

Article

Irreversibility as Thermodynamic Time

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Abstract: In Newtonian mechanics, time as well as space are perceived as absolute entities. In Einstein's special relativity, time is frame dependent. Time is also affected by gravitational field and as the field varies in space, time also varies throughout space. In the present article, a thermodynamic-based time is investigated. The entity is called "irreversibility", which is generated when availability (also known as exergy) is destroyed. Since each thermodynamic system may generate different amount of irreversibility, this quantity is system dependent. The time's arrow is automatically satisfied, since irreversibility generation always proceeds in one direction (toward future). We have demonstrated that, like common time, irreversibility is frame dependent, and affected by gravity in the similar manner as the common time. For this reason, we propose to assign the entity *irreversibility* of the system as thermodynamic time. A possible application of the thermodynamic time is an interpretation and managing of the aging of biological systems. The metabolic efficiency is related to the irreversibility of the chemical processes and affect the aging of the system. Our sensation of time-flow may be attributed to the flow of availability and destruction of it through the living system. It is shown by other authors that entropy generation (equivalent to irreversibility) is a parameter for the human life span. Since the thermodynamic time is based on a concept of thermodynamics that is universal, further applications to other subjects, such as biological clock, telomere, and cosmology are possible.

Keywords: time; availability; irreversibility; time dilation; biological clock; metabolic efficiency; telomere; mitochondria

1. Introduction

1.1. Time in classical mechanics

In Newtonian mechanics, the time in the universe is fixed regardless of location or epoch [1–4]. This means that all events can be regarded as having a distinct and definite position in space and occur at a particular moment of time. Time as one perceives is absolute and seems to flow steadily and uniformly regardless of anything external. This moment of time is taken to be the same for observers everywhere in the universe. Time is un-stretchable quantity, in terms of which, change in the whole universe could be uniquely described. The theory constructs a deterministic set of mathematical relations that allow prediction of the *future* and *past* behaviors of moving objects. All that one needs in order to do this are data in the *present* regarding these moving objects. The equation of motion in Newtonian mechanics, symmetry is maintained with respect to translation in time and reversal of time. This view held for more than 200 years because it appealed to our intuition. In analyses of most problems in physics and engineering, the Newtonian mechanics is employed as a good approximation.

1.2. Time in relativity theory

Einstein changed Newton's idea totally. In his special and general theories of relativity, time is stretchable and varied from place to place. Einstein's mechanics indicates that the time passages for two individuals moving relative to one another, or experiencing a gravitational field, are different [1,2,5–7]. These theories finally break Newtonian mechanics' rigid conception, though the flexibility of time passage becomes apparent only at high speeds or in strong gravitational fields.

Special relativity is based on the following postulates:

1. The law of physics are same in all inertial reference frames.
2. The speed of light is invariant to all observers in inertial frames.
3. Uniform motion is invariant to all inertial frames.

In the following subsections, the rates of clocks differ (1) on moving frames with a constant relative velocity and (2) on uniform gravity fields with different strength. In later Sections, it will be shown that a thermodynamic quantity *irreversibility*, \mathcal{I} , behaves like time.

1.2.1. Rates of Clocks in Standard Configuration [8]

In special relativity the Lorentz transformation equations for the primed and unprimed variables in *standard configuration*¹ are:

$$x' = \gamma(v)(x - vt), \quad (1)$$

$$y' = y, \quad (2)$$

$$z' = z, \quad (3)$$

$$t' = \gamma(v)(t - vx/c^2), \quad (4)$$

where $\gamma(v) = 1/\sqrt{1 - \beta^2}$ and $\beta = v/c$. The inverse of the last equation can be written as

$$t = \gamma(v)(t' + vx'/c^2). \quad (5)$$

Consider two inertial frames F and F' in standard configuration. The frame F' moves at velocity v relative to the frame F along the x -axis. Consider a clock at rest in F' . Let two events, 1 and 2, which occur at the same point $x'_2 = x'_1$ in F' , indicated by the interval as $\Delta t' = t'_2 - t'_1$. Substituting these values in equation (5) yields

$$\Delta t' = \Delta t \sqrt{1 - \beta^2}, \quad (6)$$

where $\Delta t = t_2 - t_1$. Observers in F observe that the moving clock is running slow. This effect, *time dilation*, is reciprocal. That is, if a clock is at rest in F , observers in F' find that it runs slow as compared with clocks at rest in their frame. The difference in the rates of two clocks is calculated next.

$$\Delta t' = \Delta t \sqrt{1 - \beta^2} = \Delta t - \left(1 - \sqrt{1 - \beta^2}\right) \Delta t,$$

$$\begin{aligned} \Delta t - \Delta t' &= \left(1 - \sqrt{1 - \beta^2}\right) \Delta t \\ &\simeq \frac{1}{2} \frac{v^2}{c^2} \Delta t, \end{aligned} \quad (7)$$

neglecting magnitude of fourth and higher order. [6] If $v = 10$ m/s, $1/2(v^2/c^2) = 5.563 \times 10^{-16}$, showing that the time dilation is very small with low velocity v .

¹ Imagine that two rigid reference frames F and F' are in uniform relative motion with velocity v . For both frames, identical units of length and time are used. Their time t, t' and their Cartesian coordinates x, y, z and x', y', z' form the coordinate systems $F : \{x, y, z, t\}$ and $F' : \{x', y', z', t'\}$. The systems are said to be in *standard configuration*, if they are arranged in the following way. The origin of F' -frame moves with velocity v along the x -axis of F , the x' -axis coincides with x -axis, while the y - and y' -axes remain parallel, so do the z - and z' -axes; and all clocks are set to zero when the two origins meet.

