ANALYSIS OF THERMAL AND ENERGY SYSTEMS

ATHENS '91

Edited by

D.A.Kouremenos
G.Tsatsaronis
C.D.Rakopoulos

TEMPERATURE OF A SYSTEM WITH ONE CONSTITUENT

WITH ONE DEGREE OF FREEDOM

Elias P. Gyftopoulos

Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

ABSTRACT

The concept of thermodynamic temperature is examined in different contexts, that is, classical thermodynamics, quantum physics, and fluctuations. It is shown that none of these contexts imposes restrictions either on the values of the amounts of constituents—or the corresponding number of degrees of freedom—or on the values of the constraints or parameters—such as the volume—of the system. So we conclude that temperature is well defined and valid for any system, including one with a single elementary particle with only one degree of freedom, such as a one–dimensional harmonic oscillator of specified frequency of oscillation.

INTRODUCTION

A long standing consensus in practically all authoritative treatises on classical thermodynamics and statistical mechanics is that thermodynamics and "its most important conception, temperature" [1] applies only to macroscopic bodies. A sample of this consensus is reflected in the following statements. Pippard states [2] "The science of thermodynamics, in the widest sense in which the word is used nowadays may be said to be concerned with the understanding and interpretation of the properties of matter in so far as they are affected by temperature... . For a consideration of the behavior of a large assembly of atoms, molecules, or other physical entities, it may be shown, with a fair degree of rigour (enough to satisfy most physicists but few pure mathematicians), that those properties of the assembly which are observable by macroscopic measurements are related in obedience with the laws of thermodynamics." Modell and Reed state [3] "The essence of the theoretical structure of classical thermodynamics is a set of natural laws governing the behavior of macroscopic systems." Callen avers [4] "By definition, suggested by the nature of macroscopic observations, thermodynamics describes only static states of macroscopic systems." Tolman indicates [5] "...And the principles of thermodynamics are devised for giving a phenomenological account of the gross behaviour of macroscopic physical systems in conditions corresponding to the specification of a limited number of thermodynamic variables such as volume, pressure, energy, temperature and entropy." Landau and Lifshitz declare [6] "Like entropy, the temperature is seen to be a purely statistical

quantity which has meaning only for macroscopic bodies." And most recently, Feshbach concludes [7] "These observations, which are based on rather simple considerations, suggest that for small systems thermodynamics is not always quantitatively valid, and therefore requires appropriate modification."

What is the justification for this consensus? A scrutiny of the foundations of thermodynamics and its relation to quantum physics reveals that there exists neither experimental nor theoretical compelling evidence in support of the consensus, and that the statistical interpretation of thermodynamics leads to serious inconsistencies [8]. In response to these conclusions, an alternative viewpoint has been developed. It is a unified, quantum but nonstatistical theory which encompasses within a single conceptual structure all systems, large and small, and all states, static and not static [9,10].

The purpose of this paper is to present only one aspect of this alternative viewpoint, that is, to prove that temperature is equally well defined for a microscopic system as it is for a macroscopic system, including a system consisting of a single elementary constituent, such as one spin with spin orientation in one direction as the only degree of freedom, and a one–dimensional harmonic oscillator of specified frequency of oscillation. The proof is discussed in three different contexts, classical thermodynamics, probabilistic derivations, and fluctuations.

CLASSICAL THERMODYNAMICS

In classical thermodynamics, whenever temperature is introduced without circular arguments, the concept is well defined in theory and very demanding in application. If the vector $\mathbf{n} = \{n_1, n_2,...,n_r\}$ denotes the types and the amounts of the r constituents of a system, and the vector $\beta = \{\beta_1, \beta_2,...,\beta_s\}$ the types and values of the s constraints or parameters of the system, the *thermodynamic temperature* is defined by the relation (Landau and Lifshitz [6], Callen [11], Gyftopoulos and Beretta [12])

$$T = (\partial E/\partial S)_{\mathbf{n},\beta} \qquad (1)$$

where E is the energy, and S the entropy of the system.

Equation 1 indicates that the concept of temperature T applies to states for which the energy E is a function only of the entropy S, the values of the amounts of the constituents $\mathbf{n}$, and the values of the constraints β. The only states for which $E = E(S,\mathbf{n},\beta)$ are the thermodynamic equilibrium or stable equilibrium states. This consequence of the first and second laws of thermodynamics [13] is often referred to as the *state principle*.

As it is well known, each stable equilibrium state has the smallest[1] energy of all the states with the same values of S, $\mathbf{n}$, and β or, alternatively, the largest entropy of all the states with the same values E, $\mathbf{n}$, and β. These two results are sometimes referred to as the *lowest energy principle* and the *highest entropy principle*, respectively [14]. For states that are not stable equilibrium, E

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[1] Spin systems have values of energy that are bounded both from below and above. For each set of values S, $\mathbf{n}$, and β, the state with the smallest energy corresponds to a positive temperature, and the state with the largest to a negative temperature.

depends on more independent variables than S, n, and β, and, therefore, Equation 1 is inappropriate.

