

An increasing number of natural phenomena do not fit into the relatively simple description of diffusion developed by Einstein a century ago

Anomalous diffusion spreads its wings

Joseph Klafter and Igor M Sokolov

AS ALL of us are no doubt aware, this year has been declared “world year of physics” to celebrate the three remarkable breakthroughs made by Albert Einstein in 1905. However, it is not so well known that Einstein’s work on Brownian motion – the random motion of tiny particles first observed and investigated by the botanist Robert Brown in 1827 – has been cited more times in the scientific literature than his more famous papers on special relativity and the quantum nature of light. In a series of publications that included his doctoral thesis, Einstein derived an equation for Brownian motion from microscopic principles – a feat that ultimately enabled Jean Perrin and others to prove the existence of atoms (see *Physics World* January pp19–22).

Einstein was not the only person thinking about this type of problem. The 27 July 1905 issue of *Nature* contained a letter with the title “The problem of the random walk”, in which the British statistician Karl Pearson proposed the following: “A man starts from the point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats this process n times. I require the probability that after n stretches he is at a distance between r and $r + \delta r$ from his starting point O .”

Pearson was interested in the way that mosquitoes spread malaria, which he showed was described by the well-known diffusion equation. As such, the displacement of a mosquito from its initial position is proportional to the square root of time, and the distribution of the positions of many such “random walkers” starting from the same origin is Gaussian in form. The random walk has since turned out to be intimately linked to Einstein’s work on Brownian motion, and has become a major tool for understanding diffusive processes in nature.

When the mean is missing

In fact, the first person to address the problem of diffusion was the German physiologist Adolf Fick, who was interested in the way that water and nutrients travel through membranes



Strange behaviour – albatrosses fly by the rules of anomalous diffusion.

in living organisms. In 1855 Fick published the famous diffusion equation, which, when written in terms of probability, is $\partial p / \partial t = D \partial^2 p / \partial x^2$, where p gives the probability of finding an object at a certain position x , at a time t , and D is the diffusion coefficient. Fick went on to show that the mean-squared displacement of an object undergoing diffusion is $2Dt$.

However, Fick’s approach was purely phenomenological, based on an analogy with Fourier’s heat equation – it took Einstein to derive the diffusion equation from first principles as part

of his work on Brownian motion. He did this by assuming that the direction of motion of a particle gets “forgotten” after a certain time, and that the mean-squared displacement during this time is finite. When Einstein combined the diffusion equation with the Boltzmann distribution for a system in thermal equilibrium, he was able to predict the properties of the unceasing motion of Brownian particles in terms of collisions with surrounding liquid molecules. This was the breakthrough that ultimately led to scientists believing in the reality of atoms.

The fact that Einstein’s explanation of diffusion and Pearson’s random walk are both based on the same two assumptions – the existence of a mean free path (the length l in Pearson’s model and the distance between collisions in Einstein’s description) and of a mean time taken to perform a step or between collisions – revealed just how ubiquitous diffusion processes are in nature. However, by the mid-1970s researchers had started to pay attention to situations in which the assumptions made by Einstein and Pearson do not hold. Surprisingly, perhaps, the way that photocopier machines operated played a major role in these developments.

Today, an increasing number of processes can be described by this “anomalous diffusion”. From the signalling of biological cells to the foraging behaviour of animals, it seems that the overall motion of an object is better described by steps that are not independent and that can take vastly different times to perform.

