Teaching the Third Law of Thermodynamics

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Abstract: This work gives a brief summary of major formulations of the third law of thermodynamics and their implications, including the impossibility of perpetual motion of the third kind. The last sections of this work review more advanced applications of the third law to systems with negative temperatures and negative heat capacities. The relevance of the third law to protecting the arrow of time in general relativity is also discussed. Additional information, which may be useful in analysis of the third law, is given in the Appendices.

This short review is written to assist lecturers in selecting a strategy for teaching the third law of thermodynamics to engineering and science students. The paper provides a good summary of the various issues associated with the third law, which are typically scattered over numerous research publications and not discussed in standard textbooks.

1. INTRODUCTION

The author of this article has taught senior (year **3**) engineering thermodynamics for a number of years. Engineering students, as probably everyone else, usually do not have any difficulties in understanding the concept of energy and the first law of thermodynamics but have more problems with the concept of entropy, the second and the third laws. This trend in learning the laws of thermodynamics seems to be quite common. Human perceptions are well-aligned with the concept of energy but the concept of entropy tends to be more elusive and typically remains outside the boundaries of the students' intuition. In thermodynamic courses taught to future engineers, the concept of entropy is traditionally introduced on the basis of the Clausius inequality, which directs how to use entropy but does not explicitly explain the physical nature of the concept. The common perception that engineering students are incompatible with statistical physics prohibits the use of the explicit definition of entropy by the Boltzmann-Planck equation

$$S = k_B \ln(\Gamma) \tag{1}$$

where k_B is the Boltzmann constant and Γ is the number of micro-states realizing a given macro-state. This equation links the mysterious entropy S to the fundamental concept of probability, which in this case is related to Γ. Despite not being trivial, the concept of probability combines well with human intuition. My experience is that students very much appreciate the explicit definition of entropy. The main trend of entropy to increase, due to the overwhelming probability

of occupying whenever possible macro-states with largest Γ, explains the second law.

While statistical physics may offer some insights and assistance in teaching the second law of thermodynamics, a similar strategy is not likely to work as an educational remedy for the third law. It seems that there are two major factors that make the third law and its implications more difficult to understand than the second law.

First, after more than 100 years since Walter Nernst published his seminal work [1], which became the beginning of the third law of thermodynamics, we still do not have a satisfactory universal formulation of this law. Some formulations of the law seem to be insufficiently general while others cannot avoid unresolved problems. Many different formulations of the third law are known; some of them differ only in semantics but many display significantly different physical understandings of the law.

Another problem in teaching the third law is its abstract character, which, when compared with the other laws, is apparently less related to core engineering concepts such as thermodynamic cycles and engines. In many textbooks the third law is presented as a convenient approach for generating thermodynamic tables by using absolute entropy. Some formulations of the third law may not have clear physical implications. Finding a concise and transparent summary of the implications of the third law of thermodynamics is still not easy.

This work is an attempt to fill this gap and assist in selecting an approach to teaching the third law. First we discuss major alternative formulations of the third law. Then, by analogy with the zeroth, first and second laws, which prohibit the perpetual motion of the zeroth, first and second kind, we logically extend this sequence and declare that the

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third law prohibits the perpetual motion of the third kind, which can deliver 100% conversion of heat into work. This interpretation pertains to the original works of Nernst [2] and is reflected in more recent publications [3]. One should be aware that the term "perpetual motion of the third kind" is sometimes used to denote a completely different process – a motion without friction and loses.

The second law, the third law and the rest of thermodynamics can also be introduced on the basis of the adiabatic accessibility principle originated by Constantine Caratheodory [4]. While this possibility has been convincingly proven by Lieb and Yngvason [5], their approach is rigorous but rather formal and not suitable for teaching. The recent book by Thess [6] fills the existing gap and presents adiabatic accessibility in a very interesting and even entertaining manner. The author has not had the opportunity to try this approach in class but believes that adiabatic accessibility can be appreciated by the students and might eventually become the mainstream approach to teaching thermodynamics.

The last part of this paper is dedicated to some less common but still very interesting topics in thermodynamics – the third law in conditions of negative temperatures or negative heat capacities. The profound connection of the third law with persevering causality in general relativity seems to be especially significant. These more advanced topics can be used to stimulate the interest and imagination of the top students but, probably, would not be suitable for the rest of the class.

2. STATEMENTS OF THE THIRD LAW

While it was Walter Nernst whose ingenious intuition led thermodynamics to establishing its third law [7], this important scientific endeavor was also contributed to by other distinguished people, most notably by Max Planck and Albert Einstein. The third law of thermodynamics has evolved from the Nernst theorem – the analysis of an entropy change in a reacting system at temperatures approaching absolute zero –, which was first proposed by Nernst and followed by a discussion between him, Einstein and Planck. Even after 100 years since this discussion took place, there is still no satisfactory universal formulation of the third law thermodynamics. Leaving historical details of this discussion aside (these can be found in an excellent paper by Kox [8]), we consider major formulations of the third law. In this consideration, we follow the broad ideas expressed by the founders of the third law rather than their exact words – on many occasions clear statements of the third law were produced much later [9, 10]. For example, Nernst did not like entropy, which is now conventionally used in various statements of the third law, and preferred to express his analysis in terms of availability. The existing statements differ not only by semantics but also have significant variations of the substance of the law; although statements tend to be derived from the ideas expressed by Planck, Nernst or Einstein and can be classified accordingly.

The most common formulation of the third law of thermodynamics belongs to Max Planck [11] who stated that

- **Planck formulation.** When temperature falls to absolute zero, the entropy of any pure crystalline substance tends to a universal constant (which can be taken to be zero)

$$S \to 0 \text{ as } T \to 0 \tag{2}$$

Entropy selected according to $S = 0$ at $T = 0$ is called absolute. If S depends on x (where x may represent any independent thermodynamic parameter such as volume or extent of a chemical reaction), then x is presumed to remain finite in (2). The Planck formulation unifies other formulations given below into a single statement but has a qualifier "pure crystalline substance", which confines application of the law to specific substances. This is not consistent with understanding the laws of thermodynamics as being the most fundamental and universally applicable principles of nature. This formulation does not comment on entropy of other substances at $T = 0$ and thus is not universally applicable.

The Planck formulation, in fact, necessitates validity of two statements of unequal universality: the Einstein statement and the Nernst theorem.

- **Einstein statement.** As the temperature falls to absolute zero, the entropy of any substance remains finite

$$S(T, x) \to S_0(x), |S_0| < \infty \text{ as } T \to 0, |x| < \infty \tag{3}$$

The limiting value S_0 may depend on x, which is presumed to remain finite at $T \to 0$. Considering expression for the entropy change in a constant volume heating process

$$S = \int_0^T \frac{C_V}{T} dT \tag{4}$$

it is easy to see that (3) presumes vanishing heat capacity

$$C_V \to 0 \text{ at } T \to 0 \tag{5}$$

since otherwise, the integral in (4) diverges and $S \to -\infty$ as $T \to 0$. A similar conclusion can be drawn for C_P by considering the heating process with constant pressure.

The statement is attributed to Einstein [12], who was first to investigate entropy of quantum systems at low temperatures and to find that the heat capacities should vanish at absolute zero; this implies that S is finite at $T \to 0$. Nernst and his group at University of Berlin undertook extensive experimental investigation of physical properties at low temperatures, which confirmed the Einstein statement [8]. It should be noted that thermodynamic systems become quantized at low temperatures and classical statistics is likely to produce incorrect results, not consistent with the Einstein statement. Hence experimental confirmation of the Einstein statement was at the same time a confirmation for quantum mechanics. The quantum theory of heat capacity was latter corrected by Debye [13] to produce a better quantitative match with Nernst's experimental results. This correction, however, does not affect the validity of the Einstein statement. Although the validity of the Einstein statement is beyond doubt, this statement does not capture all important thermodynamic properties at the limit $T \to 0$.

