Carnot cycles and a non-equilibrium absolute temperature

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Abstract. Starting from a Carnot cycle with entropy production in the heat reservoirs, we suggest a physical interpretation of a non-equilibrium absolute temperature.

1. Introduction

Some years ago, we proposed a non-equilibrium absolute temperature based on a generalised entropy (Casas-Vázquez and Jou 1981). Although we could calculate the non-equilibrium corrections with respect to the local-equilibrium absolute temperature, we were not able to provide a physical interpretation for them. The aim of the present paper is to propose such an interpretation, still limited but sufficiently illustrative, based on Carnot cycles. Historically, Carnot cycles were the basis for the first proposal of an absolute temperature scale (Thomson 1848) so they may again be a good conceptual tool to gain some insight into the meaning of the new terms appearing in the non-equilibrium absolute temperature.

In fact, the existence and the meaning of a non-equilibrium entropy and of a non-equilibrium absolute temperature are amongst the most basic and fundamental open questions in thermodynamics. To deal with them in all generality would be very difficult so recourse to simple model systems, as in this paper, is justified. Furthermore, this leads to concrete and specific answers whose physical immediateness renders them especially suggestive and pedagogical.

In §2 we review the main ideas leading to a physical interpretation of the non-equilibrium entropy used in this paper, and in §3 we propose a Carnot cycle with dissipation, leading to an interpretation of the corresponding non-equilibrium absolute temperature. In §4, we compare our results with those of kinetic theory, in order to have a microscopic model for the non-equilibrium temperature.

2. Interpretation of non-equilibrium entropy

Our proposition for a non-equilibrium absolute temperature (Casas-Vázquez and Jou 1981) was based on the generalised entropy used in extended irreversible thermodynamics (Lebon *et al* 1980, Casas-Vázquez *et al* 1984, Muller 1985). Such entropy has as variables not only the local-equilibrium ones, i.e. the internal energy and the density, but also the dissipative fluxes present in the system. We will limit ourselves to the case of heat conduction. The generalised Gibbs equation is then (Casas-Vázquez and Jou 1981, Jou and Careta 1982), for a simple fluid or an isotropic solid,

$$ds = T^{-1} \, du + T^{-1} p \, dv - (\tau v / \lambda T^2) \boldsymbol{q} \cdot d\boldsymbol{q} \tag{1}$$

with s, u and v being the entropy, internal energy and specific volume per unit mass (the reciprocal of the mass density) respectively, T and p are absolute temperature and thermodynamic pressure, q is the heat flux and λ and τ are the heat conductivity and relaxation time of the heat flux, defined according to the Maxwell–Cattaneo equation

$$\tau \delta q / \delta t + q = -\lambda \nabla T. \tag{2}$$

The justification for including the heat flux as an independent variable is precisely equation (2), for whose solution one must specify initial conditions for q, independently of those for ∇T. This equation, which generalises the classical Fourier law for heat conduction, may be justified from kinetic theory. It is useful for the description of second sound in solids at low temperatures and it avoids the paradox of infinite velocity of propagation of thermal signals from classical theory. Equation (2) should be used instead of Fourier's law when the frequency of the phenomena studied becomes of the order of the inverse of τ, as is the case in ultrasonic propagation in moderately rarefied gases and in neutron scattering experiments in liquids. For all these reasons, the consideration of the relaxation terms in (1) and (2) is not merely academic, but has a definite meaning. It provides the physical basis for our model of non-equilibrium thermodynamics.

The integrability condition of (1), namely the equality of the second-order mixed derivatives of s, leads for the absolute temperature to (Nettleton 1960, Casas-Vázquez and Jou 1981)

$$T^{-1}(u, v, q) = T_{\text{eq}}^{-1}(u, v) - \tfrac{1}{2}\delta[(\tau v / \lambda T^2)q^2]/\delta u \tag{3}$$

with $T_{\text{eq}}^{-1}(u, v)$ being the usual local-equilibrium absolute temperature and the derivative in (3) being carried out at constant v and q.

We will propose firstly an interpretation of the generalised entropy (1), which is the basis for the subsequent derivation of (3). With this aim in mind, assume a system in a steady non-equilibrium state with heat flux q_0. Take a very small part of it, so small that its temperature may be considered as uniform. The local equilibrium assumption would postulate from the start that the entropy of this small element is just the equilibrium entropy corresponding to its values of u and v. We do not make this hypothesis. Instead, we try an operational definition for the entropy to be assigned to this small system. We suddenly isolate the system, which is traversed by the heat flux q_0, and then let it attain equilibrium, i.e. let the heat flux q decay to its final equilibrium value $q = 0$.