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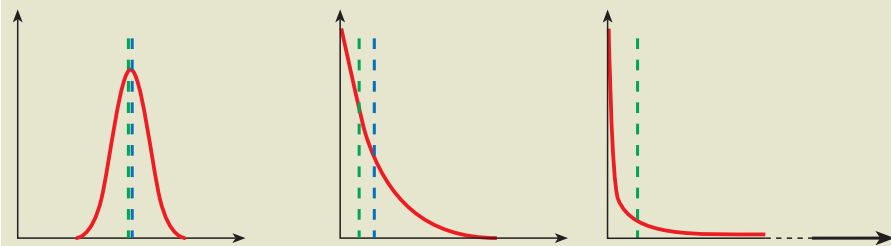
The best way to study deviations from normal Gaussian diffusion is to plot the distributions of the free path of a particle and of the time taken to travel this path. These distributions, like all distributions, have a width: if this width is narrow, then most values are concentrated around the mean value; however, if this width is large, the mean value does not represent the typical behaviour (figure 1). For example, the distribution of heights in a population is narrow because the shortest and tallest people only differ in height by a factor of about five. But the distribution of wealth in a population is very broad, as first noted by the Italian economist Vilfredo Pareto. Indeed, the spread between extreme poverty and wealth is so large that the mean of a Pareto distribution has no meaning.

Pareto-type distributions also appear in physics. In the 1920s the French mathematician Paul Lévy discovered a special family of distributions, now known as Pareto–Lévy distributions, that arise when many independent random quantities that each follow a Pareto law are added together. Different physical situations correspond to different modifications of Pearson’s more basic scheme, where all step lengths and time intervals are the same. For example, the random walker might pause between two successive steps, in which case the time between steps might be distributed according to a Pareto–Lévy law. What all these situations have in common, however, is that the walker’s behaviour is dominated by the largest steps or longest periods in which there is no motion. This means that the system’s “memory” about such rare events is never erased.

So how does all this affect the simple diffusion equation? Once again, the anomalous nature leads to a surprise, because it turns out that the ordinary derivatives in Fick’s equation need to be replaced by fractional ones such as $\partial^{1/2}y/\partial x^{1/2}$. Mathematicians have been aware of fractional derivatives for over 300 years, but, like the strange Pareto distributions that have no mean value, these derivatives only found their way into the physical sciences due to the relatively recent observations of anomalous diffusion.

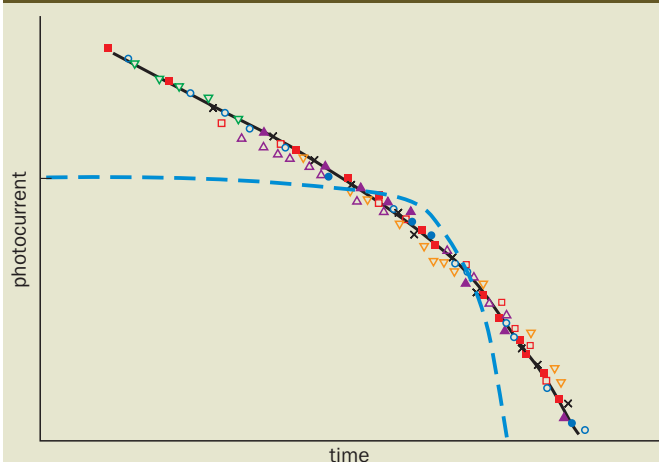
The best examples of fractional derivatives in action can be found in the modern office: both the photocopier and the laser printer rely on the transport of electrons or “holes” in amorphous semiconductors in an electric field. In the early 1970s it became clear that the movement of these charge carriers could not be described by the classic diffusion equation (figure 2). The issue was resolved in 1975 when Harvey Scher and Elliot Montroll, then at Xerox and the University of Rochester, respectively, realized that charges moving in amor-

1 Mean distributions



A statistical distribution can be characterized by its mean (blue) and its median (green). The mean is a conventional average, whereas the median divides the distribution such that half the values are higher than the median and half are lower. In the Gaussian distribution (left) the mean and the median coincide, while in the exponential distribution (middle) the mean is slightly larger than the median. The tails of both of these distributions decay very quickly, which means that very large values are highly improbable. However, in a Pareto distribution (right), which describes the distribution of wealth in a population, the mean is not well defined and there is a non-zero probability for finding very high values.

