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Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales

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We experimentally demonstrate the fluctuation theorem, which predicts appreciable and measurable violations of the second law of thermodynamics for small systems over short time scales, by following the trajectory of a colloidal particle captured in an optical trap that is translated relative to surrounding water molecules. From each particle trajectory, we calculate the entropy production/consumption over the duration of the trajectory and determine the fraction of second law-defying trajectories. Our results show entropy consumption can occur over colloidal length and time scales. ©2002 *The American Physical Society*

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Number 598 #1, July 17, 2002 by Phil Schewe, James Riordon, and Ben Stein

Pushing the Second Law to the Limit

Australian researchers have experimentally shown that microscopic systems (a nano-machine) may spontaneously become more orderly for short periods of time--a development that would be tantamount to violating the second law of thermodynamics, if it happened in a larger system. Don't worry, nature still rigorously enforces the venerable second law in macroscopic systems, but engineers will want to keep limits to the second law in mind when designing nanoscale machines. The new experiment also potentially has important ramifications for an understanding of the mechanics of life on the scale of microbes and cells.

There are numerous ways to summarize the second law of thermodynamics. One of the simplest is to note that it's impossible simply to extract the heat energy from some reservoir and use it to do work. Otherwise, machines could run on the energy in a glass of water, for example, by extracting heat and leaving behind a lump of ice. If this were possible, refrigerators and freezers could create electrical power rather than consuming it. The second law typically concerns collections of many trillions of particles--such as the molecules in an iron rod, or a cup of tea, or a helium balloon--and it works well because it is essentially a statistical statement about the collective behavior of countless particles we could never hope to track individually. In systems of only a few particles, the statistics are grainier, and circumstances may arise that would be highly improbable in large systems. Therefore, the second law of thermodynamics is not generally applied to small collections of particles.

The experiment at the Australian National University in Canberra and Griffith University in Brisbane (Edith Sevick, sevick@rsc.anu.edu.au, 011+61-2-6125-0508) looks at aspects of thermodynamics in the hazy middle ground between very small and very large systems. The

researchers used optical tweezers to grab hold of a micron-sized bead and drag it through water. By measuring the motion of the bead and calculating the minuscule forces on it, the researchers were able to show that the bead was sometimes kicked by the water molecules in such a way that energy was transferred from the water to the bead. In effect, heat energy was extracted from the reservoir and used to do work (helping to move the bead) in apparent violation of the second law.

As it turns out, when the bead was briefly moved over short distances, it was almost as likely to extract energy from the water as it was to add energy to the water. But when the bead was moved for more than about 2 seconds at a time, the second law took over again and no useful energy could be extracted from the motion of the water molecules, eliminating the possibility of micron-sized perpetual motion machines that run for more than a few seconds. Nevertheless, many physicists will be surprised to learn that the second law is not entirely valid for systems as large as the bead-and-water experiment, and for periods on the order of seconds. After all, even a cubic micron of water contains about thirty billion molecules. While it's still not possible to do useful work by turning water into ice, the experiment suggests that nanoscale machines may have to deal with phenomena that are more bizarre than most engineers realize. Such tiny devices may even end up running backwards for brief periods due to the counterintuitive energy flow. The research may also be important to biologists because many of the cells and microbes they study comprise systems comparable in size to the bead-and-water experiment. ([G.M. Wang et al.](#), *Physical Review Letters*, 29 July 2002.)

The New York Times

ON THE WEB

<http://www.nytimes.com/2002/07/30/science/physical/30ENTR.html>
July 30, 2002

Humpty Dumpty Restored: When Disorder Lurches Into Order

By KENNETH CHANG

Not all the universe is falling apart all of the time.

An experiment by scientists in Australia has shown that a small patch of disorder can momentarily lurch into order, akin to Humpty Dumpty's magically putting himself back together again.

That would appear to violate the second law of thermodynamics, which states that entropy, a measure of disorder, rises inexorably unless an outside energy source maintains things in order. A billow of smoke always disperses, never contracts.

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The experiment confirms a theory from 1993 that reconciled a longstanding paradox, that the laws of physics do not run fine forward and backward in everyday life, but they do at the atomic level, where subatomic particles collide.

That spontaneous order effect, the creation of order from disorder, is small and short-lived. But it may prove to be important in the emerging field of nanotechnology, where it could bungle future molecular-size machines by making them run backward, the researchers said.

"I think nature already does that," said Dr. Denis J. Evans, a professor of chemistry at the Australian National University. Living organisms may take advantage of the effect to kick around proteins and other

molecules until they bind together properly, Dr. Evans said. So the effect could be useful.

In the everyday world, the second law prohibits the flow of heat energy from a cooler reservoir to run a motor or do other work. Otherwise, one could imagine a machine running on the thermal energy in a glass of water — the jiggling of individual water molecules — and leaving behind a chunk of ice as the only waste.

But at a much smaller scale, the researchers have demonstrated, it is possible essentially to do just that, at least under certain circumstances.

In the experiment, reported in the current issue of *Physical Review Letters*, Dr. Evans and other scientists at the Australian National University in Canberra and Griffith University in Brisbane suspended a transparent bead one four-thousandths of an inch wide in a small puddle of water. A laser shining through the water held the bead in place. The bead's curved surface, acting like a lens, bent the laser light, exerting a force that kept it at the center of the beam.

"It just goes zip, and it quickly goes to the focal point, and it sits there," said Dr. Edith M. Sevick, a chemist at the Australian National University on the research team.

The team lowered the laser power so that it barely kept its hold onto the bead. "We can actually seeing it jiggling around right around the focal point," Dr. Sevick said.

The team used the laser to drag the bead through the puddle at a leisurely pace of one-seventh of an inch an hour, as if it were a tugboat pulling a barge.

Usually, the water exerted a slowing force. But occasionally enough water molecules bounced off the bead at the same time, reflecting a more orderly arrangement of the molecules, to push the bead ahead, as if a barge suddenly jumped in front of the tugboat pulling it.

"That's the violation," Dr. Sevick said.

The violation lasted two seconds at most, and it occurred only because the force of the laser light was minuscule, almost as slight as the force of the water molecules bouncing off the bead. Over longer periods of time or if the laser power was turned up, the effect disappeared.

"You cannot get perpetual motion machines," Dr. Sevick said. "You always get back to the second law."

Until recently, scientists could not fully explain how the second law arises. In the basic equations of motion, both those devised by Isaac Newton and the later ones of quantum mechanics, time is said to be reversible. The equations remain true even when time flowed backward.

But the equations of thermodynamics, which describe the collective random motion of many trillions of particles, do contain a definite direction of time. Heat always flows from warm to cold, never the other way around. Entropy rises, never falls.

As early as 1876, a physicist, Josef Loschmidt, pointed out that paradox. If the motion of each individual particle is reversible, why is their collective behavior irreversible?

Dr. Evans finally figured out the answer in 1993. The irreversibility arises from causality, that events in the future cannot affect the present. From that, he showed that ordered systems became exponentially less likely while the probability of disorder rose.

Computer simulations verified that the ideas worked. Still, scientists like Dr. Peter T. Cummings of the Oak Ridge National Laboratory in Tennessee said it was surprising to find a clear example in the real world of the hazy zone between very small systems and very large ones.

"It's unexpected there could be an experimental verification of this theorem," Dr. Cummings said. The Australian experiment, he said, "puts it squarely in the realm where it may have practical significance."

SCIENCE JOURNAL**Envy Microworld Life, Where Things Get Neater as Time Passes**

By Sharon Begley

08/02/2002

The Wall Street Journal

B1

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WHEN THE RESEARCH paper arrived on March 4 at Physical Review Letters, one of the world's top physics journals, editors winced. "Experimental Demonstration of Violations of the Second Law of Thermodynamics," the title boldly proclaimed.

Claims of violations of the Second Law tend to come from the same folks who talk to ET via aluminum foil, but this one, the editors quickly saw, was different, offering tantalizing hints about questions as diverse as the behavior of nanomachines, the thermodynamic arguments against evolution and the universality of nature's laws.

There are several ways to express the Second Law, but the basic idea is twofold. First, in a closed system, entropy (disorder) increases. Or as that great thermodynamicist William Butler Yeats said, things fall apart. In addition, you can't harvest heat energy from cooler surroundings and turn it into work. That, alas, precludes running a machine on the energy from the dancing molecules in a tubful of cold water and leaving behind a block of ice. If such a trick were possible, then machines could create electrical power rather than gobble it up, perpetual-motion machines could hum merrily forever, and things would become more orderly as time went by (even if your mother didn't clean up after you).

No wonder inventors and teens alike would love to repeal the Second Law. Who

wouldn't welcome a world of self-organizing closets? And no wonder the journal editors looked askance.

THEY INSISTED THAT, at minimum, the Australians add to their title, ". . . for Small Systems and Short Timescales." But by whatever name, the paper in the July 26 Phys Rev Letters announces a discovery that, in the era of nanotechnology, has startling implications: For brief periods, tiny particles can suck up entropy, converting heat from their surroundings into useful work.

That's what chemist Denis Evans of Australian National University in Canberra theorized in 1993. In the microworld, predicts his Fluctuation Theorem, systems can briefly violate the Second Law. Computer simulations validated the theorem, but as Dr. Evans says, "There's nothing like an experiment to convince people."

To do that, his colleague, Edith Sevick, floated latex beads 6 microns (millionths of a meter) across in water. Then she used "optical tweezers," an infrared laser whose light pressure confines a bead between two beams, to drag one bead at a time through the water.

The beads turned Second Law scofflaws. Water molecules in random ("Brownian") motion knocked into each bead, transferring energy to it for as long as two seconds. It was the micro version of a refrigerator sucking up the energy in that tub of water and leaving behind ice. So, although the Second Law bars that, it seems to let a nanomachine run on the Brownian motion in a drop of water, at least briefly.

