Velocity Persistence of Brownian Particles Generated in a Glow Discharge

Alan J. Hurd and Pauline Ho
Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 14 March 1989)

Quasielastic light scattering from Brownian particles in the rarefied environment of a glow discharge exhibits Gaussianlike 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.

PACS numbers: 47.45.Dt, 05.40.+j, 52.75.−d, 66.10.Cb

An ingredient of Brownian motion that is not often considered is the "free flight" steps making up the random walk. Since the velocity of a suspended Brownian particle changes on short-time scales ($\sim 10^{-8}$ s) due to the rapid (10^{21} s^{-1}) bombardment by liquid molecules,[1] a hydrodynamic, diffusional description of its transport is adequate for macroscopic length and time scales. In rarefied aerosols, however, the mean free path of diffusing particles can be large compared to optical wavelengths; on time scales comparable to the time of flight, the transport must be described by kinetic theory. In this Letter we describe light scattering experiments with particles generated in a radio frequency (rf) glow discharge in which the data are best described by ballistic transport for short times crossing over to diffusional transport for long times. We establish these regimes and discuss briefly the ramifications of polydispersity. To our knowledge, the kinetic regime has not been reported previously for Brownian particles,[2] although both regimes have been studied in gases.[3] Light scattering studies of motile bacteria[4] have also yielded Gaussian-type intensity correlation functions, like those of the kinetic regime, but for a different reason: The long mean free path of a bacterium is due to swimming rather than thermal motion.

In light scattering by homodyne photon correlation spectroscopy, the scattered intensity $I(t)$ 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 measured via the intensity correlation function,[5]

$$\langle I(0)I(t)\rangle = \int_0^\infty I(t')I(t'+t)dt' = I_0^2 + \alpha\langle E(0)E(t)\rangle^2, \quad (1)$$

where I_0 is a constant background and α is a constant factor depending on the detector. Since the instantaneous scattered field $\mathbf{E}(t)$ depends through a phase factor on the positions $\mathbf{r}_i(t)$ of N illuminated scatterers,

$$\mathbf{E}(t) = \sum_{i=1}^{N} \mathbf{E}_i e^{i\mathbf{q}\cdot\mathbf{r}_i(t)}, \quad (2)$$

the intensity fluctuates according to the changing interference conditions associated with their movement. [The scattering wave vector is $\mathbf{q} = (4\pi/\lambda)\sin(\theta/2)$, λ is the wavelength, and $\mathbf{E}_i$ is the strength of the scattering from the ith particle.]

In general, the intensity correlation function decays in the time τ for a typical particle to move a distance $\Delta r = q^{-1}$, which would reverse the phase in Eq. (2). For diffusive particles, $\tau \approx \Delta r^2/D$, 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.

In the case of ballistic particles, which we define as when the mean free path is large compared to q^{-1}, $\tau \approx \Delta r/u$, where u is the mean velocity of the particles. Thus, τ is proportional to q^{-1}. For identical particles in this limit, averaging[5] over $\mathbf{u}$ yields a Gaussian correlation function,

$$\langle E(0)E(t)\rangle = E_0^2\left\langle \sum_i e^{i\mathbf{q}\cdot\Delta\mathbf{r}_i(t)}\right\rangle = E_0^2\langle e^{i\mathbf{q}\cdot\mathbf{u}t}\rangle = E_0^2\int_0^\infty P(u)e^{i\mathbf{q}\cdot\mathbf{u}t}du = E_0^2 e^{-(1/2)q^2\langle u_z^2\rangle t^2}, \quad (3)$$

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 $\mathbf{q}$, 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.

Next, we 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 $-\beta\mathbf{u}$ and a rapidly fluctuating force $\mathbf{A}(t)$,

$$\dot{\mathbf{u}} = -\beta\mathbf{u} + \mathbf{A}(t). \quad (4)$$

Chandrasekhar[1] derived the probability $W(\mathbf{r},t;\mathbf{r}_0,\mathbf{u}_0)$ that a particle is at position $\mathbf{r}$ at time t given an initial

