

SOME HISTORICAL NOTES

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Notes for Chapter 9: Fundamental Physics

Section: Irreversibility and the Second Law of Thermodynamics

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History of thermodynamics. Basic physical notions of heat and temperature were established in the 1600s, and scientists of the time appear to have thought correctly that heat is associated with the motion of microscopic constituents of matter. But in the 1700s it became widely believed that heat was instead a separate fluid-like substance. Experiments by [James Joule](#) and others in the 1840s put this in doubt, and finally in the 1850s it became accepted that heat is in fact a form of energy. The relation between heat and energy was important for the development of steam engines, and in 1824 [Sadi Carnot](#) had captured some of the ideas of thermodynamics in his discussion of the efficiency of an idealized engine. Around 1850 [Rudolf Clausius](#) and [William Thomson \(Kelvin\)](#) stated both the First Law - that total energy is conserved - and the Second Law of Thermodynamics. The Second Law was originally formulated in terms of the fact that heat does not spontaneously flow from a colder body to a hotter. Other formulations followed quickly, and Kelvin in particular understood some of the law's general implications. The idea that gases consist of molecules in motion had been discussed in some detail by [Daniel Bernoulli](#) in 1738, but had fallen out of favor, and was revived by Clausius in 1857. Following this, [James Clerk Maxwell](#) in 1860 derived from the mechanics of individual molecular collisions the expected distribution of molecular speeds in a gas. Over the next several years the kinetic theory of gases developed rapidly, and many macroscopic properties of gases in equilibrium were computed. In 1872 [Ludwig Boltzmann](#) constructed an equation that he thought could describe the detailed time development of a gas, whether in equilibrium or not. In the 1860s Clausius had introduced entropy as a ratio of heat to temperature, and had stated the Second Law in terms of the increase of this quantity. Boltzmann then showed that his equation implied the so-called H Theorem, which states that a quantity equal to entropy in equilibrium must always increase with time. At first, it seemed that Boltzmann had successfully proved the Second Law. But then it was noticed that since molecular collisions were assumed reversible, his derivation could be run in reverse, and would then imply the opposite of the Second Law. Much later it was realized that Boltzmann's original equation implicitly assumed that molecules are uncorrelated before each collision, but not afterwards, thereby introducing a fundamental asymmetry in time. Early in the 1870s Maxwell and Kelvin appear to have already understood that the Second Law could not formally be derived from microscopic physics, but must somehow be a consequence of human inability to track large numbers of molecules. In responding to objections concerning reversibility Boltzmann realized around 1876 that in a gas there are many more states that seem random than seem orderly. This realization led him to argue that entropy must be proportional to the logarithm of the number of possible states of a system, and to formulate ideas about ergodicity. The statistical mechanics of systems of particles was put in a more general context by [Willard Gibbs](#), beginning around 1900. Gibbs introduced the notion of an ensemble - a collection of many possible states of a system, each assigned a certain probability. He argued that if the time evolution of a single state were to visit all other states in the ensemble - the so-called ergodic hypothesis - then averaged over a sufficiently long time a single state would behave in a way that was typical of the ensemble. Gibbs also gave qualitative arguments that entropy would increase if it were measured in a "coarse-grained" way in which nearby states were not distinguished. In the early 1900s the development of thermodynamics was largely overshadowed by quantum theory and little fundamental work was done on it. Nevertheless, by the 1930s, the Second Law had somehow come to be generally regarded as a principle of physics whose foundations should be questioned only as a curiosity. Despite neglect in physics, however, ergodic theory became an active area of pure mathematics, and from the 1920s to the 1960s properties related to ergodicity were established for many kinds of simple systems. When electronic computers became available in the 1950s, [Enrico Fermi](#) and others began to investigate the ergodic properties of nonlinear systems of springs. But they ended up concentrating on recurrence phenomena related to solitons, and not looking at general questions related to the Second Law. Much the same happened in the 1960s, when the first simulations of hard sphere gases were led to concentrate on the specific phenomenon of long-time tails. And by the 1970s, computer experiments were mostly oriented towards ordinary differential equations and strange attractors, rather than towards systems with large numbers of components, to which the Second Law might apply. Starting in the 1950s, it was recognized that entropy is simply the negative of the information quantity introduced in the 1940s by [Claude Shannon](#). Following statements by [John von Neumann](#), it was thought that any computational process must necessarily increase entropy, but by the early 1970s, notably with work by [Charles Bennett](#), it became accepted that this is not so (see page 1023), laying some early groundwork for relating computational and thermodynamic ideas.

Stephen Wolfram, *A New Kind of Science* (Wolfram Media, 2002), page 1019.

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