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NONEQUILIBRIUM TEMPERATURE IN THE MULTISCALE DYNAMICS AND THERMODYNAMICS

Miroslav Grmela [a*] and Liliana Restuccia [b]

Abstract. The basis for defining and measuring temperatures is an equilibration process. In externally unforced systems the equilibration process is the time evolution, driven by entropy, toward the thermodynamic equilibrium states. In the systems subjected to external forces the equilibration process is a time evolution representing the approach from a more detailed level of description to constitutive relations on a less detailed level. This approach is driven by the CR entropy that in the absence of driving forces and after the approach is completed becomes the dissipation potential (a quantity closely related to the entropy production).

1. Introduction

Sensation of cold and warm is arguably the most important message that we are receiving from the world of atoms and molecules. Roughly speaking, the temperature, that puts a scale on the cold and the warm, is a measure of the energy of the atoms which is associated with their chaotic type motion that is not directly related to the macroscopic motion of our everyday interest. The chaotic type motion of atoms nevertheless strongly influences the physical and the chemical processes that are essential for sustaining life. This is the main reason why the words temperature, cold, and warm are so ubiquitous in our everyday conversations. The thermometer invented by Galileo in 1592 is an example of attempts to make the subjective sensation of the temperature objective and quantitatively measurable.

Being equipped with microscopic, mesoscopic, and macroscopic dynamical theories of macroscopic systems, how do we define the temperature and how do we measure it (Casas-Vazquez and Jou 2003; Jou and Restuccia 2016). The answer depends on the level of description (i.e. on the amount of details that we are including in our theory and that we are directly measuring) and on the presence or the absence of external forces.

Both the definition and the measurement of the temperature are well understood if: (i) there are no external forces preventing the approach to the thermodynamic equilibrium states (or local thermodynamic equilibrium states), (ii) the macroscopic systems under investigation are in the equilibrium states (or local equilibrium states), and (iii) the chosen level of description is the level of the classical equilibrium thermodynamics. In such case the influence of the chaotic motion of atoms on the macroscopic behavior is mathematically expressed in the maximization of entropy (called MaxEnt principle). The definition of the temperature as well as its measurement are based on the maximization of the entropy under the free exchange of the energy of the chaotic type molecular motion (called an internal energy - see Section **2**).

If the level of description on which we seek to define and measure the temperature is chosen to involve more details than those included in the classical equilibrium thermodynamics (the extra details are characterized by quantities called internal state variables) then the entropy and consequently also the temperature depend on the extra details. It is important to emphasize however that the entropy (depending now on the internal variables) remains still the basis for defining the temperature. In this Note we do not investigate the complications arising from the presence of internal variables but we focus our attention on the complications arising in the presence of external forces that prevent the approach to equilibrium. For such systems the classical equilibrium thermodynamics becomes excluded from the levels of description that can be used to describe the experimentally observed behavior. We argue in Section **3** that in externally driven systems it is no more the entropy but another potential that serves as a basis for defining the temperature. We prove that in the absence of external forces the new potential has the meaning of the entropy production and the new temperature defined in terms of the new potential becomes the same as the temperature defined in terms of the entropy.

2. Approach to Equilibrium

Our objective in this Note is to define the temperature on all levels of description and also in the presence of external forces. We want to focus the presentation on the physics that is behind the definition. For this reason we look for the simplest possible setting in which we can formulate our viewpoint. We therefore limit ourselves in this Note to spatially homogeneous systems in which only the internal energy and its rate serve as state variables. In this Section we moreover restrict our investigation only to macroscopic systems that are externally unforced and are seen to reach thermodynamic equilibrium states. In Section **3** we then remove this restriction. As for the multiscale nature of our discussion, we consider three levels of description that we call *equilibrium*, *Fourier*, and *Cattaneo*. We now introduce the levels.

2.1. *Equilibrium* **level.** The state variable is the internal energy ε. A concave function $\sigma = \sigma(\varepsilon)$, where σ denotes the entropy, is called a fundamental thermodynamic relation. It is in this relation where the individual nature of the macroscopic system under investigation is expressed in the classical equilibrium thermodynamics.

