Experimental demonstration that a free-falling aerosol particle obeys a fluctuation theorem

Chun-Shang Wong, J. Goree, and Ranganathan Gopalakrishnan

Phys. Rev. E **97**, 050601 — Published 10 May 2018

DOI: 10.1103/PhysRevE.97.050601

Experimental demonstration that a free-falling aerosol particle obeys a fluctuation theorem

Chun-Shang Wong* and J. Goree
Department of Physics and Astronomy, The University of Iowa, Iowa City, Iowa 52242, USA

Ranganathan Gopalakrishnan
Department of Mechanical Engineering, The University of Memphis, Memphis, Tennessee 38152, USA

(Dated: April 26, 2018)

We investigate the fluctuating motion of an aerosol particle falling in air. Using a Millikan-like setup, we tracked a one-micron sphere falling at its terminal velocity. We observe occurrences of particles undergoing upward displacements against the force of gravity, so that negative work is done briefly. These negative-work events have a probability that is shown to obey the work fluctuation theorem. This experimental confirmation of the theorem's applicability to aerosols leads us to develop and demonstrate an application: an *in-situ* measurement of an aerosol particle's mass.

The second law of thermodynamics forbids a reversal of heating done by friction [1]. Likewise, it forbids the extraction of work from a single-temperature bath under steady conditions [2]. While the second law holds in the thermodynamic limit for large systems, small systems allow for what other authors once called "second-law violations" [3, 4]. In such events, the forbidden extraction of work from a single-temperature bath occurs temporarily. In other words, the work done fluctuates from the more common positive value to a less common negative value. The probabilities of negative and positive work are related by a fluctuation theorem.

Fluctuation theorems are typically used to describe small nonequilibrium systems [3–8] in the presence of a heat bath. These theorems have been experimentally shown to be applicable to a variety of physical systems. Physical systems that have been studied in fluctuation-theorem experiments include single colloidal particles manipulated by a laser beam in a liquid bath [9–13], single molecules [14–19], and a metallic single-electron box [20] among others [21–28]. For aerosols, there have been experiments with nanoparticles trapped by a laser beam in rarified air [29, 30]. However, for the typical case of free aerosol particles in air, fluctuation-theorem experiments are lacking, to the best of our knowledge [31].

In fluctuation-theorem experiments of all kinds, a fluctuating thermodynamic quantity is observed, such as entropy production rate [32, 33] or free energy [34]. Another fluctuating quantity can be work [35, 36], as in the experiment we report here.

Our experimental system is simply a single micron-sized aerosol particle immersed in still air. The air is the heat bath, while gravity drives the nonequilibrium process of the particle falling. We observe the particle after it attains its terminal settling velocity, so that the system is in a nonequilibrium steady state.

This Letter has two main outcomes for the motion of a falling aerosol particle. First, we confirm that the work fluctuation theorem of van Zon and Cohen [35] accurately describes the stochastic motion of a particle in free fall. Second, our confirmation enables a new application of the fluctuation theorem: a measurement of the mass of an aerosol particle can be obtained from what was previously discarded as noise.

In our experiment, the work done by gravity on a free-falling aerosol particle is given by

$$W = -mg\Delta y. \tag{1}$$

The work done by gravity [37] depends of course on the particle's vertical displacement Δy and mass m, along with the gravitational acceleration g. It will be important later that this work does not depend on other properties of the aerosol particle, such as its size or shape.

The particle's motion is a combination of free fall and Brownian motion due to stochastic collisions with air molecules [38]. On average, the particle is displaced downward and the force of gravity does positive work. Occasionally, however, the Brownian motion overcomes the free fall; when this happens, the particle is briefly displaced upwards and the work done is negative [39]. In these brief negative-work events, work is temporarily extracted from a single-temperature bath of air. The experiment that we report here demonstrates not only that these short-lived negative-work events are observable, but also that they occur with a probability that obeys the work fluctuation theorem.

