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Long-Time Correlation Effects on Displacement Distributions

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The distribution of displacements in a fluid of hard disks is found by molecular dynamics to be non-Gaussian in the long-time limit, as surmised from the moments of the distribution that yield divergent diffusion and Burnett coefficients. On the other hand, for the Lorentz gas of hard disks, the distribution of displacements is Gaussian in the long-time limit and the diffusion coefficient exists, though the autocorrelation functions have power law tails, which lead to divergent Burnett coefficients.

KEY WORDS: Displacement distributions; long-time correlations; Lorentz gas; Burnett coefficient; percolation point; non-Gaussian distribution.

It has been established through computer studies[(1)] and graph theoretical calculations[(2)] that due to persistent long-time correlations the diffusion coefficient for a hard-disk fluid diverges. Since the diffusion coefficient is related to the distribution of displacements through the rate at which the second moment of the distribution reaches its limiting value, it becomes important to establish both the rate at which the displacement distribution approaches the limiting distribution as well as the long-time limit of the displacement distribution itself, so that the proper representation of the constitutive relations, such as Fick's law, which are free of divergences, can be found. The long-time limit of this distribution function has almost invariably been thought to be Gaussian, through invoking the central limit theorem. However, the divergence of the diffusion coefficient suggests that the central limit theorem may not apply. The importance of understanding

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this divergence is due to the fact that it invalidates Navier–Stokes hydrodynamics and the Chapman–Enskog[3] expansion, where the diffusion coefficient occurs in the lowest order term of that expansion. In three dimensions, the Chapman–Enskog expansion also fails even though the diffusion coefficient exists, because the Burnett coefficient, the next higher term in the expansion, which measures the limiting rate dependence of the fourth cumulant of the distribution of displacements, diverges.[4] In order to investigate the cause of these divergences, it is desirable to study also a simpler, but still nontrivial, system in which the hydrodynamic vortex modes, believed to be responsible for the nonanalytical behavior in fluids, are absent. That is the Lorentz model, for which the long-time limit as well as the dependence of the moments and the cumulants of the displacement distribution with time are presented.

The Lorentz gas, in which a single particle diffuses through a set of randomly placed, fixed point scatterers, has a number of interesting properties. Rigorous mathematical analysis of the Lorentz model has led to a proof that the system has good ergodic properties and that certain functions obey the central limit theorem,[5] which is consistent with the displacement distribution being Gaussian. However, graph theoretical methods have shown[6] the velocity autocorrelation function in two dimensions and in the low-density limit to have a power law tail of the form α_D/t^2, where α_D is a constant and t is time. Abnormal diffusion has been observed in a different version of the Lorentz gas, called the Ehrenfest wind tree model, by computer simulation.[7] Thus, for even this simple model it is important to establish the nature of the long-time correlation and the resulting distribution of displacements.

It is important to investigate the behavior of the Lorentz gas not only at low density but over the whole density range, because the results change qualitatively. This is because, at sufficiently high density of the randomly placed scattering points, the moving particle is trapped and consequently the diffusion as well as all Burnett coefficients vanish. The lowest density at which the diffusion coefficient vanishes is called the percolation point, which has been estimated[8] to be at $n^* = 0.37 \pm 0.02$, where $n^* = nR^2$, the number density multiplied by the square of the radius of the moving particle. The percolation limit can be avoided, and order in the scattering centers can be introduced, by investigating the nonoverlapping Lorentz gas as opposed to the overlapping case discussed so far. The nonoverlapping case permits investigation of the role of the topology of the space on the distribution of displacements. That situation is generated by letting a point particle move through a representative configuration of a hard-particle fluid or solid, entirely equivalent to reversing the size of the moving particle and the scatterers.