The thermodynamic potential φ, defined by

$$\varphi(\varepsilon, \varepsilon^*) = -\sigma(\varepsilon) + \varepsilon^* \varepsilon \tag{1}$$

reaches its minimum at $\varphi_\varepsilon = 0$ which implies

$$\sigma_\varepsilon = \varepsilon^* \tag{2}$$

We use hereafter the shorthand notation for derivatives: $\varphi_\varepsilon = d\varphi/d\varepsilon$, $\sigma_\varepsilon = d\sigma/d\varepsilon$. The temperature on the *equilibrium* level, that we denote by the symbol τ and call an *equilibrium* *temperature*, is defined by

$$\sigma_\varepsilon = \frac{1}{\tau} \tag{3}$$

Let $\hat{\varepsilon}(\varepsilon^*)$ be solution of (2). The Legendre transformation $\sigma^*(\varepsilon^*)$ of $\sigma(\varepsilon)$ is

$$\sigma^*(\varepsilon^*) = \varphi(\hat{\varepsilon}(\varepsilon^*), \varepsilon^*) \tag{4}$$

No time evolution takes place on the *equilibrium* level.

2.2. *Fourier* **level.** The state variable in the Fourier theory of heat conduction is the field $e(r)$ of the internal energy (r denotes the position coordinate). Its time evolution is driven by the gradient $\partial e(r)/\partial r$ of $e(r)$. In this Note the dependence on the spatial coordinate r is absent. The state variable is thus just the internal energy $e \in \mathbb{R}$ and its time evolution is driven by the interaction with the environment. We still call this level of description, that is clearly a very simplified version of the level used in the Fourier theory, a *Fourier* level.

We begin by observing the time evolution of a system that is in contact with a thermal bath of the temperature τ. The contact allows a free exchange of the internal energy between the system and the thermal bath. Let solutions to

$$\dot{e} = -\lambda \phi_e^{(\tau)}(e,\tau) = \lambda \left(\frac{1}{\theta(e)} - \frac{1}{\tau} \right) \tag{5}$$

describe well the observed time evolution. The notation used in (5) is the following: $\dot{e} = de/dt$, t denotes the time,

$$\phi(e, e^*) = -s(e) + e^* e \tag{6}$$

$s(e)$ is a concave function that we call entropy, $\phi^{(\tau)} = [\phi]_{e^*=\frac{1}{\tau}}$, $\lambda > 0$ is a parameter, and θ, called a *Fourier temperature*, is defined by

$$s_e = \frac{1}{\theta} \tag{7}$$

In the experimental observations of the time evolution we, first of all, observe the approach to equilibrium states at which the time evolution stops. This is indeed seen in solutions to (5). We note that

$$\dot{\phi}^{(\tau)} = -\lambda \left(\phi_e^{(\tau)} \right)^2 < 0 \tag{8}$$

that directly follows from (5), implies that $\phi^{(\tau)}$ plays the role of the Lyapunov function and solutions to (5) tend to solutions to $\phi_e^{(\tau)} = 0$ (i.e. to states at which $\phi^{(\tau)}$ reaches its minimum). This then means that

$$\theta \to \tau \; as \, t \to \infty \tag{9}$$

This relation provides the basis for defining the Fourier temperature θ and for measuring the equilibrium temperature τ. The measurement consists of reaching the thermodynamic equilibrium at which the Fourier and the equilibrium temperatures become the same. The time evolution governed by (5) describes the physical process of preparing macroscopic systems to states at which the *equilibrium* level becomes applicable. It is the potential $s(e)$ that generates the preparation process. Since the preparation to equilibrium obviously precedes the equilibrium itself, we regard $s(e)$ as the primary potential introducing the concept of entropy and the equilibrium entropy $\sigma(\varepsilon)$ as a secondary potential. The equilibrium entropy $\sigma(\varepsilon)$ is just $t \to \infty$ limit of $s(e)$. Indeed, by inserting solution to $s_e = \frac{1}{\tau}$ (denoted by $\hat{e}(\tau)$ to $\phi^{(\tau)}$ we obtain the Legendre transformation $\sigma^*(\frac{1}{\tau})$ of the equilibrium entropy $\sigma(\varepsilon)$.

