

Irreversible processes and temperature

Byung Chan Eu

Department of Chemistry and Department of Physics, McGill University, Montreal, Quebec, Canada H3A 2K6

L. S. García-Colín

*Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-543,
09340 México Distrito Federal, Mexico*

(Received 30 August 1995)

The notion of nonequilibrium temperature used in extended irreversible thermodynamics (EIT) is examined from the viewpoints of thermodynamic laws and statistical mechanics in this article. It is shown that in both the phenomenological theory and statistical mechanics of irreversible processes the notion of nonequilibrium temperature in some versions of EIT inevitably came about since a nonequilibrium entropy was not derived from the thermodynamic laws but was arbitrarily assumed and consequently not given its thermodynamic foundations. It is also shown that there is no other temperature than the one established by the zeroth law of thermodynamics and based on the second law of thermodynamics, regardless of whether the system is in equilibrium or nonequilibrium. When such a notion breaks down because the temporal evolution of dynamical processes is faster than the time scale of thermometric resolution, the thermodynamics of irreversible processes (e.g., EIT) is no longer applicable. [S1063-651X(96)10709-1]

PACS number(s): 05.70.Ln, 05.20.Dd

I. INTRODUCTION

The concept of temperature has its origin in times much beyond the pioneering age of thermodynamic laws according to the historical account of thermal science by Brush [1], but the modern concept of thermodynamic temperature and the attendant thermometry rest on the basic discovery of Lord Kelvin, who recognized in the Carnot theorem [2] a universal thermodynamic basis on which to found the concept of a universal temperature scale [3]. It is now deeply entrenched in wide ranging aspects of physical science, especially, through the thermodynamics of reversible processes—equilibrium thermodynamics, and is a fundamental cornerstone of thermal science. Fitted to a universal scale, the thermodynamic temperature provides a basic yardstick against which we measure and record thermal properties of matter, regardless of the states of aggregation and whether the system is in equilibrium or not. For systems in equilibrium the concept of temperature as is now known is universally accepted. Confusion lies in the domain of nonequilibrium phenomena. The essential concept of temperature is founded on the zeroth law of thermodynamics, which should not be limited to equilibrium only, but also apply to systems in nonequilibrium states where irreversible processes occur. After all, we talk of temperatures of animate bodies removed far from equilibrium. If the irreversible processes in the body are too fast for the thermal state of the body to come to equilibrium with any conceivable thermometric device, then the zeroth law is no longer applicable and consequently the thermodynamics of irreversible processes within the framework of the currently accepted thermodynamic laws (e.g., extended irreversible thermodynamics) becomes inapplicable, and an alternative description of the processes may have to be looked for.

In recent years considerable attention has been paid to generalizations [4–8] of equilibrium thermodynamics. A

genre of generalizations where the local equilibrium hypothesis is extended to include various fluxes will be broadly called extended irreversible thermodynamics (EIT). There are different versions [6–8] of EIT reported in the literature. The points of departure are basically in the manners by which the Clausius entropy is generalized, its thermodynamic foundations or the lack of them, the concept of temperature, and the constitutive equations. These points will be further elaborated later when the main topic of this paper, namely, temperature, is discussed. In such generalizations of equilibrium thermodynamics, there naturally arise questions regarding the temperature of nonequilibrium systems and generalized forms of the Clausius entropy, which is the conjugate variable to temperature in the equilibrium theory. In the case of nonequilibrium processes the concept of temperature has become a subject of debate [9(b)–12(a)]. In this paper, we would like to analyze various strands of thought published in the literature on the concept of nonequilibrium temperature, since it is our opinion that it is crucially important to have this concept firmly clarified and enunciated if a rational development of irreversible thermodynamics is to be made. This subject can be approached from both statistical mechanical and phenomenological standpoints, which must confluence to a unified concept valid for both equilibrium and nonequilibrium. Reading through the literature on temperature in nonequilibrium statistical mechanics, one finds that equilibrium concepts appear entangled with nonequilibrium concepts in a rather vexing manner. Therefore, the first task that we must face should be to sort them out and examine their mutual relations, if any. For this reason we will go over even some well-trodden topics at the risk of appearing to be repetitive and even trite. It should not be construed as a pedantic exercise on the part of the present authors since the aim is to give a comprehensive picture of the subject under scrutiny, which represents a keystone concept for development of irreversible thermodynamics.

This paper is organized as follows. In Sec. II we briefly review how the concept of thermodynamic temperature enters the thermodynamics of reversible and irreversible processes. We then examine the concept of nonequilibrium temperature used in the version of EIT by Jou *et al.* [7] and Nettleton [12(b)] in the light of the review given on the thermodynamic concept of temperature. This then will be followed in Sec. III by a brief review of how temperature enters equilibrium statistical mechanics and the classical kinetic theory [13–15] in the early period of thermodynamics. In this connection, we also discuss the idea of Tolman [16] and its recent elaboration [17] in which attempts were made to arrive at a statistical definition of temperature. We then analyze the concept of temperature used in the statistical mechanical approach to EIT via a maximum entropy method as pursued by Jou *et al.* [7] and Nettleton [12(b),(c)]. This is then followed by examination of how the concept of temperature enters the nonequilibrium ensemble method [18(a),(b)] and argues that it is a general and logical manner of introducing the temperature concept into nonequilibrium statistical mechanics since it is firmly based on the thermodynamic laws. The manner by which the temperature concept is introduced in the nonequilibrium ensemble method is completely parallel to that of the equilibrium ensemble method of Gibbs. In Sec. IV, the proposition made by Jou and Casas-Vazquez [9(a)–(c)] for a nonequilibrium temperature is specifically analyzed and discussed. Concluding remarks are also given in this section.

II. SECOND LAW OF THERMODYNAMICS AND TEMPERATURE

Lord Kelvin [19] recognized that Carnot's theorem [2], as a precursor to the second law of thermodynamics, which he together with Clausius [20] enunciated, could serve as a means to introduce a universal temperature scale, nowadays called the thermodynamic temperature. It is well known [21] that this thermodynamic temperature scale can be made coincident with the absolute temperature scale based on the ideal gas thermometer. If the temperatures of the heat reservoirs of a Carnot cycle are denoted by T_1 and T_2 ($T_1 > T_2$) in such scale, then the efficiency ε_{rev} of the reversible Carnot cycle can be expressed in terms of temperatures as

$$\varepsilon_{\text{rev}} = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}, \quad (2.1)$$

where Q_1 and Q_2 are the heat absorbed and emitted by the system, respectively. We adopt the convention for the sign of heat that heat absorbed by the body is taken to be positive and heat emitted by the body is taken to be negative. Rearranging Eq. (2.1), we obtain

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \quad (2.1')$$

In the case of an irreversible Carnot cycle, by the Carnot theorem there holds the inequality

$$1 + \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1} \quad (2.2)$$

or

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0. \quad (2.2')$$

It must be noted that the meanings and values of the temperatures in Eqs. (2.1) and (2.2) are the same despite the differences in the meanings of Q_1 and Q_2 in them; T_1 and T_2 are the temperatures of the heat reservoirs, whereas Q_1 and Q_2 are reversible heat transfers in the case of Eq. (2.1) and are irreversible heat transfers in the case of Eq. (2.2).