THE SECOND LAW formally applies only to collections of zillions of particles -- a refrigerator, a closet, a living creature. "The Law does not preclude fluctuations on small scales and short times such as these," says physicist David Harris of the American Physical Society, which is reminiscent of the way quantum laws apply to the microworld but apparently not to the macroworld.

The results could complicate things for nanomachinists. Molecular-scale devices with the "Fantastic Voyage"-like ability to motor through blood vessels and clear obstructions, or to pluck toxic compounds from the air and water, are still only dreams. But some components -- nanoactuators and nanosensors -- exist. "If we're going to build nanomachines," says physicist Chris Jarzynski of Los Alamos National Laboratory, "we'll have to take into account that they'll be subject to this effect," either running better than normal or behaving erratically.

Creationists often invoke the Second Law to argue that life could not have begun from nonlife, let alone evolved from pond scum into Gwyneth Paltrow. The contention is, the Second Law prevents systems from growing

more organized and complex with time -- absent the hand of God.

But if the microworld can violate the Second Law, "biological machinery might take advantage of this," says Dr. Evans. Molecules could briefly extract energy from their surroundings, combining in ways that would otherwise be impossible in practice. The loophole in the Second Law -- for tiny objects for short periods of time -- might be big enough to let miracles through. All of life may be 6-5 against, as Damon Runyon said, but violations of the Second Law in the microworld might let a long shot come in.

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Search and Discovery

Blau, S. K. 2002 The unusual thermodynamics of microscopic systems. *Phys. Today* **55**, 19-21.

The Unusual Thermodynamics of Microscopic Systems

Theoretical distributions of work delivered to small objects have some surprising properties recently confirmed by experiment.

The thermodynamic behavior of microscopic systems can be quite different from that of macroscopic systems, for which fluctuations in thermodynamic quantities are usually negligible. As physicists strive to build ever smaller machines, it becomes important to understand, for example, the statistics of the work done on or by a machine as it moves from an initial to a final state. That work is not simply a function of the beginning and ending states. But--according to the usual telling of the story--the work is determined once one is given a path or process that connects the states.

The usual story is not strictly accurate. For example, in a system connected to a heat bath, uncertainties of order kT arise from the Boltzmann distribution of energies in the initial and final states, and also from energy exchange with the heat bath as the system moves along a path connecting those states. That means the work given to a system cannot be uniquely specified, even if the path is known. The energy uncertainties in macroscopic systems, though, are tiny compared to the average work. Thus, for practical purposes, one can say that two states and a connecting path determine work in those systems. If the system is microscopic, the statistical distribution of work associated with the system's change from its initial to its final state can have practical consequences.

Over the past decade, a good deal of theoretical effort has been devoted to spelling out the nature of work distributions. In the past few months, experimental tests have been conducted for two particular theoretical results--the transient fluctuation theorem of Denis Evans (Australian National University in Canberra) and Debra Searles (Griffith University in Brisbane)¹ and the nonequilibrium work relation derived by Chris Jarzynski (now at Los Alamos National Lab)².

Evans and Searles joined forces with three other colleagues from ANU to test the transient fluctuation theorem.³ At about the same time, a team from the University of California, Berkeley, and Lawrence Berkeley National Laboratory, led by Carlos Bustamante, explored the validity of the nonequilibrium work relation.⁴ Both theoretical predictions passed admirably.

Transient fluctuation theorem

The transient fluctuation theorem is one of many that tackle the statistical nature of fluctuations. Specific forms of the various theorems depend on which thermodynamic parameters (temperature, volume, and so forth) are held constant, whether the system is prepared in an equilibrium state, and other factors. The transient fluctuation theorem tested by Evans and coworkers applies to systems in a constant-temperature environment and initially at equilibrium. For the Australian team's work, in which an optical trap interacts with an experimental vessel, the theorem assumes the form

$$P(W)/P(-W) = \exp(W).$$

Here, W is a dimensionless number giving the work (divided by kT) delivered to the vessel; $P(W)$ is the probability that, in a given experiment, work W will be delivered to the vessel; and $P(-W)$ is the probability that the vessel does work W on the trap. Multiplying both sides of the above equation by $P(-W)$ and integrating over W from $-\infty$ to 0 yields an integrated version of the fluctuation theorem

$$P(W < 0)/P(W > 0) = \langle \exp(-W) \rangle_+,$$

where $P(W < 0)$ is the probability that the vessel does work on the trap and $P(W > 0)$ is the probability that the trap does work on the vessel. The angle brackets and subscript denote an average over all trajectories with positive work delivered to the vessel.

Testing transient fluctuations

To test the transient fluctuation theorem, Evans and colleagues measured the work delivered to a room-temperature vessel consisting of 6.3 μm -diameter latex beads in contact with a water bath. A focused external laser beam created an optical trap that exerts a Hooke's-law restoring force with known force constant on a bead near its focal point. Initially the vessel was at rest and a bead was allowed to come to equilibrium in the trap. Then Evans and coworkers moved the vessel at 1.25 $\mu\text{m/s}$ relative to the fixed trap. As a consequence of this movement, the bead was dragged away from the focus of the

trap and subject to an external force, which causes it to move in the trap's potential well.

the

The Australian group observed the latex bead's position 100 times per second for a total of 10 seconds. At each time step, position of the bead yielded the force exerted by the optical trap. The product of force and the distance the vessel moved gave the incremental work added to the vessel by the trap at each time step. Effects associated with the initial acceleration of the vessel were negligible.

Figure 1 shows the experimentally determined values for the right- and left-hand sides of the integrated fluctuation theorem as a function of time for the 540 trajectories studied by the Australian group. The two curves agree to within statistical error. Discrepancies at early times, for which the work values are small, may arise because of experimental limitations in measuring the position of the bead and difficulty in determining the precise time at which the vessel began to move.

The nonzero probability for negative work observed for up to about two seconds is worthy of comment. Imagine, as is often the case, that after a certain time, the bead has a higher energy than it had initially. Then, if the work done by the trap on the vessel (bead plus bath) is negative, energy has been delivered to both the bead and the optical trap interacting with the vessel. That energy came from the water bath--just the sort of energy transfer prohibited by the second law in the thermodynamic limit of infinitely large systems: Heat has been converted to work with 100% efficiency.

Nonequilibrium work relation

Bustamante and his colleagues measured the work delivered as they stretched and recompressed a folded RNA molecule that was prepared in equilibrium and kept in a constant-temperature and constant-pressure environment. Associated with the change in length of the molecule is a change in the Gibbs free energy, which can be thought of as the work needed to reversibly change the length. (For reversible processes, the work is well defined.) When one manipulates a system so as to change its free energy, a generalized form of the transient fluctuation theorem reflects that change:⁵

$$P(W)/PR(-W) = \exp(W-DG).$$

Here, PR denotes the probability distribution for the process that is the time reversal of the "forward" process yielding the distribution P, and DG is the change in the free energy (divided by kT). So, for example, in the Berkeley experiment, if the forward process is stretching the RNA molecule, the reverse process is compressing it. In the Australian experiment, time reversal takes a right-moving vessel and gives it a velocity to the left. Left-right symmetry means that for that experiment, one need not distinguish between the forward and time-reversed distributions.

Multiply both sides of the preceding equation by $PR(-W)\exp(-W)$ and integrate over W from $-\infty$ to $+\infty$. Because G is a state function, its change comes out of the work integral, and yields the result

$$\exp(-DG) <\exp(-W)>,$$

where the angle brackets denote an average over all trials. The remarkable feature of this so-called nonequilibrium work relation is that it allows extraction of information about a system's free energy change--a property of its equilibrium states--by studying the work distribution arising from a series of processes in which the system starts at equilibrium but need not be in equilibrium at any other time (including in its final state). Jarzynski derived the nonequilibrium work relation from first principles in 1997. The later elegant demonstration beginning from the generalized transient fluctuation theorem is due to Berkeley's Gavin Crooks.⁵

Testing nonequilibrium work

If one stretches a rubber band very slowly, and then lets it slowly relax, one does no net work on the band. But if the rubber band is stretched quickly, its force constant increases. Quick compression yields a reduced force constant. For rapid operation, one does net work on the band even though its final and initial states are the same.

The folded RNA molecule that Bustamante and colleagues studied is similar to the rubber band in many respects. When the Berkeley group unfolded and refolded the molecule slowly enough, increasing the applied force, say, by 5 piconewtons each second, the process was essentially reversible: In particular, to within experimental error, no net work was associated with an unfolding-refolding cycle. When they unfolded and refolded the RNA rapidly (34 and 52 pN/s) they generally did work on the molecule. But the transient fluctuation theorem asserts, and Bustamante and colleagues confirmed, that sometimes the work was negative.

To manipulate the RNA molecule, the Berkeley group attached each end of the RNA molecule to its own polystyrene bead. One bead was deliberately moved a measured distance, which stretched the RNA molecule, while the other was held in an optical trap (but also moved in response to the stretching). The Berkeley group determined the force acting on the RNA molecule by measuring the deflection of the trapping laser beams. From that force, they deduced the position of the bead in the trap.

By stretching the RNA molecule slowly and measuring the work input, the Berkeley group determined the molecule's free

energy as a function of the amount by which it was stretched. Two different rates of rapid stretching then yielded two different (extension-dependent) work distributions that were plugged into the nonequilibrium work relation to estimate the free energy as a function of extension.

Figure 2 shows the difference between the free energies calculated from Jarzynski's relation and the free energy measured in experiments conducted slowly enough to approximate them as reversible. Except for the fastest stretching rate and the greatest extensions, the two agree within experimental error, confirming the nonequilibrium work relation.

Systematic errors might account for the discrepancies. Because of the exponential averaging in Jarzynski's result, the nonequilibrium work relation strongly weights those runs for which the work is less than the free-energy change. Therefore, instrument noise tends to lead to an underestimate of the free energy, especially for large extensions, since noise piles up over the time needed to produce such extensions.