The formula for the work fluctuation theorem [35] describes the probability $p(w_\tau)$. Here, w_τ is a dimensionless work done over a specified time interval τ, and it is commonly [35] normalized by k_BT. The formula compares two probabilities; one is for a specified negative value $w_\tau = -C$ and the other is for the corresponding positive value $w_\tau = C$,

$$\ln\left[\frac{p(-C)}{p(C)}\right] = -C, \text{ as } \tau \to \infty. \tag{2}$$

As a shorthand, Eq. (2) can be written as LHS = RHS as $\tau \to \infty$.

*Electronic address: chun-shang-wong@uiowa.edu

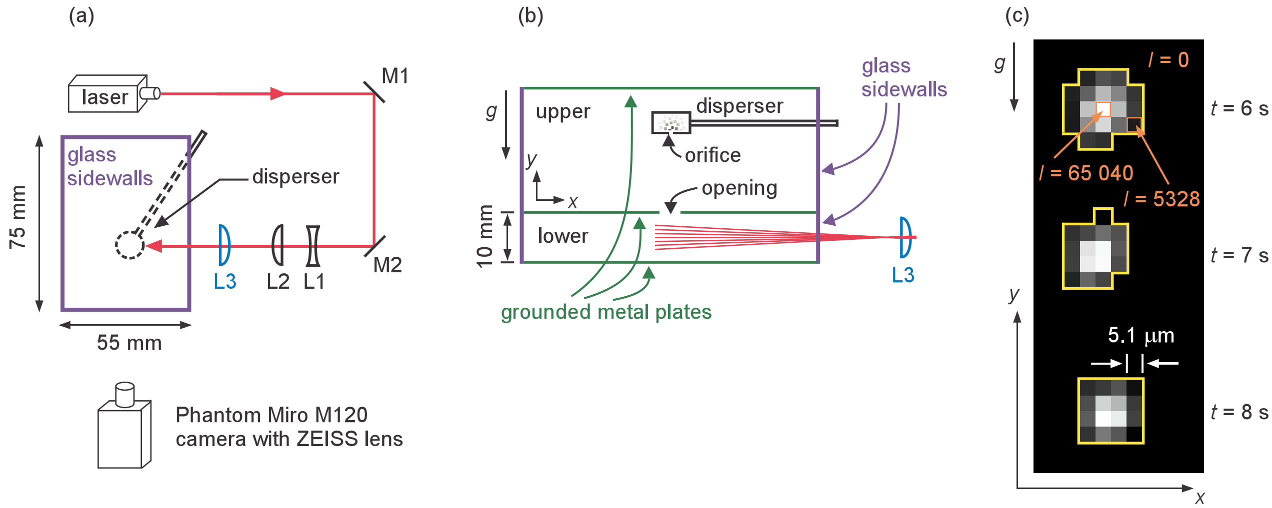

FIG. 1: (color online). Sketch of the experimental apparatus as viewed from the (a) top and (b) side. Microspheres fell from a disperser in the upper chamber. An opening limited the number of microspheres that entered lower chamber, where they were imaged by a side-view camera. Illumination of the microspheres was provided by a 15-mW HeNe laser beam that was shaped into a vertical cross section of the lower chamber. The beam-shaping optics, not drawn to scale, include: mirrors M1 and M2, spherical lenses L1 and L2, and cylindrical lens L3. The air was still. (c) Superposition of three images of the same microsphere at different times from a video. The overall downward motion is obvious at this long time interval of 1 s, and a weak horizontal diffusion can also be detected. The values of the intensity I, for each pixel within the outlined border, provide the data for particle position measurements [45]. A sample video, and all our microsphere position data, are provided in the Supplemental Material [40].