2.3. ***Cattaneo*** **level.** In this Section we investigate the same macroscopic systems under the same conditions as in the previous Section. The macroscopic systems are still allowed to reach the equilibrium at which the *equilibrium* level can be applied. The only difference is that our observations are now more detailed. In addition to the time evolution of e we also observe the rate of change of e that we denote by the symbol Q. In the context of mechanics, this generalization is analogical to the extension from observing only the positions (playing the role of e) to observing positions and velocities (playing the role of e and Q). In mechanics, this extension brings inertia. In the context of the heat transfer the inertia has been introduced by Cattaneo (1948). In our simplified setting, the Cattaneo extension of the Fourier equation (5) takes the form

$$\begin{aligned} \dot{e} &= S_Q \\ \dot{Q} &= -S_e - \Lambda S_Q \end{aligned} \tag{10}$$

The notation used in (10) is the following: Q is the extra state variable. From the first equation in (10), we see that S_Q has the physical meaning of the rate of the internal energy e. The potential $S(e,Q)$ is the entropy on the *Cattaneo* level (called hereafter the Cattaneo entropy). The symbol $\Lambda > 0$ stands for a parameter.

Now we proceed to examine solutions to (10). We begin by noting that $\dot{\Phi} = -\Lambda (\Phi_Q)^2 < 0$. This means that solutions to (10) approach, as $t \to \infty$, equilibrium states defined by $\Phi_Q - 0$. If, in addition, we make the following three requirements on the choice of Φ and Λ: (i) $\Phi_Q = 0 \Rightarrow Q = 0$, Λ is such that the term ΛS_Q dominates the right hand side of the second equation in (10), and (iii) S_e tends to $\phi_e^{(\tau)}$ as $t \to \infty$ then Q evolves faster than e which means that $\dot{Q}$ is very small for large t and thus $S_Q \to -\frac{1}{\Lambda}\phi_e^{(\tau)}$. The first equation in (10) therefore becomes the Fourier equation (5) with $\lambda = \frac{1}{\Lambda}$. We have thus shown that solutions to the Cattaneo equation (10) approach asymptotically solutions to the Fourier equation (5) and eventually the same equilibrium state as the one found in the previous Section. Also the equilibrium entropy σ implied by (10) is the same as the one implied by (5).

3. Approach to Constitutive Relations

In this Section we apply external forces that prevent approach to equilibrium. The *equilibrium* level is not applicable. Let the experimental observations indicate that the *Fourier* level remains applicable and let the time evolution on the *Fourier* level be found to be governed by

$$\dot{e} = \mathscr{E}(e) \tag{11}$$

Using the terminology established in nonequilibrium thermodynamics, we call the specification of $\mathscr{E}(e)$ a *Constitutive Relation*. We note that in the absence of external forces Eq.(11) has to be the same as the Fourier equation (5) and consequently $\mathscr{E}(e) = -\lambda\phi_e^{(\tau)}(e)$.

Since we know that the *Fourier* level provides a good description of the observed behavior, any more microscopic level time evolution (i.e. the time evolution involving more details) has to approach the *Fourier* level. This time evolution will bring thermodynamics into the setting with external forces and without the *equilibrium* level. Inspired by the Cattaneo extension (in Section **2.3**) of the *Fourier* level, we choose Q as the state variable and

$$\dot{Q} = -\Gamma \Psi^{(q)}_Q = -\Gamma \left(\frac{1}{\Theta(Q)} - q^* \right) \tag{12}$$

called *CR time evolution equation*, as the equation governing its time evolution. The quantities appearing in (12) are defined as follows: $\Gamma > 0$ is a parameter,

$$\Psi^{(q)}(Q, q^*) = -\mathscr{S}(Q) + q^* Q \tag{13}$$

is called a Constitutive-Relation thermodynamic potential or briefly *CR thermodynamic potential*, $\mathscr{S}(Q)$ is a concave function of Q that we call Constitutive-Relation entropy or briefly *CR entropy*, and

$$\mathscr{S}_Q = \frac{1}{\Theta} \tag{14}$$

defines the *CR temperature* Θ. The quantity q^* remains at this point unspecified.

Next, we investigate solutions to Eq.(12). Since (12) implies $\dot{\Psi} = -\Gamma(\Psi_Q)^2 < 0$, the potential Ψ plays the role of the Lyapunov function for the approach, as $t \to \infty$, of solutions to (12) to solutions to $\Psi_Q = 0$. that we shall call CR equilibrium sates and denoted by $\hat{Q}(q^*)$. The CR thermodynamic potential Ψ evaluated at $\hat{Q}(q^*)$ becomes the Legendre transform $\Sigma^*(q^*)$ of the CR entropy $\Sigma(q)$: $\Psi(\hat{Q}(q^*), Q^*) = \Sigma^*(q^*)$; $\Sigma(q) = [-\Sigma^*(q^*) + qq^*]_{\hat{q}^*(q)}$, where $\hat{q}^*(q)$ is a solution of $(-\Sigma^*(q^*) + qq^*)_q = 0$. We have proven that

$$\Theta \to q^* \ \ as\, t \to \infty \tag{15}$$

So far, the quantity q^*, introduced in (13), remains unspecified. It is in q^* where we make a contact with the time evolution taking place on the *Fourier* level.

