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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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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.

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."

THE WALL STREET JOURNAL. ONLINE

SCIENCE JOURNAL

Envy Microworld Life, Where Things Get Neater as Time Passes

By Sharon Begley

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The Wall Street Journal

B1

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

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 -¥ 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 mm-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 mm/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 Australian group observed the latex bead's position 100 times per second for a total of 10 seconds. At each time step, the 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 -¥ to +¥. Because G is a state function, its change comes out of the work integral, and yields the result

$$\exp(-DG) \langle \exp(-W) \rangle,$$

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.

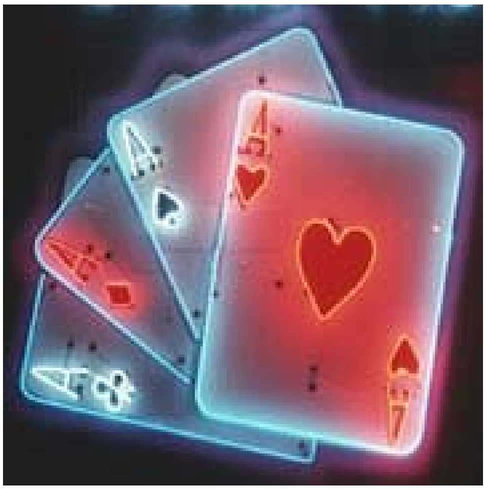
The findings suggest that the miniaturization of machines may have inherent limitations. Noting that nanomachines are not simply "rescaled versions of their larger counterparts," the researchers conclude that "as they become smaller, the probability that they will run in reverse inescapably becomes greater."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

nature scienceupdate

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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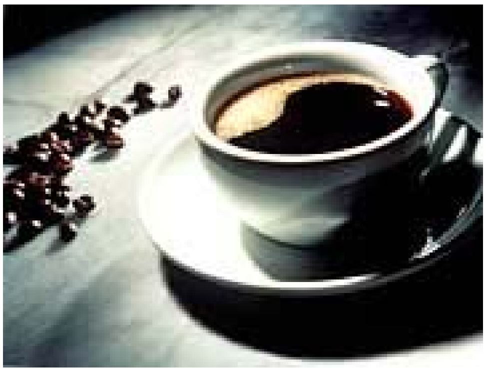
Thermodynamik

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.

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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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Second law of thermodynamics "broken"

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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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Paper abstract, Physical Review Letters

Liquid state chemical physics, ANU

Second law of thermodynamics

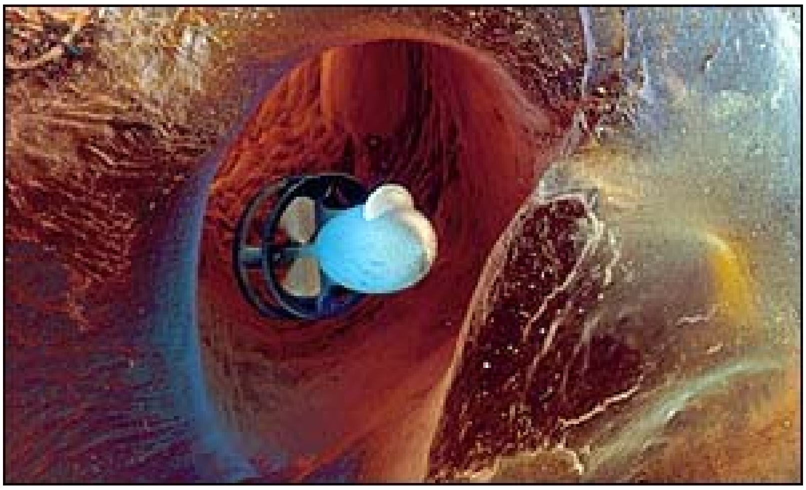
Fluctuation theorem, ANU

BBC NEWS

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 though 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.

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

Physics News Update
The AIP Bulletin of Physics News
http://www.aip.org/enews/physnews/2002/split/598-1.html

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 that 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.)

FT.com
FINANCIAL TIMES

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

By FIONA HARVEY.
245 words
25 July 2002
Financial Times
12
English

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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