Journal of Statistical Physics, Vol. 40, Nos. 5/6, 1985

The Fractal Nature of Molecular Trajectories in Fluids

D. C. Rapaport[1]

Received November 15, 1984; revised March 5, 1985

The scaled lengths of molecular trajectories obtained by molecular dynamics simulation of a hard-sphere fluid are shown to have the same fractal dimension $D = 2$ as the random walk. Self-similarity first appears on length scales typically a factor of 25 greater than the mean free-path length, whereas for the simple random walk with constant step size the onset occurs after only six steps; the reason for the slow convergence is shown to be the near exponential distribution of intercollision path lengths of the fluid molecules. The influence of density on the scaled path lengths is also discussed.

KEY WORDS: Fractals; Brownian motion; diffusion; hard sphere fluid; molecular dynamics simulation.

1. INTRODUCTION

The concept of fractal dimension as an aid to classifying the morphology of natural phenomena that display statistical self-similarity over a range of length scales is now firmly established.(1) Brownian motion is an example of a self-similar process(1); although the molecules of a (classical) fluid follow trajectories that are in principal prescribed by deterministic equations of motion, the fact that the neighborhood of a given molecule undergoes continual rapid change results in a trajectory that, to the macroscopic observer, resembles a random walk. The average motion of the molecule is in fact governed by the diffusion equation and thus its mean-square displacement grows linearly with time; this characteristic of the motion corresponds to a fractal dimension $D = 2$ for the path mapped out in space by the molecule.

---

[1] Department of Physics, Bar-Ilan University, Ramat-Gan, Israel. Present address: IBM, Dept. 48B/428, Neighborhood Road, Kingston, N.Y. 12401.

The subject of the present paper is the direct measurement of D for the trajectories obtained by computer simulation of a hard-sphere fluid. The motivation for undertaking a study of this nature was a recent report$^{(2)}$ that claimed to obtain a fractal dimension other than 2 (actually 1.65) for molecular motion in a fluid in a particular thermodynamic state; this in turn led to the suggestion that the fractal dimension is in fact a state variable of the fluid.

The main conclusion of this paper, a preliminary report of which has appeared elsewhere,$^{(3)}$ is that the result $D=2$ is indeed the correct one; the reason an alternative value was obtained lies in the relatively short trajectory length on which the measurements were based and the consequent lack of a sufficiently broad range of length scales over which observation of self-similarity is at all possible. The reason behind the slow convergence to self-similarity is also discussed and it is concluded that it is the approximate negative exponential distribution of free-path lengths between collisions that is responsible; synthesized random walks with this step distribution converge much more slowly than walks with steps of constant length.

2. THE LENGTH OF A MOLECULAR TRAJECTORY

A prerequisite to determining the length of the continuous but very jagged path taken by a fluid molecule over a given time interval is the specification of the measurement technique to be used. Several such techniques have been proposed,$^{(1)}$ the most straightforward of which is opening a pair of dividers to a separation η—the "yardstick" length or length scale—and walking the dividers along the path in such a way that each new step begins where the previous step ends. The measured trajectory length is then denoted by $L(\eta)$, a quantity equal to the number of steps multiplied by the length scale η. This approach was originally used by Richardson (see Ref. 1) in a study of the lengths of coastlines and led to the conclusion

$$L(\eta)=A\eta^{1-D} \tag{1}$$

where A is a constant. The exponent D is now referred to as the fractal dimension and is directly measurable from a plot of $\log L(\eta)$ vs. $\log \eta$. For molecular trajectories $D=2$.$^{(1)}$

It is entirely reasonable to expect that trajectories generated by computer simulation would correspond to the predicted $D=2$. The recently reported$^{(2)}$ first direct measurement of D for molecular motion however yielded the value 1.65, a result impossible to reconcile with the diffusive nature of molecular motion in fluids. The value of D was based on a molecular dynamics simulation of a 108-molecule Lennard-Jones liquid in which the trajectory of a single molecule was measured using the yardstick approach. A potential source of error in the analysis of the $L(\eta)$ data is trying to fit the results to (1) for values of η too small to warrant such a fit; it will become clear below that this premature declaration of convergence to the limiting form (1) is the reason for the incorrect D estimate.