Not only can the effect of spatial order on the distribution of displacements be investigated, but so can the effect of velocity correlations as well. One way to achieve this is to let the particle be scattered diffusively, that is randomly, at each collision, instead of the equal scattering angle condition, therby breaking up the persistence of velocity. Another way is to ignore the velocity and the collisions entirely, and let the particle move, by the standard Monte Carlo[9] sampling technique, through the fixed scatterers. Finally, a generalization of a random walk that employs a waiting time distribution[10] to determine a transition time when a particle will make a jump (correspond-

Table I. The Long-Time Behavior Represented by αt^{β} of the Velocity Autocorrelation Functions that Lead to the Diffusion (D) and Burnett *(B)* coefficients of a Two-Dimensional Lorentz Gas

n^{*a}	$-\alpha_D{}^b$	$-\beta_D$	$\alpha_B{}^c$	$-\beta_B$	$-\beta_B{}'$
0.736	0.88_8	2.1_1	-0.6_1	1.7_3	2.2_2
0.654	0.42_5	1.7_1	-0.14_2	1.2_1	1.4_2
0.654 (S)	0.40_4	1.7_1	-0.4_2	1.2_1	—
0.477	0.19_2	1.40_4	0	—	—
0.370	0.18_1	1.34_5	(0.06_2)	(0.75_4)	0.68_9
0.318	0.20_2	1.40_5	(0.11_2)	(0.71_4)	0.78_8
0.260 (N)	0.27_2	1.6_1	0.15_5	0.45_5	—
0.200	0.23_1	1.59_5	0.09_1	0.60_1	0.59_5
0.200 (S)	0.17_4	1.54_5	0.08_2	0.59_5	—
0.200 (MC)	—	—	—	0.65_7	—
0.050	0.07_1	2.0_1	0.09_3	1.0^d	1.0_1
0.030	0.02_1	2.0_1	0.05_2	1.0^d	1.0_1

[a] The first two entries use 90, the last two 1968, the rest 504 particles. Runs were 5×10^7 collisions long, except at the lowest two densities, where the velocity autocorrelation function results represent 4×10^8 collisions. Every 10^4 collisions a new random scattering configuration was generated. The entry marked (S) stands for diffusive scattering, (N) for the no overlap case, and (MC) for the Monte Carlo run.

[b] The magnitude is determined by normalizing the autocorrelation function initially to unity and a fit of the data over a range of t from 15 to 50 mean collision times, except at the lowest two densities, where the range is 10–20 collisions.

[c] The magnitude is determined by $d^2(tB)/dt^2$ being divided by $D_0{}^2$, where $D_0 = 3v^2/8\Gamma$, where Γ is the collision rate, and a fit of the data over a range of times comparable to the diffusion data. At densities 0.370 and 0.318 the autocorrelation function changes at late times, of the order of several hundred mean collision times, attributed to boundary condition effects, since that change depends on the number of particles employed. The data given hence correspond to the early-time trapped particle region.

[d] The uncertainty in the last significant number is given in the subscript numeral to the entry, except in the case where the Burnett coefficient logarithmically diverges in the range of 10–50 mean collision times.

ing to the rejections in the Monte Carlo procedure) was tried. All these different computer experiments represent an effort to find a process other than an ordinary random walk for which the cumulants might not diverge. The above generalization of the random walk predicts that if the velocity correlation function decays with the power of β_D (achieved by an assumed power law tail for the waiting time distribution), the higher order velocity autocorrelation function of the Burnett coefficient decays with the power $\beta_B' = \beta_D + 1$ in the diffusing region and with $\beta_B' = 2\beta_D + 2$ in the nondiffusing region.

The results for all these problems are summarized in Table I by a long-time asymptotic fit to the equation $\alpha_D t^{\beta_D}$ of the velocity autocorrelation function $\frac{1}{2}(d^2/dt^2)\langle\Delta x^2\rangle$ whose integral is the diffusion coefficient, and the equation $\alpha_B t^{\beta_B}$ of the autocorrelation function $(1/24)(d^2/dt^2)[\langle\Delta x\rangle^4 - 3\langle\Delta x^2\rangle^2]$ whose integral is the Burnett coefficient, where Δx is the displacement of a particle in time t and α and β are constants. The two lowest density results are consistent with the theoretical prediction of a power law decay of $\beta_D = -2$ for the velocity autocorrelation function, but the magnitude of the coefficient α_D, which should be n^*/π, is closer to n^* at both densities. Unless

