Terrestrial origin versus extraterrestrial overflow of thermodynamics

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Abstract: It is well known that matter filling either an ideally or actually isolated volume, being subjected to the Earth's gravitational field, spontaneously tends to disorder along the concentric equipotential surfaces of the Earth gravity field (i.e., to lateral statistical isotropy), and to order perpendicularly to these surfaces. In small enough volumes, the effect of the gravity gradient can be disregarded and matter can be considered as spontaneously tending to randomness (i. e., to true statistical isotropy) (1, 2). Such was the real kind and size of the 'systems' considered by Sadi Carnot and his first followers. But, historically, the choice made in the development of classical thermodynamics has been more drastic! The whole gravitational field has been disregarded and the local tendency to randomness has been justified by the Boltzmann H-theorem. As a consequence, what can be proved at a small scale (far smaller then the planet Earth), has been inferred to be valid even at a cosmic scale.

Taking into account the role played by the gravitational field, it can be proved that the existence of an equilibrium temperature gradient is unavoidable and that it does not invalidate the second law of thermodynamics. The latter will remain valid (as a special case) in the classical enunciations only locally within the system Earth. If enunciated in a more general form, its validity ca be extended to the whole system Earth and to whole similar systems. On the contrary, the extrapolation of the validity of the second law to the whole Universe could be questionable.

1. Thermodynamics and Gravity.

Dealing with the internal dynamics of the system Earth (made of the so called "solid" part and of its fluid envelope), forced departures from, and spontaneous tendencies to different kinds of equilibrium states (thermal, thermodynamic, phase, chemical, mechanical, and so on) are currently considered as being each one independent from the other ones.

The interconnection among all these specific states of equilibrium is commonly neglected since each one of them is considered and defined out of its proper context. It will be shown here that the interconnection among a number of these equilibria becomes manifest and cannot be ignored if the hydrostatic equilibrium state toward which the whole Earth system spontaneously tends is taken into account.

According to the definition given by the International Astronomical Union (IAU) in 2006, the Earth, as a planet, is a celestial body that has sufficient mass to assume "*a hydrostatic equilibrium* (n*early round) shape*". The hydrostatic equilibrium and the consequent (almost) spherical shape are justified by the action in concert of what we are used considering separately as mutual gravitational attraction and short range interactions among its structural elements (ions, atoms, molecules, crystals). Being an open system, our planet Earth has not attained and cannot attain complete hydrostatic equilibrium. In fact we witness a permanent competition between the spontaneous tendency toward equilibrium of the whole planet and departures from it produced by

- *(a)* Actual exchange of matter and energy with its environment,
- *(b)* Internal matter-energy transformations (such as the one implied by radioactive decay) that can be considered as a balanced exchange of matter and energy with its environment,
- *(c)* Exchange of matter and energy with the biosphere, that is with the whole collection of organisms living on it.

The hypothetical equilibrium configuration of the Earth considered as an isolated system would depend upon the configuration of its gravitational field, or, vice versa, the equilibrium configuration of the Earth gravitational field can be inferred from that of the equilibrium configuration toward which spontaneously the Earth tends. Some effects of the Earth's motion, contributing to the departure from spherical shape, cannot be ignored, but, since their consideration is not necessary to justify the specific departures from equilibrium that will be taken into account here, they will be disregarded. Since from direct experience we know that the matter making the system Earth shows a tendency to (statistical) disorder along closed concentric surfaces and a tendency to order perpendicularly to them[1], the existence of an abstract gravitational field characterized by homogeneity and lateral[2] isotropy and by a vertical[3] gradient can be inferred.

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[1] A clear perception of this tendency is already shown in the Lucretius' *De Rerum Natura*, and in the Galileo *Dialogo dei Massimi Sistemi*.

[2] Here and in the following, 'lateral', stands for 'on the equipotential surfaces of the Earth gravity field'.

[3] Here and in the following, 'vertical' stands for 'perpendicular to the equipotential surfaces of the Earth gravity field'.

In an infinitesimally small volume element of the Earth, considered as a closed *continuum* self-gravitating system in its global equilibrium state, the departure from homogeneity perpendicularly to the equipotential surfaces[4] may be disregarded, allowing, among other things, the definition of an isotropic tensorial quantity – namely the *pressure at a point* (or the *isotropic state of stress at a point*) – that can be treated as a scalar quantity with dimension of a force per unit area.

