The Origin of Irreversibility

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

Ludwig Boltzmann's dynamical H-Theorem (his 1872 *Stosszahlansatz*) correctly predicts the approach to equilibrium. But this apparent increase in entropy can 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, justifying what N. G. van Kampen calls a "repeated randomness" assumption. 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 show, each discrete quantum of angular momentum exchanged during individual photon collisions alters the classical paths sufficiently to destroy molecular velocity correlations.

Path erasure is a strong function of temperature, pressure, and the atomic and molecular species of the gas. We calculate path erasure times over a range of conditions, from standard temperature and pressure to the extreme low densities and temperatures of the intergalactic medium.

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 path information. The elementary process of the emission of radiation is not time reversible, as first noted by Einstein in 1909. Macroscopic physics is only statistically determined. Macroscopic processes are adequately determined when the 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 reversible.

I. INTRODUCTION

Macroscopic laws of physics, notably the phenomenological second law of thermodynamics, describe irreversible behavior. Microscopic laws, however, are described by differential equations that are deterministic and reversible, whether Newton's classical dynamical laws or the quantum mechanical equations of motion (e.g., the Schrödinger equation). Microscopic physics is time reversible for conservative systems describable by a real Hamiltonian (Bohm [1], p.415, Messiah [2], vol.II, p.673, Tolman [3], p.395). A fundamental problem in statistical mechanics is how indeterministic macroscopic irreversibility can result from deterministic and reversible microscopic motions (Ehrenfest and Ehrenfest [4], Montroll and Green [5], van Kampen [6]).

Ludwig Boltzmann's presumed proof of entropy increase (his H-Theorem) used a definition of statistical entropy that ignored molecular correlations [7]. This was described as his hypothesis of "molecular chaos" by the Ehrenfests [4]. When J. Willard Gibbs included molecular correlations between particles, he found that (his) total statistical entropy is a constant [8]. Gibbs' view was endorsed by many mathematical physicists, including Albert Einstein, as compatible with a block-universe in which total information is a conserved quantity. In the time evolution of a closed system started in a highly ordered state, the initial macroscopic order is lost (Boltzmann entropy increases) as it becomes microscopic information in the form of molecular correlations. The Gibbs entropy conserves the path information stored in molecular correlations. It is these microscopic correlations that could return the system to its initially ordered state, if the momenta of all the material particles could be reversed at any time (the physical equivalent of time reversal).

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No treatment of the irreversibility problem limited to material particles has successfully resolved the well-known objections raised during Boltzmann's lifetime These were the reversibility problem (Josef Loschmidt's "*Umkehreinwand*") and the recurrence problem (Ernst Zermelo's "*Wiederkehreinwand*") (Boltzmann [9], p.443). Boltzmann's calculations of the extraordinary improbability of these two objections showed that they can be ignored for practical purposes. For a one-tenth liter of gas, Boltzmann calculated the Poincaré recurrence time (the "*Wiederkehrsatz*") as of the order of $10^{10^{10}}$ years. But if Boltzmann's H-theorem does not indefinitely maintain the monotonic increase in entropy we observe in the universe, what mechanism can explain the irreversibility? We show that it is the indeterministic and irreversible interaction of matter and radiation.

In 1909, Einstein 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. ([10]) H. Dieter Zeh says that the inverse process is "never observed in nature." ([11])

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. We show that these quantum processes are equivalent to the irreversible “’measurements” that John von Neumann showed increase the entropy ([12], p.379-387).

Just as a material gas alone cannot produce a permanent approach to equilibrium, a non-equilibrium radiation distribution cannot by itself approach the equilibrium of Max Planck’s radiation distribution law. Gustav Kirchhoff noted that in a perfectly reflecting cavity, there is no way for monochromatic rays of one frequency to change to another frequency. But he said that a single speck of material would be enough to produce blackbody radiation. His student Planck said that a single carbon particle would be enough to change perfectly arbitrary radiation into black radiation ([13], p.44). The time necessary is not essential. We shall show that even a small amount of radiation has a similar effect on a material gas, helping it to maintain a Maxwell-Boltzmann distribution and maximum Boltzmann entropy against significant fluctuations from equilibrium.