The simple scaling relationship (1) can only be expected to apply over a limited range of length scales. At small η, $L(\eta)$ approaches a limiting value that is the true distance moved by the molecule; this is in marked contrast to a typical coastline for which the scaled length is essentially unbounded as $\eta \to 0$. At the other extreme of large η the measurement process itself becomes meaningless for a finite trajectory since the yardstick length eventually exceeds the overall span of the trajectory. Between these two limits, and for a sufficiently long trajectory, there exists a range of η over which (1) should hold. The onset of self-similarity at low η corresponds to a changeover between the observation of ballistic and diffusive motion; no *a priori* indication exists of where this should occur, hence the need for sufficiently long trajectories to allow analysis of $L(\eta)$ over a wide range of η.

3. METHOD

The trajectories whose fractal dimension is to be determined are obtained from the molecular dynamics simulation of a hard-sphere fluid. The system consists of 1372 molecules of unit diameter, subject to periodic boundary conditions, and with the size of the unit cell chosen to produce the required density. Special computational techniques are needed in order to carry out the relatively time-consuming simulations efficiently. These techniques provide an algorithmic solution to the problems of determining future collisions among the spheres based on the dynamical state at a given instant, and establishing a temporal ordering of the large number of potential future collisions. These issues will not be discussed further here since both a general survey of the subject(4) and a detailed description of the particular techniques employed in the present work(5) are available elsewhere.

The simulation is started with the molecules in a regular close-packed configuration, with initial velocities of unit magnitude and random direction, and the system is allowed to evolve over a period of time adequate for equilibration to the fluid state. Subsequently, the motions of selected molecules are tracked as the system evolves in time, and the coordinates of each collision in which these molecules are involved recorded. The recording process takes into account any crossings of the periodic boundaries that occur and which are obviously involved in the trajectory length computations. Since the motion of a molecule between collisions is rectilinear, the collision history allows a complete reconstruction of the trajectory for later analysis. Energy is conserved over the course of the simulation.

Trajectories that extended over 10^4 collisions/molecule were found to be adequate for the analysis. To produce trajectories of this length the simulations had to cover a total of 7×10^6 collisions. The calculations were repeated for three values of reduced volume v (v and the number density are related by $v = 2^{1/2}/\rho$); the run details are summarized in Table I. The trajectories of 16 molecules were recorded during each run (in contrast to the single trajectory used in Ref. 2).

The measurement of trajectory length using a yardstick (i.e., the dividers) of given length η is carried out in the following manner. If $\mathbf{r}_0$ is the point on the trajectory path corresponding to the end of the previous measurement step (or the start of the trajectory if the initial step) then the immediate task is to locate both the linear segment of the path and the point on this segment where the measurement step will end. This entails a search of the current and possibly subsequent path segments; for a particular segment of the path between the points $\mathbf{r}_1$ and $\mathbf{r}_2$ a search is made for a point lying on the segment a distance η from $\mathbf{r}_0$ by solving

$$\|(1-\beta)\,\mathbf{r}_1 + \beta\mathbf{r}_2 - \mathbf{r}_0\| = \eta \tag{2}$$

for β, subject to the restriction $0 \leqslant \beta \leqslant 1$. If two solutions are found then the smaller is taken, if none then the particular segment is not directly involved in the length measurement; if $\mathbf{r}_0$ itself lies on the segment $\mathbf{r}_1\mathbf{r}_2$ then it replaces $\mathbf{r}_1$ in (2). The small portion of the trajectory not included in the last complete measurement step is discarded; the length error introduced

Table I. Summary of the Molecular Dynamics Runs.[a]

Reduced volume (v)	Simulated time (psec)	Mean free path	Mean-square displacement
1.75	590	0.066 (0.071)	150 (136)
2.0	840	0.095 (0.101)	441 (337)
2.5	1390	0.160 (0.166)	1275 (1030)

[a] The mean free paths and mean-square displacements are measured in units of the hard-sphere diameter (= 1); error estimates are given in parentheses. The time periods covered by the runs are also shown.

by this truncation cannot exceed η itself. The total number of measurement steps multiplied by η is an estimate of $L(\eta)$, with the final results being based on averages over all the trajectories.