The probability $p(w_\tau)$ used in Eq. (2) for our experiment is a data point in a histogram. The histogram is prepared by counting observations of the work done on individual particles. For a single free-falling particle i, the normalized work w_τ done over a time interval τ is

$$w_{\tau,i} = -\frac{m_i g \Delta y_{\tau,i}}{k_B T}, \tag{3}$$

where $\Delta y_{\tau,i} = y_i(t+\tau) - y_i(t)$ is the vertical displacement of particle i observed during the time interval τ. For a sphere falling in air, Eq. (3) can be written as

$$w_{\tau,i} = -\frac{v_{s,i}^{3/2}}{D} \left\langle \frac{1}{\sqrt{v_{s,i}}} \right\rangle \Delta y_{\tau,i} \tag{4}$$

where D is a Brownian diffusion coefficient, $v_{s,i}$ is the settling velocity (also called the terminal velocity) of an individual sphere i, and the brackets $\langle ... \rangle$ indicate an average over particles. Equation (4), which is derived in the Supplemental Material [40], allows us to obtain the required histograms from particle position measurements only, without any knowledge of m_i, g, or T.

Experiment—We designed an experiment drawing upon on the heritage of Millikan's apparatus [44]. We observed individual micron-size particles in still air, using a two-chamber apparatus. This familiar design is intended to make our experiment understandable to a broad readership.

Our particle size was small enough to have frequent upward displacements, yet large enough to scatter sufficient light for imaging. For these purposes, a one-micron diameter was suitable. Our microspheres were a nearly monodisperse dry powder of a polymer, melamine-formaldehyde, that resists coagulation [40]. The air was at atmospheric pressure.

We began our experiment by loading a few milligrams of microspheres into a disperser within the upper chamber. The disperser was a centimeter-size metal can; its lower surface was aluminum foil with a 50-μm orifice. Manually agitating the disperser released microspheres into the upper chamber, where they attained their settling velocities. To avoid collisions or coagulation of microspheres, we reduced the number of microspheres that entered the lower chamber using a 6-mm opening between chambers. We illuminated a cross section within the lower chamber using a 632.8-nm steady-state laser beam. Microspheres within this illuminated cross section were imaged by a side-view camera operated at 200 frames/s. The camera's magnification was such that each pixel on its sensor imaged a 5.1-μm square in the lower chamber. The apparatus is sketched in Fig. 1.

To minimize disturbing effects, we designed our apparatus to avoid electric forces and Rayleigh-Bénard convection. Radiation-pressure forces from the illumination laser were also minimized. Further details of the design are in the Supplemental Material [40].

We performed our experiment so that it yielded the data required for both of our main outcomes. To demonstrate the work fluctuation theorem, we used vertical and horizontal particle positions, with no other inputs.

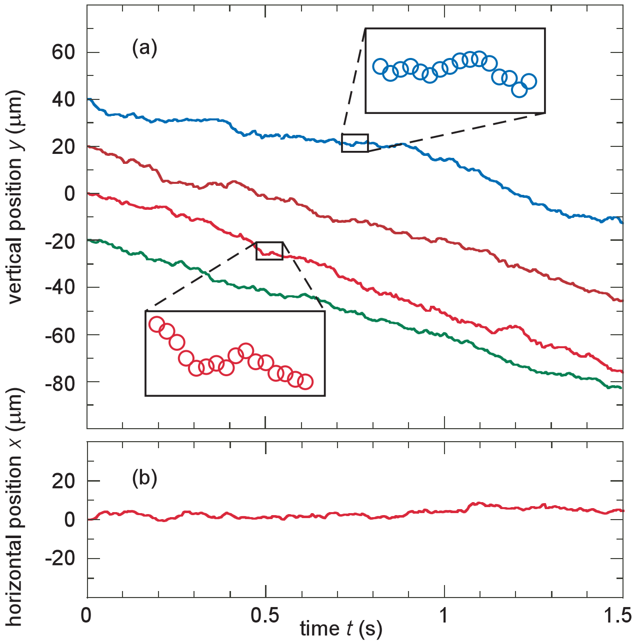

FIG. 2: (color online). Time series of microsphere positions in the lower chamber. (a) Vertical positions for four representative microspheres; curves are displaced for clarity. The downtrend trend corresponds to free-fall at a settling velocity. Due to Brownian motion, the free-fall motion occasionally reversed so that negative work is done. Such occasional events, as in the insets, have varying durations. Data points were recorded at 5 ms intervals. (b) Horizontal position of one representative microsphere. Horizontal motion consists of Brownian diffusion and a weak drift due to the illumination laser.