The final entropy will be, of course, the equilibrium entropy corresponding to u and v. The initial (non-equilibrium) entropy will be related to that final entropy by means of

$$s_{\text{eq}}(u, v) = s(u, v, q^2) + \int_{v'} \int_0^x dv \, dt \, \sigma(t) \tag{4}$$

where σ is the entropy production per unit volume and unit time. Since we have isolated the system there is no flow of entropy nor energy across the boundaries during the decay towards equilibrium.

The entropy production in the case of heat conduction may be written as (De Groot and Mazur 1962) $\sigma = q^2/\lambda T^2$. We will assume that λT^2 remains constant during the decay (here, we are neglecting the terms of order q^2 in T, because σ itself is of second

order in q). We assume furthermore, according to equation (2), that the decay of q is exponential, i.e. $q(t) = q_0 \exp(-t/\tau)$.

Integration of (4) then leads to

$$s(u, v, q^2) = s_{eq}(u, v) - \tfrac{1}{2}(\tau v'/\lambda T^2)q^2 \tag{5}$$

with v' the volume of the element considered. This argument shows the physical origin of the non-classical terms in entropy (1).

In order to obtain an estimate of how small the subsystem must be in order for q to have an exponential decay, we introduce equation (2) into the energy conservation equation

$$\rho c \, \delta T / \delta t = -\text{div } q \tag{6}$$

with c the specific heat. This gives the classical 'telegrapher's equation' with two timescales defined by τ and $\tau_L = \rho c L^2/\lambda$, with L the dimensions of the subsystem. For q to decay exponentially it is required that $\tau_L \ll \tau$. This is achieved when $L^2 \ll \lambda \tau/\rho c$.

One could also consider, as a speculative idealisation, the extreme case of a large system at uniform temperature through which heat is circulating. This would be the case of a system with very high heat conductivity because in this case the condition $L^2 \ll \tau \lambda/\rho c$ would be satisfied by the system as a whole. An example could be a crystal with purely harmonic interactions amongst neighbouring molecules, which would behave as a 'heat superconductor'. Though surprising, this may be the case of the heat reservoirs used in the classical reversible Carnot cycle, which are able to provide heat to a system at its same temperature. In this case, if the heat flux was uniform through the system, the volume integral would become simply the product of the integrand times the total volume of the system. In the general and more realistic case of non-uniform distribution of temperatures, the entropy of the system would be obtained by integration over all the small elementary volumes which compose it.

In order to deal with large systems in a more general way we suppose, exactly as in the classical theory of non-equilibrium thermodynamics and in kinetic theory, that they may subdivide in many small subsystems, each of them with an entropy given by (5). Thus, we define the entropy of the total system as the sum of the entropies of the subsystems. When writing the generalised Gibbs equation (1) per unit mass, the coefficient $(\tau/\lambda T^2)$ must be understood as the mean value of this quantity over the specific volume v in the region considered.

3. Carnot cycle with dissipation and non-equilibrium absolute temperature

We will now apply a related argument to obtain an insight into the heat-dependent terms appearing in the absolute temperature (3). With this aim we consider a system undergoing an infinitesimal Carnot cycle between a furnace and a refrigerator at respective (local-equilibrium) absolute temperatures T_1 and T_2. We consider that the heat $dQ_1 > 0$ gained from the first one and the heat $-dQ_2$ (< 0) given to the second one are exchanged during the decay of initial heat fluxes $q_1(0)$ and $q_2(0)$ through the respective thermal reservoirs. Then, dQ_1 and dQ_2 are given by

$$dQ_1 = \int_0^\infty A_1 q_1(t) \, dt = \tau_1 q_1(0) A_1 \qquad dQ_2 = \int_0^\infty A_2 q_2(t) \, dt = \tau_2 q_2(0) A_2. \tag{7}$$

This is so because q is just the heat per unit area and unit time. A_1 and A_2 are the mean areas of contact of the system with the reservoirs at T_1 and T_2, respectively, and the heat fluxes $q_i(t)$ decay exponentially according to the Maxwell–Cattaneo law.

