The measurement Einstein deemed impossible

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Particles undergoing Brownian motion move with constant velocity between Brownian kicks. Albert Einstein predicted the velocity distribution, but he wrongly thought his result would never be experimentally confirmed.

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rownian motion, the seemingly random wiggle-waggle of particles suspended in a liquid or gas, was first systematically studied by Robert Brown in 1827 and described in the *Philosophical Magazine* the next year (volume 4, page 161). When Brown used a microscope to look at particles from pollen grains immersed in water, he "observed many of them very evidently in motion." It looked like the particles were alive, so vigorously did they move.

The phenomenon of Brownian motion was first explained by Albert Einstein in 1905 as a consequence of the thermal motion of surrounding fluid molecules. Einstein's theory predicts that Brownian particles diffuse; as a consequence, their mean-square displacement $\langle (\Delta x)^2 \rangle = 2Dt$ in each dimension is proportional to a diffusion coefficient D and the measured time interval t. As illustrated in figure 1a, the motion of Brownian particles looks like a jerky and unpredictable dance, and the sudden changes in direction and speed seem to indicate that velocity is not defined. Moreover, the mean velocity $\langle v \rangle \equiv \langle (\Delta x)^2 \rangle^{1/2} / t = (2D/t)^{1/2}$ diverges as t approaches 0. If you think all that is strange, you are in good company: Einstein felt the same way.

In 1907 Einstein returned to Brownian motion and concluded that on a sufficiently short time scale, a Brownian particle must have a well-defined velocity, which he called the instantaneous velocity. During that short time, Einstein argued, the particles move ballistically, as shown in figure 1b—that is, the particle trajectory is built from segments of straight-line motion with a well-defined kinetic energy.

Furthermore, Einstein predicted that the distribution of particle velocities would obey the energy equipartition theorem, a basic rule of statistical mechanics. In other words, the probability of finding a particle with a particular velocity would be determined by the Maxwell–Boltzmann distribution, a Gaussian function of speed that otherwise depends only on temperature and the mass of the particle. Einstein then made a prediction about possible experiments, a risky move for a theorist. He said that the time scale for the instantaneous velocity is so short that it would be impossible to

measure in practice. Two years later, in 1909, Einstein wrote to Jean Perrin to congratulate the French physicist for measuring the displacement of Brownian particles with a precision Einstein "did not believe . . . possible." Measuring the instantaneous velocity, however, is a much more difficult challenge than the one so admirably met by Perrin, and entering the 21st century, it seemed that Einstein's prediction was correct. But things were soon to change.

Optical tweezers

We now take a detour to Bell Labs in the 1970s. Arthur Ashkin, a scientist at the laboratory, demonstrated something remarkable: Light could control the motion of matter. Specifically, he showed that a focused laser beam could trap small particles in water and move them around at an experimenter's will. His invention, known as the optical tweezer, has become a major tool in physics and biology. In recent years optical tweezers have been used to study Brownian motion. As a trapped particle, typically a bead of glass, undergoes such motion, it slightly deflects the trapping laser beam; the deflection can then be observed with a split photodetector. (We'll give details with figure 2.)

The split-photodetector approach has traditionally been limited by the speed of commercially available detectors. We and our colleagues realized that we could change the design of the device to speed up the detection by a big factor. Our group then built an experiment to study Brownian motion of beads in air, because the time during which a particle undergoes ballistic motion is much longer in air than in a liquid. We needed to resolve spatial motion on the order of 1 Å, within a time frame of 50 µs.

Figure 2a shows our setup, in which two counterpropa-

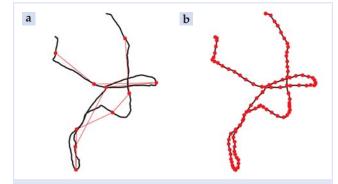


Figure 1. Brownian motion trajectories. When examined at modest measurement rates **(a)**, the observed positions (red dots) of particles executing Brownian motion appear to lie on the jerky trajectory illustrated in red. The black curve shows the underlying particle path. **(b)** Measurements at finer time scales reveal that the particle path is in fact built from short bursts of constant velocity motion.

