

CONF-8508135--1

FRACTAL BEHAVIOR OF SINGLE-PARTICLE TRAJECTORIES AND ISOSETS IN  
ISOTROPIC AND ANISOTROPIC FLUIDS\*

R. K. Kalia and P. Vashishta  
Materials Science and Technology Division  
Argonne National Laboratory  
Argonne, IL 60439

and

S. W. de Leeuw  
Michigan State University  
East Lansing, MI 48824

CONF-8508135--1

DE85 018343

August 1985

The submitted manuscript has been authored  
by a contractor of the U. S. Government  
under contract No. W-31-109-ENG-38.  
Accordingly, the U. S. Government retains a  
nonexclusive, royalty-free license to publish  
or reproduce the published form of this  
contribution, or allow others to do so, for  
U. S. Government purposes.

bsm

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**MASTER**

This submitted at the Proceedings of the IX International Workshop on  
Condensed Matter Theories, August 5-10, 1985, San Francisco, California.

\*Work supported by the U.S. Department of Energy, BES-Materials Sciences,  
under Contract W-31-109-ENG-38.

FRactal BEHAVIOR OF SINGLE-PARTICLE TRAJECTORIES AND ISOSETS IN  
ISOTROPIC AND ANISOTROPIC FLUIDS\*

R. K. Kalia and P. Vashishta

Argonne National Laboratory  
Argonne, IL 60439

and

S. W. de Leeuw

Michigan State University  
East Lansing, MI 48824

ABSTRACT

Fractal behavior associated with single-particle trajectories and isosets is observed in molecular dynamics simulations of liquids and superionic conductors. Fractal dimensions of trails and isosets are found to be 2 and 0.5, respectively. These values are shown to be universal in that they are independent of the spatial dimensionality, the nature of the interparticle interaction, and the thermodynamic state of the system.

The single-particle motion in liquids is conventionally characterized by the velocity autocorrelation function and diffusion constant. These characteristics vary from system to system and are also functions of the thermodynamic state of the system. However, certain features of the single-particle motion are independent of the nature of the interaction or the thermodynamic state of the system. These universal features are manifested in the fractal behavior of single-particle trajectories and isosets: their fractal dimensions are always 2 and 0.5, respectively.<sup>1</sup>

The fractal behavior of single-particle trajectories is related to their length.<sup>2</sup> When measured in units of a step distance  $\epsilon$ , the length of a trajectory,  $L(\epsilon)$ , decays algebraically over a certain range of  $\epsilon$ :

$$L(\epsilon) \propto \epsilon^{-\alpha} \quad (1)$$

\*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract W-31-109-ENG-38.

The exponent  $\alpha$  is called Richardson's coefficient, and the fractal dimension  $D$  is defined as

$$D = 1 + \alpha . \quad (2)$$

The fractal behavior of isosets is related to Brown functions,  $x_i(t)$ ,  $y_i(t)$ ... which describe the time variations of coordinates of a particle.<sup>2</sup> The instants of time  $\{\tau\}$  when the Brown function is equal to a given value  $x_0$  constitute an isoset. If  $x_0$  is the origin, the isoset is known as the zeroset. The gaps between successive values of  $\tau$  are described by a probability function  $\text{Pr}(G > g)$ , for finding a gap of duration  $G$  greater than a given value  $g$ . It can be shown<sup>2</sup> that

$$\text{Pr}(G > g) \propto g^{-\bar{D}} \quad (3)$$

where  $\bar{D}$  is the fractal dimension of the isoset.

Fractal behavior of single-particle trajectories was first observed by Powles and Quirke<sup>3</sup> in molecular dynamics simulations of Lennard-Jones fluid. These authors concluded that the fractal dimension  $D = 1.65$  and that  $D$  may be a function of the thermodynamic state of the system. However, Rapaport's<sup>4</sup> simulations for a hard-sphere system revealed that the asymptotic value of  $D$  inferred from very long trajectories yields the expected value  $D = 2$ .