Figure 2 does not present error bars for the estimates based on the nonequilibrium work relation. For the non-Gaussian distributions involved, conventional error analysis can be misleading. One possible estimate, based on the standard error of the mean, gives relatively small errors.⁴

Clunky small machines

A consequence of the transient fluctuation theorem is that microscopic machines will work differently from their macroscopic counterparts. If an engine is made small enough so that the work performed during a cycle is comparable to kT , then occasionally and uncontrollably it will not run as designed. Imagining a tiny car with a tiny engine, Evans observes that the car won't run straight down the interstate but will jump "two steps forward, one step back." You'll get to where you want to go, but the ride won't be smooth. "The bottom line," comments Jarzynski, "is that we're starting to understand more quantitatively the nature of thermodynamic fluctuations at the microscopic level."

Steven K. Blau

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NEWS

July 24, 2002

Second Law of Thermodynamics Violated

It seems that something odd happens to the second law of thermodynamics when systems get sufficiently small. The law states that the entropy, or disorder, of the universe increases over time and it holds steadfast for large-scale systems. For instance, whereas a hot beverage will spontaneously dissipate heat to the surrounding air (an increase in disorder), the air cannot heat the liquid without added energy. Nearly a decade ago, scientists predicted that small assemblages of molecules inside larger systems may not always abide by the principle. Now Australian researchers writing in the July 29 issue of *Physical Review Letters* report that even larger systems of thousands of molecules can also undergo fleeting energy increases that seem to violate the venerable law.

Genmiao M. Wang of the Australian National University and colleagues discovered the anomaly when they dragged a micron-sized bead through a container of water using optical tweezers. The team found that, on occasion, the water molecules interacted with the bead in such a way that energy was transferred from the liquid to the bead. These additional kicks used the random thermal motion of the water to do the work of moving the bead, in effect yielding something for nothing. For periods of movement lasting less than two seconds, the bead was almost as likely to gain energy from the water as it was to add energy to the reservoir, the investigators say. No useful amounts of energy could be extracted from the set-up, however, because the effect disappeared if the bead was moved for time intervals greater than two seconds.

The findings suggest that the miniaturization of machines may have inherent limitations. Noting that nanomachines are not simply "rescaled versions of their larger counterparts," the researchers conclude that "as they become smaller, the probability that they will run in reverse inescapably becomes greater." --Sarah Graham

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Second law broken

Small-scale energy fluctuations could limit minaturization.
23 July 2002

ED GERSTNER



Researchers have shown for the first time that, on the level of thousands of atoms and molecules, fleeting energy increases violate the second law of thermodynamics¹. This is the tenet that some energy will always be lost when converting from one type to another.

The breach may mean there is a limit to miniaturization and to our understanding of the living world. It suggests that at scales of millionths of a

millimetre - where machines may one day operate, and where cells already do - the mechanics of large systems cannot simply be scaled down.

In some ways thermodynamics is like gambling. The first law - that energy cannot be created - tells us 'you can't win'. The second says 'you can't even break even'.

In other words, there is nothing unusual about winning a single game of blackjack, but over many games the house always wins. If a player keeps playing, they must eventually lose. And in thermodynamics, you're not allowed to leave the casino - hence the robustness of the second law.

Denis J. Evans and colleagues have discovered, not how to beat the house, but what happens in the realm between a single coin toss and a weekend in Las Vegas. To do so they measured water molecules' influence the motion of tiny latex beads held between lasers.

They found that over periods of time less than two seconds, variations in the random thermal motion of water molecules occasionally gave individual beads a kick. This increased the beads' kinetic energy by a small but significant amount, in apparent violation of the second law.

The gain is short-lived, and so could never amount to a source of free energy or perpetual motion. But it is big enough to confirm what physicists have long suspected.

Law enforcement

The first and second laws of thermodynamics are considered so fundamental that the United States Patent and Trademark Office will not consider patent applications that claim to violate them - unless a working model is provided with the application.

But violation of the second law of thermodynamics by small ensembles of particles within larger systems is not a new

idea. Evans's team predicted it formally a decade ago². And in 1878, the physicist James Clerk Maxwell wrote in a book review for Nature:

The truth of the second law is ... a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules... Hence the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body.

For larger systems over normal periods of time, however, the second law of thermodynamics is absolutely rock solid.

Ed Gerstner is the Editor of Nature's Physics and Materials Portals

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Thermodynamik

Fundamentales Gesetz ist brüchig

Von Martin Paetsch



Ein Fundament der Physik, der zweite Satz der Thermodynamik, bricht in mikroskopischen Welten zusammen: Dort spielt die Natur mitunter verrückt, wie australische Forscher gezeigt haben.

Der zweite Satz der Thermodynamik ist eines der grundlegendsten physikalischen Gesetze - doch auf mikroskopischer Ebene kann es durchaus verletzt werden. In der Welt der Zellen und künftiger Nanomaschinen fließt Energie auch in die falsche Richtung, wie ein australisches Forscherteam jetzt bewiesen hat. Die Entdeckung zeigt den Ingenieuren Grenzen auf für die Entwicklung winziger Motoren und Geräte.

Während der erste Hauptsatz der Thermodynamik die Erhaltung der Energie festschreibt, hat das zweite Gesetz die Ordnung im Universum zum Thema - oder besser ihr Gegenteil. Denn in geschlossenen Systemen, so die Regel, wächst die Unordnung mit der Zeit, bestenfalls

bleibt sie konstant. Als Konsequenz daraus nimmt etwa eine heiße Tasse Kaffee keine Energie von der umgebenden kühlen Luft auf, sondern gibt selbst Wärme ab.

Allerdings ist das zweite thermodynamische Gesetz im Grunde ein statistischer Satz, der das Verhalten von vielen Milliarden Teilchen beschreibt: den Atomen und Molekülen, aus denen sich die Stoffe zusammensetzen. In kleineren Maßstäben, wo es um sehr viel weniger Partikel geht, geschehen dagegen Dinge, die in größeren Systemen praktisch unmöglich sind - das Gesetz wird gebrochen.

Den Nachweis dafür brachten die Wissenschaftler um Denis Evans von der Australian National University in Canberra mit ihrem Experiment. Die Forscher, die ihre Ergebnisse in den "Physical Review Letters" vorstellen, hatten ein wenige Mikrometer großes Kügelchen aus Latex mit Hilfe von Laserstrahlen fixiert und immer wieder mit konstanter Geschwindigkeit durch Wasser gezogen. Dabei wurde ständig die genaue Position des Objekts gemessen.

Anhand dieser Daten konnte das Team errechnen, wie sich die Unordnung des Systems - Physiker sprechen von seiner Entropie - veränderte. Tatsächlich registrierten sie in Zeitabschnitten von einigen Zehntelsekunden etwas, das dem Gesetz zufolge nicht sein dürfte: eine Abnahme der Entropie. Die Kugel hatte zusätzliche Energie aus den zufälligen Bewegungen der Wassermoleküle gewonnen. Eine solche Umwandlung in nützliche Arbeit ist nach dem zweiten thermodynamischen Satz eigentlich verboten, genauso wie heißer Kaffee, der von kühler Luft noch weiter erwärmt wird.

Während einer sehr kurzen Zeitspanne, so die Beobachtung der Forscher, war die Regelverletzung - dass nämlich das Kügelchen Energie vom Wasser aufnahm, statt selbst welche abzugeben - fast ebenso wahrscheinlich wie ihre Einhaltung. Wurde die Latexperle dagegen länger als zwei Sekunden bewegt, dann triumphierte über die Gesamtdauer betrachtet wieder das zweite thermodynamische Gesetz.

Mit ihrem Versuch konnten die Wissenschaftler experimentell das so genannte Fluktuationstheorem bestätigen. Nach dieser 1993 von Evans und Kollegen aufgestellten

Beziehung ist die Wahrscheinlichkeit einer Verletzung des Gesetzes umso größer, je kleiner das beobachtete System und je kürzer die Zeitspanne ist. Das Theorem soll den zweiten Hauptsatz der Thermodynamik mit den Gleichungen der klassischen Mechanik und der Quantenmechanik vereinen, die zeitlich umkehrbar sind.

Die Gültigkeit des zweiten thermodynamischen Gesetzes in der makroskopischen Welt lassen die Versuche zwar unberührt. Nanoingenieure könnten jedoch irgendwann an eine Grenze der Miniaturisierung stoßen. Winzige Maschinen verhalten sich, so die Schlussfolgerung der Forscher, nicht wie große: Je kleiner ein Motor ist, desto größer ist die Gefahr, dass er während des Betriebs für einen Moment in entgegengesetzter Richtung läuft.

Law and Disorder: Chance fluctuations can rule the nanorealm

Peter Weiss

Whether it's the gasoline-to-motion transformation of automobiles or the electricity-to-cooling action of refrigerators, all processes squander energy. They vent that waste in the form of heat. It's a law of thermodynamics, and no one has ever witnessed a sustained violation of it.

On the minute scales of cells and molecules, however, brief reversals of the usual rules routinely occur. Tiny mechanisms run in reverse or draw their power from random, normally untappable thermal motion in the surroundings. Such small systems, on average, still obey thermodynamics laws, although some theorists predict that certain quantum structures may not (SN: 10/7/00, p. 234: <http://www.sciencenews.org/20001007/bob1.asp>). Now, researchers in Australia report that they have experimentally confirmed a theory that enables them to predict how often and under what circumstances reversals will dominate the behavior of a classical tiny system.

The new observations could become a reality check on the burgeoning field of nanotechnology, the scientists say. Working in an unfamiliar realm, many nanodevice makers today can't predict which of their mechanisms will actually work as planned. Moreover, because the living machinery of cells and microorganisms also operates on the nanoscale, the Australian work could lead to new biological insights as well.

