Some Thoughts about Non-equilibrium Temperature

by

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Abstract

The main objective of this paper is to show that, within the present framework of the kinetic theoretical approach to irreversible thermodynamics, there is no evidence that provides a basis to modify the ordinary Fourier equation relating the heat flux in a non-equilibrium steady state to the gradient of the local equilibrium temperature. This fact is supported, among other arguments, through the kinetic foundations of generalized hydrodynamics. Some attempts have been recently proposed asserting that, in the presence of non-linearities of the state variables, such a temperature should be replaced by the non-equilibrium temperature as defined in Extended Irreversible Thermodynamics. In the approximations used for such a temperature there is so far no evidence that sustains this proposal.

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I. Basic Concepts.

The problem of extending uniquely defined thermodynamic quantities for equilibrium states of many body systems to non-equilibrium states remains still highly controversial. This situation is particularly striking when referring to the concepts of entropy and temperature. For a one-component fluid in equilibrium, the three basic laws of thermostatics are condensed in the equation

\[ T \, dS = dU + pdV, \quad (1) \]

where all symbols have their ordinary meaning. Thus, the equilibrium temperature \( T \) is related to the two state variables \( S \), the entropy as defined by Clausius, and \( U \), the internal energy, by the relation

\[ \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V. \quad (2) \]

Eq. (2) is easily generalizable to equilibrium states of more complicated systems. Any attempt to extend eq. (2) to a non-equilibrium state of any arbitrary system would imply that not only \( U \) but also the entropy \( S \) is uniquely defined for such a state. This requirement is met in Linear Irreversible Thermodynamics (LIT) through the local equilibrium assumption\(^1,2\) whereby in (2) all quantities depend on the position \( \vec{r} \) of an infinitesimal element of the system at time \( t \). The local equilibrium temperature is thus a quantity which uniquely characterizes a system’s element whose characteristic length is much longer than a mean free path, but much smaller than the length of the container holding the system. Moreover, eq. (2) contrary to statements often issued in the literature, is not the definition of temperature. It provides an equation of state of the intensive parameter \( T \) which, after use is made of the basic contents of the zeroth law, is shown to posses all properties required to define what we invariably understand as equilibrium temperature\(^3\).

Beyond local equilibrium the question which has caught the attention of many workers in this field concerns the validity of an appropriate extension of eq. (2). This question as well as how to formulate a theory for irreversible processes within the context of the laws of thermodynamics has been exhaustively discussed in other papers\(^4a,b\). Within this context, it is pertinent to mention that many efforts have been made in the past to define the entropy of a non-equilibrium state of an arbitrary system, none of which has led to a
clear cut answer. In fact, twenty years ago in a not very well known paper, J. Meixner, one of the founders of LIT, gave very convincing arguments to show that it is very unlikely that a non-equilibrium state function playing the role of the entropy may be uniquely defined. Indeed, summarizing his ideas one may assert that the conclusion reached by him is that such a function, either cannot be defined, or if it can, then it may be done so in an infinite number of ways. Without being so drastic in this last assertion, a similar conclusion was held by Grad over thirty years ago. In exploring recent literature on this question these conjectures seem to hold true in a more restricted sense. Taking a closed (constant mass) thermodynamic system undergoing an irreversible process, and assuming that the pertinent state variables describing the system’s states during such a process are stochastic variables, one can provide several definitions for non-equilibrium entropies when the process is Markovian. Yet if the system’s state at a certain time $t$ is still characterized by the histories of the independent state variables up to such a time, the process is non-Markovian, and then an entropy-like function has resisted a definition. These, in different words, are the ideas sustained by Meixner. Thus, according to this conjecture one would have none or as many intensive parameters formally playing the role of $1/T$ in eq. (2) as entropy-like functions one could define. Nevertheless, the only possible definition of non-equilibrium temperature consistent with the laws of thermodynamics is already implicit in Clausius inequality.

