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BROWNIAN TRAIL RECTIFIED.

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The experiments described here indicate when one of Nature's best fractals--the Brownian trail--becomes nonfractal.

In most ambient fluids, the trail of a Brownian particle is self-similar over many decades of length. For example, the trail of a submicron particle suspended in an ordinary liquid, recorded at equal time intervals, exhibits apparently discontinuous changes in velocity from macroscopic lengths down to molecular lengths: the trail is a random walk with no velocity "memory" from one step to the next. In ideal Brownian motion, the kinks in the trail persist to infinitesimal time intervals, i.e. it is a curve without tangents. Even in real Brownian motion in a liquid, the time interval must be shortened to $\sim 10^{-8}$ s before the velocity appears continuous.

In sufficiently rarefied environments, this time resolution at which a Brownian trail is rectified from a curve without tangents to a smoothly varying trajectory is greatly lengthened, making it possible to study the kinetic regime by dynamic light scattering. Our recent experiments with particles in a plasma have demonstrated this capability. In this regime, the particle velocity persists over a finite "step length" allowing an analogy to an ideal gas with Maxwell-Boltzmann velocities; the particle mass could be obtained from equipartition. The cross over from ballistic flight to hydrodynamic diffusion was also seen.

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INTRODUCTION

The experiments described here indicate when one of Nature's best fractals--the Brownian trail--becomes nonfractal.

In most ambient fluids, the trail of a Brownian particle is self-similar over many decades of length. For example, the trail of a submicron particle suspended in an ordinary liquid, recorded at equal time intervals, exhibits apparently discontinuous changes in velocity from macroscopic lengths down to molecular lengths: the trail is a random walk with no velocity "memory" from one step to the next. In ideal Brownian motion, the kinks in the trail persist to infinitesimal time intervals, i.e. it is a curve without tangents. Even in real Brownian motion in a liquid, the velocity appears discontinuous down to ~10^{-8} s.

In sufficiently rarefied environments, this time resolution at which a Brownian trail is rectified from a curve without tangents to a smoothly varying trajectory is greatly lengthened, making it possible to study the kinetic regime by dynamic light scattering. In recent experiments [1], we found that Brownian particles in a glow discharge exhibits Gaussian-like intensity correlation functions owing to the long mean free paths of the particles. The shape of the correlation function depends on the particles' average thermal velocity and friction coefficient, which can be related to aggregate mass and structure, and indicates a crossover from kinetic to hydrodynamic behavior.

LIGHT SCATTERING DETAILS

In homodyne photon correlation spectroscopy, the intensity of scattered light I(t) is measured at a given scattering angle θ as a function of time. The scattered field time correlation function $\langle E(0)E(t)\rangle$ is related to the displacements of each particle by $\langle E(0)E(t)\rangle=\langle\Sigma_i E_i \exp[i\mathbf{q}.\Delta\mathbf{r}_i(t)]\rangle$, where the scattering wave vector is $q=(4\pi/\lambda)\sin(\theta/2)$, λ is the wavelength, and E_i is the strength of the scattering from the ith particle.

When the particles have moved a distance $\Delta r=q^{-1}$, the phase in the scattered field reverses, causing the intensity correlation function to decay with a characteristic time τ. For diffusive particles, the characteristic time is $\tau\approx\Delta r^2/D$, where D is the diffusion constant. Hence for diffusion the decay time is proportional to q^{-2} and the (exponential) correlation function provides a measurement of D. On the other hand, for ballistic particles, which we define as when the mean free path is large compared to q^{-1}, the dephasing time is $\tau\approx\Delta r/u$, where u is the mean velocity of the particles. Thus, τ is proportional to q^{-1}. Assuming identical ballistic particles, averaging over u yields [2] a Gaussian function,

$$\langle E(0)E(t)\rangle = E_o^2 \left\langle \sum_i e^{i\mathbf{q}.\Delta\mathbf{r}_i(t)} \right\rangle = E_o^2 \langle e^{i\mathbf{q}.\mathbf{u}t}\rangle$$