2 Anomalous diffusion in photocopiers



In the 1970s researchers measured the transient photocurrent in amorphous thin films that form the core of photocopier machines (data points). The blue dashed line indicates the expected behaviour if this diffusion process followed Fick’s equation, which led Scher and Montroll to describe the process using broad distributions of waiting times. Both axes are logarithmic. This became the best known example of anomalous subdiffusion in nature. From H Scher and E Montroll 1975 *Phys. Rev. B* **12** 2455–2477

phous media tend to get trapped by local imperfections and then released due to thermal fluctuations. This means that the trapping times are more likely to be described by a Pareto distribution than a Gaussian distribution.

This idea did not go down well with other researchers because it implied that a distribution that did not have a mean value might have a physical meaning. However, the trapping times were indeed found to follow a Pareto law in many cases, which meant that the charge carriers diffused more slowly than they would in the case of normal diffusion. This type of anomalous diffusion is called “subdiffusion”, since the mean-squared displacement of particles grows slower than the first power of time in Fick’s diffusion equation.

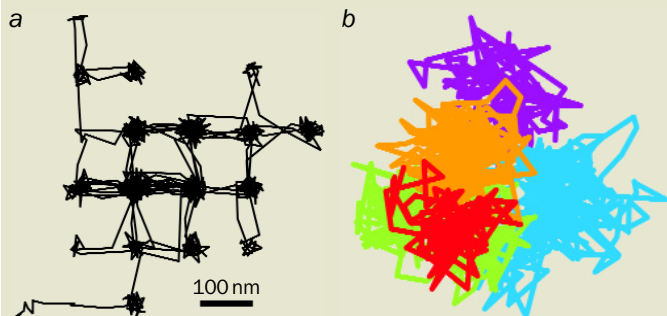


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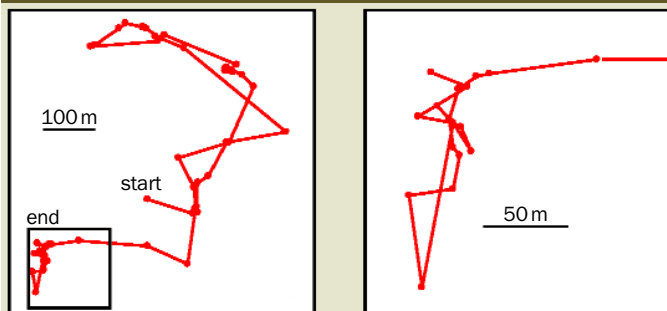


3 Subdiffusion in cells



Researchers have found that the way proteins diffuse across cell membranes can be described by anomalous diffusion that is slower than the normal case. (a) This is a simulation of such a random walk, which shows a 2 ms timeframe over which a protein “hops” between 120 nm^2 compartments thought to be formed by the cell’s cytoskeleton. (b) The experimental trajectories of proteins in the plasma membrane of a live cell (shown in a 0.025 ms timeframe) provide evidence for this trapping nature, as shown by the different colours. The long residence times in these compartments is thought to be the origin of the anomalous behaviour.

4 Superdiffusion in monkey behaviour



The typical trajectories of spider monkeys in the forest of the Mexican Yucatan peninsula display steps with variable lengths, which correspond to a diffusive process that is faster than that of normal diffusion. An example of such a trajectory is shown on the left. A magnified part of it is shown on the right; this image looks qualitatively similar to the larger-scale trajectory, which is an important property of Lévy walks. Similar behaviour is found in the foraging habits of other animals, and could mean that anomalous diffusion offers a better search strategy than that of normal diffusion.

Subdiffusion

More recent examples of subdiffusive behaviour come from hydrology. In 2000 James Kirchner and co-workers at the University of California at Berkeley showed that as a result of trapping, the travel times of contaminants in groundwater are much longer than is expected from the classic diffusion picture. Here, the mean flow of the groundwater plays the role that the electric field plays in the photocopier machine, while stagnant regions of zero velocity (such as side channels of the main flow) correspond to the traps. By modifying the diffusion equation, researchers can therefore work out how long pollutants from environmental accidents, for example, will remain before they are flushed out into lakes or the sea.

