Journal of Statistical Physics, Vol. 71, Nos. 1/2, 1993

Diffusion in a One-Dimensional Gas of Hard Point Particles

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Received July 2, 1992; final October 1, 1992

We simulate the classical diffusion of a particle of mass M in an infinite one-dimensional system of hard point particles of mass m in equilibrium. Each computer run corresponds to about 10^8 collisions of the diffusive particle. We find that $\langle vv(t)\rangle \sim 1/t^{\delta}$ for t large enough, and a crossover from an $M \neq m$ regime where $\delta = 2$ to $\delta = 3$ for $M = m$. The diffusion constant has a sharp maximum at $M = m$. We study moments $\langle x(t)^2\rangle$ and $\langle x(t)^4\rangle$, and examine the behavior of $q^2(t) = \langle x(t)^4\rangle/3\langle x(t)^2\rangle^2$. We find that $q(t) \to 1$ (consistent with a normal distribution) in the $M \to \infty$ limit (for all times t) and in the $t \to \infty$ limit for all M.

KEY WORDS: Diffusion; autocorrelation functions; long-time tails; one dimension.

1. INTRODUCTION

Some fundamental questions about diffusion phenomena, such as the long-time behavior of the time-dependent velocity autocorrelation function $\langle vv(t)\rangle$ (from which the diffusion coefficient D follows), remain unclear. Long-time tails were unexpectedly found numerically over two decades ago by Alder and Wainwright[(1)] (see refs. 2 for reviews). Further computer work which supports and extends the original results has been carried out.[(3)] There is some experimental evidence for long-time tails from the diffusion of large particles suspended in fluids[(4)] and from neutron scattering experiments from which self-diffusion can be inferred.[(5)] Theoretical

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0022-4715/93/0400-0225$07.00/0

arguments[2,6] have also been given for their existence as well as for the values of A and δ, defined by

$$\langle vv(t)\rangle \to (-A/t^{\delta}) \qquad \text{as} \quad t\to\infty \tag{1}$$

However, some scepticism remains (e.g., ref. 7) that these results have not been established sufficiently firmly (e.g., numerical results used to determine δ extend over a range of values of $\langle vv(t)\rangle$ which is only a small fraction of a decade). A few exact results have, however, been established in the thermodynamic limit for a simplified model: diffusive motion of a particle of mass M (which we call "the test particle" hereafter) in a gas of hard point particles of mass m each, in thermal equilibrium, in one dimension. This is one of the simplest models of diffusion one can think of. In fact, motion of the test particle proceeds independently of whether the gas particles collide among themselves elastically as hard point particles or whether they move freely as in an ideal gas; this is because the only effect of such collisions is to exchange the identity of pairs of them as they collide. Despite the simplicity of the model, a sort of diffusion does take place in it. Upper and lower bounds for D have been obtained,[8] and its exact value is known[9] for $M=m$. It has also been shown[10] analytically for this model that $\langle vv(t)\rangle$ does have long-time tails and that $\delta=3$ for $M=m$. [Computer results[11] for a one-dimensional system of particles with Lennard-Jones interactions also give $\delta=3$, albeit for a somewhat small range of values of $\langle vv(t)\rangle$.] For $d\geqslant 2$, the mechanism for diffusion seems to be a different one[2]; the rule[3] $\delta=d/2$ is expected then.

There remain some unanswered questions about diffusion in an equilibrium one-dimensional system of hard point particles: (a) it is not known how δ or A varies with M; (b) doubts have been raised about whether the displacement does become a Gaussian random variable in the infinite-time limit[12,13]; (c) values of D have been computed only for a few values of M,[13,14] but the overall M dependence of D is not yet clear (there is an interesting question[14] about its $M\to 0$ limit, and its behavior in the neighborhood of $M=0$ is unknown).