- **Nernst (heat) theorem.** The entropy change of a system in any reversible isothermal process tends to zero as the temperature of the process tends to absolute zero.

$$S(T,x) - S(T, x + \Delta x) \to 0 \ \text{ as } \ T \to 0, |x| < \infty, |\Delta x| < \infty \qquad (6)$$

The change in x is presumed to remain finite at $T \to 0$. Assuming "smooth" differentiation, the Nernst theorem obviously implies that

$$\left(\frac{\partial S}{\partial x} \right)_T \to 0 \quad \text{as } T \to 0 \qquad (7)$$

The Nernst theorem, although valid in many cases, is unlikely to be universal. On many occasions Einstein disputed Nernst's arguments aimed at deriving the heat theorem from the second law [8]. The main problem with the theorem is that the entropy S cannot be independent of x at $T = 0$ when some uncertainties are allowed to remain in the system at $T = 0$. Indeed, if a mixture of two or more components (which can be different substances or different isotopes of the same substance) can be brought to the state of $T = 0$, then there must be uncertainties in positions of the molecules representing specific components of the mixture, since the positions of two different molecules can be swapped to form a new microstate. Assuming that x is the molar fraction of one of the components, we conclude that presence of these uncertainties should depend on x. The Planck formulation unifies two independent statements – the Einstein statement and the Nernst theorem – and patches the Nernst theorem by restricting application of the Planck formulation to pure crystalline substances. The third law represents a statement which physically is related to the second law, but logically is independent from the second law.

Another formulation of the third law is represented by the following principle:

- **Nernst (unattainability) principle.** Any thermodynamic process cannot reach the temperature of absolute zero by a finite number of steps and within a finite time.

The Nernst principle was introduced by Nernst [2] to support the Nernst theorem [1] and to counter Einstein's objections. The Nernst principle implies that an isentropic process (adiabatic expansion or a similar reversible adiabatic process that can be used to reduce temperature below that of the environment) cannot start at any small positive T and finish at absolute zero when volume and other extensive parameters remain limited, that is

$$S(T,x) - S(0, x + \Delta x) > 0 \ \text{ when } \ T > 0, |x| < \infty, |\Delta x| < \infty \qquad (8)$$

If expression (8) is not valid and $S(T,x) = S(0, x + \Delta x)$, then the isentropic process starting at (T,x) and finishing at $(0, x + \Delta x)$ reaches the absolute zero. According to the present understanding of the Nernst principle, $S(T,x) = S(0, x + \Delta x)$ might be possible but then the isentropic process connecting (T,x) and $(0, x + \Delta x)$ must be impeded by other physical factors, for example, the process may require an infinite time.

Equivalence of the Nernst principle and the Nernst theorem has repeatedly been proven in the literature [14]. These proofs are illustrated by Fig. (**1a,b**) demonstrating the possibility or impossibility of an isentropic process reaching $T = 0$ while $x_1 \leq x \leq x_2$ (the bounding lines represent $x = x_1$ and $x = x_2$). Case (**a**) corresponds to the validity of the Nernst principle and the Nernst theorem while case (**b**) violates both of these statements. Achieving $T = 0$ in case (**a**) requires an infinite number of steps as shown in the figure. The Carnot cycle reaching $T = 0$, which is called the Carnot-Nernst cycle, is possible in case (**b**) and is also shown in the figure. It should be noted that proofs of equivalence of Nernst principle and Nernst theorem involve a number of additional assumptions [15, 16] as illustrated by examples (**c**), (**d**), (**e**) and (**f**). Cases (**c**) and (**e**) indicate that the Nernst principle can be valid while the Nernst theorem is not. Case (**c**) violates the Einstein statement while case (**e**) allows for fragmented dependence of S on x and shows boundaries $x_1 \leq x \leq x_2$ and $x_3 \leq x \leq x_4$. Cases (**d**) and (**f**) demonstrate validity of the Nernst theorem and violation of the Nernst principle. Case (**d**) considers a special entropy state with $S(T,x) = 0$ at $T > 0$ - a system with these properties and Bose-Einstein statistics is discussed by Wheeler [16]. Case (**f**) implies negative heat capacities due to $\partial S / \partial T < 0$ at $T \to 0$ and $x = x_1$.

While universality of the Nernst theorem is doubtful, it seems that the Nernst principle has better chances of success. The difficulty of reaching $T = 0$ is supported by experimental evidence. Interactions of a paramagnetic with a magnetic field are commonly used to reach low absolute temperatures. The lowest recorded experimental temperature of $T = 10^{-10}$ K was achieved in a piece of rhodium metal by YKI research group at Helsinki University of Technology in 2010 [17] (this report needs further confirmation). Unattainability of $T = 0$ can be explained by limitations imposed by the Nernst theorem, when this theorem is valid, or by other restrictions, when the Nernst theorem is incorrect. For example, reversible transition between mixed and unmixed states requires selectively permeable membranes; diffusion between components and through these membranes is likely be terminated at $T = 0$. Thus, although the process illustrated at Fig. (**1b**) is possible for mixtures, this process may need an infinite time to complete. We use a weakened version of the Nernst principle referring to both "finite number of steps"' and "finite time" to stress its non-equivalence with the Nernst theorem.

Wreszinski and Abdalla [18] recently gave new formulation of the third law, which is based on the concept of adiabatic accessibility [4-6], stating that zero temperatures $T = 0$ are adiabatically inaccessible from any point where $T > 0$. The formulation is equivalent to the Nernst principle. This work [18] also includes a proof of the Nernst theorem from the Nernst principle using the adiabatic accessibility concept and imposing two additional conditions, which exclude cases shown in Figs. (**1c** and **1e**).

In a summary, we have two major formulations of the third law: the most reliable but relatively weak Einstein
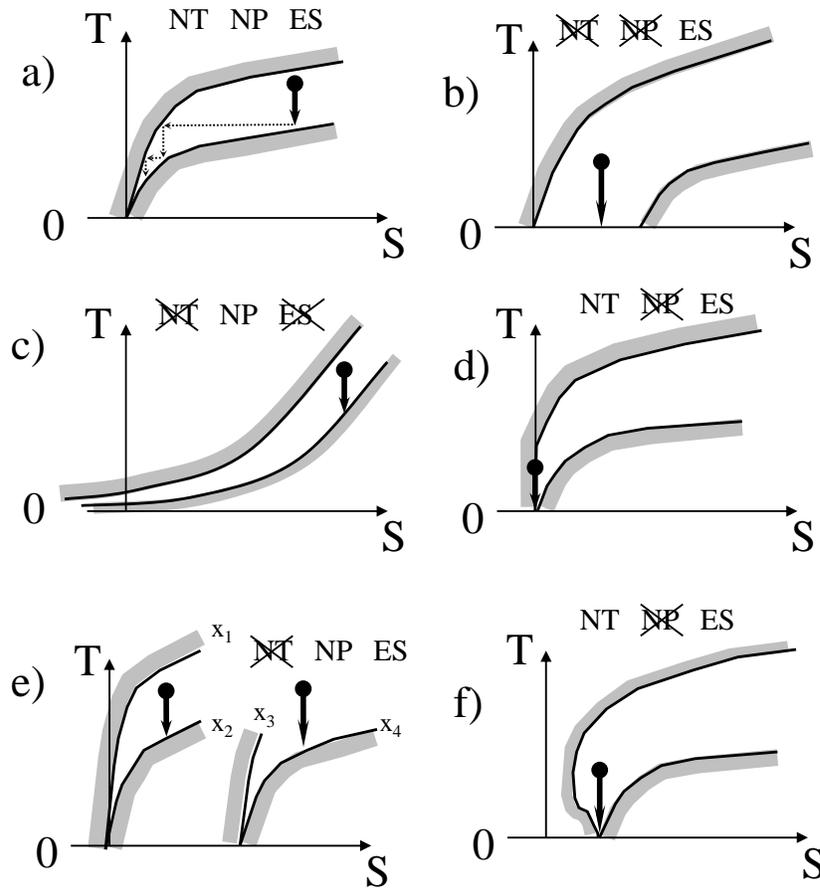
Fig. (1). Entropy behavior near absolute zero. The lines of constant x bounding isentropic expansion are shown. Violations of the Nernst theorem (NT), Nernst principle (NP) and Einstein statement (ES) are indicated above each figure. The dotted arrows in Fig. (**a**) show the infinite number of steps needed to reach absolute zero by a sequence of isentropic and isothermal processes. The dashed arrows in Fig. (**b**) demonstrate the Carnot-Nernst cycle.

