Thermodynamics – the Origin of Irreversibility and Entropy

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To understand the difference between reversibility and irreversibility, and thereby begin to understand entropy, consider a game of pitch and catch on skateboards as illustrated in figure 1. Because there is an exchange of momentum between the ball and the players, the players will ineluctably drift apart. If the game is prolonged, their recessional velocity will eventually exceed their ability to throw the ball fast enough to continue playing.

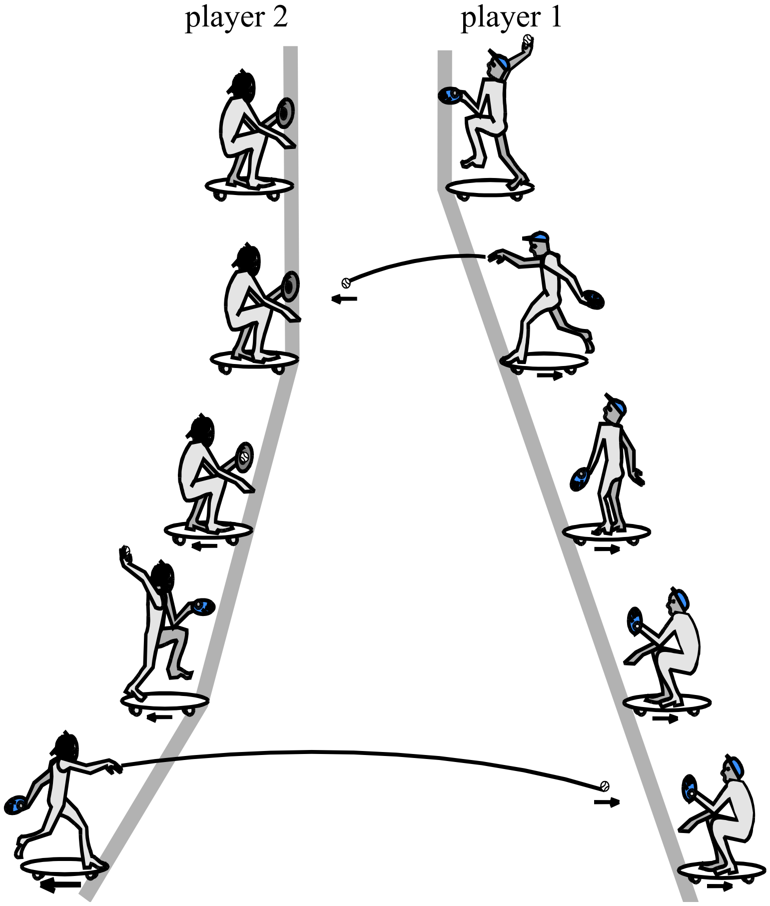

Figure 1: The dynamics of a 'catch' sequence on skateboards

A direct reversal of velocities at any point in the sequence would step by step restore their altered status until they were once again in close proximity with zero relative velocity. Thereafter they would proceed to drift apart again. In short, their interactions are *reversible*. Energy and momentum are conserved whether velocities are reversed or not.

If we add a couple of constraints the situation becomes totally different. Suppose that each player can only throw the ball at precisely 100 feet per second. Further, let us suppose that each player can catch a ball if it is traveling at 100 feet per second or greater but not if it is traveling more slowly. They begin at some separation with approaching relative velocity. Player 1 throws the ball at 100 feet per second relative to himself, but his recoil velocity reduces this velocity slightly. However, if player 2 is approaching at a relative velocity greater than this recoil velocity he can catch the ball, recoiling slightly as he does. This exchange can continue until the sum of their recoil velocities brings them to a relative standstill or to actually receding slightly. At this point it is game over; the ball has become uncatchable because the recoil velocity will reduce the ball's speed for the catcher below 100 feet per second. These rules of engagement make the interactions *irreversible*. By reversing all velocities, we have a situation with a receding relative velocity rather than an approaching one, rendering the ball uncatchable in every case.

background on the impasse in thermodynamics

The word thermodynamics suggests a conjoining of heat with mechanical motions of physical objects. It is a fact, however, that no amount of motion of particles is in itself tantamount to 'heat' as traditionally understood. The motion of particles is *not* uniquely responsible for generating blackbody or even thermal radiation. Such motions are indeed an 'indicator' of internal kinetic energy and in as much as molecules striking walls of containers produce pressure that causes mercury to rise in an old-fashioned thermometer, this energy would be assigned a temperature. But consider: if you were struck by a high-speed particle you would be bruised. If high energy radiation struck you, you would be burned. Heat is more directly associated with radiation than with particles.

