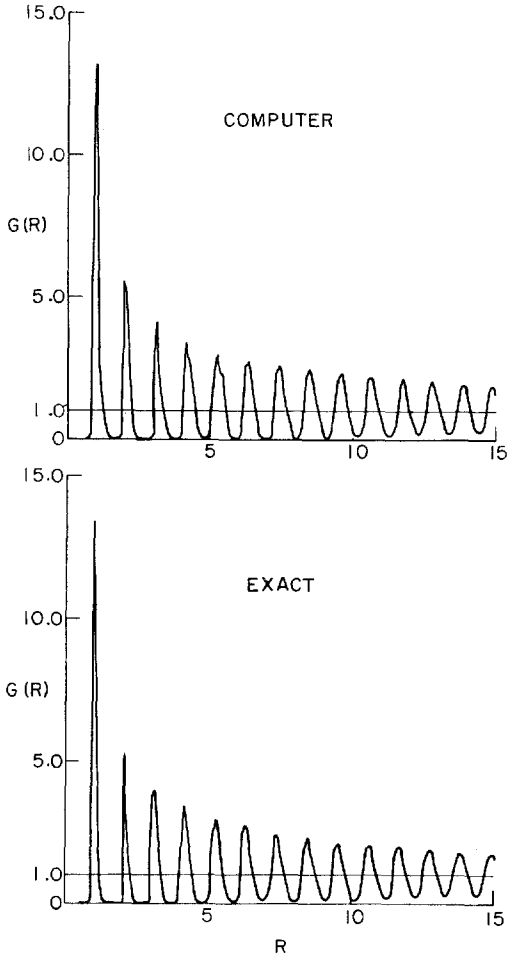


FIG. 1. Comparison between the machine pair correlation function and the exact one. $R$ is in units of $\sigma$.

ing result found by Jepsen was the asymptotic decay of the velocity autocorrelation function of a labeled particle $\langle V_0(t)V_0(0)\rangle$. It decays as $t^{-3}$ in contradistinction to the $t^{-d/2}(d=2, 3)$ dependence found by other workers[3] in two and three dimensions. Furthermore, the tail is negative whereas in two and three dimensions it is positive. Lebowitz *et al.*[4] have extended Jepsen's results to an infinite system of rods with diameter $\sigma$. Lebowitz *et al.* find that the normalized velocity autocorrelation function, $\psi(t)$, can be almost perfectly represented by

$$\psi(t) = \exp[-4nt/(1-n\sigma)(\pi m\beta)^{1/2}] . \tag{5}$$

Here $n$ is the number density, $m$ the particle mass, and $\beta = 1/kT$. The exact $\psi(t)$ disagrees with this expression for

$$t \geq (\pi\beta m)^{1/2}(1-\sigma n)/n , \tag{6}$$

where the exact $\psi(t)$ becomes negative and very small ($\approx -6\times10^{-3}$). In our units this time is $\approx 31$ steps but the computer calculations are not accurate enough to detect the tiny negative region.

We have determined $\psi(t)$ from the HR trajectory information by using the following averaging procedure:

$$\psi(t) = \frac{(N_p N_t)^{-1}\sum_{j=1}^{N_p}\sum_{i=1}^{N_t} V_j(t+i)\,V_j(i)}{(N_p N_t)^{-1}\sum_{j=1}^{N_p}\sum_{i=1}^{N_t} V_j(i)\,V_j(i)} , \tag{7}$$

where $N_p = 1000$ (the number of particles) and $N_t = 400$ (the number of time origins). The exact and machine results are presented in Fig. 2. The agreement is very good. However, in order to see the $t^{-3}$ decay it would be necessary to do an exceedingly accurate calculation for a long time and so this interesting property cannot be investigated with our data. In fact our $\psi(t)$ has a positive noisy tail for times larger than $4\times10^{-13}$ sec.

