Glowing beacons reveal hidden order in dynamical systems

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A dynamical system in which repeated measurements on a single particle yield the same mean result as a single measurement of the whole ensemble is said to be ergodic. The ergodic theorem expresses a fundamental physical principle, and its validity for diffusive processes has now been demonstrated.

The so-called ergodic theorem formulates a fundamental physical principle relating to the behavior of dynamical systems. Essentially the theorem states that in a multiparticle system each individual particle behaves just as "chaotically" as does the system as a whole. In other words, one can extrapolate from the behavior of a single element to that of the whole system. Strangely enough, in spite of its wide-ranging implications, the theorem has not been rigorously tested experimentally.

A collaborative effort mounted by Professor Christoph Bräuchle's team in the Department of Chemistry at LMU Munich and Professor Jörg Kärger's group at Leipzig University has now confirmed the validity of the theorem by measuring the diffusive behavior of ensembles of particles and the trajectories of single molecules in the same system. Using fluorescent molecules as tracers and high-resolution imaging methods, the LMU investigators were able to track the paths of individual molecules, while the Leipzig group studied the collective behavior of the whole ensemble. "It will be very interesting to take a closer look at systems that do not conform to the tenets of the ergodic theorem and to determine the reasons for their aberrant behavior," says Bräuchle.

The term "diffusion" refers to the random motion of particles, such as atoms and molecules, under the influence of thermal energy. This physical process is an essential component of innumerable phenomena in nature, and also plays a crucial role in many technological procedures. For instance, in virtually all chemical reactions, diffusion is responsible for bringing reactants sufficiently close together to enable them to react at all. It is generally accepted that the ergodic theorem is applicable to the dynamics of diffusive processes. The theory basically states that repeated measurements of a given variable – such as the distance covered by a particle in a given time interval – should yield the same average value as a single measurement of the same variable on a collection of particles – provided the system considered is in a state of equilibrium. However, as Kärger points out, "although diffusive processes have been investigated for the past 150 years, the principle of ergodicity has not yet been experimentally verified." This is because it has so far been possible to quantify diffusive processes only by means of ensemble measurements – i.e. measurements of many particles simultaneously. One of the most informative methods for this purpose is pulsed-field gradient nuclear magnetic resonance (PFG-NMR), a technique for which Kärger and his group are well known. The actual trajectory of a single particle, on the other hand, could not be observed directly. "With the development of single-molecule spectroscopy and single-molecule microscopy, we can now follow the trajectories – and therefore monitor the diffusion behavior – of single molecules," Bräuchle explains. Optical tracking methods visualize molecules on the basis of their fluorescence, making it possible for their positions to be localized and monitored with a precision of a few nanometers.

This still leaves one problem to be solved - successful application of the two methods requires very different, indeed apparently conflicting, conditions. NMR measurements need high concentrations of molecules with large diffusion coefficients, while single-molecule spectroscopy works best with extremely dilute solutions of species with small diffusion coefficients. By using particular organic dyes with high fluorescence yields in combination with porous silicate glasses containing networks of nanometer-sized channels in which the dye molecules can diffuse, the researchers were able to create conditions that were compatible with both methods. This experimental set-up allowed them to perform single-molecule and ensemble measurements on the same system.

When the two teams compared their data, they found that the diffusion coefficients (the parameter that describes diffusive motion) obtained by the two techniques agreed with each other – providing the first experimental confirmation of the ergodic theorem in this context. The next step will be to examine systems in which the theory does not apply. "The diffusion of nanoparticles in cells looks like an interesting example," says Bräuchle, "and for us the important thing is to find out why the ergodic theorem doesn't hold in this case."

More information: Single-particle and ensemble diffusivities - Test of ergodicity, F. Feil, S. Naumov, J. Michaelis, R. Valiullin, D. Enke, J. Kärger, C. Bräuchle
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