NON-EQUILIBRIUM TEMPERATURES IN SYSTEMS WITH INTERNAL VARIABLES

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ABSTRACT

Temperature is a concept common to all thermodynamic approaches. Different approaches may consider temperature from different perspectives. For instance, in rational thermodynamics, it is considered as a primitive quantity. In extended thermodynamics, temperature is assumed to depend also on the fluxes. In statistical theories, temperature may be related to the form of the distribution functions. In theories with internal variables, each variable could have in principle its own temperature. Thus, a comparative discussion of the several thermodynamic approaches requires as a preliminary condition to compare and clarify the role of temperature. In this contribution we discuss different definitions of non-equilibrium temperature in systems with internal variables, that may be measured only by suitable methods and cannot be controlled with the same immediateness as in the case of classical variables.

In equilibrium thermodynamics, there are different definitions of temperature (thermometric, caloric, entropic, kinetic, vibrational, configurational, fluctuational, and so on) and they lead to the same value. Here, we focus our attention on: i)empirical (or thermometric) temperature, based on the zeroth law; ii) entropic temperature, defined by the second law of thermodynamics as

$$\frac{1}{T} \stackrel{\cdot}{\equiv} \left(\frac{\partial S}{\partial U} \right), \tag{1}$$

where S is the entropy of the system; iii) caloric temperature, based on the first law of thermodynamics and called caloric, because it uses the so-called caloric equation. For instance

$$U = U(T, V, N_i), \tag{2}$$

with V the volume, N_i the number of particles of the species i and U the internal energy defined by the first principle.

The aim of this paper is to discuss these three temperatures in different thermodynamic approaches in non-equilibrium steady states, in presence of an external energy flux and to find the transformation laws relating the several temperatures. In equilibrium states all the above definitions of empirical, caloric and entropic temperatures lead to same value T. Out of equilibrium, equipartition is not to be expected and then in non-equilibrium steady states, when, for instance, the system is crossed by an energy flux and the variables do not depend on time, these temperatures are different from each other.

As an example, in a system composed of matter and radiation, a thermometer with purely reflecting walls will give the temperature of matter, as it will be insensitive to radiation. In contrast, a thermometer with perfectly black walls will yield a temperature related both to matter and radiation. In equilibrium, both thermometers will give the same temperature, but in a non-equilibrium steady state (for instance, with photons transmitting heat and colliding against the particles of a gas) these thermometers will give different temperatures.

Another situation with several -or many-temperatures arises in mixtures of gases with internal degrees of freedom and at high temperatures, as in the entry of spaceships into a planetary atmosphere. In such a case, one may have different kinetic temperatures for different gases, and different electronic temperatures (related to the relative occupancy of electrons at the several energy levels), and different vibrational and rotational temperatures. All these temperatures may be experimentally obtained by means of spectrometric methods, by measuring the intensity of the spectral lines emitted by the gases.

These different temperatures yields a very rich information about the system: about their internal energy transfers and their internal energy contents for the several degrees of freedom. Thus, one of the aims of this contribution is finding the transformation laws relating several thermometric, entropic, caloric and other temperatures in systems in equilibrium steady state submitted to given energy flux.

First, we present an example related to a statistical approach, a two level system with N_1 particles at level 1 (with energy E_1) and N_2 particles at level 2 (with energy 2). For instance, this example could refer to electrons in two electronic levels. In an equilibrium state we define a caloric temperature T as

$$k_B T \equiv \frac{N_1}{N} E_1 + \frac{N_2}{N} E_2, \tag{3}$$

with N the total number of particles $N = N_1 + N_2$, and k_B the Boltzmann constant. The thermometric temperature is defined by

$$k_B T \equiv \frac{E_2 - E_1}{ln(N_1/N_2)}. \tag{4}$$

The entropy has the form

$$S=-k\left(\frac{N_1}{N}ln\,N_1/N+\frac{N_2}{N}ln\,N_2/N\right), \tag{5}$$

and the entropic temperature is given by

$$\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)=\frac{\partial}{\partial U}\left[-k_B\left(\frac{N_1}{N}ln\,N_1/N+\frac{N_2}{N}ln\,N_2/N\right)\right], \tag{6}$$