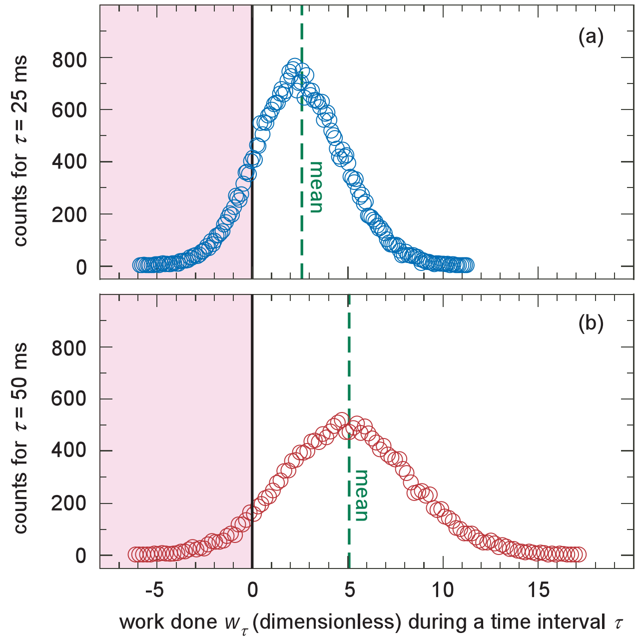

FIG. 3: (color online). Histograms of the normalized work done on microspheres during an interval τ. The occurrence of negative-work events is quantified by data points in the shaded portions of these histograms. These negative-work events are more probable for (a) τ = 25 ms than for (b) a longer τ = 50 ms. We prepared histograms by analyzing experimental time-series data for 69 microspheres, and counting observations of w_τ.

To demonstrate the mass-measurement method, we used just the vertical positions, along with inputs of our air temperature measurement $T = 295$ K and the known local gravitational acceleration [46] $g = 9.804$ m/s^2. Other experimental conditions, which were not used in any of our calculations, are given in the Supplemental Material [40].

Particle tracking—A time series of a microsphere's coordinates was obtained by image analysis. Positions were measured [45] with a random error [40] of about ± 0.1 μm. We tracked 69 individual microspheres by following them in consecutive frames, for at least 10 s. Vertical and horizontal displacements were analyzed for separate purposes.

The vertical motion, Fig. 2(a), has thermal fluctuations that are the focus of this Letter. The vertical motion also has a downward trend, corresponding to a terminal settling velocity that averaged 51.5 μm/s. Most importantly, this downward trend is occasionally overcome by upward fluctuations, as seen in the insets of Fig. 2(a). For such an upward displacement, the work done on the microspheres is negative.

The horizontal motion, Fig. 2(b), was analyzed to provide a normalization parameter for the fluctuation theorem demonstration. Horizontal displacements are dominated by fluctuations due to air-molecule impacts. An analysis of mean-square displacements yielded a Brownian diffusion coefficient $D = 26.4$ μm^2/s. This value, along with our settling-velocity measurements, is used in the denominator of Eq. (4). In this way, our demonstration of the work fluctuation theorem is accomplished using only data for the microsphere positions, without any measurement of m, g, or T.

Histograms—For the fluctuation theorem demonstration, we prepared histograms of w_τ. We began by dividing the time series for a single microsphere's vertical position into non-overlapping segments of a specified time interval τ. Each segment yielded one observation of $w_{\tau,i}$ computed using Eq. (4). Using ten different values of τ in the range 5 ms to 200 ms, we prepared ten histograms. Two of these histograms are presented in Fig. 3; the others are in Supplemental Material [40].

Negative-work events, which are the focus of the fluctuation theorem, are clearly seen in the shaded portions of Fig. 3. These negative-work events are more common for a short time interval τ = 25 ms in Fig. 3(a) than for a longer interval τ = 50 ms in Fig. 3(b). No matter the time interval, these negative fluctuations of the work are always less frequent than positive fluctuations, so that the mean values of histograms are positive.