statement and somewhat less certain but more informative Nernst principle. Currently available scientific evidence tends to support the validity of the Nernst principle. The Nernst theorem, although linked to the Nernst principle, is not fully equivalent to this principle. This theorem does not seem to be universal and, as was first noted by Einstein, is likely to be incorrect as a general statement. The Nernst theorem, however, should be correct for pure substances, providing useful information for analysis of thermodynamic properties at $T \rightarrow 0$; some of these properties are given in Appendix **A**. Planck's formulation unifies the Nernst theorem with the Einstein statement but is thus applicable only to pure substances.

It is interesting that the Nernst principle and the Einstein statement can be combined to produce the following formulation of the third law:

- **Nernst (Nernst - Einstein) formulation.** A thermo-dynamic state with zero absolute temperature can not be reached from any thermodynamic state with a positive absolute temperature through a finite isentropic process limited in time and space, although the entropy change between these states is finite.

This statement implies that

$$0 < S(T,x) - S(0, x + \Delta x) < \infty \quad \text{when} \quad 0 < T < \infty, |x| < \infty, |\Delta x| < \infty \quad (9)$$

or, possibly in some cases, $S(T,x) = S(0, x + \Delta x)$ but the isentropic process connecting these states needs an infinite time for its completion. When Nernst [2] introduced his unattainability principle, he formulated and understood this principle in context of validity of the Einstein statement. If the Einstein statement is not valid and $S \rightarrow -\infty$ as $T \rightarrow 0$, then unattainability of $T = 0$ is quite obvious.

3. PERPETUAL MOTION OF THE THIRD KIND

The importance of the laws of thermodynamics is not solely related to their formal validity; these laws should have a clear physical meaning and applied significance. Thermodynamics has a very strong engineering element embedded into this discipline. We might still not know whether irreversibility of the real world is related only to the temporal boundary conditions imposed on the Universe or there is some other ongoing fundamental irreversibility weaved into the matter. Conventional physics, including both classical and quantum mechanics (but not the interactions of quantum and classical worlds, which may

cause quantum decoherence), is fundamentally reversible. Thermodynamics may not have all of the needed scientific explanations, but it admits the obvious (i.e. the irreversibility of the surrounding world), postulates this in form of its laws and proceeds further to investigate their implications.

The fundamental implications of the laws of thermodynamics are related to engines - devices that are capable of converting heat into work. Converting work into heat is irreversible: all work can be converted to heat but not all heat can be converted to work. The zeroth, first and second laws of thermodynamics impose restrictions that prohibit certain types of engines – these can be conventionally called perpetual motions of the zeroth, first and second kind depending on which laws these engines violate. The n-th law of thermodynamics can be formulated by simply stating that perpetual motion of the n-th kind is impossible. These perpetual engines are illustrated in Fig. (**2**). The first engine represents a possible engine placed into an impossible situation banned by zeroth law of thermodynamics, when temperatures of the reservoirs are not transitive, which symbolically can be represented by $T_H > T_C > T_0 > T_H$, where $T_H > T_C$ means that the heat naturally flows from T_H to T_C. Note that the second law is also violated by this setup. The second engine illustrates the impossibility of producing work out of nothing, which is banned by the first law. The

third engine produces work out of heat without any side effects – this violates the second law.

As in case of the other laws, the third law should have a clear physical interpretation. Since we have two formulations – the Einstein statement and the Nernst principle - we consider two corresponding versions of perpetual motion of the third kind.

The first perpetual engine of the third kind (Fig. (**3a**)) violates the Einstein statement of the third law: it uses the Carnot-Nernst cycle with a compact cooling reservoir at $T_C = 0$ and infinitely small entropy $S = -\infty$ (the cycle's working fluid is presumed to have vanishing heat capacity at $T \to 0$). The amount of heat disposed by the Carnot cycle into the cooler is zero under these conditions ($Q_C = Q_H T_C / T_H \to 0$ as $T_C \to 0$) and all of Q_H is converted into work. The cooler, however, must receive the entropy ΔS_H lost by the heater. Since its entropy is infinitely negative, the state of the cooler is not affected by this entropy dump. One can unify the Carnot-Nernst cycle with the compact cooler and call this an engine converting heat into work. This perpetual engine clearly contradicts if not the letter then the spirit of the second law. Unlimited entropy sinks, which allow for extraction of unlimited work from the environment, are banned by the Einstein statement of the third law. The physical meaning of this statement is a
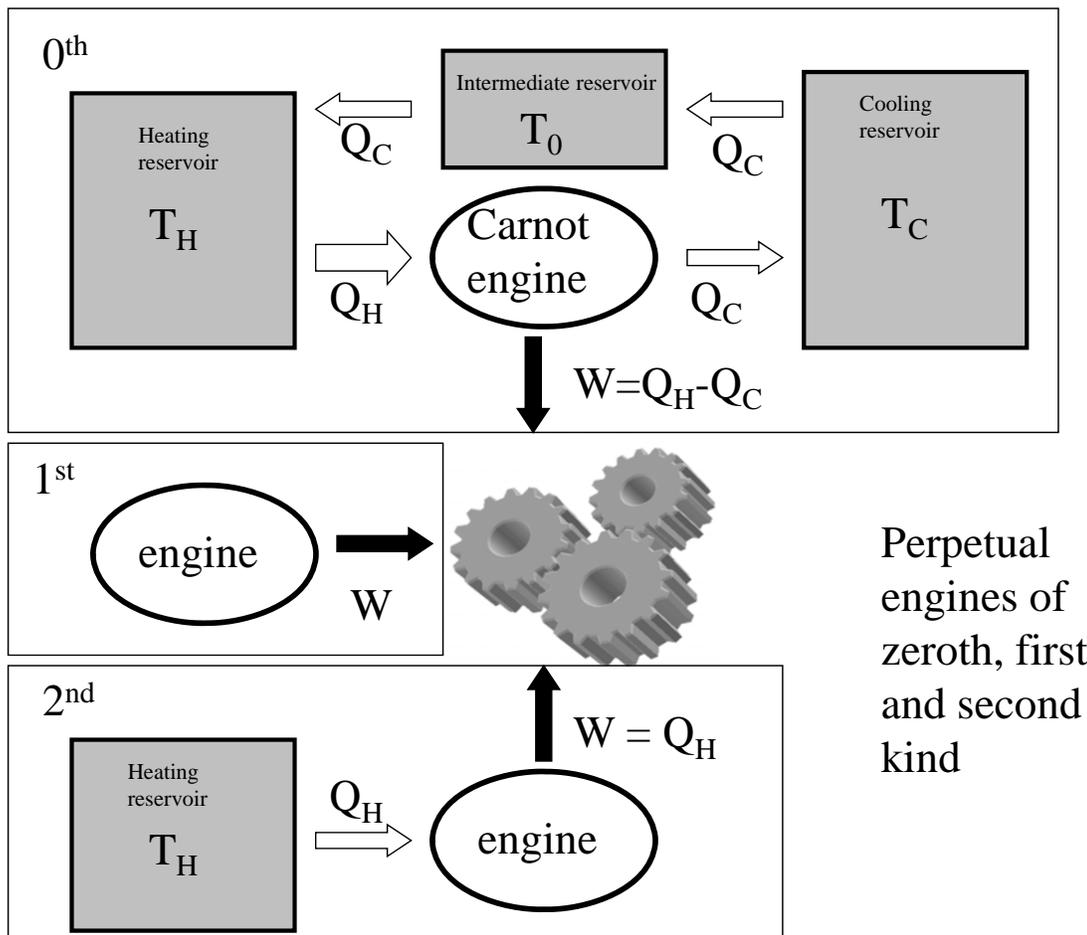
Fig. (2). Perpetual motion engines of the zeroth, first and second kinds.

