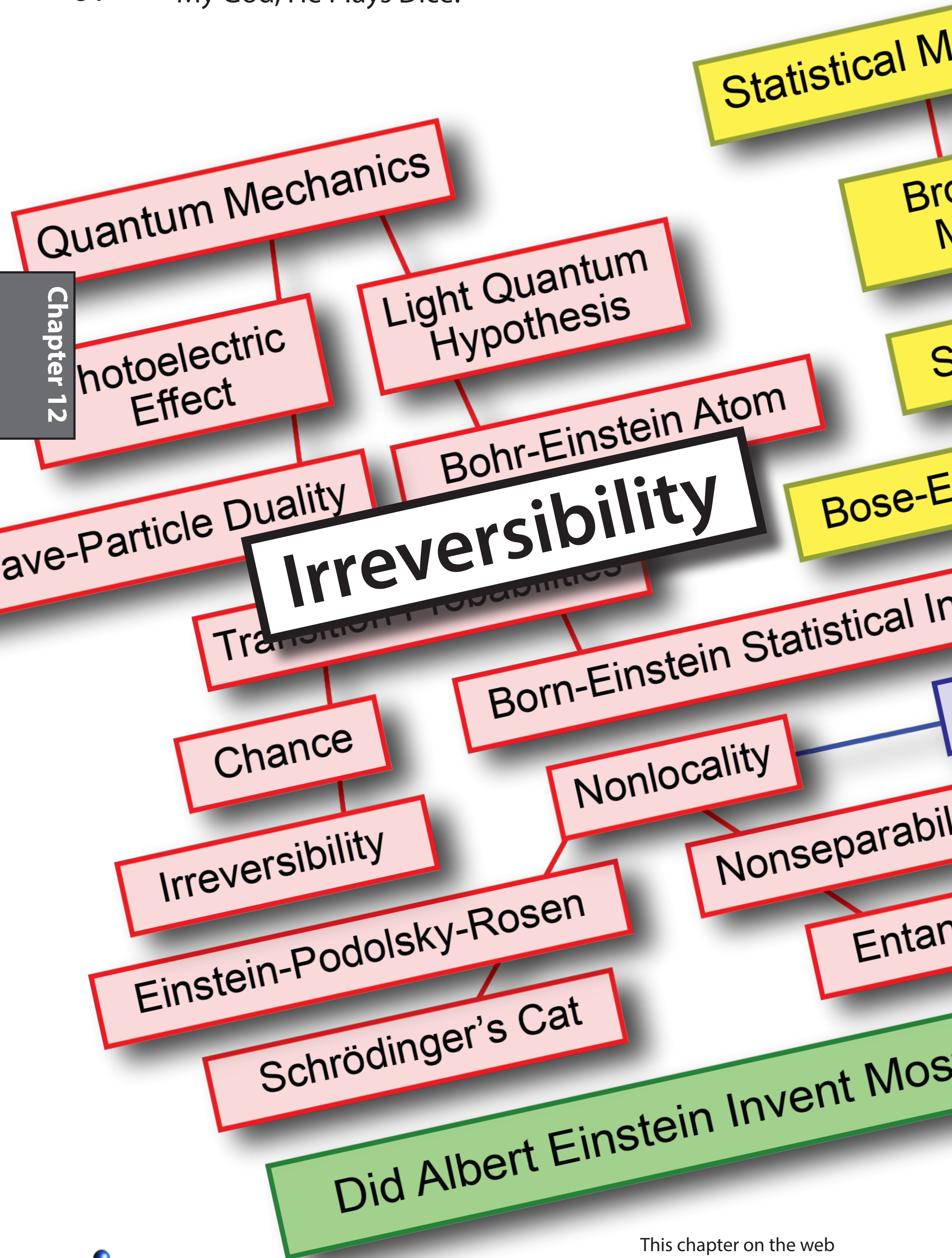
Irreversibility



Microscopic Irreversibility

In the 1870's, Ludwig Boltzmann developed his transport equation and his dynamical H-theorem to show exactly how gases with large numbers of particles have *macroscopic* irreversibility.

We see this fact every day when things mix but never unmix. Imagine putting 50 white and 50 black balls into a box and shaking them, now pour out 50 each into two smaller boxes and consider the possibility that one contains all black, the other all white.