To track transient reversals of a thermodynamics law, Denis J. Evans of the Australian National University in Canberra and his colleagues manipulated latex beads about the size of red blood cells. They used an infrared laser as if it were an ultratiny tweezers.

Imagine pulling a toy submarine through calm water by a rope tied to its prow. Because the water provides drag, the boat will lag behind the puller and rope, that is, unless it gets some sort of push.

That's roughly what happens to the latex beads. When Evans and his colleagues tugged their beads through water with their optical tweezers, sometimes a bead would slightly lead the laser, says Debra J. Searles of Griffith University, a member of the team. In such instances, the random motion of the water molecules was contributing to the bead's forward motion.

In tests that spanned from one-hundredth of a second to 10 seconds, the scientists found that for periods up to almost 2 seconds, the thermodynamic reversals could dominate the bead-dragging runs. The results, scheduled to appear in the July 29 *Physical Review Letters*, confirm predictions of a theory about the effect of random fluctuations developed by Evans and Searles almost a decade ago.

Searles says the new findings will come as a surprise to most scientists because the prevailing wisdom has been that such reversals have a major impact only on much smaller scales of size and time. "It's a tiny bead, but it's still a lot of atoms," she says.

Daniel P. Sheehan of the University of San Diego is not wowed by the size at which the effects appear. After all, he notes, ever since the 19th-century discovery of Brownian motion—the jiggling of pollen-grain-size particles in fluids because of random molecular bombardment—scientists have known that thermal motion can push fairly big particles around.

However, Sheehan was impressed by how long the thermodynamic reversals could dominate in the new tests. "It goes against my intuition that you could see [that effect] for as long as a tenth of a second," he says.

The result suggests that random thermal fluctuations could become a proverbial monkey wrench for many nanomachines, Searles says. Instead of going forward, for example, they might sometimes go backward. Even so, she says, nanomachine makers may find the new work useful as a tool for predicting whether their plans may go awry.

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From *Science News*, Vol. 162, No. 4, July 27, 2002, p. 51.

The World's No.1 Science & Technology News Service

Second law of thermodynamics "broken"

09:21 19 July 02

NewScientist.com news service

One of the most fundamental rules of physics, the second law of thermodynamics, has for the first time been shown not to hold for microscopic systems.

The demonstration, by chemical physicists in Australia, could place a fundamental limit on miniaturisation, because it suggests that the micro-scale devices envisaged by nanotechnologists will not behave like simple scaled-down versions of their larger counterparts - they could sometimes run backwards.

The second law states that a closed system will remain the same or become more disordered over time, i.e. its entropy will always increase. It is the reason a cup of tea loses heat to its surroundings, rather than being heated by the air around it.

"In a typical room, for example, the air molecules are most likely to be distributed evenly, which is the overall result of their individual random motion", says theoretical physicist Andrew Davies of Glasgow University. "But because of this randomness there is always a probability that suddenly all the air will bunch up in one corner." Thankfully this probability is so small it never happens on human timescales.

To the limit

Physicists knew that at atomic scales over very short periods of time, statistical mechanics is pushed beyond its limit, and the second law does not apply. Put another way, situations that break the second law become much more probable.

But the new experiment probed the uncertain middle ground between extremely small-scale systems and macroscopic systems and showed that the second law can also be consistently broken at micron scale, over time periods of up to two seconds.

Researchers led by Denis Evans at the Australian National University in Canberra measured changes in the entropy of latex beads, each a few micrometres across and suspended in water.

By using a precise laser beam to trap the beads, the team were able to measure the movement of the beads very frequently, and hence repeatedly calculate the entropy of the system at short time intervals.

Running in reverse

They found that the change in entropy was negative over time intervals of a few tenths of a second, revealing nature running in reverse. In this case, the bead was gaining energy from the random motion of the water molecule - the small-scale equivalent of the cup of tea getting hotter. But over time intervals of more than two seconds, on overall positive entropy change was measured and normality restored.

The team say their experiment provides the first evidence that the second law of thermodynamics is violated at appreciable time and length scales.

Their results are also in good agreement with predictions of the "fluctuation theorem", a theory developed at ANU 10 years ago to reconcile the second law with the behaviour of particles at microscopic scales.

"The results imply that the fluctuation theorem has important ramifications for nanotechnology and indeed for how life itself functions", claim the researchers.

Journal reference: *Physical Review Letters* (vol 89, 050601)

Matthew Chalmers

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Weblinks

[Paper abstract, Physical Review Letters](#)

[Liquid state chemical physics, ANU](#)

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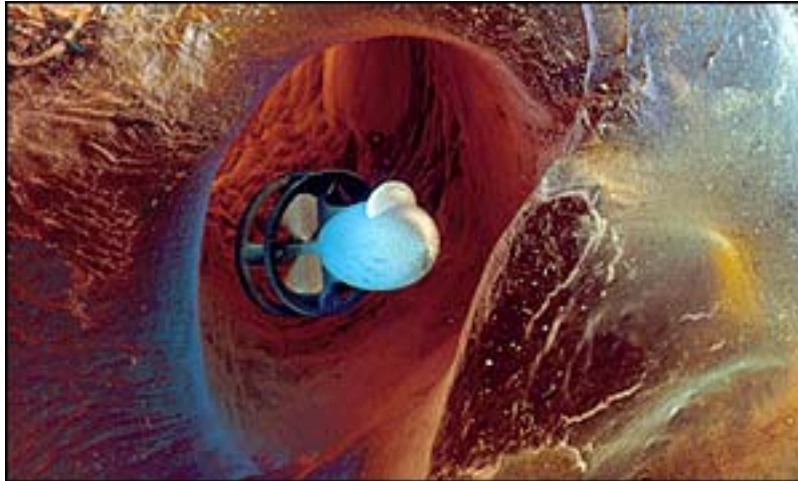
[Fluctuation theorem, ANU](#)



<http://news.bbc.co.uk/1/hi/sci/tech/2135779.stm>

Change to World Thursday, 18 July, 2002, 11:09 GMT 12:09 UK

Beads of doubt



Future vision: Nano-subs would seek and destroy cancer
(Image by Science Photo Library)

By Dr David Whitehouse

BBC News Online science editor One of the most important principles of physics, that disorder, or entropy, always increases, has been shown to be untrue.

This result has profound consequences for any chemical or physical process that occurs over short times and in small regions

ANU team Scientists at the Australian National University (ANU) have carried out an experiment involving lasers and microscopic beads that disobeys the so-called Second Law of Thermodynamics, something many scientists had considered impossible.

The finding has implications for nanotechnology - the design and construction of molecular machines. They may not work as expected.

It may also help scientists better understand DNA and proteins, molecules that form the basis of life and whose behaviour in some circumstances is not fully explained.

No discussion

Flanders and Swann wrote a famous song entitled The First And Second Law about what entropy meant and its implications for the physical world. It has become a mantra for generations of scientists.

The law of entropy, or the Second Law of Thermodynamics, is one of the bedrocks on which modern theoretical physics is based. It is one of a handful of laws about which physicists feel most certain.

So much so that there is a common adage that if anyone has a theory that violates the Second Law then, without any discussion, that theory must certainly be wrong.

The Second Law states that the entropy - or disorder - of a closed system always increases. Put simply, it says that things fall apart, disorder overcomes everything - eventually. But when this principle is applied to small systems such as collections of molecules there is a paradox.

Human scales

This Second Law of Thermodynamics says that the disorder of the Universe can only increase in time, but the equations of classical and quantum mechanics, the laws that govern the behaviour of the very small, are time reversible.

A few years ago, a tentative theoretical solution to this paradox was proposed - the so-called Fluctuation Theorem - stating that the chances of the Second Law being violated increases as the system in question gets smaller.

This means that at human scales, the Second Law dominates and machines only ever run in one direction. However, when working at molecular scales and over extremely short periods of time, things can take place in either direction.

Now, scientists have demonstrated that principle experimentally.

Fraction of a second

Professor Denis Evans and colleagues at the Research School of Chemistry at the Australian National University put 100 tiny beads

into a water-filled container. They fired a laser beam at one of the beads, electrically charging the tiny particle and trapping it.

The container holding the beads was then moved from side to side a thousand times a second so that the trapped bead would be dragged first one way and then the other.

The researchers discovered that in such a tiny system, entropy can sometimes decrease rather than increase.

This effect was seen when the researchers looked at the bead's behaviour for a tenth of a second. Any longer and the effect was lost.

Emerging science

The scientists say their finding could be important for the emerging science of nanotechnology. Researchers envisage a time when tiny machines no more than a few billionths of a metre across surge through our bodies to deliver drugs and destroy disease-causing pathogens.

This research means that on the very small scales of space and time such machines may not work the way we expect them to.

Essentially, the smaller a machine is, the greater the chance that it will run backwards. It could be extremely difficult to control.

The researchers said: "This result has profound consequences for any chemical or physical process that occurs over short times and in small regions."

The ANU work is published in Physical Review Letters.

ABC NewsRadio

 *StarStuff*

<http://www.abc.net.au/newsradio/star.htm>



INSIDE TRACK - Bad news for nanomachines - TECHNOLOGY WORTH WATCHING.

By FIONA HARVEY.

245 words

25 July 2002

Financial Times

12

English

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The second law of thermodynamics has been broken and it is bad news for nanomachines.

Scientists have speculated for many years that while the second law of thermodynamics - which states that energy tends to dissipate from bodies into their surroundings - appears to be true in the case of large systems, it might not always hold true in the case of very small systems. The first evidence for this theory comes from the Australian National University and is published in the current edition of Physical Review Letters.

The Australian scientists dragged a tiny bead of latex through some water using a pair of "optical tweezers", consisting of two laser beams that trapped and held the bead. They examined closely the way the water interacted with the bead, and found that while for most of the bead's passage through the water a small amount of energy was transferred from the bead to the water, for short periods of up to two seconds the bead gained energy from the water.