$$= E_o^2 \int_0^\infty P(u)\, e^{iq.ut}\, du = E_o^2\, e^{-\frac{1}{2}q^2\langle u_z^2\rangle t^2}, \quad (1)$$

where $P(u)=[m/2\pi kT]^{3/2}\exp[-mu^2/2kT]$ is the Maxwell velocity distribution, $\langle u_z^2\rangle=kT/m$ is the mean square value of the velocity component along q, and we have assumed that the particles are uncorrelated in position. Hence in

this kinetic limit the decay time $\tau=[q\langle u_z^2\rangle^{1/2}]^{-1}$ gives a direct measure of the particle mass m through energy equipartition.

For particles that are not fully in the kinetic limit, it is necessary to generalize our treatment of the correlation function to obtain an expression suitable for the crossover between kinetic and hydrodynamic behavior. From the Langevin equation for the motion of a particle in the presence of a friction force $-\beta u$ and a rapidly fluctuating force, Chandrasekhar [3] derived the probability $W(r,t;r_o,u_o)$ that a particle is at position r at time t given an initial position r_o and initial velocity u_o,

$$W(r,t;r_o,u_o) = W_o\, e^{-R^2/R_o^2} \quad , \qquad (2)$$

where

$$R_o^2 = \frac{2kT}{m\beta^2}\,[2\beta t-3+4e^{-\beta t}-e^{-2\beta t}] \quad ,$$

$W_o=\pi^{-3/2}R_o^{-3}$, and $R=r-r_o-fu_o$ with $f=[1-\exp(-\beta t)]/\beta$. β^{-1} is the persistence time, or "braking time," of velocity fluctuations. Considering r_o and u_o to be constant, the phase factor $\langle\exp[iq.(r-r_o)]\rangle$ averaged over $W(r)$ is just $\exp(iq.fu_o)\exp(-q^2R_o^2/4)$, independent of r_o. Assuming that the probability function for u_o is the Maxwellian distribution $P(u_o)$, the field correlation function, including the kinetic-hydrodynamic crossover, is

$$\langle E(0)E(t)\rangle = E_o^2\, \exp[-2q^2\langle u_z^2\rangle\beta^{-2}g(\beta t)] \quad , \qquad (3)$$

where $g(x)=-1+x+e^{-x}$.

For times long compared to the persistence time β^{-1}, Eq. (3) has an exponential form, $\exp(-q^2Dt)$, where $D=kT/m\beta$ is the diffusion constant; for short times Eq. (1) is recovered. As expected, the mean square displacement $\langle\Delta r^2\rangle=(6kT/m\beta^2)g(\beta t)$, which can be obtained [3] by averaging $|r-r_o|^2$ over $W(r)$, is just $\langle u_z^2\rangle t^2$ for t smaller than β^{-1} and 6Dt for t greater than β^{-1}.

Polydispersity can affect the shape of the correlation function. As a trial cluster mass distribution, we explored the power-law form expected for an aggregating system with a constant source of primary particles [4], $N(m)\sim m^{-\varepsilon}\exp(-m/m_o)$, where m_o is a cutoff mass. The polydisperse, kinetic limit is found by averaging Eq. (1) over $m^2N(m)$ (for small q),

$$\langle E(0)E(t)\rangle = E_o'^2 \int_0^\infty m^2\, N(m)\, e^{-q^2(kT/2m)t^2}\, dm \qquad (4)$$

$$= E_o'^2\, 2^{\varepsilon-2}(t/t_o)^{3-\varepsilon}\, K_{3-\varepsilon}(t/t_o)$$

where E_o' is a constant, $t_o^2=m_o/(q^2kT)$, and $K_\nu(x)$ is the ν-order Bessel function of imaginary argument. Assuming β to be mass independent (see below), the general polydisperse case, including the kinetic-hydrodynamic crossover as in Eq. (3), can be obtained by replacing t^2 by $\beta^{-2}g(\beta t)$.