In 1876, Josef Loschmidt criticized his younger colleague Boltzmann's attempt to derive from classical dynamics the increasing entropy required by the second law of thermodynamics. Loschmidt's criticism was based on the simple idea that the laws of classical dynamics are time reversible. Consequently, if we just turn the time around, the time evolution of the system should lead to decreasing entropy.

But we cannot turn time around. This is the intimate connection between time and the increasing entropy of the second law of thermodynamics that Arthur Stanley Eddington later called the Arrow of Time.[1]

We saw in chapter 4 that Max Planck hoped for many years to show that the second law of thermodynamics and its irreversible increase in entropy are universal and absolute laws. Planck hoped some irreversibility might emerge from a study of the interaction of matter and radiation. We now know his intuition was correct about that interaction, but wrong about the *absolute* nature of the second law. Irreversibility is a *statistical* phenomenon.

Microscopic time *reversibility* remains one of the foundational assumptions of classical mechanics. This is because the classical differential equations (Newton's laws) that describe the motion are time reversible. So are Maxwell's laws of electromagnetism.

Our first problem in the preface, known since the nineteenth century, is how can we reconcile macroscopic irreversibility with microscopic reversibility? The short answer is quantum mechanics. The laws of classical mechanics are adequate only for statistical averages over a large number of quantum particles.

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1 See Doyle, 2016a, chapter 23.

A careful quantum analysis shows that microscopic reversibility fails in the case of two particles in collision - provided the quantum mechanical interaction with radiation is taken into account. Planck was looking in the right place.

As we saw in the last chapter, Einstein found that when a light quantum is emitted (or absorbed) there is a transfer of momentum *hv/c* to the particle. Since the direction of emission is random, the gas particle suffers a random and irreversible change in direction, because the outgoing radiation is irreversible. Einstein's discovery of ontological chance, despite the fact that he did not like it, is the basis for understanding microscopic irreversibility.

Some scientists still believe that microscopic time reversibility is true because the deterministic linear Schrödinger equation itself is time reversible. But the Schrödinger equation only describes the deterministic time evolution of the *probabilities* of various quantum events. It does not determine individual events. As Einstein knew, quantum mechanics is *statistical*. Max Born put this distinction concisely

> The motion of the particle follows the laws of probability, but the probability itself propagates in accord with causal laws.[2]

When a quantum event occurs, if there is a record of the event (if new information enters the universe), the previous probabilities of multiple *possible* events collapse to the occurrence of just one *actual* event. This is the collapse of the wave function that John von Neumann called process 1.[3]

An irreversible event that leaves a record (stable new information) may become a measurement, if and when the new information is observed. Measurements are fundamentally and irreducibly irreversible, as many quantum physicists believed.

When particles collide, even structureless particles should not be treated as individual particles with single-particle wave functions, but as a single system with a two- or multiple-particle wave function, because particles are now entangled.[4]

Treating two atoms in collision as a temporary molecule means we must use molecular, rather than atomic, wave functions. The

2 "Quantum mechanics of collision processes," *Zeit. Phys.*, 38, 804 (1927)
3 See chapter 23.
4 See chapter 27.

quantum description of the molecule now transforms the six independent degrees of freedom for two atoms into three for the molecule's center of mass and three more that describe vibrational and rotational quantum states.

The possibility of quantum transitions between closely spaced vibrational and rotational energy levels in the "quasi-molecule' introduces indeterminacy in the future paths of the separate atoms. The classical path information needed to ensure the deterministic dynamical behavior has been partially erased. The memory of the past needed to predict the future has been lost.

Quantum transitions, especially the random emission of radiation. erases information about the particle's past motions.

Even assuming the practical impossibility of a perfect classical time reversal, in which we simply turn the two particles around, quantum physics requires two measurements to locate the two particles, followed by two state preparations to send them in the opposite direction.

Heisenberg indeterminacy puts calculable limits on the accuracy with which perfect reversed paths could be achieved.

Let us assume this impossible task can be completed, and it sends the two particles into the reverse collision paths. But on the return path, there is still only a finite probability that a "sum over histories" calculation will produce the same (or reversed) quantum transitions between vibrational and rotational states that occurred in the first collision. Reversibility is not impossible, but extremely improbable,

Thus a quantum description of a two-particle collision establishes the microscopic irreversibility that Boltzmann sometimes described as his assumption of "molecular disorder." In his second (1877) statistical derivation of the H-theorem, Boltzmann used a statistical approach and the molecular disorder assumption to get away from the time-reversibility assumptions of classical dynamics.