The entropy balance during a cycle must now take into account the irreversibilities of the cycle, as in finite-time thermodynamics (Curzon and Ahlborn 1975, Andresen *et al* 1977a, b). Whereas the reversible Carnot cycle may be formulated in a very general form, this is not the case when some dissipative process is taking place. In the latter case, one must construct a model incorporating those irreversibilities actively involved during the cycle, because the explicit and detailed consideration of all the irreversibilities would be disproportionately time-consuming and complicated in relation to the new results one wished to obtain. In our case, the model for the entropy production due to the irreversibility of the decay of the fluxes has already been formulated and evaluated in (4) and (5).

We have, for the entropy balance during a cycle,

$$-dQ_1/T_1 + dQ_2/T_2 = \tfrac{1}{2}(V_1\tau_1/\lambda_1 T_1^2)q_1^2 + \tfrac{1}{2}(V_2\tau_2/\lambda_2 T^2)q_2^2 \geq 0 \qquad (8)$$

with V_i and λ_i the respective volumes and heat conductivities of the heat reservoirs. We assume that the machine is endoreversible (Andresen *et al* 1977a, b), i.e. that all the irreversibilities take place in the reservoirs and not in the system at work. This amounts to assuming that the relaxation time of the system is much less than those of the reservoirs. Here we suppose that the relaxation process takes place in the whole volume V of the reservoirs. This is not a fundamental hypothesis. V could also be considered as the volume of the region of the reservoirs where the relaxation takes place, as for instance the region of contact between them and the system. Note, finally, that in the limit of infinite heat conductivity the dissipative terms in (8) formally vanish and we recover the well known result for the reversible Carnot cycle.

Expression (8) may be written in the form

$$-dQ_1[(1/T_1) + (1/dQ_1)\tfrac{1}{2}(V_1\tau_1/\lambda_1 T_1^2)q_1^2]$$
$$+ dQ_2[(1/T)_2 - \tfrac{1}{2}(1/dQ_2)(V_2\tau_2/\lambda_2 T_2^2)q_2^2] = 0. \qquad (9)$$

If the equilibrium absolute temperature of the reservoirs is changed by the expressions within square brackets, which we will call $(1/T_1')$ and $(1/T_2')$, the efficiency of this dissipative Carnot cycle will be given by the classical expression for the Carnot efficiency $\eta = (T_1 - T_2)/T_1$ but with the T_i replaced by the T_i'.

Now, we want to compare the 'temperatures' T' suggested by (9) with those appearing in (3), obtained by derivation of s with respect to u. We have

$$(1/T_1') = (1/T_1) + \tfrac{1}{2}(1/dQ_1)(V_1\tau_1/\lambda_1 T_1^2)q_1^2$$
$$(1/T_2') = (1/T_2) - \tfrac{1}{2}(1/dQ_2)(V_2\tau_2/\lambda_2 T_2^2)q_2^2. \qquad (10)$$

But dQ_1 and dQ_2 may be written in terms of the variations of the internal energy of the reservoirs as $dQ_1 = -(\Delta U_1)$ and $dQ_2 = (\Delta U_2)$. In the limit of small ΔU, the 'temperatures' defined in (10) reduce to our absolute temperatures as defined by (3). This is because the terms in q^2 may also be written as increments, compared with the vanishing entropy production of the classical case. In this way, they could be written as $\tfrac{1}{2}(1/\Delta U)[\Delta(V\tau/\lambda T^2)]$, and their limit for small heat pulses (ΔU going to zero) would be the derivative appearing in (3). This may also be seen from another point of view; if, according to the specification of (3), we assume that $q_1(0)$ and $q_2(0)$ are fixed and that the geometry (V, A) is also fixed, then we could change—conceptually,

though not in a strictly actual physical sense—dQ_1 and dQ_2 by modifying τ_1 and τ_2. This is also the only way to modify the corresponding entropy productions, since the conductivities and temperatures have been taken as fixed—this hypothesis is consistent with that made in going from (4) to (5) and could be slightly relaxed both there and here. As a consequence, the expressions (10) may be written as

$$(1/T_1') = (1/T_1) - \tfrac{1}{2}\delta[(V_1\tau_1/\lambda_1 T_1^2)q_1^2(0)]/\delta U_1$$

$$(1/T_2') = (1/T_2) - \tfrac{1}{2}\delta[(V_2\tau_2/\lambda_2 T_2^2)q_2^2(0)]/\delta U_2 \tag{11}$$

because both the numerators and denominators are linear in the τ.