EXPERIMENTAL DETAILS

The apparatus for our experiments has been described in detail elsewhere [5]. Near the center of a large aluminum chamber (46 cm on a side), fitted with windows for optical access, two 12-cm-dia circular metal screens formed a horizontal parallel plate capacitor with spacing 2.5 cm. After evacuation, a 1-to-7 gaseous mixture of silane (SiH_4) and ammonia (NH_3) flowed continuously through the chamber, maintaining a pressure of about 0.3 Torr at a total flow rate of 80 standard cc min^{-1}. When the electrodes were energized with 30 W rf power at 13.56 MHz, a bright, stable discharge could be seen between the screens, except in nonluminous "sheath" regions within 0.5 cm of the screens. Reactions produced solid particles (a

Si-N-H material [5] similar to silicon diimide $[Si(NH)_2]_n$) throughout the plasma, as was evident by scattered laser light. Particles collected on filter paper were found by transmission electron microscopy to consist of aggregates of primary particles ranging in size from 10 nm to 200 nm.

Vertically polarized laser light (λ=633 nm) was focussed using a 50 cm focal length lens, and the light scattered from the particle laden plasma was collected with a similar lens in individual runs at horizontal scattering angles from θ=2° to 15°, i.e. with the scattering wave vector q parallel to the electrodes. The scattered light was focussed on a 200 μm masking pinhole to reject flare light, then passed to a photomultiplier tube. By autocorrelating the photocurrent, we obtained $\langle I(0)I(t)\rangle$, an example of which is shown in Fig. 1. We also made measurements at various vertical scattering angles (q perpendicular to the electrodes), pressures, and positions in the plasma; measurements of the time-averaged intensity $\langle I\rangle$ yielded an average radius of gyration of R_g=0.36 ± 0.05 μm. Thus the dynamic measurements were taken at $q<R_g$.

ANALYSIS

A fit with Eq. (3) (monodisperse, with a kinetic-hydrodynamic crossover) and its residuals are shown in Fig. 1 and can be seen to be satisfactory for all t. In general, fits to the monodisperse model with a kinetic-hydrodynamic crossover were better (smaller and more random residuals) than for the fully kinetic models. As shown below, the ambient pressure is such that we would expect the clusters to be in a crossover regime. For most purposes a fit to a pure Gaussian, $\exp(-t^2/\tau^2)$ from Eq. (1), in the limit $t\to 0$ was adequate to extract the decay time $\tau=q^{-1}\langle u^2\rangle^{-1/2}$, although these fits are incorrect for large t. Of course, the general polydisperse case, mentioned below Eq. (4), could also be used, but it would be difficult to improve on the fits to the monodisperse model.

We found that the velocity $\langle u_z^2\rangle^{1/2}=(\tau q)^{-1}$ is independent of q; this establishes free flight transport as the reason for the slow, initially Gaussian decay of $\langle I(0)I(t)\rangle$. The rms velocity $(\tau q)^{-1}$ was 4.7 ± 0.5 cm s^{-1}, corresponding to an average mass $m=1.9\times10^{-15}$ g using $\langle u_z^2\rangle=kT/m$. Here we have assumed room temperature for the particles and gas [6]. Given a typical primary particle radius of ~10 nm and a material density [5] of 1.8 g cm^{-3}, this mass equals ~300 primary particles. The density m/R_g^3 of a typical cluster is of order 10^{-2} g cm^{-3}, indicating a very open structure.