To demonstrate the work fluctuation theorem, we obtain the LHS and RHS of Eq. (2). To start, we choose values of C and τ. The RHS is simply $-C$. The LHS is computed from data in the w_τ histogram at both $w_\tau = -C$ and $w_\tau = C$. We plotted the RHS as a line with slope -1, and we plotted the LHS as data points, in Fig. 4. Error bars in Fig. 4 reflect counting statistics in the histograms, and do not include other measurement errors [40].

Fluctuation-theorem results—We find an agreement between the LHS and RHS in Fig. 4. In this comparison, individual data points for the LHS mostly coincide, within error bars, with the line representing the RHS. This agreement serves as our demonstration of the work fluctuation theorem. We find consistent agreement across many dozens of such comparisons in Fig. 4 and Fig. SM3 of the Supplemental Material [40]. The only overall discrepancies we find between the LHS and RHS are for short times, $\tau < 25$ ms, when displacements are so small that our finite random errors in positions can have an effect, as explained in the Supplemental Material [40].

New method of measuring aerosol particle mass—In aerosol science, fluctuations in experiments are commonly discarded as useless noise, so that only time-average quantities are retained when measuring aerosol particle properties. We demonstrate here that a useful measurement can actually be obtained from what has been previously disregarded as noise. In particular, we demonstrate a new method of mass measurement for an aerosol particle using fluctuations in its vertical motion. This method is made possible by our demonstration, above, that the fluctuation theorem is applicable to a free-falling aerosol particle.

The data for our method consist only of images of particles as they fall in still air, along with values of g and T. The images are used only to obtain the vertical displacements; horizontal displacements and horizontal diffusion are not measured. The vertical displacements are analyzed using Eqs. (2) and (3), with mass as a free parameter that is adjusted to achieve agreement between the LHS and RHS of Eq. (2). This method can be done either for an individual particle or an average of multiple non-interacting particles.

For the microspheres used in the present experimental demonstration, our new method of mass measurement yielded $m = (8.07 \pm 0.10) \times 10^{-16}$ kg. This value agreed within 0.8% of the reference mass measurement of Ref. [47]. Further details on the implementation of our new mass measurement method are also provided in Ref. [47].

Advantages of our new method include requiring very little information about the particle. Prior knowledge of the size and density of the particle are not needed because, as mentioned earlier, they do not enter the two formulas used here, Eqs. (2) and (3). Moreover, it is not necessary for the particle to be spherical [48] nor does it matter if it is rotating, so long as its center of mass can be tracked. Another advantage is that the instrumentation is uncomplicated; it is the same as for our fluctuation-theorem experiment in Fig. 1. No electric charging of particles is required. There is no power supply for particle manipulation or any detector to analyze particles after they land.

