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Note on the Fractal Dimension of Hard Sphere Trajectories

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Using Monte Carlo molecular dynamics, a new, careful study is made of the approach of the trajectory of a typical particle in a hard sphere fluid to that of a Brownian particle, discussed before by Powles and Quirke and Rapaport. The apparent fractal dimension of the trajectory, as a function of reduced length scale, $\Delta(\eta)$, characterizes the transition from mechanical to Brownian motion and differs markedly from 2 in all present computer simulations.

KEY WORDS: Brownian motion; self-diffusion; hard spheres; molecular dynamics; Monte Carlo; fractal dimension.

The geometry of the trajectory of a molecule has been studied in the last year, stirred by Mandelbrot's monograph on the geometry of irregular shapes.[1] Mandelbrot argued that the particle trajectories in an N-particle system would, for large N, essentially be that of a Brownian particle, with fractal dimension $\Delta = 2$.

Recently, a molecular dynamics calculation was carried out by Powles and Quirke for a system of 108 Lennard–Jones particles,[2] subject to periodic boundary conditions at values of density and temperature characteristic of a dense liquid. They concluded that $\Delta = 1.65$ and that Δ might be a function of the thermodynamic state of the system. Their results were criticized by Rapaport[3] who studied a system of 1372 hard spheres with periodic boundary conditions at three distinct densities. He concluded that $\Delta = 2$ in each case and that the reason that Powles and Quirke had found a smaller value was that their trajectory was not long enough.

While this criticism is justified, Rapaport's argument does not clarify the matter entirely. He reported results for the fractal length as a function

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of length scale ε which were consistent, at the largest values of the length scale, with the $\Delta = 2$ interpretation but which contained such large statistical uncertainty as to be consistent with the Powles–Quirke value as well. Moreover, at a given density, Rapaport studied the dependence of his results neither on the number of particles in the system nor on the overall length of the trajectory. The former dependence is needed to show that the calculations are relevant for the system in the thermodynamic limit. The latter is important, since his data extend into a regime of length scales ε where the fractal length depends strongly on the overall length of the trajectory; therefore, his conclusion regarding the fractal dimension, which depends critically on the large length-scale data, is not well substantiated.

In this note we study the behavior of the fractal dimension of hard sphere trajectories at a single fluid density. However, rather than simply observing the fractal length for a single system, we study the fractal dimension as a function of length scale for a number of system sizes and trajectory lengths, so that we can extrapolate to large values of each of these parameters. Also we resolve the very large statistical uncertainties seen in Rapaport's results by using much more extensive averaging. From such results, then, we attempt to observe the transition from dynamical behavior ($\Delta = 1$) at small ε to Brownian behavior ($\Delta = 2$) at large ε. Our results show a slow approach of Δ to an asymptote, on a length scale of at least 100 mean free paths. Indeed we conclude that the fractal dimension of 2 cannot be observed for trajectories as short as considered by either Rapaport or us. Somewhat in the spirit of Powles and Quirke, we observe that the way Δ approaches 2 with increasing length scale may well be a function of the thermodynamic state.

Our calculations were carried out using Monte Carlo molecular dynamics, the details of which will be discussed elsewhere. The apparent fractal dimension of a trajectory was defined, using Richardson's definition $\Delta(\varepsilon) = 1 - d[\ln L(\varepsilon)]/d(\ln \varepsilon)$.[1] The fractal length $L(\varepsilon)$ as a function of length scale ε is obtained from the ensemble average of the trajectory length of a particle by applying dividers of length ε along the trajectory generated to a final time t_f. Thus both L and Δ will depend on the parameter t_f and the number of particles N. To obtain the dependence on t_f we consider trajectories with t_f varying from $200t_{00}$ to $6000t_{00}$, where t_{00} is the Boltzmann mean free time. At the volume of twice close-packing for which the calculations were done, the actual mean free time, t_0, is about $t_{00}/3$, so that our longest trajectories are about double those of Rapaport. The trajectory calculations were performed with roughly 14 digits of numerical precision, so that the trajectories are typically accurate out to times of about 50 mean free times.[4] Nonetheless, we expect that fractal lengths computed with our approximate trajectories will remain meaningful

even for longer times, just as calculations of the equation of state and the velocity autocorrelation function appear to be unaffected by the precision of the trajectory.[4,5]