The velocity persistence times β^{-1} obtained from the fits for various q were consistently in the range 88 ± 8 μs, which we now argue is a reasonable value. According to kinetic theory [7], the drag per unit mass for a free-molecular (size << gas mean free path) sphere of radius a and mass m_p is

$$\beta_o = \frac{8}{3}\rho\left(\frac{2\pi kT}{m'}\right)^{1/2}\left(1+\frac{\pi\alpha'}{8}\right)\frac{a^2}{m_p}$$

where ρ is the gas (mass) density, m' is the gas molecular weight, and α' is an "accomodation coefficient" of order 1 representing the fraction of gas molecules reflecting from the surface in equilibrium. A free-molecular aggregate of N such primary particles, sufficiently open in structure that ballistic gas molecules can pass through it [8], will have a collision cross section ~Na^2. Dividing by the cluster mass renders β independent of N, $\beta\approx\beta_o$. Using the appropriate parameters, we obtain $\beta^{-1}\approx$70 μs, in reasonable agreement with the measured value (88 μs) considering the approximations. (This value corresponds to a mean free path $\langle u_z^2\rangle^{1/2}/\beta$=4.1 μm, which can be compared to q^{-1}=2.9 μm at our smallest scattering angle.)

The fact that a monodisperse model fits the data may be an indication that the particles were spatially sorted according to charge by the plasma potential [6]. These results could be considered a test of the validity of

the Maxwellian velocity distribution P(u) for the particles; in the kinetic regime the particles act like a "gas" of micron-size molecules.

In summary, Brownian particles describe a path that is fractal only above the length scale defined by their mean free path. For particles suspended at sufficiently low pressure, this distance is extended into the optical regime. In our light scattering experiments, we were able to access wavevectors small enough to resolve not only the ballistic flight but the crossover from ballistic to diffusive (fractal) behavior as well. While the velocity of all Brownian particles must be continuous at some small length scale, our experiments appear to be the first instance studied in which the "Brownian steps" of a real random walker could be resolved.

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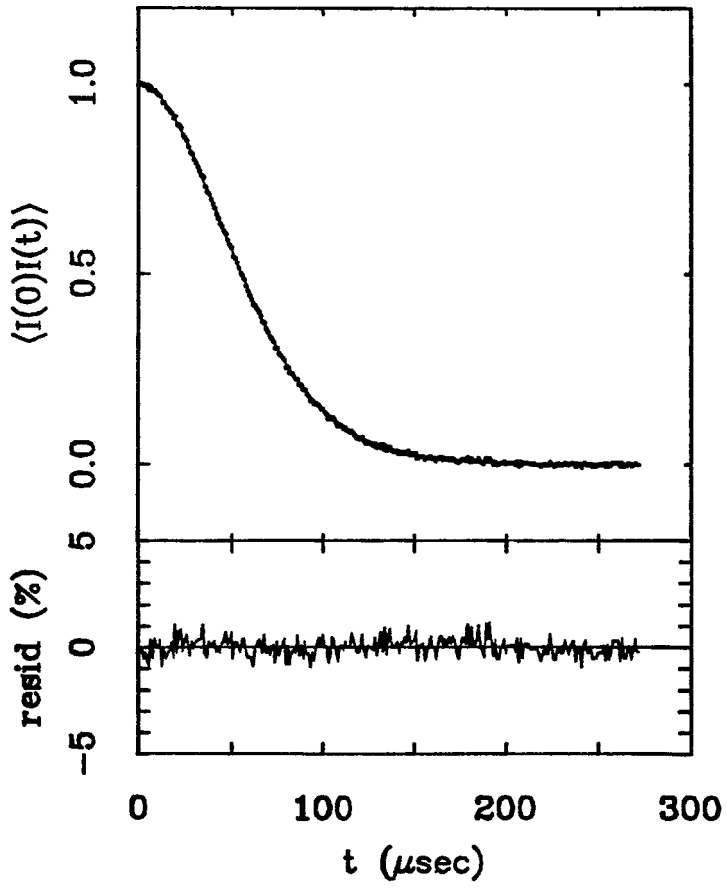

Figure 1. Intensity autocorrelation function ($q=3.47\times10^3$ cm^{-1}) for particles generated in rf glow discharge and fit to monodisperse model, Eq. (3), with a kinetic-hydrodynamic crossover; residuals are at the bottom.