Of course, one might consider states that depend on more independent variables than S, n, and β, and define a property T by either a partial derivative similar to that in Equation 1 by keeping all variables fixed except for S, or some other procedure. Though such a definition might be well specified, it would be useless for the thermodynamics of stable equilibrium states.

To clarify the last assertion, we recall a criterion for two systems A and B to be in mutual stable equilibrium, that is, for the composite of two systems A and B to be in a thermodynamic equilibrium state. The criterion is that the entropy of the state of the composite system be the largest of all the states with the same values of energy $E^A + E^B$, amounts $n^A + n^B$, and constraints $\beta^A + \beta^B$. It can be readily shown that a necessary condition for this criterion to be satisfied is that

$$[(\partial E/\partial S)_{n,\beta}]^A = [(\partial E/\partial S)_{n,\beta}]^B \tag{2}$$

or, equivalently,

$$T^A = T^B \tag{3}$$

namely, that A and B be in temperature equality. The temperature equality is important not only as a necessary condition for mutual stable equilibrium but also as a unique operational tool for finding the value of the temperature by means of a null measurement.

Because only the thermodynamic temperature satisfies the temperature equality, any definition of T different from Equation 1 might be well prescribed but irrelevant to the requirements of mutual stable equilibrium between systems and, therefore, to the most important and unique operational technique we use in temperature measurements.

As a result of this review of all the procedures of classical thermodynamics that lead to the definition of the thermodynamic temperature by Equation 1, we find that none requires that any restrictions be imposed either on the types and values of the amounts of the constituents, or on the types and values of the constraints. So we must reach the inescapable conclusion that, in classical thermodynamics, the concept of thermodynamic temperature is valid equally well for a system with large amounts of constituents—large values of the corresponding number of degrees of freedom—and large values of constraints, such as a large volume, as it is for a system consisting of a single structureless particle, confined over a short straight line, namely, a system with one constituent with one degree of freedom.

PROBABILISTIC DERIVATIONS

Ever since the inception of thermodynamics in the 1850's, countless efforts have been devoted to reconciling the contrasts between the predictions of mechanics and thermodynamics. For example, in the context of mechanics all the energy of a system above the ground state can be transferred out of the system in the form of work. However, in the context of thermodynamics, the energy that

can be transferred out of the system in the form of work is smaller than the energy above the ground state, and it can be even zero.

Though perhaps expressed in different terms, the contrast just cited has been the subject of intensive inquiry and controversy. Invariably a reconciliation is proposed in terms of a statistical interpretation of thermodynamics.[2]

Whenever a statistical interpretation of thermodynamics is attempted, the question arises whether the thermodynamic temperature is restricted not only to systems in thermodynamic equilibrium but also to systems with particular values of either the amounts of constituents, or the constraints, or both. As already indicated, practically all treatises on statistical thermodynamics assert that thermodynamics, in general, and the concept of temperature, in particular, apply to macroscopic systems only [4–6]—systems with constituents with innumerable degrees of freedom—because only then the statistical interpretation is valid. Close scrutiny of the issue, however, reveals that such an assertion is entirely unfounded. The first scientist to make this observation was Gibbs [15] himself, and the problem was worked upon also by Wilson [16].

We can state unequivocally that, even in the context of a statistical interpretation of thermodynamics, temperature is equally well defined for systems with a single constituent with one degree of freedom as it is for systems with many constituents and correspondingly many degrees of freedom, and for systems with any values of the constraints. We can illustrate the rationale of this conclusion by using the language of quantum physics.

We consider a system with a Hamiltonian operator $\hat{H}$ and a well defined energy eigenvalue problem

$$\hat{H}\ u_i = \epsilon_i\ u_i \quad \text{for} \quad i = 1, 2,... \quad (4)$$

where for simplicity we assume a discrete energy eigenvalue spectrum ϵ_i, denote each eigenstate by a different subscript i, and recognize that each ϵ_i is a function $\epsilon_i(n,\beta)$ of the values of the amounts of constituents n, and the values of the constraints β. We impose no restriction on the values of either the amounts n and, therefore, the corresponding number of degrees of freedom, or the constraints β because none is required by the specification of the energy eigenvalue problem. In other words, the energy eigenvalue problem may correspond to one spin with two energy eigenstates, two spins with four energy eigenstates, one structureless particle or a harmonic oscillator in a box (large or small, one–dimensional or three–dimensional) with an indefinite number of energy eigenstates, or many molecules in a box (large or small) again with an indefinite number of energy eigenstates.

