The Fourth Law of Thermodynamics[@]

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Abstract

This paper discusses differences between equilibrium, steady state and non-equilibrium both in terms of energy transfer as well as probability of occupation. Steady state is the optimal solution in information processing, traffic management, electric transmission, heat exchangers and international politics. Next, the paper reviews the zeroth, the first, the second and the third laws of thermodynamics. The existence of negative temperatures in small, isolated subsystems does pose a question whether the first law would remain valid if one is able to construct a heat engine, which uses these states as sink. Such processes may be discovered in future, which make operation of such an engine possible. In order to avoid logical inconsistencies, the fourth law of thermodynamics is presented, which states that it is not possible to run a *Carnot Engine* or any other physical heat engine between a source having a positive (absolute) temperature and a sink having a negative (absolute) temperature.

*Keywords***:** Laws of thermodynamics, negative temperatures, heat engine, steady state

1. Introduction

Thermodynamics is a fundamental discipline in physics and engineering sciences concerned with the understanding and the interpretation of temperature-dependent properties of matter. Two of the six paradigms of physics come from thermodynamics [1, 2]. Having a solid mathematical formulation, thermodynamics (combined with statistical mechanics) is one of the core areas of physics, foundation of engineering sciences and plays a pivotal role in technological innovations. In addition, chemical sciences and technologies, biological sciences and technologies, geological sciences and technologies, economics and financial sciences, political science and international relations benefit from some form of laws of thermodynamics. In this paper laws of thermodynamics are reviewed and possibility of introducing a fourth law explored.

2. Equilibrium, Steady State and Non-Equilibrium

2.1 Energy-Transfer Considerations

In terms of energy transfer, equilibrium could be understood as a situation in which there is no net transfer of energy, data or information. Steady state is a situation employing transfer of energy, data or information at a uniform rate. Steady state is the optimal solution in information processing, traffic management, electric transmission, heat exchangers and international politics. Non-equilibrium is a situation, in which transfer of energy, data or information takes place at a variable rate.

2.2 Probability-of-Occupation Considerations

In terms of probability of occupation, equilibrium implies same probability of occupation in different states, which is not varying with time; steady state means different probability of occupation in different states, at the same time not varying with time, whereas non-equilibrium corresponds to probability of occupation in different states varying with time.

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2.3 Examples

A layman can think of equilibrium as curfew imposed in the city, no traffic on roads. Traffic on a highway would be a good example of steady state. Traffic on a road serving a busy market may be considered as a non-equilibrium situation.

In thermodynamics, if two bodies are at the same temperature, there shall be no net transfer of heat from one to another, although the amount of heat possessed by both of them may differ. This is called thermodynamic equilibrium. In calorimetry, equilibrium is achieved through stirring the mixture in order to determine specific heat of a substance. In Searle's method of determining thermal conductivity of a metallic rod, one end of the rod is heated by passing steam through a tube wrapped around it. After circulating, the steam is condensed by dipping the rubber pipe into cool water. Two thermometers are inserted, one where steam is about to transfer heat to the conducting rod, and the other measuring temperature of the steam coming out after transferring heat to the rod. Similarly, water is circulated through a tube on the other end of the conducting rod, so that heat is taken away by water. Two thermometers, also, measure temperatures of the water. One of them records temperature of water coming from tap and the one water, which has taken away heat of the rod. Initially, temperatures on all thermometers vary (non-equilibrium). However, if the flow is adjusted properly, the temperatures become constant, although showing different values on each thermometer. When this happens, steady state is reached. Note that if all the temperatures become equal, there is no transfer of heat possible, and this will be a situation of equilibrium.

In electrodynamics, if two bodies are at the same potential, there shall be no net transfer of charge (flow of current) from one to another, although the amount of charge on each of them may not be equal. State of equilibrium means open circuit (no flow of current). Steady state (constant flow of current) is required in electroplating and experiment of mechanical equivalent of heat by electrical method.

Siphon is a good example to describe concepts of equilibrium, steady state and non-equilibrium in the context of gravitational field. If the two arms of liquid column have same height, there will be no flow (equal gravitational potential). This is an example of equilibrium. Both arms may not necessarily have the same diameter; hence the amount of liquid may vary in each arm. If one of the arms is higher (and care is taken to keep difference in heights same by adding suitable amount of liquid in the column, which is higher), there will be a uniform flow from the higher arm to the lower arm — example of steady state. If the difference of heights does not remain constant (ordinary flow), the situation will be that of non-equilibrium.

3. Laws of Thermodynamics

3.1 The Zeroth Law

Fowler and Planck stated the zeroth law in 1930, long after the first, the second and the third law were widely understood. This is the reason that the law is named as the zeroth law. This law serves as foundation to the other laws. It allows one to define temperature in a non-circular way without referring to entropy, its conjugate variable. A system is said to be in thermal equilibrium with another system when it is in thermal contact with the other system (diathermally connected — heat is allowed to exchange between the two systems) and its thermodynamic parameters do not change in time [3]. The zeroth law may be stated as: If system *A* and system *B* are in thermal equilibrium with system *C*, then system *A* is in thermal equilibrium with system *B.* This law appears to employ transitive property of numbers if equality is replaced by thermal equilibrium.

3.2 The First Law

Mayer Joule and Helmholz were behind the development of the first law of thermodynamics. The first law of thermodynamics is considered as the first paradigm of physics by the author [1]. This law is no more than a statement of the law of conservation of energy, realizing that heat is a form of energy. Below are some of the statements of the first law:
a) The total energy, in any process in an isolated system, remains the same.
b) The energy provided to a thermodynamic system is utilized in doing external work and increasing internal energy of the system [1].