Most texts on statistical mechanics say that the quantum treatment of statistical mechanics reaches no conclusions different from the classical treatment. Richard Tolman (Tolman [3], p.8) claimed 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 [14], p. 292) said “The transition from classical to statistical mechanics does not introduce any fundamental changes.” 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 there is no net momentum transfer to the particles. The radiation distribution, like the distribution of particles, is indeed statistically isotropic, but, as we show, 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 (van Kampen [6], pp.58-59, 449–456). Van Kampen has criticized approximation methods that claim to produce irreversibility as lacking an underlying physical explanation, i.e., a specific mechanism that could justify the approach to equilibrium as a Markovian process (van Kampen [15], cited by van Vliet [16]).

“Path erasure” of molecular correlation information during collisions justifies “repeated randomness” assumptions and validates the Boltzmann assumption of molecular chaos.

II. PATH ERASURE

At the standard temperature and pressure of gases considered in classical statistical physics, interaction between matter and radiation has usually been ignored. Electronic transitions between atomic energy levels require relatively high-energies (order of electron volts), justifying the usual treatment of gas particles as not interacting with radiation. But excitation of vibrational and rotational states in some molecules is possible with collision energies commonly present at room temperatures (.03 eV). And free atoms close enough to collide are most accurately described by the use of ”quasi-molecular” wave functions (Doyle [17]). During these 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 the classical paths they would have followed without radiation interaction.

Assuming motion reversal of such atoms after a collision, the reversed 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.

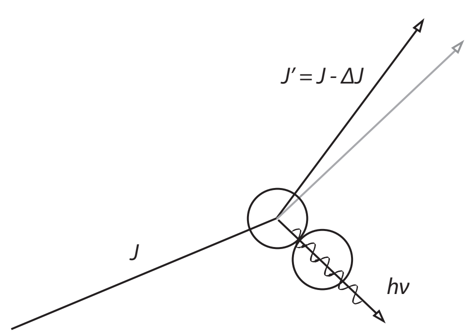

FIG. 1. The emitted photon carries away one unit of angular momentum, so the path of the collision is altered, erasing its memory of the incoming path before the collision.

The emission of the photon is described by a spherical outgoing probability amplitude wave. But when that photon is absorbed, by collision with another particle or the wall of the container, the emitting particle experiences a recoil momentum $h\nu/c$ in a random direction [18].

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 the reverse 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. Detailed balancing ensures that on average the reverse effect occurs in the gas. So there is no macroscopic "net effect." But it is extremely improbable for any given pair of particles to experience the exact opposite transition with an incoming photon.

Note that it was a two-particle original collision that emitted a photon, but the reverse process is a three-body collision. Three- and higher-number collisions are traditionally ignored in statistical mechanics.

Furthermore, where particles can in principle be motion reversed, to produce a time-reversed electromagnetic radiation field would involve advanced electromagnetic potentials, as Wheeler and Feynman considered in their absorber theory of radiation (Wheeler and Feynman [19]), but later rejected. "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 reversible (Einstein [10]). The extraordinary initial conditions required for such advanced potentials are "never observed in nature," as H.D. Zeh says in his studies of the direction of time

(Zeh [20]). Water waves, sound waves, electromagnetic waves, and quantum probability amplitude waves all share a "radiation arrow of time" whose direction coincides with the thermodynamic arrow of entropy and the cosmological arrow of the expansion of the universe. All of these arrows may find a shared basis in the irreversibility of quantum interactions between radiation and matter.

Actual photons are not required. Many types of "rearrangement collisions," mediated by the exchange of virtual photons, are 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 (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 might introduce the small quantum change of one unit 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.

