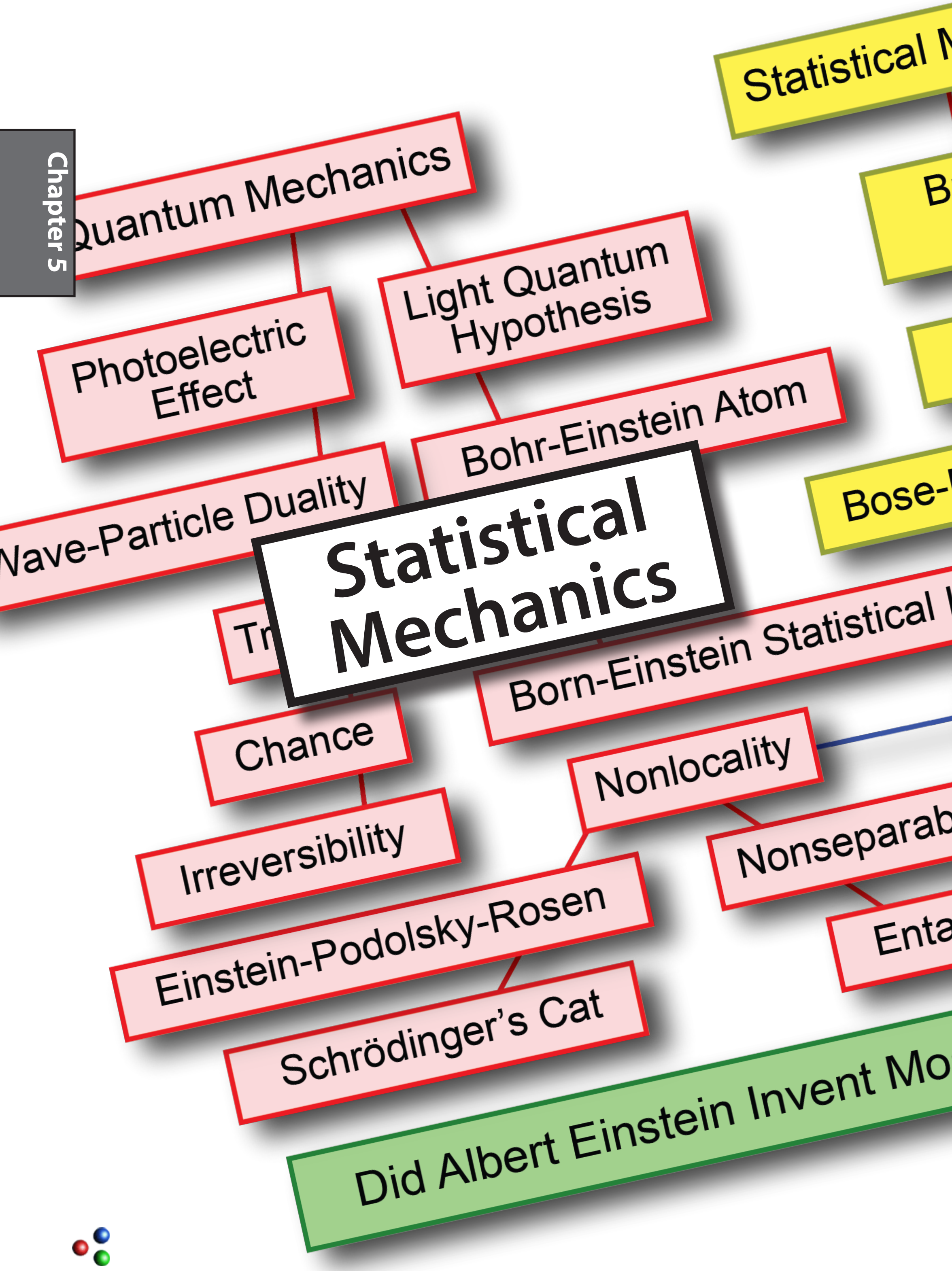
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Statistical Mechanics

Statistical mechanics and thermodynamics are nineteenth-century *classical* physics, but they contain the seeds of the ideas that ALBERT EINSTEIN would use to create *quantum* theory in the twentieth, especially the work of his *annus mirabilis* of 1905.