In non-equilibrium steady states,for the same two-level system, submitted to an external energy flux, we obtain the following relations for non-equilibrium temperatures thermometric, caloric and entropic, respectively:

$$T_{neq,th}=T\frac{1}{1-\frac{ln[1+(\gamma/\alpha)q]}{E_2-E_1}k_BT}, \tag{7}$$

where T is the equilibrium temperature, α and β are the transition rates from 1 to 2 and from 2 to 1 respectively, and γ is the energy absorption coefficient of N_1 particles.

$$T_{neq,cal}=T\frac{\alpha+\beta}{\alpha+\beta+\gamma q}\frac{E_1+(\alpha+\gamma q)\beta^{-1}E_2}{E_1+\alpha\beta^{-1}E_2}. \tag{8}$$

The entropy in presence of q takes the form

$$S=S_{eq}-k_B\frac{\gamma^2}{\beta^2}\left[\frac{N}{N_1}+\frac{N}{N_2}\right]q^2, \tag{9}$$

with S_{eq} the entropy at equilibrium and this leads to the following non-equilibrium entropic temperature

$$\frac{1}{T_{neq,entr}}=\frac{1}{T}+k_B\frac{\gamma^2}{\beta^2}\frac{1}{(E_1-E_2)N}\left[\frac{N^2}{N_1^2}-\frac{N^2}{N_2^2}\right]q^2. \tag{10}$$

These three temperatures are different from each other and are related to the equilibrium temperature T. Analogous results are obtained in the same statistical approach for a three-level system, with N_1, N_2 and N_3 particles at levels 1, 2 and 3 with energies $E_1<E_2<E_3$, and possible internal transitions $1\rightarrow 2\rightarrow 3\rightarrow 1$ in presence of an external energy flux $\mathbf{q}$. In kinetic theory in the case of an ideal gas, at equilibrium state the caloric temperature concides with the kinetic temperature through the relation

$$\frac{3}{2}k_BT=<\frac{1}{2}mC^2>, \tag{11}$$

where m and C are the mass and the velocity intensity of a gas particle. In non-equilibrium states, we have to consider the distribution function

$$f(\mathbf{r},C,t)=f_{eq}(\mathbf{r},C,t)[1+\Phi], \tag{12}$$

with f_{eq} the equilibrium distribution function and Φ a non-equilibrium contribution. The ”entropy” s obtained from the H-function has the form

$$s=s_{eq}-\frac{1}{2}k_B\int f_{eq}\Phi^2dC, \tag{13}$$

with s the entropy per unit volume and s_{eq} local-equilibrium

entropy. In presence of a heat flux, the entropy has the form, up to the second order in the heat flux,

$$s=s_{eq}-\frac{\tau}{2\lambda T^2}\mathbf{q}\cdot\mathbf{q}, \tag{14}$$

where τ is the collision time and λ the thermal conductivity. Then, we obtain the following non-equilibrium entropic temperature

$$\frac{1}{T_{neq,ent}}=\frac{1}{T}+\frac{2}{5}\frac{nm}{p^3T}\mathbf{q}\cdot\mathbf{q}. \tag{15}$$

This non-equilibrium temperature corresponds to the kinetic temperature in the plane perpendicular to the heat flux. Thus, if the heat flux is in the z direction, we find the following relations

$$<\frac{1}{2}mC_x^2>=<\frac{1}{2}mC_y^2>=\frac{1}{2}k_BT_{neq,ent}<\frac{1}{2}k_BT$$

and

$$<\frac{1}{2}mC_z^2>=\frac{1}{2}k_B(3T_{neq,ent}-2T)>\frac{1}{2}k_BT. \tag{16}$$

In the framework of continuum thermodynamics we discuss the caloric and entropic non-equilibrium temperatures in a crystal with defects of dislocation in non-equilibrium steady states, when it is crossed by a given energy flux. We have in mind, for instance, the walls of a fusion nuclear reactor, which are submitted to an intense neutron flux supplied by the nuclear reaction. The local structure of dislocations lines, which form a network of very thin capillary tubes disturbing the otherwise perfect periodicity of the crystal lattice is described by the dislocation core tensor a_{ij}, its flux V_{ijk} and a field source A_{ij}. a_{ij} gives the local density of the dislocation channels along several directions [5]. Assuming that The evolution equation for the tensorial internal variable is the following

