Negative Absolute Temperature: An Introduction to Statistical Mechanics

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Abstract

A recent paper in *Science*[1] discussed an experiment that produced a collection of particles with kinetic energy corresponding to a negative absolute temperature. What does that even mean? We'll cover an introduction to statistical mechanical definitions of concepts like entropy and temperature as a way to develop an understanding of what it means for a system to have a negative absolute temperature.

Questions to answer:

1. What is thermodynamics?
2. What is statistical mechanics?
3. What is a "state"?
4. What is entropy?
5. What is temperature?
6. So, how can temperature be negative?
7. Can you make a negative temperature in real life?

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[1] `http://arxiv.org/abs/1211.0545`

1 What is thermodynamics?

You've probably heard of thermodynamics before. It's the physics of how heat, energy, work, and temperature of systems behave. Originally, it was developed by engineers who wanted to learn how to make more efficient steam engines. Over the course of the Nineteenth Century, physicists developed the **Four Laws of Thermodynamics**:

Zeroth Law

If two systems are both in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

This gives us a meaning for "temperature": any objects at the same temperature can be in contact without one getting hotter and the other colder.

First Law

The energy of the universe is conserved. Energy flows in and out of a system as heat and work.

This means that perpetual motion machines that supply more energy than they consume are impossible: the energy flows into and out of a system have to be equal once you consider all forms of work and heat.

Second Law

An isolated system, if not already in its state of thermodynamic equilibrium, spontaneously evolves towards it.

This gives us a concept of "entropy". An isolated system always gets closer to equilibrium; the closer it is to equilibrium, the higher its entropy.

Third Law

The entropy of a system approaches a constant minimum value as the temperature approaches zero.

This gives us a meaning for the idea of "absolute zero" and "absolute temperature"—Kelvin as opposed to Fahrenheit or Celsius. When the temperature of a system is lowered far enough, it reaches a state where it is as far from equilibrium as it can be, absolute zero.

These laws weren't things that they had directly proven to be true. Instead, they were experimental discoveries that held true in many different sorts of experiments. By using them as axioms, physicists were able to derive many other rules about the behavior of heat, energy, work, and temperature.

2 What is statistical mechanics?

The laws of thermodynamics describe the properties of macroscopic objects as though they are single entities: the temperature of a kettle of water, the work done by a quantity of expanding steam, and so on. However, everyday materials are made of huge numbers of microscopic particles—atoms and molecules—that can be studied individually.

Just as the macroscopic chemical properties of materials can be understood in terms of the microscopic properties of the atoms and molecules that they're made of, the laws of thermodynamics can be derived from the microscopic behavior of the atoms and particles in a system. Statistical mechanics is, in essence, the study of how the laws of thermodynamics emerge from the behavior of individual atoms and molecules.

3 What is a "state"?

When physicists talk about the "state" of a system, they mean a complete description of all its properties. Two systems are in the same state if they're identical, such that calculations done about one will describe the other equally well.

There are two types of states that we care about in statistical mechanics:

Macrostate

The macrostate of a system is the collection of properties that you could observe directly without knowing anything about its atomic structure. For example, its temperature, its pressure, and the amount of heat it contains or work it can do. This is the only sort of state that thermodynamics considers.

Microstate

The microstate of a system is a full description of the properties of each atom or molecule in it. A simple example might be 6N numbers for a set of N helium atoms: three position coordinates and three components of the velocity vector of each atom.

The microstate description of a system is much more detailed than the macrostate description, and there will generally be many microstates that correspond to the same macrostate.

The fundamental assumption of statistical mechanics—called "equipartition"—is that a system in a given macrostate is equally likely to be in any of the microstates that correspond to that macrostate. Such microstates are described as "accessible".

4 What is entropy?

As a simple model, consider a system containing one mole of helium gas with a total internal energy of one kilojoule. In this case, we can describe the number of accessible microstates as: $g(N, U)$ where g is the number of states and it depends on the number of particles, N and the total internal energy of the system, U.

Suppose, now, we have two systems in contact: system 1, with an internal energy of U_1, and system 2, with an internal energy of U_2. If particles cannot travel between the systems, but energy can, then the macrostate is fully described by two numbers, U, and U_1, since conservation of energy tells us that $U_2 = U - U_1$.