1.2.2. Rates of Clocks in Gravitational Field

In a uniform gravity field, a clock h sitting on a high shelf will run faster than a clock ℓ on the floor. If clock h is the emitter of light with frequency ω_h and clock ℓ is the receiver, Feynman [5] finds the frequency at the receiver as follows. A photon of frequency ω_h has energy $\varepsilon_h = \hbar\omega_h$. Since emitted energy ε_h has the gravitational mass ε_h/c^2 the photon has a mass $\hbar\omega_h/c^2$, and is attracted by the earth. In falling the distance $H = H_h - H_\ell$ it gains an additional energy $(\hbar\omega_h/c^2)gH$, so it arrives at the receiver with the energy

$$\varepsilon_\ell = \hbar\omega_\ell = \hbar\omega_h \left(1 + \frac{gH}{c^2}\right).$$

Rewriting

$$(\text{Rate at the receiver } \omega_\ell) = (\text{Rate of emission } \omega_h) \left(1 + \frac{gH}{c^2}\right), \quad (8)$$

If we write the Equation in terms of the time rate

$$\frac{1}{\Delta t_\ell} = \frac{1}{\Delta t_h} \left(1 + \frac{gH}{c^2}\right),$$

or

$$\frac{\Delta t_h}{\Delta t_\ell} = 1 + \frac{gH}{c^2}. \quad (9)$$

For $H = 20$ m, $gH/c^2 = 2.182 \times 10^{-15}$, that is for an altitude difference of 20 meters at the earth's surface, the time difference, $\Delta t_h - \Delta t_\ell$, is only about two parts in 10^{15} . Note that the quantity gH/c^2 is non-dimensional.

1.3. Various Aspects of Time

Eddington had the following view on motion and time. [9] Motion is generally recognized by the disappearance of particle at one point of space and the appearance of apparently identical particle at a neighboring point. The kinematical conception of motion implies change – disappearance at one point and reappearance at another point – but no change is detectable. Note that acceleration is not defined as change of velocity; it is an independent entity

Misner et al. stated that "Time is defined so that motion looks simple". [10] According to this definition, the 'time' is introduced as a tool so that the time coordinate of a local Lorentz frame is so defined that motion looks simple. Thus, "time" is treated merely as a parameter following the change of state of a system in a process; any other perceived characteristics of time, such as time flow, or asymmetry of time have been ignored.

Barbour and Rovelli [11,12] argued that time had no role to play as an independent element of reality. Callender [3] cited examples of time emerging from timelessness. Smolin [13,14] maintained the existence of time. There is a notion referred to as block time. The time does not flow at all, but is laid out in its entirety. It is a timescape, analogous to a landscape, with all past and future events located there together.

Whitehead says "There is time because there are happenings, and apart from these happenings there is nothing." [15] Here a "happening" is not sharply defined; but it is more like a moment which has an inner structure of its own. Each moment contains both the memories of the past with the potentialities for future development.

Measuring time using devices other than clocks is nothing new. In *Stitches in Time* [16], Stromberg describes a technique to date silk based on its chemical composition. Silk proteins are made of amino acids. Each amino acid has two possible variants: left-handed, known as "L" amino acids, and right-handed, referred to as "D". The amino acids produced by most living systems – like silkworms – are left-handed. As silk proteins age, some of the amino acids rearrange themselves into the D variant.

By looking at the ratio of D to L amino acids in a silk thread, the age of the thread can be determined. Although a calibration process may be involved, the dating can be accomplished in principle.

In both Newtonian and Einstein mechanics, the time passage is symmetric. The dynamical equations is symmetrical under a reversal of the direction of time. What we are conscious of is a memory of the past tinged with an expectation of the future [17]. Once the occurrence of an event has passed, the event has become a memory and cannot be repeated or corrected. In the words of Bohm [18]: "Although the present is, it cannot be specified in words or thought without slipping into the past." Penrose [19] stated that central to our feeling of awareness is the sensation of the progression of time. The future is an un-trailed territory that is hidden behind a mist. Because of this unknown nature of the future, stock market, lottery, and insurance, etc. can have their businesses.² Our experience shows that time is asymmetric to the past and the future, and analogous to the flight of an arrow. This means that if we arrange events in chronological order along an axis, the time appears to be asymmetric with respect to the axis. This also means that the events are irreversible; the events cannot be played back as a movie playing backward.

The physical basis of the direction of time has been discussed by many authors [2,20–26]. There appears to have arrow of time of different origins: the thermodynamic arrow of time, psychological arrow of time, the arrow of time of retarded electromagnetic radiation, cosmological time asymmetry, and others. It is observed that most of the processes occurring in the universe follow macroscopic thermodynamic laws. Exceptions are some quantum mechanical processes that involve a small number of particles.

Good examples showing the asymmetry of time are biological systems. All biological systems are subject to continuous irreversible changes through their entire lives. There is a type of people called *progerin* who grows much faster than ordinary people. This indicates that time passage depends on individual systems.

Sarlis introduced natural time which may reveal properties that are usually hidden when studying the system in conventional time. [27] An entropy has been defined, and complexity measures based on this entropy, as well as its value under time reversal has been introduced and found applications in various complex systems. Martyushev and Shaiapin consider advantages of the measure of time based on the entropy change under irreversible process. [28] This measure of time proves to be nonlinearly related to reference measure assumed uniform by convention.

According to the Copenhagen interpretation of quantum mechanics, quantum evolution is governed by the Schrödinger equation, which is time symmetric, and by wave function collapse, which is time irreversible. Despite the post-measurement state being entirely stochastic in formulation of quantum mechanics, a link to the thermodynamic arrow has been proposed. Thus, the modern physical view of wave function collapse, the quantum de-coherence, the quantum arrow of time is a consequence of the thermodynamic arrow of time. [25]

Based on the foregoing description involving the evolution and the nature of time, we list various aspects of time as follows:

1. Time is asymmetrical with respect to the event axis (world line). This is commonly called the arrow of time.
2. One suspects that the arrow of time is somehow connected to the principle of entropy increase for the system. The entropy of an isolated system may supply the direction of time, because it increases as the system experiences a change of state. However, this principle is for an isolated system, and the system in question is in general not isolated.
3. Time is frame-dependent and field-dependent; every system has its own clock with its own time. Within a star with a strong gravitational field, the rate of a clock can vary from point to point. This is evident from the theory of relativity.

² Based on speculation, sheer guess, or prediction.

Time can be abstracted from change [29], which may be motion or other measures. The examples given in the previous paragraphs use change in entropy. The present article investigates the feasibility of describing other changes, or going further in assigning a quantity as time itself. The proposed quantity is *irreversibility*, which is the destruction of availability (exergy). This is described in the following Sections.