In view of this result, which holds true for non-equilibrium states, one may raise the question about the physical meaning of the quantity $\Theta$ defined by:

$$\frac{1}{\Theta} = \left( \frac{\partial \eta}{\partial u} \right)_{v,\ldots},$$

(3)

where $\eta$ is one of such entropy-like functions and $u$ the specific internal energy, a dynamical quantity which may be uniquely defined. Here $(\quad)_{v,\ldots}$ means that in eq. (3) the specific volume and other pertinent extensive state variables are kept fixed in taking the partial derivative. However, following the postulates of Extended Irreversible Thermodynamics (EIT) we shall refer to $\Theta$ as a non-equilibrium temperature and to $\eta$ as an entropy-like function. As far as $\Theta$ is concerned, here taken as an unknown function of all the variables on which $\eta$ depends, it has been proposed to regard it as the phenomenological temperature,
that is as the reading provided by a thermometer introduced into the system assuming that local thermal equilibrium is reached by both systems. What we wish to emphasize in this paper is that so far, available molecular theories have not provided a suitable and reliable molecular interpretation for this quantity, whereas they reinforce the unique validity of the local equilibrium temperature.

In Section II we will briefly summarize the arguments that motivated this work. In Section III we go into the core of the paper showing that the kinetic theoretical considerations are insufficient to give a molecular interpretation of \( \Theta \). We also argue that at present, other microscopic methods have not yet solved the question and in our opinion will hardly do so.

II. Background.

For the sake of simplicity and to make contact with other approaches we shall restrict ourselves to the examination of a system defined by a rigid heat conductor\(^8\) characterized by its internal energy density \( u(\vec{r}, t) \) and the heat flux \( \vec{q}(\vec{r}, t) \) raised to the status of independent variable. According to the basic postulate of Müller\(^8c,9\) concerning the phenomenological structure of EIT, we assume that a regular and continuous function exists depending on the independent state variables, which acts like a generalized thermodynamic potential namely, an entropy like function. In the case of our rigid conductor we call this function, as in eq. (3), \( \eta = \eta(u, \vec{q}) \), and therefore,

\[
d\eta = \left( \frac{\partial \eta}{\partial u} \right)_{\vec{q}} du + \left( \frac{\partial \eta}{\partial \vec{q}} \right)_{u} \cdot d\vec{q}
\]

By analogy with eq. (1) and according to eq. (3) we define the non-equilibrium temperature \( \Theta(u, \vec{q})^{-1} \). Notice that \( \eta \) and \( \Theta \) being both scalars and functions of \( \vec{q} \), must be functions of all scalar invariants of \( \vec{q} \), namely \( q^2 = \vec{q} \cdot \vec{q} \). Thus, to the lowest order in \( \vec{q} \), we may write that

\[
\eta = s_0 - \frac{\alpha}{2} q^2, \quad (5)
\]

\[
\frac{1}{\Theta} = \frac{1}{T} - \frac{\alpha'}{2} q^2. \quad (6)
\]
where \( s_0(u) \) is the local equilibrium entropy, \( \alpha \) depends on \( u \) and \( \alpha' = d\alpha/du \), and \( T \) is the local equilibrium temperature as related to the local state variable \( u \) through \( s_0 \). Emphasis should be made however, that in eq. (6) the quantity \( \Theta \) is not the full nonequilibrium temperature as defined in eq. (3), but only an approximate expression that contains deviations from \( T^{-1} \) by quadratic terms in \( \vec{q} \).

On the other hand \((\partial \eta/\partial \vec{q})_u\) being a vector, must in general be of the form

\[
\left( \frac{\partial \eta}{\partial \vec{q}} \right)_u = -A(u, \vec{q}) \vec{q}.
\]

and using eq. (5) one gets \( A(u, 0) = \alpha(u) \). The time derivative of \( \eta \) is then written

\[
\dot{\eta} = \Theta^{-1} \dot{u} - A \vec{q} \dot{\vec{q}}.
\] (7)

where \( \dot{x} \equiv dx/dt \).