Einstein wrote three papers on statistical mechanics between 1902 and 1904 He put earlier ideas on a firmer basis. Einstein claimed that although JAMES CLERK MAXWELL's and LUDWIG BOLTZMANN's theories had come close, they had not provided a foundation for a general theory of heat based on their kinetic theory of gases, which depend on the existence of microscopic atoms and molecules. In his 1902 paper, Einstein did so, deriving the equipartition theory of the distribution of energy among the degrees of freedom of a system that is in equilibrium with a large heat reservoir that maintains the system temperature.

But, Einstein said in his second paper (1903), a general theory of heat should be able to explain both thermal equilibrium and the second law of thermodynamics *independent of* the kinetic theory. The laws of *macroscopic* phenomenological thermodynamics do not depend on the existence of microscopic atoms and molecules. His second paper derived the second law based solely on the probability of distributions of states, Boltzmann's entropy, $S = k \log W$, which Einstein redefined, as the fraction of time the system spends in each state. This work, he said, bases thermodynamics on general *principles* like the impossibility of building a perpetual motion machine.

In his third paper (1904), Einstein again derived the second law and the entropy, using the same statistical method used by Boltzmann in his theory of the ideal gas and by Planck in his derivation of the radiation law. Einstein investigated the significance of what Planck had called Boltzmann's constant k. With the dimensions of ergs/degeree, as a multiplier of the absolute temperature T, $\frac{1}{2}kT$ gives us a measure of the average energy in each degree of freedom. But Einstein showed that k is also a measure of the thermal stability of the system, how much it departs from equilibrium in the form of energy *fluctuations*.

What Did Statistics Mean for Einstein?

In 1904, Einstein was only 25 years old, but in two years he had independently derived or rederived the work of the previous three decades in the kinetic theory of gases and statistical mechanics.

As we saw in chapter 2 on chance, most scientists did not believe that the appearance of randomly distributed events is any proof that there is ontological chance in the universe. For them, regularities in the "normal" distribution implied underlying unknown laws determining events. And Einstein was no exception.

The use of "statistical" methods is justified by the apparent impossibility of knowing the detailed paths of an incredibly large number of particles. One might think that increasing the number of particles would make their study increasingly complex, but the opposite is true. The regularities that appear when averaging over their large numbers gives us mean values for the important quantities of classical thermodynamics like energy and entropy.

In principle, the motions of individual particles obey the laws of classical mechanics. They are *deterministic*, and *time reversible*. In 1904, Einstein certainly subscribed to this view, until 1909 at least.

So when Boltzmann's H-theorem had shown in 1872 that the entropy in an isolated system can only increase, it was that the increase in entropy is only *statistically irreversible*.

Before Boltzmann, we saw in chapter 3 it was Maxwell who first derived a mathematical expression for the distribution of gas particles among different velocities. He assumed the particles were distributed at random and used probabilities from the theory of errors to derive the shape of the distribution. There is some evidence that Maxwell was a skeptic about determinism and may thus have accepted that randomness as ontological chance.

But Boltzmann clearly accepted that his macroscopic irreversibility did not prove the existence of *microscopic irreversibility*. He had considered the possibility of some "molecular chaos." But even without something microscopically random, Boltzmann's statistical irreversibility does explain the increase in entropy, despite his critics Josef Loschmidt and Ernst Zermelo.

What Then Are the Fluctuations?

In the last of his papers on statistical mechanics, Einstein derived expressions for expected *fluctuations* away from thermal equilibrium. Fluctuations would be examples of entropy decreasing slightly, proving that the second law is not an *absolute* law, but only a statistical one, as both Maxwell and Boltzmann had accepted.

Boltzmann had calculated the size of fluctuations and declared them to be *unobservable* in normal gases. One year after his 1904 paper, Einstein would demonstrate that molecular fluctuations are *indirectly* observable and can explain the Brownian motion. Einstein's prediction and its experimental confirmation by Jean Perrin a few years later would prove the existence of atoms.

Einstein also expressed the possibility in his 1904 paper that a general theory of physical systems would apply equally to matter and radiation. He thought fluctuations would be even more important for radiation, especially for radiation with wavelengths comparable to the size of their container. He showed that the largest fluctuations in energy would be for particles of average energy.