thermodynamic the declaration of existence of quantum mechanics, which does not allow allocation of unlimited information within a limited volume due to quantum uncertainty.

The second perpetual engine of the third kind shown in Fig. (**3b**) violates the Nernst principle and works with a large cooling reservoir at $T = 0$, which serves as an entropy sink. The engine uses the Carnot-Nernst cycle and converts 100% of heat into work while dumping the excess entropy ΔS_H into the cooling reservoir. The Nernst principle prohibits reaching $T = 0$ in the cycle and does not allow conversion of 100% of heat into work under these conditions. Entropy can be interpreted as negative information - i.e. absence of information about the exact micro-state of the system. The Nernst principle allows for reduction of the energy content of information by lowering T but does not permit the complete decoupling of information and energy that occurs at $T = 0$.

4. NEGATIVE TEMPERATURES

Thermodynamic systems may have negative temperatures [19, 20]. A simple thermodynamic system involving only two energy levels is sufficient to bring negative temperatures into consideration. The thermodynamic relations for this system are derived in Appendix **B**. The entropy S and

inverse temperature $1/T$, obtained in Appendix **B**, are plotted in Fig. (**4**) against energy E. It can be seen that the region of negative temperatures lies above the region of positive temperatures with $T = +0$ being the lowest possible temperature and $T = -0$ being the highest possible temperature. As the energy of the system increases from $E = 0$, particles may now be allocated at both energy levels and this increases uncertainty and entropy. As the energy increases further towards it maximal value $E = E_1$, most of the particles are pushed towards the high energy level and this decreases uncertainty and entropy. Note that the function $S(E)$ is symmetric and $T(E)$ is antisymmetric with respect to the point $E = E_1 / 2$ for this example.

We can define quality of energy as being determined by the function $\beta = -1/T$ so that higher quality corresponds to larger (more positive) β. The quality of work corresponds to the quality of heat at $T = \infty$ and $\beta = 0$. Energy can easily lose its quality and be transferred from higher to lower β but upgrading the quality of energy is subject to the usual restrictions of the second law of thermodynamics. This law can be formulated by stating that energy cannot be transferred from a lower quality state to a higher quality state without any side effects on the environment.
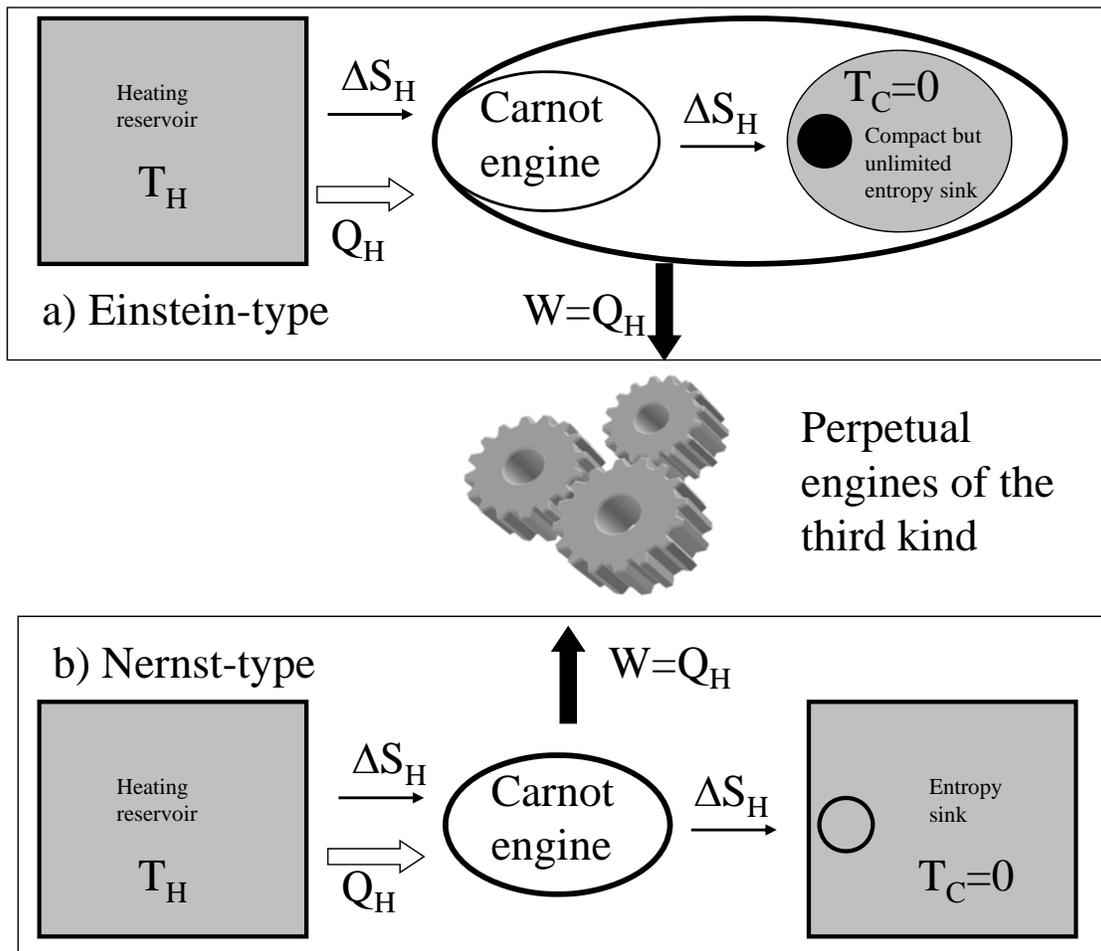

Fig. (3). Perpetual motion engines of the third kind: **a**) violating the Einstein statement and **b**) violating the Nernst principle.
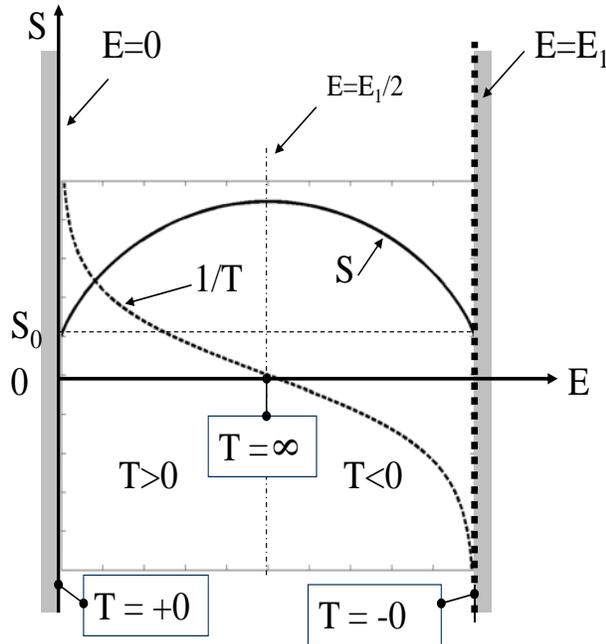
Fig. (4). Negative temperatures in thermodynamics.

