Quantum Erasure of Classical Path Information by Photon Interactions and Rearrangement Collisions

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Photon emission and absorption during molecular collisions is shown to destroy nonlocal molecular correlations, thus justifying Ludwig Boltzmann's assumption of "molecular chaos" (*molekular ungeordnete*) and James Clerk Maxwell's assumption that molecular velocities are not correlated. The information about particle paths that would be needed to implement a deterministic motion reversal is actually erased, justifying what N. G. van Kampen calls the "repeated randomness" assumption needed to validate the H-Theorem. Boltzmann's original *Stosszahlansatz* correctly predicts the approach to equilibrium. Quantum physics shows the deterministic reversibility objections of Boltzmann's critics to be untenable, removing a major defense from the thesis of classical physical determinism. We calculate the characteristic times of quantum erasure over a range of conditions, from standard temperature and pressure to the extreme low densities and temperatures of the intergalactic medium. We find the quantum erasure time τ_{QE} is intermediate between Boltzmann's relaxation time τ_B and the cosmologically long Poincaré recurrence time τ_P. The Loschmidt reversibility objection to Boltzmann's H-Theorem is removed by a quantum-mechanical treatment of collisions and microscopic irreversibility is established..

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A quantum-mechanical treatment of collisions between atoms or molecules shows that a hypothetical reversal of all the velocities following a collision would only very rarely follow the original path backwards, when interactions with a thermal radiation field and rearrangement collisions are taken into account. It does not preserve path information, as would classical dynamics. Although the deterministic Schrödinger equation of motion for a two-particle isolated system is time reversible, the ideal conditions needed for isolating two particles are shown to be unrealizable in normal gas conditions. 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.

Consider the collision of two atoms. Electronic transitions between atomic energy levels require relatively high-energies (order of electron volts), but excitation of vibrational and rotational states in molecules are possible with collision energies commonly present at room temperatures (.03 eV). When the atoms are close enough to collide they are best described as a "quasi-molecule." (Doyle, 1968) During collisions, discrete atomic spectral lines are broadened into a continuum by the "quasi-molecule" translational energy, which is not quantized. Low-energy photon emission (or absorption) during a collision alters the angular momentum of the quasi-molecule, deflecting the colliding atoms from their classical paths.

Assuming motion reversal of the atoms, the subsequent collision is highly unlikely to absorb a photon at exactly the right time and with the exact opposite momentum required to produce the precise time-reversed trajectory assumed for classical particles. When the colliding atoms emit a specific energy photon, for example, one corresponding to a discrete vibrational- or rotational-state transition during the collision, the likelihood of an identical energy photon being available during the hypothetical time-reversed collision, combined with the small probability of the opposite quasi-molecular-state transition, is vanishingly small.

The energy of collision at standard temperature is more than enough to cause transitions between rotational eigenstates, accompanied by the *emission* (or absorption) of a photon. Rotational transitions which increase (or decrease) the particles' combined angular momentum by ΔJ, would cause the quasi-molecules to follow paths that diverge from those of colliding atoms that experience no photon interactions, as shown in Figure 1.

At some time t after the collision, theoretically (if not practically) 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 if a photon had been 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 overall momentum), allowing the colliding atoms to reverse its original path. While this is not impossible, it is extraordinarily improbable.

We note in passing that there are many more rearrangement collisions possible, in which more exotic transitions might occur. These are dependent on the type of particle. For a hydrogen atom, there is a probability that during a collision one of the electrons might flip from parallel to the atom's nuclear spin

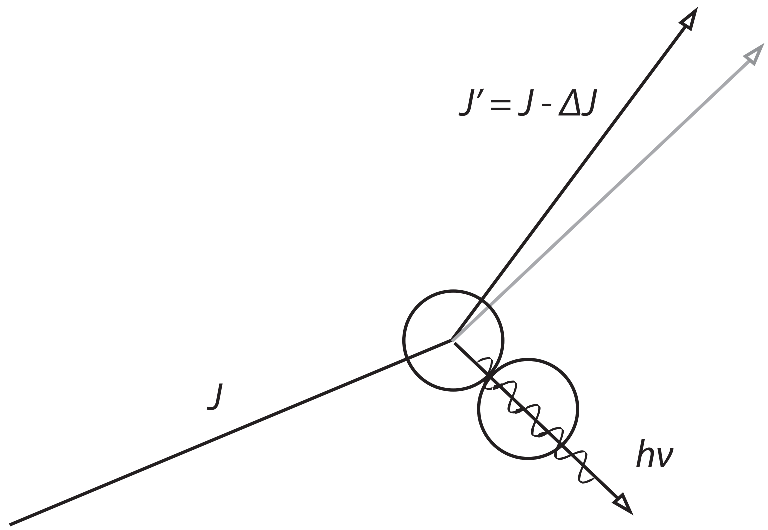

FIG. 1 The emitted photon carries away one unit of angular momentum, so the path of the collision is altered, losing its memory of the incoming path before the collision.