Regardless of the specifics of the energy eigenvalue problem, it is well known that each thermodynamic equilibrium state of the system has values of energy and entropy given by the relations

$$E = \Sigma_i\ x_i \epsilon_i \quad S = -k\ \Sigma_i\ x_i \ln x_i \quad 1 = \Sigma_i\ x_i \quad x_i \geq 0 \quad (5)$$

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[2] A statistical interpretation means that probabilities are introduced because of lack of information. They can be eliminated by improved information.

where the distribution x_i is determined by the highest entropy principle, that is, by the requirement that S be a maximum subject to a given value E, the summation $\Sigma_i\, x_i$ being equal to unity, and fixed values of either the amounts of constituents n and the constraints β or, equivalently, a fixed vector $\epsilon = \{\epsilon_1, \epsilon_2,...\}$. The coefficient k is Boltzmann's constant. The result of this constrained maximization is [17]

$$x_i = \exp(-\epsilon_i/k\,\lambda_1)/\lambda_2 \quad \text{for} \quad i = 1, 2,... \tag{6}$$

where λ_1 and λ_2 are the two Lagrange multipliers of the constrained maximization problem. Upon substituting Equation 6 into $\Sigma_i\, x_i = 1$, we find

$$\lambda_2 = \Sigma_i \exp(-\epsilon_i/k\,\lambda_1) \tag{7}$$

and

$$x_i = \exp(-\epsilon_i/k\,\lambda_1)/\Sigma_i \exp(-\epsilon_i/k\,\lambda_1) \quad \text{for } i = 1,2,... \tag{8}$$

Moreover, upon substituting Equation 8 into $E = \Sigma_i\, x_i\epsilon_i$, we find λ_1 as a function E. We can easily show that each value of E yields one and only one value λ_1. The distribution represented by Equation 8 is called *canonical*.

Now we raise the question "For given values of E, n, and β or, equivalently, E and ϵ, is the Lagrange multiplier λ_1 related to any property other than E of the corresponding thermodynamic or stable equilibrium state?" The answer is yes, and we find it as follows. We compute the partial derivatives $[\partial E/\partial(1/\lambda_1)]_\epsilon = [\partial E/\partial(1/\lambda_1)]_{n,\beta}$ and $[\partial S/\partial(1/\lambda_1)]_\epsilon = [\partial S/\partial(1/\lambda_1)]_{n,\beta}$ and then take their ratio. We can easily show that

$$\left[\frac{\partial E}{\partial(1/\lambda_1)}\right]_{n,\beta} = \frac{E^2 - \Sigma_i\, x_i\epsilon_i^2}{k} \tag{9}$$

$$\left[\frac{\partial S}{\partial(1/\lambda_1)}\right]_{n,\beta} = \frac{E^2 - \Sigma_i\, x_i\epsilon_i^2}{k\lambda_1} \tag{10}$$

and, upon solving Equations 9 and 10 for λ_1, that

$$\lambda_1 = \left[\frac{\partial E}{\partial(1/\lambda_1)}\right]_{n,\beta} \Big/ \left[\frac{\partial S}{\partial(1/\lambda_1)}\right]_{n,\beta} = \left[\frac{\partial E}{\partial S}\right]_{n,\beta} \tag{11}$$

We see that λ_1 equals $[\partial E/\partial S]_{n,\beta}$. But, in classical thermodynamics, $[\partial E/\partial S]_{n,\beta}$ is defined as the thermodynamic temperature T and, therefore,

$$\lambda_1 = T \tag{12}$$

It is clear that no aspect of this statistical interpretation of thermodynamic equilibrium imposes any restriction whatever on n and β. The statement of the energy eigenvalue problem, Equations 5, and the constrained maximization procedure are all not conditioned by the magnitudes of n and β. So here, as in classical thermodynamics, we must reach the inescapable conclusion that temperature is defined for stable equilibrium states of systems with constituents with any number of degrees of freedom, including unity, with any number of distinct energy eigenvalues equal to or greater than two, and any values of constraints, including a small or large volume.

This elegant and concise derivation of the canonical distribution (Equation 8), and the identification of the exponent λ_1 with the thermodynamic temperature (Equation 12) do not require the consideration of either a heat bath or interactions between subsystems of a large system, as often claimed in most of the literature on statistical physics [18,19]. The reason is that each of these two artifices is neither necessary nor correct.