These observations could be bad news for the development of nanomachines, because they suggest that the motion and workings of such tiny machines - only a few molecules in size - could be disrupted in unpredictable ways by sudden transfers of energy from their surroundings, in contradiction of the second law. Australian National University, Canberra; tel: 0061 2 6125 5111; www.anu.edu.au

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LIFESTYLE
QUEST

In the short run, the law has an exception

SCOTT LAFEE

152 words

24 July 2002

The San Diego Union-Tribune

1,2,6,7

F-10

English (Copyright 2002)

Australian scientists say they have proved experimentally that the second law of thermodynamics does not hold true for microscopic systems.

The second law states that a closed system will remain the same or become more disordered. It's the law that dictates that a cup of tea loses heat to its surroundings rather than becoming hotter.

But on the atomic scale, the rule doesn't seem to apply. Researchers at Australian National University in Canberra measured minute changes in latex beads suspended in water and illuminated by a laser.

They found that, for brief but appreciable moments of time – a few tenths of a second – the beads actually gained energy from the random movement of surrounding water molecules.

Over time intervals of more than two seconds, however, the beads lost energy, thus reasserting the primacy of the second law.

Find this article at:

http://www.signonsandiego.com/news/science/20020724-9999_1c24second.html

URL: <http://www.chemweb.com/alchem/articles/1027071098597.html>

**Second Law of
Thermodynamics can break
down at Nanoscale Size
Range**

25 July 2002

Stop those scientists! They broke the second law of thermodynamics! The second law states that some energy will always be lost when converting from one form of energy to another.

Hundreds of inventors have tried and failed to develop devices that violate the second law. Now researchers have shown for the first time that the second law can break down under special circumstances [1].

In systems containing thousands of molecules, the scale of nanomachines and living cells, transient energy increases can occur that violate the second law.

Denis Evans and colleagues at the Australian National University and Griffith University measured the effect of water molecules on the motion of colloidal latex beads held in an optical trap between laser beams.

Over time periods of less than two seconds, variations in the random thermal motion of water molecules occasionally gave individual beads a 'kick' increasing their kinetic energy by a small but significant amount and altering bead trajectory.

The team calculated the entropy change over the duration of each particle trajectory. Results indicated that a significant fraction of the observed bead trajectories defied the second law.

This observation suggests that there is a limit to miniaturisation and to our understanding of living cell behaviour. The increased energy observed is a short-lived microscale phenomenon and thus could not power a perpetual motion machine.

However, the effect is large enough to confirm a long-standing speculation that small assemblages of atoms or molecules could violate the second law. Evans's research team developed a 'fluctuation theorem' that predicted violation of the second law in small systems ten years ago [2].

Indeed, as long ago as 1878, renowned physicist James Clerk Maxwell wrote in a book review for the journal *Nature*: "The truth of the second law is ... a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules... Hence the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body."

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John K. Borchardt

The Canberra Times

TO SERVE THE NATIONAL CITY AND THROUGH IT THE NATION

http://canberra.yourguide.com.au/detail.asp?story_id=172306&y=2002&m=8&class=Features&subclass=Science&category=Feature&class_id=17

Breaking a law of physics

By SIMON GROSE

IN the ANU Research School of Chemistry they are proving physics wrong.

Professor Dennis Evans, the Dean of the school, and his team of researchers attracted media attention around

the world after one of their experiments violated the second law of thermodynamics.

That's the one that says that if you have a hot cup of coffee in a cold room, the coffee will get cooler, rather than the room get warmer.

But to break this golden rule they had to use small things, like a bead less than one tenth of a millimetre in diameter floating in a pond of water in a very sensitive apparatus.

"It can measure forces down to 5×10^{-10} newtons," Evans said last week.

"The smaller the force, the longer you can observe the violation of the second law. If the force was larger you wouldn't be able to see it for so long." In the experiment, reported in Physical Review Letters, they used a laser beaming up through the water to drag the bead very slowly in one direction. They used the laser at as low a power as possible, just enough to keep the ball trapped in its beam.

The water slowed the ball's progress, but occasionally the ball jumped ahead of the laser when random arrangements of water molecules bouncing around it pushed it forward. That broke a law of physics, a phenomenon that has been noted before at nano level.

"If you make nano machines so small that the energy or the entropy produced per duty cycle of the machine becomes comparable to the thermal energy of a single water molecule in a solution, then you start getting into this regime where it will run backwards a fair percentage of the time," Evans said. "Like your Holden Commodore, taking heat, CO₂, water, and all the rest of it out of the atmosphere, and generating petrol."

The research provides a practical demonstration of a theoretical resolution of the conflict between the second law of thermodynamics and equations of classical and quantum mechanics which are time reversible. The resolution

proposed in 1993 by Evans and Debra Searles of Griffith University was a Fluctuation Theorem. This states that the probability of the second law of thermodynamics being violated decreases exponentially as the size of the system increases.

Possible applications of the work relate to biology where molecular interactions occur at such a small scale that the findings may be relevant. It also shows that there may be limits to the performance of nanomachines.

"What we want to do is a continuous version," Evans said. Rather than moving the laser in one direction, they will move it around in a circle and in other patterns.

"This will be a steady state rather than these transient states just after you start," Evans said.

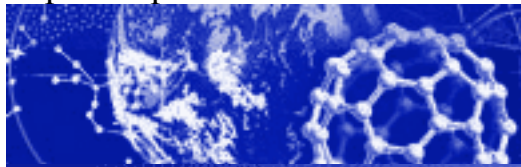
"Mathematically there are a lot of differences between the two.

"In those experiments I predict that we will see some really crazy things where the ball will start to move before you turn the switch on, because of the connection between the second law of thermodynamics and causality."

Computer modelling has shown this is likely. "Even a decade ago I didn't think you could extend thermodynamics to really small systems and relatively short times," Evans said.

"It's amazing that in the 21st century you can make a new statement about such an old subject."

Relevant links



Physik allg.

19.07.2002

2. Hauptsatz der Thermodynamik verletzt: In Nanomaschinen kann die Entropie abnehmen

In kleinen physikalischen Systeme mit Abmessungen im Nanometerbereich kann bei periodischen Bewegungen die Entropie abnehmen. Sie verletzen damit den zweiten Hauptsatz der Thermodynamik, der besagt, dass die Entropie bei Kreisprozessen stets ansteigt oder im besten Fall gleich bleibt. Ein australisches Forscherteam hat nun erstmals eine Entropieabnahme experimentell nachgewiesen und damit eine vor zehn Jahren aufgestellte Theorie bestätigt. Darüber berichtet das Fachblatt *Physical Review Letters* (Band 89, Referenznummer 050601).

Das Experiment der Forscher um Denis Evans von der australischen Nationaluniversität untersuchte die bei der periodischen Bewegung einer nur wenige Mikrometer großen Latexkugel auftretenden Entropieänderungen. Dazu fingen die Forscher eine in einer Flüssigkeitszelle schwebende Kugel mittels des Laserstrahls einer Laserpinzette ein. Die Kugel war damit durch elektrostatische Kräfte an den Brennpunkt des Strahls gebunden.

Die Forscher bewegten nun die Flüssigkeitszelle mit einer Frequenz von 54 Hertz vorwärts und rückwärts, so dass die in ihr schwebende Latexkugel mit dieser Frequenz durch den Brennpunkt des Laserstrahls wanderte. Mittels einer Hochgeschwindigkeitskamera hielt das Team den Ort der Kugel Tausend mal pro Sekunde fest. Dies ermöglichte die Bestimmung der Bahnkurven der Kugel, und daraus wiederum ließen sich die wirkenden Kräfte und die mit dieser Bewegung verbundenen Entropieänderungen bestimmen.

Unter den aufgenommenen Bahnkurven fanden sich in der Tat einige, bei denen das System während eines Zyklus Entropie verbrauchte und somit gegen den zweiten Hauptsatz der Thermodynamik verstieß. Diese Entropieabnahme ließ sich jedoch nur bei sehr kurzen Beobachtungszeiten von wenigen Sekundenbruchteilen beobachten. Eine über wenige Zehntelsekunden durchgeführte Entropiebilanz dieses Prozesses konnte so in der Tat eine Entropieabnahme aufzeigen – wenn die Bilanz allerdings über mehrere Sekunden durchgeführt wurde, so nahm die Entropie zu.

Die Forscher konnten damit eine von ihnen vor zehn Jahren aufgestellte Theorie bestätigen. In ihrer so genannten Fluktuations-These hatten sie vorausgesagt, dass kleine Systeme über kurze Zeiträume Entropie verbrauchen können.

Die Entropieabnahme könnte für die Funktionsweise von Nanomachinen von Bedeutung sein. Wenn deren Entropie abnimmt, würden sie quasi "rückwärts" laufen. Die Fluktuationstheorie kann den Forschern nach auch zur Untersuchung von biologischen Protein-Motoren angewendet werden.

Weitere Meldungen zum Thema Entropie finden Sie im Archiv von wissenschaft.de.

Stefan Maier



Nanotechnology doesn't respect second law of thermodynamics

Washington, July 20 (ANI):

The second law of thermodynamics, a rule that physicists swear by, does not hold water, as far as microscopic systems are concerned.

Miniaturisation doesn't exactly work as a scaled down version of its larger counterparts showed Australian chemical physicists.

Nanotechnologists say that they could sometimes run backwards on some basic physical rules, reports NewScientist.

According to the second law, a closed system will remain the same or become more disordered over time, i.e. its entropy will always increase. It is the reason a cup of tea loses heat to its surroundings, rather than being heated by the air around it.

Physicists knew that at atomic scales over very short periods of time, statistical mechanics is pushed beyond its limit, and the second law does not apply. Put another way, situations that break the second law become much more probable.

But the new experiment probed the uncertain middle ground between extremely small-scale systems and macroscopic systems and showed that the second law can also be consistently broken at micron scale, over time periods of up to two seconds.