The above departure from homogeneity can be disregarded even when dealing with *finite* subsystems[5] of the system Earth, comparatively small with respect to the whole system, but large enough to contain a very large numbers of structural elements (such as ions, atoms, molecules, and grain crystals); within them the vertical gradients are so small that can be disregarded so that they can be considered isotropic[6]. Resorting to this approximation, one is allowed to conclude that, if a self-gravitating system such as the Earth, considered as hypothetically isolated, could attain its state of global equilibrium, any small element confined between two close enough equipotential surfaces would be characterized by the *same*:

average homogeneous composition,
average density,
statistically isotropic structure,
average isotropic pressure,
and average temperature.

On any equipotential surface, the instantaneous positions of ions, atoms and molecules should - over a certain scale - be considered as randomly distributed, the average distance among them as statistically uniform in every direction, their motion characterized by the same average velocity in every direction, and each direction as equally probable for their orientation and the direction of their velocity; sections of structural elements of higher order (such as crystal grains in a polycrystalline aggregate) should have a homogeneous average size, and their boundaries and structure should be randomly oriented.

In the system Earth, the spontaneous tendency toward hydrostatic equilibrium manifests itself through various physical processes. Because of the large variety of materials and of their behavior in different environmental conditions, different physical processes take place with rates that can be quite different. Therefore, each naturally or artificially confined (≈ isolated, that is, not exchanging appreciable amounts of matter and heat with their environment) subsystem may achieve and temporarily preserve a number of different equilibrium states. For any equilibrium state, in small subsystems with homogeneous composition (even if made of several phases which do not separate under the action of gravity), the instantaneous positions of ions, atoms and molecules may be - *over a certain scale* - considered as randomly distributed *in space*, the average distance among them as statistically uniform in every direction *in space*, their motion characterized by the same average velocity in every direction *in space*, and each direction *in space* as equally probable for their orientation and the direction of their velocity; structural elements of higher order (such as crystal grains in a polycrystalline aggregate) as characterized by a homogeneous average size with their boundary and lattices randomly oriented *in space*. Therefore, these *local and temporary* equilibrium states may be considered as characterized by approximately isotropic (≈ disordered) structure as well as by average homogeneous pressure and temperature, and, if we consider subsystems made of a single component, or of several phases which do not separate under the action of gravity, by homogeneous average density. Each equilibrium state of any subsystem would be characterized by its proper pressure, temperature and degree of disorder (which is also dependent on the amplitude and space and time frequency of fluctuations).

Simply because of the existence of the Earth's gravity field, any of these isolated systems spontaneously tends to disorder and to homogenize its temperature through heat transfer, from warmer parts to colder ones. The recognition that heat *spontaneously* flows only from a hotter body to a colder one, may be considered in the present context (that is, dealing with small subsystems of a self gravitating planet) as equivalent to the Clausius formulation of the second law of thermodynamics, stating that "a transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible". Tendency to disorder and spontaneous flow of heat from hotter regions of a system to colder ones involved by the tendency to hydrostatic equilibrium is in agreement with the second law of thermodynamics. Therefore the second law may be seen as a mere implication of the spontaneous tendency to hydrostatic equilibrium.

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[4] Here and the following, the expression 'equipotential surfaces' stands for 'equipotential surfaces of the Earth gravity field'

[5] The word 'subsystem' will be used in the following to make reference to a finite material system subjected to the Earth gravitational field, that is, to a naturally or artificially isolated 'solid' and/or fluid portion of the whole system Earth, consisting either of natural components of our planet or of artificial compounds.

[6] In the following, such subsystems of the system Earth will be simply called 'small subsystems.

The size of the above approximately isolated actual subsystems is of the order of the ones on which observers and experimenters, mostly motivated by the growing interest in heat-engines, originally focused their attention. The development of classical thermodynamics springs up from their observations and experiments.

In statistical thermodynamics, the dynamical structure of a system - that was considered irrelevant, and then ignored, in classical thermodynamics - came on stage. Since the rewarding success of classical thermodynamics was obtained considering the gravitational field as external (and the potential gravitational energy as non contributing to the internal energy of a system), even the possible influence of gravity in determining the inner structure of a thermodynamic system in equilibrium remained out of sight, so creating the need for an alternative explanation. The solution was found making the assumption that the molecules of a gas, whatever its original state and independently from the existence of external fields, soon or later must (or have a very high probability to) move randomly, with no preferred direction, at an average speed.