Taking to the limit of an infinite number of infinitesimal cycles and combining (2.1') and (2.2'), Clausius obtained his famous inequality [23]

$$N = - \oint \frac{dQ}{T} \geq 0. \quad (2.3)$$

The N is called the uncompensated heat—Clausius called it the uncompensated transformation value. It vanishes identically in the case of reversible processes and is positive otherwise. The important point that must be remembered is that even if the process involved in the cycle is irreversible, the temperature T is that of a heat reservoir that is in thermal contact with the system undergoing the infinitesimal process in question and also in equilibrium with a thermometer used to measure its temperature. By the zeroth law of thermodynamics this temperature is also the temperature of the body (i.e., the working substance). The reason for this is that since the Carnot cycle is decomposed into an infinite number of infinitesimal Carnot cycles when the inequality (2.2) is cast into the inequality (2.3), the temperature of the working substance undergoing an irreversible process characteristic of the infinitesimal Carnot cycle of interest is necessarily the same as T , the temperature of one of the heat reservoirs. And when Eq. (2.3) is cast into a local form, this temperature must be regarded as the local temperature of the body in question. Viewed in this way [22], the heat reservoir of the infinitesimal cycle in question may double as a thermometer in the absolute temperature scale that indicates the temperature value T . It is very important to recognize this meaning of T in the Clausius inequality for an irreversible cycle since the Clausius inequality is the crucial mathematical representation of the second law of thermodynamics and the starting point of the mathematical formulation of thermodynamics on the basis of the first and second laws. *The body undergoes an irreversible process and T is the thermodynamic temperature of the infinitesimal body as well as the heat reservoir, which can act as a thermometer. There is no other kind of temperature evident in the formulation of the Clausius inequality for irreversible processes, namely, in the mathematical representation of the second law of thermodynamics.*

In his 1865 article [23], Clausius suggested to calculate N by using a cycle consisting of an irreversible segment and a reversible segment, which reversibly restores the system to the original state. In this case, Eq. (2.3) may be written as

$$N = \Delta S_e - \int_{\text{irrev}} \frac{dQ}{T}, \quad (2.3')$$

where ΔS_e is the entropy change for the reversible process that restores the system to the original state and the integration is over the irreversible segment of the cycle. An account of the road to the Clausius entropy is referred to in Cropper's paper [24]. The procedure using Eq. (2.3') for N is unsuitable for developing a theory of irreversible processes. The inequality (2.3) must be differently interpreted for the purpose mentioned: we interpret the compensated and uncompensated heats as two independent physical entities that exactly balance each other so as to form the equation as in Eq. (2.3); see p. 43 of Ref. [6] and Ref. [22].

It has been shown in recent works [6,22] by one of the present authors that, if the uncompensated heat is expressed in the form of a cyclic integral

$$N = \oint dN, \quad (2.4)$$

then the Clausius inequality (2.3) can be cast into a vanishing cyclic integral

$$\oint \left(\frac{dQ}{T} + dN \right) = 0. \quad (2.5)$$

This vanishing integral implies that there exists an exact differential of a quantity called calortropy [18(a)] Ψ in thermodynamic space defined later:

$$d\Psi = \frac{dQ}{T} + dN. \quad (2.6)$$

Here dN is always positive and vanishes only if the process in the segment in question is reversible. If dN were negative, it would be possible to devise a cycle that contravenes the second law of thermodynamics, but that is impossible. The differential form $d\Psi$ can be put into a local balance equation

$$\rho \frac{d\hat{\Psi}}{dt} = -\nabla \cdot (\mathbf{Q}^c/T) + \Xi_c(\mathbf{r},t), \quad (2.7)$$

where $\hat{\Psi}$, \mathbf{Q}^c , and Ξ_c are defined such that

$$\Psi = \int_V d\mathbf{r} \rho \hat{\Psi}(\mathbf{r},t), \quad (2.8a)$$

$$T^{-1} \frac{dQ}{dt} = - \int_V d\mathbf{r} \nabla \cdot (\mathbf{Q}^c/T), \quad (2.8b)$$

$$\frac{dN}{dt} = \int_V d\mathbf{r} \Xi_c(\mathbf{r},t), \quad (2.8c)$$

with ρ denoting the mass density, and d/dt in Eq. (2.7) stands for the substantial time derivative. The temperature T in Eq. (2.7) is the local absolute temperature at position \mathbf{r} and time t .

If the internal energy density, specific volume, mass fractions, and nonconserved variables are denoted by \mathcal{E} , v , c_a , and $\hat{\Phi}_{ka}$ ($k \geq 1$, $r \geq a \geq 1$), respectively, for an r -component mixture, it is useful to introduce a thermodynamic space spanned by $\mathfrak{G} = (\mathcal{E}, v, c_a, \hat{\Phi}_{ka} : k \geq 1, r \geq a \geq 1)$. It can then be shown that under a set of propositions [22] regarding \mathbf{Q}^c

and Ξ_c the calortropy balance equation (2.7) can be put into a differential form for $d_t \hat{\Psi}$ as follows:

$$d_t \hat{\Psi} = T^{-1} \left[d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right], \quad (2.9)$$

where $d_t = d/dt$ and p , $\hat{\mu}_a$, and X_{ka} are variables conjugate to v , c_a , and $\hat{\Phi}_{ka}$, respectively. They are local variables depending on position \mathbf{r} and time t . It must be emphasized that T is the local temperature of the nonequilibrium system that is given in the absolute temperature scale and that under the propositions [22] for \mathbf{Q}^c and Ξ_c , which put (2.7) in the differential form as in Eq. (2.9), there is no other temperature suggested by the Clausius inequality, namely, the second law of thermodynamics. The T is what is provided by thermometry on the irreversible system, and that is a parameter in terms of which the calortropy density $\hat{\Psi}$ is determined with the help of the constitutive relations for p , $\hat{\mu}_a$, and X_{ka} in space \mathfrak{G} . The differential form (2.9) tells us that $\hat{\Psi}$ is not determined by some other means but the constitutive relations and T , when the differential form is integrated in space \mathfrak{G} . Recall that the situation is the same in the case of equilibrium thermodynamics since there is no direct way of measuring the Clausius entropy; calorimetry and other thermodynamic measurements make it possible to calculate the Clausius entropy. The case of nonequilibrium therefore would be no exception. In fact, when such a concept of temperature is rendered meaningless, since the irreversible processes are faster than the time scale of thermometric resolution, the Clausius inequality is no longer applicable. We then have no mathematical representation for the second law of thermodynamics on which to build a thermodynamics of irreversible processes; in such an event there is a question of whether thermodynamics is a meaningful description of the process in hand. It is very important to recognize the crucial position that the Clausius inequality occupies in thermodynamics and the meaning of T therein that we have elucidated here. A mathematical study [25] of Eq. (2.9) shows that T^{-1} is mathematically an integrating factor for the differential form

$$\Omega = d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka}. \quad (2.9')$$

That is, this differential form Ω is made an exact differential form in space \mathfrak{G} by the integrating factor T^{-1} . [We emphasize that Ω is a symbol for the 1-form [26] on the right-hand side of Eq. (2.9'); it is not a function nor a differential of a function.]

The differential form (2.9) reduces to the well-known local equilibrium Gibbs relation for the Clausius entropy S_e if $X_{ka} = 0$ or $d_t \hat{\Phi}_{ka} = 0$ or both:

$$d_t \hat{\Psi}_{\text{eq}} = T_e^{-1} \left(d_t \mathcal{E} + p_e d_t v - \sum_{a=1}^r \hat{\mu}_a^e d_t c_a \right) = d_t S_e, \quad (2.10)$$

where the subscript or superscript e is affixed on the coefficients to the differentials to indicate that the parameters affixed with e are equilibrium quantities such that

$$T_e = \lim_{\Phi \rightarrow 0} T(\hat{\Phi}), \quad p_e = \lim_{\Phi \rightarrow 0} p(\hat{\Phi}), \quad \hat{\mu}_a^e = \lim_{\Phi \rightarrow 0} \hat{\mu}_a(\hat{\Phi}). \quad (2.11)$$

It must be recognized that T_e , albeit in the limit of $\Phi_{ka} \rightarrow 0$, is not of a different temperature scale from that of T ; both T_e and T are in the same absolute temperature scale, but their numerical values are different because of the irreversible processes. The differential form (2.9) implies that there holds the relation

$$T^{-1} = \left(\frac{\partial \hat{\Psi}}{\partial \mathcal{E}} \right)_{v,c,\hat{\Phi}}. \quad (2.12)$$

This gives the tangent to the $\hat{\Psi}$ surface along the \mathcal{E} axis in space $\mathfrak{G}_\psi \equiv \mathfrak{G} \cup \hat{\Psi}$ and T^{-1} is a constitutive relation, which, together with other constitutive relations for p , $\hat{\mu}_a$, and X_{ka} , determines the surface $\hat{\Psi}$ in \mathfrak{G}_ψ . Equation (2.12) is often regarded [7,9(a)–(c),12(b)] as an equation defining “non-equilibrium temperature” T in analogy to the equilibrium thermodynamic relation arising from Eq. (2.10)

$$T_e^{-1} = \left(\frac{\partial S_e}{\partial \mathcal{E}} \right)_{v,c}. \quad (2.12')$$