First, we consider the situation when the system under investigation is not subjected to external forces. This means that after the CR time evolution of Q, governed by (12), is completed, the time evolution of e begins and brings the system to the thermodynamic equilibrium. In such case we choose $\mathscr{S}(Q)$, and q^* in such a way that q^* is the Fourier constitutive relation $-\lambda\phi^{(\tau)}(e)$ and $\Sigma^*(q^*)$ is the production $\lambda\left(\phi^{(\tau)}\right)^2$ of the Fourier thermodynamic potential $\phi^{(\tau)}(e)$. We easily see that such choice is: $q^* = \phi^{(\tau)}_e$; $\mathscr{S}(Q) = -\frac{Q^2}{2\lambda}$. We also note that with the choice $q^* = \phi^{(\tau)}_e$ and with leaving the choice of $\mathscr{S}$ open, we obtain a generalized Fourier time evolution equation

$$\dot{e} = -\left[\Sigma^*_{q^*}(q^*)\right]_{q^* = \phi^{(\tau)}_e} \tag{16}$$

The potential $\Sigma^*_{q^*}(q^*)$ appearing in (16) is called a dissipation potential (see more in Grmela 2015). We see that in the particular case when $\Sigma^*(q^*) = \frac{\lambda}{2}(q^*)^2$, the generalized Fourier equation (16) becomes the classical Fourier equation (5. For the generalized Fourier equation (16), the equation (8) becomes

$$\dot{\phi}^{(\tau)} = -\left[q^* \Sigma^*_{q^*}(q^*)\right]_{q^* = \phi^{(\tau)}_e} < 0 \tag{17}$$

The inequality in (17) is a consequence of the convexity of $\Sigma^*_{q^*}(q^*)$ and the property $[\Sigma^*_{q^*}(q^*)]_{q^*=0} = 0$. We see therefore that also in the case of the generalized Fourier theory represented by (16), the thermodynamic potential $\phi^{(\tau)}$ plays the role of the Lyapunov function for the approach to thermodynamic equilibrium states that are solutions to $\phi^{(\tau)}{}_e = 0$.

Summing up, we have seen that in the particular case when the external forces are absent and the system reaches eventually the equilibrium state the CR entropy $\mathscr{S}(Q)$ turns into the dissipation potential in the generalized Fourier equation (16).

Now we comment about the measurement of the temperatures τ and θ. First, we recall the measurement of the equilibrium temperature τ. In the context of the analysis in Section **2**), the role of the thermometer plays the system with the internal energy e serving as the state variable and the thermal bath is the system whose temperature we measure. In order that the relation (9) can actually be used to measure τ, we need to know in addition: (i) the complete set of state variables (denoted (e,η)) that are involved in the Fourier equilibration process in the thermometer, (ii) the fundamental thermodynamic relation $s(e,\eta)$ representing the thermometer, (iii) the properties of the interface between the thermometer and the thermal bath; the interface is required to allow a free passage of e while the changes in η, that arise due to the interactions on the interface. are controlled. If all this is known then the temperature τ is read in η (e.g. the volume), reached at the equilibrium, that corresponds (through the known fundamental thermodynamic relation) to the temperature τ. This is indeed how the measurements of the equilibrium temperature are made. The difficulties arise when η involves internal state variables that are not controlled on the thermometer-bath interface.

Next, we replace the Fourier equilibration (9) with with the CR equilibration (15) in which we choose $q^* = \lambda\left(\frac{1}{\theta(e)} - \frac{1}{\tau}\right)$. This equilibration provides a basis for the measurement of the Fourier temperature θ with the thermometer whose states are characterized by Q. Again, in order that the relation (15) can be actually used to measure θ, we need to know in addition: (i) a full set of state variables that we denote by (Q,ξ), (ii) the fundamental thermodynamic relation $\mathscr{S}(Q,\xi)$, and (iii) properties of the interface. At this point we only know that the CR entropy $\mathscr{S}(Q,\xi)$ exists (since both the Fourier and the the more microscopic level with state variables (Q,ξ) serving as state variables provide a good description of the observed behavior). A more detailed investigation, that is outside the scope of this Note, is needed to obtain the rest of the required information.