The state of negative temperatures is highly unstable and it cannot have conventional volume as separating the volume into smaller parts moving stochastically with macro-velocities increases the entropy. Indeed, the quality of kinetic energy (work) is $T = \infty$ and is below the quality of energy at negative temperatures. For these systems, shattering into small pieces appears to be thermodynamically beneficial. A strict proof of this statement is given in the famous course on theoretical physics of Landau & Lifshits [20]. Negative temperatures may, however, exist in systems that do not posses macroscopic momentum. Both Ramsey [19] and Landau & Lifshits [20] nominate a physical system that may possess negative temperatures during time interval of a measurable duration: interactions of nuclear spins with each other and a magnetic field in a crystal. After a fast change in direction of magnetic field this system is in a state with a negative temperature, which will last until the energy is transferred to the rest of the crystal.

Now we return to the third law of thermodynamics. It is most likely that difficulties and restrictions for reaching positive zero $T = +0$, which are stated by the third law of thermodynamics, are also applicable to negative zero $T = -0$. In the absence of experimental data, this statement may seem speculative but, considering the difficulties of reaching any negative temperatures, achieving $T = -0$ would not be any easier than achieving $T = +0$. In the example given in Appendix **B**, an instantaneous reverse of the direction of the magnetic field changes state E to $E_0 - E$ so that T is changed to $-T$. Hence reaching $T = -0$ allows us to reach $T = +0$ and vice versa.

5. NEGATIVE HEAT CAPACITIES

Thermodynamic systems with negative heat capacities $C < 0$ are unusual objects [21]. In particular, they cannot be

divided into equilibrated subsystems, say A and B, and, as proven by Schrödinger [22] (see Appendix **C**), and cannot be treated by conventional methods of statistical physics (i.e. using the partition function) since these methods imply the existence of equilibrium between subsystems. Indeed, if A and B are initially at equilibrium and $C_A < 0$ and $C_B < 0$ this equilibrium is unstable. Let a small amount of heat δQ to be passed from A to B, then T_A tend to increase and T_B tend to decrease and this encourages further heat transfer from A to B which further increases T_A and decreases T_B. The initial equilibrium between A and B is unstable.

An object with $C < 0$ can however be in equilibrium with a reservoir having positive capacity $C_r > 0$ provided $|C| > C_r$. Indeed, if initially $T = T_r$ and δQ is passed from the object to the reservoir; both T and T_r increase but according to condition $|C| > C_r$, the temperature T_r increases more than T, encouraging heat transfer back from the reservoir to the object.

Although thermodynamic states with negative heat capacity are unstable, such cases have been found among conventional thermodynamic objects with a short existence time [23]. Here, we consider thermodynamic objects with persistent negative heat capacities $C < 0$, and term them thermodynamics stars and thermodynamic black holes due to the vague similarity of their thermodynamic properties to those of real stars and black holes. The heat capacity of a star is negative in Newtonian gravity as considered in Appendix **D**.

5.1. Thermodynamic Stars and Black Holes

The environment is a reservoir with a very large size and capacity so its temperature T_0 does not change. Equilibrium of an object with negative C and the environment is always unstable. Assume that the temperature of the object T is slightly above that of the environment T_0. In this case the object tends to lose some energy due to heat transfer. Since its heat capacity is negative, this would further increase T resulting in more energy loss. The process will continue until the object loses all of its energy; due to obvious similarity we will call these cases *thermodynamic stars*. If a thermodynamic star loses its energy at a rapidly increasing pace as determined by its rapidly rising temperature, it may explode – i.e. reach negative temperatures before losing all of its energy and then disintegrate into small pieces as discussed in the previous section.

We, however, are more interested in an opposite case when T is slightly below the environmental temperature T_0. In this case energy tends to be transferred to the object from the environment, resulting in further temperature T decrease and energy E increase. As T drops to very low values, extracting energy from the object by thermodynamic means becomes practically impossible (as this would need even smaller temperatures). In this case the object can be

termed a *thermodynamic black hole*. Depending on the nature of the limiting state $T \to 0$ we divide thermodynamic black holes into three types:

- **Type 1:** S and E remain bounded. This type is consistent with the Einstein statement but may violate the Nernst theorem and the Nernst principle.

- **Type 2:** E remains bounded but S is not. This type obviously violates the Einstein statement and most likely the Nernst theorem.

- **Type 3:** both S and E are not bounded. This type complies with the Nernst principle but may violate the other statements.

These types of thermodynamic black holes are illustrated in Fig. (**5**). Note that, according to equation (22), $\partial^2 S / \partial E^2$ is positive when C is negative (hence the case $S \to const$, $E \to \infty$ cannot occur). A type 1 black hole reaching $T = 0$ cannot lose any heat since it has the lowest possible temperature and cannot gain any heat since its gaining capacity is saturated – it is thermodynamically locked from its surroundings.

We now examine gravitational black holes, whose major characteristics are listed in Appendix **E**.

5.2. Schwarzschild Black Holes

The Schwarzschild black holes are the simplest type of gravitational black holes and are controlled by a single parameter – the mass of the hole M –, which determines the radius, surface area and volume of the hole [24].

$$r_S = 2\frac{\gamma}{c^2}M, \quad A = 4\pi r_S^2, \quad V = \frac{4}{3}\pi r_S^3 \qquad (10)$$

Here we refer, of course, to the dimensions of the event horizon, which, for Schwarzschild black holes, is a sphere surrounding the time/space singularity. Nothing, not even light, can escape from within the event horizon. It is interesting that the relativistic expression for the radius of the Schwarzschild event horizon r_S coincides with the corresponding Newtonian expression.
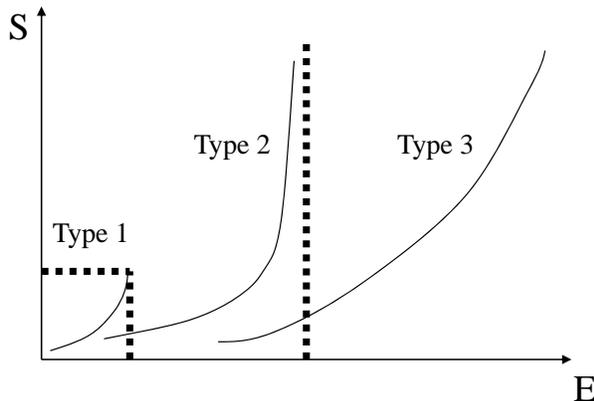

Fig. (5). Three types of thermodynamic black holes.

