

Further insights on the new concept of heat for open systems

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Abstract

A new definition of heat for open systems, with a number of advantages over previous definitions, was introduced in [2013; *Int. J. Therm.*, 16(3), 102–108]. We extend the previous work by analyzing the production of entropy and showing that the new definition of heat appears naturally as the proper flow [«flux density»] conjugate to the gradient of temperature, with the previous definitions only considering a subset of the physical effects associated to this gradient. We also revisit the transfer of heat in multicomponent systems, confirming the identity derived in the previous work for the identification of thermal effects associated to each one of the chemical potentials in the system.

The new definition of heat was previously obtained within the scope of the traditional thermodynamics of irreversible processes (TIP), which has a limited field of applicability to macroscopic systems with not too strong gradients and not too fast processes. We extend now the new definition of heat to more general situations and to the quantum level of description using a standard non-commutative phase space, with the former TIP-level definition recovered from partial integration.

1 Introduction

A new definition of heat for open systems, with a number of advantages over previous definitions, was introduced in [1]. The new definition was motivated by the analysis of the components of the flow [2] of entropy for open systems and the identification of the entropy per mole transferred by the flux of mass. The flow of heat was then found to be proportional to a 'thermal' entropy flux where the entropy transferred through a mass flow had been subtracted. In this work we will use all the conventions in the former paper [1].

In the next section, we show how the analysis of the production of entropy provides further physical insight on the new definition of heat as the proper flow conjugate to the gradient of temperature, and show how the previous definitions only considered a subset of the physical effects associated to this gradient. In a posterior section, we revisit the transfer of heat in multicomponent systems, confirming the identity derived in [1], for the identification of thermal effects associated to each one of the chemical potentials in the system.

The new definition was previously obtained [1] within the scope of the traditional thermodynamics of irreversible processes (TIP), which has a limited field of applicability to macroscopic systems with no too strong gradients and not too fast processes. We will show in a final section of this paper how the new definition of heat can be extended to more general situations and to the quantum level of description.

2 Heat flux in the production of entropy

We begin by considering a simple system defined by one-component element of volume, at rest, that can interchange internal energy and matter, without chemical reactions, and that verify the generalized GIBBS equation [3]

$$Tds = du - \mu dn, \tag{1}$$

for thermodynamic temperature T , density of entropy s , density of internal energy u , chemical potential μ , and mole unit per unit volume n .

The production of entropy σ_S for this system is given by

$$\sigma_S = \mathbf{J}_U \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_N \cdot \nabla \left(\frac{\mu}{T} \right), \quad (2)$$

where \mathbf{J}_U and \mathbf{J}_N are the flows [2] of internal energy and matter, respectively. This will be our starting point for the analysis of the new definition of heat flux. Systems more complex will be considered later.

DEGROOT & MAZUR, FOX, JOU, CASAS-VAZQUEZ, & LEBON and BALESU –see [1] and references cited therein– identify the heat flux as the flow conjugate to the first gradient of (inverse) temperature, i.e.; $\mathbf{J}_{Q^{DM}} \stackrel{\text{def}}{=} \mathbf{J}_U$. Using this definition, (2) can be rewritten as

$$\sigma_S = \mathbf{J}_{Q^{DM}} \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_N \cdot \nabla \left(\frac{\mu}{T} \right). \quad (3)$$

Besides all the defects inherent to this definition [1], we can observe that it is only considering partially the effects of the gradient of temperature.

Precisely CALLEN and MISNER, THORNE, & WHEELER –see [1] and references cited therein– also consider the gradient of temperature in the second term of (2) and propose $\mathbf{J}_{Q^C} \stackrel{\text{def}}{=} \mathbf{J}_U - \mu \mathbf{J}_N$. Now the production of entropy (2) takes the simple form

$$\sigma_S = \mathbf{J}_{Q^C} \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_N \cdot \frac{\nabla \mu}{T}. \quad (4)$$

Their definition has still all the deficiencies mentioned in the former work [1], but its more important weakness is that their definition does not account for all the effects generated by the gradient of temperature, because it is ignoring thermal effects associated to the chemical potential.