Since the arrangement of particles in one system doesn't affect the arrangement of particles in the other—except by restricting the energy available—the total number of accessible microstates for a macrostate defined by U without specifying U_1 is:

$$g(U) = \sum_{U_1} g_1(U_1) \times g_2(U - U_1)$$

Our assumption of equipartition tells us that the most probable macrostate—defined in terms of U and U_1—will be the one that contributes the largest term to this series. We can call this macrostate "thermal equilibrium", since probability tells us that the system will naturally return to it if given enough time.

Since this macrostate is a maximum of g in terms of U_1, an infinitesimal change in U_1—an infinitesimal interchange in energy—results in no change in the number of states. Thus:

$$dg = \left(\frac{\partial g_1}{\partial U_1}\right) g_2 dU_1 + \left(\frac{\partial g_2}{\partial U_2}\right) g_1 dU_2 = 0$$

Since $dU_1 = -dU_2$, divide both sides by $g_1 g_2 dU_1$ to get a condition for thermal equilibrium:

$$\frac{1}{g_1}\left(\frac{\partial g_1}{\partial U_1}\right) = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial U_2}\right)$$

We recognize the derivative of a natural log here and rewrite this as

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right) = \left(\frac{\partial \sigma_2}{\partial U_2}\right)$$

where $\sigma \equiv \ln g$ is called the "entropy" of the system. This definition of entropy makes intuitive sense, since it always increases with the number of microstates available for a given macrostate. We also see—consistent with thermodynamics—that the entropy of the system will be conserved if and only if the system is in thermal equilibrium.

5 What is temperature?

We have just derived a definition of thermal equilibrium in terms the microstates of a system. However, thermodynamics tells us another equality that must be satisfied at thermal equilibrium: $T_1 = T_2$. This immediately gives us a statistical mechanics definition of temperature:

$$\beta = \left(\frac{\partial \sigma}{\partial U}\right)$$

The units of this definition of temperature, if U is in J, are J^{-1}, since σ is the log of a pure number. This relates to our everyday definition of temperature in Kelvin, T, as

$$\beta \equiv \frac{1}{k_B T}$$

where k_B is Boltzmann's constant, a fundamental physical constant.

This definition gives us an understanding of what temperature physically *means*. β is the rate of change of entropy with respect to energy, and T is inversely proportional to β. So, a system with a low value of T—a high value of β—will have a very big increase in entropy for a small increase in energy. As T increases—and β decreases—the entropy gain from a given increase in energy will get smaller and smaller.

With a little thought, we can see that this makes sense. If we have two systems at temperatures T_1 and T_2, with $T_2 > T_1$, we expect that the system at T_2 should lose energy to the system at T_1 until they reach the same temperature.

Conservation of energy tells us that the T_1 system gains the same amount of energy that the T_2 system loses. Since the system at T_2 has a higher value of T, it has a smaller value of $\frac{\partial \sigma}{\partial U}$, and thus the entropy of the T_2 system decreases at a lower rate than the entropy of the T_1 system increases. Thus, the combined entropy increases, as we expect for spontaneous processes.

Once the systems are the same temperature, $T_1 = T_2$, so any energy transfer between them conserves entropy as well as energy, and thus energy flow isn't favored in one direction: the system is in equilibrium.

6 So, how can temperature be negative?

Our definition of temperature as

$$\frac{1}{k_B T} \equiv \beta = \left(\frac{\partial \sigma}{\partial U}\right)$$

indicates what would be necessary for temperature to be negative: increasing the energy of the system would have to decrease entropy. In other words, supplying more energy would have have to decrease the number of accessible microstates.

For the sorts of temperature we're most familiar with thinking of, such as that of gas molecules in a container, this doesn't make any sense. While there's a lower bound on kinetic energy and velocity of a gas molecule, there's no upper bound: you can always have the molecules move slightly faster. This means that increasing the energy available should always increase the number of microstates available: there are always more higher-energy states that molecules can reach only when the energy of the system increases. That said, as the number of states accessible increases compared to the number of molecules, adding energy has a smaller effect on the number of states. So, as we increase the energy of the system, T goes from 0 to ∞ and β goes from ∞ to 0.