Erwin Schrödinger said, for example:

> *"We know all atoms to perform all the time a completely disordered heat motion, which, so to speak, opposes itself to their orderly behavior and does not allow the events that happen between a small number of atoms to enroll themselves according to any recognizable laws. Only in the cooperation of an enormously large number of atoms do statistical laws begin to operate and control the behavior of these assemblies with an accuracy increasing as the number of atoms involved increases. It is in that way that the events acquire truly orderly features."*[1]

This fallacious argument that is shared by many great minds of science, maintains in essence that the scientific reductionist agenda is invalid – that there must indeed be 'emergent' phenomena that pertain only at upper levels of complexity and (importantly) have no counterparts at lower levels of reality. Significant flaws in this argument involve presumptions without supporting evidence or explanation that "completely disordered heat motion" is comprised of something *other than*, and presumably *opposed* and *superior* to, "orderly behavior" associated with "events that happen between a small number of atoms." This has never been established, nor could it be. And furthermore, it totally opposes assumptions of the kinetic theory of gases that most nearly account for a very wide range of related thermodynamic phenomena.

The equipartitioning of energy among various constituents and modes of behavior would be completed to a very high degree with a relatively small number of confined constituent particles. If, in fact, "heat motions" of an ensemble of particles were to constitute a uniquely irreversible behavior pattern counter to the otherwise understood reversible processes in which smaller numbers of atoms "enroll themselves", the statistical treatment of the latter reversible processes could *not* suffice as the explanation of the former. Boltzmann's collision analyses do *not* demonstrate how one distribution of velocities evolves into another no matter how fervently he remonstrated. They demonstrate only that

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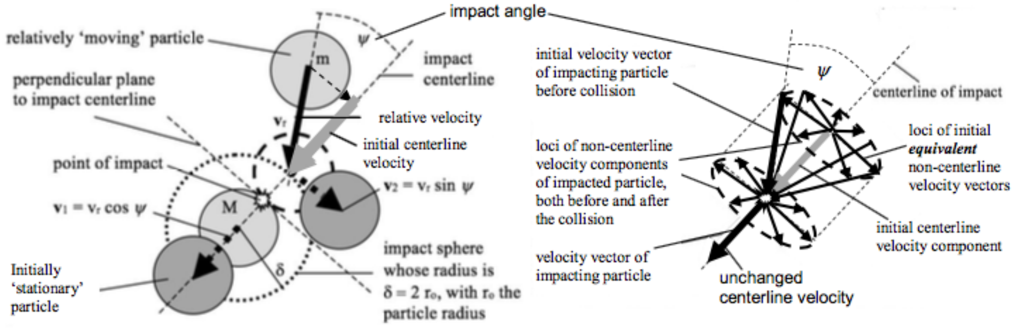
[1] Erwin Schrödinger, ***What is Life?*** Doubleday, New York, 1956. The surrounding dialog was taken from Bonn.

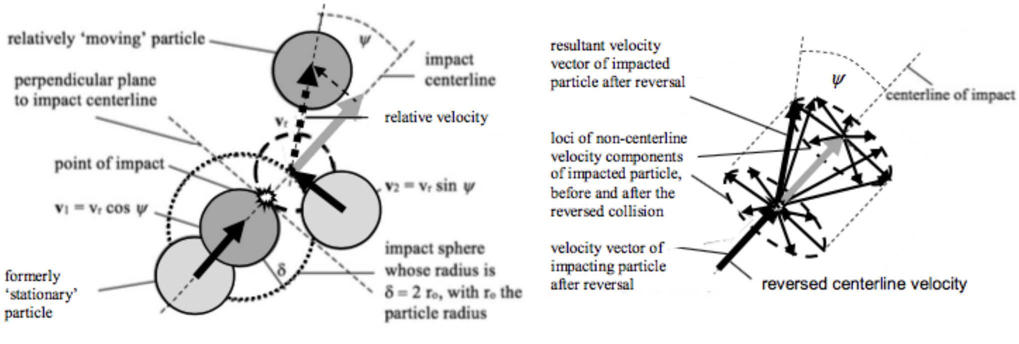
a Maxwell/Boltzmann distribution of particle velocities would be *maintained* by elastic collisions. That is also all that statistical mechanics can legitimately claim. Significantly, statistics most certainly do *not* "operate and control the behavior" of an associated assembly; statistics are merely descriptive with more or less distortion associated with whatever data compression characterizes the statistical approach.

Boltzmann had meaningful achievements, but whether elastic collisions occur or not, it is only the velocities (energy and momentum) of the particles, as Maxwell explained, that determines the equilibrium distribution known as the Maxwell-Boltzmann distribution.