2. Availability and Irreversibility

The concept of availability is based on the macroscopic and phenomenological character of thermodynamics [30–32]. The conservation of energy for a control mass can be expressed as [31,33]

$$dE = \delta Q - \delta W. \quad (10)$$

The entropy equation can be written as

$$dS = \frac{\delta Q}{T} + \delta\sigma, \quad (11)$$

where σ is *entropy production* which can be stated as:

$\delta\sigma > 0$ internally irreversible process,

$\delta\sigma = 0$ internally reversible process,

$\delta\sigma < 0$ impossible process.

A quantity *availability* (also called exergy, work potential, *Arbeitsfähigkeit*) has been used by engineers to assess the maximum work that can be obtained for a combined system, closed or open, in a given environmental condition. It is known that all macro-processes are irreversible, and the availability is destroyed. The destruction of availability is called *irreversibility*.

2.1. Availability of Closed Systems

If the state of a thermodynamic system departs from that of the environment, an opportunity exists for developing work. For a combined system of a control mass (closed system) plus the environment, the work W_c for the combined system is given by [31]

$$W_c = (E - U_0) + p_0(V - V_0) - T_0(S - S_0) - T_0\sigma_c. \quad (12)$$

Since $T_0\sigma_c$ is positive when irreversibilities are present and vanishes in the limiting case where there are no irreversibilities, the maximum theoretical value for W_c is obtained by setting $T_0\sigma_c$ to zero in Eq. (12):

$$\mathcal{A} = W_{c, \max} = (E - U_0) + p_0(V - V_0) - T_0(S - S_0). \quad (13)$$

The function \mathcal{A} is called *availability* for the control mass. To sum up, the availability is defined as the maximum theoretical useful work obtained if a system is brought into thermodynamic equilibrium with the environment by means of processes in which the system interacts with this environment [34]. In the general case, a control mass may experience both heat and work interactions with other systems, not necessarily including the environment, and there is some availability destruction within it during such interactions.

$$\Delta\mathcal{A} = \int_1^2 \left(1 - \frac{T_0}{T_b}\right) \delta Q - (W - p_0\Delta V) - \mathcal{I}, \quad (14)$$

heat transfer work interaction irreversibility

where $\Delta\mathcal{A} = \Delta E + p_0\Delta V - T_0\Delta S$. The term irreversibility $\mathcal{I} (= T_0\sigma)$ accounts for the destruction of availability due to irreversible processes within the control mass.

2.2. Flow Availability [31,34]

Including heat transfer and matter flow at the boundary surface (open system), the "rate equation" for availability can be written as

$$\dot{\mathcal{A}}_{cv} = \int_a \left(1 - \frac{T_0}{T_b}\right) q_s'' da - \left(\dot{W}_{cv} - p_0 \frac{V_{cv}}{dt}\right) + \sum_i \dot{m}_i a_{fi} + \sum_e \dot{m}_e a_{fe} - \dot{\mathcal{I}}, \quad (15)$$

where the flow availability is expressed per unit mass basis:

$$a_f = (h - h_0) + \frac{v^2 - v_0^2}{2} + g(z - z_0) - T_0(s - s_0) + \sum_{i=1}^k y_i (\mu_{i0} - \mu_i^0),$$

where y_i and μ_i are mass fraction and the chemical potential of i -species (per unit mass). The kinetic and potential energy terms are included in the equation. It may be noted that Equation (15) is a general case of Equation (14).

3. Special Features of Irreversibility

We proceed to describe the time-like behavior of the irreversibility in this section.

3.1. Irreversibility and Frame Dependence

We shall demonstrate that the irreversibility \mathcal{I} is frame dependent, similar to common time used in science. Planck and Einstein considered thermodynamic systems which are in the *standard configuration*. [33,35] First, we note that irreversibility can be expressed as $\mathcal{I} = T_0\sigma$. [31] In the standard configuration of frame F and frame F' , the quantities T_0 and σ are related by the following equations (page 159, Tolman). [33]

$$\gamma(v)T_{0F'} = T_{0F} \quad (16)$$

$$\sigma_{F'} = \sigma_F \quad (17)$$

Then

$$\frac{\mathcal{I}_{F'}}{\mathcal{I}_F} = \frac{T_{0F'}\sigma_{F'}}{T_{0F}\sigma_F} = \frac{T_{0F}\sigma_{F'}}{\gamma(v)T_{0F}\sigma_F} = \sqrt{1 - \frac{v^2}{c^2}} \quad (18)$$

$$\mathcal{I}_{F'} = \sqrt{1 - \frac{v^2}{c^2}} \mathcal{I}_F \text{ implies } \mathcal{I}_{F'} < \mathcal{I}_F$$

The difference in value is

$$\begin{aligned} \mathcal{I}_F - \mathcal{I}_{F'} &= \mathcal{I}_F - \sqrt{1 - \frac{v^2}{c^2}} \mathcal{I}_{F'} \\ &= \mathcal{I}_F \left[1 - \sqrt{1 - \frac{v^2}{c^2}} \right] \\ &\simeq \frac{1}{2} \frac{v^2}{c^2} \mathcal{I}_F, \end{aligned} \quad (19)$$

neglecting magnitude of fourth and higher order. Comparing this result with Equation (7), we see that "time" and irreversibility behave similarly. i.e.,

$$\frac{\Delta t'}{\Delta t} = 1 - \frac{1}{2} \frac{v^2}{c^2} = \frac{\mathcal{I}_{F'}}{\mathcal{I}_F} \quad (20)$$

3.2. Irreversibility in a Gravitational Field

In this section, we analyze the effects of a gravitation field on the value of irreversibility \mathcal{I} . The objective is to compare the result of this thought experiment with the gravitational field on 'time' as described in Section 1.2.2.