Expressions (11) are identical to (3), so that we have a physical interpretation of the non-equilibrium absolute temperature in (3) in terms of the efficiency of Carnot cycles, in a close parallel with the identification of the usual absolute temperature.

Note, incidentally, that, as was to be expected, the efficiency of this Carnot cycle with dissipation is less than the ideal reversible one. The efficiency is

$$\eta = dW/dQ = 1 - (T_2'/T_1') \leqslant 1 - (T_2/T_1) \tag{12}$$

and the inequality is due to the fact that, according to (9), $T_1' \leqslant T_1$ whereas $T_2' \geqslant T_2$ (note that both dQ_1 and dQ_2 are positive).

4. Comparison with kinetic theory

An investigation of the meaning of both temperatures—the local-equilibrium one and the generalised one—at a more microscopic level may also be helpful in understanding the role of both temperatures. We will concentrate our attention to the simplest case, namely a moderately dilute gas in such conditions that its evolution may be described by means of the Boltzmann equation.

In kinetic theory, the absolute temperature appearing in the velocity distribution function through the mean value of the energy of the particles, is given by

$$\tfrac{3}{2}kTn = \int \tfrac{1}{2}mc^2 f \, dv \tag{13}$$

m being the mass of a molecule, c its relative velocity with respect to the mean velocity u, and k the Boltzmann constant.

Out of equilibrium, but near to it, the velocity distribution function is usually developed in the form

$$f = f_{eq}(1 + \phi_1) \tag{14}$$

where f_{eq} the Maxwell–Boltzmann equilibrium (or local-equilibrium) distribution function and ϕ_1 a function of the deviation from equilibrium (∇T in the Chapman–Enskog method and q in the Grad method) we assumed small with respect to unity. In order to determine the five parameters appearing in f, i.e. n (particle number density), u (mean velocity) and T (temperature), one imposes the condition

$$n = \int f \, dv \qquad nmu = \int mvf \, dv \qquad \tfrac{3}{2}kTn = \int \tfrac{1}{2}mc^2 f \, dv \tag{15}$$

where v is the molecular velocity.

These relations lead to the following conditions on f:

$$\int f \, d\boldsymbol{v} = \int f_{eq} \, d\boldsymbol{v} \qquad \int f\boldsymbol{v} \, d\boldsymbol{v} = \int f_{eq}\boldsymbol{v} \, d\boldsymbol{v} \qquad \int fc^2 \, d\boldsymbol{v} = \int f_{eq}c^2 \, d\boldsymbol{v} \qquad (16)$$

so that $f_{eq}\phi_1$ does not contribute to the first five moments of the (non-equilibrium) velocity distribution function. In such a way, only the classical local-equilibrium absolute temperature usually appears in kinetic theory, as defined by (13), and there is no contribution to it from the non-equilibrium part.

The question now is: from where may another 'absolute temperature' appear in kinetic theory? One finds the answer when considering the entropy, which is defined as

$$\rho s = -k \int f \ln f \, d\boldsymbol{v}. \qquad (17)$$

Introducing (14) into (17) and developing it up to second order in ϕ_1, one obtains (De Groot and Mazur 1962)

$$\rho s = \rho s_{eq} - \tfrac{1}{2}k \int f_{eq}\phi_1^2 \, d\boldsymbol{v}. \qquad (18)$$

Here, ρs_{eq} is the local-equilibrium entropy defined as

$$\rho s_{eq} = -k \int f_{eq} \ln f_{eq} \, d\boldsymbol{v}. \qquad (19)$$

The derivative of the entropy (18) with respect to the internal energy (at constant volume) also gives rise to an 'absolute temperature', which is different from the local equilibrium one obtained by differentiation of ρs with respect to u. Whereas in the local-equilibrium theory both absolute temperatures (that defined from the mean value of the energy and that defined as the derivative of the entropy) coincide, this is no longer the case when the local-equilibrium assumption is abandoned.