Boltzmann made much of there being two complimentary types of collision to maintain a distribution, one altering the distribution, the other restoring it as shown in panels a and b in figure 2. Certainly, in any ensemble of many particles there would be a high incidence of collision, but what about that (however short) interval following a collision that alters the distribution awaiting the one that will restore it? In point of fact, there is but one kind of elastic (reversible) collision. In panels a and b of figure 2, two physically identical participating particles are shown, an impacting and an impacted particle. In a very significant sense, at whatever velocity or grazing angle such an elastic collision occurs, there will be no change in energy, momentum, or even velocity components. The only change is with regard to which of the two participants possesses the various velocity components before and after collision, which is all that a distribution of velocities demands. So, the distribution itself remains unchanged after every collision. Boltzmann believed he had demonstrated that elastic collisions taking place within an ensemble of particles would suffice to inevitably drive any system to a Maxwell-Boltzmann distribution of velocities (kinetic energies). But he hadn't. Elastic collisions *cannot* drive a system to equilibrium. This was the essence of a criticism by Lochschmidt.



a. Geometry of grazing collisions **c.** Component velocities before and after impact (forward)



b. Collision with velocity reversal **d.** Component velocities before and after impact (reverse)

Figure 2: The inconsequential net result of an elastic (completely reversible) collision

Boltzmann's work did not include radiant energy, so although it is typically stated, as we have seen, that 'heat' is tantamount to the motion of particles, it isn't. Thermodynamics associates 'internal energy' with 'heat' by virtue of the associated pressure against a container wall. This is within the purview of the ideal gas law, PV = nRT that applies only *after* 'inelastic' (irreversible) interactions with radiation have driven the system to equilibrium. It is certainly well-understood that the ideal gas law applies exclusively to thermodynamic systems that are in equilibrium. But how such a system reaches a state of equilibrium is not adequately understood. The fact that only inelastic collisions produce equilibrium is a caveat that too seldom accompanies the claim. Inelastic collisions are only those involving interactions between particulate matter and radiation.

How do particles and photons relate to each other?

The very existence of radiation requires non-elastic collisions of particles. A hydrogen atom, for example, that collides with another hydrogen atom at high enough speed will 'knock off' an electron or at least 'jar it loose', such that it absorbs enough energy to bump it up to a higher internal energy level. In either case some of the excess relative-velocity-related kinetic energy is freed up in loosening attachment of the oppositely charged electron and proton. These will eventually collapse back into lower energy states releasing radiant energy in the process. Or, two colliding atoms will bind together upon contact sharing their electrons to form a stable molecule of H_2, also releasing energy. In all such *inelastic* collisions, the released energy will be in the form of radiation, a different form of energy altogether from the rest mass and kinetic energy of particles. We know it is of a 'different kind' because the relationships between conservation laws of energy and momentum differ for photons of radiation and for particles.

The energy and momentum of a particle *are not* directly proportional to each other. The energy of a photon of radiation on the other hand *is* directly proportional to an analogous expression for momentum associated with that photon. There are dramatic consequences that derive from this very essential difference between the rather flexible energy-momentum relationship of particulate components of a gas and the similar (but more constrained) energy-momentum relationship of radiation associated with that very same gas. The disparity in these relationships is a well-known fact. But those who have tackled related issues have typically continued to be unaccountably oblivious to the role of this essential difference in the context of analyses employed by both Boltzmann (who was understandably unaware of it altogether) and Einstein in developing their respective models of particles and radiation. Incompatibility of energy and momentum relationships introduces stringent additional constraints on conservation principles employed in determining the effects of interactions within thermodynamic systems.

In analyzing these interactions using classical Newtonian mechanics the applicable functional relationship between the conserved kinetic energy $E_k(p)$ and the momentum p of a particle exhibits the following nonlinear (squared) relationship,

$$E_k(p) = p^2 / 2m_o$$

This is shown as the dotted line in figure 3 where m_o is the constant (rest) mass of the submicroscopic particle independent of the particle's velocity.

Einstein's relativity theory demands a revision of these classical formulas for particulate matter with the mass of a particle now dependent on its relative velocity. The relevant relativistic equations become respectively:

$E_T(v) = m(v)\, c^2$, and $p(v) = m(v)\, v$, where

$m(v) = m_o / (1 - v^2 / c^2)^{½}$.

The dynamic mass m(v) depends on its relative motion with respect to the observer for whom the equations apply. The universal constant speed of light is c. So that the kinetic energy of a particle is:

$E_k(v) = E_T (v) - E_{rm} = m(v)\, c^2 - m_o\, c^2 = \sqrt{(p(v))^2 + (m_o\, c^2)^2}\ )$

It is the kinetic portion of the total energy of the particle that results when one subtracts the 'rest mass energy' E_{rm} from the total. Other than for small velocities, we no longer have the direct square relationship between momentum and kinetic energy. The relationship remains nonlinear, but now it is a little more complicated. As can be easily seen, this functionality becomes closer and closer to the linear relationship exhibited by radiation as the relative velocity of a particle becomes closer and closer to that of the speed of light. This is shown as the dark solid line in figure 3.