Making the choice of considering the above assumption as correct, no matter if the Boltzmann "proof" is accepted or not, instead of attributing to gravity its determinant role, the field of application of thermodynamics widens dramatically: from application to the tiny volume of a subsystems of a self-gravitating system (small enough to be considered isotropic when in a state of equilibrium), to application to the infinity.

It is amazing that, while hardly anybody dares to question the choice of the latter, or indeed of the whole universe, everybody finds correct the attribution of lateral statistical isotropy and vertical gradient of composition and grain size, shown by the polycrystalline medium of our planet, to the control of gravity. Yet, what is valid for a solid phase should be valid for a fluid: in compliance with the principles of symmetry of physical phenomena enunciated by Pierre Curie (4)!

2. Equilibrium temperature gradient.

The existence of a vertical gradient of temperature accompanying those of pressure and density has been suspected or maintained by physicists. Ups and downs of the debate on this subject are widely exposed by Dreyer et al. (5). The reason for the eventual refusal to accept the possibility of such a gradient is that it would invalidate the second law of thermodynamics. Among other things, it cannot be inferred from the above quoted symmetry principles of physical phenomena, because the existence of a field having the structure of the gravitational one would be a necessary but not sufficient condition. Anyway, the reason supporting the existence of an equilibrium temperature gradient can be found on condition that the determinant role of gravity is recognized. Doing so, the second law would not be questioned, provided that it is enunciated in a more general form, valid not only for a small portion of the planet Earth, but also for larger parts of it and for the whole planet.

The Achilles' heel of the assumption that the Earth gravitational field does not have any influence on the spontaneous tendency to equilibrium in a thermodynamic system can be unveiled just by considering an accidental allusion to hydrostatics made by Boltzmann in one of the papers (3) he wrote during the debate with his detractors. In this paper, while dealing with gases, he stated: "... it follows that, despite the presence of external forces, each direction in space is equally probable for the direction of the velocity of any one of the molecules, moreover, that in each volume element of the gas, the distribution of velocities of the gas is of the same form as in a gas of the same temperature on which no external forces act. The effect of the external forces consists only in a variation of the density in the gas from point to point, and namely in a way that is already known from hydrostatics."[7]

In agreement with the Maxwell statistical derivation of the velocity distribution of gas molecules under equilibrium conditions, one must recognize that an *indefinitely* (or even *infinitely*) *extended* random distribution of moving molecules in space can be *indefinitely maintained with time* only on condition that any one of them travels at the same average velocity and that each direction in space is equally probable for the direction of the velocity of any one of them. Boltzmann, concentrating his attention on the change a distribution of gas molecules should undergo when approaching equilibrium, concluded that it tends to the Maxwellian form. Unfortunately, the existence, or the acquisition, of the Maxwell equilibrium distribution

[7] "*... folgt, daß trotz der Wirksamkeit der äußeren Kräfte für die Richtung der Geschwindigkeit irgend eines der Moleküle jede Richtung im Raume gleich wahrscheinlich ist, ferner dass in jedem Raumelemente des Gases die Geschwindigkeitsvertheilung des Gases genau ebenso beschaffen ist, wie in einem Gase von gleicher Temperatur, auf das keine Aussenkräfte wirken. Der Effect der äusseren Kräfte besteht blos darin, dass sich die Dichte im Gase von Stelle zu Stelle verändert und zwar in einer Weise, welche schon aus der Hydrostatik bekannt ist.*"

cannot assure the permanence with time of a non homogeneous distribution of molecules as the one resulting from hydrostatic adjustment in the gravity field. One has to conclude that, if - as in the specific case of a portion of the Earth's atmosphere in hydrostatic equilibrium - a vertical gradient of density should be preserved with time, the gas molecules must move with different average velocities in different directions and the velocity directions in space must not be equally probable. In the above case a larger number of molecules at higher average velocity should move downwards and a small number of them should move at slower velocity upwards, so balancing the opposite fluxes in any direction. As a consequence, in a subsystem of a self-gravitating planet in an hypothetical state of equilibrium, a permanent vertical gradient of temperature would be, not only possible, but unavoidable.