Nevertheless, eq. (6) is the starting point of recent discussions\(^8,10\) concerning the possibility of measuring \( \Theta \) by some kind of experiments. The argument invoked in these efforts is that eq. (7), the equation for the energy balance and the definition of a vector \( \vec{J}_\eta = \Theta^{-1} \vec{q} \), leads to a balance equation for \( \eta \), in which the production term \( \sigma_\eta \) has the form

\[
\sigma_\eta = \vec{q}(\nabla \Theta^{-1} - \rho A \dot{\vec{q}}),
\] (8)

and this quantity, arguing compatibility with the second law, is assumed to be non-negative. Then it is proposed that due to the structure of eq. (8)

\[
\nabla \Theta^{-1} - \rho A \dot{\vec{q}} = \mu \vec{q}
\] (9)

and \( \mu \geq 0 \). Therefore the time evolution equation for \( \vec{q} \) is to be of the Maxwell-Cattaneo-Vernotte (MCV) form, namely

\[
\tau \dot{\vec{q}} + \vec{q} = -\lambda \nabla \Theta,
\] (10)

where \( \tau = \rho A/\mu \) and \( \lambda = 1/\mu \Theta^2 \). Now, \( \tau, \lambda \) and \( \Theta \) are in general functions of \( u \) and \( \vec{q} \), so that eq. (10) is a highly nonlinear equation for \( \vec{q} \). When we limit ourselves to the approximation used in eq. (5), \( \lambda \) and \( \tau \) become functions of \( u \) only. Moreover, the complete
linearization of eq. (10) is achieved with $T$ in place of $\Theta$, yielding the ordinary MCV equation.$^6$

The quantity $\Theta$ may be pressumably identified with the phenomenological temperature, instead of $T$ as occurs in LIT. Thus, when we consider steady state situations, eq. (10) acts as a generalized Fourier law, namely

$$\vec{q} = -\lambda \nabla \Theta, \quad (11)$$

that may give some physical content to the non-equilibrium temperature defined in eq. (3). Once we accept that the relation between temperature and heat flux is given by eq. (10) or (11), then $\Theta$ becomes the only temperature that can be measured$^{10b}$, and it is not possible to measure the local equilibrium temperature $T$ independently, but only to calculate it through eq. (6).

The question we want to raise in this paper concerns the possibility of sustaining the validity of eq. (10) from both, kinetic and statistical mechanical models of matter. As we shall argue in the following section there is no such evidence. That means that to the order of approximation involved in eqs. (5) and (6), the difference between $T(\vec{r}, t)$ and $\Theta(\vec{r}, t)$, if any, is completely negligible. In all cases the quantity that preserves its physical identity is $T$. This is shown to be true in general in ref. (4b).

**III. Kinetic and Statistical Interpretation of the Non-equilibrium Temperature.**

We begin by considering the definition of the non-equilibrium temperature $\Theta$ in the case of a dilute gas whose dynamics is governed by the Boltzmann equation.$^{11}$ We recall the reader that when this equation is multiplied by $\ln f$, (we assume that the integrals converge and that $f$ vanishes in the boundaries of the velocity subspace) integration over the $\vec{v}$-space leads to a balance type equation for the entropy as defined by $\rho \eta = -k \int f \ln f d\vec{v}$, in which the entropy production is non-negative. This property is inherent to the Boltzmann equation and must be obeyed by any exact solution $f$ of the full non-linear equation. Such solutions are still unknown for realistic systems. One therefore resorts to approximate methods of solution among which Grad’s moments solution$^{11}$ is rather pertinent to
the problem posed here. This method is based upon the expansion of the single particle distribution function around its local equilibrium (Maxwellian) form, as an infinite series in Hermite tensorial polynomials whose coefficients \( a^{(s)}(\vec{r}, t) \), known as Grad’s moments, perform here the role of the local state variables describing states beyond the local-equilibrium one. Nevertheless, for practical reasons the infinite series is in general truncated at some stage, although there exists no well defined criterion that indicates how or where such truncation must be performed. In the case of the thirteen moment approximation\(^{11,12} \), it is well known that the physical fluxes namely, the stress tensor \( T \) and the heat flux \( \vec{q} \) are raised to the status of independent variables. Taking a system such that its states depend only on \( \vec{q} \) (shear free systems), then the single particle distribution function is given by

\[
f(\vec{r}, \vec{c}, t) = f^{(0)}(\vec{r}, \vec{c}, t) \left\{ 1 + \frac{2}{5} \frac{m}{pk_B T} \left( \frac{mc^2}{2k_B T} - \frac{5}{2} \right) \vec{q} \cdot \vec{c} \right\} .
\]