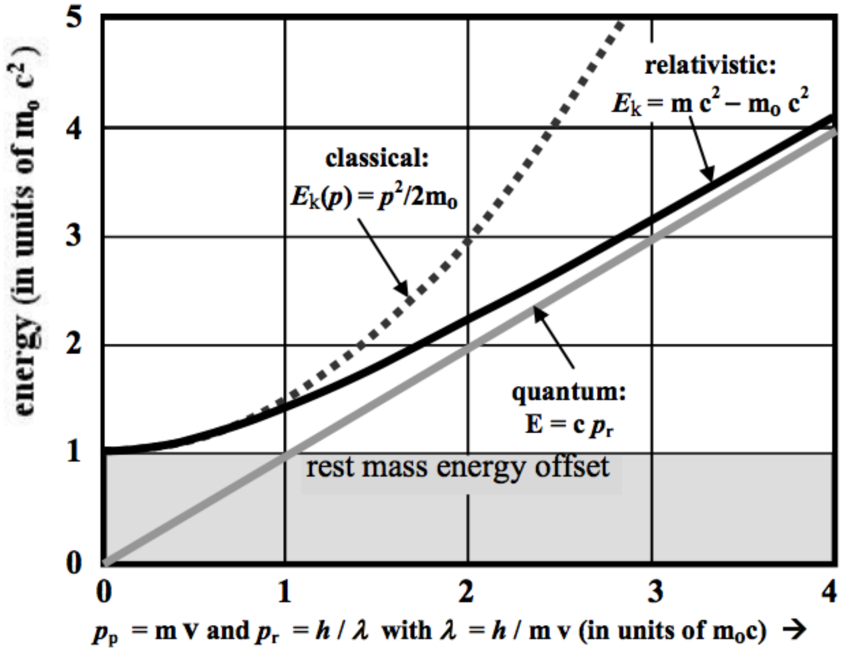


Figure 3: Energy and momentum relationships for particles and photons

The quantum behavior of photons of electromagnetic radiation on the other hand is constrained by an energy-to-momentum relationship that is strictly linear. This is in part because the rest mass of a photon is zero and also because of the wavelength dependence exhibited in the quantum theory of radiation where the commensurate energy and momentum parameters are given by:

$E_T(\lambda) = h\ c / \lambda$ and $p_r(\lambda) = h / \lambda$

Here λ is the wavelength of the radiation and h is Plank's constant. Notice that the frequency ν of such radiation is given by $\nu = c / \lambda$. Thus, photons (unlike their particulate component counterparts) are constrained by a precisely articulated proportionality such that:

$E(p_r) = c\ p_r$

This is shown by a light solid line superimposed on the plots of figure 3. Even for the proper relativistic equations, this differs significantly from the situation that applies to particulate components although, as illustrated, the differences do become much less at extremely high energies.

What is the nature of inelastic collisions?

There is but a single quantum (photon) of radiation released/absorbed by each inelastic collision. A distribution of particle velocities involved in such non-elastic collisions will produce, and be associated with, a separate distribution of radiation frequencies, each released photon stealing energy and momentum from the particulate kinetic energy and momentum of the interacting particles. If the energy distribution of the particles is in equilibrium, i.e., if it is of a Maxwell-Boltzmann form, then the distribution of radiation will also be thermal radiation of the 'blackbody' form with the same *total* energy as the particle kinetic energy 'partition'. ('Partition' applies to the separation of energy types of the various components in a thermodynamic system.) But, although the total energy is the same, the distributions of the energies of the two partitions will be different, very different.

This is where Planck's and Einstein's Quantum Theory of Radiation enters the picture. Non-elastic particle collisions of every kind exhibit quantum levels of radiation absorption and/or emission. The quanta that are emitted and absorbed by particles are indivisible. The precise balance of exchange of quanta is admirably explained in Einstein's seminal paper on that subject.[2] He explained how it all plays together to produce the Planck blackbody spectrum.