If an equilibrium vertical temperature gradient should characterize a relatively large isolated subsystem in a state of equilibrium, no flow of heat could take place between any two portions of it, even if they are at different temperatures. To conciliate the existence of an equilibrium gradient and the validity of the second law, one has to assume that the whole isolated system Earth and any isolated part of it, must, when in equilibrium, be characterized by uniform specific entropy and that the ***necessary*** *spontaneous tendency to homogenization of specific entropy, and not the spontaneous tendency to homogenization of temperature, is responsible for heat flow*. Only in the small enough subsystems considered in the previous paragraph - and characterized at equilibrium by (approximately) uniform temperature - a homogenization of specific entropy (approximately) involves homogenization of temperature as well as of pressure and density.

The above quoted Clausius postulate (whatever Clausius' intention was) remains acceptable, given that it does not exclude in an explicit way that heat may *not necessarily flow* wherever a gradient or difference of temperature exists.

If two large isolated subsystems A and B, with the same composition and each one in a different state of equilibrium with different equilibrium temperature and pressure gradients, are put in connection to form a composite system C, flow of heat and matter will take place bringing the whole system C in a new state of equilibrium characterized by equilibrium temperature and pressure gradients different from those of the subsystems A and B. In agreement with the enunciation of the second law that refers to entropy, at equilibrium, the entropy of the system C must be higher than the sum of the entropies of the subsystems A and B.

3. Heterogeneous systems.

The existence of vertical equilibrium temperature gradients has been introduced above having in mind subsystems composed by a single chemical substance – preferably a fluid – in order to consider states of complete equilibrium, comprehensive of both thermodynamic and hydrostatic equilibrium. Therefore, the considered equilibrium temperature gradients are characterized by coincidence of isothermal surfaces and equipotential surfaces.

Both a natural or artificial thermodynamic subsystem may be laterally heterogeneous – if made, for instance, of a solid and a fluid, or by two different solids put side by side – and its heterogeneity may last for a long time. For practical purposes, it can be convenient to consider them in a state of equilibrium even if they are far from hydrostatic equilibrium. Heat transfer can take place in a time far shorter from that required to attain the equilibrium arrangement of different phases in the gravitational field according to their density. It is currently taken for granted that such a system reaches thermal equilibrium, that is uniform temperature, without reaching hydrostatic equilibrium. In large heterogeneous subsystems it should be not ignored that the isothermal surfaces could not coincide with the equipotential surface. Lateral temperature gradients may persist for very long time even if they cannot be considered as *equilibrium* gradients like the vertical ones. Only in small heterogeneous subsystems the actual departure from uniformity may be so slight that it can be ignored.

As a consequence, the zeroth law of thermodynamics should be considered as *approximately* valid within any small subsystem which is necessarily *heterogeneous* (in the above sense), at least because a thermometer is included in it.

4. Hydrostatic equilibrium *sensu lato*.

The hydrostatic equilibrium *s. s.* (*sensu strictu* = in a restricted sense), currently considered as responsible for the equilibrium arrangement of components of different density and/or for the equilibrium density gradient in a single component in the gravitational field, is different from the hydrostatic equilibrium *s. l.* (*sensu lato* = in a broad sense) that should characterize the system Earth in its global state of equilibrium and a large subsystem of it in its complete equilibrium. Actually hydrostatic equilibrium *s. l.* involves all the specific equilibria here considered. It can be observed both in natural and artificial systems that a departure from one of them involves some departure from all the others, and that the tendency to a specific equilibrium involves the tendency to all the other ones.

Therefore, chemical and phase equilibria, as well as thermodynamic and hydrostatic *s. s.* equilibria, are facets of the same global equilibrium in the whole system Earth and of complete equilibrium in large subsystems of it. In addition, miscibility or non-miscibility of different components, as well as spontaneous isotropization of structure and state of stress in small subsystems are controlled by the spontaneous tendency to specific entropy homogenization, that is, to the tendency to hydrostatic equilibrium *sensu lato*. Complete equilibrium, specific entropy homogeneity and hydrostatic equilibrium *sensu lato* can be considered as synonyms. The expression 'global equilibrium' has been used above to refer to complete equilibrium of the whole self-gravitating system Earth (if its motion is disregarded).