Suppose this is the definition of T_e , as is thought by some authors [7,9(a)–(c),12(a)–(c)] in EIT. The T_e can be obtained from Eq. (2.12') if and only if S_e is known, but the differential form (2.10), obtained from the second law by Clausius, does not permit us to determine S_e unless T_e , p_e , and $\hat{\mu}_a^e$ are known as functions of \mathcal{E} , v , and c_a , or \mathcal{E} , p_e , and $\hat{\mu}_a^e$ are known as functions of T_e , v , and c_a . As mentioned earlier, thermodynamics does not provide a means to measure S_e directly as a primitive variable. *Therefore, it is clear that Eq. (2.12') is not a definition of T_e ; rather, it is a relation by which the Clausius entropy S_e may be determined in terms of T_e with the help of the caloric equation of state that relates \mathcal{E} to T_e , the equation of state, and the chemical potentials.* The meaning of T_e has been already fixed universally by the Carnot theorem and the second law of thermodynamics—this is Kelvin's thermodynamic temperature. A similar conclusion can be drawn from Eq. (2.12); it is not a defining equation for T , but an equation by means of which $\hat{\Psi}$ may be determined in terms of T and variables in \mathfrak{G} , provided that \mathcal{E} is given as a function of T and other variables in \mathfrak{G} . *Calortropy $\hat{\Psi}$ cannot be directly measured by means of macroscopic irreversible thermodynamic techniques and one of the tasks of irreversible thermodynamics is to devise ways to measure indirectly the values of $\hat{\Psi}$ for given irreversible processes.* We take an analogy from our everyday affairs: $\hat{\Psi}$ is like a filing cabinet (or more aptly, a computer diskette or a magnetic tape) containing information on the physical properties of the macroscopic systems of interest. We make up the “filing system,” for later use, only on careful analysis of the system properties via constitutive equations. It is practically impossible to guess and assume beforehand a mathematical form for $\hat{\Psi}$ in space \mathfrak{G} so as to

construct all the constitutive equations of matter from it. In fact, the situation is quite opposite because the content of $\hat{\Psi}$ is determined on integration of Eq. (2.9) with the help of the constitutive relations for the coefficients to the differentials in Eq. (2.9). The meaning of T has been also fixed unambiguously by the second law of thermodynamics and given an operational meaning through the temperature scale universally fixed (e.g., the absolute temperature scale) as is for T_e in the case of reversible processes, and thermometry on the system determines T . It is now clear that irreversible processes do not alter the situation. A definition of a physical quantity implies a means of measurement, at least in principle, for the quantity, but this important criterion is absent in the case of Eq. (2.12) as a definition for T . Therefore, we conclude that Eq. (2.12) as a definition for T in the phenomenological theory is a misguided notion and cannot serve the desired role, although it is usually thought as such by many authors [e.g., Refs. [7,9(a)–(c)] and [12(a)–(c)]] in EIT.

Before proceeding further on the discussion of Refs. [7, 9, 12], we digress and mention the differential form obtained by Keizer [5], since it is relevant to the present discussion and the viewpoint toward T in it is similar to ours here. He develops a theory of irreversible processes on the basis of a fluctuation theory for macroscopic variables that fluctuate from the thermodynamically determined set of values. The theory involves a differential form for what he calls the Σ function, which appears to be comparable to the Pfaffian form in Eq. (2.9). In the differential form for Σ there appears the inverse temperature T^{-1} as an integrating factor in the manner of Eq. (2.9), and this T is considered to be a local temperature whose numerical value is recorded by a thermometer inserted at the point of interest at time t . It, however, must be pointed out that this differential form has not been shown, in contrast to Eq. (2.9), to have descended from the second law of thermodynamics or the Clausius inequality in Ref. [5] or in the references cited therein, although the Caratheodory principle is substituted for the second law as the basis for the differential form. For irreversible processes the said principle is not as self-evident as the case of reversible processes because of the presence of the uncompensated heat. Nevertheless, there is a convergence of the viewpoints held by Keizer and by the present authors with regard to the operational meaning of the T factor appearing in the differential forms for the $\hat{\Psi}$ and Σ functions. These convergent viewpoints toward T are in contrast to those held by the authors of Refs. [9] and [12].

We now examine how inevitably the notion of nonequilibrium temperature arises in the version of EIT described in Refs. [7,9(a)–(c),12(a)–(c)]. In this version, the Clausius entropy is straightforwardly generalized so as to be a function of nonconserved variables as well as the conserved variables. We denote it by S . This assumption formally yields a differential form for $d_t S$ similar to Eq. (2.9) in mathematical structure:

$$d_t S = T^{-1} \left[d_t \mathcal{E} + p' d_t v - \sum_{a=1}^r \hat{\mu}'_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X'_{ka} d_t \hat{\Phi}_{ka} \right], \quad (2.13)$$

only if the tangents to S are defined by the relations

$$T'^{-1} = \left(\frac{\partial S}{\partial \mathcal{E}} \right)_{v,c,\hat{\Phi}}, \quad (2.14a)$$

$$p' T'^{-1} = \left(\frac{\partial S}{\partial v} \right)_{\mathcal{E},c,\hat{\Phi}}, \quad (2.14b)$$

$$-\hat{\mu}'_a T'^{-1} = \left(\frac{\partial S}{\partial c_a} \right)_{\mathcal{E},v,c',\hat{\Phi}}, \quad (2.14c)$$

$$X'_{ka} T'^{-1} = \left(\frac{\partial S}{\partial \hat{\Phi}_{ka}} \right)_{\mathcal{E},v,c,\hat{\Phi}'}. \quad (2.14d)$$

Thus, the notion of nonequilibrium temperature, together with those of nonequilibrium pressure and chemical potentials, has arisen in EIT as a quantity derivable from S because it is assumed that S is known in space \mathfrak{G} and rooted in thermodynamic laws and its differential form is given by a 1-form reminiscent of the equilibrium Gibbs relation (2.10). [The prime on the subscript in the derivatives in Eq. (2.14) means exclusion of the variable in the derivative.] However, the differential form (2.13) simply implies that S is determinable as a function of variables in \mathfrak{G} , provided that T'^{-1} , $p' T'^{-1}$, $\hat{\mu}'_a T'^{-1}$, and $X'_{ka} T'^{-1}$ are given in \mathfrak{G} and the differential form satisfies the integrability conditions; the definitions (2.14a)–(2.14d) by no means make the tangents thermodynamically operational quantities nor are the derivatives determined by Eqs. (2.14a)–(2.14d) unless S is explicitly known in \mathfrak{G} . Therefore, the idea that Eq. (2.14a) defines the temperature of the nonequilibrium system appears to have originated from the thought that S is somehow known *a priori* in space \mathfrak{G} , but this is hardly true because all that is assumed about S is that there exists a function in \mathfrak{G} that satisfies the differential form (2.13). *We do not even know the meaning of S from the stand-point of thermodynamic laws since the Clausius entropy is defined for reversible processes only and the differential form (2.13) of its purported generalization S is completely detached from the second law of thermodynamics as it stands under the assumption made on S .* The notion that T' is some sort of temperature, in fact, appears to have derived from analogy to the equilibrium Gibbs relation, but the latter holds only for reversible processes and in no way does it imply that a similar relation will hold for nonequilibrium. Equation (2.13) in Refs. [7, 9, 12] does not descend from the thermodynamic laws and has no relation to the latter. If one compares Eq. (2.13) with Eq. (2.9) and makes the correspondence

$$\hat{\Psi} \Leftrightarrow S, \quad (2.15)$$

then and only then may T' in Eq. (2.13) be made to correspond to T in Eq. (2.9) and thereby given a thermodynamic operational meaning. But then, this procedure of assuming such an S only to make correspondence with the phenomenological quantity $\hat{\Psi}$ is not warranted since Eq. (2.9) is already provided by the thermodynamic laws, and the procedure involving S is superfluous. Putting it differently, one may say that the versions of EIT as in Refs. [7,12(b)–(c)]

cannot be regarded as thermodynamic theories until the fundamental relation, such as (2.9), has been derived from the thermodynamic laws.

