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Microscopic Irreversibility

In 1876, Josef Loschmidt criticized his younger colleague Ludwig Boltzmann's 1866 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 turned the time around, the time evolution of the system should lead to decreasing entropy.

This is the intimate connection between time and the second law of thermodynamics that Arthur Stanley Eddington later called the Arrow of Time.[1]

Microscopic time reversibility is one of the foundational assumptions of both classical mechanics and quantum mechanics. But a careful quantum analysis shows that reversibility fails even in the most ideal conditions - the case of two particles in collision - provided the quantum mechanical interaction with radiation is taken into account.

Our proof of microscopic irreversibility provides a new justification for Boltzmann's assumption of "molecular disorder" and strengthens his proof of *H*-Theorem.

In quantum mechanics, microscopic time reversibility is assumed to be true by some scientists 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.

When a quantum event occurs, if there is a record of the event (if new information enters the universe), the 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**.[2]

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

1 See chapter 24
2 See chapter 20 and appendix C

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-particle wave function, because they are now entangled.[3]

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

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 can be achieved.

Let us assume this impossible task can be completed, and it sends the two particles back along the reverse collision paths. On the return path, there is 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. Perfect reversal is not impossible but extremely improbable.

Thus a quantum description of a two-particle collision establishes the microscopic irreversibility that Boltzmann sometimes

3 See chapter 21 on entanglement.

described as his assumption of "molecular disorder." In his second (1877) 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 Irreversibility

The path information required for microscopic reversibility of particle paths is destroyed or erased by local interactions with radiation and other particles.

Boltzmann's dynamical H-Theorem (his 1872 *Stosszahlansatz*) correctly predicts the approach to equilibrium. But this apparent increase in entropy could be reversed, according to Josef Loschmidt's time-reversibility objection and Ernst Zermelo's recurrence objection. We show that the addition of electromagnetic radiation adds an irreducible element of randomness to atomic and molecular motions, erasing classical path information, just as the addition of a small speck of material can thermalize a non-equilibrium radiation field. Path erasure prevents reversibility and maintains a high entropy state indefinitely. Statistical fluctuations from equilibrium are damped by path erasure.

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.

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 we will show, 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 all path information. The elementary process of the emission of radiation is not time reversible, as first noted by Albert 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, he said.

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 very rarely follow the original path backwards. 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 equivalent to the irreversible "measurements" that von Neumann showed increase the entropy.[4]

4 See appendix C

In classical physics, if we time reverse a collision, two particles will reverse their vectors and go back along their original paths.

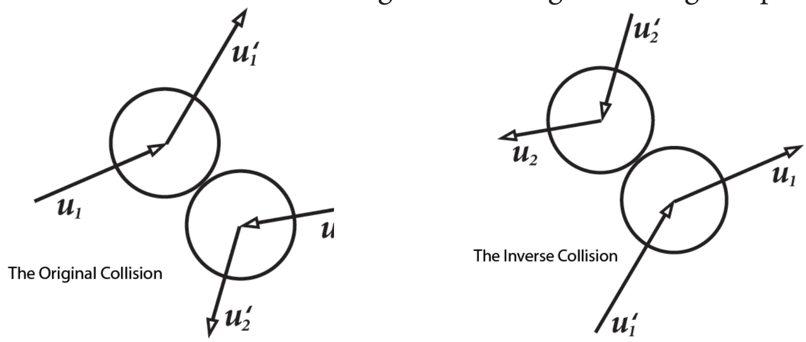

Figure 1-31. Classical particle collisions are perfectly time reversible.

Now consider a quantum collision between two atoms that results in the emission of a photon, deflecting the classical paths.

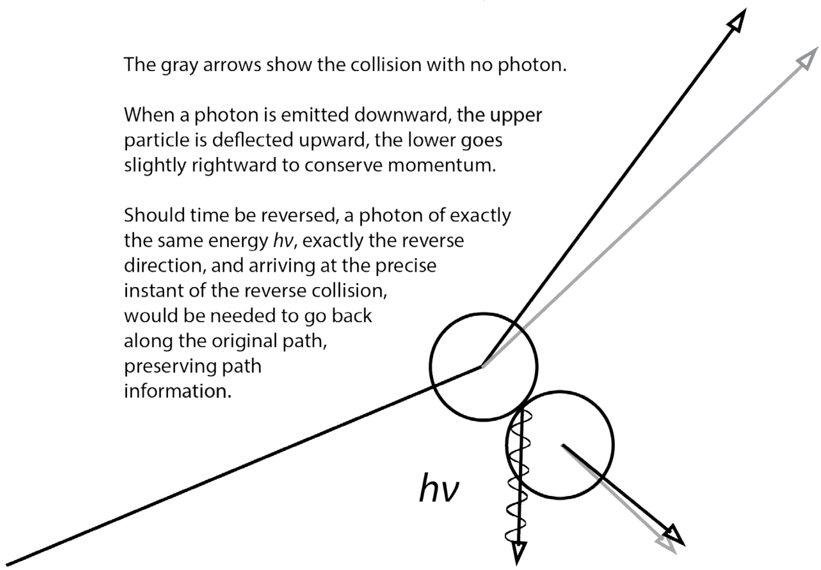

Figure 1-30. Quantum particle collisions are not time reversible.

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. But since a photon was emitted, traversing the original path requires us to calculate the probability that at precisely the right time a photon of the same frequency is absorbed by the quasi-molecule, corresponding to a quantum jump back to the original rotational-vibrational state (conserving energy), with the photon direction exactly opposite to the original absorption (conserving momentum), allowing the colliding atoms to reverse its original path. 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, for example.) In fact, Einstein started with Boltzmann's assumption of detailed balancing, along with the "Boltzmann principle" 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 absorption of radiation. Einstein also derived Planck's radiation law and Bohr's two "quantum postulates." But Einstein distinctly denied any 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."[5]

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 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.[6]

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5 "On the Development of Our Views Concerning the Nature and Constitution of Radiation," 1909, *Einstein Collected Papers*, vol.2, p.387

6 "On the Quantum Theory of Radiation," *Einstein Collected Papers*, vol.6, p.213