5. Discussion

Agreeing on the assumptions made at the beginning of this note (see points *a*, *b* and *c*), the whole system Earth can be considered as a thermodynamic open system: for it and for any portion (subsystem) of it, the first law of thermodynamics, expressing the conservation of energy, would be considered as valid.

Accepting the role played by the Earth gravitational field in shaping the structure to which the Earth would spontaneously tend in absence of external actions, the second law should be considered valid in its classical formulations only for any subsystem of the self-gravitating system Earth enough small to be considered isotropic when in equilibrium and in which vertical gradients can be disregarded. Its validity may be extended to larger subsystems and to the whole system Earth by recognizing that:

- flow of heat takes place in closed systems of any size because of the unavoidable spontaneous tendency to homogenization of specific entropy,
- and tendency to homogenization of specific entropy can be considered as associated with tendency to homogenization of temperature only in the above defined small subsystems.

The existence of an equilibrium temperature in non-self-gravitating system in a gravitational field with radial symmetry that is created by a mass can be justified without considering relativistc effects that have been suggested, or are accepted, by some authors(5, 6, 7).

The conclusions above reached raise a variety of doubts, questions, and, why not, good hopes. Only some will be here summarily mentioned.

The dismantling of a taboo, namely that of the incompatibility of an equilibrium vertical temperature gradient with thermodynamic equilibrium, in the 'solid' Earth interior, in the oceans, and in the atmosphere, should have some useful returns.

Notwithstanding the expected problems to be faced in discriminating equilibrium and non-equilibrium components of temperature gradients, a better understanding of the dynamics of the Earth's interior, of oceanography and meteorology could be obtained. At least, it would be a warning for some technicians and investors: they should expect also some failure when trying to look for the exploitation of temperature differences at large vertical distances.

Anyhow, the most perplexing question is also the basic one: are the laws of the *internal* dynamics of the planet Earth a representative sample of those of the whole Universe? Or, more specifically: may the 'terrestrial' laws of classical thermodynamics be considered valid in any extraterrestrial domain that does not consist in another analogous celestial body?

The extrapolation of the validity of the second law of thermodynamics to the whole Universe has been already stated in an emphatically way by Clausius (8) in 1865. The original banishment of the crucial role played by the Earth gravitational field has been confirmed thanks to the Maxwell derivation and the Boltzmann elaboration of the gas molecules distribution, since no limits were imposed to the extension of the volume occupied by the considered gas. Unfortunately, "Once the error is based like a foundation stone in the ground, everything is built thereupon, nevermore it returns to light."[8].

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[8] *Liegt der Irrtum nur erst*
wie ein Grundstein im Boden,
immer baut man darauf,
nimmermehr kommt er an [den] Tag.
Dreyer et al. (5) quote these lines by Goethe and Schiller (Xenien) in the heading of the paragraph "Entropy and Gravity".

Provided that it has been an error!

References

1. Guzzetta G., Riflessioni di un geologo su calore, gravità e tempo, (in Italian), Alfredo Guida Editore, Napoli, 2001

2. Guzzetta G., *Thermo-gravitational equilibrium*, Jour. of Theoretics, **6-4**, p. 1-5 (2004).

3. Boltzmann L., Über das Wärmegleichgewicht von Gasen, auf welche äußere Kräfte wirken, Wien. Sitzungsber. II, **72**, 427(1876).

4. Curie P., *Sur la symétrie dans les phénoménes physiques; symétrie d'un champ electrique et d'un champ magnetique*, Journal de Physique, **3**, p. 393-415 (1894).

5. Dreyer W., Müller W-H., and Weiss W., *Tales of thermodynamics and obscure applications of the second law*, Cont. Mech. and Thermodyn., **12**, 3, p. 151-184 (2000).

6. Tolman R. C., and Ehrenfest P., *Temperature equilibrium in a static gravitational field*. Phys. Rev., **36**, 1791 (1930).

7. Eckart C., *The thermodynamics of irreversible processes III: Relativistic theory of the\simple fluid*, Phys. Rev., **58**, 919 (1940).

8. Clausius R., *Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie*, Poggendorffs Annalen, **125**, 353-400 (1865).