Entropy is a messy concept, especially without equilibrium

Most people who pay attention to science know that entropy always increases. But many are unfamiliar with the fine print about when that rule really applies. It doesn’t always. In some situations, entropy isn’t even easy to define.

That’s especially the case for systems not in equilibrium, as two leading authorities on the second law of thermodynamics point out in a new paper (arxiv.org/abs/1305.3912).

“While entropy is fairly unambiguously well defined for equilibrium states, a good part of the matter in the universe, if not most of it, is not in an equilibrium state. It does not have a well-defined entropy,” write Elliott Lieb of Princeton University and Jakob Yngvason of the University of Vienna.

Consequently the notion that “entropy always increases” isn’t always so clear-cut. “If one does not know precisely what entropy is for non-equilibrium systems, the notion of increase cannot be properly quantified,” Lieb and Yngvason assert.

Many attempts to define non-equilibrium entropy have been attempted, and some are useful for practical purposes. But as a fundamental concept, entropy ought to be a quantity that permits precise predictions of what a system will do in well-defined situations, in Lieb and Yngvason’s view.

Their point is that in an isolated system (no input or output of energy allowed), some changes are possible and some aren’t. The second law of thermodynamics requires that those changes are always accompanied by an increase (or at least no decrease) in a quantity called entropy.

In popular discussions, entropy is often equated with “disorder.” But in thermodynamics, it’s really more about probability than messiness. Entropy is a measure of how probable a particular arrangement of a system is. Since there are usually many ways to be messy, but very few ways to be neatly ordered, high entropy generally corresponds to high messiness. A system in equilibrium is at its maximum possible entropy, as dictated by the second law.

Lieb and Yngvason point out that the second law does not depend on any particular model of how nature works — it doesn’t even require the existence of atoms. It’s rooted in relationships between things like temperature and pressure that don’t depend on details about the nature of matter.

“The Second Law is one of the few really fundamental physical laws. It is independent of models and its consequences are far reaching,” Lieb and Yngvason write.

In previous work they had attempted to establish the second law’s foundations in the form of simple basic principles and experimental facts. “Our approach is independent of concepts from statistical mechanics and model making,” they noted.

In their new work, Lieb and Yngvason explore ways of extending their concept of entropy to non-equilibrium situations.

“It may not be possible in general to define one unique entropy for non-equilibrium states that fulfills all the roles of entropy for equilibrium states,” they argue. “Instead one has to expect a whole range of entropies lying between two extremes.”

Tom Siegfried May 28, 2013

It’s possible, in special cases, that the two extreme entropies coincide and so some non-equilibrium systems do have a precise entropy. But not often. One requirement for such cases is that the system be reproducible, a nontrivial restriction for systems not in equilibrium.

“In fact,” Lieb and Yngvason say, “it is hard to talk about the properties of states that occur only once in the span of the universe, but that is often the case for non-equilibrium states.”

It’s not obvious, for instance, that there is any meaning to the concept of the entropy of an exploding bomb, they point out.

Lieb and Yngvason’s analysis digs deeply into the technical underpinnings of entropy and the second law. They’ve exposed weaknesses in applying it to systems that don’t fit the circumstances where it’s valid and the usual concept of entropy is meaningful. They emphasize a key concept, called “comparability,” which has to do with whether one state of a system can “precede” another. That idea is rooted in Max Planck’s way of expressing the second law: system X precedes system Y if you can change X into Y in such a way that the ultimate effect on its surroundings is the rise or fall of a weight. Moving a weight, of course, is all about doing work, and the second law’s most famous application is in describing how entropy quantifies the amount of useful work you can get out of a certain amount of energy.

It is only when comparability holds that entropy is well-defined for non-equilibrium systems, and usually they aren’t comparable. “Comparability for non-equilibrium states … can certainly not be expected in general,” Lieb and Yngvason say.

Textbooks would have you believe that all this stuff about entropy and the second law, work and entropy and energy, is all completely understood. But when you look a little closer, everything about entropy doesn’t seem to be completely in order.

Papers like Lieb and Yngvason’s reveal that it’s not just popular culture that’s confused about entropy. All in all, the fact that not all experts agree on these things should be taken as a sign that some supposedly well-established science actually isn’t. There is, in fact, confusion among scientists about one of the most fundamental laws of nature. Maybe that’s good. Probably not, though.

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