The Einstein energy, Bekenstein-Hawking entropy and Hawking temperature of the black hole are given by [24]

$$E = Mc^2, \quad S = 4\pi\frac{\gamma k_B}{c\hbar}M^2, \quad T = \frac{\hbar c^3}{8\pi\gamma k_B}\frac{1}{M} \qquad (11)$$

These equations are combined into conventional

$$dE = TdS \qquad (12)$$

Note that Schwarzschild black holes have negative heat capacities

$$C = T\frac{\partial S}{\partial T} = \frac{\partial S}{\partial M}\left(\frac{\partial \ln(T)}{\partial M}\right)^{-1} = -2S \qquad (13)$$

The Bekenstein entropy can be estimated from the quantum uncertainty principle $\Delta E\,\Delta t \sim \hbar$ where ΔE is minimal energy of a quantum wave and Δt is its maximal life time. Inside the horizon, the radial coordinate r becomes time-like (one can say that time t and space distance r "swap" their coordinates) and $\Delta t \sim r_S / c$, hence $\Delta E \sim \hbar c^3 / (\gamma M)$. The ratio $E / \Delta E$ then represents an estimate for the maximal number of quantum waves within the horizon. Assuming that each wave may have at least 2 states, say with positive and negative spins, we obtain the following estimate for the corresponding number of macro-states $\Gamma \sim 2^{E/\Delta E} \sim \exp(E / \Delta E)$. The Boltzmann-Planck equation (1) indicates that $S \sim k_B E / \Delta E \sim k_B\gamma M^2 / (\hbar c)$. This estimate and equation (12) necessitate that $T \sim \hbar c^3 / (\gamma k_B M)$. According to a more rigorous theory developed by Hawking [25] (in the wake of Zeldovich's [26, 27] analysis indicating that rotating black holes emit radiation), black holes can radiate due to quantum fluctuations appearing everywhere including the event horizon. As field disturbances propagate away from the hole, they experience red shift due to relativistic time delays in strong gravity. The Hawking temperature is the effective temperature of a black hole as observed from a remote location. It is useful to note numerical values of the constants:

$$T \approx \frac{1.2 \times 10^{23}\,\text{kg}}{M}\,\text{K}, \quad S \approx 3.6 \times 10^{-7} M^2 \frac{\text{J}}{\text{kg}^2\text{K}}, \quad r_S \approx 1.48 \times 10^{-27} M \frac{\text{m}}{\text{kg}}$$

It is generally believed that, due to restrictions of quantum mechanics, the Bekenstein-Hawking entropy of Schwarzschild black holes represents the maximum possible entropy allocated within a given volume. A black hole works as the ultimate shredding machine: all information entering the black hole is destroyed introducing maximal uncertainty (although mass, charge and angular momentum are preserved). The carrying mass is packed to maximal possible density and reaches maximal entropy. While in absence of gravity the state of maximal entropy is achieved by a uniform dispersal of a given matter over the available volume, shrinking the same matter into a singularity point is favored by the second law of thermodynamics in the presence of a gravitational pull. The relatively small number of black holes, that presumably existed in the early Universe,

is responsible for its initial low-entropy state that provides thermodynamic exergy needed for powering stars and galaxies. The Universe works as if it was a very large thermodynamic engine!

We now examine compliance with the formulations of the third law. In terms of the classification given above, Schwarzschild black holes are of type 3 and they clearly comply with the Nernst principle. Since mass and volume are not restricted at the limit $T \to 0$ (and so is the specific volume $V/M \to \infty$), the Nernst theorem is not formally violated due to non-compliance with its condition of keeping the secondary thermodynamic parameter x finite. The thermodynamic quantities characterizing the black hole behave differently as $T \to 0$ depending on whether they are considered on "per mass" or "per volume" basis. Entropy and capacity per volume comply with the Planck and Einstein statements and the Nernst theorem $C/V \to -0$, $S/V \to +0$ as $T \to 0$ and $M \to \infty$, while the same quantities per mass do not: $C/M \to -\infty, S/M \to +\infty$ as $T \to 0$ and $M \to \infty$.

5.3. Kerr-Newman Black Holes

Kerr-Newman black holes are rotating and electrically charged black holes, characterized by three parameters: mass M, angular momentum J and charge q. These black holes have a very complex space-time structure, which possesses only cylindrical (but not spherical) symmetry. The generalization of the equations presented in the previous subsection leads us to [24]

$$T = \frac{\hbar}{ck_B}\frac{\kappa}{2\pi}, \quad S = k_B \frac{A}{4l_p^2}, \quad l_p^2 = \frac{\gamma\hbar}{c^3} \tag{14}$$

$$dE = TdS + \Omega dJ + \Phi dq \tag{15}$$

where κ is the surface gravity and l_p is the Planck length scale. The definitions of the angular rotation speed Ω and the electrical potential Φ, as well as the associated equations expressing κ and A in terms of M, J and q, are given in Appendix **E**. The heat capacity of Kerr-Newman black hole may be negative or positive depending on the values of the parameters M, J and q.

A major feature of Kerr-Newman black holes is that zero temperature may be achieved with finite values of the parameters M J, and q; this hole belongs to type 1. Indeed equation (46) indicates that $\kappa = 0$ and $T = 0$ when

$$\tilde{M}^2 = \tilde{q}^2 + \frac{\tilde{J}^2}{\tilde{M}^2} \tag{16}$$

This state of a black hole is called extreme. For the sake of simplicity, we use normalized (geometric) values of the parameters marked by "tilde" and defined in the Appendix. The entropy in this state tends to a finite limit

$$S \to k_B \frac{A_0}{4l_p^2}, A \to A_0 = 4\pi(2\tilde{M}^2 - \tilde{q}^2) \quad \text{as} \quad T \to 0 \tag{17}$$

Note that $\tilde{M}^2 \geq \tilde{q}^2$ according to (16) and $A_0 > 0$. One can see that this extreme state complies with the Einstein statement but clearly violates the Nernst theorem. Indeed, the entropy S can, in principle, be changed by dropping suitably selected charged particles into the black hole and changing A_0 without altering condition (16), that is at $T = 0$. If a black hole can physically reach its extreme state, this would also violate the Nernst principle. This appears to be quite important for modern physics and is discussed in the rest of this section.

Charged and rotating black holes have not one event horizon but two: the inner and the outer. As the black hole reaches its extreme state these horizons approach each other and finally merge. If any further increase in charge and angular momentum or decrease in mass occurs, and the event horizons disappear as indicated by A becoming complex in equation (43). The singularity, which is normally hidden behind the horizons, becomes "naked". If this happens anywhere in the Universe, the nature of the Universe changes: we can gain access to non-chronal regions previously protected by the horizons, where many wonderful things such as closed time-like curves and time travel are possible. The implications of this possibility for our understanding of the Universe involve violations of the causality principle and are so severe that Roger Penrose suggested the "cosmic censorship" principle prohibiting naked singularities [28].

Thermodynamics, which is fundamentally linked to the arrow of time, likes the possibility of time travel even less than the other sciences. The Nernst principle, however, prohibits reaching the extreme state since it has $T = 0$ and protects causality in general and irreversibility of the second law in particular. While a rigorous proof of the unattainability statement for Kerr-Newman black holes can be found in the literature [29], we restrict our consideration to a simple illustration. As any thermodynamic object, a black hole radiates energy with intensity $dE/dt \sim AT^4$. We may try to reach extreme state by radiating energy (and mass) of the black hole while keeping its charge the same. If the energy $E_0 = M_0 c^2$ corresponds to the extreme state, then, according to (46) and (43), $T \sim \kappa \sim (E - E_0)^{1/2}$ and $A \to A_0$ as $E \to E_0$. Hence, we obtain $dE/dt \sim (E - E_0)^2$ resulting in $E - E_0 \sim 1/t$. In accordance with the Nernst principle, an infinite time (as measured by a remote observer) is needed for a black hole to reach its extreme state.