The main thrust of Einstein's seminal article is that exchanges of radiation energy between particles are quantized. But he did this without specifically taking into account the relative velocities of the participants. He did, of course, state that the transfer of momentum between particles and radiation results in compatibility between the Maxwell-Boltzmann distribution of kinetic energy of particles and the Planck blackbody distribution of radiant energy. That they are thus intricately linked was clearly demonstrated in the article. However, although he did summarily address the relationship of changes between particle momentum and Doppler changes in wavelength that bridge the gap between distributions, he mysteriously ignored the relativistic formula he had introduced in his earlier work. His

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[2] Albert Einstein, "On the Quantum Theory of Radiation," (originally published in March 3, 1917 exactly one century ago), Sources of Quantum Mechanics, Dover, New York, 1967. (p. 64)

relativistic formula includes the hitherto unprecedented gamma factor producing a transverse Doppler effect over and above whatever recessional effect might also be involved. This ominous omission of not taking his own work into account allowed irreversible interactions at the submicroscopic level of reality to go undiscovered for another century. That discovery is that not all interactions at the submicroscopic level of reality are reversible; in fact, a majority are not. This is where irreversibility and entropy originate.

Although relativistic aberration and Doppler formulas are symmetrical with regard to velocity reversal and all conservation laws would be satisfied by such a reversal, still, there can be no reversibility of the exchange itself. By reversing velocities, we would have two molecules that had been approaching each other now receding from each other. Receding molecules cannot (without coincidental shifting to another *different* discrete energy level) exchange quantized photons because the quantum restriction would be compromised by the Doppler shift. This is directly analogous to our brief analysis pertaining to figure 1. Both of the phenomena that affect the constraint on the energy and momentum involved in a photon exchange had been identified by Einstein earlier in his career. Of course, this constraint does not mean that the original interaction is precluded or that there are not similar (although certainly not precisely *reversed*) interactions that can proceed in the *opposite* direction, but those interactions would involve different participants. Thus – counter to virtually every commentary to the contrary – reversibility does *not* occur on all (or in fact *any*) interactions mediated by photons at the submicroscopic level of reality. Despite centuries of avowals that all interactions at the submicroscopic level are reversible, irreversibility and thus entropy originate at this lowest level as adamant reductionists have always insisted they must.

Why are the interactions that are mediated by photons irreversible?

With the introduction of Einstein's special theory of relativity, the expectations for the Doppler Effect on radiation changed. Einstein's second postulate, that the velocity of light is the same for all observers (and thus for all absorbers of radiation) independent of their relative motion with regard to the source of that radiation in a vacuum, required a different explanation of observed phenomena. That explanation, like most of what follows in Einstein's theory of relativity can be simply derived from the applicable Lorentz transformation equations. Thus, a revised Doppler formula came into being:

$\lambda' = \lambda \gamma (1 - v/c \cos \theta)$, with: $\gamma = 1 / (1 - v^2 /c^2)^{1/2}$

The additional 'gamma factor' contributes very little to the effect unless the relative velocity v of the source with regard to the observer is significant with respect to the speed of light, a caveat very seldom applicable to mundane interactions. However, when relative velocities are large the effect of this factor becomes appreciable. Refer to figure 4 where the magnitude of the Doppler Effect is illustrated for both the classical and relativistic formulas.

Clearly, when there are interactions between molecules whose relative velocities are not aligned with the centerline, there is an additional effect on interactions that must be taken into account. As illustrated in figures 4, when $\theta = \pi/2$ there is a change in wavelength even where none had previously been predicted by the classical formula. A transverse Doppler effect has to be taken into account. Since it is a second order effect in v/c it is extremely small in virtually every situation of interacting molecules with temperatures that are typically realized. However small in any particular instance, the effect modifies the results of every interaction and thereby contributes to irreversibility as we will see.