position $\mathbf{r}_0$ and initial velocity $\mathbf{u}_0$,

$$W(\mathbf{r},t;\mathbf{r}_0,\mathbf{u}_0)=W_0 e^{-R^2/R_0^2}, \quad (5)$$

where

$$R_0^2=\frac{2kT}{m\beta^2}[2\beta t-3+4e^{-\beta t}-e^{-2\beta t}],$$

$W_0=\pi^{-3/2}R_0^{-3}$, and $\mathbf{R}=\mathbf{r}-\mathbf{r}_0-f\mathbf{u}_0$ with $f=[1-\exp(-\beta t)]/\beta$. By averaging Eq. (4) over time periods long compared to fluctuations in $\mathbf{A}(t)$, we obtain the relation $d\langle\mathbf{u}\rangle/dt=-\beta\langle\mathbf{u}\rangle$. Thus, β^{-1} can be seen to be the persistence time, or "braking time," of velocity fluctuations. Considering $\mathbf{r}_0$ and $\mathbf{u}_0$ to be constant, the phase factor $\langle\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}_0)]\rangle$ averaged over $W(\mathbf{r})$ is just $\exp(i\mathbf{q}\cdot f\mathbf{u}_0)\exp(-q^2R_0^2/4)$, independent of $\mathbf{r}_0$. Assuming that the probability function for $\mathbf{u}_0$ is the Maxwellian distribution $P(u_0)$, the field correlation function, including the kinetic-hydrodynamic crossover, is

$$\langle E(0)E(t)\rangle=E_0^2\exp[-2q^2\langle u_z^2\rangle\beta^{-2}g(\beta t)], \quad (6)$$

where $g(x)=-1+x+e^{-x}$; $\langle I(0)I(t)\rangle$ can be found by Eq. (1).

For times long compared to the persistence time β^{-1}, Eq. (6) has an exponential form, $\exp(-q^2Dt)$, where $D=kT/m\beta$ is the diffusion constant, whereas for short times Eq. (3) is recovered. As expected, the mean square displacement[1] $\langle\Delta r^2\rangle=(6kT/m\beta^2)g(\beta t)$, which can be obtained by averaging $|\mathbf{r}-\mathbf{r}_0|^2$ over $W(\mathbf{r})$, 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,[6] $N(m)\sim m^{-\epsilon}\exp(-m/m_0)$, where m_0 is a cutoff mass. The *polydisperse*, kinetic limit is found by averaging Eq. (3) over $m^2N(m)$ (for small q),

$$\langle E(0)E(t)\rangle=E_0'^2\int_0^\infty m^2N(m)e^{-q^2(kT/2m)t^2}dm$$
$$=E_0'^2 2^{\epsilon-2}(t/t_0)^{3-\epsilon}K_{3-\epsilon}(t/t_0), \quad (7)$$

where E_0' is a constant, $t_0^2=m_0/q^2kT$, 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. (6), can be obtained by replacing t^2 by $\beta^{-2}g(\beta t)$.

The apparatus for our experiments has been described in detail elsewhere.[7] We used a large aluminum chamber (46 cm on a side) fitted with windows for optical access. Near the center of the box, two 12-cm-diam circular metal screens formed a horizontal parallel-plate capacitor with spacing 2.5 cm. One electrode was grounded to the box and the other was attached to an rf generator through an impedance-matching circuit ("symmetrical geometry"[8]). 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 cm^3min^{-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 between the silane and ammonia gases produced solid particles (a Si-N-H material[7] similar to silicon diimide $[Si(NH)_2]_n$) throughout the plasma, as was evident by scattered laser light. Particles collected by deposition on filter paper in the box were found[7] by transmission electron microscopy to consist of aggregates of primary particles ranging in size from 10 to 200 nm.

The light scattering from particles was greatest in the glowing plasma within 0.2 cm of the sheath boundary, and it was in this region that we performed the experiments reported here. Since no particles could be seen inside the dark space of the sheath, we believe that the particles may have been negatively charged.[8] However, since the scattering wave vector was parallel to the electrodes, rf-field-driven particle motions would be perpendicular to $\mathbf{q}$ in these experiments and should not affect the measurements. Particle densities of order 10^8 cm^{-3} have been measured by light scattering in similar plasmas.[9]

Vertically polarized laser light ($\lambda=633$ nm) was focused 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 $\theta=2°$ to 15°, i.e., with the scattering wave vector $\mathbf{q}$ 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 autocorrelation of the photocurrent, we obtained $\langle I(0)I(t)\rangle$, an example of which is shown in Fig. 1. We also made measurements with vertical scattering angles ($\mathbf{q}$ perpendicular to the electrodes), pressure dependence, position dependence in the plasma, and static intensity, the details of which will be given in a subsequent publication. We mention only that the average radius of gyration from static intensity was found to be $R_g=0.36\pm0.05$ μm and that the dynamic measurements were taken at $q<R_g$.