On the basis of the considerations made up to this point, we conclude that the notion of nonequilibrium temperature in the versions of EIT by Jou and co-workers [7,9(a)–(c)] and Nettleton [12(b),(c)] has arisen because the assumption made on a nonequilibrium entropy has no relation to the second law of thermodynamics. A thermodynamic theory should be based on the thermodynamic laws.

III. STATISTICAL MECHANICS AND TEMPERATURE

The meaning of temperature has been an important subject of quest in statistical mechanics and kinetic theory. In particular, in EIT the question of the temperature of a nonequilibrium system has been approached from the standpoint of kinetic theory of matter. In order to put the kinetic theory approach in a historical setting, let us trace how the concept of temperature arose in the classical kinetic theory and statistical mechanics. According to Brush [1], Bernoulli [13] for the first time calculated the temperature of an ideal gas in terms of the average kinetic energy of gas molecules. This was forgotten, but later revived independently by Herapath [14] and Waterston [15], whose works were never given deserved credit by their contemporaries. The basic point of their theory is that the average kinetic energy of the molecules in the gas is a measure of the temperature of the gas. This basic notion played an important seminal role in the development of thermodynamics and has survived to this day. For example, in his seminal paper [27] of 1946 on the kinetic theory of fluids Kirkwood defined the temperature of a fluid (gas or liquid) in terms of the mean kinetic energy of the fluid, and this definition has been used for temperature in molecular dynamics simulations [28]. The same definition has been used in the case of dilute gases, as is evident in the well-known monographs [29,30] on kinetic theory of gases. In the case of dense fluids the definition of temperature is intimately related to the question of bulk viscosity, and divergent views toward it are expressed in the literature [31,32]. In the statistical approaches to EIT in which dilute monatomic gases are taken as a model, the temperature of the system is generally defined in the same manner as those mentioned earlier. However, the statistical definition of temperature by means of the average kinetic energy is not without a hitch, as will be discussed presently. We first review how temperature generally enters statistical thermodynamics. This is evident in the well-known treatises in statistical mechanics [33–35], but we will discuss it to complete the picture of the matter under examination and for the sake of the flow of reasoning.

A. Gibbs ensemble method and temperature

In the Gibbs ensemble theory [33–35], the canonical distribution function of a system at equilibrium is assumed to be in the form

$$f = \exp(-\beta H) / \langle \exp(-\beta H) \rangle, \quad (3.1)$$

where H is the Hamiltonian of the system and β is an as-yet-undetermined parameter. The angular brackets denote inte-

gration in the phase space. The average energy E is then given by the statistical formula

$$E = \langle Hf \rangle, \quad (3.2)$$

from which the parameter β may be determined in terms of E . If the particles interact, then the Hamiltonian contains an interaction potential-energy term and the relation between β and E is not simple and universal because the equipartition law no longer remains valid unless the interaction potential energies happen to be quadratic in coordinates of the particles. In the case of an ideal gas the relation becomes rather simple, and by using the ideal gas equation of state given in terms of absolute temperature T and the well-known relation

$$p = 2E/3V, \quad (3.3)$$

where V is the volume, we find that

$$\beta = 1/k_B T, \quad (3.4)$$

where k_B is the Boltzmann constant. Such an identification of β is not possible by way of calculating the average kinetic energy if the particles are quantum mechanical or relativistic, even if the gas is ideal, because E is not a simple function of β , although Eq. (3.3) may still hold. Again, the equipartition law breaks down in these cases. To use the concept of temperature even for relativistic cases, Tolman [16] introduced a generalized equipartition law, and this approach has been used by later authors [17] to obtain an expression that appears to give temperature as the average of an operator in the cases of quantum gases. However, close examination reveals that the aforementioned generalized equipartition law is a rearrangement of the normalization condition of the distribution function and consequently the temperature operator defined is devoid of an evident physical meaning. This point becomes even more cogent in the case of dense fluids where interactions of particles become important, since the temperature operator consequently is not identifiable in a universal form.

In general, the parameter β in the canonical form (3.1) is determined with the help of thermodynamics by comparing the statistical entropy and other statistically computed mechanical observables with the Clausius entropy and the phenomenological thermodynamic observables. Such a calculation led Boltzmann [36] to realize that his H function could serve as a statistical formula for the Clausius entropy in the case of a dilute gas in equilibrium. In the later synthesis by Gibbs [33] of the Maxwell-Boltzmann statistical theory, such correspondence determines the parameter β in the canonical form by the relation as in Eq. (3.4) for all forms of aggregation of matter in equilibrium. Recall that T in Eq. (3.4) is the thermodynamic temperature of the heat reservoir, the scale of which may be made coincident with the absolute temperature scale [37]. It is the very temperature appearing in the Clausius inequality for a reversible process:

$$\oint dS_e = \oint_{\text{rev}} \frac{dQ}{T} = 0, \quad (3.5)$$

where $dS_e = dQ/T$ is the global (Clausius) entropy change as defined by Clausius for a reversible process. This manner of

identifying β is free from the assumption on the nature of matter and is universal and rigorous inasmuch as the second law of thermodynamics is universal and axiomatic. Thus, we see that the parameter β in the canonical distribution function (3.1) is given in terms of the absolute temperature by virtue of thermodynamics, which indispensably and unavoidably manifests itself in the process of correspondence between thermodynamics and the statistical theory of matter simply because we insist that the canonical form (3.1) describe the thermodynamic system at the statistical level, and, fortunately, the statistically derived formula for dS_e matches with the phenomenological theory formula for the same. This is the beauty of the canonical distribution function. From the purely mathematical and probabilistic standpoint detached from thermodynamics the parameter β is related to the mean energy E and *nothing like Eq. (3.4) can be inferred within the framework of the probability theory alone*. In fact, the ideal gas represents a degenerate case, since it happens that $E = \frac{3}{2}nk_B T$ by virtue of mathematics and this relation happens to be consistent with Eqs. (3.3) and (3.4) as well as the equilibrium Gibbs relation for dS_e ; an accidental mutual consistency no longer enjoyed by the ideal quantum gases [6,38] and ideal relativistic gases [6,39] owing to the fact that E is no longer a simple linear function of β^{-1} . This is an observation on well-known statistical-mechanical results from a nonconventional angle. If a unified description of diverse, but seemingly related, facts in physical phenomena is one of the important goals of physics, then the aforementioned aspect regarding the relation of E to temperature tells us otherwise about the role of kinetic energy in connection with temperature in statistical thermodynamics. The relation between temperature and kinetic energy is subtler than commonly thought in kinetic theory.

In summary, for the equilibrium canonical form and the parameter β therein, the temperature enters the statistical-mechanical formalism through the correspondence between the phenomenological (i.e., thermodynamic) equilibrium Gibbs relation and the corresponding statistically computed relation. The concept that the average kinetic energy is the statistical definition of temperature is not universal and therefore does not meet the universality condition required for a temperature scale from the viewpoint of rigorous thermometry [40]. In any case, the equilibrium Gibbs ensemble theory can do without the statistical definition of temperature as long as there is the equilibrium Gibbs relation for the entropy change provided by the thermodynamic laws for reversible processes, since then the parameter β in the canonical distribution function can be determined by the method of thermodynamic correspondence between the thermodynamic phenomenology and the statistical thermodynamic theory.

B. Some versions of EIT and temperature

The statistical foundations of EIT have been investigated by means of the Boltzmann equation by a number of authors. Some [7,41–43] approached the subject by using approximate distribution functions; in another [7,12(b)] a maximum entropy method was taken; and in still another [6,18(a)] a rigorous approach was pursued. The first two approaches will be grouped as version *A* since they represent the same line of viewpoint. The last one taken in Refs. [6] and [18(a)] will be called version *B*. These two versions will be consid-

ered separately. In both versions the temperature of a non-equilibrium monatomic ideal gas mixture is “defined” by the mean kinetic energy

$$\rho\mathcal{E} = \sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 f_a \rangle \equiv \frac{3}{2} n k_B \theta, \quad (3.6)$$

where θ is the nonequilibrium temperature, C_a is the peculiar velocity, n is the number density, and f_a is a singlet distribution function obeying the Boltzmann equation. However, the interpretation of θ is made differently in versions *A* and *B*. The Boltzmann kinetic theory provides a statistical formula, the H function, that at a quick glance appears to meet the billing for the Clausius entropy and its nonequilibrium generalization. The H function gives the Boltzmann entropy density

$$\rho S = -k_B \sum_{a=1}^r \langle f_a (\ln f_a - 1) \rangle, \quad (3.7)$$

where the angular brackets mean integration in velocity. This formula is also common to versions *A* and *B*, but its role in the theory of irreversible processes is significantly different in the two versions.