Lebowitz and co-workers have also determined $D$,

$$D_{\text{exact}} = (1-n\sigma)/n(2\pi\beta m)^{1/2} . \tag{8}$$

For our conditions $D_{\text{exact}} = 1.28\times10^{-5}$ cm$^2$/sec. The diffusion coefficient can be determined in two ways from the dynamics:

(1) Integrating $\psi(t)$ via the Green–Kubo relation,

$$D_{gk} = \langle v^2\rangle \int_0^\infty dt\,\psi(t) . \tag{9}$$

(2) Finding the slope of the mean-square displacement vs time and using the Einstein formula,

$$D_s = (1/2t)\langle[x(t)-x(0)]^2\rangle . \tag{10}$$

A Simpson integration of the machine $\psi(t)$ up to the point at which the exponential went to zero gave $D_{gk} = (1.42\pm.01)\times10^{-5}$ cm$^2$/sec. From Lebowitz's exponential expression, $D$ exponent was found to be $1.42\times10^{-5}$ cm$^2$/sec. These results are expected to be larger than the exact value because the negative tail has been neglected. The mean-square displacement gives further evidence of the "noisy" tail effects in the machine $\psi(t)$. For short times there is excellent agreement between $\langle\Delta X^2\rangle$ determined directly on the computer from the dynamics and $\langle\Delta X^2\rangle$ found by substituting the exponential approximation for the exact $\psi(t)$ into

$$\langle\Delta x^2(t)\rangle = 2\int_0^t dt(t-\tau)\psi(\tau)\langle v^2\rangle . \tag{11}$$

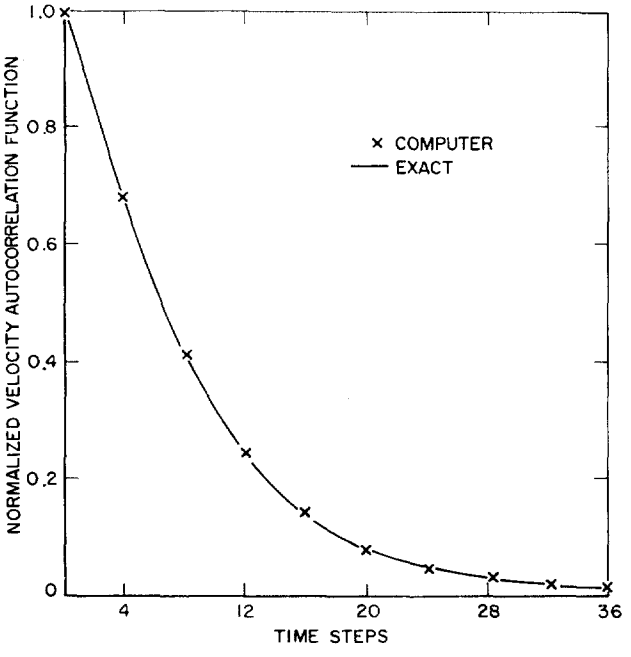


FIG. 2. Comparison between the machine normalized velocity autocorrelation function and the exact one. Each time step is $1\times10^{-14}$ sec.

The above expression can be derived from the definition of $x(t)$ in terms of the time integral of $v(t)$. The $\langle \Delta x^2(t) \rangle$ results are shown in Fig. 3. The error estimate is obtained from the Zwanzig–Ailawadi[5] expression. The slope gave $D_s = 1.42 \times 10^{-5}$ cm$^2$/sec when only times at which the $\langle \Delta x^2 \rangle$ functions agreed were used. If the full time scale was used, $D_s$ of the machine calculation was $(2.26 \pm 0.41) \times 10^{-5}$ cm$^2$/sec. which is larger than the exact value. This discrepancy is again due to the positive noisy tail which hides the negative $t^{-3}$ tail.

Hence, we conclude that the agreement between the machine calculations and the exact results is quite good up to the time when the $t^{-3}$ tail sets in.

## ACKNOWLEDGMENTS

The authors thank the Columbia University Computer Center for a generous grant of machine time. We would also like to thank the referees for their pertinent remarks which have helped us to improve our paper.