We consider the irreversibility of a system with mass m as it is lowered from height $z = H_h$ to height $z = 0$ (datum). Equation (14) will be used. This process has no heat transfer δQ , no work W , no change in the volume ΔV , and no entropy change ΔS , so that

$$\Delta \mathcal{A} = -\mathcal{I} \text{ or } \mathcal{I} = -\Delta \mathcal{A}$$

This implies that during the process, availability is destroyed. The kinetic energy is not considered, so that E consists of internal energy U and potential energy mgz . For the process $h = h \rightarrow 0$

$$\begin{aligned} \mathcal{I}_h &= -\Delta E_h \\ &= -(E_0 - E_h) \\ &= -[(U_0 + 0) - (U_h + mgH_h)] \\ &= mgH_h, \end{aligned} \quad (21)$$

assuming $U_h = U_0$ (mainly a function of T). Next, we consider the irreversibility of the same system which is lowered from height $z = H_\ell$ to the height $z = 0$, where $H_\ell < H_h$. For the process $\ell = \ell \rightarrow 0$, we have

$$\begin{aligned} \mathcal{I}_\ell &= -\Delta E_\ell \\ &= -(E_0 - E_\ell) \\ &= -[(U_0 + 0) - (U_\ell + mgH_\ell)] \\ &= mgH_\ell, \end{aligned} \quad (22)$$

assuming again $U_\ell = U_0$. The irreversibility of lowering the system from H_h to H_ℓ is

$$\mathcal{I}_h - \mathcal{I}_\ell = mgH_h - mgH_\ell = mg(H_h - H_\ell) = mgH.$$

Next, dividing both sides by \mathcal{I}_ℓ yields

$$\frac{\mathcal{I}_h - \mathcal{I}_\ell}{\mathcal{I}_\ell} = \frac{\mathcal{I}_h}{\mathcal{I}_\ell} - 1 = \frac{mgH}{mgH_\ell} = \frac{mgH}{E_\ell - E_0} \approx \frac{gH}{c^2}, \quad (23)$$

where we make approximation $E_\ell - E_0 \approx E_\ell \approx mc^2$, and finally obtain

$$\frac{\mathcal{I}_h}{\mathcal{I}_\ell} \approx 1 + \frac{gH}{c^2} \quad (24)$$

Comparing Equation (24) with Equation (9), we observe the similarity between time and irreversibility in the presence of gravity field, i.e.,

$$\frac{\Delta t_h}{\Delta t_\ell} = 1 + \frac{gH}{c^2} \approx \frac{\mathcal{I}_h}{\mathcal{I}_\ell}. \quad (25)$$

3.3. Irreversibility as Thermodynamic Time

The entity *irreversibility* \mathcal{I} possesses the following characteristics:

1. The entity \mathcal{I} is always positive and zero in the limit. The notion of irreversibility presupposes "time's arrow", because the direction of the process is always in the direction towards future.
2. The entity is associated with a system and can be defined for either a closed or an open system.

3. The entity is the destruction of availability which represents the maximum possible work for the given system plus the environment.
4. The entity has the dimension of energy. The energy we are dealing with here is not conserved and is availability destruction.
5. The entity is frame dependent in the similar manner as "time" in two moving inertial frames. Here, we compare $\mathcal{S}_F > \mathcal{S}_{F'}$ in Equation (19) with Equation (7) which gives $\Delta t > \Delta t'$. The similarity between the expressions for Δt and \mathcal{S} are identical as shown by Equation (20).
6. The entity is affected by a gravity field in the similar manner as time. For systems lowering from different heights in a gravitational field, Equation (24) shows $\mathcal{S}_h > \mathcal{S}_\ell$. We compare this with Equation(9), which gives $\Delta t_h > \Delta t_\ell$, and again we find the identical expressions between Δt and \mathcal{S} as shown by Equation (25).

Based on the forgoing similarity of \mathcal{S} and Δt , we propose to use \mathcal{S} as a "thermodynamic measure" of time. We may envision that as availability destruction of a system takes place, the conditions in the system changes, and this change is the "time" for the system. Since irreversibility is a macroscopic measure of the system, the irreversibility is a macroscopic entity. Because of its macroscopic nature, this entity does not exist in quantum mechanics.

4. Irreversibility of Various Systems

Once the thermodynamic time \mathcal{S} is defined, we may want to find where it is operating. A thermodynamic system may be closed or open, biological or inanimate. The systems interact with its environment, and in the process destroy availability and generate irreversibility (or entropy because $\mathcal{S} = T_0\sigma$). This signifies as degradation of the useful energy of the system, and we have interpreted this as the passage of time for the system, i.e., the system possesses its own time.

For inanimate systems, irreversibility can also be generated. This includes oxidation, erosion, or heat transfer. Since thermodynamic time is a function of irreversibility production, some lifeless systems like diamond or gold, which produce only small amount of irreversibility, have slow thermodynamic time. This implies that time proceeds slowly for these systems.

4.1. Irreversibility Generation

4.1.1. Energy Management

In biological systems, a living cell is an open system with continuous energy and matter interactions with the environment, and operating away from equilibrium as an organized and dissipative structure. [36] Every developed and adapted biological system extracts useful energy from outside, converts, stores it, and uses for muscular contraction, substrate transport, protein synthesis, and other energy utilizing processes. This energy management in a living cell is called the bio-energetics, and the useful energy is the availability, which is destroyed in every irreversible process because of the entropy production. Mitochondria in a living cell contain the inner and outer membranes made of bilayers, which may influence the coupling and local gradients of ions, molecules, and macromolecules in the regulation of energy metabolism. [37] The energy source for the phosphorylation (OP) is the oxidation of reducing equivalents of nutrients via the respiratory chain. The converted availability is the adenosine triphosphate (ATP) produced through the oxidative phosphorylation (OP) coupled to respiration in which the availability originates from oxidation of reducing equivalents of nutrients. (The inner membrane houses the respiratory chain and ATP synthesis in oxidative phosphorylation.)

A living cell uses the ATP for all the energy demanding activities; it has to maintain non-vanishing thermodynamic forces, such as electrochemical potential gradient, and is an open, non-equilibrium system, which manages the availability destruction and power production to adapt the fluctuation in energy demand and production within mitochondria. In biological reactions the rate is ultimately controlled by enzymes and other proteins of complex structure and high molecular weight. [38] Eyring

considered the situation for which irreversible thermodynamics using Onsager reciprocal relations apply. The energy consumption and coupling effect in living system were also considered.