1. Version *A* and temperature

In Refs. [7] and [9(a)–(c)] the nonequilibrium temperature θ is also defined in terms of the energy derivative of S :

$$\theta^{-1} = \left(\frac{\partial S}{\partial \mathcal{E}} \right). \quad (3.8)$$

The same relation can be inferred from the differential form for dS in Refs. [12(b),12(c)]. The two definitions (3.6) and (3.8), being for the same attribute of the system, must be self-consistent. Temperature, being the most basic quantity in thermal physics, must be rigorously defined and consistent with the thermodynamic laws. Therefore, one cannot afford an inconsistency between Eqs. (3.6) and (3.8), for example. In Refs. [7,9(c),12(b)], in addition to Eqs. (3.6) and (3.8) where θ appears, f_a enters expressed in a nonequilibrium canonical form f_a^m ,

$$f_a^m = \exp[-\beta(H_a + \boldsymbol{\gamma}_a \cdot \mathbf{A}_a)] / \langle \exp[-\beta(H_a + \boldsymbol{\gamma}_a \cdot \mathbf{A}_a)] \rangle, \quad (3.9)$$

where $\boldsymbol{\gamma}_a$ is a row vector of undetermined multipliers and \mathbf{A}_a is a column vector consisting of conjugate variables to the undetermined multipliers. These latter variables depend on the velocities of the particles. The f_a^m in Eq. (3.9) allegedly yields “a maximum” ρS in Eq. (3.7), since it is obtained by “maximizing” the entropy. (The term maximization or extremization used in this context is incorrect, but we will not dwell on it here since it is beside the point of this paper.) In the aforementioned references, β is claimed to be related to nonequilibrium temperature θ by the formula

$$\beta = 1/k_B \theta \quad (3.10)$$

because with Eq. (3.9) S is asserted to be given, within the framework of the maximum entropy method, by the postulated differential form

$$\theta d_t S = d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \boldsymbol{\gamma}_a \cdot d_t \mathbf{A}_a, \quad (3.11)$$

and furthermore Eq. (3.11) is, by virtue of the formal analogy to the equilibrium Gibbs relation, simply asserted to be a representation of the thermodynamic laws for irreversible processes and for nonequilibrium. Hence the term nonequilibrium temperature for θ . Equation (3.10) follows from Eqs. (3.8) and (3.9) if Eq. (3.11) is indeed true. We now examine Eq. (3.11). Equation (3.11) does not follow unless

$$\rho S = -k_B \sum_{a=1}^r \langle f_a^m (\ln f_a^m - 1) \rangle \quad (3.12)$$

and additional conditions on $d_t \mathbf{A}_a$, that is, the evolution equations for \mathbf{A}_a are met. These conditions are elucidated in Ref. [18(a)], where it is shown that all is not well with Eqs. (3.11) and (3.12). In any case, if f_a^m is the distribution function maximizing S , then there is a fluctuation in f_a . This fluctuation cannot be neglected. Even if f_a^m is such that there hold the conditions

$$\langle (f_a - f_a^m) \rangle = 0, \quad \langle (f_a - f_a^m) H_a \rangle = 0, \quad \langle (f_a - f_a^m) \mathbf{A}_a \rangle = 0, \quad (3.13)$$

there exists the relative Boltzmann entropy $S_r[f|f^m]$, such that [18(a)]

$$\rho S = -k_B \sum_{a=1}^r \langle f_a (\ln f_a^m - 1) \rangle - \rho S_r[f|f^m], \quad (3.14)$$

where

$$\rho S_r[f|f^m] = k_B \sum_{a=1}^r \langle f_a \ln(f_a / f_a^m) \rangle. \quad (3.15)$$

This relative Boltzmann entropy does not vanish away from the state “maximizing” S . (Note that S is a maximum only at equilibrium reached in long time [6].) Therefore, Eq. (3.12) must be an approximation that neglects $S_r[f|f^m]$. Furthermore, a nonvanishing $S_r[f|f^m]$ makes Eq. (3.9) inconsistent with Eq. (3.8), that is, Eq. (3.8) is not true. The reason for this will become evident in the subsequent discussion. Even if they were consistent with each other, Eq. (3.11) would be given a thermodynamic status, only if it was made to correspond to its thermodynamic counterpart derived from the thermodynamic laws. However, since such a thermodynamic counterpart is absent not only for the Boltzmann entropy but also in the nonequilibrium entropy S in version *A* (EIT developed in Refs. [7,8,9(a)–(c),12(b)]) it is not possible to endow Eq. (3.11) with a thermodynamic status. Therefore Eq. (3.8) does not define a thermodynamically operational quantity; it is simply a symbolic relation between S and θ in a probabilistic theory of dynamical objects, which holds under the assumption that $S_r[f|f^m] = 0$ and under the conditions on $d_t \mathbf{A}_a$ that can be inferred from Refs. [18(a), 22]. If these restrictions are not met, the Pfaffian form (3.11) does not hold for $d_t S$ and Eq. (3.8) does not follow. In fact, it is easy to show that the assumption $S_r[f|f^m] = 0$ is incompatible with the conditions on $d_t \mathbf{A}_a$ [18(a),22], and Eq. (3.11)

is not true. A similar conclusion that Eq. (3.11) is not true has been recently drawn by Ichiyangi [44] from the viewpoint of the Onsager-Machlup theory.

2. Version B and temperature

In Refs. [6, 18(a)] it is shown that the sufficient conditions for conserved variables to remain constant in space-time are the matching conditions

$$\rho\mathcal{E} = \sum_{a=1}^r \langle \frac{1}{2}m_a C_a^2 f_a \rangle = \sum_{a=1}^r \langle \frac{1}{2}m_a C_a^2 f_a^m \rangle = \rho_e \mathcal{E}_e, \quad (3.16a)$$

$$\rho = \sum_{a=1}^r \langle m_a f_a \rangle = \sum_{a=1}^r \langle m_a f_a^m \rangle = \rho_e, \quad (3.16b)$$

$$\rho\mathbf{u} = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a \rangle = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^m \rangle = \rho_e \mathbf{u}. \quad (3.16c)$$

Furthermore, if the nonequilibrium canonical form is given in terms of the complete set of tensor Hermite polynomials $\mathcal{H}^{(k)}(\mathbf{w}_a)$ of reduced peculiar velocity $\mathbf{w}_a = \sqrt{\beta m_a} \mathbf{C}_a$ by the formula

$$f_a^c = \exp \left\{ -\beta \left[H_a + \sum_{k \geq 1} X_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) - m_a \hat{\mu}_a \right] \right\}, \quad (3.17)$$

where β and X_{ka} are as-yet-undetermined parameters and $\hat{\mu}_a$ is the normalization factor, then with the statistical definition of calortropy $\hat{\Psi}$

$$\rho \hat{\Psi} = -k_B \sum_{a=1}^r \langle f_a (\ln f_a^c - 1) \rangle \quad (3.18)$$

and the relative Boltzmann entropy

$$\rho S_r[f|f^c] = k_B \sum_{a=1}^r \langle f_a \ln(f_a/f_a^c) \rangle, \quad (3.19)$$

it is possible to show that the differential form for $d_t \hat{\Psi}$ is given by

$$d_t \hat{\Psi} = T^{-1} \left[d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right]. \quad (3.20)$$

Here $\hat{\Phi}_{ka}$ is defined by the statistical formula

$$\Phi_{ka} = \rho \hat{\Phi}_{ka} = \langle f_a \mathcal{H}^{(k)}(\mathbf{w}_a) \rangle. \quad (3.21)$$