A fit with Eq. (6) (monodisperse, with a kinetic-hydrodynamic crossover) and its residuals are shown in Fig. 1(a) and can be seen to be satisfactory for all t. The solid curve in Fig. 1(b) is a fit by a pure Gaussian, Eq. (3) (monodisperse, fully kinetic), with its residuals plotted below as a solid line. The residuals for fitting with Eq. (7) (polydisperse, fully kinetic) are also seen in the lower part of Fig. 1(b) (dotted curve). In general, fits by the monodisperse model with a kinetic-hydrodynamic crossover were better (smaller, more random residuals) than for the fully kinetic models. As shown below, the

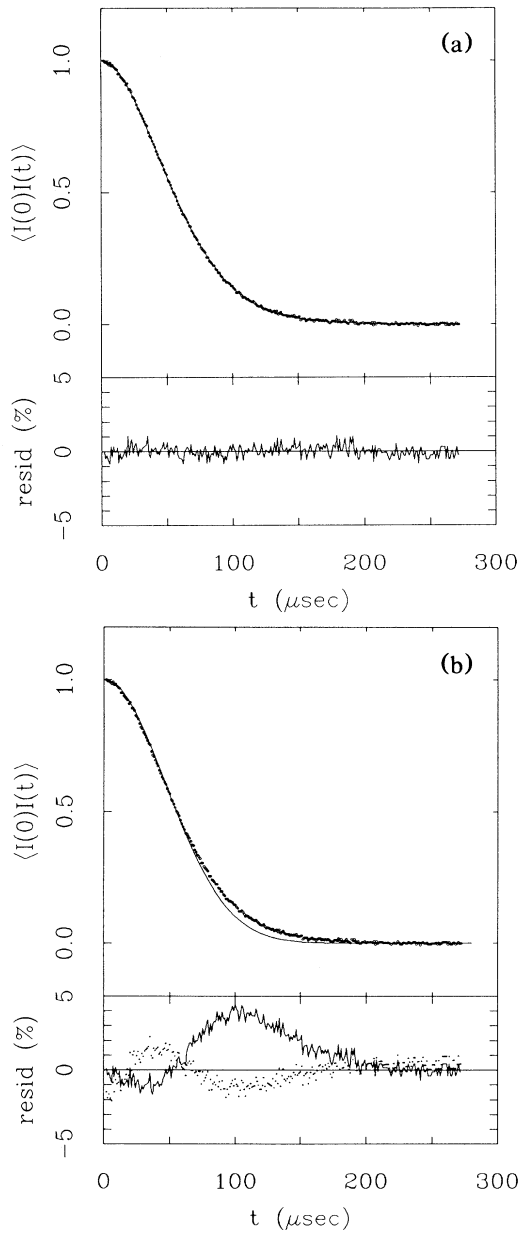

FIG. 1. Intensity autocorrelation function for particles generated in rf glow discharge, $q=3.47\times10^{3}$ cm^{-1}. (a) Fit by monodisperse model, Eq. (6), with a kinetic-hydrodynamic crossover; its residuals are shown at the bottom. (b) Fit by monodisperse kinetic model, Eq. (3) (Gaussian), with residuals shown by the solid line at the bottom. The dotted residuals at the bottom correspond to a polydisperse model in the kinetic limit, Eq. (7).

ambient pressure is such that we would expect the clusters to be in a crossover regime. For most purposes a fit by a pure Gaussian, $\exp(-t^2/\tau^2)$ from Eq. (3), in the limit $t\rightarrow 0$ was adequate to extract the decay time $\tau=q^{-1}\langle u^2\rangle^{-1/2}$, although these fits are incorrect for

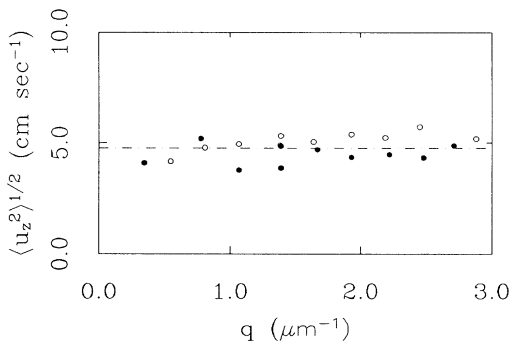

FIG. 2. rms velocity, $\langle u_z^2\rangle^{1/2}=(\tau q)^{-1}=4.7$ cm s^{-1}, vs scattering wave vector q for two consecutive scans in the scattering angle.

large t. Of course, the general polydisperse case, mentioned below Eq. (7), could also be used, but little additional information would be gained because it would be difficult to improve on the fits with the monodisperse model.