(triplet state) to anti-parallel. This hyperfine structure transition produces the long-wavelength 21-cm line of radio astronomy. Nuclear spins might make a similar transition, changing the quasi molecule from ortho-H_2 to para-H_2. Any of these transitions would introduce the small quantum change of angular momentum needed to deflect the colliding particles from their classical paths, erasing their memory of past positions and paths, and effectively invalidating deterministic statistical physics.

We conclude that even if we could prepare the velocities of gas molecules with the exact opposite velocities (the condition that Loschmidt thought would be equivalent to reversing the time), the entropy would decrease only for a short time (as Boltzmann accepted) until statistically irreversible quantum mechanical interactions with the radiation field or rearrangement of the internal quantum states of the colliding particles dominates after the characteristic quantum erasure time $\tau_{QE}$of the gas..

We find that quantum mechanics provides the molecular disorder or chaos that Boltzmann and the British physicists thought might serve to guarantee his H-theorem, that entropy always increases. Reversing all velocities is of course not the same as reversing time. But unlike most earlier research, we conclude that microscopic quantum irreversibility would ensure the increase of entropy in such hypothetical situations. Most texts on statistical mechanics say that the quantum treatment of statistical mechanics reaches no conclusions different from the classical treatment.[1] This is because both classical and quantum statistical mechanics describe ensembles of systems. The quantum systems are in “mixed states,” disregarding the interference terms in the density matrix of the “pure states” density operator.

It has been argued that photon interactions can be ignored because radiation is isotropic and thus

[1] Richard Tolman ((Tolman, 1938), p.8) claimed (mistakenly, in my view) that the “principle of dynamical reversibility” holds also in quantum mechanics in appropriate form, indicating that quantum theory supplies no new kind of element for understanding the actual irreversibility in the macroscopic behavior of physical systems. D. ter Haar ((ter Haar, 1955), p. 292) said ”The transition from classical to statistical mechanics does not introduce any fundamental changes.”

there is no net momentum transfer to the particles. This is indeed correct, because radiation, like the distribution of particles, is statistically isotropic, but, as we have shown, each discrete quantum of angular momentum exchanged during individual photon collisions alters the classical paths sufficiently to destroy molecular velocity correlations. Photon interactions (and rearrangement collisions) may therefore justify the "repeated randomness assumption" of N. G. van Kampen.[2]

We describe this insight as the "quantum erasure" of path information during collisions. It provides a solid basis for the Boltzmann assumption of molecular chaos. Molecular velocities are not correlated as a consequence of past collisions. Quantum path information erasure is a strong form of decoherence. We show that information "leaked" or "delocalized" into the environment is not recoverable, in principle and in practice. It is erased.

I. THE CHARACTERISTIC TIME OF QUANTUM ERASURE OF CLASSICAL PATH INFORMATION

The time scale for the quantum erasure of classical path information τ_{QE} depends on the number of collisions per second and the efficiency of erasure (the cross-section for erasure σ_{QE}). The cross section is highly wavelength and species dependent, reflecting the internal quantum structure of the colliding atoms or molecules.

A complete solution requires the time-independent Boltzmann equation

$$\frac{\partial f()}{\partial t} = \tag{1}$$

A. Standard Temperature and Pressure

Assuming that we have a gas in an isolated container with perfectly reflecting adiabatic walls at standard temperature and pressure, the number density of particles is

$$n \approx 2.5 \times 10^{19}/cm^3 \tag{2}$$

From the equipartition theorem,

$$\frac{1}{2}m\bar{v^2} = \frac{3}{2}kT. \tag{3}$$

The mean velocity of typical atmospheric molecules such as N_2 (mass 5×10^{-23} g) is

[2] Van Kampen (van Kampen, 2007), pp.449–456.

$$\bar{v} \approx 5 \times 10^4 cm/s. \tag{4}$$

The mean free path of molecules between collisions depends on the molecular diameter D and the effective scattering cross-section σ. For N_2, $D \approx 2 \times 10^{-8}$ and the geometric cross-section $\sigma \approx 6 \times 10^{-16}$.