In this paper we report the results of our molecular dynamics calculations on several liquids whose Hamiltonians may be written as

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} u \left( \frac{\sigma}{r_{ij}} \right)^n . \quad (4)$$

Here  $u$  measures the strength of the interaction, and  $\sigma$  the size of the particles. The exponent  $n$  determines the steepness and range of the force law. We have chosen these systems because of the relative simplicity in characterizing their thermodynamic state by a single dimensionless variable

$$\Gamma = u \left( \frac{\sigma}{r_0} \right)^n / k_B T , \quad (5)$$

where  $r_0$  is the mean interparticle separation:  $\pi r_0^3 = \rho^{-1}$ ,  $\rho$  being the number density of the system. By varying the exponent  $n$  we can study the effects of the range and steepness of the interaction. Special values of  $n$  correspond to experimentally studied systems.

- (1)  $n=1$ . If we write  $u\sigma$  in Eq. (4) as  $e^2$  the Hamiltonian describes the interaction between electrons confined to move in a plane. Charge neutrality is maintained by adding a uniform background of positive charge. This Hamiltonian has been used to model electrons on the surface of liquid helium, which has been studied by a variety of experimental techniques and simulations.<sup>5,6</sup> In particular, it has been shown that the system undergoes a fluid-solid transition at  $\Gamma_f = 125 \pm 4$ .
- (2)  $n=3$ . Replacing  $u\sigma^3$  by  $\mu^2$  the energy of interaction in Eq. (4) corresponds to dipoles whose moments,  $\mu$ , point perpendicular to the plane of motion. To a good approximation, this model describes a system of polystyrene spheres floating on water<sup>7</sup> or immersed in a ferromagnetic fluid sandwiched between glass plates and under the influence of a magnetic field perpendicular to the plates.<sup>8</sup>

Dynamical simulations<sup>9</sup> have shown that the system solidifies at  $\Gamma_f = 62 \pm 3$ .

- (3)  $n=12$ . The potential energy in Eq. (4) is the repulsive part of the Lennard-Jones potential. It is used as a model for the interaction of inert-gas atoms at high densities. Computer simulation studies<sup>10</sup> indicate a solid-fluid transition at  $\Gamma_f = 0.98 \pi^6$ .

Trajectories of the particles in these systems were obtained by the method of molecular dynamics (MD). As is well known, this technique is used to generate a sequence of dynamic states of the system by numerical integration of the equations of motion. We used a fifth-order predictor-corrector method for this integration.<sup>6</sup> MD calculations were performed for systems containing 256 particles in a rectangular cell whose sides  $L_x$  and  $L_y$  were in the ratio  $L_x/L_y = 2/\sqrt{3}$ . Periodic boundary conditions were imposed on the system.

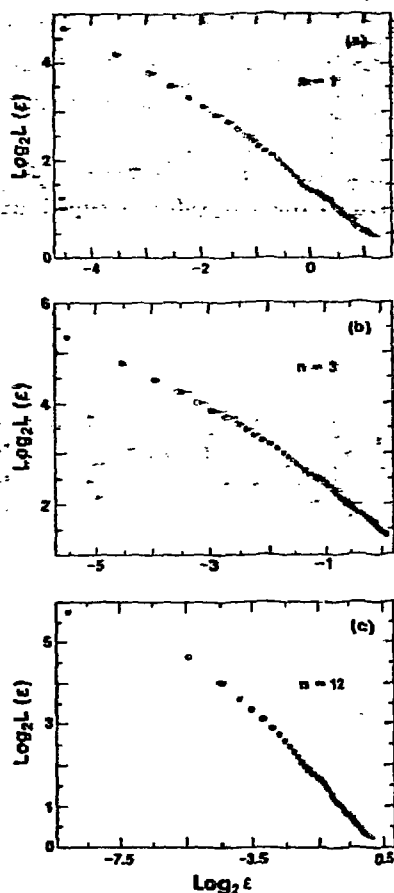


Figure 1: Variation of the length,  $L(\epsilon)$ , of a single-particle trajectory with the step distance  $\epsilon$  for  $n=1, 3$  and  $12$  systems at  $T_f/T=0.29$ .  $T_f$  is the freezing temperature.