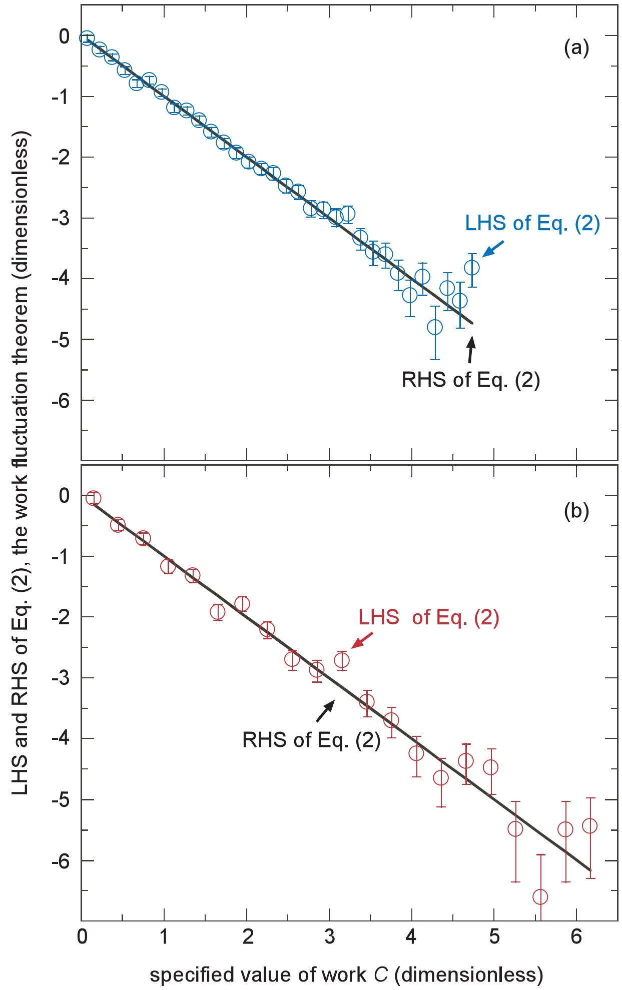

FIG. 4: (color online). Demonstration of the work fluctuation theorem, as shown by the agreement of the data points with the lines for (a) $\tau = 25$ ms and for (b) $\tau = 50$ ms. The data points and the lines correspond to the LHS and RHS of Eq. (2), respectively. We obtained LHS values with an input of experimental data from the histograms in Fig. 3.

Conclusion—In an experiment using a simplified version of Millikan's apparatus, it was demonstrated that the fluctuation theorem is applicable to an aerosol particle as it falls. Individual microspheres under the influence of gravity were tracked by video microscopy, capturing not only their steady downward settling velocity, but also their fluctuations arising from impacts with air molecules. The occasional upward fluctuations of a microsphere's motion correspond to negative work done on a microsphere. The probability of the negative-work events was confirmed to obey the work fluctuation theorem.

For aerosol science, our confirmation of the work fluctuation theorem's applicability makes possible a new mass measurement method. This measurement requires no electrical charging; it uses imaging of the vertical motion of a free-falling particle, without any need for knowledge of the particle's shape, size, or density. This measurement exploits stochastic fluctuations that until now have generally been dismissed as noise in the motion of a drifting particle.

We thank R. Belousov for helpful discussions. Work at the University of Iowa was supported by the National Science Foundation, the Department of Energy, and NASA.

