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Onset of Brownian Motion in a One-Dimensional Fluid*

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In this article we describe a computer study of the onset of Brownian motion in a model, one-dimensional system. It is shown that clusters of particles behave like Brownian particles in the limit of large mass. The normalized velocity autocorrelation functions and the corresponding memory functions of these clusters have been determined and compared to theoretical predictions. An interesting result of this study is the mass independence of the self-diffusion coefficient.

In this article we describe a computer study of the onset of Brownian motion in a model one-dimensional system.¹ The model consists of 1000 equal mass particles interacting via a pairwise, additive, truncated Lennard-Jones potential with the potential parameters ($\epsilon/k=119.8^\circ\text{K}$, $\sigma=3.405 \text{ \AA}$) and periodic boundary conditions. This set of 1000 particles is then grouped into various sized contiguous clusters. Each cluster has a mass equal to the total mass of its constituents ($M=nm$) and a velocity equal to the average velocity of its constituents: Clusters of mass $M=10m, 25m, 40m, 50m, 60m, 75m, 90m$, and $100m$ have been analyzed.

Our purpose in this study is to investigate the onset of Brownian motion as a function of B mass. Toward this end, we study the mass independence of the normalized velocity autocorrelation function $\psi_M(t)$, and its memory $K_M(t)$, which are related by the equation

$$\partial_t \psi_M(t) = -M^{-1} \int_0^t d\tau K_M(\tau) \psi_M(t-\tau). \quad (1)$$

We find that:

(1) The mean-square force on a B particle becomes independent of the mass for masses above $M \geq 75m$ (see Table I).

(2) $\psi_M(t)$ approaches a linear form above $M \geq 25m$ and its decay constant is equal to ζ/M where ζ is mass independent (see Fig. 1 and Table I).

(3) The memory function, $K_M(t)$, becomes mass independent for masses above $M \geq 40m$ (see Fig. (2)).

(4) The self-diffusion coefficient, D , is mass independent for all masses (see Table I).

The conclusions are based on the data in the table and in Figs. 1 and 2.

In addition, the normalized velocity correlation function for a group of 100 particles randomly sampled from the 1000-particle system, was determined. The

TABLE I. Mass dependence of dynamical properties.

M/m	D	β	ζ	$K(0)$
1	0.053 ^a	14	14	442
10	0.048 ^b	1.6	16	318
25	0.046	0.64 ^c	16	243
40	0.038	0.49	19	200
50	0.042	0.35	17	180
60	0.046	0.27	16	169
75	0.051	0.19	14	149
90	0.049	0.17	15	141
100	0.047	0.16	16	139

^a $\langle r^2(\tau) \rangle = 2D\tau$.

^b $D = \int_0^\infty d\tau \langle V(\tau)V(0) \rangle$,

$D = T^*/\zeta$, $T^* = 0.735$, $\zeta = (M/m)\beta$.

^c Least squares fit of $\ln\psi(\tau)$.

particles in the group are not contiguous. As can be seen from Fig. 3, this correlation function is identical, within machine error, to the normalized velocity correlation function of a single fluid atom; thus showing that the linear time decay observed in clusters of contiguous atoms is not due to a statistical effect.

We regard the model system as being very close, but not identical, to the models used to derive the Langevin equation, or the Fokker-Planck equation from mechanics.²⁻⁶ These derivations are based on a three-dimensional model in which the mass of the *B* particle increases, but its interaction potential remains the same. Our *B* particle experiences forces which depend on its size, but due to the finite range of the potential, the forces become independent of the size as the mass increases. Thus, for sufficiently large clusters ($M \geq 75m$) [see Table I for the mean-square forces, $K(0)$], our results are quite similar to the theoretical predictions in that the theoretical decay is exponential which for $t \ll M/\zeta$ has a linear form.^{6a} Our model differs in one other respect from the theoretical model. It has internal

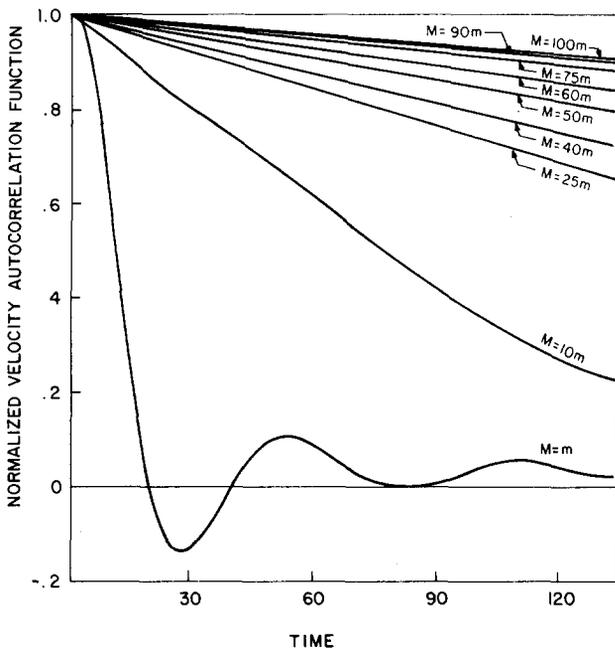


FIG. 1. Mass dependence of the normalized velocity autocorrelation function. Time is in units of 10^{-14} sec.

degrees of freedom. Nevertheless, this model shows essential agreement with the theoretical models.