The intra-cellular organelles, mitochondria, transfer the food we eat and the air we breathe into an electric potential that drive processes like DNA replication or protein building. [39,40] Mitochondria generate more than 90 % of cellular energy. The mitochondria turn food's hydrogen and carbon and inhaled oxygen into carbon dioxide (CO_2), water and adenosine triphosphate, or ATP, which stores energy. Mitochondria produce energy for moving body parts by combining nutrients with oxygen through breathing. The more abundant the number of mitochondria and the more active they are, the higher the ability to remove radical oxygen in the body. As mitochondria lose its ability, cells lose ability to use oxygen, and the body has excess radical oxygen and damage cells. Mitochondria exist in muscles and muscles lose their mass with aging. It is possible that at age 40 we lose 20 % of muscle mass. As muscles mass decreases, energy production of mitochondria also decreases, the mobility decreases, and causing additional muscle loss. Since heart and liver are supported by muscles, organ metabolism decrease and mobility also decrease. As the result the simple management of preventing invader or stress cannot be done, and inflammation occurs easily.

4.1.2. Metabolic Efficiency

Silva and Annamalai [41,42] correlated life-span entropy generation and the aging of human. The organs considered are brain, heart, kidney, liver, adipose tissue, skeletal muscles, and the rest of organs. To estimate entropy generation during a human life span, an availability analysis is applied to the metabolic oxidation of the 3 main nutrient groups: carbohydrates, fats, and proteins, in order to obtain the entropy generated for each of them under isothermal conditions.

Entropy generated over the life span of average individuals (natural death) was found to be 11,404 kJ/K per kg of body mass. The entropy generated predicts a life span of 73.78 and 81.61 years for the average U.S. male and female individuals respectively, which are values that closely match the average life span from statistics (74.63 and 80.36 years). These articles assume that entropy generation is the mechanism to biological aging, and that life comes to an end when entropy generation reaches its maximum.

The overall oxidation of carbohydrates ($C_6H_{12}O_6$) is considered as an example:



The chemical energy in the form of ATP is used in the body for muscular work, osmotic work, and the synthesis of new molecules. ATP is the "energy currency" of the living organism, and it is through the free energy release by conversion of ATP to adenosine diphosphate (ADP) that the cells can perform non-spontaneous reactions required to maintain life: for example, ion transport against concentration gradients.

For carbohydrates oxidation, the metabolic efficiency η is calculated as [41]

$$\eta = \frac{\text{ATP energy}}{\text{chemical energy}} \approx 34\%$$

It can be seen that only a part of the available energy has been converted into chemical energy within the ATP molecules. The difference is wasted as entropic heat. Other type of availability destructions accompanies muscular construction, substrate transport, protein synthesis, and other energy utilizing processes. Some examples of irreversibility production are given in the in Section 3.3. Nutrients are modeled as carbohydrates, fats, and proteins, whose main properties are shown in Table 1.

Table 1 Metabolic Efficiency of Nutrients [41]

Nutrient	Formula	Metabolic Efficiency
Carbohydrates	$C_6H_{12}O_6$	34%
Fats	$C_{4.57}H_{9.03}N_{1.27}O_{2.75}S_{0.046}$	32%
Proteins	$C_{16}H_{32}O_2$	10%

These articles provide a strong and tangible support for the postulated thermodynamic time. The entropy generation σ in this article is basically the same as the irreversibility \mathcal{I} ($= T_0\sigma$), the thermodynamic time. As indicated by Denbigh [43], the concept of irreversibility has a much wider field of application than has the concept of entropy generation. In addition, irreversibility has the dimension of energy which may be easier to visualize and control. In relation to this article, a person with accelerated aging (*progerin*) may have metabolism that involves excessive irreversibility in the cell systems (low metabolic efficiency), so that, according to our present argument, the aging for this person is faster than for ordinary people.

4.2. Biological Clock and its mechanism

There are evidences that living organisms possess biological clocks which enable them to make accurate time measurements. [1,44]

Circadian rhythm³ Plants extend their leaves in the hours of daylight and fold them at night. These movements continue even if the plants are kept in constant darkness. This circadian rhythms are now known to be exhibited by almost all plants and animals.

Tide cycle Green flatworms (*convoluta*) come to the surface of the sand at high tide and then bury themselves in the sand as it dries. This rhythm continues when they are placed in an aquarium where there are no tides.

Lunar cycle The palolo-worm reproduces only during the neap tides of the last quarter Moon in October or November. The brown alga (*Dictyota dichotoma*) liberates its male and female gametes at certain localities twice in a lunar cycle to increase the chance of fertilization.

Circannual rhythm A species of ground squirrel that inhabits the Rocky Mountains was found to exhibit an annual biological rhythm. The annual growth and shedding of antlers by deer is controlled by an intrinsic clock.

Diseases related to biological clocks Cancer, Parkinson's disease, seasonal depression and attention-deficit disorder have all been linked to defects in biological clocks.

Clocks in our cells Greenwood reports that our cells respond to the drug differently at different time of the day. [45] This indicates that the effectiveness of drug depends on biological time which is based on the energy flow in the body (irreversibility).

The brain center consisting of cerebral cortex governs perception, memory and conscious thought. [44] The cerebral cortex with the cognitive power are involved in interval timing. The brain structure that are involved in the task consume more oxygen than those that are not involved. The consumption of oxygen is chemical reactions resulting in energy flow and irreversibility.

The problem of time flowing in our sensation may be interpreted as the sensation of irreversibility occurring in our body. Note that the irreversibility is the destruction of availability which accompanies chemical reactions in our body. It may be postulated that perception of availability destruction in our brains provides a sensation of time flow. We have gained little insights into the question of why we perceive time to flow or, indeed, why we perceive at all. The physiology of timing mechanisms is not completely understood.

4.3. Telomere and Irreversibility

In 1990s, Bill Andrews, the director of molecular biology at the Bay Area biotech firm Geron, helped identify the human telomere gene. [46] Telomerase is an enzyme that maintains the ends of our

³ from the Latin *circa* ("about") and *diem* ("a day")

cell's chromosomes, called telomeres. Telomeres get shorter each time a cell divides, and when they get too short the cell can no longer make fresh copies of itself. If we live long enough, the tissues and organ systems that depend on continued cell replication begin to falter.