Even if we could prepare gas molecules with the exact opposite velocities - the condition that Loschmidt thought would be equivalent to reversing the time (discussed by Boltzmann in Boltzmann [21]), the entropy would decrease only for a short time (as Boltzmann accepted). Statistically irreversible quantum-mechanical interactions with the radiation field or rearrangement of the internal quantum states of the colliding particles would slow the entropy decrease after the characteristic path erasure time τ_{PE} of the gas.

We find that quantum mechanics provides the molecular disorder or chaos that Boltzmann and some British physicists (Burbury [22]) 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 maintain the increased entropy in such hypothetical situations.

III. THE CHARACTERISTIC TIME OF ERASURE OF CLASSICAL PATH INFORMATION

The time scale for the erasure of classical microscopic path information τ_{PE} depends on the number of collisions per second and the efficiency of erasure (the cross-section for erasure σ_{PE}). The cross section is highly wavelength and species dependent, reflecting the internal quantum structure of the colliding atoms or molecules. The collision rate depends on the temperature (average particle velocity squared), volume, and pressure (particle density).

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

$$n \approx 2.5 \times 10^{19}/cm^3 \tag{1}$$

From the equipartition theorem,

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

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

$$\bar{v} \approx 5 \times 10^4 cm/s. \tag{3}$$

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

$$l_{mfp} = \frac{1}{n\sigma} \approx 3 \times 10^{-5} cm. \quad (4)$$

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

$$\tau = \frac{l_{mfp}}{\bar{v}} \approx 6 \times 10^{-10} s, \quad (5)$$

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 path erasure time τ_{PE} 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,

$$d = \Delta\theta \cdot l_{mfp}. \quad (6)$$

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,

$$u(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad (7)$$

The number density of photons of frequency ν is therefore

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

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

$$n_\nu = 8 \times 10^{-4} cm^{-3} sec^{-1} \quad (9)$$

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.

$$\frac{P}{A} = \sigma T^4. \quad (10)$$

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 path 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, 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 ($\approx .03eV$) 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 (or molecules) is transferred to the quasi-molecule (conserving total angular momentum), the outgoing paths of the particles are altered indeterministically from the expected classical paths, a third example of irreversible path erasure.

IV. DECOHERENCE AND IRREVERSIBILITY

The "decoherence program" (Zeh [11], Joos and Zeh [23], Joos *et al.* [24], **?**], Tegmark and Wheeler [25]) describes "environmental monitoring" of entangled systems by photons (even cosmic microwave background radiation) as the principal source of decoherence. For coherent systems, the matrix of the density operator contains significant off-diagonal terms. These carry the phase information necessary for interference. In decohering, the "pure state" evolves into a "mixed state" for which the off-diagonal terms can be neglected. Complex probability amplitudes (characteristic of quantum systems) become real probabilities and this constitutes the quantum-to-classical transition, they argue (Joos *et al.* [24]).

These authors, with many colleague scientists (and philosophers of science) who pursue the "foundations of physics," generally deny the indeterministic collapse of the wave function. Following early work of Erwin Schrödinger, David Bohm, and Hugh Everett, they accept Dirac's principle of superposition but deny his "projection postulate" (von Neumann's Process 1). They claim that collapses and "quantum jumps" are only *apparent*. They see collapses as branch points in which the "universal wave function," evolving according to the deterministic Schrödinger equation, divides and creates multiple universes instantaneously. It is "embarrassing that nobody has provided a testable deterministic equation specifying precisely when the mysterious collapse is supposed to occur" (Tegmark and Wheeler [25]).

