

Title: Maxwell and a Third 2nd Law of Thermodynamics

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Abstract: It has long been recognized that there are two distinct laws that go by the name of the Second Law of Thermodynamics. The original says that there can be no process resulting in a net decrease in the total entropy of all bodies involved. A consequence of the kinetic theory of heat is that this law will not be strictly true; statistical fluctuations will result in small spontaneous transfers of heat from a cooler to a warmer body. The currently accepted version of the Second Law is probabilistic: tiny spontaneous transfers of heat from a cooler to a warmer body will be occurring all the time, while a larger transfer is not impossible, merely improbable. There can be no process whose expected result is a net decrease in total entropy.

According to Maxwell, the Second Law has only statistical validity, and this statement is easily read as an endorsement of the probabilistic version. I argue that a close reading of Maxwell, with attention to his use of "statistical," shows that the version of the second law endorsed by Maxwell is strictly weaker than our probabilistic version. According to Maxwell, even the probable truth of the second law is limited to situations in which we deal with matter only in bulk and are unable to observe or manipulate individual molecules. Maxwell's version does not rule out a device that could, predictably and reliably, transfer heat from a cooler to a warmer body without a compensating increase in entropy. I will discuss the evidence we have for these two laws, Maxwell's and ours.

Maxwell and a Third 2nd Law of Thermodynamics

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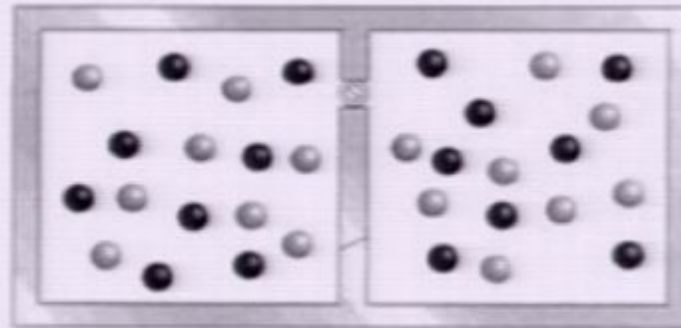
The University of Western Ontario

James Clerk Maxwell

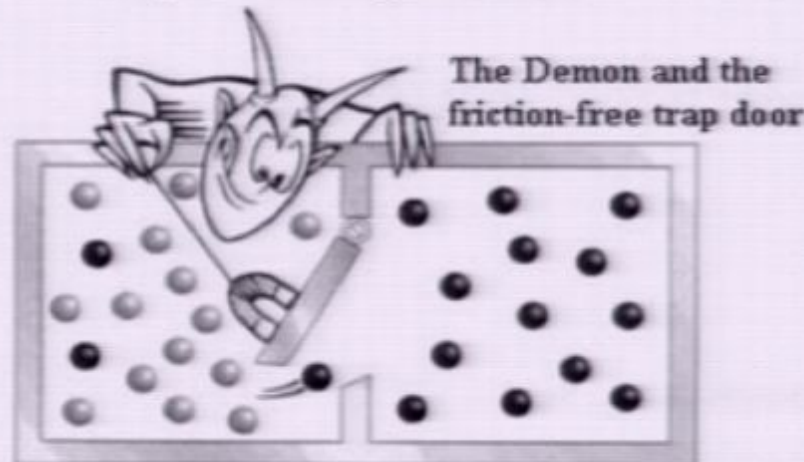


1831-1879

His demon



System at Equilibrium



**The Demon and the
friction-free trap door**

**System with Lower Entropy
(in violation of the Second Law)**

“Catechism on Demons”

(from an undated letter to P.G. Tait)

Concerning Demons

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Concerning Demons

1. Who gave them this name? Thomson.
2. What were they by nature? Very small BUT lively beings incapable of doing work but able to open and shut valves which move without friction or inertia.
3. What was their chief end? To show that the 2nd Law of Thermodynamics has only a statistical certainty.

In case anyone was wondering...



William Thomson
(Lord Kelvin)

The word 'demon', which originally in Greek meant a supernatural being, has never been properly used to signify a real or ideal personification of malignity.

2nd Law of Thermodynamics, original version



Rudolf Clausius
1822 - 1888

Heat cannot pass from a colder body to a warmer body without some other change connected with it occurring at the same time.

2nd Law of Thermodynamics, probabilistic version



J. Willard Gibbs,
1839 - 1903

the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.