4. RESULTS

The fact that the distribution of free-path lengths is practically density independent when scaled by the mean free-path length$^{(6)}$ suggests that the trajectory length measurements should be similarly scaled in order to isolate the effect of density on the "shape" of the trajectory (i.e., the v dependence of L). If λ denotes the mean free-path (itself a function of v) and the reduced quantities $\bar{L} = L/\lambda$ and $\bar{\eta} = \eta/\lambda$ are defined, then (1) becomes

$$\bar{L}(\bar{\eta}) = \bar{A}\bar{\eta}^{1-D} \tag{3}$$

where

$$\bar{A} = \lambda^{-D}A$$

Any v dependence not covered by the variation in mean free path is now confined to the coefficient $\bar{A}$.

Figure 1 shows the (natural) log–log graphs of $\bar{L}$ against $\bar{\eta}$ for the different v, averaged over the individual trajectories. The linear portion of each graph should have gradient -1 if $D = 2$, as is indeed the case. Error bars are omitted for clarity—see however$^{(3)}$ where the unreduced quantities are shown and error bars included. The spread of values of $L(\eta)$ over the different trajectories is not greatly influenced by the value of η; the relative spread does of course increase with η and the graphs terminate when this becomes significant.

The three sets of data become superimposed as $\bar{\eta} \to 1$; this is to be expected since the small-$\bar{\eta}$ limit of $\bar{L}$ is simply the total number of collisions participating in the trajectory. The scaling behavior implied by (3) does not appear at a common value of $\bar{\eta}$ for the different v and the graphs do not coincide in the linear region indicating that $\bar{A}$ is explicitly v dependent. Estimates of $\bar{\eta}$ at which linearity first appears are by their nature subjective; the values suggested by the data are 23, 26, and 31 for $v = 1.75$, 2.0, and 2.5, respectively, i.e., the rate of approach to self-similarity drops with increasing v.

The upper limit to η for which meaningful estimates of $L(\eta)$ are to be expected is a value close to the r.m.s. displacement of the molecule over the course of the trajectory—the end-to-end distance of the path. The logarithm of the ratio (end-to-end distance)/λ follows from Table I and

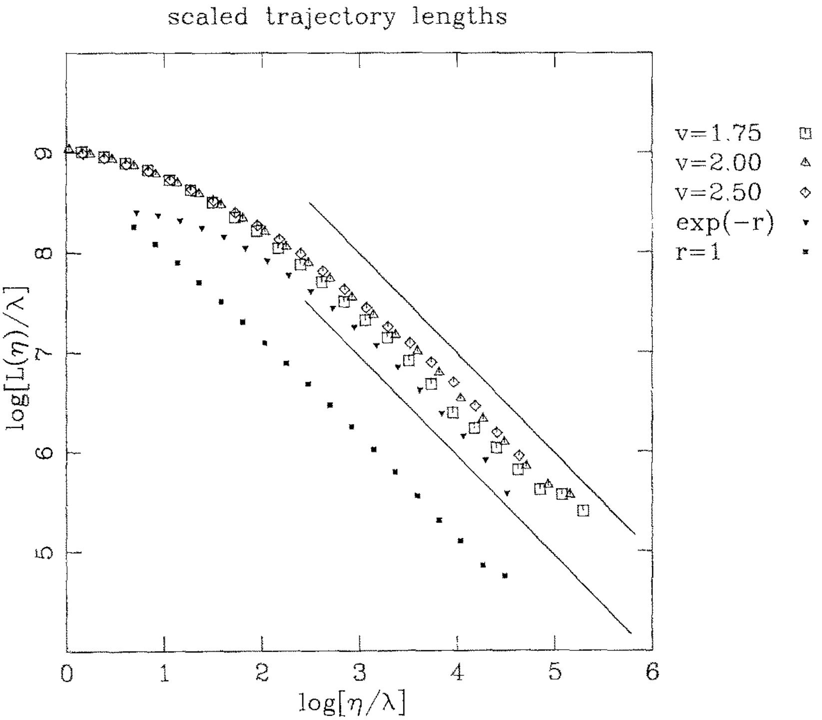

Fig. 1. Log–log (natural) plot of scaled trajectory length L as a function of measurement scale length η; both quantities have been divided by the mean free path length λ. Scaled lengths of random walks with constant (■) and negative exponentially distributed (▼) step sizes are also shown. The straight lines have gradient -1 and show the expected slope for $D=2$.

equals 5.3 ± 0.1 for the three values of v; this is essentially the value of $\log \bar{\eta}$ at which the graphs in Fig. 1 terminate owing to lack of reliable scaled length estimates.