6. CONCLUDING REMARKS

The importance of thermodynamic laws lies not only in the formal correctness of thermodynamic statements but also in their universal applicability and physical significance. The third law is an independent statement, which acts as a "guardian angel" for the second law. There is still no perfect formulation for the third law of thermodynamics. Planck's statement and the Nernst theorem are not universal (or likely to be incorrect if formulated as general statements). The

Einstein statement is, to the best of our knowledge, correct and universal but it is weaker than generally expected from the third law of thermodynamics. The considered version of the Nernst principle, which is not fully equivalent to the Nernst theorem, seems to be both universal and correct and is a good candidate for the third law. Recent developments in cosmological thermodynamics tend to support this view: thermodynamics of black holes violates the Nernst theorem but is considered to uphold the Einstein statement and the Nernst principle. The relation between the Nernst principle and protection of causality by cosmic censorship seems profound and produces a very strong argument in favor of formulating the third law of thermodynamics on the basis of this principle.

Both the Einstein statement and the Nernst principle have physical and engineering implications and can be recommended to represent the third law in thermodynamic courses (separately or as the combined Nernst-Einstein formulation). It is probably better to keep the existing

uncertainty in choosing the best formulation of the third law outside the scope of engineering thermodynamic courses – this would be confusing for the students. Selecting a single general formulation and focusing on physical implications rather than on mathematical strictness of the formulation seems to be the best approach. The engineering interpretation of the law – no perpetual motion of the third kind is possible – is a way to induce the students' interest and convince them of the importance of the law. The best engineering and science students may also benefit from a wider discussion of the role of the laws of thermodynamics in the Universe.

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CONFLICT OF INTEREST

Declared none.

APPENDICES

A. Thermodynamic Relations

This Appendix presents thermodynamic relations, which can be useful in analysis of the third law and its implications [20]. We begin with the well-known Maxwell relations which are derived from the commutative properties of partial derivatives (for example $\partial^2 G/(\partial T \partial P) = \partial^2 G/(\partial P \partial T)$). Differentials of energy E, enthalpy H, Gibbs G and Helmholtz F free energies indicate

$$\frac{\partial(S,T)}{\partial(P,T)} = -\frac{\partial(V,P)}{\partial(T,P)} = \frac{\partial G}{\partial T \partial P}, \quad \frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(P,V)}{\partial(T,V)} = \frac{\partial F}{\partial T \partial V} \tag{18}$$

$$\frac{\partial(T,S)}{\partial(V,S)} = -\frac{\partial(P,V)}{\partial(S,V)} = \frac{\partial E}{\partial S \partial V}, \quad \frac{\partial(T,S)}{\partial(P,S)} = \frac{\partial(V,P)}{\partial(S,P)} = \frac{\partial H}{\partial S \partial P} \tag{19}$$

Here partial derivatives are expressed in terms of Jacobians – this can be quite useful in derivations. For example $\partial S/\partial T$ with constant V can be equivalently interpreted as Jacobian for replacement of variables (T,V) by (S,V). The following definitions are related to heat capacities

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\partial(S,V)}{\partial(T,V)} = \left(\frac{\partial E}{\partial T}\right)_V \tag{20}$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\frac{\partial(S,P)}{\partial(T,P)} = \left(\frac{\partial H}{\partial T}\right)_P \tag{21}$$

$$\frac{1}{C_V} = \frac{1}{T}\left(\frac{\partial^2 E}{\partial S^2}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial S}\right)^3\left(\frac{\partial^2 S}{\partial E^2}\right)_V = T^2\left(\frac{\partial^2 S}{\partial E^2}\right)_V \tag{22}$$

The ratio of adiabatic to isothermal compressibilities is linked to heat capacities

$$\frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{\frac{\partial(P,S)}{\partial(V,S)}}{\frac{\partial(P,T)}{\partial(V,T)}} = \frac{T\frac{\partial(P,S)}{\partial(P,T)}}{T\frac{\partial(V,S)}{\partial(V,T)}} = \frac{C_P}{C_V} \tag{23}$$

The difference between C_P and C_V is evaluated by representing entropy as $S = S(T,V(T,P))$ so that

$$C_P - C_V = -T\frac{\partial(S,T)}{\partial(V,T)}\frac{\partial(V,P)}{\partial(T,P)} =$$

$$= -T \frac{\partial(P,V)}{\partial(T,V)} \frac{\partial(V,P)}{\partial(T,P)} = T \frac{\partial(S,T)}{\partial(V,T)} \frac{\partial(S,T)}{\partial(P,T)} \tag{24}$$

Maxwell relations (18) and (19) are used here. The Nernst heat theorem (6) requires (7) that is $(\partial S / \partial x)_T \to 0$ as $T \to 0$ where x can be any thermodynamic parameter, for example V or P. Hence

$$\frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(P,V)}{\partial(T,V)} \to 0, \ \frac{\partial(S,T)}{\partial(P,T)} = -\frac{\partial(V,P)}{\partial(T,P)} \to 0 \quad \text{as} \quad T \to 0 \tag{25}$$

In conjunction with (24), these relations imply that

$$\frac{C_P}{C_V} \to 1 \quad \text{as} \quad T \to 0 \tag{26}$$

The derivative, which indicates the rate of reduction of temperature in adiabatic expansion,

$$\frac{\partial(T,S)}{\partial(V,S)} = \frac{\partial(T,S)}{\partial(V,T)} \frac{\partial(V,T)}{\partial(V,S)} = -\left(\frac{\partial S}{\partial V}\right)_T \frac{T}{C_V} \to 0 \quad \text{as} \quad T \to 0 \tag{27}$$

vanishes under restrictions of the Nernst theorem according to (25). Here we use V and $P = (\partial E / \partial V)_S$ but these relationships can be generalized for any other consistent thermodynamic variables, say x and $y = (\partial E / \partial x)_S$.

B. A Simple Thermodynamic System with Negative Temperatures

Let us consider a simple example: n particles can occupy one of the two energy levels 0 and E_1 (this can be practically achieved when, for example, particle spins can take two values $+\frac{1}{2}$ and $-\frac{1}{2}$ in a magnetic filed). These levels are degenerate, with k_0 and k_1 representing the corresponding degeneracy factors. Classical statistics is assumed implying that $k_0, k_1 \gg n$. There is no need to evaluate the partition function for this simple case. Indeed, assuming that $n_1 = n - n_0$ particles are located at the energy level E_1, the system energy is determined by

$$E = E_1 n_1 \tag{28}$$

The n_1 indistinguishable particles can be allocated on k_1 sublevels of the level E_1 by $\Gamma_1 = k_1^{n_1} / n_1!$ micro-states. Similarly, $\Gamma_0 = k_0^{n_0} / n_0!$. According to the Boltzmann-Planck equation (1) entropy S is linked to $\Gamma = \Gamma_0 \Gamma_1$ by the equation

$$S = k_B \ln(\Gamma_0 \Gamma_1) = -k_B \left(n_0 \ln\left(\frac{n_0}{ek_0}\right) + n_1 \ln\left(\frac{n_1}{ek_1}\right) \right) \tag{29}$$

Here we use $\ln(n!) = n \ln(n / e) + \dots$ and conventionally neglect smaller terms. With the use of

$$S = -k_B n \left(\left(1 - \frac{E}{E_1}\right) \ln\left(\frac{n}{ek_0}\left(1 - \frac{E}{E_1}\right)\right) + \frac{E}{E_1} \ln\left(\frac{n}{ek_1} \frac{E}{E_1}\right) \right) \tag{30}$$