“On the Equilibrium of Heterogeneous Substances” (1876)

2nd Law of Thermodynamics, probabilistic version

Although there will be local fluctuations in temperature and pressure, there can be no process that *consistently* and *reliably* exploits them to transfer heat from a cooler to a warmer body without producing a compensating increase in entropy elsewhere.

Maxwell on violations of the 2nd Law

Nature, Review of Tait's *Thermodynamics* (1878)

If we ... consider a finite number of molecules, ... the average properties of this group, though subject to smaller variations than those of a single molecule, are still every now and then deviating very considerably from the theoretical mean of the whole system, because the molecules which form the group do not submit their procedure as individuals to the laws which prescribe the behaviour of the average or mean molecule.

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 on violations of the 2nd Law

This calculation belongs of course to molecular theory and not to pure thermodynamics, but it shows that we have reason for believing the truth of the second law to be of the nature of a strong probability...

From *Theory of Heat*.

“Limitation of the Second Law of Thermodynamics”

One of the best established facts in thermodynamics is that it is impossible in a system enclosed in an envelope which permits neither change of volume nor passage of heat, and in which both the temperature and the pressure are everywhere the same, to produce any inequality of temperature or pressure without the expenditure of work. This is the second law of thermodynamics, and it is undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving the separate molecules of which they are made up.

From *Theory of Heat*.

“Limitation of the Second Law of Thermodynamics”

But if we conceive of a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributed are still as essentially as finite as our own, would be able to do what is **at present impossible to us**.

... He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics.

From *Theory of Heat*.

“Limitation of the Second Law of Thermodynamics”

This is only one of the instances in which conclusions which we have drawn from our experience of bodies consisting of an immense number of molecules may be found not to be applicable to the more delicate observations and experiments which we may suppose made by one who can perceive and handle the individual molecules which we deal with only in large masses.

The meaning of “statistical”

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- Originally: knowledge relevant to a statesman.
- By Maxwell's time: systematic compilation of population and economic method.

Maxwell on statistical method

The modern atomists have therefore adopted a method which is, I believe, new in the department of mathematical physics, though it has long been in use of the section of Statistics. ... The number of individuals is far too great to allow of their tracing the history of each separately, so that, in order to reduce their labour within human limits, they concentrate their attention on a small number of artificial group. The varying number of individuals in each group, and not the varying state of each individual, is the primary datum from which they work.

The 2nd Law as a statistical certainty

- Statistical certainty: predictable regularity that stems from dealing with a large population *en masse*.

A Third Second Law of Thermodynamics

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- For Maxwell, even the probable truth of the 2nd Law is limited to situations in which molecules are dealt with, not individually, but *en masse*.

A Third Second Law of Thermodynamics

- For Maxwell, even the probable truth of the 2nd Law is limited to situations in which molecules are dealt with, not individually, but *en masse*.
- A demon---or a human, with the right equipment---might be able to *predictably and reliably* produce large entropy decreases.

Digression: Poincaré on the reality of fluctuations

- Poincaré 1893: Recurrence theorem shows that entropy, having increased, must again decrease.

I do not know if it has been remarked the English kinetic theories can extricate themselves from this contradiction.

... According to this theory, to see heat pass from a cold body to a warm one, it will not be necessary to have the acute vision, the intelligence, and the dexterity of Maxwell's demon; it will suffice to have a little patience.

Digression: Poincaré on the reality of fluctuations

- Poincaré 1904, on Gouy's interpretation of Brownian motion.

If, then, these movements never cease, or rather are reborn without ceasing, without borrowing anything from an external source of energy, what ought we to believe? ... we see under our eyes now motion transformed into heat by friction, now heat changed inversely into motion, and that without loss since the movement lasts forever. This is contrary to the principle of Carnot. If this be so, to see the world return backward, we no longer have need of the infinitely subtle eye of Maxwell's demon; our microscope suffices us.

