Evidence for Failure of Millikan's Law of Particle Fall in Gases

Yong W. Kim and Paul D. Fedele
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015

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Discovery of a new phenomenon is reported for submicron spheres undergoing a fall in nitrogen in the density range of 1 to 22 atm at 293 K. The measured fall rate of a single test particle increases with density if the particle is sufficiently small that its Brownian diffusion velocity becomes comparable to its velocity of fall, in contradiction to the Millikan law of fall embodying the concept of slip. The trend appears to reverse smoothly to that of Millikan's in the limit of large particle radius.

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In the course of our experimental investigations into Brownian fluctuations in general and the persistent velocity autocorrelation in particular,[1] as guided by intense theoretical activities in statistical physics of the last decade, it has come to light that the Millikan law of fall, embodying the notion of decreasing slip with increasing gas density,[2] breaks down in the regime where the Brownian particle is so small that its Brownian diffusion velocity becomes comparable to its velocity of fall. In this Letter, we report the experimental evidence, together with an account of our exhaustive search for the underlying physics of the new phenomenon, which presents a special opportunity for theoretical analyses as the first simple and dramatic example in nonequilibrium steady-state problems of current interest.[3]

In our experiment, a single particle is held for up to 15 h in a variable-density Brownian cell as shown in Fig. 1. An image of the particle under illumination by an argon ion laser (514.5 nm at <20 mW cw) is displayed on a television monitor with a total magnification of 328 ± 8, giving a $0.39 \times 0.55\text{-mm}^2$ laboratory field of view. The exact particle size remains unknown but is approximately in the range of 0.10 to 0.45 μm in radius.

Each experimental run proceeds as follows: Droplets of mineral oil (density of 0.88 g/cm^3) are first generated in the sealed settling chamber. After a 15-min wait gate valve V_2 is opened to introduce a number of particles into the Brownian cell by sedimentation. In the next hour and a half a single particle of desirable fall rate is selected and charged by uv illumination. Six electrodes, defining the 1.02-cm cube working volume within the Brownian cell, are used to manipulate the particle.

The settling chamber (and the pressure vessel through the sintered metal filter cage) is then evacuated and refilled with dry nitrogen to rid it of excess particles and oil vapor. The distance of fall in a 10-sec period is measured repeatedly for up to 980 times for the test particle at each pressure. During each 10-sec fall, all six electrodes are grounded to the Brownian cell, and the laser illumination is interrupted by means of a timer-controlled electromagnetic shutter.

The fluid density in the cell is increased by slowly bleeding high-pressure nitrogen into the vessel through needle valve V_1 with V_2 open. The rate of pressurization has been $\lesssim 5$ atm/h.

In Fig. 2 a summary of our experimental results is given for 24 different runs grouped into nine data sets. Also shown in the figure is the Millikan fall rate for comparison. For a particle

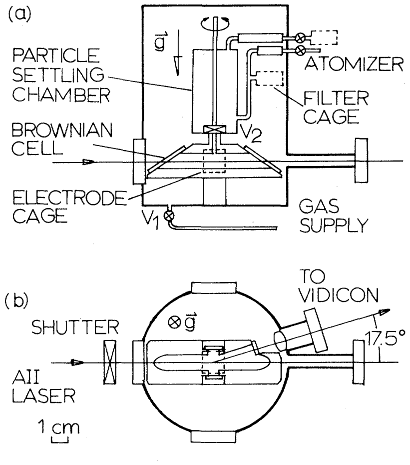

FIG. 1. (a) Side and (b) top views of the variable-density Brownian-cell assembly. The following precautions are taken to insure thermal isolation of the cell: (i) No metallic links exist between the cell and vessel, both constructed of aluminum. (ii) The assembly is mounted on a vibration- and thermally isolated optical table. (iii) During each measurement period, the cell is sealed vacuum tight (a vacuum of $<10^{-5}$ Torr can be sustained).