4. Concluding Remarks

Temperature is a very useful measure of the energy of the chaotic type atomic motion that strongly influences the behavior of macroscopic systems. Classical equilibrium thermodynamics and equilibrium statistical mechanics provide an excellent setting for defining and measuring the temperature at equilibrium (or local equilibrium) states. But even in the Gibbs classical statistical mechanics it is not obvious which type of molecular motion (and the energy associated with it) is involved in determining the equilibrium temperature and which is not. For example in the van der Waals gas the total molecular energy is a sum of three terms: kinetic energy, long range attractive energy, and the short range repulsive energy. As shown in van Kampen (1964), only the first two generate the chaotic type motion entering the temperature, the third enters the entropy as a constraint. It has then been shown in Grmela (1971) that the spatial nonlocality of molecular collisions (due to the short range repulsive forces), introduced in the Enskog kinetic equation, contribute to the time reversible, nondissipative part of the time evolution. Another example of this type can be found in the statistical mechanics of polymers. The conformation variations of the polymer macromolecules enter the entropy and not the chaotic type motion involved in the determination of the equilibrium temperature.

The chaotic type atomic motion remains to play a very important role also in externally driven systems that are prevented from reaching the thermodynamic equilibrium. How can we extend the theoretical and the experimental understanding of the equilibrium temperature to externally driven systems that are kept out of equilibrium? In this Note we suggest such extension. First, we cast the equilibrium theory to the form in which the temperature emerges as a natural concept in the equilibration process. The extension then consists of replacing the equilibration process in which the thermodynamic equilibrium states are approached with other equilibration processes that take place also in externally driven systems.

Why do we regard the equilibration process as the essence of the definition of the temperature? We do it for two reasons. First, the equilibration is a dissipative process involving the chaotic type microscopic motion. This means that by concentrating on the equilibration process we actually identify the type of motion that we want to address in the concept of the temperature (chaotic type motion) and put our attention on it. Second, the measurement of the temperature is reaching the equilibrium in two systems (one is the thermometer and the other the system whose temperature we measure) exchanging freely the internal energy involved in the chaotic type motion.

From the mathematical point of view, the equilibration process is formulated as a gradient dynamical system. The time evolution is driven by a potential that at the equilibrium reaches its extremum. In the equilibration leading to the thermodynamic equilibrium the potential is the entropy and the state variable evolving toward the equilibrium is the internal energy. The temperature makes it appearance in the condition for the equilibrium. The inverse of the temperature is the conjugate of the internal energy with respect to the entropy.

In order to extend this viewpoint of the temperature to externally driven systems in which the equilibration to thermodynamic equilibrium states is absent, we have to identify another type of equilibration process involving a more detailed characterization of the internal energy. If it is established that the behavior of the externally driven system under investigation can be well described on a mesoscopic level of description (e.g. on the level of fluid mechanics) then any more microscopic level (i.e. a level taking into account more details) has to approach to the mesoscopic level. This approach (called in Grmela (2017) reducing dynamics) is then the equilibration process which can serve us to define the temperature. In this Note we have worked out a simple illustrative example.

While the association of the temperature with the approach to the thermodynamic equilibrium states is well known, its extension to the approach of a more microscopic to a less microscopic level of description appears to be new. Among the many viewpoints of the temperature listed in Casas-Vazquez and Jou (2003) and Jou and Restuccia (2016) the closest to the one presented in Section **3** is the recognition of the temperature in the relation between the entropy flux and the heat flux. We expect that this type of relation (that is not associated in Casas-Vazquez and Jou (2003) and Jou and Restuccia (2016) with the reducing dynamics) will arise in the generalization of Section **3** to spatially inhomogeneous systems.

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[a] École Polytechnique de Montréal,
C.P.6079 suc. Centre-ville,
Montréal, H3C 3A7, Québec, Canada

[b] Università degli Studi di Messina
Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra
Contrada Papardo, 98166 Messina, Italy

[*] E-mail address: miroslav.grmela@polymtl.ca

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