To clarify the last assertion, first we note that the canonical distribution is obtained from the constrained maximization of the entropy, and that the temperature is either determined by the energy or derived by differentiation of the energy with respect to entropy along a path of stable equilibrium states. As such, both x_i and T are properties of stable equilibrium states, in the same sense that energy, enthalpy, and Gibbs free energy are properties of these states. So, x_i and T are not and need not be tied to a bath or thermostat. A trivial illustration of this conclusion is the maintenance of cold, lukewarm, hot, or superheated water inside a well manufactured thermos bottle, in the same environment, be it outer space, or an oven. The temperature of the water is determined solely by the amount of energy of the water and not any other factor whatsoever. Another illustration is the creation of a thermonuclear plasma inside an electromagnetic nest of forces. Here again the temperature of the plasma is solely a function of the energy transferred to the plasma and not the environment in which the thermonuclear plasma is created.

Next, we recall that for a body to be a system with properties, such as energy and entropy, it must have a Hamiltonian operator that is separable from the Hamiltonian operators of systems in the environment, and probabilities associated with measurement results that are statistically independent of the probabilities associated with measurement results on systems in the environment [20]. In principle, neither separability nor statistical independence is satisfied in the presence of interactions of a body with a bath or thermostat, especially if the body consists of one particle of a dense phase.

An important question that transcends the issues surrounding the definition of temperature relates to the meaning of the distribution x_i. In statistical mechanics, the distribution represents probabilities that reflect lack of information about the exact state of the system. Such probabilities can be eliminated by improved information. Although more than a century old, this interpretation leads to inconsistencies [8]. The inconsistencies disappear if we recognize the

existence of quantum—theoretic probability distributions[3] associated with a homogeneous ensemble even though its density operator may have the form traditionally associated with inhomogeneous quantal ensembles (mixtures of pure states or wave functions). The discussion of this important discovery is beyond the scope of this paper but can be found in References 9, 21, and 22.

FLUCTUATIONS

Concerns about the applicability of the concept of temperature to small systems are sometimes expressed in terms of the magnitude of fluctuations [7]. Because the term fluctuation is not defined explicitly in Reference 7, we examine its two principal meanings and find that neither implies any restriction on the concept of temperature.

One meaning of the term fluctuation relates to the standard deviation of a probability distribution associated with measurement results of a quantum observable. For example, the Δx and Δp_x that appear in the Heisenberg uncertainty relation $\Delta x \, \Delta p_x \geq \hbar$ are related to the standard deviations of position x and momentum p_x measurement results, respectively, where $\hbar$ is Planck's constant divided by 2π. Regardless of the magnitude of this type of fluctuation of a quantum observable, the (expectation) value of the observable is well defined, and no restriction is imposed on its validity. If temperature were a quantum observable, and its measurement results had a standard deviation or fluctuation, this fluctuation would not impose a limitation on the validity of the concept of temperature. So the fluctuation of temperature discussed in Reference 7, on the basis of which the author concludes that "for small systems thermodynamics is not always quantitatively valid," cannot be related to a standard deviation.

Besides temperature is not an observable in the sense of quantum physics. The reason is that temperature is a property only of stable equilibrium states whereas a quantum observable represents a property of any state, stable equilibrium or not. Because it is not a quantum observable, temperature measurement results are not associated with a spectrum of eigenvalues and a corresponding probability distribution. It follows that no standard-deviation-like fluctuation is associated with temperature.

The other meaning of the term fluctuation relates to changes of value of a property as a function of time, that is to variations of the property about some mean value as time goes on. If observed, such fluctuations imply that the system is not in a thermodynamic equilibrium state[4] and, therefore, the concept of temperature is inapplicable not because the value of the number of degrees of freedom is small or large but because of departure from equilibrium. So, if the

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[3] Quantum—theoretic probability distributions are conceived to be inherent to natural phenomena, and cannot be eliminated by improved information.

[4] It is important to recall that, by definition, when a system is in a thermodynamic equilibrium state or stable equilibrium state, the system is isolated, none of its properties changes as a function of time, and no change of the state can be brought about without net effects on other systems in the environment.

large fluctuations discussed in Reference 7 are of this second type, they cannot be used to decide the validity of the concept of temperature because they arise from nonequilibrium. In fact, as pointed out by Kittel [23], the expression "temperature fluctuation" is an oxymoron because temperature refers to a stable equilibrium state that does not vary with time, whereas here fluctuation results from a state that does vary with time.

A third, statistical notion of the term temperature fluctuation has been given by Mandelbrot [24]. Although correct in the context of statistics, the notion described by Mandelbrot is never used either in measurements or in theoretical explanations of temperature. So his arguments are not germane to the concepts, principles, and procedures of thermodynamics.

CONCLUSION

The discussions of temperature from the standpoints of classical thermodynamics, probabilistic interpretations, and fluctuations disclose no restriction imposed on the concept of temperature by the number of degrees of freedom of the constituents of the system. Accordingly, we conclude that the thermodynamic temperature is a well defined concept that applies equally well to both macroscopic and microscopic systems, including a system with one constituent with one degree of freedom.

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