Two choices can be made for $L(\varepsilon)$ depending on whether one does or does not include the final portion of the trajectory, beyond the point where the dividers last intersect the trajectory. These two different choices correspond to those made by Powles and Quirke and Rapaport, respectively. By averaging the $L(\varepsilon)$ over each of the N particles in the system and also over a number of initial phases, selected through the Metropolis Monte Carlo technique, we have reduced the statistical uncertainties to much lower levels than previously reported.

We carried out calculations for systems of $N = 108$, 500, 1372, and 4000 particles and only included results for $L(\varepsilon)$ for those ε for which the precise treatment of the tail portion of the trajectory was not important. In Fig. 1, the apparent fractal dimension $\Delta(\eta)$ is plotted as a function of $\eta = \varepsilon/l$, where l is the actual mean free path of the system. The values of $\Delta(\eta)$ were derived by extrapolating the measured values of $\Delta(\eta; t_f, N)$ (obtained by numerical differentiation of the $L(\varepsilon)$ data) using the double limit $N \to \infty$, $t_f \to \infty$ of the least-squares fit $\Delta(\eta; t_f, N) = \Delta(\eta) + a(\eta)/t_f + b(\eta)/N$ to our data. We do not show results for $\eta > 60$, even though our calculations include reliable results for the $L(\varepsilon)$ for ε as large as $200l$, because uncertainties introduced both in the numerical differentiation to obtain Δ and the extrapolations in N and t_f result in much less precise estimates of Δ for larger values of η. To illustrate the effects of our fitting, Fig. 1 also shows the data for our largest value of N for $t_f = 2000t_{00}$. While Fig. 1 does not contradict $\Delta = 2$ for large η, it does not prove it either. The difference with Rapaport's result is related to his use of fractal lengths out to values of $\eta = 180$, which (for his value of t_f) is about twice the value of η for which the two different definitions of $L(\varepsilon)$ agree. The function $\Delta(\eta)$ in Fig. 1 exhibits an unexpectedly slow transition from dynamical motion ($\Delta = 1$) to presumably Brownian motion ($\Delta = 2$). In fact, the value 2 will certainly not be achieved before $\eta = 100$, clearly requiring trajectories with lengths considerably in excess of those studied up to now. Moreover, the function $\Delta(\eta)$ may well depend on the thermodynamic state.

We conclude with the following remarks.

1. The slow approach of Δ to 2 is a consequence of the dynamic nature of the hard sphere trajectory, as opposed to the random nature of that of a Brownian particle. The dynamics imposes restrictions on the motion of a particle that translate into velocity correlations that only vanish after about 25 collisions.[4,6]