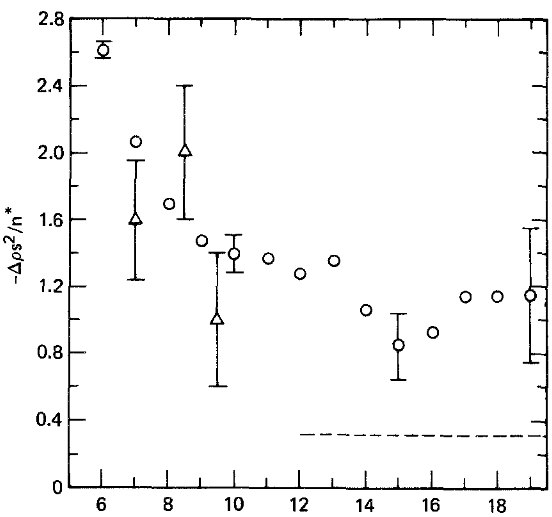

Fig. 1. The low-density velocity autocorrelation function for the Lorentz gas as a function of mean collision time s. The deviation of the velocity autocorrelation function $\rho(s)$, normalized so that $\rho(0) = 1$, from an exponential $\rho_0(s) = \exp(-4s/3)$, that is, $-[\rho(s) - \rho_0(s)]s^2/n^*$, is plotted at $n^* = 0.05$. The circles, representing the present run of about 4×10^8 collisions, are compared to an earlier run[11] (triangles) in which the average of four low densities is represented for a total of 10^8 collisions. The dashed line represents the low-density theoretical prediction.

there is a drastic change of this coefficient at still lower densities, this indicates, as shown in Fig. 1, some theoretical deficiency.

The negative tail of the Lorentz gas is caused by a long sequence of backscattering events that lead to a higher than random probability of return of a particle to its starting position. These same events lead to the logarithmic divergence of the Burnett coefficient at low density, as indicated in Table I, confirming the theoretical prediction of the random walk with a waiting time distribution that β_B is one power larger than β_D. Note also, as in the fluid, that the coefficient α_B is of opposite sign to that of α_D. A plausible cause for this behavior is that some particles diffuse for larger distances in passages of less than average density, and these are weighted more heavily in the fourth moment.

At higher densities, the value of $-\beta_D$ decreases to a minimum value of 4/3 at the percolation density near 0.37, but interestingly enough, the Burnett coefficient diverges even beyond the percolation density to $n^* = 0.477$, in a region where the diffusion coefficient is zero. The autocorrelation function leading to the Burnett coefficient loses its long-time tail at a density near 0.477, as shown in Table I by $\alpha_B = 0$. Beyond this density, α_B changes sign, the Burnett coefficient converges, but its value is zero. These observations are consistent with the prediction of the random walk with a waiting time distribution, as shown in Table I by the column labeled β_B'. The waiting time distribution also predicts an intermediate region where the diffusion coefficient vanishes and the Burnett coefficient diverges. Finally, it is interesting to note from Table I, from the various alternate versions of the Lorentz problems investigated, that neither the detailed topology of the space nor the kinematics of the particle motion affects the power law of the tail significantly.

The effect of these long-time correlations on the nature of the limiting distribution itself also can be deduced from the computer-generated information. The difference in the distribution of displacement between the two-dimensional Lorentz gas and the fluid of disks is indicated in Fig. 2. In the upper part of the figure, the fourth cumulant divided by the second moment squared is shown for the two systems. Even though both fourth cumulants diverge, the distribution can still be Gaussian if this ratio vanishes in the long-time limit. The ratio test for the Lorentz gas is hence consistent with a Gaussian distribution in the long-time limit and in the diffusion region, while the one for the fluid is not. A part of the actual distribution is shown in the lower part of the plot and this gives more direct evidence of the Gaussian nature of the distribution of displacements for the Lorentz gas. The figure also gives evidence that the non-Gaussian displacement distribution for the disk fluid is not due to the finite number of particles used in the computer calculations. Both plots in Fig. 2 show that fewer particles than predicted by a Gaussian