In the 1950s, research biologists began to view aging itself as the disease. [46] When free radicals scavenge electrons from their neighbors, they set in motion some ugly chain reactions. Cholesterol molecules become oxidized and begin to interact with the artery walls to form atherosclerosis-causing plaque, for instance, or the DNA in the cell nucleus suffers mutations, laying the ground work for cancer. Later refinements of this theory emphasize the role of the mitochondria, the cellular power plant that help convert glucose into energy. As the mitochondria age, they spew out increasing amount of the free radicals that hamper energy production and damage the entire cell, accelerating our all-systems decline. Among cell biologists, these mechanisms remain to this day the most accepted ways of explaining the aging of our body.

The life expectancy of an American a century ago was just 54 years; an infant born today may live to 78 years. [47] There are two approaches to longevity research aim to extend the average life span. One camp focuses on curing disease and replacing damaged body parts via stem cell therapies. Another camp focuses on slowing the aging process on the cellular and molecular levels.

If the present postulate of thermodynamic time is accepted, slowing the aging process means reducing the irreversibility in the metabolism of a body. As research shows, heat transfer, diffusion, chemical reactions, and fluid flow can bring about irreversibility, one can monitor all body activities and may reduce irreversibility. In contrast to individual organs, telomeres are at the ends of cell's chromosomes. Although the size of the systems are many orders of difference, they are the subjects of study for body's aging.

Telomeres get shorter each time a cell divides, and they get too short the cell can no longer make fresh copies of itself. At this time, the tissues and organ systems that depend on continued cell replication begin to falter. Telomere shortening is considered one of the cellular timing mechanisms controlling aging [48].

Chronic stress has been linked to shortening of telomeres, in particular, in women who are in the highly stressful situation of being caregivers for disabled or chronically ill children. The thermodynamic state of high body stresses is high irreversibility production or low metabolic efficiency. To reduce stress, meditation has been found useful. The thermodynamic state sought by meditation is supposed to be of low irreversibility state, making it low production of irreversibility and slow aging. One of the important questions is how chronic stress affects telomeres [49]. We may cite metabolic efficiency relating to irreversibility production. High metabolic efficiency (less irreversibility) reduces amount of heat transferred to blood or lower temperature rise in blood slows down the aging process. This in turn slow down the shortening of telomeres.

5. Concluding Remarks

Irreversibility of a system is proposed to be the *thermodynamic time* of the system. As the consequence, the proposed time is local and system-dependent. The irreversibility is shown to behave like ordinary time for two uniformly moving frames in standard configuration and varies with variation in a gravitational field.

The overall picture is that as the availability (exergy) of the system is destroyed, the thermodynamic time progresses, like the progress of the common time (clock which is artificial). As we know, the irreversibility of all systems increases. If the system is biological, we may call this aging.

5.1. Thermodynamic Time and Its Applications

In Section 3.2 we have seen the calculation of irreversibility for a closed system. If we desire not to have the size (mass) of the system as a parameter, we may use \mathcal{I}/m , so that the size of the system may not become a parameter and comparison between various systems can be performed, i.e.

$$\Delta\tau_1 = C_1 \frac{\mathcal{I}}{m},$$

where τ_1 is a thermodynamic time and C_1 , a dimensional constant. The treatment of human aging by Silva and Annamalai [41,42] cited in Section 4.1 have used open systems. Since for an open system mass and energy are not fixed, analysis is more complicated. Here, we may use the instantaneous values of \mathcal{I}/m , \mathcal{I}/E , or \mathcal{I}/\mathcal{A} within the control volume. Using \mathcal{I}/E as an example,

$$\Delta\tau_2 = C_2 \frac{\mathcal{I}}{E},$$

where τ_2 is another thermodynamic time and C_2 , a non-dimensional constant.

It is natural to ask how \mathcal{I} and Δt is related. From the work of Silva and Annamalai [41], the following numbers can be listed.

1. Entropy generated, kJ/kg-K: Male, 11508; Female, 11299
2. $T_0 = 37^\circ\text{C} = 310\text{ K}$
3. Irreversibility generated, MJ/kg: Male, 3567; Female, 3503
4. Equivalent human age, year : Male, 74.63; Female, 80.36
5. \mathcal{I}/m J/kg-s: Male, 1.52; Female, 1.38

This results may be interpreted as that a human male destroys about 1.5 joule of useful energy per kg body weight every second in his life span.

5.2. Impacts and Implications of Thermodynamic Time

As pointed out previously, thermodynamic time \mathcal{I} has the dimension of energy. Many phenomena in biological systems where duration is involved, such as aging, biological clocks, and defects in biological clocks (Parkinson's disease) may be closely related to energy flow through irreversibility [44,46,47]. Our sensation of time-flow may be explained as the availability flow and destruction of it (irreversibility) in the body and brain. The irreversibility comes from heat transfer, diffusion, fluid viscous dissipation, and chemical reactions, which operate at the cellular level [31,36,50]. Some examples are given in Appendix A. By reducing the irreversibility in the metabolism of a body, the aging process may be slowed down.

Since irreversibility is based on a thermodynamic concept which is universal, further application to other fields, such as cosmology (the Big Bang or black holes), are possible.