The Origin of Microscopic Irreversibility

The path information required for microscopic reversibility of particle paths is destroyed or erased by local interactions with radiation and other particles in the environment. This is the origin of microscopic irreversibility.

Photon emission and absorption during molecular collisions is shown to destroy nonlocal molecular correlations, justifying Boltzmann's assumption of "molecular chaos" (*molekular ungeordnete*) as well as Maxwell's earlier assumption that molecular velocities are not correlated. These molecular correlations were retained in WILLARD GIBBS' formulation of entropy. But the microscopic information implicit in classical particle paths (which would be needed to implement Loschmidt's deterministic motion reversal) is actually *erased*. Boltzmann's physical insight was correct that his increased entropy is irreversible, not just macroscopically but microscopically.

It has been argued that photon interactions can be ignored because radiation is *isotropic* and thus there is no *net* momentum transfer to the particles. The radiation distribution, like the distribution of particles, is indeed *statistically* isotropic, but, as Einstein showed in 1916, each discrete quantum of angular momentum exchanged during individual photon collisions alters the classical paths sufficiently to destroy molecular velocity correlations.

Reversibility is closely related to the maintenance of path information forward in time that is required to assert that physics is *deterministic*. Indeterministic interactions between matter and radiation erase that information. The elementary process of the emission of radiation is not time reversible, as first noted by Einstein in 1909. He argued that the elementary process of light radiation does not have reversibility ("*Umkehrbarkeit*"). The reverse process ("*umgekehrte Prozess*") does not exist as an elementary process.

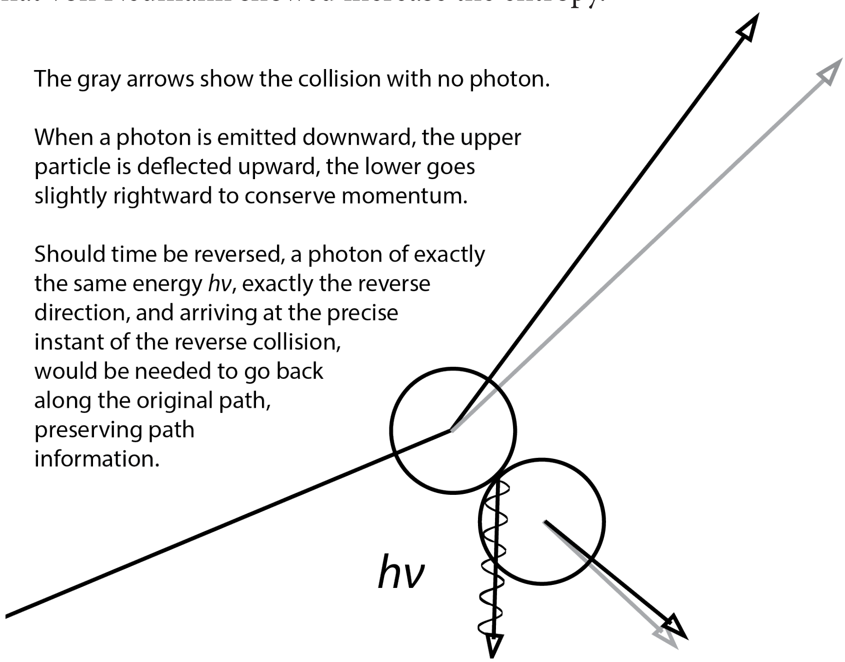
Macroscopic physics is only *statistically* determined. Macroscopic processes are adequately determined when the mass *m* of an object is large compared to the Planck quantum of action *h* (when there are large numbers of quantum particles).

But the information-destroying elementary processes of emission and absorption of radiation ensure that macroscopic processes are not individually reversible.

When interactions with a thermal radiation field and rearrangement collisions are taken into account, a quantum-mechanical treatment of collisions between material particles shows that a hypothetical reversal of all the velocities following a collision would only extremely rarely follow the original path backwards.

A rearrangement collision is one in which the internal energy of one or both of the colliding particles changes because of a quantum jump between its internal energy levels. These internal energy levels and jumps between them were first seen by Einstein in his 1907 work on specific heats (chapter 8).