In order to obtain a more explicit view of that which we have commented on, we may go to the expressions obtained in Grad's method (Grad 1958). In the case when the system is submitted to a heat flux $\boldsymbol{q}$, the ϕ_1 is given by

$$\phi_1 = \tfrac{2}{5}(m/pk^2T^2)[\tfrac{1}{2}mc^2 - \tfrac{5}{2}kT]\boldsymbol{c} \cdot \boldsymbol{q} \qquad (20)$$

where p is the pressure, and one obtains for the entropy (18)

$$\rho s = \rho s_{eq} - (m/5pkT^2)\boldsymbol{q} \cdot \boldsymbol{q}. \qquad (21)$$

Furthermore, by introducing (14) and (20) into the linearised Boltzmann equation, one finds for the evolution of the heat flux (amongst other terms which are of no interest here)

$$d\boldsymbol{q}/dt = -(2\rho\beta/3)\boldsymbol{q} - (5pk/2m)\nabla T + \text{other terms} \qquad (22)$$

where β is a parameter related to an integral of the collision term.

The latter equation, when compared to the Maxwell–Cattaneo one (2), allows us to identify $\tau = \tfrac{3}{2}(1/\rho\beta)$ and $\lambda = \tfrac{5}{2}(pk/m)\tau$. When this relation between λ and τ is taken into account, one sees that the entropy (21) is just a particular case of our macroscopic entropy defined by (1) or (5)—here we are working at unit volume—because $\tau/2\lambda T^2 = m/(5pkT^2)$.

As a conclusion, the 'absolute temperature' obtained by differentiating the entropy of kinetic theory with respect to internal energy—at constant volume—is just a particular case of our macroscopic definition (3). However, in contrast to the local-equilibrium absolute temperature, its meaning is not physically evident. We hope this paper is able to provide some understanding of it.

Note, finally, in relation to our argument of § 2, that when the gas is suddenly isolated the velocity distribution function is not the local-equilibrium one, but still has a non-equilibrium part, $f_{eq}\phi_1$, which will decay to zero in a short time of order τ. Perhaps this microscopic point of view may be of some help in understanding the meaning of the relaxation to the equilibrium we have mentioned in §§ 2 and 3.

5. Concluding remarks

Some of the assumptions made here, though seemingly artificial (such as a heat reservoir at uniform temperature which gives or takes heat from a system at the same temperature) are also shared by the classical Carnot cycle. Other assumptions, such as the endoreversible character of the cycle (entropy production only takes place in the reservoirs but not in the system), are shared by most finite-time thermodynamic developments. On the other side, the interpretation of the non-equilibrium temperature as proposed here depends on a very peculiar and specific process. This is rather inescapable because when dealing with dissipative processes one must propose some definite mechanism of entropy production in order to be able to obtain explicit results. The mechanism chosen here has been the relaxation of the heat fluxes. This is of course consistent with the whole formalism of extended thermodynamics which up to now has focused its attention on an exponential relaxation of the fluxes.

The procedure presented in this paper somewhat clarifies the problem of the measurement of generalised temperature. This could not be achieved with a fast and small thermometer, which would give the local-equilibrium temperature (i.e. that related to the mutual equilibrium of the system and the thermometer), but with a complex combination of that thermometer with some kind of heat fluxmeter, such as a bolometer. Here we provide a very theoretical but physically definite method to obtain T, namely through the efficiency of an infinitesimal Carnot cycle run by short thermal pulses. Therefore, there is some parallel with the theoretical method proposed by Lord Kelvin (Thomson 1848) for the 'measurement' or, at least, for the theoretical justification of the absolute character of the scale defined by the air thermometer at constant pressure.

It is worth mentioning that in situations when the viscous pressure tensor p^v must be taken into account, the continuity of the heat flux across a thermometric wall does not guarantee the continuity of the absolute temperature. The jump in $1/T$ appears related to the jump in P^v as (Muller 1985)

$$[1/T]q \cdot n - [P^v] \cdot q \cdot n = 0 \tag{23}$$

with n the normal to the wall. Here we do not have this problem, since we have assumed vanishing P^v. In more general situations, the continuity is required not only of q but also of P^v across the thermometric wall in order to be sure of the continuity of T.

In summary, we think that, in spite of its limitations, the interpretation proposed here is sufficiently enlightening with respect to the physical meaning of the non-equilibrium absolute temperature previously proposed in extended thermodynamics.

Furthermore, it suggests a connection between two new kinds of thermodynamic developments (extended thermodynamics and finite-time thermodynamics) which were previously considered to be uncorrelated.

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