Denis Evans, Australian National University measured changes in the entropy of latex beads, each a few micrometres across and suspended in water, using a precise laser beam to trap the beads. The team were able to measure the movement of the beads very frequently, and hence repeatedly calculate the entropy of the system at short time intervals.

They found that the bead was gaining energy from the random motion of the water molecule. But over time intervals of more than two seconds, on overall positive entropy change was measured and normality restored.

The team say their experiment provides the first evidence that the second law of thermodynamics is violated at appreciable time and length scales. Their results are also in good agreement with predictions of the "fluctuation theorem", a theory developed 10 years ago to reconcile the second law with the behaviour of particles at microscopic scales.

"The results imply that the fluctuation theorem has important ramifications for nanotechnology and indeed for how life itself functions", the researchers opine.

<http://radio.weblogs.com/0105910/2002/08/10.html>

Roland Piquepaille's Technology Trends

How new technologies are modifying our way of life



samedi 10 août 2002

Thermodynamics Law Hits Snag With Nano-Exceptions

Two days ago, I told you about my fascination with quantum computing. Today, let's talk about another scientific subject: nanotechnology. But I warn you: it's going to be technical.

We'll start with the abstract of a paper published by the Physical Review Letters in its July 29, 2002 issue.

Ready for the abstract? Here we go.

The title is "Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales."

We experimentally demonstrate the fluctuation theorem, which predicts appreciable and measurable violations of the second law of thermodynamics for small systems over short time scales, by following the trajectory of a colloidal particle captured in an optical trap that is translated relative to surrounding water molecules. From each particle trajectory, we calculate the entropy production/consumption over the duration of the trajectory and determine the fraction of second law-defying trajectories. Our results show entropy consumption can occur over colloidal length and time scales.

Of course, this abstract is not written in "English for Dummies." So let's turn to the Science section of the Wall Street Journal (WSJ) for explanations in -- almost -- plain english.

Sharon Begley wrote a story for the Journal on August 2, 2002. Unfortunately, you have to be a paid subscriber of the WSJ to read the full contents of the article. Here are some quotes.

There are several ways to express the Second Law, but the basic idea is twofold. First, in a closed system, entropy (disorder) increases. Or as that great thermodynamicist William Butler Yeats said, things fall apart.

In addition, you can't harvest heat energy from cooler surroundings and turn it into work. If such a trick were possible, then machines could create electrical power rather than gobble it up, perpetual-motion machines could hum merrily forever.

Chemist Denis Evans of Australian National University in Canberra theorized in 1993 that "for brief periods, tiny particles

can suck up entropy, converting heat from their surroundings into useful work."

With the help of his colleagues, he did some experiments which -- apparently -- prove this is possible to break the Second Law of Thermodynamics for as long as two seconds.

If the microworld can violate the Second Law, "biological machinery might take advantage of this," says Dr. Evans. Molecules could briefly extract energy from their surroundings, combining in ways that would otherwise be impossible in practice. The loophole in the Second Law -- for tiny objects for short periods of time -- might be big enough to let miracles through.

Nanoproducts will be real one day -- but when?

Source: Sharon Begley, The Wall Street Journal, August 2, 2002; Physical Review Letters, July 29, 2002

An den Grenzen der Thermodynamik

Die drei Hauptsätze der Thermodynamik gehören zu den ehernen Gesetzen der Physik. Unter anderem besagen sie, dass es unmöglich ist, Maschinen zu bauen, die mehr Energie erzeugen als verbrauchen. Zumindest auf molekularer und atomarer Ebene gerät aber der Zweite Hauptsatz der Thermodynamik ins Wanken - wie nun erstmals experimentell bewiesen wurde.

Eine Frage der System-Größe

Wie Ed Gerstner, der Herausgeber der beiden Online-Portale zu Physik und Materialien der Fachzeitschrift "Nature" schreibt, könnte dies bedeuten, dass es eine Art natürliche Grenze der Miniaturisierung und unseres Verständnisses der belebten Welt gibt.

In einer Größenordnung von ein paar Millionstel Millimeter - eine Größenordnung, in der Zellen bereits jetzt, in einigen Jahren aber auch Maschinen operieren werden - werden die Gesetze der Mechanik großer Systeme scheinbar nicht angewandt.

Drei Hauptsätze der Thermodynamik

Für die Thermodynamik sind die drei Hauptsätze der Wärmelehre maßgebend:

1. Hauptsatz - der Energieerhaltungssatz: Wärme kann in andere Energieformen übergeführt oder aus diesen erzeugt werden, sie kann aber nicht aus nichts entstehen.
2. Hauptsatz - der Entropiesatz: die Entropie - eine von Rudolf Julius Emanuel (Clausius) eingeführte Rechengröße, die in der Wärmelehre den Zustand eines Systems (z.B. Gas oder Flüssigkeit) charakterisiert - kann bei Zustandsänderungen des Systems nicht abnehmen.
3. Hauptsatz - das Nernst'sche Wärmetheorem: die Entropie jeder Substanz geht gegen Null, wenn die Temperatur bei ansonsten festen Bedingungen gegen Null strebt.

Online Skript Thermodynamik und Statistische Physik

Wassermoleküle vs. Latex-Tröpfchen

Wie kam es zu dieser Einschätzung? Emil Mittag, Debra J. Searles und Kollegen zweier australischer Universitäten hatten den Einfluss von Wassermolekülen auf die Bewegung von winzigen Latex-Tropfen untersucht, die durch Laserstrahlen fixiert wurden.

Sie fanden heraus, dass Variationen in der zufälligen thermischen Bewegung der Wassermoleküle innerhalb von Zeitspannen von weniger als zwei Sekunden einzelne Tröpfchen anstießen.

Dies führte zu einer zwar kleinen, aber signifikanten Erhöhung ihrer kinetischen Energie - eine Verletzung des zweiten Hauptsatzes der Thermodynamik.

Keine "freie" Energie, kein Perpetuum mobile

Der Energiegewinn, so die Forscher, sei nur von kurzer Dauer gewesen und könnte insofern niemals zu einer Quelle "freier" Energie oder einem Perpetuum mobile führen.

Er war aber groß genug, um das zu bestätigen, was sich die Physiker ohnehin lange schon dachten.

Der Zweite Hauptsatz der Thermodynamik

Der Entropiesatz wurde auf verschiedene Weisen ausgedrückt. Eine Variante: Wärme kann niemals spontan, d.h. ohne Arbeitszufuhr von außen, von einem kälteren auf einen wärmeren Körper übergehen (Clausius). Eine weitere: Es ist unmöglich, eine periodisch arbeitende Maschine zu konstruieren, die nichts anderes bewirkt als die Erzeugung mechanischer Arbeit unter Abkühlung eines Wärmereservoirs (Unmöglichkeit eines Perpetuum mobile II; Planck und Thomson).

Ludwig Boltzmann wiederum erkannte, dass der Entropiesatz gleichbedeutend ist mit der Wahrscheinlichkeitsaussage: Die auf die einzelnen Moleküle eines Körpers verteilte Bewegungsenergie geht stets von einem weniger wahrscheinlichen Verteilungszustand in einen wahrscheinlicheren über, nicht aber umgekehrt. Sind z. B. alle Luftmoleküle zu Anfang in einer Ecke eines Zimmers, so verteilen sie sich gleichmäßig in diesem Zimmer: die Entropie nimmt zu. Es ist jedoch praktisch ausgeschlossen, dass umgekehrt die gleichmäßig verteilten Moleküle sich einmal alle in einer Zimmerecke ansammeln.

Mehr über den zweiten Hauptsatz der Thermodynamik

Theoretische Vorhersage bestand seit langem

Denn die Verletzung des Zweiten Gesetzes der Thermodynamik bei kleinsten Teilchen-Mengen innerhalb größerer Systeme ist keine neue Idee. Das Forscherteam um Searles und Mittag hat es bereits vor mehr als zehn Jahren theoretisch vorher gesagt.

Und schon 1878 schrieb der schottische Physiker James Clerk Maxwell: "Die Wahrheit des Zweiten Gesetzes der Thermodynamik ist ... statistisch, nicht mathematisch, da sie auf der Tatsache beruht, dass die Systeme, mit denen wir uns beschäftigen, aus Millionen von Molekülen bestehen ... Daher wird das Gesetz auch bei jeder ausreichend kleinen Gruppe von Molekülen, die zu einem größeren System gehören, kontinuierlich und bis zu einem bemerkenswertem Ausmaß verletzt."

Analogie zum Glücksspiel

Ed Gerstner verglich die Thermodynamik in der Online-Ausgabe von "Nature" mit einem fortwährenden Glücksspiel. Der erste Hauptsatz, wonach keine Energie aus nichts geschaffen werden kann, bedeutet in diesem Zusammenhang: "Man kann nicht gewinnen." Der zweite: "Man kann nicht einmal ohne Verluste spielen."

Mit anderen Worten: Es ist nicht besonders ungewöhnlich, ein einzelnes Glücksspiel zu gewinnen. Nach sehr vielen Spielen gewinnt aber immer die Bank.

Oder im Sinne der Thermodynamik: Man kann das Kasino gar nie verlassen, daher rühre auch die Robustheit des Zweiten Gesetzes -

zumindest bei größeren Systemen und über einen größeren Beobachtungszeitraum hinweg.

Die Original-Studie von Emil Mittag, Debra J. Searles und Kollegen unter dem Titel "Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales" erscheint in den Physical Review Letters vom 29. Juli 2002 (89, 050601).

Original-Abstract

Grundbegriffe der Thermodynamik

Grundlagen der Thermodynamik

Physical Review Letters

Nature Science Update

Breaking even



The first law of thermodynamics states that it is impossible to create energy from nothing — or in other words, in terms of energy, you can't win.