Figure 2 shows 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 $\langle I(0)I(t)\rangle$. Flowing aerosols[10] can also give rise to a Gaussian-type decay (due to the transit of particles through the Gaussian intensity profile of a laser), but the decay is q-independent (unlike ours) and depends on the width of the incident beam. As a check, we defocused the incident laser and observed no difference in the correlation function.

We found the root mean square velocity $(\tau q)^{-1}$ to be 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.[8] (Although the electrons in a glow discharge have effective temperatures of order 10^5 K, the molecules are not equilibrated with the electrons.) Given a typical primary particle radius of ~10 nm and a material density[7] of 1.8 g cm^{-3}, this mass equals ~300 primary particles. Clearly the clusters observed *ex situ* aggregated to some extent in the plasma as well as during deposition. Furthermore, the density m/R_g^3 of a typical cluster is of order 10^{-2} g cm^{-3}, indicating a very open structure.

Finally, 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, the drag per unit mass for a free-molecular (size $\ll$ gas mean free path) *sphere* of radius a and mass m_p is[11]

$$\beta_0=\frac{8}{3}\rho\left(\frac{2\pi kT}{m'}\right)^{1/2}\left(1+\frac{\pi\alpha'}{8}\right)^2\frac{a}{m_p},$$

where ρ is the gas (mass) density, m' is the gas molecular weight, and α' is an "accommodation 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,[12] will have a collision cross section $\sim Na^2$. Dividing by the cluster mass renders β independent of N, $\beta \simeq \beta_0$. Using the parameters appropriate for our experiment, we obtain $\beta^{-1} \simeq 70$ 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.)

In summary, the observed velocity persistence times combined with the shape of the light scattering correlation function show that the particles in the glow disdcharge were in a kinetic-hydrodynamic crossover regime. 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.[8] These results could be considered as 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. We have assumed no hydrodynamic memory effects,[13] which could be interesting in this kinetic-hydrodynamic regime.

We gratefully acknowledge fruitful interactions with Richard J. Buss, Francois Leyvraz, Andy Glines, Bill Flower, and especially Chris Sorensen, who has conceived of similar experiments. This work was supported by Sandia National Laboratories under DOE Contract No. DE-AC04-76-DP00789.

[1]S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943). Reprinted in N. Wax, *Selected Papers on Noise and Stochastic Processes* (Dover, New York, 1954).

[2]B. Dahneke (private communication). B. Dahneke and D. K. Hutchins have utilized a dynamic light scattering technique to measure the mass, size, and other properties of individual particles by measurement of their motions over periods in which the kinetic, crossover, and hydrodynamic regimes are resolved.

[3]N. A. Clark, Phys. Rev. A **12**, 232 (1975).

[4]D. W. Schaefer and B. J. Berne, Biophys. J. **15**, 253 (1975), and references therein.

[5]B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), Sec. 5.6.

[6]E. M. Hendriks and M. H. Ernst, J. Colloid Interface Sci. **97**, 176 (1984); T. Vicsek, P. Meakin, and F. Family, Phys. Rev. A **32**, 1122 (1985); Z. Racz, Phys. Rev. A **32**, 1129 (1985).

[7]P. Ho, R. J. Buss, and R. E. Loehman, J. Mater. Res. (to be published).

[8]B. Chapman, *Glow Discharge Processes* (Wiley, New York, 1980).

[9]K. G. Spears, R. P. Kampf, and T. J. Robinson, J. Phys. Chem. **92**, 5297 (1988).

[10]T. W. Taylor and C. M. Sorensen, Appl. Opt. **25**, 2421 (1986).

[11]P. S. Epstein, Phys. Rev. **23**, 710 (1924).

[12]A "sufficiently open" structure would have a fractal dimension less than 2. (The fractal dimension for cluster-cluster aggregation is 1.8.) This was first pointed out to us by Tom Witten. See also R. D. Mountain, G. W. Mulholland, and H. Baum, J. Colloid Interface Sci. **114**, 67 (1986).

[13]R. Zwanzig and M. Bixon, J. Fluid Mech. **69**, 21 (1975).