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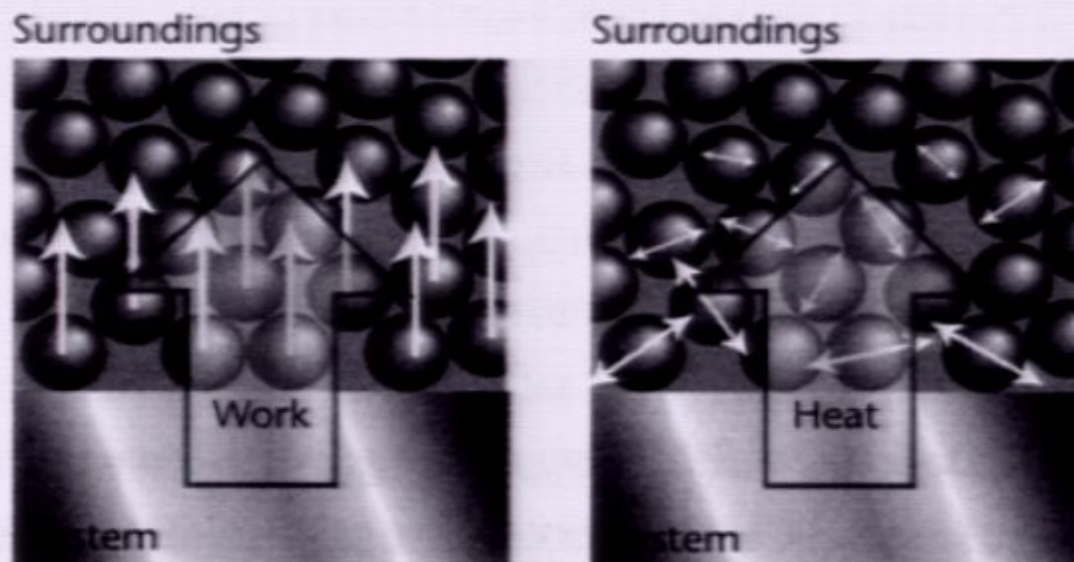
Digression: Poincaré on the reality of fluctuations

- 1912, after Perrin's agreeing measurements of Avogadro's number from disparate sources.

The brilliant determinations of the number of atoms computed by Mr. Perrin have completed the triumph of atomism. What makes it all the more convincing are the multiple correspondences between results obtained by entirely different processes The atom of the chemist is now a reality.