Molecular dynamics simulations yield the positions  $\vec{r}_i(0), \vec{r}_i(\Delta t), \dots, \vec{r}_i(n\Delta t)$  of the particles  $i = 1, 2, \dots, N$  at regular time intervals  $\Delta t$  where  $\Delta t$  is the time step used in integrating the equations of motion. Since  $\Delta t$  is sufficiently small, the particles may be assumed to travel along straight lines between successive time intervals. The length  $L(\epsilon)$  is now calculated for a given value of the step distance  $\epsilon$  by counting the number

of times a rigid rod of length  $\epsilon$  fits into the trajectory. End corrections are taken as fractions. In the limit  $\epsilon \rightarrow 0$ , the length  $L(\epsilon)$  corresponds to the length of the trajectory as if it were stretched out into a straight line. This length is  $L_1 = \bar{v} t$  where  $\bar{v} = (2 k_B T/m)^{1/2}$  is the thermal speed and  $t$  the duration of the MD simulation. For large values of  $\epsilon$  the length will be given by the separation between the end points of the trajectory and this is close to the root mean square distance of the trajectories.

Figure 1 shows the log-log plot of the length  $L(\epsilon)$  as a function of the step distance  $\epsilon$  for  $n=1, 3$ , and  $12$  systems. It is apparent that there is a range of  $\epsilon$  ( $\sim 10$ ) over which  $L(\epsilon)$  decreases linearly on the logarithmic scale. The slopes of these linear regions give Richardson's coefficient  $\alpha$  which is related to the fractal dimension  $D$  by Eq. (2). The data in Fig. 1 show that  $D$  is always 2, regardless of the nature of the interparticle interaction in the system. However, this is true only if the trajectories are sufficiently long ( $\sim 10^5 \Delta t$ ). For shorter trajectories ( $30,000 \Delta t$ ) the fractal dimension  $D$  is less than 2; the higher the temperature, the larger the deviation from  $D = 2$ . Thus, the fractal dimension approaches 2 in an asymptotic way when the trajectories are sufficiently long. MD calculations also show that the fractal dimension has the same universal value in different thermodynamic states.

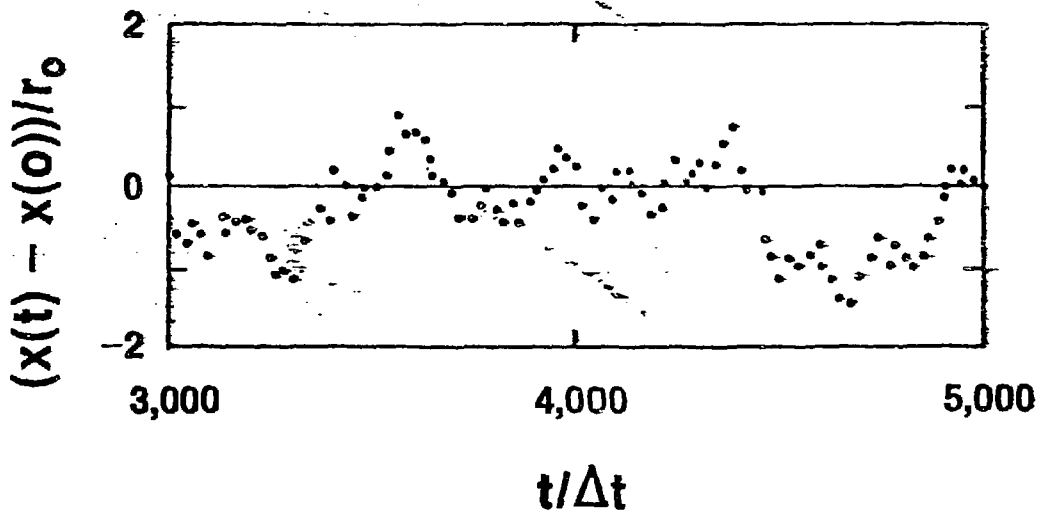


Figure 2: Time variation of a Brown function measured relative to its value at  $t=0$  for  $n=1$  system. The function is plotted at intervals of 20  $\Delta t$  where  $\Delta t = 2.5 \times 10^{-12}$  sec.

The probability function for gaps was calculated from Brown functions  $\{x_i(t), y_i(t)\}$  generated by MD simulations. A plot of Brown function is shown in Fig. 2. Members of an isoset are the instants of time when the Brown function equals a given value  $x_0$ . These members tend to cluster, but the clusters themselves are distributed sparsely. The gaps  $G$  are the durations between successive members of an isoset. The probability function  $\text{Pr}(G > g)$  is the number of gaps of duration  $G$  greater than a given value  $g$ , normalized by the total number of gaps. Figure 3 shows a log-log plot of  $P(g)$  as a function of  $g$  for the three systems at the same reduced temperature  $T_f/T = 0.29$ . The slopes yield 0.5 for the fractal dimension  $\bar{D}$  in the three systems. That  $\bar{D} = 0.5$  holds at other values

of  $\bar{\Gamma}$  too, implying that  $\bar{D}$  is also independent of the thermodynamic state of the system.