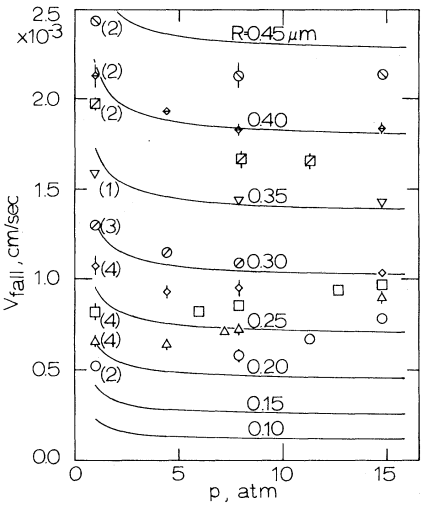

FIG. 2. Measured fall rates of mineral-oil drops in nitrogen as a function of gas density. A number of particles whose fall rates at 1 atm fall within a narrow range have been grouped together in a data set and the number of particles in each set is given in parentheses. Such a grouping not only helps improve the statistics but, more importantly, also facilitates examination of the density dependence at many more different densities than is possible with a single test particle in an 8- to 15-h period. Solid curves are computed from Eq. (1) for representative particle radii.

of radius R and mass m in the gas of density ρ and shear viscosity η, it is

$$v_{\text{fall}}(\text{Millikan}) = (m - m_f)g/\xi(\rho, R), \tag{1}$$

where

$$\xi(\rho, R) = \frac{6\pi\eta R}{[1 + (A + Be^{-CR/l})l/R]}, \tag{2}$$

and $m_f = 4\pi\rho R^3/3$. For oil drops in air, Millikan gives $A = 0.864$, $B = 0.290$, and $C = 1.25$. l denotes the mean free path as given by $\eta = 0.3502\rho\bar{c}l$, where $\bar{c}$ is the most probable molecular velocity at temperature T.[4]

For large-fall-rate particles, the data indicate a density dependence resembling that of the Millikan law. As the particles of decreasing fall rate are examined, the measured density dependence undergoes a gradual transition to one where the particle fall rate increases with increasing density. This is completely opposite to the Millikan behavior!

The Millikan experiment differs from ours in several important respects: (i) The particle radius was >0.3285 μm in the Millikan experiment while in our case it has been in the approximate range of 0.10 to 0.45 μm. (ii) Millikan's gas density range of 0.1626 to 76 cm Hg at room temperature differs significantly from our range of 76 to 1600 cm Hg. (iii) In all cases of Millikan's measurements, Brownian displacements were small compared with the typical fall distance of 1 cm, whereas all of our particles have been those with Brownian displacements comparable to or greater than the distance of fall. (iv) The Millikan data consist of a series of measurements made for different particles, each studied at only one density. Ours is the only experiment in which a single test particle has been actually taken through a range of gas density in order to examine the density dependence of the particle fall rate.[5]

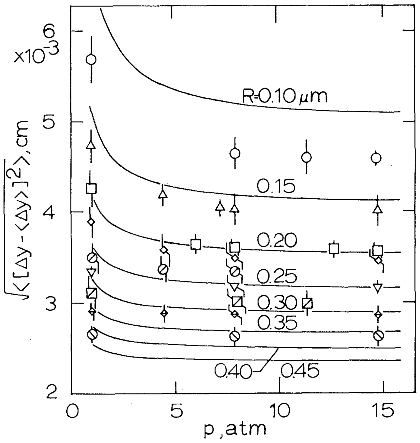

FIG. 3. Measured density dependence of the root mean square displacement about the mean for $\Delta t = 10$ sec. Symbols for individual data points follow the convention of Fig. 2. Calculated values from the Millikan law of drag are shown for comparison (solid curves).