[1] M. Planck, *Treatise on Thermodynamics* (Longmans, Green and Co., London, 1903), p. 81.
[2] N.-L.-S. Carnot, in *Reflections on the Motive Power of Heat*, edited by R. H Thurston, (John Wiley & Sons, New York, 1897).
[3] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[4] U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).
[5] D. J. Evans and D. J. Searles, Adv. Phys. **51**, 1529 (2002).
[6] F. Ritort, Adv. Chem. Phys. **137**, 31 (2008).
[7] E. M. Sevick, R. Prabhakar, S. R. Williams, and D. J. Searles, Annu. Rev. Phys. Chem. **59**, 603 (2008).
[8] C. Jarzynski, Annu. Rev. Phys. Chem. **2**, 329 (2011).
[9] G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **89**, 050601 (2002).
[10] D. M. Carberry, J. C. Reid, G. M. Wang, E. M. Sevick, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **92**, 140601 (2004).
[11] J. C. Reid, D. M. Carberry, G. M. Wang, E. M. Sevick, D. J. Searles, and D. J. Evans, Phys. Rev. E **70**, 016111 (2004).
[12] G. M. Wang, D. M. Carberry, J. C. Reid, E. M. Sevick, and D. J. Evans, J. Phys. Condens. Matter, **17**, 32393244, (2005).
[13] G. M. Wang, J. C. Reid, D. M. Carberry, D. R. M. Williams, E. M. Sevick, and D. J. Evans, Phys. Rev. E **71**, 046142 (2005).
[14] G. Hummer and A. Szabo, Proc. Natl. Acad. Sci. U.S.A. **98**, 3658 (2001).
[15] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco Jr., and C. Bustamante, Science **296**, 1832 (2002).
[16] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr., and C. Bustamante, Nature (London) **437**, 231 (2005).
[17] A. Alemany, A. Mossa, I. Junier, and F. Ritort, Nat. Phys. **8**, 688 (2012).
[18] D. Nickelsen and A. Engel, Phys. Rev. Lett. **110**, 214501 (2013).
[19] J. Camunas-Soler, A. Alemany, F. Ritort, Science **355**, 412-415 (2017).
[20] O.-P. Saira, Y. Yoon, T. Tanttu, M. Möttönen, D. V. Averin, and J. P. Pekola, Phys. Rev. Lett. **109**, 180601 (2012).
[21] S. Ciliberto, S. Joubaud, and A. Petrosyan, J. Stat. Mech. (**2010**) P12003.
[22] N. Garnier and S. Ciliberto, Phys. Rev. E **71**, 060101 (2005).
[23] S. Schuler, T. Speck, C. Tietz, J. Wrachtrup, and U. Seifert, Phys. Rev. Lett. **94**, 180602 (2005).
[24] F. Douarche, S. Joubaud, N. B. Garnier, A. Petrosyan, and S. Ciliberto, Phys. Rev. Lett. **97**, 140603 (2006).
[25] A. Naert, Europhys. Lett. **97**, 20010 (2012).
[26] T. B. Batalhão, A. M. Souza, R. S. Sarthour, I. S. Oliveira, M. Paternostro, E. Lutz, and R. M. Serra, Phys. Rev. Lett. **115**, 190601 (2015).
[27] S. Ciliberto, Phys. Rev. X **7**, 021051 (2017).
[28] C.-S. Wong, J. Goree, Z. Haralson, and B. Liu, Nat. Phys. **14**, 21-24 (2018).
[29] J. Gieseler, R. Quidant, C. Dellago, and L. Novotny, Nat. Nanotechnol. **9**, 358 (2014).
[30] T. M. Hoang, R. Pan, J. Ahn, J. Bang, H. T. Quan, and T. Li, Phys. Rev. Lett. **120**, 080602 (2018).
[31] The fluctuation theorem of stochastic thermodynamics should not be confused with the correlation-fluctuation theorem, which has been applied to aerosols.
[32] D. J. Evans and D. J. Searles, Phys. Rev. E **50**, 1645 (1994).
[33] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[34] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[35] R. van Zon, and E. G. D. Cohen, Phys. Rev. E **67**, 046102 (2003).
[36] K. Sekimoto, Prog. Theor. Phys. Supp. **130**, 17 (1998).
[37] The quantity termed work, described by the work fluctuation theorem of van Zon and Cohen [35], is the done by the force that provides nonequilibrium. In our experiment, this force is the steady gradient of gravitational potential energy, not stochastic forces due to the bath.
[38] In the simplest approximation, the particle's motion can be described a combination of a first-order moment (drift as seen in the lab frame) and a second-order moment (diffusion as seen in a co-moving frame), but the motion can also include higher order moments, as in R. Belousov, E. G. D. Cohen, C.-S. Wong, J. A. Goree, and Y. Feng, Phys. Rev. E **93**, 042125 (2016).
[39] R. D. Astumian, Am. J. Phys. **74**, 683 (2006).
[40] See Supplemental Material at [URL will be inserted by publisher] for further details, which includes Refs. [41–43].
[41] J. Pavlů, A. Velyhan, I. Richterová, Z. Němeček, J. Šafránková, I. Čermák, and P. Žilavý, IEEE Trans. Plasma Sci. **32**, 704-708 (2004).
[42] J. Carstensen, H. Jung, F. Greiner, and A. Piel, Phys. Plasmas **18**, 033701 (2011).
[43] M. Mikikian, L. Boufendi, A. Bouchoule, H. M. Thomas, G. E. Morfill, A. P. Nefedov, V. E. Fortov, and PKE-Nefedov Team, New J. Phys. **5**, 19 (2003).
[44] R. A. Millikan, Phys. Rev. **32**, 349-397 (1911).
[45] Y. Feng, J. Goree, and B. Liu, Rev. Sci. Instrum. **78**, 053704 (2007).
[46] N. K. Pavlis, S. A. Holmes, S. C. Kenyon, and J. K. Factor, J. Geophys. Res. **117**, B04406 (2012).
[47] C.-S. Wong, J. Goree, and R. Gopalakrishnan (unpublished).
[48] Since Eq. (4) is not used in this new mass-measurement method, there is no assumption of spherical shape.