According to standard quantum mechanics, there are many possibilities of jumping into different eigenstates. The calculated probabiities of such jumps are confirmed with unparalleled accuracy by quantum experiments. One of these eigenstates is selected at random. The new state is actualized or realized, at which moment all those probabilities of the other possible states vanish instantly. The "collapse" of the wave function is nothing more than the vanishing of those abstract (immaterial) probabilities, wherever they previously had non-zero values in configuration space. This Einstein saw as *nonlocal* behavior that might violate his relativity principle, perhaps as early as 1905 (Einstein [26]). In 1909, he saw that the elementary process of radiation emission is not reversible (Einstein [26]).

Nothing irreversible ever happens in a universe evolving deterministically. The total information in the universe is a constant. The present is determined by the past and it completely determines the future. In the absence of radiation, collisions between material particles are microscopically reversible, leading to Loschmidt's claim that if their motions could be instantly reversed, Boltzmann's entropy would decrease. In the absence of matter, there is no interaction between photons that could make a nonequilibrium radiation distribution approach equilibrium. In a perfectly reflecting container (an unrealizable idealization) there is no mechanism for photons to change frequencies.

All this perfect reversibility and determinism disappears when photons interact with material particles, as Einstein was the first to see. The decoherence "foundationists" are correct that radiation interaction can decohere entangled systems. But more importantly, photon interactions can destroy path information, create Boltzmann's molecular disorder, and irreversibly increase the entropy. They are also intimately involved in information-*creating* "measurements," which decrease local entropy at the same time as they increase global entropy.

Dirac and von Neumann described the process of measurement as irreversible. We trace this irreversibility to the elementary process of radiation-matter interactions, which as Einstein first saw was a proces involving pure chance. Even in the "no collapse" deterministic many-worlds interpretation preferred by the "foundationists," is it not still a matter of chance which of the many universes we wind up in after performing a quantum measurement? John Bell thought the many-worlds interpretation to be "extravagant" and the anthropomorphism of universe behavior depending on measurements by scientists (with Ph.D's) to be extreme.

The "decoherence program" finds the two laws for the evolution of quantum systems - the deterministic Schrödinger equation on the one hand ant the indeterministic "collapse" on the other - to be logically inconsistent. They choose to accept and exaggerate the reversible determinism and deny the irreversible indeterminism. We show that the proper view is to calculate the motion of material particles and light quanta with the information-conserving deterministic Schrödinger equation, but when light and matter interact we must calculate with scattering matrices and Hamiltonians that are indeterministic and not conservative.

Even if just one photon in an elementary process erases the path information of a single material particle, it means that the future is not completely determined by the past. The future is not reversible. Unlike the decoherence of "foundationists," this is indeterministic and *irreversible decoherence.*

V. CONCLUSION

Irreversible 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 (or time-reversed past) paths indeterminate. Although the average direction of photons is isotropic, individual photon interactions are not isotropic. They are directed and alter particle paths indeterministically, destroying microscopic molecular velocity correlations. Rearrangement collisions without the emission or absorption of radiation also erase past information. The characteristic time of this path erasure (τ_{PE}) is much longer than Boltzmann's relaxation time (τ_B) for the approach to apparent 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 would only evolve toward lower entropy states for times of order τ_{PE}. Boltzmann knew this intuitively, but could not establish it without a physical basis for his molecular disorder assumption. A physical mechanism for molecular chaos (or a "repeated randomness" assumption) is provided by the erasure of path information during individual collisions. The maintenance of molecular correlations needed for a deterministic, time-reversible microphysics is prevented by path erasure in time scales consistent with observations. Boltzmann's intuition about recurrence has also been shown to be correct in a universe in which both entropy and macroscopic information are increasing. Both the Loschmidt reversibility objection and the Zermelo recurrence objection to Boltzmann's proof of the second law that entropy always increases have been removed.

The indeterministic interactions of matter and radiation are the fundamental source of thermodynamic irreversibility. They also may be involved in other "arrows of time" like the radiation arrow and the cosmological arrow. Decoherence theorists are correct that photons play a critical role, but it is precisely because they cause the irreversible collapse of many possibilites to a single actuality, both in experimental measurements and in the largely unobserved universe.

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