NOMENCLATURE

- a : area
- a_f : flow availability per unit mass
- c : velocity of light
- E : energy
- F, F' : coordinate systems
- g : acceleration of gravity
- H : height separation
- h : enthalpy
- J_i : energy flow
- L_{ij} : cross coefficient in Onsager reciprocal relation
- m : mass

\dot{m} : mass flow rate
 p : pressure
 Q : heat energy
 q'' : heat flux per unit area
 S : entropy
 s : entropy per unit mass
 T : temperature
 t : time
 U : internal energy
 V : volume
 v : velocity
 W : work
 x, y, z : Cartesian coordinates
 y_i : mass fraction of i-species
 z : elevation above some datum
 \mathcal{A} : availability
 β : v/c
 $\varepsilon_h, \varepsilon_\ell$: energy states of a photon
 γ : $1/\sqrt{1-\beta^2}$
 \hbar : Planck's quantum mechanical constant
 \mathcal{I} : irreversibility
 μ : viscosity
 μ_i : chemical potential of i-species
 σ : entropy production
 ω : frequency of light
 Δ : difference
 η : efficiency
 τ : thermodynamic time

Superscripts

$\dot{}$: rate
 $'$: moving frame
 0 : environment

Subscripts

$1, 2$: location
 b : boundary
 c : combined
 cv : control volume
 D : datum
 e : exit
 F, F' : frames
 f : flow
 h : high
 i : in
 ℓ : low
 s : surface
 0 : dead state; environment for pressure and temperature

Appendix A Examples of Availability and Irreversibility

The irreversibility \mathcal{I} will play the center role in this paper that examples from various fields and situations are given in this section. It is noted that the dimension of \mathcal{I} is energy, the destruction of availability. Also note that for all systems

$$\mathcal{I} \geq 0.$$

Example 1: Heat Transfer [31]

A steady heat transfer of energy takes place through a rod. The ends of the rod are held constant temperatures T_1 and T_2 , it is insulated along its length, and its state does not change with time. Determine the irreversibility. Let $T_1 > T_2 > T_0$

The heat energy flow into the rod during a specified time interval is denoted Q . An energy equation for the rod at steady state shows that the energy out by heat transfer is $(-Q)$. Applying Eq.(14) to the rod, noting that no work is done and the rod is at steady-state

$$0 = \left(1 - \frac{T_0}{T_1}\right) Q - \left(1 - \frac{T_0}{T_2}\right) Q - \mathcal{I}$$

Solving for \mathcal{I} and reducing

$$\begin{aligned} \mathcal{I} &= \left(1 - \frac{T_0}{T_1}\right) Q - \left(1 - \frac{T_0}{T_2}\right) Q \\ &= T_0 \left[\frac{Q}{T_1 T_2} (T_1 - T_2) \right] > 0 \end{aligned} \quad (\text{A1})$$

The irreversibility occurs due to heat transfer through a finite temperature difference.

Example 2: Heat Transfer Heat transfer between two bodies with finite temperature difference is common in nature. A solid mass m_s initially at temperature T_{si} is immersed in a closed tank containing m_w of water initially at T_{wi} . Heat transfer from the tank contents can be neglected. Determine the amount of irreversibility produced. $T_{si} \neq T_{wi}$

The final equilibrium temperature T_f can be determined from an energy balance for the closed system (water plus solid):

$$T_f = \frac{m_s c_s}{m_s c_s + m_w c_w} T_{si} + \frac{m_w c_w}{m_s c_s + m_w c_w} T_{wi},$$

Since the solid and water are incompressible, $\Delta V = 0$, and from the energy balance $\Delta U|_{solid} + \Delta U|_{water} = 0$, Equation (13) gives

$$\Delta \mathcal{A} = -T_0 (\Delta S|_{solid} + \Delta S|_{water}) \quad (\text{A2})$$

For the system using Equation(14)

$$\Delta \mathcal{A} = \underbrace{\int_1^2 \left(1 - \frac{T_0}{T_b}\right) \delta Q}_0 - \underbrace{(W - p_0 \Delta V)}_0 - \mathcal{I}$$

Therefore the irreversibility is

$$\mathcal{I} = -\Delta \mathcal{A} = T_0 (\Delta S|_{solid} + \Delta S|_{water}) > 0.$$

The quantity within the bracket is the total entropy change of the isolated system (solid plus water) and must increase. There are many instances of interaction between bodies of finite temperature difference. When this happens, availability destruction of the combined system occurs. Note that the energy of the system remains constant for this case.

Example 3: Diffusion of ideal gases Diffusion of fluids is observed commonly in nature. Here, we consider n_1 moles of gas 1 at pressure p and temperature T mixing with n_2 moles of gas 2 also at p and T in an adiabatic process. The final mixture pressure is p . Assuming ideal gases. The irreversibility is to be determined.

Using ideal gas equation, the final temperature is

$$T_f = T$$

The availability change for the system is

$$\Delta \mathcal{A} = \mathcal{A}_f - \mathcal{A}_i = \Delta E + p\Delta V - T_0\Delta S$$

But

$$\begin{aligned} \Delta E &= (U_f - U_i) + \Delta KE + \Delta PE \\ &= Q - W + \Delta KE + \Delta PE \\ &= 0, \end{aligned} \quad (\text{A3})$$

Since all terms on the right-hand side are zero, where KE denotes kinetic energy, and PE, potential energy. Also $\Delta V = 0$, so that

$$\Delta \mathcal{A} = -T_0\Delta S = -T_0(S_f - S_i) \quad (\text{A4})$$

The initial entropy of the system is

$$S_i = n_1\bar{s}_1(T, p) + n_2\bar{s}_2(T, p)$$

Since each gas initially exists separately at T and p , each of the specific entropies appearing in the expression is evaluated at T, p . The entropy of the system at the final state is

$$S_f = n_1\bar{s}_1(T, x_1p) + n_2\bar{s}_2(T, x_2p),$$

where x is the mole fraction.

$$\begin{aligned} \Delta \mathcal{A} &= -T_0 [n_1\bar{s}_1(T, x_1p) + n_2\bar{s}_2(T, x_2p) - n_1\bar{s}_1(T, p) - n_2\bar{s}_2(T, p)] \\ &= -T_0 [n_1(\bar{s}_1(T, x_1p) - \bar{s}_1(T, p)) + n_2(\bar{s}_2(T, x_2p) - \bar{s}_2(T, p))] \\ &= -T_0 \left[-n_1\bar{R} \ln \left(\frac{x_1p}{p} \right) - n_2\bar{R} \ln \left(\frac{x_2p}{p} \right) \right] \\ &= T_0\bar{R}(n_1 \ln x_1 + n_2 \ln x_2) \\ &= -\mathcal{I} \end{aligned} \quad (\text{A5})$$

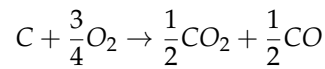
Therefore

$$\mathcal{I} = -T_0\bar{R}(n_1 \ln x_1 + n_2 \ln x_2) > 0,$$

since $x_1 < 1$, $x_2 < 1$. This means that the availability is destroyed in this process. The destruction of the availability is equal to the irreversibility $\mathcal{I} > 0$ for the process.