We address these questions here and provide some numerically based answers for them. We follow the motion of the test particle of mass M for about 10^8 collisions within an infinite one-dimensional gas of hard point particles which is in equilibrium at temperature T. We obtain neat long-time tails of $\langle vv(t)\rangle$; some are shown in Figs. 1a and 1b. Note that the x-axis variables are different in Figs. 1a and 1b. Figure 1b shows that the long-time tail of $\langle vv(t)\rangle$ oscillates for M small enough. Repeated collisions of a *light* test particle with its two neighbors lead to this effect in one dimension. The $\log_{10}[\langle vv(t)\rangle]$ is shown in Figs. 2a and 2b versus $\log_{10}(t)$

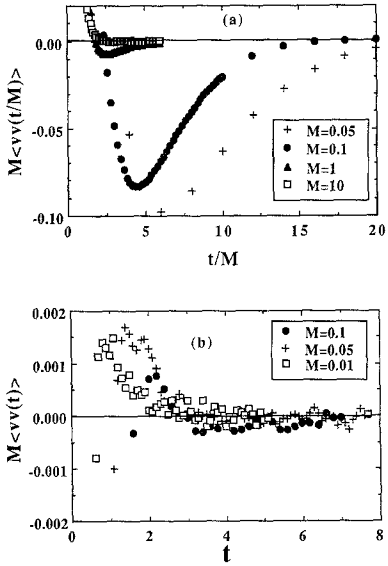

Fig. 1. Plots of $M\langle vv(t)\rangle$, for several values of M, (a) versus t/M and (b) versus t.

for large t for values of M not far from m. The δ [defined in Eq. (1)] is obtained from such data points. Interestingly, our numerical result suggest the following behavior: (i) $\delta = 3$ for $M = m$, as predicted by Jepsen,[10] but $\delta = 2$ for $M \neq m$ in the neighborhood of $M = m$; (ii) there is a finite cross-over time τ_c for $M \neq m$ such that an effective $\delta = 3$ behavior prevails for $t < \tau_c$ and the $\delta = 2$ behavior only emerges for $t \gg \tau_c$. The diffusion constant D is obtained from the second moment $\langle x(t)^2\rangle$ of the displacement $x(t)$ which the test particle undergoes in time t. The result for D is shown in Fig. 3. Finally, in order to check whether displacements of the test particle are normally distributed, we monitor the quantity $q(t)$ defined by

$$q(t)^2 = \langle [x(t)]^4\rangle / 3\langle [x(t)]^2\rangle^2 \tag{2}$$

For normal processes, $q(t) = 1$. Our results for $q(t)$ are summarized in Fig. 4.

2. METHOD

A description of our algorithm follows. We simulate an infinite system working with an *open* finite system of N particles (we keep N rather small: $N = 32$ throughout unless stated otherwise) on a line segment $\mathscr{L}$ of length $N\rho^{-1}$ centered on the test particle. We move $\mathscr{L}$ (within an infinite bath) so that the test particle remains at its center. Particles move in and out of

$\mathscr{L}$ because (a) particles move and (b) $\mathscr{L}$ itself moves. We next describe this procedure in some detail and why the errors it brings about are negligible. We start out with the test particle at $x=0$ and N particles randomly distributed within $-(1/2)N\rho^{-1}$ and $(1/2)N\rho^{-1}$. Normally distributed speeds u are assigned to each of the N bath particles, such that $\langle u^2\rangle = kT/m = 1$; the test particle is also given a random speed v, normally distributed, such that $\langle v^2\rangle = m/M$. Let $t_1 = 0.05N\rho^{-1}$ (a particle entering one end of $\mathscr{L}$, traveling at a speed 10 times $\langle u^2\rangle^{1/2}$, reaches the center of $\mathscr{L}$ in time t_1). As the gas particles merely exchange identities upon collision, we do not keep track of their collisions; the motion of the test particle proceeds as if they were free and we therefore treat them so. We let all particles move freely until the test particle collides or until t_1—*whatever happens first*. At that time t' ($t' \leqslant t_1$), $\mathscr{L}$ is shifted to have $x(t')$ at its center, and all particles not within $\mathscr{L}$ are discarded thereafter. Now, even if $\mathscr{L}$ had not moved, particles would have streamed into and out of it. The motion of $\mathscr{L}$ only modifies things slightly. Accordingly, we shoot particles into $\mathscr{L}$ as they would have come in from the bath, thus neglecting correlations which might have developed between them and the test particle at the center of $\mathscr{L}$. We show below that, for $N > 16$, the effect of this approximation is negligible on the quantities of interest here [such as $\langle vv(t)\rangle$] for the relevant values of t. We then iterate the process, we let all particles move freely until the test particle collides or until t_1, and so on.