Furthermore, the second law states that, in converting energy from one type to another, some of that energy will be always be lost in a different form — or in other words, you can't even break even. These two laws are considered so fundamental that the United States Patent and Trademark Office will not even consider patent applications that claim to violate them (that is, unless a working model is provided with the application). But writing in *Physical Review Letters* this week, Genmiao Wang and colleagues suggest that violations of the second law of thermodynamics, albeit at small scales and over short periods of time, can and do occur.

The idea that the second law of thermodynamics could be violated by small ensembles of particles within larger systems is not new. In 1878, James Clerk Maxwell (writing in a book review for *Nature*) noted:

"The truth of the second law is ... a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules... Hence the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body. (Maxwell, J. C., Tait's "Thermodynamics" II, *Nature* 17, 278–280 (7 February 1878)).

For larger systems over normal periods of time, however, the second law of thermodynamics is sound.

To explain all this apparent paradox, a useful analogy can be drawn to gambling. Although there is nothing unusual about winning a single game of 'black-jack', it is a matter of statistical fact that over many games, the house always wins. Therefore, if a player keeps playing, they must eventually lose. And in thermodynamics, you're not allowed to leave the casino — hence the robustness of the second law. The interesting question posed by Wang et al., however, is not how to beat the house, but what happens in the realm between a single coin toss and a weekend in Las Vegas?

At length scales where nanomachines may one day operate — and indeed, biological systems such as living cells already do — violation of the second law may have important phenomenological implications. In a previous work, one of the authors developed a framework called the fluctuation theorem to quantitatively describe such violations in finite systems (Evans et al. *Phys. Rev. Lett.* 71, 2401–2404 (1993)). In the new work, Wang et al. experimentally confirm the predictions of this theorem by observing the influence of water

molecules on the motion of microsized latex beads held in an optical trap.

They find that over timescales of less than 2 s, fluctuations in the random thermal motion of water molecules can occasionally give individual beads a kick, increasing their kinetic energy by a small but measurable amount, in apparent violation of the second law of thermodynamics.

The gain is short-lived, and so could never amount to a source of free energy or perpetual motion. But the results do suggest that as technology approaches ever-smaller dimensions, our understanding of statistical mechanics may have to be more sophisticated than a simple scaling down of macroscopic models.

For more materials science and nanotechnology highlights, and free full text access (until 31st October) to all materials and nanotech papers published in Nature, go to Materials Update.

Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales

G. M. WANG, E. M. SEVICK, EMIL MITTAG, DEBRA J. SEARLES & DENIS J. EVANS

We experimentally demonstrate the fluctuation theorem, which predicts appreciable and measurable violations of the second law of thermodynamics for small systems over short time scales, by following the trajectory of a colloidal particle captured in an optical trap that is translated relative to surrounding water molecules. From each particle trajectory, we calculate the entropy production/consumption over the duration of the trajectory and determine the fraction of second law-defying trajectories. Our results show entropy consumption can occur over colloidal length and time scales.

Physical Review Letters 29, 050601 (15 July 2002)

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Kleine Systeme widersetzen sich dem zweiten Hauptsatz der Thermodynamik

Beitrag von Olli [] zu:

RE: RE: zweiter Hauptsatz???

Da ich keinen Zugang habe, komme ich leider nicht an den Volltext ran, aber laut Abstract scheint tats%ochlich der 2. HS verletzt:

Experimental Demonstration of Violations of the Second Law of
Thermodynamics for Small Systems and Short Time Scales

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We experimentally demonstrate the fluctuation theorem, which predicts appreciable and measurable violations of the second law of thermodynamics for small systems over short time scales, by following the trajectory of a colloidal particle captured in an optical trap that is translated relative to surrounding water molecules. From each particle trajectory, we calculate the entropy production/consumption over the duration of the trajectory and determine the fraction of second lawñdefying trajectories. Our results show entropy consumption can occur over colloidal length and time scales.

<http://link.aps.org/abstract/PRL/v89/e050601>

The Australian

Edition 1TUE 01 OCT 2002, Page C03

Taking up the nano challenge

By Karen Dearne

Australia is among the frontrunners in the race to make machines so tiny they are invisible to the eye, Karen Dearne reports

THE race to make things smaller is gathering pace -- and Australia wants a piece of the action.

While the "art of building substances atom by atom" remains a dream, nanotechnology is nevertheless throwing up many new products and tantalising possibilities.

A three-day nanotechnology conference held in Sydney recently -- the first of its kind -- attracted several hundred research scientists, technical experts, consultants, venture capitalists and companies keen to enter the field.

Professor Michael Barber of the Australian Academy of Sciences says nanotechnology

is fascinating because it draws on physics, chemistry and biology in ways that challenge fundamental scientific laws.

Nanotech is also about delivering useful products, and these include nanomaterials, biosensors and

enhanced computing and telecommunications services.

Quantum computing offers high potential, and the "sheer genius and capabilities" of Australians

in this area are highly sought-after, Barber says.

The new ARC Centre for Quantum Computing -- involving some 60 research staff and students

from the University of New South Wales, University of Queensland and University of Melbourne --

is building a revolutionary solid state machine using the silicon material system.

Quantum processors are expected to leapfrog traditional computers by many orders of magnitude,

opening up unthought-of realms for research and technologies.

"Nanotechnology is known as a disruptive technology, because it's so hard to predict the effects and changes it will

bring," Barber says.

"The major threats and opportunities will certainly fall upon our existing resources, agricultural

and manufacturing industries."

Dr Vijoleta Braach-Maksvytis, chair of the CSIRO Science Forum, says there are more than 500

start-up nanotech companies globally, and most multinational IT, pharmaceutical and chemical companies are actively researching nanotechnologies

Some older technologies, such as microelectronics and powder/slurry goods are being rebadged as nanotech, while quantum computing, semiconductors and biotechnology are coming under the nano umbrella.

“We're basically at the raw material level with nanotechnology

, and the analogy of that is like discovering gold," she says. For example, the quantum effects of simply reducing the size of a material creates a range of new materials.

Nano-processing will revolutionise manufacturing, enabling much cheaper bottom-up, or self-assembly of components such as silicon chips.

Braach-Maksvytis says Australia's Flinders University was the first in the world to offer a degree

course in nanotechnology, in 1999.

“Interest in nanotechnology has risen dramatically in the past 18 months," she says. “We have key skills in training, and a mindset that embraces innovation.

“We have to be aware of the waves of skills shortages we've seen in IT, and think about how we can reskill and retrain people to meet the challenge."

Nanomachinery

GROUNDBREAKING work led by Professor Denis Evans of the ANU Research School of Chemistry has demonstrated that things work quite differently at very small scales of time and space.

A nanometre (1nm) equals 1 billionth of a metre. When working at the nanoscale over extremely short periods, things can work in either direction.

As a result, nano-engines can either consume fuel to produce work, heat and waste or they can

consume work, heat and waste to produce fuel. As the size of the engine gets smaller, the probabilities that the engine will run forwards or

backwards become more nearly equal. Evans suggests this will place a fundamental limit on the work that can be performed by nanomachines.

Mimicking nature

MICROSCOPIC self-assembling machines, neural computing, robots too small to be seen by the naked eye - that's the challenge for CSIRO's Telecommunications and Industrial Physics team.

Scientists are looking to nature to develop technologies that are smaller, cheaper, faster and more environmentally friendly.

Nature is proving inspirational - the new field of biomimetics involves engineering systems that

mimic natural plant and animal systems at the molecular level, resulting in the creation of novel

advanced structures, materials and devices.

Nanosized materials are being developed for application in polymers, pharmaceuticals and drug

delivery systems, cosmetics and sunscreens, paints, barrier coatings, inks and textiles.

Column: Australian IT, Computers, Cutting Edge

Section: FEATURES

<http://www.manilatimes.net/national/2002/oct/01/life/20021001lif3.html>

SCIENCE

A violation of the second law

By Rony Diaz

For the first time, a deviation from the second law of thermodynamics was shown in an experiment.

The feat was accomplished by a team of the Australian National University led by Dr. Denis Evans. He predicted it 10 years ago. (G. Wang et al 2002 Phys. Rev. Lett.)

The discovery could help in designing nanomachines and in explaining how small biological systems — protein motors, for example — work. All this was reported on July 16, 2002 in PhysicsWeb (<http://physicsweb.org/article/news/6/7/11>).

The first law of thermodynamics states that the total energy of the universe is constant. This is also known as the conservation of energy.

The second law says that the total entropy or disorder of the universe is continually increasing. This is one of the most profound — and, among philosophers and some scientists, controversial — laws of physics.

There are any number of ways of stating the second law that accords with experience and can be expressed mathematically.

Some of these are the following:

Isolated systems inevitably become less organized. In an isolated system, usable energy is constantly decreasing. Heat flows from hot to cold places, thereby equalizing temperature.

Without the second law, a car could run forever because energy is conserved. Without it, we wouldn't have to ingest heat in the form of food. Perpetual motion machines would become possible. And so forth and so on.

The second law prevents all this from happening. The level of disorder in the world for all isolated systems, whether as small as a box filled with liquid or gas or as large as the solar system, is constantly rising irreversibly.

The deepest and most puzzling implication of the second law is the so-called "arrow of time." This provides a definition of the direction of time with its statement that isolated systems will adjust itself, as time passes, so that disorder is as great as possible. In short, time moves forward, never backward.

The second law is less a law (as the word is commonly understood) and more a set of probabilities.

In probability theory, all states are equally likely, given enough time.

Think of a box with two compartments. One is filled with water and the other with ink. Remove the wall. The water and the ink will mix into a disorganized and probable configuration of a liquid less clear than water and less murky than ink.

The probability that the two liquids would unmix to return to their original ordered states is overwhelming prohibitive.

The conclusion: (a) an isolated system naturally changes to more probable configuration; (b) an isolated system redistributes available energy equally among its parts; and (c) isolated systems evolve toward increasing disorder.