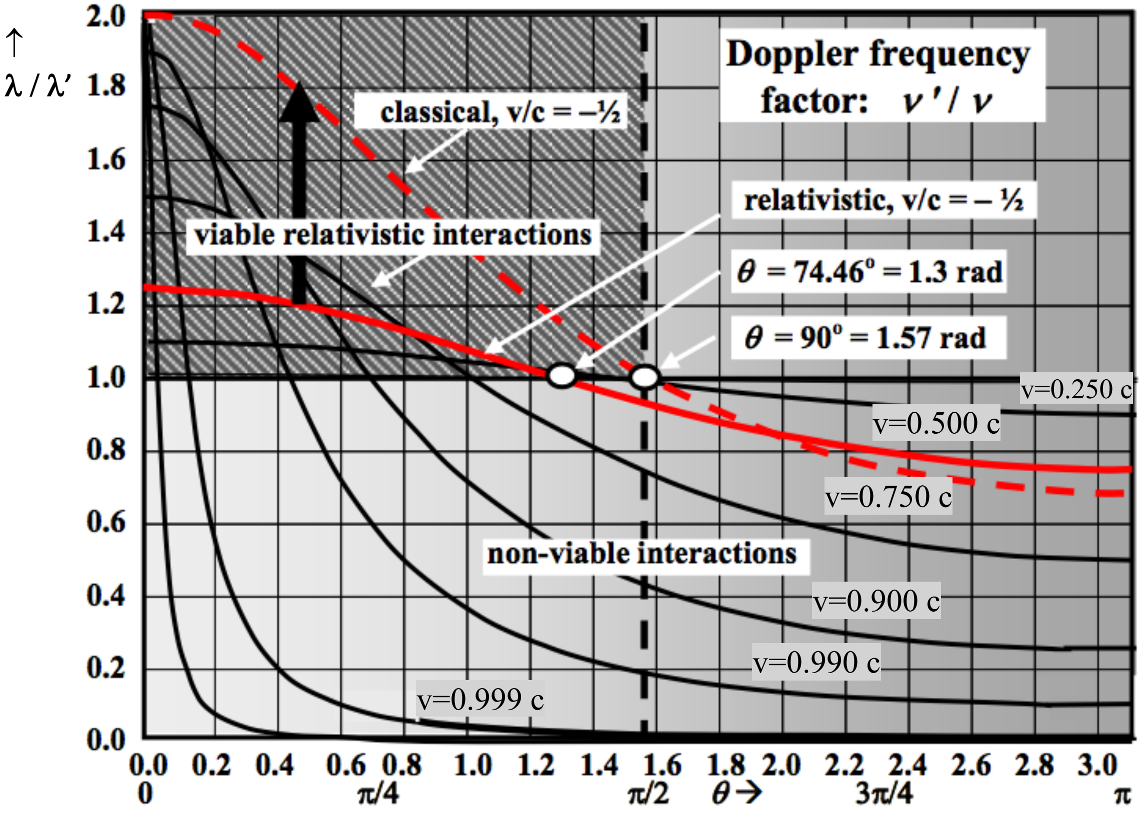


Figure 4: Doppler wavelength factor in classical and relativistic physics

Furthermore, in addition to the issue of transverse Doppler, there are the ever-present quantum effects that constrain molecular interactions due to the photoelectric effect. Among Albert Einstein's major discoveries during the first decade of the 20th century, the photoelectric effect is of particular interest here. It was significant to the acceptance that light transmission involves discreet quanta of energy, or 'photons' as G. N. Lewis would first denominate them in 1926. The significance of the discovery was that matter can only absorb entire photons of electromagnetic energy. This imposes an additional constraint on interactions such that: if a photon of a given frequency (energy) is emitted by one molecule, a similar molecule in relative motion can only absorb that photon if its relative velocity is such that the photon has enough energy (in the absorbing molecule's frame of reference) to raise the internal molecular energy to a next discrete quantum level. This constraint is so severe that it actually precludes at least half of all otherwise-allowed interactions from even occurring.

If the ratio λ / λ' is less than unity (i.e., the molecules are receding from each other), then there is insufficient energy in the redshifted photon for the receding molecule to be able to absorb it and therefore no interaction results. What this means in essence is that interactions cannot occur between molecules that are receding from each other. In fact, for an appreciable relative velocity no interaction will occur unless it is initiated well in advance of the time at which the molecules are at their closest approach. In figure 4 that is indicated by the angle at which $\lambda / \lambda' = 1.0$. So, the quantum-relativistic criterion for even the possibility of interaction is $1.0 \geq \lambda / \lambda'$ which results in the following:

$$0 \geq \cos\theta \geq (1 - (1 - v^2 /c^2)^{1/2}) / (v/c) \approx \tfrac{1}{2}\, v/c$$

The interactions for which the relative velocity and angle of approach are compatible with this constraint are only those shown in the upper left quadrant of the plot in figure 4. Solid curves all represent the relativistic formula for approach velocities. For direct comparison, a plot using the Doppler formula of classical physics is shown for $v = c / 2$ as the dashed curve in the figure. All curves for the classical non-relativistic formula cross the abscissa at $\theta = \pi/2$. Using a correct relativistic Doppler formula, this is only precisely true for $v = 0$.

In all situations, whether molecules can absorb radiation is determined by quantum theory. But this is complicated by relativistic Doppler phenomena. Together they impose severe constraints that preclude reversibility because, if one reverses velocities of approaching particles, the fact that they will then be receding from each other precludes interaction. Molecules that are receding from each other have passed their window of opportunity for interaction. We are now equipped to determine combinations of angles, distances, and relative velocities that can at least accommodate mediated particle/radiation interactions. From this vantage, we can assess the possibility of viable interactions as illustrated in figure 5.