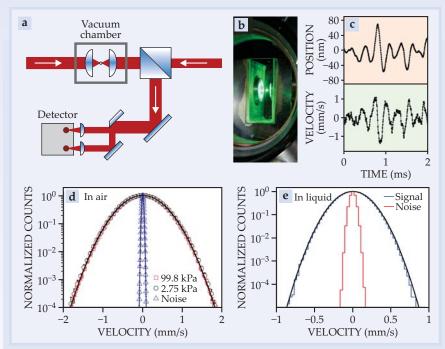


Figure 2. The instantaneous velocity of a Brownian particle. (a) To observe the ballistic motion of a particle undergoing Brownian motion, we used a counterpropagating dual-beam optical tweezer and a split-detection system. The beam entering from the left is reflected downward after it has passed through a trapped bead inside a vacuum chamber. It is then split by a mirror with a sharp edge and detected. Splitting the beam allows us to remove sensitivity-compromising effects due to intensity fluctuations in the laser. (b) A trapped bead can be indefinitely suspended in air. (c) The plots show a position component (top) and the corresponding instantaneous velocity component (bottom) of a 3-µm-diameter silica bead trapped in air at 2.75 kPa. (d) These distributions of instantaneous velocities were measured for a 3-µm-diameter silica bead in air at two different pressures.

The solid black curves here and in the following panel represent Maxwell–Boltzmann distributions. **(e)** This instantaneous velocity distribution was obtained for a 3.7-µm-diameter barium titanate microsphere in acetone.

gating laser beams—the optical tweezer—are focused to a single spot where a glass bead is trapped. You might wonder how we got a bead to that exact location. The procedure was actually a little tricky. We spread dry beads on a glass slide and positioned the slide above the optical tweezer. The slide was shaken violently to detach beads, which fell due to gravity. We repeated that process until we detected a single trapped bead (see figure 2b). As long as the laser beams were on, we could keep the bead for as long as we liked. Once the bead was trapped, we recorded its motion with the split photodetector. Typical traces are shown in figure 2c; the lower one represents the first measurements of the instantaneous velocity of a Brownian particle, a feat that Einstein said was impossible.

From many velocity measurements, we can construct a velocity probability distribution, and as figure 2d shows, our results are in excellent agreement with the theoretically predicted Maxwell–Boltzmann distribution. From the measured velocity distribution we can also calculate the average kinetic energy of the glass bead. At temperature T, each velocity component contributes a factor of $\frac{1}{K}_B T$ to the kinetic energy (k_B is Boltzmann's constant), the same as a molecule of air.

On to liquids

A skeptic might say, "All that is great, but Einstein said the instantaneous velocity could not be measured in a liquid, and you did the experiment in air." That's a valid point, so we decided to go for broke and repeat the experiment with a Brownian particle in liquid—a task easier said than done. The required spatial resolution for a bead in water is 10 picometers, and the necessary time resolution is 5 nanoseconds! We realized that meeting those specs with our detection system was impossible. So we switched from glass to barium titanate, which is denser, so it maintains velocity for a longer time; it also has a higher index of refraction, so it deflects the laser light more strongly. Instead of water we used acetone, which has much lower viscosity.

Still, we had to push the limits of technology to operate our system at much higher laser power; ultimately we were limited by the quantum noise of the light. At last, we succeeded in observing the instantaneous velocity in a liquid and, as figure 2e shows, verified that the velocities lie on the Maxwell–Boltzmann distribution but, as had been theoretically anticipated, with the actual mass of the microsphere replaced by an effective mass.

Now that we have a test bed for Brownian motion, we can use it to address fundamental questions in statistical mechanics. For example, does the system strictly obey the energy equipartition theorem, or could there be deviations? With pulsed lasers, we now have a tool for extending our measurements to much shorter time scales-even down to subnanosecond scales—for which the compressibility of liquid becomes important. We should be able to see how the bead initially moves as if the liquid was not present, but then starts dragging its surrounding medium along. We can also drive the bead far from thermal equilibrium with a sudden kick and then track its return to equilibrium. Theorists have speculated that the onset of irreversibility is due to quantum entanglement with the environment. Could one possibly see that phenomenon in short-time Brownian motion? It is safe to say that Einstein would be surprised, and hopefully pleased, that a simple physical system is proving to be such a fertile testing ground.

Additional resources

- ▶ A. Einstein, "Theoretical observations on the Brownian motion," in *Investigations on the Theory of the Brownian Movement*, A. D. Cowper, trans., Dover (1956), p. 63.
- ▶ A. Ashkin, "Acceleration and trapping of particles by radiation pressure," *Phys. Rev. Lett.* **24**, 156 (1970).
- ▶ T. Li et al., "Measurement of the instantaneous velocity of a Brownian particle." *Science* **328**, 1673 (2010).
- a Brownian particle," *Science* **328**, 1673 (2010). ► S. Kheifets et al., "Observation of Brownian motion in liquids at short times: Instantaneous velocity and memory loss," *Science* **343**, 1493 (2014).
- ► Science in the Classroom, "Experiments Einstein Could Only Dream Of," http://scienceintheclassroom.org.