Figure 3 shows the density dependence of the root mean square displacement ($\Delta t = 10$ sec) in the vertical direction for the same nine data sets as in Fig. 2. Also shown are the predictions from the Millikan law for representative particle radii: $\langle[\Delta y - \langle\Delta y\rangle]^2\rangle = 2kT\Delta t/\xi(\rho, R)$, where k denotes the Boltzmann constant. Overall, the observed density dependence is in line with the general trend of the Millikan law for all test-particle sizes, although some systematic departure from the Millikan behavior emerges at higher gas densities, independently of the particle size.[6]

Since our initial observation a great deal of effort has been exerted to establish that the observed phenomenon is not due to the following effects:

(i) *Electrostatic effects.*—In a series of experiments we have looked for a possible dependence on the electrical charge by varying the charge on a single particle from Q_0 to $\sim Q_0/2$, $\sim Q_0/4$, and $\sim Q_0/8$. We made measurements for several particles in this way, at either 1 or 15 atm, and found no dependence. Also, the maximum charge in our experiment has been $<60e$ and the particle is no more than 0.3 mm displaced from the center of the conducting cube of electrodes. This shows that the image charge force is too small compared with gravity to explain the phenomenon.

(ii) Residual fluid motions due to pressurization.—There is a rapidly decaying flow pattern near the center of the cell shortly after each pressurization, and an hour of waiting time is allowed before commencing a measurement. Once every 35 measurements, a 35-point average is computed. When six consecutive 35-point averages fail to show any recognizable time dependence, the subsequent 420 fall-rate measurements are used for final analysis. In addition, on three separate occasions a single test particle has been studied at five densities, three while increasing in density and two while decreasing. These measurements show that the phenomenon is completely reversible in density. The observed size dependence of the departure from the Millikan law cannot be accounted for by fluid motions of this kind in any event.

(iii) Thermal effects.—Precautions described earlier eliminated all possibilities of thermal gradient in the cell. This has also been verified by sustained application of the procedure used under item (ii) at several pressures.

(iv) Leaks.—There is no measurable decrease of pressure in the sealed pressure vessel in a 72-h period. Taking the resolution of the 18-in. Heise gauge as the upper bound, a leak rate of $<4\times10^{-6}$ cm^3/sec at 22 atm is obtained and it sets the upper bound for the flow speed due to leaks at $<4\times10^{-6}$ cm/sec. This is again too small to be of any consequence.

(v) Laser effects.—Under strict laser alignment and constant-power operation, continuous illumination has no measurable effects on the fall rate. But we have gone further and totally blocked the laser beam from the cell during each fall.

(vi) Systematics in the measurement procedure.—The majority of the measurements shown in Fig. 2 have been made in the volume element measuring 0.08 mm in width, 0.3 mm in height, and 0.2 mm in depth at the center of the electrode cage. We have in a series of measurements raised the particle through one part of the fluid and let it fall through a different region separated from the first by as much as 0.4 mm. Also the time between successive falls has been varied from about half a second to twenty seconds. No systematic connection between the fall rate and experimental protocol has been found.

(vii) Changes in the particle properties.—The nitrogen gas supply contains no known condensable species which can change the test particle size or mass at higher densities. The water-vapor content in nitrogen is <8 ppm and at 22 atm and 293 K the partial pressure of water remains at least 2 orders of magnitude below the saturated vapor pressure of 17.54 Torr. By any estimation the solubility of nitrogen in oil is $<3\%$ by volume, again too small to be of consequence. Remember that the partial pressure of oil in the Brownian cell remains unchanged during pressurization. Adsorption of nitrogen on the particle does not offer any plausible explanation. One can also dismiss the possibility that the particle may actually be a balloon.

The data reported here are limited to a single time interval of 10 sec, although small-sample measurements at other intervals have been taken. There are no theoretical or experimental indications that our observation is unique to this particular time interval.

The complete experimental evidence on hand indicates that the observed phenomenon is a manifestation of a hitherto unrecognized new physics which compliments the slip[2] in determining the law of fall with a density dependence opposite to that of the slip. In this picture, the Millikan law of fall is only an asymptotic one valid in the slip-dominated regime. The new physics has to do with the nonsteady nature of the process of fall for small particles.