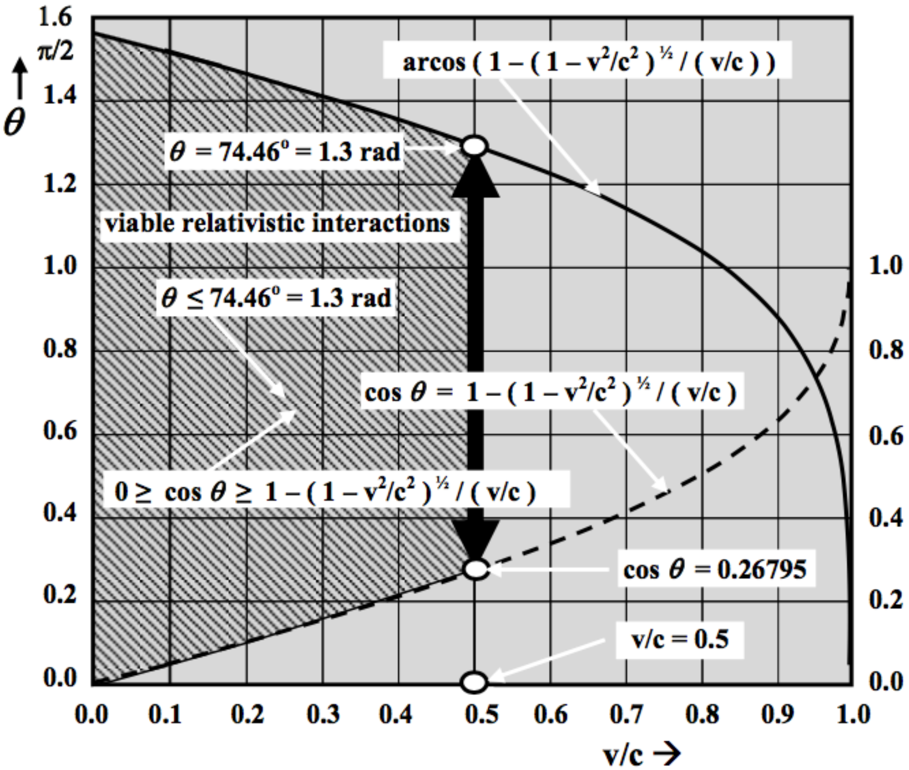
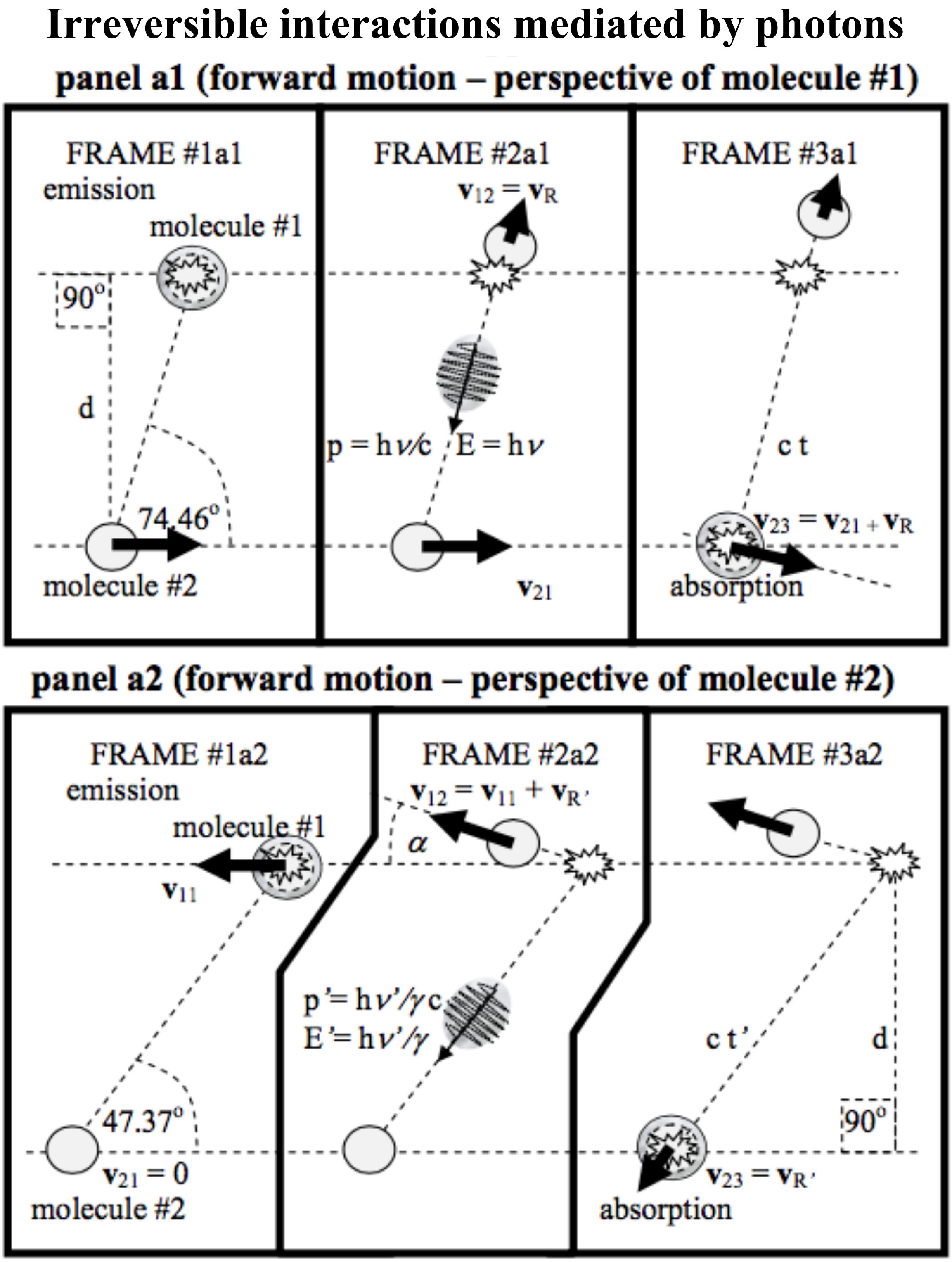