Einstein argued that the general principle of *equipartition of energy* among all the degrees of freedom of a system should be extended to radiation. But he was concerned that radiation, as a continuous theory, might have infinite degrees of freedom. A system of *N* gas particles has a finite number of degrees of freedom, which determines the finite number of states *W* and the system's entropy.

Einstein's speculation that the kinetic-molecular theory of statistical mechanics should also apply to radiation shows us an Einstein on the verge of discovering the particulate or "quantum" nature of radiation, which most physicists would not accept for another one or two decades at least.

We saw in chapter 4 that the term "quantum" was introduced into physics in 1900 by Max Planck, who hypothesized that the total energy of the mechanical oscillators generating the radiation field must be limited to integer multiples of a quantity $h\nu$, where ν is the radiation frequency and h is a new constant with the dimensions of action (energy x time *or* momentum x distance). Planck did not think the radiation itself is quantized. But his quantizing the energy states of the matter did allow him to avoid infinities and use Boltzmann's definition of entropy as disorder and probability.

Einstein saw that Planck had used Boltzmann's probabilistic and statistical methods to arrive at an equation describing the distribution of frequencies in blackbody radiation. [1]

But Einstein also saw that Planck did not think that the radiation field itself could be described as particles. Nevertheless, Planck clearly had found the right equation. His radiation law fit the experimental data perfectly. But Einstein thought Planck had luckily stumbled on his equation for the wrong physical reasons. Indeed, a proper derivation would not be given for two more decades, when Einstein himself finally explained it in 1925 as the result of *quantum statistics* that have no place in classical statistical mechanics. [2]

Had Gibbs Done Everything Before Einstein?

Some historians and philosophers of science think that Josiah Willard Gibbs completed all the important work in statistical mechanics before Einstein. Gibbs had worked on statistical physics for many decades. Einstein had not read Gibbs, and when he finally did, he said his own work added little to Gibbs. But he was wrong.

Gibbs earned the first American Ph.D. in Engineering from Yale in 1863. He went to France where he studied with the great Joseph Liouville, who formulated the theorem that the phase-space volume of a system evolving under a conservative Hamiltonian function is a constant along the system's trajectory. This led to the conclusion that entropy is a conserved quantity, like mass, energy, momentum, etc.

In his short text *Principles in Statistical Mechanics,* published the year before his death in 1903, Gibbs coined the English term phase space and the name for the new field - statistical mechanics. This book brought him his most fame. But it was not his first work. Gibbs had published many articles on thermodynamics and was well known in Europe, though not by Einstein. Einstein independently rederived much of Gibbs's past work.

Einstein, by comparison, was an unknown developing his first ideas about a molecular basis for thermodynamics. His readings were probably limited to Boltzmann's *Lectures on Gas Theory*.

1 See chapter 4.

2 See chapter 22.

Gibbs transformed the earlier work in "kinetic gas theory" by Boltzmann, making it more mathematically rigorous. Gibbs made kinetic gas theory obsolete, but he lacked the deep physical insight of either Boltzmann or Einstein.

Perhaps inspired by the examples of other conservation laws in physics discovered during his lifetime, Gibbs disagreed with Boltzmann's view that information is "lost" when the entropy increases. For Gibbs, every particle is in principle distinguishable and identifiable. For Boltzmann, two gases on either side of a partition with particles distinguishable from one another, but otherwise identical, will increase their entropy when the partition is removed and they are allowed to mix.

For Gibbs, this suggested a paradox, what if the gases on both side were identical? On Boltzmann's view, the entropy would not go up, because there would be no "mixing." Entropy seems to depend on what we know about the particles? For Gibbs, complete information about every particle, their identities, their classical paths, would give us a constant entropy, essentially zero.

For Gibbs, information is conserved when macroscopic order disappears because it simply changes into microscopic (thus invisible) order as the path information of all the gas particles is preserved. As Boltzmann's mentor Josef Loschmidt had argued in the early 1870's, if the velocities of all the particles could be reversed at an instant, the future evolution of the gas would move in the direction of decreasing entropy. All the original order would reappear.