$$\frac{da_{ij}}{dt}+V_{ijk,k}=A_{ij}. \tag{17}$$

where a_{ij} is the dislocation core tensor, $V_{ijk}$is its flux and A_{ij} is a field source. The tensor a_{ij}, introduced by Maruszewski [5], . Assuming for the dislocation flux $V_{ijk}=-D\frac{\partial a_{ij}}{\partial x_k}$, with D a diffusion coefficient for dislocations and A_{ij} is the net formation tensor (formation- destruction)of dislocations lines, we obtain

$$\frac{da_{ij}}{dt}-D\nabla^2a_{ij}=A_{ij,eq}+\tilde{\alpha}q_iq_j, \tag{18}$$

where $A_{ij,eq}$ is the net formation at equilibrium and $q_i q_j$ is a second contribution related to thermal stresses. The equilibrium temperature and the non-equilibrium entropic temperatures are defined by

$$\theta_{eq}^{-1} \doteq \left(\frac{\partial s}{\partial u}\right)_{\mathbf{q}=0} ; \qquad \theta_{neq}^{-1} \doteq \left(\frac{\partial s}{\partial u}\right)_{\mathbf{q}\neq 0} . \tag{19}$$

The quantity θ_{neq}^{-1} can be expanded around the reciprocal equilibrium temperature obtaining the following result in the first approximation

$$\theta_{neq}^{-1} = \theta_{eq}^{-1} - \theta_{eq}^{-2} \frac{\partial \theta_{eq}}{\partial a_{ij}} \Delta a_{ij}, \tag{20}$$

with

$$\Delta a_{ij} = a_{ij}(\mathbf{q} \neq 0) - a_{ij}(\mathbf{q} = 0). \tag{21}$$

Then, in the first approximation, the non-equilibrium temperature θ_{neq} will be related to the equilibrium temperature as

$$\theta_{neq} = \frac{\theta_{eq}}{1 - \theta_{eq}^{-1} \frac{\partial \theta_{eq}}{\partial a_{ij}} \Delta a_{ij}} \approx T \left(1 + T^{-1} \left(\frac{\partial T}{\partial a_{ij}}\right) \Delta a_{ij}\right) =$$

$$T + \left(\frac{\partial T}{\partial a_{ij}}\right) \Delta a_{ij}. \tag{22}$$

To define the caloric of temperature related to the internal variable a_{ij}, first we consider the caloric equation of state at the equilibrium: $U_{dis} = U\left(a_{ij}(T, \varepsilon_{kl}), T, \varepsilon_{kl}\right)$, where we have taken in consideration that at equilibrium the internal variable depends on temperature and the stress tensor. Then, we define the caloric non-equilibrium temperature field T_{neq} related to a_{ij} in a steady state, assuming that out the equilibrium the internal energy has the same form as in equilibrium in presence of $\mathbf{q}$.

$$U_{dis}\left(a_{ij}(T_{neq}, \varepsilon_{kl}, \mathbf{q} = 0), T_{neq}, \varepsilon_{kl}\right) \doteq U_{dis}\left(a_{ij}\left(T, \varepsilon_{kl}, \mathbf{q}\right), T, \varepsilon_{kl}\right). \tag{23}$$

Then, in the first approximation the non-equilibrium caloric temperature will be related to equilibrium temperature by

$$T_{neq} = T + \left(\frac{\partial T}{\partial U_{dis}}\right) \Delta U_{dis} = T + \left(\frac{1}{c_{dis}}\right) \Delta U_{dis}, \tag{24}$$

where c_{dis} is the specific heat associated to the changes of the internal energy of dislocation lines, per unit volume. we see that in this order of approximation both non-equilibrium temperatures (entropic and caloric) coincide.

In [1] it was seen that in the case of a crystal with dislocations, the entropy flux has the form

$$J_k^S = \theta^{-1} q_k - \pi_{ij} \theta^{-1} V_{ijk}, \tag{25}$$

where the variable π_{ij} is the conjugate to a_{ij} and it was been proposed to define the reciprocal of non-equilibrium thermodynamic temperature as the coefficient linking the heat flux $\mathbf{q}$ with the entropy flux $\mathbf{J}^S$. Based on the idea of perfect interfaces between systems, in which both the heat flux and the entropy flux would be continuous, Muller gave the definition of the so-called ”coldness”, namely, of the reciprocal of absolute temperature.

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