Definitions (3.18) and (3.19) imply that

$$S = \hat{\Psi} - S_r[\mathbf{f}|\mathbf{f}^c], \quad (3.22a)$$

$$d_t S = d_t \hat{\Psi} - d_t S_r[\mathbf{f}|\mathbf{f}^c], \quad (3.22b)$$

but $S_r[\mathbf{f}|\mathbf{f}^c] \neq 0$ and $d_t S_r[\mathbf{f}|\mathbf{f}^c] \neq 0$ for systems away from equilibrium [18(a),(b)]. Nevertheless, since $d_t \hat{\Psi}$ in (3.20) is in a 1-form similar to (2.9) it is possible to correspond the statistically derived differential form (3.20) to the phenom-

enological thermodynamic differential form (2.9) obtained from the thermodynamic laws. We thereby obtain a relation between β and T

$$\beta = 1/k_B T, \quad (3.23)$$

which identifies the parameter β in terms of inverse thermodynamic temperature T^{-1} . The point of this analysis then is that in version A of EIT the nonequilibrium entropy S as in Eq. (3.12) must be replaced by the calortropy, since the right-hand side of Eq. (3.12) with Eq. (3.13) is precisely $\rho \hat{\Psi}$ as defined by Eq. (3.18) if the conditions in Eq. (3.13) are imposed. Then and only then is it possible to make the thermodynamic correspondence as described earlier and the thermodynamic temperature is related to $\hat{\Psi}$ by the derivative

$$T^{-1} = \left(\frac{\partial \hat{\Psi}}{\partial \mathcal{E}} \right)_{v,c,\hat{\Phi}}. \quad (3.24)$$

We emphasize that, by virtue of the correspondence of Eq. (2.9) with Eq. (3.20), T here is the thermodynamic temperature as in Eq. (2.9). Thus, Eq. (3.24) provides a way to determine $\hat{\Psi}$ in terms of T unless one elects to calculate $\hat{\Psi}$ statistically, but it should not be construed as a definition of T . If one had exactly calculated $\hat{\Psi}$ and \mathcal{E} by using the nonequilibrium canonical form (3.17), then Eq. (3.24) would reproduce Eq. (3.23) and thereby serve as a check for the correctness of the calculation performed. In practice, by using the nonequilibrium partition function \mathbb{Z} [18(b)], Eq. (3.24) may be cast into the constitutive equation, namely, the statistical formula for the caloric equation of state

$$C_v = T \left(\frac{\partial \Psi}{\partial T} \right)_{v,c,\hat{\Phi}} = k_B T \left(\frac{\partial^2}{\partial T^2} T \ln \mathbb{Z} \right)_{v,c,\hat{\Phi}}. \quad (3.25)$$

Here

$$\begin{aligned} \mathbb{Z} &= \prod_{a=1}^r \mathbb{Z}_a^{N_a} = \exp \left(-\beta \sum_{a=1}^r \mu_a N_a \right) \\ &= \prod_{a=1}^r \left\{ n_a^{-1} \left\langle \exp \left[-\beta \left(H_a + \sum_{k \geq 1} X_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) \right) \right] \right\rangle \right\}^{N_a} \end{aligned}$$

with N_a denoting $N_a = V \rho c_a / m_a$. If C_v is treated as a phenomenological quantity, the first equality in Eq. (3.25) determines $\hat{\Psi}$ from the knowledge of C_v . If the second equality is used, C_v is calculated from the knowledge of \mathbb{Z} . However, in no cases does (3.25) define T ; rather, C_v is given in terms of the empirical parameter T . Phenomenologically, the important task of determining $\hat{\Psi}$, together with p , $\hat{\mu}_a$, and X_{ka} , belongs to the realm of irreversible thermodynamics. In this connection, we would like to add here a note on $\hat{\mu}_a$. By using the previously cited fluctuation theory, Keizer [5] has deduced from the differential form for his Σ function the constitutive parameters $\hat{\mu}_a$ as empirical chemical potentials on the same footing as the temperature. That is, $\hat{\mu}_a$ are thermodynamics-based in the same sense as the temperature, even if the system is displaced from equilibrium. Keizer and Chang [45] measured the electromotive force of a reacting nonequilibrium system by means of the conventional method and detected a nonequilibrium effect. This result is corroborated

rated by Hjelmfelt and Ross [46], although they are not completely certain as to the conclusion of Keizer *et al.* The implication of these experiments is that there is no necessity of making a distinction between the equilibrium and nonequilibrium chemical potentials, which only differ in their numerical values, but of simply measuring them as usual in a nonequilibrium condition. They do not appear as two different quantities in macroscopic equations describing irreversible processes in the manner θ and T appear in the theory of Refs. [9(a)–(c)], which will be discussed in the subsequent sections. It is important to remember that no equilibrium thermodynamic measurements are truly measurements on ideal reversible processes, and there are always elements of departure from the ideality, but the latter feature does not require, for example, another thermometric scale different from that for the ideal measurements.

In summary of the statistical aspect of temperature, we have pointed out that the mean kinetic energy does not generally serve as a statistical definition of temperature; $\hat{\Psi}$ is not completely determined in thermodynamic space \mathfrak{G} until β is made to correspond to the thermodynamic temperature and thus its thermodynamic meaning elucidated and therefore, (3.24) or a similar form with $\hat{\Psi}$ replaced by S does not define temperature, but simply gives the parameter β in terms of undetermined T . Consequently, if statistical mechanics is to have a relevance to irreversible thermodynamics or simply thermodynamics, temperature or β appearing in either equilibrium or nonequilibrium statistical mechanics must be the phenomenological temperature appearing in thermodynamics, namely, the thermodynamic temperature. Therefore, in the spirit of the Gibbs ensemble theory the temperature of the system, whether equilibrium or nonequilibrium, is a phenomenological attribute of the system, even in the statistical theory of molecular systems. The present authors believe that the misconception about this subtle but important point has been the cause of numerous confusing results and propositions in EIT.

3. Further comment on nonequilibrium temperature

In a recent paper [12(a)], Nettleton asserts that the nonequilibrium temperature defined in Refs. [7,9(c)] can be well approximated by the equilibrium temperature. We put his assertion in the notation of the present paper. The temperatures of nonequilibrium and local equilibrium systems are defined, respectively, by the formulas

$$\frac{3}{2}nk_B\theta = \sum_{a=1}^r \langle \frac{1}{2}m_a C_a^2 f_a \rangle, \quad (3.26a)$$

$$\frac{3}{2}nk_B T_e = \sum_{a=1}^r \langle \frac{1}{2}m_a C_a^2 f_a^e \rangle. \quad (3.26b)$$

Then, according to his calculation

$$\theta = T_e + \Delta\theta. \quad (3.27)$$

The nonequilibrium temperature appears in this form in Refs. [9(a)–(c)]. Since $\Delta\theta$ is on the order of 10^{-2} for a hard-sphere fluid [12(a)], he concludes that θ may be replaced by the local equilibrium temperature T_e to a good approximation for all densities. In the case of liquids or dense gases, his

calculation simply shows that the temperature defined in molecular dynamics simulations [28] is tolerable as an approximation. It by no means should be construed as the acceptability of the definition (3.26a) of nonequilibrium temperature since temperature cannot be defined approximately if one is to use it as a gauge to measure all thermal properties of matter. An approximate scale of temperature would be simply nonscientific. Furthermore, as discussed earlier, S must be replaced by $\hat{\Psi}$, and θ is simply the local temperature. In the case of dilute monatomic gases, his calculation just points out that the notion of nonequilibrium temperature is perpetuated by an incorrect understanding of kinetic theory and thus is meaningless, since the matching conditions given in Eq. (3.16) guarantee that the nonequilibrium temperature θ defined by Eq. (3.26a) is identical to the local thermodynamic temperature T_e , namely, $\Delta\theta=0$ identically. Therefore, the differences in temperatures he obtained for various cases of transport processes are simply due to the numerical errors incurred by the approximation made for the distribution function if his calculation is specialized to dilute monatomic gases. The comments made earlier in connection with the nonequilibrium temperature also apply to his calculations made for a dense hard-sphere fluid, since he, too, defines the nonequilibrium temperature with (3.8) or (3.26a).