## APPENDIX A

The hard rod (HR) potential has the form Eq. (1). Since particles move with constant velocity until collisions occur, the HR equations of motion reduce to algebraic expressions instead of differential equations. We have adopted the Alder–Wainwright[6] scheme to one dimension in order to solve the equations of motion. Let $X_i^0$ and $X_j^0$ be the positions of particles $i$ and $j$ at $t = 0$. Then the positions at time $t$, $X_i$ and $X_j$, are $X_i = X_i^0 + V_i^0 t$ and likewise for $X_j$. Here $V_i^0$ is the velocity of $i$ at $t = 0$. Thus, $X_{ij} = (X_i^0 - X_j^0) + (V_i^0 - V_j^0)t$. At the time of a collision between $i$ and $j$, $t^c$, $X_{ij} = -1$, where the negative sign enters from the convention $X_i < X_j$. Hence,

$$t^c = -(1 + X_{ij}^0)/V_{ij}^0 \ . \tag{A1}$$

Clearly $|X_{ij}^0| \geq 1$ or else particles would penetrate each other. Also if $V_{ij}^0 < 0$ the particles move away from each other and cannot possibly collide. This information reduces the number of pairs which have to be examined.

In order to minimize surface effects and to simulate an infinite system periodic boundary conditions are imposed on the equations of motion. This means that if

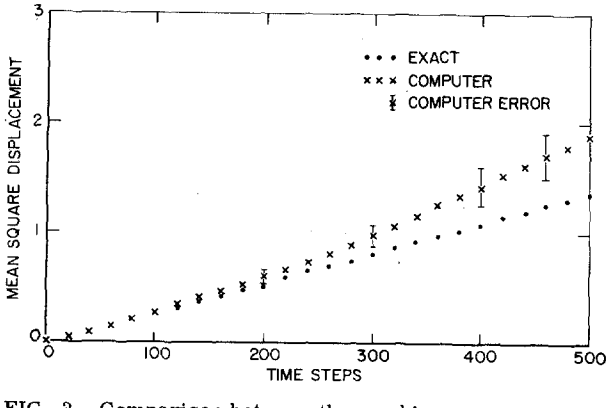


FIG. 3. Comparison between the machine mean-square displacement and the exact one. The error bars are calculated from the Zwanzig–Ailawadi formula. Each time step is $1 \times 10^{-14}$ sec.

$X_i$ is the position of particle $i$ in the line, there are two periodic images at $X_i \pm L$ where $L$ is the length of the basic cell. $L$ is determined by fixing the number density $N/L$. The particles at the ends of the line can collide with these periodic images. The boundary conditions have the consequence that when a particle leaves the line through one end, its image enters the other end, thus preserving the number of particles in the line.

The initial configuration is specified as follows: starting with $N$ particles ($N = 1000$), the one-dimensional number density (0.935 in reduced units or 0.2746 particles/Å) is selected to correspond to a three-dimensional Ar liquid ($mn = 1.374$ g/cc where $mn$ is the mass density). Particles are initially placed on lattice sites. The particle velocities are selected from a Maxwellian distribution whose temperature is preassigned as 88.14 °K. The rejection method of Kahn[7] was used in the selection process. These initial conditions are used to determine $t_{ij}^c$ for all colliding pairs. The shortest $t^c$ is selected from the list and all the particles moved for this time, $t_s^c$, to their new positions $X = X^0 + V^0 t_s^c$. At this time particles $i$ and $j$ collide. Since hard collisions take place, all that happens is that the equal mass particles (mass of Ar) exchange velocities. A cycle is started by subtracting $t_s^c$ from all the other listed times. It is then necessary to recompute the collision times involving the pair which collided at $t_s^c$ since they now have new velocities. If these new times are larger than the longest one on the list they are discarded; otherwise they replace their old values. The next shortest time is selected from the list and the process repeated until all the tabulated times are exhausted.

The particles involved in the collision, the time of the collision, and the positions and velocities of the entire system are stored on 9-track magnetic tape. The above process yields data at unequally spaced collision times; it is simpler to treat data at equal intervals. The collision time scheme can be converted into an equally spaced one by considering the collision times as ordered by their magnitude on the time axis. Dividing this axis into equal intervals of length $\Delta t$, it is simple to transform the data. Just find the largest $t^c$ in a given interval and use the stored positions and velocities at $t^c$ to "move" to the end of the interval. Then $X = X^c + V^c \times (N\Delta t - t^c)$ and $V = V^c$ since no new collisions have occurred. $N$ is the number of the equally spaced time interval. The time step, $\Delta t$, is chosen as $1 \times 10^{-14}$ sec.