Nevertheless, Gibbs's idea of the conservation of information is still widely held today by mathematical physicists. And most texts on statistical mechanics still claim that microscopic collisions between particles are reversible. Some explicitly claim that quantum mechanics changes nothing, because they limit themselves to the unitary (conservative and deterministic) evolution of the Schrödinger equation and ignore the collapse of the wave function.

So if Gibbs does not calculate the permutations of molecules in "microstates" and their combinations into the "complexions" of Boltzmann's "macrostates," what exactly is his statistical thinking?

It is the statistics of a large number of identical thermodynamic systems that he calls “ensembles.” Boltzmann had also considered such large numbers of identical systems, averaging over them and assuming the averages give the same results as time averages over a single system. Such systems are called *ergodic*.

Maxwell thought that Boltzmann’s ergodic hypothesis requires that the time evolution of a system pass through every point consistent with the energy. If the system is continuous, there are an infinite number of such points.

Boltzmann relaxed the ergodic requirement, dividing what Gibbs later called “phase space” into finite cells that Boltzmann described as “coarse graining.” Quantum mechanics would later find reasons for particles being confined to phase-space volumes equal to the cube of Planck’s quantum of action h^3. This is not because space is quantized but because material particles cannot get closer together than Heisenberg’s uncertainty principle allows. $\Delta p\, \Delta x = h$.

Both Boltzmann and Gibbs considered two kinds of ensembles. Boltzmann called his ensembles *monodes*. Boltzmann’s *ergode* is known since Gibbs as the microcanonical ensemble, in which energy is constant. In Gibbs’s canonical ensemble energy may change. Boltzmann called it a *holode*. Einstein’s focus was on the canonical ensemble. For him, the canonical is one where energy may be exchanged with a very large connected heat reservoir, which helped Einstein to define the absolute temperature T.

Where Gibbs ignored the microscopic behavior of molecules, Einstein followed Boltzmann in considering the motions and behavior of molecules, atoms, even electrons, and then photons.

Gibbs’ statistical mechanics provided a formal basis for all the classical results of thermodynamics. But he discovered nothing new in atomic and molecular physics.

By contrast, Einstein’s statistical mechanics gave him insight into things previously thought to be unobservable - the motions of molecules that explain the Brownian motion,[3] the behavior of electrons in metals as electrical and thermal conductors, the existence of energy levels in solids that explains anomalies in their specific heat,[4] and even let him discover the particle nature of light.[5]

3 Chapter 7.
4 Chapter 8.
5 Chapter 6.

Einstein's study of *fluctuations* let him see both the particle nature and the wave nature of light as separate terms in his analysis of entropy. In the final section of his 1904 paper, Einstein applied his calculations to radiation.

He thought that energy fluctuations would be extreme if the radiation is confined to a volume of space with dimensions of the same order of magnitude as the wavelength of the radiation.

While Einstein may or may not be correct about the maximum of fluctuations, he did derive the wavelength of the maximum of radiation λ_{max}, showing it is inversely proportional to the absolute temperature *T*. Einstein estimated theoretically that

$\lambda_{max} = 0.42/T$

Wien had discovered this relationship ten years earlier empirically as his displacement law. Wien had found

$\lambda_{max} = 0.293/T$.

Einstein wrote

> One can see that both the kind of dependence on the temperature and the order of magnitude of λ_m can be correctly determined from the general molecular theory of heat, and considering the broad generality of our assumptions, I believe that this agreement must not be attributed to chance. [6]

Einstein's work on statistical mechanics thus goes well beyond that of Boltzmann and Gibbs. The work of Gibbs did not depend on the existence of material particles and that of Boltzmann had nothing to do with radiation.

The tools Einstein developed in his three papers on statistical mechanics, especially his ability to calculate microscopic fluctuations, gave him profound insights into both matter and light.

All this work may be largely forgotten today, especially in many modern texts on quantum physics that prefer the conservative Gibbs formalism to that of Einstein. But Einstein's next three papers, all published in just one year often called his *annus mirabilis*, were all based on his young ability to see far beyond his older colleagues.

In particular, Einstein had a knack for seeing what goes on at the microscopic level that he called an "objective reality."

6 On the General Molecular Theory of Heat, §5 Application to Radiation, *Annalen der Physik*, 14 (1904) pp.354-362.