There are, however, several points which are clarified by the computer study. Recall that the memory function in Eq. (1) is explicitly⁷

$$K_M(t) = \langle F_B \exp(iQLt) F_B \rangle / kT, \quad (2)$$

where F_B is the force on the *B* particle and Q is a projection operator,

$$Q \equiv 1 - P, \quad P \equiv V \langle V \dots \rangle / \langle V^2 \rangle,$$

onto the orthogonal subspace of V in the Hilbert space of dynamical variables. Since the force, F_B , is not expected to change with the mass of the cluster (for $M \geq 75m$), the only mass dependence in $K_M(t)$ must arise from the dynamics which is contained in

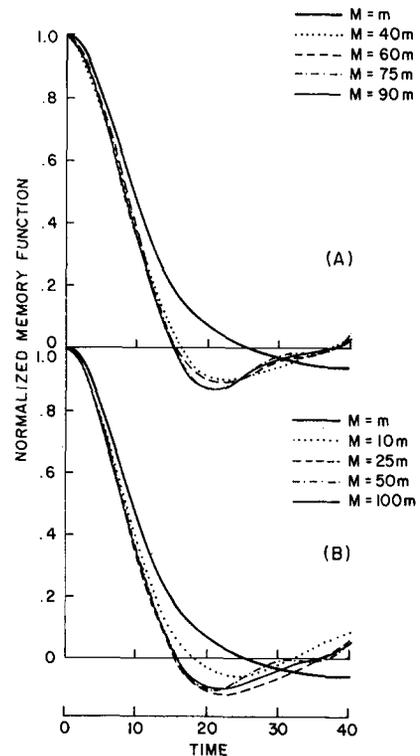


FIG. 2. Mass dependence of the normalized memory obtained by inverting Eq. (1) numerically. Time is in units of 10^{-14} sec.

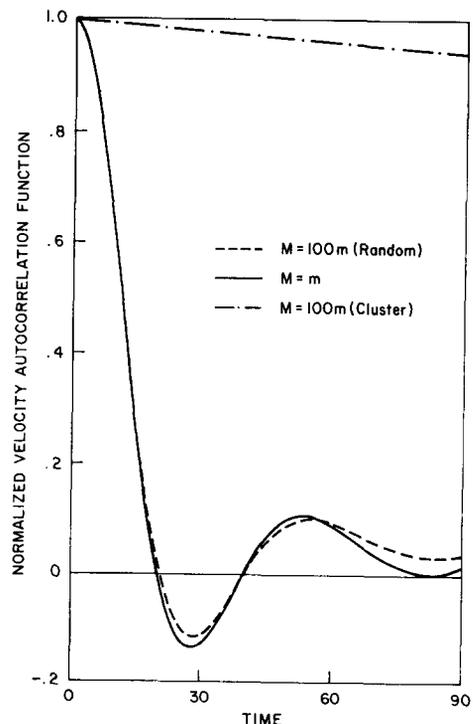


FIG. 3. Comparison of the normalized velocity autocorrelation function for clusters selected randomly and contiguously. Time is in units of 10^{-14} sec.

the propagator $\exp(iQLt)$. The Liouville operator L is the sum of a fluid operator L_f and a B -particle operator L_B . The theoretical treatments assume that as the mass of the B particle increases relative to the host, L_B ceases to contribute and

$$K_M(t) \xrightarrow{M \rightarrow \infty} \langle F_B \exp(iL_f t) F_B \rangle / kT,$$

so that the memory function becomes an autocorrelation function in a "Hamiltonian system."⁷ The computer experiment shows that this happens at a mass of $M \geq 40m$. Moreover, from Eq. (1) we see that as M increases, the time rate of change of ψ_M , $\partial_t \psi_M$, decreases due to the factor M^{-1} . Thus for sufficiently high masses, $\psi_M(t)$ varies slowly compared with $K_M(t)$, there is a separation of time scales, and Eq. (1) reduces to

$$\partial_t \psi_M(t) = -(\zeta/M) \psi_M(t)$$

with

$$\zeta = \int_0^\infty dt K_M(t).$$

Since $K_M(t)$ is independent of the mass, the friction constant, ζ , is independent of the mass.

One of the interesting conclusions of this study is that the self-diffusion coefficient, D , is independent of the mass (see Table I). Although there is no theoretical explanation of this we conjecture that it is due to two competing mechanisms:

- (a) The heavier the B particle, the slower it moves.
- (b) The heavier the B particle, the larger is its mo-

mentum, and the smaller is the effect of solvent forces on its motion.

Thus, although massive particles move slowly on the average they have so much inertia that they continue along the same path for a longer time than light particles. The net effect is that in a time t , massive particles will move the same distance as light particles.

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^{6a} *Note added in proof*: R. Rubin has computed the velocity correlation function for contiguous clusters in a one dimensional harmonic lattice. He finds that the velocity correlation function decays linearly, with a mass independent diffusion coefficient. A very interesting conclusion of his study is that the velocity correlation function never becomes exponential.

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