“Les Rapports de la Matière et de l'Éther,” in *Dernières Pensées*

Heat transfer *v* Doing work

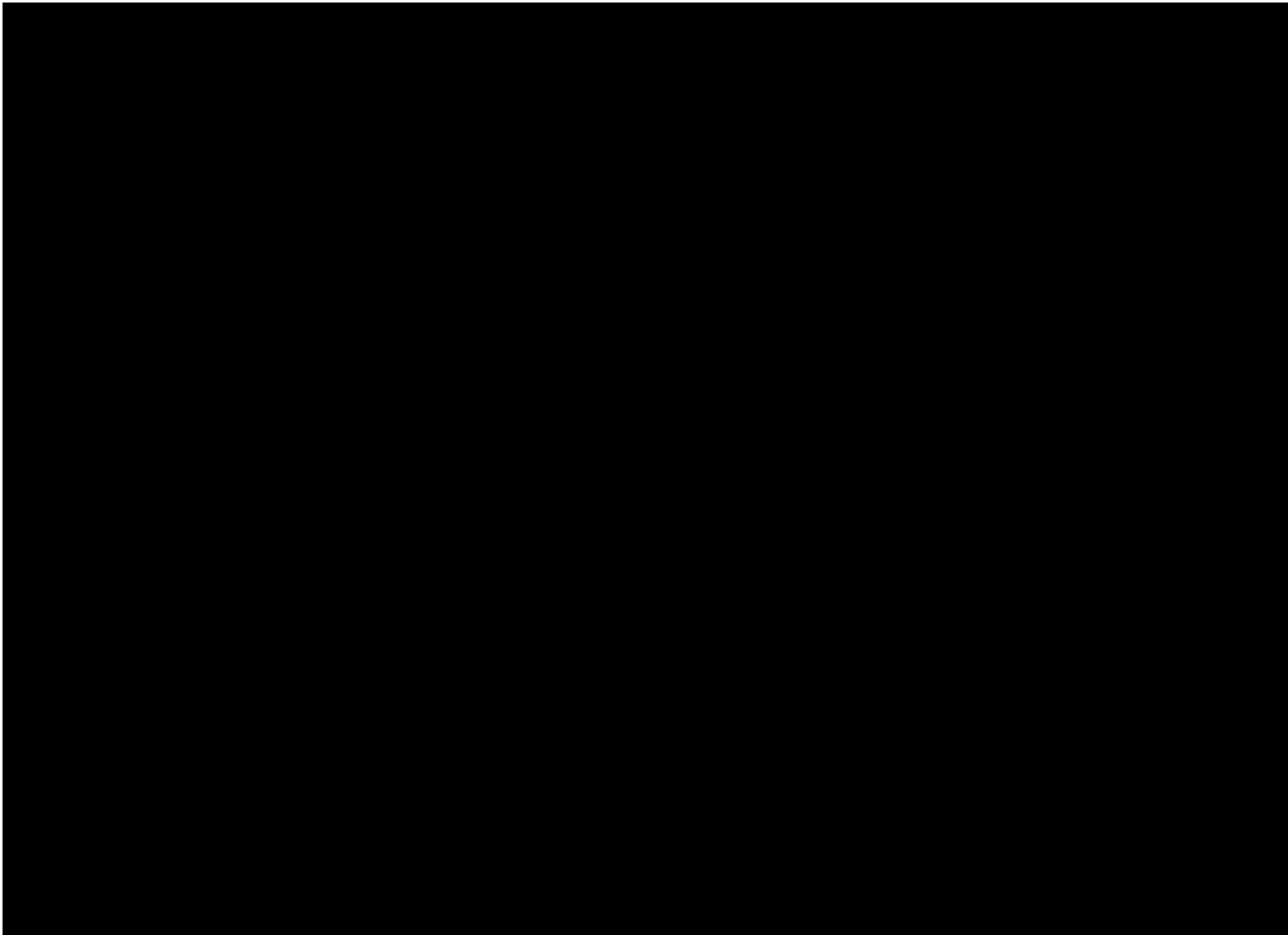


8. The molecular distinction between the transfer of energy as work (left) and heat (right). Doing work results in the uniform motion of atoms in the surroundings; heating stimulates their disorderly motion.

Heat, work, and entropy as anthropocentric concepts

- We have only to suppose our senses sharpened to such a degree that we could trace the motions of molecules as easily as we now trace those of large bodies, and the distinction between work and heat would vanish, for the communication of heat would be seen to be a communication of energy of the same kind as that which we call work.

From review of Tait's *Thermodynamics*, *Nature*, 1878



$$\Delta S = \int \frac{\delta Q}{T}$$

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Heat, work, and entropy as anthropocentric concepts

Available energy is energy which we can direct into any desired channel. Dissipated energy is energy we cannot lay hold of and direct at pleasure, such as the energy of the confused agitation of molecules which we call heat. Now, confusion, like the correlative term order, is not a property of material things in themselves, but only in relation to the mind which perceives them. A memorandum-book does not, provided it is neatly written, appear confused to an illiterate person, or to the owner of who understands thoroughly, but to any other person able to read it appears to be inextricably confused.

Similarly the notion of dissipated energy could not occur to a being who could not turn any of the energies of nature to his own account, or to one who could trace the motion of every molecule and seize it at the right moment. It is only to a being in the intermediate stage, who can lay hold of some forms of energy while others elude his grasp, that energy appears to be passing inevitably from the available to the dissipated state.

“Diffusion,” *Encyclopedia Britannica*, 1878

Cf E.T. Jaynes

- “the correct statement of the second law is not that an entropy decrease is impossible in principle, or even improbable; rather that it cannot be achieved reproducibly by manipulating the macrovariables $\{X_1, \dots, X_n\}$ that we have chosen to define our macrostate.”

