Caloric and entropic temperatures in non-equilibrium steady states

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HIGHLIGHTS

- Caloric and entropic definitions of nonequilibrium temperature are compared.
- Influence of energy flux on temperature of internal variables is studied.
- Effects of a heat flux on caloric and entropic temperatures.
- Ideal gases and two-level systems are considered.

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ABSTRACT

We examine the non-equilibrium consequences of two different definitions of temperature in systems out of equilibrium: one is based on the internal energy (caloric temperature), and the other one on the entropy (entropic temperature). We discuss the relation between the values obtained from these two definitions in ideal gases and in two-level systems.

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0. Introduction

Understanding temperature in non-equilibrium thermodynamic theories is a relevant challenge when going beyond the local-equilibrium theory [1–8]. In a comprehensive review on this topic, Casas-Vazquez and Jou [1] have emphasized the diversity of ways to define temperature and, correspondingly, to measure it or numerically evaluate it. For instance, one may do so on the basis of the internal energy of some degrees of freedom, as the average kinetic energy (kinetic temperature), the average vibrational energy (vibrational temperature), or some averages of the intermolecular potential energy (configurational temperature), or one may start from the Gibbs equation, and relate the temperature to the derivative of the internal energy with respect to the entropy (absolute temperature). One may also explore other definitions, as the relation between entropy flux and heat flux, or the second moments of the fluctuations of the variables, or the Einstein relation between diffusion and particle mobility, and so on.

In equilibrium states, all these definitions lead to the same value for the temperature, but in non-equilibrium steady states they lead to different values. This is not a theoretical inconsistency, because the several temperatures defined in this way give information on different aspects of the system, as for instance on different degrees of freedom. Out of equilibrium,

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equipartition is not to be expected, and therefore the "temperatures" of the different degrees of freedom will be different from each other, and each of them may be measured with different kinds of thermometers (for instance, the intensity of the several spectral lines in a radiation spectrum gives information on vibrational, rotational and electronic temperatures of excited atoms or molecules).

Following the proposal in Ref. [1], we think that a task for non-equilibrium thermodynamics beyond local equilibrium is not so much to insist on the priority of one particular definition on all the other ones, but to recognize that the different temperatures are giving different informations – with different degrees of usefulness or interest, of course, depending on the problem being analyzed –, and to try to establish connections between them. In Refs. [9,10], for instance, the relation between local-equilibrium temperature, kinetic temperature in the three spatial directions, thermodynamic temperature related to the non-equilibrium entropy, and fluctuation–dissipation temperature has been explicitly obtained in an ideal gas in Couette flow. These results were extended in Ref. [11] to a mixture of ideal gases in Couette flow. In Ref. [12], the relation between kinetic temperature and configurational temperature in a forced harmonic oscillator was studied.

Here, we explore the relation between the caloric and the entropic definitions of temperature and illustrate it in systems submitted to a heat flux. We discuss the relation between them, in ideal gases and in two-level systems, keeping the discussion to a minimum formal complication and focusing on conceptual aspects. In Section 1, we state the caloric and entropic definitions of temperature. In Section 2, we apply them to non-equilibrium steady states in ideal gases and in two-level systems, respectively. In Sections 3 and 4, we explicitly illustrate them in detail. Section 5 is devoted to conclusions and to entropy flux.

1. Temperature definitions in equilibrium thermodynamics

Equilibrium thermodynamics is restricted to equilibrium states, which do not change with time and do not sustain net exchange fluxes of energy, mass, momentum, electric charge and so on with the outside. Furthermore, these equilibrium states are homogeneous in their intensive variables, i.e. they do not depend explicitly on the spatial coordinates, like temperature, pressure, chemical potentials and so on, but they can describe multiphase systems and multicomponent systems.

In equilibrium thermodynamics there are several definitions of temperature: *empirical* (based on the zeroth law), *caloric* (based on the first law), and *entropic* (based on the second law) amongst others. The meaning of the caloric and the entropic temperatures is deeply different. The caloric one is related to the *energy contents* of the system, whereas the entropic one is related to the capacity of *energy exchange* with other systems. Here, we remind the reader of these definitions.

1.1. Definitions

Empirical definition:

Empirical (or thermometric) temperature θ_{emp} is defined by the zeroth law, which states the transitive character of thermal equilibrium. In particular, it states that if a state A of a system is in thermal equilibrium with state B of another system, and state B is in thermal equilibrium with state C of a third system, states A and C are in mutual thermal equilibrium.

Entropic definition:

The most fundamental definition of temperature, in equilibrium thermodynamics, is that of absolute temperature, appearing in the Gibbs equation [13,14]. Namely

$$\frac{1}{\theta_{eq}} \doteqdot \left(\frac{\partial S}{\partial U} \right)_{all\ other\ extensive\ variables}.$$ (1)

The subscript "all other extensive variables" besides the parenthesis means that the derivative of the entropy S with respect to the internal energy U must be carried out keeping constant all the other extensive variables appearing in the entropy, as for instance the volume V, the number of particles N_i of the species i, the total magnetization $\mathbf{M}$, and so on.

Caloric definition:

Another usual definition of temperature T_{eq} – we will call it the caloric definition, because it uses the so-called caloric equation of state relating internal energy and temperature – is obtained from the internal energy U, as for instance

$$U = U(T_{eq}, V, N_i).$$ (2)

Since U is defined by the first principle, definition (2) of temperature is related to this principle. It is less fundamental than the other two definitions of temperature, but it is most widely used in kinetic theory.

From a more microscopic basis, there are other possible definitions of temperature, as kinetic translational temperature, rotational temperature, potential temperature, electronic temperature, arising in kinetic theory of gases, or fluctuation temperature, or definitions of temperature based on the relative occupation on several energy levels in statistical physics. Some of these microscopic expressions will be used as illustrations in Sections 3 and 4.