The approximation just described makes the algorithm fast. It allows us to follow the test particle for about 10^8 collisions (most of our runs went up to 2×10^8 collisions). In order to justify it, we next show that the algorithm erases the memory of past collisions only at sufficiently long times after they have taken place. We now estimate the probability that after the test particle collides with another particle they move away from each other at least a distance $l = (1/2)N\rho^{-1}$, and move closer thereafter until they collide again—all within a time t. It can be checked (at least numerically) that the probability is largest if the other particle (which moves freely between collisions) is at rest, and we shall restrict ourselves to this (worst) case. Let the probability for such an event be $P(l, t)$. Let us assume for the rest of this argument that the test particle does a simple random walk while the other one remains at the origin. Now note that the probability $P_o(l, t)$ that a random walker goes out to l within time t with no further requirement (no need to return to the origin) fulfills $P(l, t) = P_o(2l, t)$; furthermore, the probability $p_+(l, t)$ that the random walker is beyond l *at* time t fulfills $2p_+(l, t) = P_o(l, t)$. It follows that $P(l, t) = 2p_+(2l, t)$. On the other hand,

$$p_+(l, t) \approx (2\pi Dt)^{-1/2} \int_l \exp(-x^2/2Dt)\, dx.$$

We shall be interested in the case $l^2/2Dt \gg 1$. Then, it follows that $P(l, t) \approx (1/y\sqrt{\pi})\exp(-y^2)$, where $y^2 = 2l^2/Dt$. Consider, for instance, $M = m$; we have obtained correlation functions only for $t < 8$ in this case (see below for units and see Figs. 2a, 2b, and 3 for numbers); putting in $D \approx 0.8$ and $x = 16$ (from $l = (1/2)N\rho^{-1}$ and $N = 32$), it follows that $y^2 > 80$, which gives a very small P. The most unfavorable case is for $M = 10m$. We have obtained correlation functions for up to $t = 40$ for $M = 10m$; putting in $D \approx 0.63$ and $l = 32$ gives $y^2 > 20$. The probability for the event under consideration is therefore always less than 10^{-9}, which is very small. Furthermore, some checks were run using $\mathscr{L}$ twice as long ($N = 64$); no noticeable differences were found in the results obtained.

We next describe the method used to compute $\langle vv(t)\rangle$, $\langle x(t)^2\rangle$, and $\langle x(t)^4\rangle$. We keep track of values of v and x at times t' given by $t'_n = n\,\Delta t$, where n is an integer, $\Delta t \sim \tau/10$, and τ is the relaxation time associated with $\langle vv(t)\rangle$. We do not keep a record of all values of v and x (a total of $\sim 10^9$ values for $M = m$, for instance), as it would be of an unmanageable length; rather, we compute these correlation functions right along as the values of v and x are generated, keeping in the computer memory only a reasonably small string of ($\sim 10^3$) the latest consecutive values. We do it as follows; let $k \equiv n$: mod(J) (recall that $n = t'_n/\Delta t$; we usually let $J = 1024$) and evaluate $v(k)$ and $x(k)$ only at J values of k. Each time some new values of x and v are determined (say, the set of values between the latest two collisions), they are recorded at the corresponding values of k; the values of v and x at times t_{k-J} are automatically overwritten (i.e., replaced by new values of v and x). To obtain $\langle vv(t_n)\rangle$, we first define $\tilde{n} = k - n$: mod(J), and add the term $v(k)\,v(\tilde{n})$ to the proper cumulative function each time a new value $v(k)$ is added to the string {similarly, we keep adding terms like $[x(k) - x(\tilde{n})]^2$ to obtain $\langle x(t_n)^2\rangle$}. For $M = m$, for instance, $\tau = 0.44$ and $\Delta t = 0.044$, and we made two runs which went on up to $t \approx 2 \times 10^8$; therefore all data points shown in Fig. 2b for $M = m$ stand for averages over nearly 10^{10} terms.