If $k_0 = k_1 = k$, then

$$S = -k_B n \left(\left(1 - \frac{E}{E_1}\right) \ln\left(\left(1 - \frac{E}{E_1}\right)\right) + \frac{E}{E_1} \ln\left(\frac{E}{E_1}\right) \right) + S_0 \tag{31}$$

where constant S_0 is defined by

$$S_0 = -k_B n \ln\left(\frac{n}{ek}\right) \tag{32}$$

The temperature T is determined by

$$\frac{1}{T} = \frac{dS}{dE} = \frac{k_B n}{E_1} \ln\left(\frac{E_1}{E} - 1\right) = -\frac{k_B n}{E_1} \ln\left(\frac{E_1}{E_1 - E} - 1\right) \tag{33}$$

C. Partition Function and Positiveness of Heat Capacities

Schrödinger [22] proved that a system whose thermodynamics is characterized by the partition function Z and statistical sums

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i \exp\left(-\frac{E_i}{k_B T}\right) \tag{34}$$

$$Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right), \tag{35}$$

must have a non-negative heat capacity. Indeed

$$C = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{Z} \sum_i \frac{E_i^2}{k_B^2 T^2} \exp\left(-\frac{E_i}{k_B T}\right) - \frac{\langle E \rangle Z}{Z^2} \frac{\partial Z}{\partial T} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B^2 T^2} \geq 0, \tag{36}$$

where we use

$$\frac{\partial Z}{\partial T} = \frac{\langle E \rangle}{k_B^2 T^2} Z \tag{37}$$

This indicates that Gibbs methods based on evaluating the partition function are not applicable to systems with negative heat capacities.

D. Newtonian Dust Star – A System with Negative Heat Capacity

In astrophysics, the energy of particles interacting by gravity with each other is

$$E = U + K \tag{38}$$

the sum of kinetic energy K and potential energy U of gravitational interactions. According to the Virial theorem (41), which is proved below, $U = -2K$ in classical gravity with the gravitational potential $\phi \sim -1/r$. Note that the kinetic energy is always positive, while potential energy in the gravitational field is negative attaining zero in remote locations. Hence $E = -K$ and the kinetic energy K of n moving particles is linked to the temperature by [21]

$$-E = K = \frac{3}{2} n k_B T \tag{39}$$

Evaluation of heat capacity

$$C = \frac{dE}{dT} = -\frac{3}{2} n k_B \tag{40}$$

yields negative values for C. Hence, when the particles forming a star lose energy due to radiation, the temperature of the star increases [21].

The Virial theorem is proved by the following equation

$$\underbrace{\frac{d^2}{dt^2} \frac{1}{2} \sum_i m_i r_i^2}_{\approx 0} = \underbrace{\frac{1}{2} \sum_i m_i \dot{r}_i^2}_{K} + \underbrace{\sum_i m_i \mathbf{r}_i \cdot \ddot{\mathbf{r}}_i}_{\frac{a}{2} U} \tag{41}$$

for a system of $i = 1, ..., n$ particles with masses m_i and locations $\mathbf{r}_i$. In a stationary state, the average distance between particles does not change and the first term is close to zero. The second term is obviously linked to kinetic energy K while the connection of the last term to U can be demonstrated as follows

$$\sum_i m_i \mathbf{r}_i \cdot \ddot{\mathbf{r}}_i = \sum_i \sum_{j \neq i} \mathbf{r}_i \cdot \mathbf{F}_{ij} = \frac{1}{2} \sum_i \sum_{j \neq i} \left(\mathbf{r}_i - \mathbf{r}_j\right) \cdot \mathbf{F}_{ij}$$

$$= -\frac{1}{2} \sum_i \sum_{j \neq i} r_{ij} \frac{d\phi_{ij}}{dr_{ij}} = \frac{1}{2} \sum_i \sum_{j \neq i} a\phi_{ij} = \frac{a}{2} U$$

Hence $U = -2a^{-1}K$. Newton's third law $\mathbf{F}_{ij} = -\mathbf{F}_{ji} = -\nabla\phi_{ij}$ is applied here while using potential $\phi_{ij}(r_{ij}) \sim -1/r_{ij}^a$, where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $a = 1$ in a gravitational field.

E. Gravitational Black Holes

General stationary **Kerr-Newman black holes** are characterized by three parameters: mass M, angular momentum J and charge q. In general relativity, it is convenient to use so called geometric units, which are denoted here by the "tilde" symbol:

$$\tilde{M} = M\frac{\gamma}{c^2}, \ \tilde{E} = E\frac{\gamma}{c^4}, \ \tilde{q} = q\frac{1}{c^2}\left(\frac{\gamma}{4\pi\varepsilon_0}\right)^{1/2},$$

$$\tilde{J} = J\frac{\gamma}{c^3}, \ \tilde{\kappa} = \frac{\kappa}{c^2}, \tilde{A} = A \tag{42}$$

where c is the speed of light, γ is the gravitational constant and ε_0 is the electric constant. Geometric mass $\tilde{M}$, energy $\tilde{E}$, and charge $\tilde{q}$ are measured in length units (m); geometric angular momentum $\tilde{J}$ and area $\tilde{A}$ are measured in area units (m^2); geometric surface gravity $\tilde{\kappa}$ is measured in inverse length units (1/m). The area of the event horizon – the surface of no-return surrounding the black hole – is given by [24]

$$\frac{A}{4\pi} = 2\tilde{M}\left(\tilde{M} + \left(\tilde{M}^2 - \tilde{q}^2 - \frac{\tilde{J}^2}{\tilde{M}^2}\right)^{1/2}\right) - \tilde{q}^2 \tag{43}$$

Differentiation of this equation results in

$$d\tilde{M} = \frac{\tilde{\kappa}}{8\pi}dA + \tilde{\Omega}d\tilde{J} + \tilde{\Phi}d\tilde{q} \tag{44}$$

where

$$\tilde{\Omega} = \frac{\partial\tilde{M}}{\partial\tilde{J}} = 4\pi\frac{\tilde{J}}{\tilde{M}A}, \ \tilde{\Phi} = \frac{\partial\tilde{M}}{\partial\tilde{q}} = \frac{2\pi\tilde{q}^3}{\tilde{M}A} + \frac{\tilde{q}}{2\tilde{M}} \tag{45}$$

and

$$\tilde{\kappa} = \frac{4\pi}{A}\left(\tilde{M}^2 - \tilde{q}^2 - \frac{\tilde{J}^2}{\tilde{M}^2}\right)^{1/2} \tag{46}$$

represents geometric surface gravity – free fall acceleration evaluated at the event horizon and rescaled by so-called red shift to produce finite values. The red shift is responsible for slowing down time in very strong gravitational fields. The conventional form of the same differential is

$$dE = \frac{c^2}{8\pi\gamma}\kappa dA + \Omega dJ + \Phi dq \tag{47}$$

where

$$\Omega = c\tilde{\Omega}, \ \Phi = \left(\frac{c^4}{4\pi\gamma\varepsilon_0}\right)^{1/2}\tilde{\Phi} \tag{48}$$

All equations simplify in case of **Schwarzschild black holes** [24], which do not have rotation or electric charge: $J = 0$ and $q = 0$. A Schwarzschild black hole is spherically symmetric; its properties are determined by one parameter – the mass M:

$$A = 16\pi\tilde{M}^2 = 16\pi\frac{\gamma^2}{c^4}M^2, \ \tilde{\kappa} = \frac{1}{4\tilde{M}}, \ \kappa = \frac{c^4}{4\gamma}\frac{1}{M} \tag{49}$$

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