The second law was deeply disturbing to some thinkers and scientists.

The great Isaac Newton in *Optiks* (1704) wrote that "Motion is much more apt to be lost than got and is always upon decay" and that the anomalies in the orbits of planets will apt to increase, till this system wants a reformation" by God. It is God that prevents the world from evolving toward decay and disorder.

Scientists in the 19th and early 20th centuries were not as ready as Newton to accept Divine intervention as the reason the universe did not run down.

William Rankine (1829-1872), an engineer and specialist in heat engines, tried to find a way around the second law. He theorized that in deep space there were huge walls that kept the energy lost by decaying systems from escaping and refocused it into usable form again.

Lord Kelvin himself, one of the discoverers of the second law, could not fully accept its logical outcome. In 1862, he wrote: "[It was] impossible to conceive a limit to the extent of matter in the universe; and therefore science points rather to an endless progress ... than to a single finite mechanism, running down like a clock, and stopping forever."

The idea of progress that was espoused by the likes of the philosopher Herbert Spencer taught that "natural and artificial forces are causing the world to become more and more developed, advanced, organized, and moral with time."

As late as 1928, the Nobel laureate for physics, Robert Millikan, put forward the hypothesis that in outer space, atoms were continually being formed out of less organized particles and that cosmic rays were produced during the formation of these atoms. "With the aid of this assumption," he said, "one would be able to regard the universe as in a steady state now and also banish forever the nihilistic doctrine of the ultimate heat death."

Thermal extinction was thought to be the inexorable consequence of the second law as the total store of usable energy diminishes over time. This is the warmist doctrine that intrigued and alarmed people in the mid-19th century.

But in 1929, a year after Millikan's hypothesis, the astronomer Edwin Hubble provided observational evidence that the universe is not in a steady state but is expanding as all the galaxies rushed away from each other.

Now to return to Denis Evans' and his team's discovery.

The second law applies, according to them, only to large systems over significant periods of time. It does not apply to small isolated systems over very short periods of time.

To explain the behavior of small systems, Evans and his colleagues proposed the "fluctuation theorem" that calculates the probability that entropy will be consumed at any point in a given cycle. Measurable deviations from the second were thereby found.

The experiment proceeded in this way. One hundred latex beads, each 6.3 μm across, were put in a cell filled with water. The cell was put on a stage of a microscope. A laser was focused on one of the beads, inducing a dipole moment that drew the bead to the most energetic region of the electric field in the laser beam. The force that acted on the particle near the point of the focus of the laser was harmonic.

The microscope stage was moved backward and forward, dragging the bead away from the laser focus. The movement was through 540 cycles in 10 seconds; the position of the bead was measured repeatedly every second. Putting together these measurements with the output of the laser and the drag of the water, the team was able to calculate the forces acting on the bead and the quantity of entropy as it moved.

They discovered that in some trajectories entropy was consumed rather than generated. This effect was detected in the behavior of the bead in a tenth or less of a second. Over periods approaching two seconds, the proportion of entropy-consuming states decreased. Above two seconds, none were seen.

The results of the experiment approximated closely a computer simulation of the fluctuation theorem.

The discovery of this violation of the second law does not falsify it. It, however, makes us more keenly aware that there are still many phenomena in nature that we still have to understand.

R&D

News of science, medicine, and technology



Physicists Learn to Turn Back Time

by Maia Weinstock

According to the Second Law of Thermodynamics, any isolated system tends to grow more disorderly over time—the fundamental reason the mess in your sink only gets worse if you don't wash the dishes. But Denis Evans, a physicist at the Australian National University, has found that the second law can sometimes be forced to run backward. To physicists, this is a discovery equivalent to finding that the dishes washed themselves while you waited.

Evans and his colleagues searched for flaws in the second law by adding fine latex beads, each less than a millionth of an inch wide, to a water-filled cell big enough to fit on a microscopic stage. The researchers shook the cell in a precise rhythm and used a laser beam to track the progress of a single bead within the chamber. They found that when they observed the bead for periods of no more than a tenth of a second, the bead's path caused the system to become more orderly—the opposite of what is supposed to happen.

The experiment proved what Evans and his colleague Debra Searles had predicted nine years earlier: Measurable violations of the second law are possible at extremely small scales; at larger scales, however,

they vanish into the overall trend toward disorder. This loophole could eventually help engineers design miniature machines, such as rotors built from a single protein molecule. It could also aid in the investigation of the very nature of causality. The second law defines the arrow of time—why those dishes do not get un-dirty, or why you cannot un-spill spilled milk. The existence of some flexibility in the law hints that events could temporarily run backward but only over minuscule distances. Humans will not be able to make themselves young again. Current theory "still prohibits time reversal for large systems," Evans says.

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Small systems defy second law

16 July 2002

A deviation from the second law of thermodynamics has been demonstrated experimentally for the first time. Denis Evans of the Australian National University and colleagues have shown that entropy can be consumed - rather than generated - in small systems over short periods of time. The achievement fulfils a prediction made by Evans and colleagues ten years ago (G Wang *et al* 2002 *Phys. Rev. Lett.* 89 050601).

The second law of thermodynamics says that the entropy - or disorder - of an isolated system undergoing a cyclic process will increase or remain the same. But this law only applies to large systems over significant periods of time. To explain the behaviour of smaller systems, Evans and colleagues devised their 'fluctuation theorem', which calculates the probability that entropy will be consumed at any point in the cycle. They found that it predicted that measurable violations of the second law would take place in small systems over short time-scales.

To test the idea, the researchers put about 100 latex beads - each 6.3 μm across - into a water-filled cell, which was placed on the stage of a microscope. The researchers focused a laser onto one of the beads, which induced a dipole moment in the bead and drew it towards the most

intense region of the electric field in the laser beam. The force acting on the particle near the laser focus was harmonic.

With the bead trapped, the researchers moved the microscope stage backwards and forwards repeatedly, dragging the bead in and out of the laser focus. The stage moved through 540 such cycles in ten seconds, and the team measured the position of the bead a thousand times every second. Combining these measurements with the laser power and fluid drag, Evans' team was able to calculate the forces acting on the bead - and its entropy production - as it moved.

Evans and co-workers found that - during some trajectories - entropy was consumed rather than generated. This effect was seen when the researchers looked at the bead's behaviour over periods of about a tenth of a second. Over periods approaching two seconds, the proportion of entropy-consuming trajectories fell, and above two seconds, none were observed. The team also found that their results closely fitted a computer simulation of the fluctuation theorem.

Evans and colleagues say that their discovery could be important in the design of nanomachines. They also point out that as thermodynamic systems become smaller, the probability that they will run 'in reverse' increases, and this could improve our understanding of how many small biological systems - such as 'protein motors' - work.

Author

Katie Pennicott is Editor of PhysicsWeb

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Katie Pennicott

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Media Release

When disorder turns into order – the fluctuation theorem explained at annual Moyal Lecture

5 October 2004

The Australian National University's Professor Denis Evans, who led the team of scientists who proved what was once considered impossible – that the Second Law of Thermodynamics could be violated – is the recipient of the 2004 Moyal Medal and will present the annual Moyal Lecture at Macquarie University on October 22.

The Second Law of Thermodynamics states that in a closed system entropy (disorder) increases unless an outside energy source maintains things in order. It is one of the laws of Nature about which physicists feel most certain, and is one of the foundations of modern theoretical physics.

In 2002 Evans ran an experiment proving that on a microscopic scale, under certain conditions and for a very short time, entropy can actually decrease rather than increase. This confirmed his 1993 theory, known as the Fluctuation Theorem, in which he predicted that in the microworld systems can briefly violate the Second Law.

This may have important implications for the emerging field of nanotechnology, where it could cause molecular-sized machines to run backwards making them difficult to control.

The work Evans and his team created international headlines when it was published in the *Physical Review Letters*, the refereed journal of the American Physical Society in 2002.

During his lecture at Macquarie University, Evans will explain the Fluctuation Theorem and describe the experiments he successfully conducted nearly 10 years later to verify its validity.

The annual Moyal Lecture honours the late Professor José Enrique Moyal, one of Australia's most remarkable scientists and former professor of mathematics at the ANU and Macquarie University. Moyal's insights into the interaction between mathematics, physics and statistics led him to make contributions to these subjects which have had far-reaching ramifications in all three fields.

His wife, Ann, a distinguished historian of science, made the seed donation to Macquarie to set up the annual Moyal lecture and medal. Many of Professor Moyal's past colleagues and students have contributed to the fund.

The lecture series aims to influence and interest graduates and postgraduate students, as well as to provide a meeting ground for researchers in these disciplines from universities in the region.

The Moyal Lecture will commence at 7 pm on Friday 22 October in Building E6A Room 102, Macquarie University. The lecture will be followed by a discussion session, supper and drinks. Bookings are not required.

Contact for inquiries: Associate Professor John Corbett, Tel (02) 98508945
Media Manager: Kathy Vozella, Tel (02) 98507456 or 0408 168918

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R&D**

Physicists Learn to Turn Back Time

By Maia Weinstock

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The experiment proved what Evans and his colleague Debra Searles had predicted nine years earlier: Measurable violations of the second law are possible at extremely small scales; at larger scales, however, they vanish into the overall trend toward disorder. This loophole could eventually help engineers design miniature machines, such as rotors built from a single protein molecule. It could also aid in the investigation of the very nature of causality. The second law defines the arrow of time—why those dishes do not get un-dirty, or why you cannot un-spill spilled milk. The existence of some flexibility in the law hints that events could temporarily run backward but only over minuscule distances. Humans will not be able to make themselves young again. Current theory "still prohibits time reversal for large systems," Evans says.

"Physicists Learn to Turn Back Time." Find out more about the second law of thermodynamics at www.secondlaw.com.

An in-depth history of research on entropy:
www.panspermia.org/seconlaw.htm.