The mean free path for hard inelastic spheres is

$$l_{mfp} = \frac{1}{n\sigma} \approx 3 \times 10^{-5} cm. \tag{5}$$

Thus $l_{mfp} \gg D$ and the average molecule travels thousands of molecular diameters between collisions. If the angular deflection due to quantum processes during the collision is even one part in a thousand, the molecule will completely miss the next collision on its classical path.

The mean time τ between collisions is

$$\tau = \frac{l_{mfp}}{\bar{v}} \approx 6 \times 10^{-10} s, \tag{6}$$

and the collision rate per molecule $\approx 2 \times 10^9 s^{-1}$.

This was the source of Boltzmann's estimate for the "relaxation time" for the approach of the gas to equilibrium as 10^{-9} seconds..

The quantum erasure time τ_{qe} for the loss of classical path information is much longer than the Boltzmann relaxation time τ_B, because it depends on the fraction of collisions that involve a photon interaction (emission or absorption) or a rearrangement collision. This depends on the quantum internal structure of the specific atoms and molecules in the gas.

Given the change in angular momentum resulting from quantum transitions (some multiple of $\hbar$), we can calculate the average angular deflection $\Delta\theta$ of the path after the collision . An angular deflection $\Delta\theta$ leads to the particle missing the next collision by a distance d,

$$d = \Delta\theta \cdot l_{mfp}. \tag{7}$$

When d is greater than the molecular diameter D, just one photon interaction is enough to invalidate the deterministic thesis that classical path information (like all information in classical dynamical physics) is conserved.

B. Photon absorptions

An estimate of the photon interaction rate can be made by calculating the number of photons that collide with the gas particles while they are in a "quasi-molecular' state with rotational and vibrational levels in the continuum.

The density of photons in the equilibrium radiation field can be determined from the Planck radiation law for spectral energy density as a function of frequency,

$$u(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{8}$$

The number density of photons of frequency ν is therefore

$$n_\nu = \frac{u(\nu, T)}{h\nu} = \frac{8\pi\nu^2}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}. \tag{9}$$

At room temperature and at $\nu = 3 \times 10^{13}$ $(\frac{k \cdot 300}{h})$, this gives us approximately

$$n_\nu = 8 \times 10^{-4} cm^{-3} sec^{-1} \tag{10}$$

as the number of photons per unit frequency interval near the maximum blackbody radiation at 300K.

To calculate the flux of photons, we can use the Stefan-Boltzmann law for the energy radiated from the surface, which in equilibrium is the amount falling on the surface.

$$\frac{P}{A} = \sigma T^4. \tag{11}$$

where σ is the Stefan-Boltzmann constant, 5.67×10^{-5} $erg\ cm^{-2} sec^{-1} K^{-4}$. At 300K, the flux of thermal photons is of the order of 10^{17} photons per cm^2.

Multiplying the geometrical cross-section of a quasi-molecule ($10^{-16} cm^2$) by the photon flux, we find the number of photon interactions with the quasi-molecules is very low, about one per second, compared to 10^8 particle collisions per second, so the quantum erasure rate must be very slow compared to Boltzmann's relaxation time to equilibrium (order of $10^{-9} sec$).

And not all of these photon interactions result in absorption or Raman scattering because 1) the geometric cross-section is larger than the cross-sections for absorption and for Raman scattering, and 2) the cross sections are strong functions of the photon frequency ν.

If the spectrum consists of discrete lines and molecular bands, a large fraction of photons simply pass by. Fortunately, there several broadening of the spectral lines by relative motion of the atoms (the translational energy between the atoms is not quantized) means there is a continuous absorption spectrum rather than the discrete lines of the individual atoms.

Thermal photons have enough energy ($\approx .03 eV$) to excite the first few rotational energy levels of a typical quasi-molecule.

C. Photon emissions

We can also attempt to estimate the number of collisions that excite internal energy levels during the collision, which are followed quickly ($10^{-8} sec$) by emission of photon, carrying away angular momentum. In thermal equilibrium, these emissions are in detailed balance with absorptions equal to emissions.

With 10^9 collisions per second and the collision energy at $300K$ about .03 eV, we would expect many low-lying rotational states to be occupied after each collision. But if the excited-state lifetimes are too long, the particles will suffer another collision before emitting a photon, and this perhaps accounts for the very low emission rate that would balance absorptions.