2. Although the mean square displacement of a particle is linear in

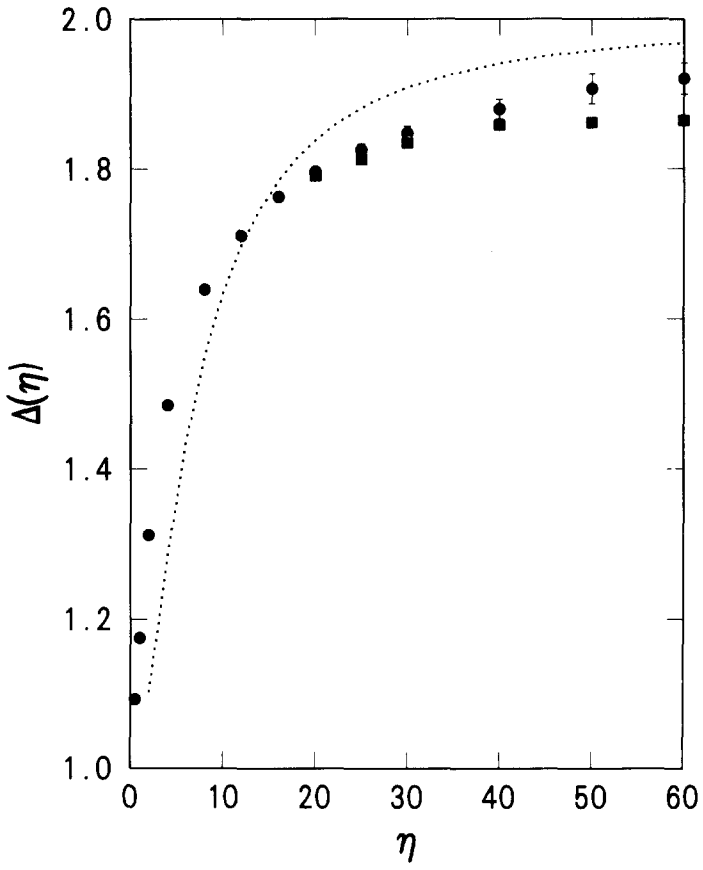

Fig. 1. Apparent fractal dimension $\Delta(\eta)$ as a function of reduced length scale η, in units of the mean free path. The circles are the extrapolation of our results to the limits of infinite trajectory length and number of particles. The squares are the results for the longest trajectory ($t_f = 2000 t_{00}$) for our largest system ($N = 4000$). Where no squares are shown, the circles and squares overlap. The curve is an approximate theoretical result.

the time after 25 collisions, $\Delta \neq 2$ after even 60 collisions. This is because our largest ε is not very large compared to $25l$, the value of the root mean square displacement for which the diffusive regime begins. Therefore, each time one puts a divider of length ε along the trajectory to obtain $L(\varepsilon)$, the dynamically correlated, nonrandom and nondiffusive part of the trajectory that is included is considerable. A calculation of the fractal length based on the approximate relation, $L(\varepsilon) = [t_f/t(\varepsilon)]\,\varepsilon$ in which $t(\varepsilon)$ is the time at which the root mean square displacement is ε, yields the curve shown in Fig. 1, which shows a similar slow approach to the Brownian limit. To

obtain this curve, the mean square displacement was obtained by (twice) integrating a simple approximation for the observed velocity autocorrelation function,[4] $\langle v_1 \cdot v_1(t) \rangle = 2D/[\pi(t/2t_0)^2]$, where v_1 is the velocity of particle 1 and D is the self-diffusion constant, taken to be 1.2 times the Enskog value at this density.[6] Thus, although from a dynamical point of view a particle trajectory is that of a Brownian particle after 25 mean free times, from a geometric point of view this can only be seen using length scales far in excess of 25 mean free paths.

3. The new function $\Delta(\eta)$ characterizes the "space-filling" capacity of the trajectory as measured at length scale η. $\Delta < 2$ means that the particle appears not to move sufficiently randomly and not to backtrack sufficiently often to obtain the value $\Delta = 2$ typical for the Wiener process and Brownian motion. The least space-filling motion is the purely dynamical one of a single particle along a straight line for which $\Delta = 1$. On the other hand, a value $\Delta > 2$ is expected when the backtracking is more than in a random motion, as in the overlapping wind-tree model.[7] The reason that under normal conditions in nature one finds $\Delta = 2$ is that the number of particles involved as well as the ε scale used are so large that the dynamically correlated portion of ε is completely negligible compared to the random portion. Then the Wiener process and diffusion are excellent approximations. Our calculations show that this is not necessarily true on the scale accessible in molecular dynamics. The function $\Delta(\eta)$ characterizes then the approach to Brownian motion by indicating the apparent space-filling capacity of a particle trajectory as a function of length scale.

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