The next logical step consists on using the GIBBS & DUHEM equation associated to (1) to obtain an identity that links gradients of chemical potential to gradients of temperature

$$s \nabla T - \nabla p = -n \nabla \mu, \quad (5)$$

which applied on (2) yields

$$\sigma_S = \left[\mathbf{J}_U - \left(\mu + \frac{T s}{n} \right) \mathbf{J}_N \right] \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_N \cdot \frac{\nabla p}{T n}. \quad (6)$$

Precisely the term between square brackets corresponds to the new heat flux defined in the former work [1] by

$$\mathbf{J}_Q \stackrel{\text{def}}{=} \mathbf{J}_U - \left(\mu + \frac{T s}{n} \right) \mathbf{J}_N. \quad (7)$$

It is now evident that the new definition of heat flux introduced in [1] acquires further physical meaning as the more general conjugate flow to the gradient of (inverse) temperature, with previous definitions in the literature, $\mathbf{J}_{Q^{\text{DM}}}$ and $\mathbf{J}_{Q^{\text{C}}}$ recovered from it as incomplete cases.

3 Revisiting multicomponent systems

As noted previously [1] the extension of the definition (7) to multicomponent systems described by the generalized GIBBS equation

$$Tds = du - \sum_k \mu_k dn_k \quad (8)$$

is not straightforward due to the interrelation between the different chemical potentials. The difficulty was solved by using an identity that equipartitions the overall thermal effects between each one of the chemical potentials in the system. This could give the false impression that the multicomponent heat flux [1, 2]

$$\mathbf{J}_Q \stackrel{\text{def}}{=} \mathbf{J}_U - \sum_k \left(\mu_k + \frac{Ts}{\sum_i n_i} \right) \mathbf{J}_{N_k}. \quad (9)$$

is only valid when one ignores the deviations from thermal equipartition of the contribution to the heat of each one of the chemical potentials. However, it can be shown that the above definition is exact because the deviations self-cancel in the system as a whole. To demonstrate this we can introduce an average chemical potential defined by

$$\langle \mu \rangle d\nu \stackrel{\text{def}}{=} \sum_k \mu_k dn_k, \quad (10)$$

where $\nu \stackrel{\text{def}}{=} \sum_k n_k$. This allows us to rewrite (8) as

$$Tds = du - \langle \mu \rangle d\nu, \quad (11)$$

which is formally equivalent to the monocomponent case (1). We can then take the formal heat flow for (11) and replace $\mathbf{J}_\nu \rightarrow \sum_k \mathbf{J}_{N_k}$, $\langle \mu \rangle \mathbf{J}_\nu \rightarrow \sum_k \mu_k \mathbf{J}_{N_k}$, and $\nu \rightarrow \sum_k n_k$ to formally re-derive the expression (9) valid for the multicomponent system.

Note that (10) implies that the deviations of the chemical potentials from the average self-cancel, i.e., $\sum_k (\delta \mu_k) dn_k = 0$. The physical explanation for the self-cancellation

is that the thermodynamic description consider the system as a whole and (8) uses the total entropy and total internal energy of the system, instead S and U of each component. As a consequence, the energetic and entropic contributions that we can formally associate to each component play no role during the extraction of thermal effects from the flow of internal energy \mathbf{J}_U and from the flow of entropy \mathbf{J}_S in the general case [1]:

$$\mathbf{J}_S = \frac{\mathbf{J}_Q}{T} + \sum_k \left(\frac{s}{\sum_i n_i} \right) \mathbf{J}_{N_k}, \quad (12)$$

$$\mathbf{J}_U = \mathbf{J}_Q + \sum_j \zeta_j \mathbf{J}_{Z_j} + \sum_k \left(\mu_k + \frac{T s}{\sum_i n_i} \right) \mathbf{J}_{N_k}. \quad (13)$$

4 Extension beyond TIP

Until now, and in the previous work [1], we restricted the discussion to systems described by the thermodynamics of irreversible processes (TIP). This is an excellent approximation when there are not large gradients and/or fast processes, otherwise a generalized formalism is needed.