Example 4: Carbon combustion [31]

Many reactions produces irreversibility. Consider a steady-state reaction



We assume that the combustor operates adiabatically and with negligible kinetic and potential energy changes. The environment includes oxygen and carbon dioxide, but not carbon or carbon monoxide. The irreversibility per mole of carbon is

$$\begin{aligned} \bar{\mathcal{J}} &= [\bar{h}_C(T, p) - T_0\bar{s}_C(T, p) - \mu_C^0] + \frac{3}{4}[\bar{h}_{O_2}(T, p) - T_0\bar{s}_{O_2}(T, p) - \mu_{O_2}^0] \\ &\quad - \frac{1}{2}[\bar{h}_{CO_2}(T') - T_0\bar{s}_{CO_2}(T', x_{CO_2}p') - \mu_{CO_2}^0] \\ &\quad - \frac{1}{2}[\bar{h}_{CO}(T') - T_0\bar{s}_{CO}(T', x_{CO}p') - \mu_{CO}^0] \end{aligned} \quad (A6)$$

where T' is the temperature of the combustion products. Since carbon and carbon monoxide do not exist in the environment, they can be derived from the equilibrium condition applying to the reaction of formation of them from environmental substances. This process gives

$$\begin{aligned} \mu_C^0 &= \mu_{CO_2}^0 - \mu_{O_2}^0 \\ \mu_{CO}^0 &= \mu_{CO_2}^0 - \frac{1}{2}\mu_{O_2}^0 \end{aligned} \quad (A7)$$

Inserting Eq. (A7) into Eq. (A6) and collecting like terms

$$\begin{aligned} \bar{\mathcal{J}} &= T_0 \left[\frac{1}{2}\bar{s}_{CO_2}(T', x_{CO_2}p') + \frac{1}{2}\bar{s}_{CO}(T', x_{CO}p') - \bar{s}_C(T, p) - \frac{3}{4}\bar{s}_{O_2}(T, p) \right] \\ &\quad + \left[\bar{h}_C(T, p) + \frac{3}{4}\bar{h}_{O_2} - \frac{1}{2}\bar{h}_{CO_2}(T') - \frac{1}{2}\bar{h}_{CO}(T') \right] \\ &\quad + \left[-(\mu_{CO_2}^0 - \mu_{O_2}^0) - \frac{3}{4}\mu_{O_2}^0 + \frac{1}{2}\mu_{CO_2}^0 + \frac{1}{2}(\mu_{CO_2}^0 - \frac{1}{2}\mu_{O_2}^0) \right] \end{aligned}$$

The second term on the right side vanishes by application of an energy equation for the adiabatic combustor at steady state. The third term vanishes identically. For the first term, the expression reduces to $\bar{\mathcal{J}} = T_0\bar{\sigma} \geq 0$, where $\bar{\sigma}$ is the entropy production per mole of carbon.

Example 5: Irreversibility in Pipe Flow [50]

Many systems involve flow of a viscous fluid through a conduit. We consider the steady laminar flow of an incompressible fluid through a horizontal pipe with radius r_0 . This type of flow may simulate flows in biological systems. There is a uniform heat flux q'' around its circumference. The axial velocity profile for the fluid is

$$v_x = \frac{r_0^2}{4\mu} \left[-\frac{dp}{dx} \right] \left[1 - \left(\frac{r}{r_0} \right)^2 \right] \quad (A8)$$

where μ denotes the fluid viscosity and $\frac{dp}{dx}$, the pressure gradient. The temperature distribution for large (x/x_0) is

$$T - T_{x=0} = \frac{q''r_0}{k} \left[-4 \left(\frac{x}{x_0} \right) - \left(\frac{r}{r_0} \right)^2 + \frac{1}{4} \left(\frac{r}{r_0} \right)^4 + \frac{7}{24} \right] \quad (A9)$$

where $x_0 = \rho c_p v_{max} r_0^2 / k$, k is the fluid thermal conductivity and $T_{x=0}$ is the uniform fluid temperature at $x = 0$. The equation for local rate of entropy generation per unit volume can be expressed in cylindrical coordinates

$$\sigma = \frac{k}{T^2} \left[\left(\frac{\partial T}{\partial x} \right)^2 + \left(\frac{\partial T}{\partial r} \right)^2 \right] + \frac{\nu}{T} \left(\frac{\partial v_x}{\partial r} \right)^2 \quad (\text{A10})$$

Combining Eqs. A8 to A10 and neglecting axial conduction, we obtain

$$\sigma = \frac{1}{k} \left\{ \frac{q''}{T} \left[\left(\frac{r}{r_0} \right)^3 - 2 \left(\frac{r}{r_0} \right) \right] \right\}^2 + \frac{4\mu v_{max}^2 r^2}{Tr_0^4} \quad (\text{A11})$$

The rate of entropy generation per unit of pipe length, σ' , is determined by integration

$$\sigma' = 2\pi r_0^2 \int_0^1 \sigma \cdot \frac{r}{r_0} \cdot d \left(\frac{r}{r_0} \right)$$

Performing the integral and assuming the temperature variation over the pipe cross-section is small yields

$$\sigma' = \frac{11(q')^2}{48\pi k T^2} + \frac{8\mu(\dot{m}_f)^2}{\pi T \rho^2 r_0^4} \quad (\text{A12})$$

where \dot{m}_f is the mass flow rate, ρ is the fluid density, and q' is the heat transfer rate per unit of length $q' = 2\pi r_0 q''$.

Since the irreversibility per unit of length is $\mathcal{S}' = T_0 \sigma' \geq 0$, the irreversibility consists of two effects: one due to heat transfer (the first term on the right of Eq. (A12)) and the other to fluid friction (the second term). For turbulent flows, similar derivation may be made using appropriate turbulence model.

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