Since there is no *a priori* guarantee that the initial arbitrary configuration is an equilibrium one, the approach to equilibrium must be monitored by following some dynamical quantity. For the HR system the temperature is a constant of the motion and so the pressure is used to follow the approach to equilibrium. The pressure equation can be obtained from the virial theorem as modified for HR,

$$\frac{PL}{NkT} = 1 + \frac{m}{NkT}\frac{dZ}{dt} \ ; \quad Z = \sum_{\substack{\text{all} \\ \text{coll}}} X_{ij} V_{ij} \ , \tag{A2}$$

where $P$ is the pressure, $L$ the line length, $N$ the number of rods, $k$ Boltzmann's constant, $T$ the temperature, $m$ the rod mass, and $Z$ the "momentum sum." Thus, the

pressure can be determined from the slope of $Z$ vs time. Figure 4 shows the results for 2000 collisions $\simeq 69$ equal time steps. A least squares fit for the segment from collision 750–1000 (32–39 steps) gave $P = 4.613 \times 10^{-6}$ dyn whereas collision 1750–2000 (63–69 steps) gave $P = 5.176 \times 10^{-6}$ dyn. Since there is an exact equation of state for one-dimensional hard rods (see Appendix B) the equilibrium pressure ($P_e$) is known to be $5.136 \times 10^{-6}$ dyn. Thus, equilibrium is reached in 69 steps. The HR trajectory was continued for 700 additional steps. The run time was 11 min on Columbia's IBM 360/91-75.

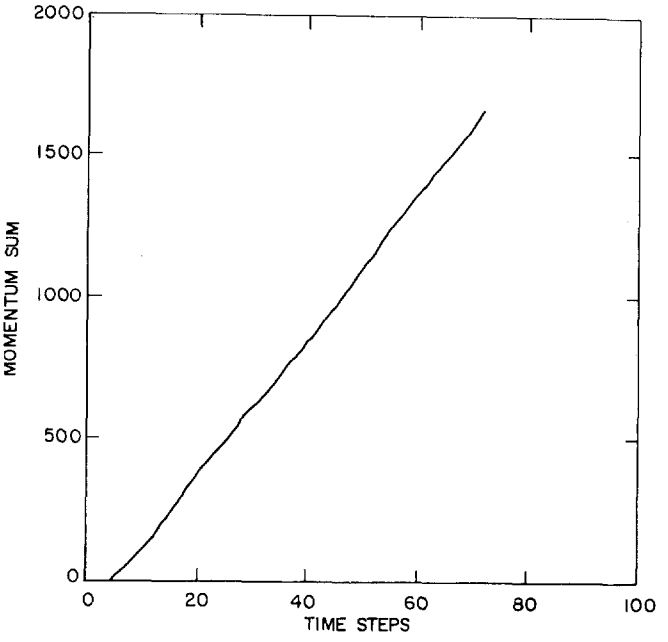


FIG. 4. Impulse term of the virial equation of state for the HR 1000 system. Each time step is $1 \times 10^{-14}$ sec. Equilibrium is reached in 69 steps.

## APPENDIX B

In general the canonical partition function for a system of $N$ rods of length $\sigma$ located at positions $x_1$, $x_2, \cdots x_N$ is given by

$$Z(L,N) = \frac{1}{N!} \int dx_1 \cdots \int dx_N \exp[-\beta V(x_1, \cdots, x_N)] \tag{B1}$$

where $V(x_1, \cdots, x_N)$ is the interatomic potential and $\beta = 1/kT$. This expression can be evaluated for a periodic system of period $L$ if the variables are changed into relative ones where one of the rods serves as the origin. Moreover, the $N-1$ relative distances are restricted for a hard potential because such a potential forces the particle order to be maintained. Then Eq. (B1) becomes

$$Z(L,N) = \frac{L(N-1)!}{N!} \int_{\sigma(N-1)}^{L-\sigma} dx_{1N} \cdots \int_{2\sigma}^{x_{14}-\sigma} dx_{13} \int_{\sigma}^{x_{13}-\sigma} dx_{12} \tag{B2}$$