Here \( f^{(0)} \) is the ordinary local Maxwellian distribution function, \( m \) the mass of the particles \( p \) and \( T \) the local pressure and temperature respectively, \( k_B \) Boltzmann’s constant, \( \vec{q} \) the heat flux and \( \vec{c} \equiv \vec{v} - \vec{u}(\vec{r}, t) \) the chaotic or thermal velocity. \( \vec{u}(\vec{r}, t) \) is the local hydrodynamic velocity defined as the first moment of \( f \). It is important to recall that in kinetic theory of dilute gases the local equilibrium temperature is interpreted as \( \frac{1}{2} mc^2 \) where the averages must be taken with (12). Thus, there is no room to bring in the non-equilibrium temperature \( \Theta \) in any logical way. Nevertheless, when the entropy of the gas is computed using eq. (12) one performs an integration in which \( \ln f = \ln f^{(0)} + \ln(1 + x) \), where \( 1 + x \) is the expression within the curly brackets in (12) and \( x \) is regarded as small compared with 1. So that retaining terms up to order \( x^2 \), one is lead to the result\(^{13} \)

\[
\rho \eta = \rho s_0 - \frac{m}{5pk_B T^2} \vec{q} \cdot \vec{q} ,
\]

which is precisely of the form expressed by eq. (5). The coefficient \( \alpha = m/5pk_B T^2 \) can be rewritten in terms of \( v \) and \( u \), using the local forms of the equation of state and the equation for the internal energy. Thus, eq. (13) leads to a temperature \( \Theta \) whose form is that of eq. (6) and need not be written explicitely. This result shows an inconsistency between the tenets of kinetic theory of gases where \( T(\vec{r}, t) \) is defined as \( \langle 1/2mc^2 \rangle \) and eq.
6. In the best case, it simply relates the local equilibrium temperature \( T(\vec{r}, t) \) with \( \Theta \) but we insist, defines neither of them.

Now, according to our discussion in section II, eq. (13) should be consistent with an equation of motion for \( \vec{q} \) of the form exhibited by eq. (10). We must then examine the nature of the equation for \( \vec{q} \). The full non-linear equation is complicated enough but certainly not of the form required by (10)\(^{12,13}\). Its linearized version, the one consistent with eq. (13), is

\[
\frac{\partial \vec{q}}{\partial t} + \frac{5pk_B}{2m} \text{grad } T = \frac{-16}{15}n\Omega^{(2,2)}\vec{q},
\]

where \( \Omega^{(2,2)} \) is a well known collision integral. Notice that eq. (14), as expected from the interpretation of \( T(\vec{r}, t) \) contains \( \text{grad } T(\vec{r}, t) \) and not \( \text{grad } \Theta \) with \( \Theta \) given by eq (6). The non-linearities in \( \eta \) arising from the quadratic term in the heat flux do not have any influence whatsoever upon the kinetic interpretation of \( T(\vec{r}, t) \). In the best of cases, this simply means that to the order of approximation involved in eqs. (5) and (6) the difference between \( T \) and \( \Theta \) is negligible. In fact the only physically meaningful quantity is \( T \).

One may pursue this analysis to incorporate more and more moments into the description of the states of the gas. In the case of 26 moments\(^{15}\), which is illustrative enough, one gets, using the same approximations as above, linearizing the \( \ln f \) term to compute the entropy and the equations of motion for the moments, that \( \rho\eta \) may always be written as the difference of two terms, \( \rho s_0 \) minus a sum of terms, \( \text{some quadratic in the fluxes. Nevertheless, for the same reason as above the difference between the two temperatures, remains negligible. This result should not surprise us. If Grad’s, or any other method is devised to seek approximate solutions to the Boltzmann equation, the only well defined temperature is } T \text{ taken as the average of the thermal kinetic energy. The quantity } \Theta \text{ as calculated from eq. (3) has no physical meaning as it depends on the degree of approximation used to compute the function } \eta. \text{ Thus, the kinetic theory of a dilute gas where no potential energy contributes to the total energy, manifestly indicates that the only variable which is justified as a physically meaningful temperature, is the local equilibrium temperature } T(\vec{r}, t). \text{ This is also consistent with the laws of thermodynamics}^{4c}.