The present simulations are of a duration sufficient to permit measurement of $L(\eta)$ for η as large as 150λ; the trajectories themselves extend over $10^4\lambda$. The earlier work(2) on the other hand involved trajectories of approximate length 500λ with a corresponding reduction in the upper limit of η. Given that the onset of self-similarity occurs in the neighborhood of $\eta = 25\lambda$, it is clear that the limiting linear region of L could not be probed in depth and hence an erroneous D was obtained.

The fact that different models are used in the two simulations should have no bearing on the conclusions. It has been shown(6) that the free-path distribution in a hard-sphere fluid is unaffected by the addition of a square-well potential. Since there is no reason that the trajectories of the square-well and Lennard-Jones fluids should differ in any essential way, because in both cases the molecular motion is governed by a diffusive mechanism, the value of D should be the same for both models.

A further consequence of Fig. 1 is that there is clearly more density dependence in the nature of the trajectory than is implied by the fact that the free-path distributions are essentially independent of density when scaled by λ.(6) On the other hand this may not come as such a surprise since the velocity autocorrelation function undergoes a qualitative change for v near 2(7): at low v (high density) the short-time correlations are negative, a characteristic that disappears as v increases. In view of the close connection between the velocity autocorrelation and the diffusive motion, a more complex relationship between the trajectory "shape" and v exists; the free-path distribution itself is not a sufficiently sensitive indicator of this dependence.

5. ANALYSIS OF RANDOM WALKS

In order to determine whether the relatively slow approach to self-similarity observed in the case of molecular trajectories is also typical of random walks in general, an analysis similar to that described above was carried out for two kinds of random walk in the continuum. The first was a walk with constant unit step size, the second a walk with step size r determined by the probability distribution $P(r) = \exp(-r)$. This negative exponential is a reasonably close approximation to the free-path distribution in a hard-sphere fluid(6) when the path lengths are scaled by λ.

For both kinds of walk 100 samples of 10^4 steps were generated and the scaled lengths measured as before. The resulting values for $L(\eta)$ are included in Fig. 1.

The constant-step walk settles down to linear behavior relatively quickly and requires that η be only approximately six times the step size. The convergence is considerably slower for the walk with exponentially distributed step size where linearity requires that η be at least 16 times the mean step size (itself equal to unity). The slower approach to self-similarity is a consequence of the need to smooth out the large fluctuations in step size inherent in the exponential distribution (for which the variance is also unity). Because of the similar distribution involved, the same explanation also applies to the molecular trajectories. It is also apparent that the exponential does not give a particularly good description of the trajectories insofar as $L(\eta)$ is concerned. This too is not unexpected given that neither the exponential, nor a more complicated functional form that treats collision statistics more carefully, are capable of fully accounting for the free-path distribution.(6)

Note Added: In this paper the emphasis is on how the trajectory lengths vary under change of measurement scale. A related but distinct problem concerns the effect of a change of time scale and, in particular, the question of whether, over macroscopic time scales, molecular motion retains its Brownian nature.(8) I thank Professor J. L. Lebowitz for bringing this work to my attention.

REFERENCES

1. B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Fransisco, 1982).
2. J. G. Powles and N. Quirke, *Phys. Rev. Lett.* **52**:1571 (1984).
3. D. C. Rapaport, *Phys. Rev. Lett.* **53**:1965 (1984).
4. J. J. Erpenbeck and W. W. Wood, *Modern Theoretical Chemistry*, Vol. 6B, B. J. Berne, ed. (Plenum Press, New York, 1977).
5. D. C. Rapaport, *J. Comp. Phys.* **34**:184 (1980).
6. B. J. Alder and T. Einwohner, *J. Chem. Phys.* **43**:3399 (1965); T. Einwohner and B. J. Alder, *J. Chem. Phys.* **49**:1458 (1968).
7. B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* **53**:3813 (1970).
8. D. Durr, S. Goldstein, and J. L. Lebowitz, *J. Stat. Phys.* **30**:519 (1983).