In 2004 Marco Dentz and colleagues, including Scher at the Weizmann Institute in Israel, formulated a theory that takes into account these extremely long retention times and distinguishes between normal and anomalous diffusion. In particular the researchers investigated the effects of the system memory on contaminant patterns over long periods, concluding that the standard diffusion equation needs to be replaced by the fractional version.

Biology also contains a wealth of subdiffusive phenomena, such as the way some that proteins diffuse across cell membranes. This process is central to the transmission of signals to the inside of cells, but its precise details are controversial because the process cannot be explained by normal Brownian motion. Earlier this year, Akihiro Kusumi and co-workers at Nagoya University in Japan performed experiments in which they tracked a single protein molecule in the plasma membrane of live cells. Fluorescent-molecule video imaging revealed that the molecules spend relatively long times trapped between nanometre-sized compartments in the actin cytoskeleton of the cell (figure 3). This, claimed Kusumi and co-workers, was the origin of the anomalous diffusion.

Subdiffusion has also been observed in fluctuating proteins – systems in which the distance between a donor and an acceptor within a single protein constantly changes. Earlier this year Sunney Xie and co-workers at Harvard University used the electron-transfer reaction to measure how this distance fluctuates in real time. The result was a strong departure from Brownian behaviour, which could help biologists understand the specific functions of certain proteins.

Superdiffusion

The examples of anomalous diffusion we have discussed so far describe random walks in which particles halt between steps. However, another possibility for anomalous diffusion is that the random walker remains in motion without changing direction for a time that follows a Pareto–Lévy distribution. In this case the step lengths and the waiting times – not just the former – have a broad distribution. Such “Lévy walks”, so named by one of the present authors (JK) and Michael Shlesinger of the US Office of Naval Research in 1985, correspond to a process in which the mean-squared displacement grows *faster* than it does in normal diffusion. Such processes are therefore termed superdiffusive.

Unlike the spread of Pearson’s mosquitoes, which was described by a simple random walk, the flight of albatrosses can be described by a Lévy-walk model, as Eugene Stanley of Boston University and co-workers discovered in 1996. These large seabirds fly at an approximately constant velocity, and the broad distribution of times between changes of direction leads to a pattern of long straight lines interrupted by localized random motions. Such trajectories can be rationalized as an efficient search strategy that leads the birds to new areas, rather than a simple diffusion trajectory in which places are revisited many times.

The search patterns of many animals resemble those of the albatross, with the behaviour of bacteria, plankton and even jackals following the Pareto–Lévy law. Indeed, last year Gabriel Ramos-Fernandez and co-workers at Mexico University found that the movement of spider monkeys also followed a Lévy walk (figure 4). While the actual reason for this anomalous behaviour is not clear, it has been shown that Lévy walks outperform normal Brownian random walks as a strategy for finding randomly located objects.

Similar to these Lévy-walk trails are the trajectories of particles in some inanimate systems. For example, in the periodic “egg crate” potential – which represents the motion of a particle on the surface of a perfect crystal – the only turning angles allowed are those obeying the symmetry of the crystal. This can lead to very long steps in the motion of heavy particles on crystalline surfaces, although the precise form of this

diffusion depends on the friction between the surface and the particle. Last year Jose Maria Sancho of Barcelona University and co-workers, including one of the present authors (IS), simulated the motion of large molecules and metal clusters across crystalline surfaces. The result was Lévy-walk behaviour that was able to explain the unusual diffusion observed experimentally in such systems.

Lévy walks have also been seen in the transport of particles in flows. In a classic experiment performed in 1994, Harry Swinney's group at the University of Texas at Austin used tracer particles to reveal superdiffusion in a rapidly rotating annular tank. Like the foraging behaviour of the spider monkey, this process combines long flights with a broad distribution of trapping times at flow vortices, which has helped researchers to understand how particles such as pollutants spread in the ocean and the atmosphere.