Figure 5: Domain of allowed molecular interactions in relativistic physics

In figure 6 we have illustrated a viable interaction mediated by a photon exchange. It is viable from both participant perspectives, but unlike the elastic interactions illustrated in figures 3.a and 3.b this interaction cannot be reversed. By reversing velocities the viability of interaction is eliminated.



Irreversible interactions mediated by photons

panel a1 (forward motion – perspective of molecule #1)

panel a2 (forward motion – perspective of molecule #2)

Figure 6: A consequential asymmetry in mediated particle interactions

Thermodynamic calculations can only be performed for systems at or near equilibrium. Boltzmann and Einstein failed to identify mechanisms by which thermodynamic systems are driven to equilibrium. At equilibrium extreme component energies are reduced and the amount of internal energy available to do work is thereby reduced as well even though the total amount of energy is conserved. But they both identified mechanisms that maintain the status quo of a system in equilibrium, with Einstein identifying how distributions in each partition (particles and radiation) are synchronized by exchanges of momentum.

conclusions with regard to irreversibility and entropy

Far from being elusive phenomena that emerge out of nowhere once systems become so complex that accountability is lost, irreversibility and entropy originate right before our eyes in the interactions between as few as two interacting particles. Boltzmann believed his analyses of elastic collisions had demonstrated an ineluctable trend toward equilibrium and a Maxwell distribution of velocities (energies). He was wrong. What he had shown was that elastic collisions would maintain the status quo for whatever distribution had already been established. Had he employed his previous discoveries, Einstein could have demonstrated a century ago that the exchange of photons between particles will eventually drive a thermodynamic system to equilibrium and the Maxwell-Boltzmann distribution of energy. Of course, what he did demonstrate was that when these exchanges occur in a thermodynamic system in equilibrium, the Plank blackbody distribution of photon energy is compatible with a Maxwell-Boltzmann distribution of particulate energy. But exchanges occur whether a system is in equilibrium or not, and these mediated interactions provide the thermalization whose intricacies have not been given the attention they most certainly deserve.

The fact that every interaction mediated by a photon exchange is irreversible produces the fundamental property of thermodynamic systems in equilibrium – the stabilization of particle velocities (energies). Every photon exchange reduces the relative velocity of the two participants of the exchange.

A thermodynamic system of gases in equilibrium cannot perform work. When it is heated or compressed, as in a steam (or combustion) engine it *can* do work, but in that process, extremes of velocities that drive pistons are eventually reduced beyond usefulness. There is no internal process whereby a thermodynamic system can restore capabilities of performing work once a Maxwell-Boltzmann distribution of energies has been achieved. The capability to do work must always come from an infusion of energy from outside a thermodynamic system in equilibrium – and some of it will not be productive.

Entropy cannot be adequately explained by probability analyses, as for example the misguided claim that the likelihood of all the molecules in a room converging to one corner of that room being so small that one can for all practical purposes just ignore the possibility. No! That is physically impossible, not just improbable. The conservation of momentum would be violated if all the molecules in a room suddenly (for however short a period of time) were to converge to one corner. That is not the universe we live in. The actual cause of irreversibility and entropy is not emergent and 'mysterious heat motions' of particles once individual accountability has been lost; it is in each and every interaction mediated by a photon.