IV. DISCUSSION AND CONCLUDING REMARKS

Having analyzed the general aspects of temperature of nonequilibrium systems, we now discuss in more detail the main point of the recent proposition by Jou and Casas-Vazquez [9(a)–(c)] for experiment on nonequilibrium temperature. As we have seen in the previous sections, the concept of temperature is intimately tied up with the notion of entropy and its nonequilibrium generalization. The aforementioned authors take the viewpoint that ‘‘EIT does not pretend to be an exact theory, but rather a model which allows for formulation of a nonequilibrium thermodynamic theory not based *a priori* on the local-equilibrium hypothesis.’’ Thermodynamics, reversible or irreversible, is an axiomatic theory that studies the consequences of the axioms summarizing macroscopic processes occurring in nature. From this viewpoint toward the subject, the following comment is made on the aforementioned quotation: An approximate thermodynamics loses its *raison d’être*, since it deprives itself of the authority to rule on the thermodynamic correctness of macroscopic theories, which we develop for macroscopic irreversible processes. By thermodynamic correctness we mean the strict conformation to the thermodynamic laws and their consequences. Notwithstanding this maxim, guided by the viewpoint just quoted, a nonequilibrium temperature θ was defined in Refs. [9(a)–(c)] by means of an approximate form for a ‘‘generalized entropy’’ for a rigid heat conductor

$$S(\mathcal{E}, \mathbf{q}) = S_{\text{eq}}(\mathcal{E}) - (v\tau/2\lambda T^2) \mathbf{q} \cdot \mathbf{q}, \quad (4.1)$$

where \mathcal{E} is the internal energy, $S_{\text{eq}}(\mathcal{E})$ is the local equilibrium entropy, T is the local equilibrium absolute temperature, \mathbf{q} is the heat flux, λ is the thermal conductivity, and τ is the relaxation time of \mathbf{q} that obeys the evolution equation

$$\tau \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \nabla \theta. \quad (4.2)$$

The quantity θ is the ‘‘generalized absolute temperature’’ defined earlier in (3.8). Thus, for the approximate $S(\mathcal{E}, \mathbf{q})$ in Eq. (4.1)

$$\theta^{-1} = T^{-1} - \gamma \mathbf{q} \cdot \mathbf{q}, \quad (4.3)$$

$$\gamma = \frac{\partial}{\partial \mathcal{E}} (v \tau / 2\lambda T^2). \quad (4.4)$$

Let us now return to (4.1) and mull over its origin and meaning. The first fundamental assumption is the extendability of the Clausius entropy into the domain of nonequilibrium, and the second entails the dependence of S on the local equilibrium absolute temperature and other parameters of the specific form as in Eq. (4.1). They are a pair of assumptions subordinating one to the other. They have no relation to the thermodynamic laws and, especially, the second law. To justify Eqs. (4.1) and (4.3) the dilute gas kinetic theory of Boltzmann has been used [9,47]. As has been pointed out in the last paragraph of Sec. III, if the gas is a dilute Boltzmannian gas, then the matching conditions (3.16) imply that $\theta = T$ (local temperature) identically if the temperatures are defined by Eqs. (3.26a) and (3.26b) as also in Ref. [9(a)]. Thus, we conclude that θ is the local absolute temperature. In fact, the second term on the right-hand side of Eq. (4.3) is a consequence of using an approximation to compute Eq. (3.6) or (3.26a). It is known that a rigorous formulation [18(a),(b)] of the theory using Eq. (3.17) shows otherwise. A similar point is also brought up in a recent paper [48] where the Boltzmann equation is ‘‘solved’’ by using Grad’s moment expansion that takes the infinite number of moments in the series as local conserved variables. The resulting expression for the Boltzmann entropy density defined in Eq. (3.7) shows that, as is already indicated in Sec. III B 3, the quantity θ^{-1} as defined in Eq. (3.8) is identical to the inverse of the local temperature introduced through Eq. (3.16a) for ideal gases.

Although it is not mentioned in the aforementioned references that λ and τ depend on T , they must be dependent on T , since T appears on the right-hand side of Eq. (4.1). On the other hand, they also appear in Eq. (4.2) where θ also appears. Since the constitutive equation (4.2) is supposed to involve the ‘‘nonequilibrium temperature,’’ should τ and λ then be regarded as functions of θ ? This dilemma can be resolved by assuming that τ and λ are either constants or $\theta = T$ as suggested by the matching conditions (3.16). The assumption that they are constants is too restrictive since even hard-sphere fluids have temperature-dependent thermal conductivities. Therefore, suppose that $\theta \neq T$, as suggested by (4.3), and further $\tau = \tau(T)$ and $\lambda = \lambda(T)$ in conformation to the assumption (4.1). This supposition has a difficulty at the hydrodynamic level of calculation, as is discussed below.

First, let us recall that the internal energy is a function of ‘‘nonequilibrium temperature’’ θ , not T , in version A of EIT: Therefore, the energy balance equation provides an evolution equation of θ which may be formally written as

$$\frac{\partial \theta}{\partial t} = F(\theta, \mathbf{q}). \quad (4.5)$$

This interpretation is consistent with (4.2). If $\lambda = \lambda(T)$ and $\tau = \tau(T)$, the coupled pair of equations (4.2) and (4.5) cannot be solved for θ and \mathbf{q} unless the local temperature T is given its spatial distribution. However, it is clear that the profile of T cannot be known from the set of equations (4.2) and (4.5) given. This suggests that the theory based on ‘‘nonequilibrium temperature’’ θ is either incomplete or ill posed. The trouble lies in θ . If this is replaced by the local temperature T , the aforementioned difficulty never arises. The indeterminability of θ also implies that \mathbf{q} is not determined and consequently neither is the generalized entropy S . Therefore, the concept of ‘‘nonequilibrium temperature’’ unhinges the entire structure of irreversible thermodynamics they intend to construct. As we have shown in Sec. III, temperature does not permit a margin for an approximation. Especially, if the generalized entropy is not based on the second law, no mathematically and thermodynamically consistent theory of irreversible processes can be expected. Besides, definition (4.3) is in fact under determined. The point is, there is no ‘‘nonequilibrium temperature’’; we have only the thermodynamic temperature coincident with the absolute temperature regardless of whether the system is in equilibrium or nonequilibrium. If the system is in nonequilibrium the thermometer may read a different local temperature from the local temperature of the same system at equilibrium in the same temperature scale. The concept of nonequilibrium temperature is a path that leads up a blind alley in thermodynamics and hydrodynamics.

Second, even if one proceeds directly from the differential of $S = S(\mathcal{E}, \mathbf{q})$ by following the steps outlined in Ref. [9(c)] where the Boltzmann kinetic theory underlies the analysis, the parameters λ and τ in Eq. (4.2) are, in general, functions of \mathcal{E} and \mathbf{q} . Thus Eq. (4.2) is at best a nonlinear differential equation for \mathbf{q} , which, together with the energy conservation equation

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{q} - \mathbf{P} : \nabla \mathbf{u} \quad (4.6)$$

constitutes a set of evolution equations for the thermodynamic state variables \mathcal{E} and \mathbf{q} that must be solved subject to the initial and boundary conditions appropriate for the problem at hand. Since this problem is not solvable in a general form even if analytic solutions are possible, it is doubtful that the steady-state equations of (4.2) and (4.6)

$$\mathbf{q} = -\lambda \nabla \theta, \quad (4.7a)$$

$$\nabla \cdot \mathbf{q} = 0, \quad (4.7b)$$

define a temperature scale that should be universal. (Note that we are assuming there is no flow of the gas, namely, $\mathbf{u} = \mathbf{0}$.) These equations will also have to be consistent with S as expressed by Eq. (4.1). Since the latter expression for S has been inspired by the Grad moment solution to the Boltzmann equation, the evolution equation obtained for \mathbf{q} by such a method ought to be such that Eqs. (4.7a) and (4.7b) should follow within the framework of the moment method. That is not the case. No matter how many moments are included in the solution [49,50], no kinetic theory support for Eq. (4.7a) is attained, but one generally gets

$$\mathbf{q} = -\lambda(\mathbf{r}, t) \nabla T(\mathbf{r}, t), \quad (4.8)$$

where the thermal conductivity is generally position and time dependent or, in the Fourier space, wave number and frequency dependent. It must be emphasized that $T(\mathbf{r}, t)$ appears but θ does not in this expression. This is consistent with generalized hydrodynamics, the validity of which is supported by experiment [51]. These arguments presented here reinforce the unphysical character of a theory based on Eqs. (4.1) and (4.2). In any case, it seems clear that the definition and scale of temperature cannot be system dependent contrary to the implication of Eq. (4.2) to the opposite effect. However, the universality of temperature is the most important aspect of the temperature concept in thermodynamics, both reversible and irreversible.