3. RESULTS AND DISCUSSION

The results obtained are given next. We use units of ρ^{-1}, $\rho^{-1}(m/kT)^{1/2}$, and m for length, time, and mass, respectively; diffusion constants are correspondingly given in units of $\rho^{-1}(kT/m)^{1/2}$. (It takes a unit of time for a gas particle with a mean square thermal velocity to move a distance ρ^{-1}, and $\langle v^2\rangle = 1/M$ in these units.) Figure 2a exhibits long-time tails for $M = 1/2$, 3/4, 4/3, and 2. Clearly, δ does not seem to vary and A depends weakly on M ($\delta \approx 2$ and $A \approx 0.3$ for these four values of M).

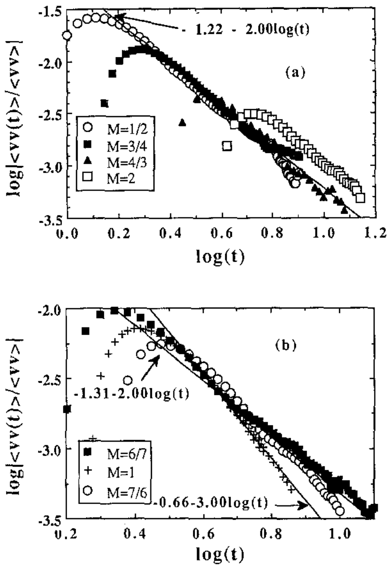

Fig. 2. (a) Plot of $\log_{10}|\langle vv(t)\rangle/\langle v^2\rangle|$ versus $\log_{10}(t)$ for $M=1/2$, $3/4$, $4/3$, and 2. A straight line for $\langle vv(t)\rangle \to -A/t^{\delta}$ is shown for $A\approx 0.3$ and $\delta=2$. All data points in this figure stand for averages over at least 10^8 collisions of the test particle. (b) Same as in (a) for $M=6/7$, 1, and 7/6. The two straight lines shown correspond to $\delta=2$ and $\delta=3$. All data points in this figure stand for averages over at least 4×10^8 collisions of the test particle.

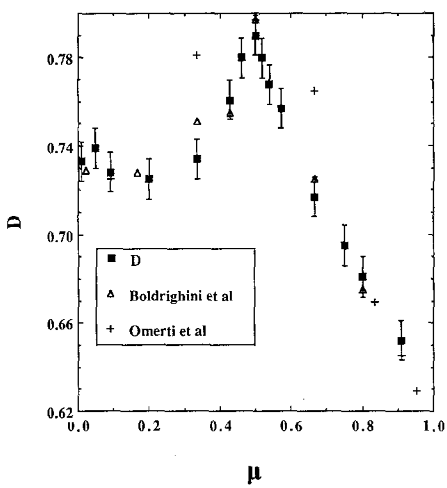

Fig. 3. Results of our own, from ref. 13, and from ref. 14 for D for various values of μ $(1/\mu \equiv 1 + m/M)$.

Similar results are shown in Fig. 2b for $M = 6/7$, 1, and 7/6. Note that all three sets of data points show approximately the same slope ($\delta = 3$) for $t < 0.7$; the data points for $M = 13/14$ and 14/13 (not shown) also seem to follow a $\delta = 2$ straight line for $t > 0.7$. These results are the basis for our inference that there is a crossover from a $\delta = 2$ to a $\delta = 3$ behavior as $|M - 1| \to 0$.