Although the deterministic Schrödinger equation of motion for an isolated two-particle material system is time reversible (for conservative systems), the quantum mechanics of radiation interactions during collisions does not preserve particle path information, as does classical dynamics. Particle interactions with photons in the thermal radiation field and rearrangement collisions that change the internal states of the colliding particles are shown to be microscopically irreversible for all practical purposes. These quantum processes are involved in the irreversible "measurements" that von Neumann showed increase the entropy.



Consider a collision between two atoms that results in the emission of a photon.

At some time *t* after the collision, let's assume we can reverse the separating atoms, sending them back toward the reverse collision. If there had been no photon emission, the most likely path is an exact traversal of the original path back before the collision.

But since a photon was emitted, traversing the original path requires us to calculate the probability that at precisely the moment of a reversed collision a photon of exactly the same frequency is absorbed by the quasi-molecule, corresponding to a quantum jump back to the original rotational-vibrational state, with the photon absorption direction exactly opposite to the original emission, allowing the colliding atoms to reverse their original paths. While this is not impossible, it is extraordinarily improbable.

The uncertainty principle would prevent an experimenter from preparing the two material particles with the precise positions and reverse momenta needed to follow the exact return paths to the collision point. Moreover, the Schrödinger equation of motion for the two particles would only provide a probability that the particles would again collide.

As to the photon, let us assume with Einstein that a light quantum is "directed" and so could be somehow aimed perfectly at the collision point. Even so, there is only a probability, not a certainty, that the photon would be absorbed.

We conclude that collisions of particles that involve radiation are not microscopically reversible.

Detailed Balancing

It is mistakenly believed that the detailed balancing of forward and reverse chemical reactions in thermal equilibrium, including the Onsager reciprocal relations, for example, depend somehow on the principle of microscopic reversibility.

Einstein's work is sometimes cited as proof of detailed balancing and microscopic reversibility. The *Wikipedia* article is an example.[5] In fact, Einstein started with Boltzmann's assumption of detailed balancing, along with the assumption that the probability of states with energy E is reduced by the exponential "Boltzmann factor," $f(E) \sim e^{-E/kT}$, to derive the transition probabilities for emission and

5 https://en.wikipedia.org/wiki/detailed_balance

absorption of radiation. Einstein then *derived* Planck's radiation law and Bohr's "quantum postulate" that $E_m - E_n = h\nu$. But Einstein denied symmetry in the elementary processes of emission and absorption.

As early as 1909, he noted that the elementary process is not "invertible." There are outgoing spherical waves of radiation, but incoming spherical waves are never seen.

> "In the kinetic theory of molecules, for every process in which only a few elementary particles participate (e.g., molecular collisions), the inverse process also exists. But that is not the case for the elementary processes of radiation. According to our prevailing theory, an oscillating ion generates a spherical wave that propagates outwards. The inverse process does not exist as an elementary process. A converging spherical wave is mathematically possible, to be sure; but to approach its realization requires a vast number of emitting entities. The elementary process of emission is not invertible." [6]

The elementary process of the emission and absorption of radiation is asymmetric, because the process is "directed." The apparent isotropy of the emission of radiation, when averaged over a large number of light quanta, is only what Einstein called "pseudo-isotropy" (*Pseudoisotropie*), a consequence of time averages over large numbers of events. Einstein often substituted time averages for space averages, or averages over the possible states of a system in statistical mechanics.

Detailed balancing is thus a consequence of averaging over extremely large numbers of particles in equilibrium. This is the same limit that produces the so-called "quantum-to-classical" transition. And it is the same condition that gives us the "adequate" statistical determinism in the macroscopic, everyday world.

Neither detailed balancing nor the adequate determinism that we see in classical Newtonian experiments does anything to deny that, at the microscopic quantum level, events are completely statistical, involving ontological chance. The interaction of radiation with matter has "a 'chance'-dependent value and a 'chance'-dependent sign" (emission or absorption), said Einstein in 1917.[7]

Reversibility is remotely possible, but extraordinarily improbable.

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6 "On the Development of Our Views Concerning the Nature and Constitution of Radiation," 1909, CPAE, vol.2, p.387

7 "On the Quantum Theory of Radiation," *CPAE*, vol.6, p.213