In conclusion of this paper, we have discussed how temperature enters the thermodynamics of irreversible processes and the nonequilibrium canonical distribution function in the statistical-mechanical formulation of irreversible thermodynamics and that it does ultimately originate from the Clausius inequality. Consideration of both equilibrium and nonequilibrium theories shows that the inverse temperature parameter β appearing in the nonequilibrium canonical distribution function cannot be generally determined without the help of the phenomenological extended Gibbs relation for the calortropy obtained from the second law of thermodynamics, namely, the Clausius inequality, and that the mean

kinetic energy as the definition of temperature in even the case of dilute gases is too special to be generally useful for fluids other than dilute Boltzmann gases. The aforementioned parameter β is given by the local phenomenological temperature, and there is no other temperature admissible than that by the zeroth law and the second law; it is the quantity that is associated with the heat reservoirs, even when the system is away from equilibrium. When this notion of temperature does not hold to be valid, the extended theory of irreversible processes that we know from the literature is no longer applicable and we pass the realm of irreversible thermodynamics governed by the thermodynamic laws into a nonthermodynamic realm of many-particle phenomena that is as yet uncharted. The notion that the “nonequilibrium temperature” θ can be defined by the relation (3.8) is not connected with the thermodynamic principles, and we have shown that it can give rise to difficulties kinetically, thermodynamically, and hydrodynamically.

ACKNOWLEDGMENTS

This work has been supported in part by the Natural Sciences and Engineering Research Council of Canada and one of the authors (LGC) is a member of the Sistema Nacional de Investigadores, Mexico.

-
- [1] S. G. Brush, *The Kind of Motion We Call Heat* (North-Holland, Amsterdam, 1976), Vols. 1 and 2.
- [2] S. Carnot, *Réflexions sur la Puissance Motrice du Feu et sur les Machines* (Bachelier, Paris, 1824) [English translation (Smith, Gloucester, MA, 1977)].
- [3] For scholarly accounts of this and related subjects, see *The Second Law of Thermodynamics*, edited by J. Kestin (Dowden, Hutchinson & Ross, Stroudsburg, PA, 1976).
- [4] B. Andresen, R. S. Berry, A. Nitzan, and P. Salamon, *Phys. Rev. A* **15**, 2086 (1977); P. Salamon, B. Andresen, and R. S. Berry, *ibid.* **15**, 2094 (1977); M. Rubin, *ibid.* **A 19**, 1272 (1979); **19**, 1277 (1979); P. Salamon, Y. B. Band, and O. Kafri, *J. Appl. Phys.* **53**, 197 (1982).
- [5] J. Keizer, *Statistical Thermodynamics of Irreversible Processes* (Springer, Berlin, 1987).
- [6] B. C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992).
- [7] D. Jou, J. Casas-Vazquez, and G. Lebon, *Extended Irreversible Thermodynamics* (Springer, Berlin, 1993).
- [8] I. Müller and T. Ruggeri, *Extended Thermodynamics* (Springer, Berlin, 1993).
- [9] (a) D. Jou and J. Casas-Vazquez, *Phys. Rev. E* **45**, 8371 (1992); (b) D. Jou and J. Casas-Vazquez, *Phys. Rev. E* **48**, 3201 (1993); (c) D. Jou and J. Casas-Vazquez, *Phys. Rev. E* **49**, 1040 (1994).
- [10] W. G. Hoover, B. L. Holian, and H. A. Posch, *Phys. Rev. E* **48**, 3196 (1993).
- [11] K. Henjes, *Phys. Rev. E* **48**, 3199 (1993).
- [12] (a) R. E. Nettleton, *Can. J. Phys.* **72**, 106 (1994); (b) R. E. Nettleton, *J. Phys. A* **21**, 3939 (1988); (c) R. E. Nettleton, *J. Phys. A* **22**, L353 (1989).
- [13] S. G. Brush, *The Kind of Motion We Call Heat* (Ref. [1]), Vol. 1, pp. 19–22.
- [14] S. G. Brush, *The Kind of Motion We Call Heat* (Ref. [1]), Vol. 1, Chap. 2.
- [15] See S. G. Brush, *The Kind of Motion We Call Heat* (Ref. [1]), Vol. 1, Chap. 3.
- [16] R. C. Tolman, *Phys. Rev.* **11**, 261 (1918).
- [17] V. J. Menon and D. C. Agrawal, *Am. J. Phys.* **59**, 258 (1991); *J. Phys. A* **25**, 4517 (1992).
- [18] B. C. Eu, *J. Chem Phys.* **102**, 7169 (1995); (b) B. C. Eu, *J. Chem. Phys.* **103**, 10 652 (1995).
- [19] See *The Second Law of Thermodynamics*, (Ref. [3]), pp. 52–58 and 59–86.
- [20] See *The Second Law of Thermodynamics*, (Ref. [3]), pp. 133–161 and 162–193.
- [21] J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1960).
- [22] B. C. Eu, *Phys. Rev. E* **51**, 768 (1995).
- [23] R. Clausius, *Ann. Phys. (Leipzig)* **125**, 355 (1865).
- [24] W. H. Cropper, *Am. J. Phys.* **54**, 1068 (1986). In this paper, the evolution of the entropy concept in the work of Clausius is examined, but no new insight to entropy is provided.
- [25] M. Chen and B. C. Eu, *J. Math. Phys.* **34**, 3012 (1993).
- [26] D. G. B. Edelen, *Exterior Calculus* (Wiley, New York, 1985).
- [27] J. G. Kirkwood, *J. Chem. Phys.* **14**, 180 (1946).
- [28] W. G. Hoover, *Molecular Dynamics* (Springer, Berlin, 1986).
- [29] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases*, 3rd. ed. (Cambridge University Press, London, 1970).
- [30] J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).

- [31] L. S. García-Colín and M. S. Green, *Phys. Rev.* **150**, 153 (1966); M. H. Ernst, *Physica* **32**, 252 (1966).
- [32] H. van Beijren, J. Karkheck, and J. V. Sengers, *Phys. Rev. A* **37**, 2247 (1988).
- [33] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Longmans, Green & Co., New York, 1928).
- [34] R. C. Tolman, *The Principles of Statistical Mechanics* (Dover, New York, 1979).
- [35] T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).
- [36] L. Boltzmann, *Lectures on Gas Theory*, translated by S. G. Brush (University of California, Berkeley, 1964).
- [37] G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, RI, 1963), Chap. 1.
- [38] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1958).
- [39] S. R. de Groot, W. A. van Leeuwen, and Ch. G. van Weert, *Relativistic Kinetic Theory* (North-Holland, Amsterdam, 1980).
- [40] *Temperature*, edited by J. F. Schooley (AIP, New York, 1982), Vol. 5.
- [41] I. Müller, *Z. Phys.* **198**, 329 (1967).
- [42] R. M. Velasco and L. S. García-Colín, *J. Stat. Phys.* **69**, 217 (1992).
- [43] L. S. García-Colín, M. Lopez de Haro, R. F. Rodriguez, J. Casas-Vazquez, and D. Jou, *J. Stat. Phys.* **37**, 465 (1984).
- [44] M. Ichiyangi, *Physica A* **215**, 123 (1995).
- [45] J. Keizer and O.-K. Chang, *J. Chem. Phys.* **87**, 4064 (1987).
- [46] A. Hjelmfelt and J. Ross, *J. Phys. Chem.* **98**, 9900 (1994).
- [47] R. Dominguez and D. Jou, *Phys. Rev E* **51**, 158 (1995).
- [48] L. S. García-Colín, *Mol. Phys.* **86**, 697 (1995).
- [49] R. M. Velasco and L. S. García-Colín, *Phys. Rev. A* **44**, 4961 (1991).
- [50] R. M. Velasco and L. S. García-Colín, *J. Non-Equil. Thermodyn.* **20**, 1 (1995).
- [51] S. Yip and J.-P. Boon, *Molecular Hydrodynamics* (Dover, Mineola, NY, 1991).