A question for us

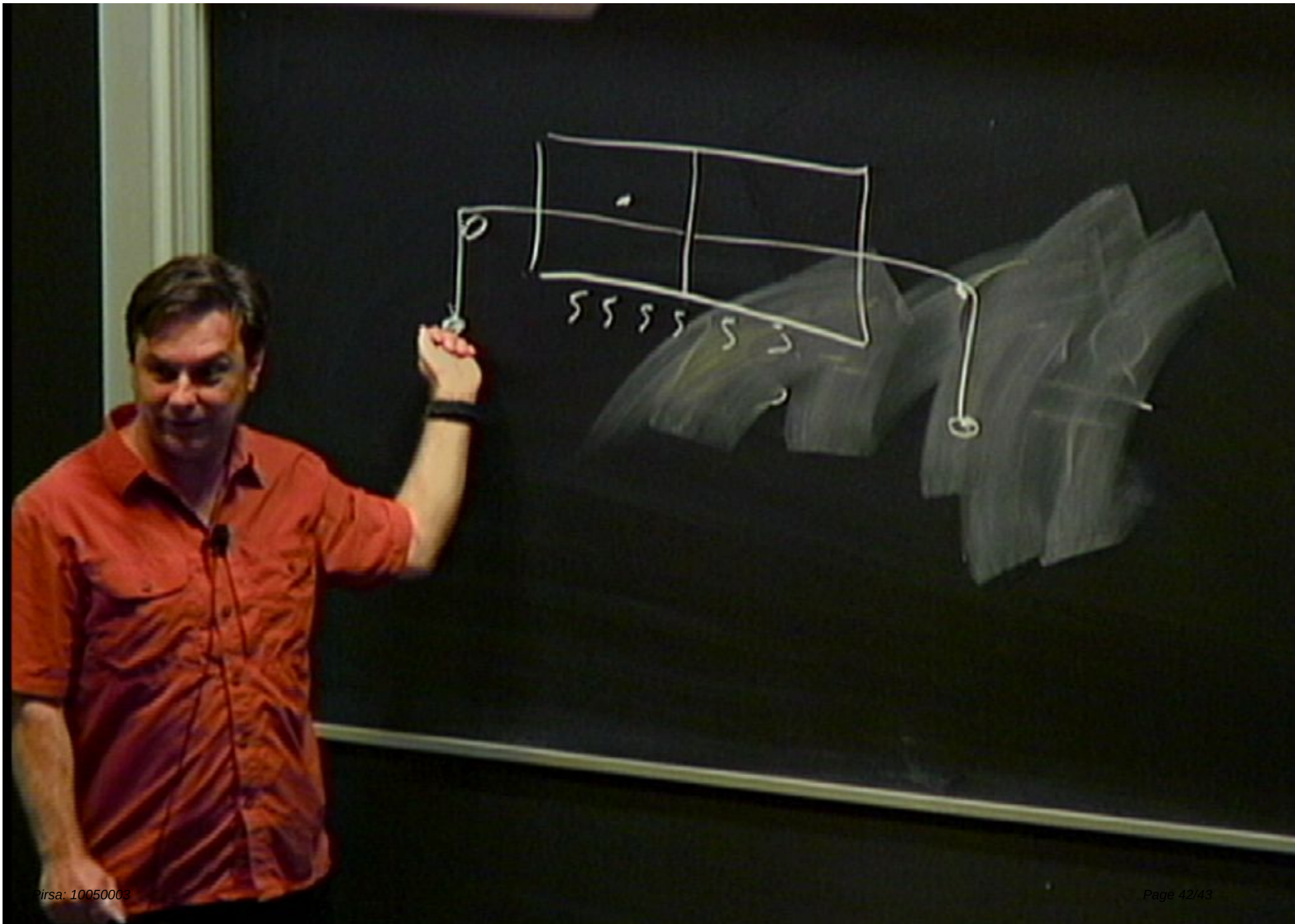
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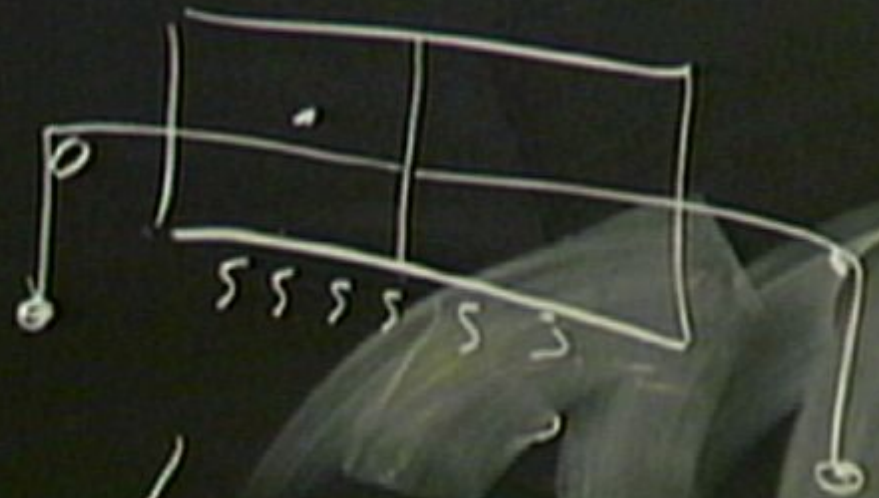
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- What could we say to a thoroughly modern Maxwell, for whom even the probabilistic version of the 2nd Law is limited to situations in which molecules are dealt with in bulk?





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