D. (

Rearrangement collisions)

In a rearrangement collision no photons are emitted or absorbed but virtual photons mediate the interaction between the colliding particles, allowing the quantum states of the two particles to change. If internal angular momentum of the atoms is transferred to the quasi-molecule (conserving total angular momentum), the outgoing paths are altered indeterministically from the expected classical paths, a third example of quantum erasure.

[Inverse of the collisional excitation of internal states]

II. THE INTERGALACTIC MEDIUM (IGM)

From the time in the early universe when the temperature was low enough for electrons to combine with protons (the recombination era) and the universe became transparent, the greatest fraction of gas in the universe was hydrogen atoms traveling alone. Can the paths of these atoms be adequately understood by classical dynamics?

The average density of the universe today is only about one hydrogen atom per cubic meter, perhaps 10 to 100 times that number in parts of the intergalactic medium, so the collision rate with other atoms is extremely low and the mean free path between collisions is extremely large.

Nevertheless, the collisions are energetic enough and frequent enough to populate the upper state in the hyperfine structure of the hydrogen ground state. Spontaneous emission from the excited state is highly forbidden (it is a magnetic dipole transition), with a probability of $2.9 \times 10^{-15} s^{-1}$. The excited state is metastable with a half-life of approximately 10 million years.

Even with such extreme low density and enormous mean free paths, however, the assumption of classical dynamics and deterministic, information-preserving classical paths is clearly inapplicable. There are enough emissions of 21-cm photons to provide astronomers with their major tool for tracing out the spiral structure of galaxies as well as intergalactic voids and filamentary structures.

Every hydrogen-line photon came from an atom that has suffered at least one collision and had its classical deterministic path altered by the indeterministic emission of that photon, which at that moment erased any information about prior classical path information.

III. QUANTUM ERASURE AS DECOHERENCE

H. D. Zeh(Zeh, 2010), E. Joos (Joos and Zeh, 1985), Wojciech Zurek, (Zurek, 1991), and their many colleagues argue that a single photon can "decohere" a quantum system. We agree that modest quantum events such as the absorption or emission of a single photon can introduce new information into the universe, and that such events can therefore be regarded as "measurements," even if there are no observers.

Experimental evidence for such decoherence is provided by the work of Gerhard Rempe, whose interferometry experiments with heavy Rubidium atoms has shown that a weak beam of low-energy microwave photons on one path excites an atom near that path into a different state. Discovering "which-way" information about the path followed by the atom causes its coherent wave function to decohere and reduce the quantum interference pattern proportional to the number of microwave photons. (Durr *et al.*, 1998)

The dynamical picture of particles moving along paths between collisions is more or less the same whether the equations of motion are classical or quantum.The Schrödinger description is just as deterministic as the classical, and quantum statistical physics arrives at the same conclusions as classical statistical physics, because they both ignore quantum events such as the photons absorbed or emitted as a result of collisions.

Decoherence theorists are correct when they say that our simply looking at a quantum system is enough to decohere it.(Joos *et al.*, 2003) But the essential thing that decoheres a system is a photon, either emitted or scattered by the system, that allows us to observe it. When the hydrogen atoms in the intergalactic medium emit a 21-cm line photon every ten million years or so, they are changing their past path, which was coherent and deterministic over those ten million years, to a new path that is fundamentally indeterministic. We can regard that as a virtual measurement, which has the potential of becoming our measurement if and when we observe the photon.

Just as we never see macroscopic superpositions of states, we never observe spontaneous entropy reduction. Whether the particle paths are treated by classical dynamical or quantum Schrödinger equations of motion, the paths are deterministic. It is only when we include the fundamentally indeterministic transitions between internal quantum states during collisions that irreversibility appears. It is the existence of "measurements" by the particles themselves, with accompanying "collapses" of the wave functions and quantum erasure of path information, that gives us the familiar macroscopic observation that entropy always increases.

IV. CONCLUSION

Interactions of atoms and molecules with thermal radiation during collisions erase the classical or quantum path information about previous paths of the particles, and make future paths undetermined. Although the average direction of photons is isotropic, individual photon interactions alter particle paths indeterministically in specific new directions, destroying any molecular velocity correlations. The characteristic time of this quantum erasure (τ_{QE}) is much longer than Boltzmann's relaxation time (τ_B) for the approach to equilibrium, but it is much shorter than the Poincaré recurrence time (τ_P). Even if an experimenter could reverse the motions of all the particles of an equilibrium gas, the system could only briefly evolve deterministically toward lower entropy states. The development of the molecular correlations needed for long-lasting and significant entropy reduction is prevented by quantum erasure in time scales consistent with observations.

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