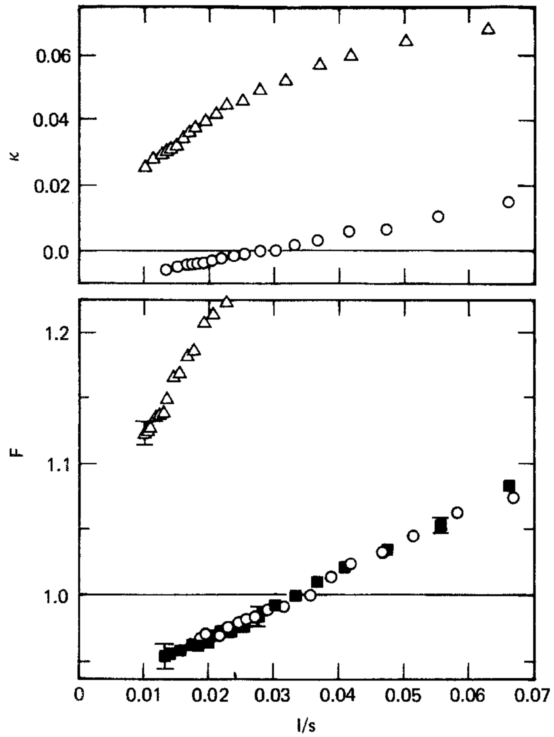

Fig. 2. Comparison between a system of hard disks and a two-dimensional Lorentz gas of the fourth cumulant and of the distribution of displacements. The upper plot shows $K(s) = [\langle \Delta x^4(s) \rangle - 3\langle \Delta x^2(s) \rangle^2]/3\langle \Delta x^2(s) \rangle^2$ against $1/s$, where s is time measured in collision times. The lower plot shows the distribution of displacements normalized by a Gaussian of the same half-width, that is, the same $\sigma = \langle \Delta x^2(s) \rangle^{1/2}$, in the interval between 3.1σ and 3.3σ against $1/s$ as well. The triangles represent a Lorentz gas at $n^* = 0.1$, while the circles correspond to a disk fluid of 1968 particles and the squares of 4012 particles at an area relative to the close-packed area A/A_0 of 3. The error bars are indicated, but for the upper figure are smaller than the size of the plotting characters in the about 10^8 collision runs.

distribution are present at large distances at long times, presumably because the coherent vortex mode leads particles back to the center. More details about the evolution of the distribution of displacements will be given in a subsequent publication, but it is evident that the Markovian approximation is not valid for the rate at which moments of the distribution approach their limiting value for even some of the simplest models for which the limiting distribution is Gaussian. More importantly, left open is the question whether the limiting distribution is Gaussian in three-dimensional fluids in which long-range correlations are also known to exist.

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REFERENCES

1. B. J. Alder and T. E. Wainwright, *Phys. Rev. A* **1**:18 (1970).
2. I. M. deSchepper and M. H. Ernst, *Physica* **87A**:35 (1977).
3. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, 1970), Chapter 8.
4. W. W. Wood, *Fundamental Problems in Statistical Mechanics, Vol. 3*, E. D. G. Cohen, ed. (1975), p. 331.
5. L. A. Bunimovich, *Theory Probability Appl.* **19**:65 (1974); Y. Sinai, *Russ. Math. Surv.* **25**:137 (1970).
6. M. M. Ernst and A. Weyland, *Phys. Lett.* **34A**:39 (1971).
7. W. W. Wood and F. Lado, *J. Comp. Phys.* **7**:528 (1971).
8. S. W. Haan and R. Zwanzig, *J. Phys. A: Math. Gen.* **10**:1547 (1977).
9. N. C. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**:1087 (1953).
10. E. W. Montroll and G. H. Weiss, *J. Math. Phys.* **6**:167 (1965).
11. C. Bruin, *Physica* **72**:261 (1974).