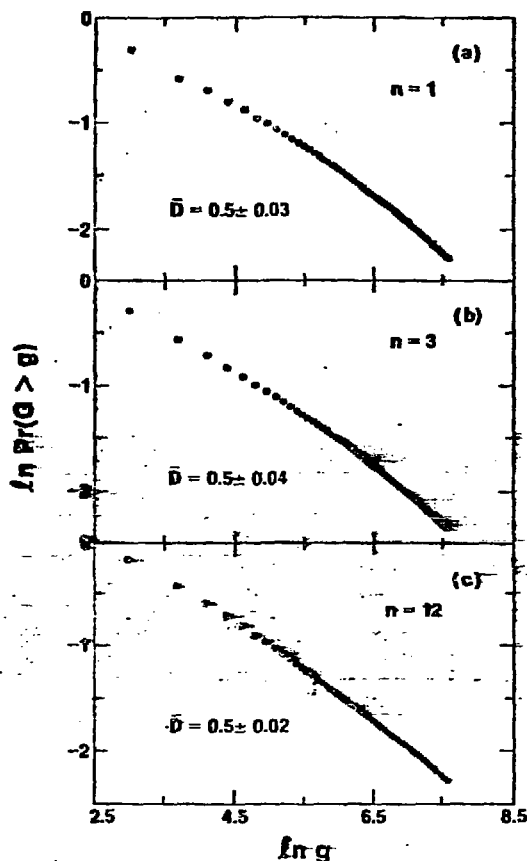


Figure 3: The probability function  $\text{Pr}(G>g)$  for finding gaps  $G$  of duration greater than  $g$  at  $T_f/T=0.29$ . The gaps are measured in units of an MD time step  $\Delta t$ .

In conclusion, MD simulations for a variety of systems in 2 spatial dimensions reveal fractal behavior associated with trajectories and isosets of single particle motion. The fractal dimensions of trajectories and isosets are 2 and 0.5, respectively, irrespective of the nature of the interparticle interaction or thermodynamic state of the system. Recently, we have investigated the fractal behavior of diffusing Ag ions in the superionic phase of  $\text{Ag}_2\text{S}$ . MD calculations have shown that the Ag ions diffuse anisotropically along certain directions in the lattice of S particles. Fractal dimensions  $D$  and  $\bar{D}$  for Ag ions are again 2 and 0.5, respectively. These results confirm the universal nature of fractal dimensions of trails and isosets.

#### REFERENCES

1. R. K. Kalia, S. W. de Leeuw, and P. Vashishta, to be published; S. W. de Leeuw, R. K. Kalia, and P. Vashishta, to be published.
2. B. B. Mandelbrot, The Fractal Geometry of Nature (Freeman, San Francisco, 1982).
3. J. G. Powles and N. Quirke, *Phys. Rev. Lett.* **52**, 1571 (1984).
4. D. C. Rapaport, *Phys. Rev. Lett.* **3**, 1965 (1984).
5. C. C. Grimes, *Surf. Sci.* **73**, 379 (1978); R. Mehrotra, B. M. Guenin, and A. J. Dahm, *Phys. Rev. Lett.* **48**, 641 (1982).

6. P. Vashishta and R. K. Kalia, in Melting, Localization and Chaos, ed. R. K. Kalia and P. Vashishta (North-Holland, NY), 1982, p. 43.
7. P. Pieranski, Phys. Rev. Lett. 45, 569 (1980).
8. A. T. Skjeltorp, Phys. Rev. Lett. 51, 2306 (1983).
9. R. K. Kalia and P. Vashishta, J. Phys. C14, L643 (1981).
10. F. van Swol, L. V. Woodcock and J. N. Cape, J. Chem. Phys. 73, 913 (1980); J. Q. Broughton, G. H. Gilmer and J. D. Weeks, Phys. Rev. B25, 4651 (1982).