The modified Langevin equation[1] with the gravity term added in an *ad hoc* fashion does not appear to have the necessary physics by itself. Our suggestion is that the fluctuating-force autocorrelation function becomes direction dependent because of the presence of a slowly decaying flow field around the test particle. The flow field has two contributions, one from the steady fall due to gravity and another from the fluctuating events. A likely consequence of the direction dependence would be that more downward events take place than those upward, all in time scales comparable to the particle relaxation time $[m/\xi(\rho,R)]$. The mean distance of fall would be sensitive to this direction dependence whereas the rms displacement would not in any obvious way, resulting in a breakdown of the classical relationship, $\langle[\Delta y$

$-\langle \Delta y\rangle]^2\rangle \propto \langle \Delta y\rangle$, as can be seen from Figs. 2 and 3.

The rather explosive growth of the departure from the Millikan behavior in going from the slip-dominated regime (large-particle limit) to the new physics regime (small-particle limit) suggests a certain nonlinear coupling between the slowly decaying flow field and the fluctuating force. The strength of the coupling increases with increasing Brownian diffusion velocity and the Basset contribution, i.e., the persistence of the flow field, indeed grows as $\sqrt{p}$. No exact theory is available at present.

We benefitted from numerous discussions with colleagues in formulating many questions which influenced the course of the experiment. In particular we acknowledge the help of Professor R. J. Emrich and Professor J. A. McLennan. This work has been supported in part by Grant No. PHY-79-9267 from the National Science Foundation. One of us (P.D.F.) receives additional support as a Byllesby graduate fellow.

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[4] In computing the Millikan fall rate in nitrogen we have used the shear viscosity of nitrogen at 293 K and the values of A, B, and C for oil drops in air. See R. A. Millikan, Phys. Rev. 21, 217 (1923).

[5] There are two references in the literature where the fall-rate measurements by Millikan for a single test particle at several pressures were hinted: one in Ref. 4 and another in P. S. Epstein, Rev. Mod. Phys. 20, 10 (1948). No evidence can be found, however, indicative of the existence or actual use of such single-particle data in obtaining the Millikan law of fall.

[6] The departure of $\langle[\Delta y - \langle\Delta y\rangle]^2\rangle$ from the Millikan law can be accounted for by the correction to the Brownian diffusion constant due to the persistence of the velocity autocorrelation function. See B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970); Y. W. Kim, Bull. Am. Phys. Soc. 18, 1468 (1973).

Ab Initio Force Constants of GaAs: A New Approach to Calculation of Phonons and Dielectric Properties

K. Kunc
Laboratoire de Physique des Solides associé au Centre National de la Recherche Scientifique, Université Pierre et Marie Curie, F-75230 Paris-Cedex 05, France

and

Richard M. Martin
Xerox Palo Alto Research Centers, Palo Alto, California 94304, and Departement de Recherches Physiques, Université Pierre et Marie Curie, F-75230 Paris-Cedex 05, France

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It is shown that self-consistent calculations of the electronic charge density in large periodic cells containing a single displaced atom provide all the information needed for *ab initio* determination of force constants, phonon dispersion curves, effective charges, and the static dielectric constant. Results are presented for GaAs.

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Two methods have been developed to calculate structural energies from the electron-ion Hamiltonian, (1) perturbation expansions[1] for phonons considered as small perturbations upon the crystal structure and (2) direct calculations[2-7] of the total energy of a crystal with "frozen phonon" displacements of arbitrary magnitude, treated on an equal basis with the energy of the undistorted lattice. The simplicity of the direct method has made it possible to carry out accurate calculations[2-7] with no essential approximations other than the local density form for exchange and correlation.[8] Remarkable successes have been found for Si, Ge, and GaAs including prediction of stable crystal structures,[3] displacive phase transitions,[4] elastic constants,[2,6] and frequencies,[2-6] pressure dependences,[2-6] and anharmonic terms[2,4,6] for phonons at $k = 0$ and at