Anomalous is normal

Our picture of diffusion 100 years after Einstein published his groundbreaking papers has clearly become much broader, quite literally. We now know that the simple picture based on the diffusion equation is just one of a whole range of possible behaviours that stem from a random-walk picture. Broad distributions with no mean values seemed unphysical at the beginning of the 20th century but have now been found to be extremely useful tools that are not that exotic after all.

The challenge now is to find the actual reasons for the sub- and superdiffusion we observe in particular natural systems, and how to apply this knowledge so that we can mani-

pulate dynamical processes on various scales. In particular, we would like to know what the biological implications of anomalous diffusion are. But the clear picture that has emerged over the last few decades is that although these phenomena are called anomalous, they are abundant in everyday life: anomalous is normal!

Further reading

M Dentz *et al.* 2004 Time behavior of solute transport in heterogeneous media: transition from anomalous to normal transport *Adv. Water Resources* **27** 155–173

R Fernandez *et al.* 2004 Lévy walk patterns in the foraging movements of spider monkeys (*Ateles geoffroyi*) *Behav. Ecol. Sociol.* **55** 223–230

R Metzler and J Klafter 2004 The restaurant at the end of the random walk: recent developments in the description of anomalous transport by fractional dynamics *J. Phys. A: Math. Gen.* **37** 1505–1535

W Min *et al.* 2005 Observation of a power-law memory kernel for fluctuations within a single protein molecule *Phys. Rev. Lett.* **94** 198302

K Ritchie *et al.* 2005 Detection of non-Brownian diffusion in the cell membrane in single molecule tracking *Biophysic. J.* **88** 2266–2277

J M Sancho *et al.* 2004 Diffusion on a solid surface: anomalous is normal *Phys. Rev. Lett.* **92** 250601

I M Sokolov, J Klafter and A Blumen 2002 Fractional kinetics *Physics Today* November pp48–54

C Tsallis 1997 Lévy distributions *Physics World* July pp42–45

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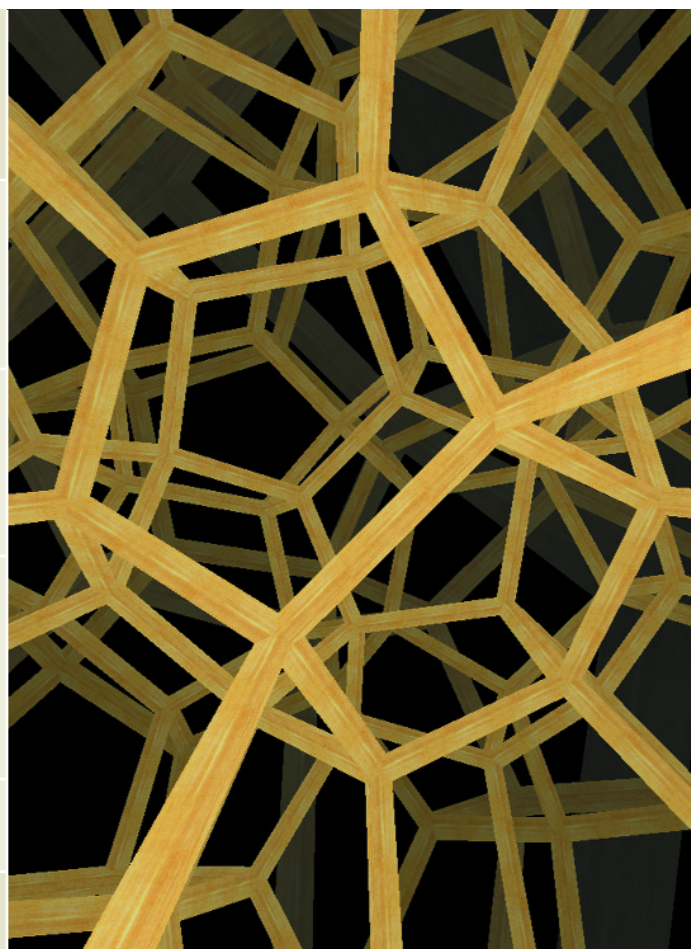
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