A generalized formalism can be obtained by extending the number of variables of the classic thermodynamic space. This is the extended thermodynamics approach. Its main problem is the lack of consensus on which is the relevant set of extended thermodynamic variables or even its number [4–7].

We follow an alternative approach based in the successive elimination of equilibrium constraints for introducing higher levels of detail in the description. On the simplest level of description, the thermodynamic system is at internal equilibrium as a whole and has entropy $S[t]$ –in this section, we do not list other thermodynamic quantities by simplicity–, which can vary by interchanges of energy and/or matter with surrounds.

The next level of description consists on considering a system which is not in thermodynamic equilibrium as a whole, but is composed of small elements of volume at equilibrium and with entropic density given by $s(x; t)$. Those are the systems studied in the sections 2 and 3.

We can further generalize the description by considering that each element of volume is not at internal equilibrium but can be decomposed into subelements, living now in a six-dimensional phase space, and with entropic phase space density given by $s(p, x; t)$. Note the hierarchies of the descriptions, where each level can be obtain upon integrating the inferior levels

$$S[t] = \int s(x; t) dx = \iint s(p, x; t) dp dx. \quad (14)$$

The next generalization would consist on considering quantum phenomena, finally deriving a local quantum phase space entropic density $\tilde{s}(p, x; t) \stackrel{\text{def}}{=} -k_B \tilde{f} \ln \tilde{f}$, where k_B is the BOLTZMANN constant, and $\tilde{f}(p, x; t)$ the quantum WIGNER function [5].

Once reached this point, we only need to replace now the quantities in previous definition of heat [1] by their formal quantum analogs in the non-commutative phase space to obtain a quantum general definition of heat

$$\tilde{\mathbf{J}}_Q \stackrel{\text{def}}{=} \tilde{\mathbf{J}}_U - \sum_j \tilde{\zeta}_j \tilde{\mathbf{J}}_{Z_j} - \sum_c \left(\tilde{\mu}_c + \frac{T \tilde{s}}{\sum_i \tilde{n}_i} \right) \tilde{\mathbf{J}}_{N_c}. \quad (15)$$

Of course, the partial integration of (15) yields, in the classical limit, the flow \mathbf{J}_Q used in (12) and (13)

$$\mathbf{J}_Q(x; t) = \lim_{\hbar \rightarrow 0} \int \tilde{\mathbf{J}}_Q(p, x; t) dp. \quad (16)$$

References and notes

- [1] Non-redundant and natural variables definition of heat valid for open systems
2013: *Int. J. Therm.*, 16(3), 102–108. GONZÁLEZ ÁLVAREZ, JUAN RAMÓN
- [2] We use here the term «*flux*» for \mathbf{J}_Y because readers must be more familiar with this old terminology. However, recent official recommendation by IUPAP and IUPAC propose the term «*flux density*» for \mathbf{J}_Y .

Some references are completely inconsistent regarding the terminology. See the discussion on [1]

The recent «*flux density*» term by IUPAP and IUPAC is still open to objections. Last recommendations propose the more adequate and unambiguous term «*areic flux*».

- [3] Survey of fundamental laws **1971**: *In Physical Chemistry, An Advanced Treatise; Volume I Thermodynamics; Academic Press, Inc.; London; Wilhelm Jost (Editor)*. HAASE, R.
- [4] Extended Irreversible Thermodynamics; fourth edition **2010**: *Springer; New York*. JOU, DAVID; CASAS-VÁZQUEZ, JOSÉ; LEBON, GEORGY.
- [5] Nonequilibrium Statistical Mechanics: Ensemble Method **1998**: *Kluwer Academic Publishers; Dordrecht*. CHANG EU, BYUNG.
- [6] Statistical Thermodynamics of Nonequilibrium Processes **1987**: *Springer-Verlag; New York*. KEIZER, JOEL.
- [7] Rational Extended Thermodynamics; second edition **1998**: *Springer; New York*. MÜLLER I; RUGGERI, T.