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Entropy and the Tao of Counting

A Brief Introduction to Statistical Mechanics and the Second Law of Thermodynamics

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For Thi and Thuan

Preface

The second law of thermodynamics, which says that a certain quantity called entropy always increases, is the law that scientists believe gives the direction to time's arrow. It is the reason why so many everyday events happen only one way. Heat flows from hot to cold. Stirring milk into coffee always mixes it, never unmixes it. Friction slows things down, never speeds them up. Even the evolution of the universe and its ultimate fate depend on entropy. It is no surprise that there are numerous books and articles on the subjects of entropy and the second law of thermodynamics. So why write another book, even a short one, on the subject?

In 1854 Rudolf Clausius showed that there was a well-defined thermodynamic quantity for which, in 1865, he coined the name entropy. In his words "*The energy of the universe remains constant. The entropy of the universe tends to a maximum.*" Entropy could be measured and its behavior described, but what it *was* remained a mystery. Twelve years later Ludwig Boltzmann provided the answer in atomistic, probabilistic terms and helped create the field of statistical mechanics.

Boltzmann's explanation was the first, and arguably still the best, explanation of entropy. His classic paper, published in 1877, is probably never read anymore yet something can still be learned by reading it. One of the things Boltzmann explains very clearly is that there are two equally important contributions to entropy: one from the distribution of atoms in space and the other from the motion of atoms (heat); in other words from the distribution of kinetic energy among the atoms.[1] However, many introductory books and articles on entropy do not give equal attention to each. The spatial contribution by its nature is just easier to visualize and explain. Explanations of the kinetic energy contribution to entropy often use fossilized concepts like Carnot cycles and efficiencies of heat engines. It is also customary to teach thermodynamics before statistical mechanics, because the former is thought to be easier, and this follows their historical order of

[1] We now know of four sources of entropy in the universe. The third is radiation: photons have entropy, a fact also discovered by Boltzmann. The fourth is black holes. These require a level of physics and mathematics beyond the scope of this book.