Our values for D follow from the relation $D = d\langle [x(t)]^2 \rangle / dt$ for t large enough, and the values of $\langle [x(t)]^2 \rangle$, which are obtained as described above. A plot of data points for it versus the reduced mass μ ($1/\mu \equiv 1 + m/M$) is shown in Fig. 3. There is reasonable agreement with the values found by Omerti *et al.*[13] and Boldrighini *et al.*[14] which were obtained by somewhat different methods. The value found for $M = 1$ agrees with the exact[9] one of $(2/\pi)^{1/2}$. The values for D span the whole range between the bounds known[8, 15] for it. It seems that (just as in ref. 14) D does not approach its $M = 1$ values as $M \to 0$. We do not, however, find this surprising: while the momentum of the test particle vanishes as $M \to 0$, its mean energy does not (it is $kT/2$, independent of M), and, consequently, two particles "squeezing" the test particle in a collision conserve momentum but do *not* conserve energy. On the other hand, a "massless" test particle would not affect the motion of the two particles flanking it at all; diffusion would therefore then take place as for $M = 1$. Finally, there seems to be a cusp in D at $\mu = 0.5$. It is quite likely associated with the crossover effect discussed above.

We have something to say about doubts raised[12] whether diffusion in this system is a Wiener process. We monitor the quantity $q(t)$, defined in

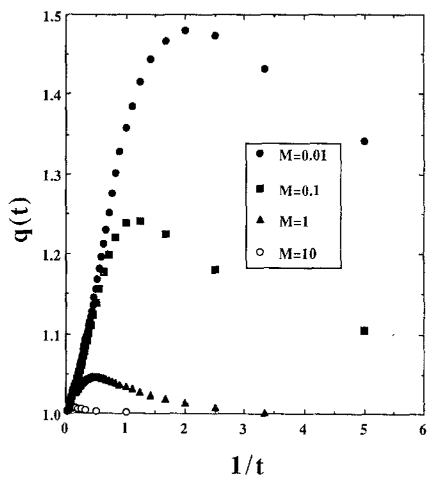

Fig. 4. Quantity $q(t)$ versus t for various values of M.

Eq. (2). For normal processes, $q(t)=1$. Our results for $q(t)$ are summarized in Fig. 4. Clearly, $q(t)\to 1$ as $t\to\infty$, for all M; furthermore, $q(t)\to 1$ as $M\to\infty$, for all times t, in agreement with the rigorous results of Sźasz and Tóth.[15] Clearly, this behavior of $q(t)$ is *not* a sufficient condition for a Wiener process, but it is a necessary one.

We next make a comment on the relaxation time and on the time t_c at which $\langle vv(t)\rangle$ becomes negative. If there were no long-time tails and if $\langle vv(t)\rangle=\langle v^2\rangle \exp(-t/\tau)$, then $D=2\langle v^2\rangle\tau$ would follow, and, consequently, we would have $2\tau/M=D$. Instead, we find that the rule $2\tau/M=(2/\pi\mu)^{1/2}$, where $\tau=1/[d(\ln\langle vv(t)\rangle)/dt]_{t=0}$, fits, within statistical errors, our results.[3] Not surprisingly, these two expressions for $2\tau/M$ agree in the $M\to\infty$ limit ($\mu\to 1$). A rough numerical guide (it fits the data within about 20%) for how t_c behaves, to which we ascribe no particular theoretical significance, is given by $t_c\approx(1.5+5.6\mu)\tau$, for $0.1<\mu<0.9$.

There is an additional reason why long-time tails become increasingly harder to detect as M increases: the "amplitude" A [$-A$ is the minimum value of $M\langle vv(t)\rangle$] of the tails becomes very small for large M. More quantitatively, $A\approx 0.0067M^{-1/2}$ for $1<M<4$. For this reason, we were unable to determine δ for large values of M.

We give no physical picture here for the interesting $M=1$ singular behavior of $\langle vv(t)\rangle$ for long times, nor for the associated cusp of D (see Fig. 3).

ACKNOWLEDGMENTS

We are very grateful to Joel L. Lebowitz for several leading comments and to Profs. D. Szász and B. Tóth for a very helpful critique of our work. Financial support from the Dirección General de Investigación Científica y Técnica of Spain (projects # PB88-0487 and PB91-0709), the Commission of the European Economic Community (grant # CI1.0409.), from CONICIT, and from Fundayacucho of Venezuela is gratefully acknowledged.

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