So, the temperature of canister of gas molecules can never have a negative temperature. However, one can imagine a system that would. Imagine a system of molecules that can have only two possible states. For example, a row of N bar magnets on an axis sitting in a strong external magnetic field. If a magnet is aligned with the field, it has an energy of 0; if it is aligned against the field it has an energy of E.

Clearly, in the lowest energy macrostate, this system has only one possible microstate—all magnets aligned with the field—and so an entropy of zero, which will increase if you increase the energy so that a magnet can be aligned against the field. If we continue to increase the energy, the entropy also goes up as more magnets are aligned against the field.

However, when we reach the point where ${}^{N}/_{2}$ magnets are aligned with the field, we've reached a point of maximum entropy. Adding an energy of E to the system will cause another magnet to be aligned against the field, which will result in a situation that, entropically speaking, is identical to when one less than ${}^{N}/_{2}$ magnets was aligned with the field. Adding more energy will decrease the entropy until we reach an energy of NE, at which point all magnets are aligned with the field and entropy is again zero.

So, in this system, as we increase the energy, β ranges from ∞ to 0 to $-\infty$ and T ranges from 0 to ∞, jumps to $-\infty$, and then ranges back to approach 0 from the negative side.

As this suggests, negative temperatures are in fact *hotter* than positive temperatures. Not only do they involve higher energies, but since the system's entropy decreases when its energy increases, the overall entropy of the universe will always increase—and so the process will be spontaneous—when energy flows from a negative temperature system to a positive temperature system.

7 Can you make a negative temperature in real life?

You've just been bombarded with a lot of math proving that the statistical mechanics definition of temperature allows for negative values from time to time. However, since statistical mechanics is physics, it's not enough for us to show that the math allows something. We should want to understand a physical system where it could actually occur.

It isn't automatically necessary that one exist. For example, "tachyons"—particles that can *only* travel faster than light—are a valid solution to Einstein's General Relativity equations. However, there is no evidence that they actually exist in our universe. And, as we've already noted, the model of temperature that's most familiar to us—the one used in the ideal gas model—doesn't allow negative temperatures because there is no maximum energy for particles.

Besides the existence of a maximum energy level, there is another practical constraint on negative-temperature systems. They must not easily exchange energy with systems around them—including the mechanical and kinetic energy of particles—that are at positive temperatures. If they can exchange energy with these systems easily then, since they are "hotter" than positive temperature systems, they'll rapidly lose energy to the positive-temperature systems until they reach equilibrium at the same temperature.

It turns out that there are several sorts of physical systems that meet these requirements. One classic example of this is nuclear magnetic resonance spectroscopy, also called NMR or MRI. An NMR system studies chemical compounds by manipulating the magnetic moments of atomic nuclei. Due to a quantum mechanical property called "spin", all nuclei of a particular isotope will act as magnets with a particular strength. However, since different atoms in a molecule have different electron densities around them, you can learn about the structure of a molecule from the behavior of these magnets in a large external field.

An NMR spectrometer consists of a large magnet that surrounds the sample with a strong and uniform magnetic field and a smaller magnet that is used to produce pulsed magnetic fields to manipulate the behavior of the nuclear magnets. The strong external field causes the nuclear magnets to align either with or against it, where the energy is lowest when they are aligned with the field and highest when they are aligned with it. This produces a system with a maximum as well as a minimum total energy.

Furthermore, since there is weak coupling between the alignments of the nuclear magnets and the physical arrangement of the molecules, there is very limited energy exchange between these two systems and it takes a relatively long time for the temperature of the nuclear magnet alignments to come into thermal equilibrium with the temperature of the molecules in the sample. That means that if the pulsed magnet is used to push the nuclear magnets into a state where they're all aligned against the external field—which is a state with a negative temperature—they'll stay there for an extended period. In fact, it's possible to prepare two sets of nuclei with different magnet-alignment temperatures and bring them into contact so that one can observe them coming into thermal equilibrium with each other.