3.3 The Second Law
The second law of thermodynamics is attributed to Carnot and Clausius. The second law defines entropy, which may be understood as a measure of deficiency of information. It states that the entropy of an isolated macroscopic system either remains the same or increases. In the words of Kittel and Kroemer, "If a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will increase monotonically in successive instants of time." [3]

3.4 The Third Law
The German chemist, Walther Nernst is considered as formulator of the third law of thermodynamics. The third law of thermodynamics implied that it is impossible to cool a system to absolute zero. Otherwise, it will be possible to operate a *Carnot Engine* with the heat sink at absolute zero. This would violate the second law of thermodynamics. The earliest statement of this law is that at absolute zero the entropy difference becomes nonexistent between all those configurations of a system, which are in internal thermal equilibrium with each other [4].

3.5 Negative Temperatures
The third law of thermodynamics does not rule out the existence of negative absolute temperature state. However, it cannot be reached by crossing 0 K. The concept is physically meaningful for a system that satisfies the following restrictions [5-7]:

a) There must be a finite upper limit to the spectrum of energy states. Otherwise, a system at a negative temperature would have infinite energy. Hence, a freely moving particle or a harmonic oscillator cannot have negative temperatures, for there is no upper bound on their energies. Only certain degrees of freedom of a particle can be at a negative temperature, *e. g.*, nuclear-spin orientation in a magnetic field.

b) The system must be internal thermal equilibrium. The states must have occupancies in accord with the Boltzmann factor selected for the appropriate negative temperature.

c) The states that are in negative temperature must be isolated and inaccessible to these states of the body that are at a positive temperature.

Negative temperatures correspond to higher energies than positive temperatures. In other words, negative temperatures are hotter than positive temperatures. Consequently, when a system at a negative temperature is brought into contact with a system at a positive temperature, energy will be transferred from the negative temperature to the positive temperature.

Nuclear and electronic spin systems can achieve negative temperatures by suitable radio frequency techniques. The nuclei make a sub-system of the solid and are isolated from rest of the solid by perfect vacuum, which exist between the nuclei and the electrons of an atom. In a true sub-system, negative absolute temperatures are obtained not by removing from the system all the energy of the thermal motion (*i. e.*, passing through 0 K), but by adding to the sub-system a greater amount of energy than the one, which corresponds to infinite absolute temperature. Note that such a behavior is exhibited in trigonometric functions. The graph of tangent versus angle jumps from positive infinity to negative infinity at 90^0 (or $\pi/2$ radian).

4. The Fourth Law of Thermodynamics

4.1 Literature Review
The first mention of a fourth law of thermodynamics seems to have occurred in the 1930s lectures of Nernst. Around 1952, people started to consider Norwegian-born American physical chemist, Lars Onasager's 1929 reciprocal relations as a fourth law. In 1972, Peter Landberg started to refer as fourth law, the Belgian chemist, Ilya Prigogine's far-from-equilibrium theories, applied to living systems. In the context of economic thermodynamics, the 1977 Nicholas Georgescu-Roegen's statement, "In a closed system (such as human society), it is impossible to completely recover the matter involved in the production of work", is popularly known as the fourth law. In the 1990s, Sven Jorgensen promoted the statement "ecosystems attempt to develop towards a higher level of energy" as a tentative fourth law. In 2000, American biochemist, Stuart Kauffman gave a version of fourth law, which is based on the logic of thermodynamic work cycles. According to Kauffman, in the context of Darwinian evolution there must exist chemical systems that act to better their own interest. During 2006-9, Romanian-born American chemical engineer, Adrian Bejan referred his 1996 constructal theory as a fourth law of thermodynamics,

which brought life and time explicitly into thermodynamics and created a bridge between biology and physics. Morel and Fleck proposed a fourth law of thermodynamics that extended the domain of thermodynamics by incorporating evolving systems [8]. In their own words, “Systems increase entropy at the maximum rate available to them”. This law requires that identical systems under identical conditions behave identically.

4.2 Need

The question arises that if negative temperatures exist in small, isolated subsystems whether the first law would remain valid if one is able to construct a heat engine, which uses these states as sink. In this case, a *Carnot Engine* operated with such a heat sink may have an efficiency exceeding unity (violation of the first law of thermodynamics). Such negative-temperature states exit in sub-systems of solid, which are isolated from the rest of the solid by perfect vacuum existing between the nuclei and the electrons of an atom. In order to avoid logical inconsistencies, a fourth law of thermodynamics is needed, which can rule out operation of such an engine.

4.3 Statement

It is not possible to design a *Carnot Engine* or any other physical heat engine, whose source has a positive (absolute) temperature and sink has a negative (absolute) temperature.

4.4 Physical Possibilities

Although, at this stage it seems, almost, technologically impossible to operate a heat engine involving the above-described mechanism, quantum tunneling and processes similar to Hawking radiation may be discovered in future, which could make operation of such an engine possible.

5. Conclusion

Laws of thermodynamics give an axiomatic basis of thermodynamics, defining fundamental physical quantities, including energy, entropy and temperature. They bring about the concept of thermodynamic systems and give a framework of transport and conversion of heat and work in thermodynamic processes. These laws are, formally, valid only in the thermodynamic limit, meaning that a certain microscopic system may be described, practically, by an infinite number of microscopic states to satisfy the laws of statistics. Statistical fluctuations are present in every finite system in their thermodynamic parameters, namely, pressure, temperature, entropy. However, these are negligible for macroscopic systems. In fact, the laws of thermodynamics occupy the status of fundamental laws of physics.

Dedication

This lecture was dedicated to the loving memory of the speaker’s teacher and inspirer, (Late) Salim Ahmed, who taught him courses entitled Theory of Relativity and Methods of Mathematical Physics as faculty member of Department of Physics, University of Karachi. He, then, proceeded to United States for his graduate studies. At the time of his death he was associated with Hamdard University.

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