Further support for the above conclusions comes from the full solution to the Boltz-
mann equation. Indeed, the result arising from the full infinite series for \( f \) namely, when no truncations are performed has been recently obtained\(^{16}\). The full linearized \( \eta \)-function is given by

\[
\rho \eta = \rho s_0 - \frac{n k_B}{2} \sum_{r=1}^{\infty} \frac{1}{r!} a^{(r)}(\vec{r},t) a^{(r)}(\vec{r},t),
\]

so that here the temperature \( \Theta \) becomes identical to the local equilibrium temperature if the moments, not the fluxes, are defined as the state variables. This deserves some comments. It appears that if an exact solution to the Boltzmann equation is used to compute the function \( \rho \eta \) even in the linear approximation, the phenomenological temperature \( \Theta \) is adequately interpreted by the kinetic temperature \( T \). Notice that this would not be the case of the physical fluxes \( \vec{q} \) and \( \mathcal{T} \) are taken as variables instead of the moments \( a^{(2)} \) and \( a^{(3)} \) to which they are related. Moreover the higher moments are independent state variables whose influence on the state of the gas appears through the wave vector and frequency dependence of the transport coefficients\(^{17-19}\).

Another point that needs be considered, is the steady state equation of heat conduction in relation to eq. 11. In the thirteen moments approximation such an equation, as it has been explicitly shown in ref. 17, is identical in form with Fourier’s law in which the local temperature \( T \) is involved. Pursuing the results of ref. 17, the calculations with the 26-moments approximation are in very good agreement with the results of generalized hydrodynamics\(^{20,21}\). These calculations show that the classical Fourier law is still valid and need not to be replaced by the non-linear form of eq. (11). The thermal conductivity is wave vector dependent (see eq. (4.8) and (4.9) in ref. 17) and these results agree with those obtained by Alder et al.\(^{21}\) using numerical methods.

We may thus conclude that, on the basis of the Grad’s moment solution to the Boltzmann equation, the correct consistency condition between the the kinetic interpretation temperature through the average kinetic energy of the molecules and eq. (3) is only achieved if the exact solution, the infinite series for \( f(\vec{r},\vec{c},t) \), is used. The kinetic temperature \( T(\vec{r},t) \) is related to \( \Theta \) as defined in eq. (3) through equations which depend on the number of moments raised to the status of state variables. It is then clear that \( \Theta \) has no bearing whatsoever on the physical description of the state of the gas.
One could now turn this question over to the realm of more microscopic theories capable with dealing with systems other than the dilute gas. This has been done for instance by Nettleton for real fluids\textsuperscript{22–24} where the temperature is associated with the intensive variable conjugate to the systems energy (Hamiltonian). Then of course the temperature defined through the average kinetic energy differs from the one interpreted as the average of the total energy. Although for equilibrium states this is inmaterial\textsuperscript{4b}, for non-equilibrium states the question is which of the two gives a theoretical value which is in closest agreement with the one obtained through a thermometer reading. The answer is yet to be given. It is perhaps appropriate at this stage to remind the reader that this is an old question. Already in 1966\textsuperscript{25,26} discussions where offered to point out the difference between two non-equilibrium temperatures defined as it is mentioned above. As it turns out, these definitions are related with the evaluation of the bulk viscosity. The value of this coefficient is different depending on which interpretation of temperature is adopted. Clearly the most appropriate one would be that which leads to a bulk viscosity that is in better agreement with experiment. Unfortunately this is a difficult quantity to measure, but some progress along these lines has been made for dense fluids\textsuperscript{27}.

We conclude that the non-linearities present in the quantities $\eta$ and $\Theta$ indeed reflect themselves in measurable properties of the system such as its transport coefficients, but they have no effect whatsoever in the steady state expressions for the non conserved variables, let them be the fluxes or in general the moments of the distribution function $f$ for dilute gases. This same fact seems to hold for other systems except that the details of this influence is much harder to exhibit, although some hints have been given using more sophisticated methods of statistical mechanics\textsuperscript{24,28–34}.

In our opinion Meixner’s conjecture seems to prevail for nonequilibrium processes beyond local equilibrium. One may define several functions $\eta$ and consequently will obtain an equal number of equations of state for $\Theta$. Nevertheless, the only non-equilibrium temperature which has a clear physical meaning and is consistent with the laws of thermodynamics is $T(\vec{r}, t)$. Therefore, no quantity $\Theta$ defined or introduced into a non-equilibrium theory through eq. (3) has any bearing whatsoever with the concept of temperature.
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