where the $L$ comes from integration over the reference rod and the $(N-1)!$ comes from the possible ways of labeling the other $N-1$ rods. Equation (B2) is evaluated by setting $W_j = X_{1,j+1} - j\sigma$ as the new variables. Thus,

$$Z(L,N) = L(L - N\sigma)^{N-1}/N! \ . \tag{B3}$$

The pressure for this system is

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial L}\right)_{\beta} = kT\left(\frac{1}{L} + \frac{N-1}{L-N\sigma}\right) . \tag{B4}$$

The pair correlation function, $g^{(2)}(x_1, x_2)$, can be determined from the theory of distribution functions,

$$g^{(2)}(x_1, x_2) = \rho_N^{(2)}(x_1, x_2)/[\rho_N^{(1)}(x)]^2 \tag{B5a}$$

and

$$\rho_N^{(2)}(x_1, x_2) = \frac{\int dx_N \cdots \int dx_3 \exp[-\beta V(x_1, \cdots, x_N)]}{\int dx_N \cdots \int dx_1 \exp[-\beta V(x_1, \cdots, x_N)]} . \tag{B5b}$$

Here $x_1$ and $x_2$ refer to any two particles in the system. Consider these particles as fixed at $x_1$ and $x_2$. They divide the system into two regions because of the hard potential: a length $x_2 - x_1$ containing $N_1$ particles and a length $L - (x_2 - x_1)$ containing $N_2$ particles such that $N_1 + N_2 = N - 2$. Hence, Eq. (B5b) becomes

$$\rho_N^{(2)}(x_1, x_2) = \sum_{N_1, N_2} \frac{\tilde{Z}(x_2 - x_1, N_1)\tilde{Z}(L - (x_2 - x_1), N_2)}{Z(L,N)} \tag{B6}$$

where $Z(L,N)$ is the partition function for $N$ particles in a periodic line and $\tilde{Z}(w,N')$ is the partition function for $N'$ particles on a line of length $w$ which is bounded by two other fixed particles. The sum is over all possible combinations of $N_1$ and $N_2$. It is simple to show that

$$\tilde{Z}(w,N') = [w - (N'+1)\sigma]^{N'}/N'! \ . \tag{B7}$$

Furthermore, the hard potential introduces a step function $\theta(x)$ such that

$$\theta(x) = 0, \ x < 0$$
$$= 1, \ x > 0 \ . \tag{B8}$$

Let $y = x_2 - x_1$. Since $\rho^{(1)}(x) = N/L$ Eq. (B5a) reduces to

$$g^{(2)}(y) = \frac{L}{N} \sum_{N_1=0}^{N-2} \frac{[y - (N_1+1)\sigma]^{N_1}(1 - \{[y - (N_1+1)\sigma]/(l-\sigma)N\})^{N-N_1-2}(N-1)!}{N_1!(N-N_1-2)!(l-\sigma)^{N_1+1}N^{N_1+1}} \theta[y - (N_1+1)\sigma] . \tag{B9}$$

It is of interest to see if the periodic $g^{(2)}(y)$ becomes equal to the thermodynamic limit ($N \to \infty$) case determined by Salsburg *et al.*[8] If $N \to \infty$,

$$(1 - a/N)^N \to e^{-a}$$

and

$$(N-1)!/(N-N_1-2)!N^{N_1+1} \to 1 \ ,$$

then

$$g_{\infty}^{(2)}(y) = l \sum_{k=1}^{N} \frac{(y - k\sigma)^{k-1} \exp[-(y - k\sigma)/(l-\sigma)]\theta(y - k\sigma)}{(k-1)!(l-\sigma)^k} , \tag{B11}$$

(B10)

$$l = L/N ,$$

which is exactly the form obtained by Salsburg *et al.*

*Supported by Grant No. NSF GP 22881.

†Work done in partial fulfillment of the Ph.D. degree at Columbia University. NIH Predoctoral Fellow. Present address: National Bureau of Standards, Washington, D.C. 20234.

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