Non-redundant and natural variables definition of heat valid for open systems

JUAN RAMÓN GONZÁLEZ ÁLVAREZ

juanrga

C:/Simancas 26, E-36208 (Bouzas) Vigo, Pontevedra, Spain

C:/Carrasqueira, 128, E-36331 (Coruxo) Vigo, Pontevedra, Spain

http://juanrga.com

Twitter: @juanrga

2011, Nov 04, 11:45

Abstract

Although an unambiguous definition of heat is available in the classical thermodynamics for closed systems, the question of how best to define heat transfer in open systems is not yet settled.

This article begins by reviewing the different definitions of heat for open systems used by CALLEN, CASAS-VÁZQUEZ, DEGROOT, FOX, HAASE, JOU, KONDEPUDI, LEBON, MAZUR, MISNER, PRIGOGINE, SMITH, THORNE, and by WHEELER in irreversible thermodynamics, emphasizing their main pros and cons. In a posterior section, this author introduces a new definition of heat that avoids the main difficulties of the existent definitions and provides us (i) a non-redundant definition that (ii) agrees with the definition used in the kinetic theory of gases, (iii) uses natural variables for the thermodynamic potentials, and (iv) properly generalizes the classical thermodynamic expressions to open systems.

1

1 Introduction

The true nature of heat, as a form of energy that can interconvert to other forms of energy, was established after much debate in the last part of the 19th century [1]. However, an unambiguous definition was lacking until BORN introduced his definition in 1921 [2]:

$$Q \equiv \Delta E - W, \tag{1}$$

with E and W being the total energy and work, respectively.

Although this definition (1) is not valid for open systems [1, 2] –i.e., for systems that can interchange matter as well as energy–, this restriction has not been, in practice, a difficulty for its usage in the classical thermodynamic theory of equilibrium; essentially, because the basic problem of classical thermodynamics is, according to CALLEN, «*the determination of the equilibrium state that eventually results after the removal of internal constraints in an isolated, composite system*» [3, 4] .

The difficulties begin with the extension of classical thermodynamics to irreversible processes. In irreversible thermodynamics, thermodynamic systems in a nonequilibrium state are divided into small elements of volume and each element is assumed to be locally at equilibrium [5]. Now, these elements of volume can interchange matter with adjacent elements, which requires a definition of heat also valid for open systems.

The importance of a generalization of the closed-systems definition of heat has been emphasized many years ago; however, in despite of the existence of several generalizations, the question of how best to define heat transfer in open systems is not yet settled [6].

The next section reviews the available definitions of heat for open systems in irreversible thermodynamics, emphasizing their main pros and cons. In a posterior section, this author introduces a new definition of heat that avoids the main difficulties of the existent definitions.

2 Review of available definitions

We start by considering an element of volume that can interchange internal energy and matter –more general systems will be considered in the next section–. The local production of entropy σ and the entropy flow J_S are

$$\sigma = J_U \nabla \left(\frac{1}{T} \right) - \sum_k J_k \nabla \left(\frac{\mu_k}{T} \right) \tag{2}$$

and

$$J_S = \frac{1}{T}\left(J_U - \sum_k \mu_k J_k\right),$$ (3)

where J_U is the flow of internal energy, T the absolute temperature, and J_k and μ_k the flow and chemical potential of the component k, respectively.

The production of entropy (2) is the usual product of flows and thermodynamic forces. A first definition of heat follows from considering it as the flow associated with the gradient of temperature in the first product, i.e., $J_Q^{[1]} \equiv J_U$. The production of entropy can be rewritten as

$$\sigma = J_Q^{[1]}\nabla\left(\frac{1}{T}\right) - \sum_k J_k\nabla\left(\frac{\mu_k}{T}\right)$$ (4)

and the entropy flow as

$$J_S = \frac{1}{T}\left(J_Q^{[1]} - \sum_k \mu_k J_k\right).$$ (5)

This definition is preferred by DeGroot & Mazur [7], and used by Fox [8] and Jou, Casas-Vázquez, & Lebon in irreversible thermodynamics [9], by Misner, Thorne, & Wheeler in curved spacetime thermodynamics [10], and by Jou, Casas-Vázquez, & Lebon in extended thermodynamics [9] —although in the two last cases the production (4) and flow (5) are generalized to curved spacetime and to an extended thermodynamic space, respectively–. The flow $J_Q^{[1]}$ is noted by Kondepudi & Prigogine in their study of alternative definitions [1] and is the standard in the kinetic theory of gases [11].

The main advantages of this first definition are its agreement with the kinetic definition, its use of natural variables for the thermodynamic potentials, and its distinction between closed and isolated systems. The main objection is found in its redundancy. Effectively, any instance of $J_Q^{[1]}$ in the equations could be substituted by J_U without physical or mathematical changes, doing unneeded the introduction of the concept of heat in the formalism.

A second definition of heat follows by separating the gradient of μ_k from the gradient of $(1/T)$ in (2). Using

$$\nabla\left(\frac{\mu_k}{T}\right) = \mu_k\nabla\left(\frac{1}{T}\right) + \left(\frac{1}{T}\right)\nabla\mu_k,$$ (6)

the production of entropy can be rewritten as

$$\sigma = J_Q^{[2]}\nabla\left(\frac{1}{T}\right) - \sum_k\left(\frac{J_k}{T}\right)\nabla\mu_k$$ (7)

and the entropy flow as

$$J_S = \frac{J_Q^{[2]}}{T},$$ (8)

for a heat flow $J_Q^{[2]} \equiv J_U - \sum_k \mu_k J_k$. This definition is used by Callen [3] and is noted by DeGroot & Mazur and by Kondepudi & Prigogine in their study of alternative definitions [1, 7].

The main advantages of this second definition are its use of natural variables for the thermodynamic potentials and its non-redundancy. The main objections being the disagreement with the kinetic definition and that it does not distinguish closed from open systems.

The first objection acquires more relevance, when we note that Callen interprets, «*in a very rough intuitive way*», the term $\mu_k J_k$ as a «*current density of potential energy*», so that he concludes that his $J_Q^{[2]}$ represents a kind of «*kinetic energy current density*» extracted from the total internal energy flow J_U [3].

The second objection is not less important. Effectively, integrating the entropy flow (8) over the area A of the whole thermodynamic system and multiplying by dt we obtain the well-known classical result

$$d_e S \equiv dt \int_A J_S \, dA = \frac{dQ^{[2]}}{T},$$ (9)

which is valid for closed but not for open systems [1, 7]. Precisely Callen introduces his heat flow from $J_Q^{[2]} = TJ_S$, in analogy with $dQ = TdS$ for reversible processes in a closed system, but this generates the following difficulty.

Consider an open thermodynamic system. Adding or eliminating mass from the system at constant temperature adds or eliminate entropy, because this is an extensive quantity. Although this process is not usually considered a heating or cooling process, the use of $J_Q^{[2]}$ obligates us to interpret as heat any transfer of entropy inside or outside the system.

A third definition of heat can be obtained by noting that the gradient of chemical potential $\nabla \mu_k$ in (6) is still a function of the temperature. Using the next separation, where s_k is the partial molar entropy of component k [1],

$$\nabla \mu_k = (\nabla \mu_k)_T - s_k \nabla T$$ (10)

and using (6), the production of entropy (2) can be rewritten as

$$\sigma = J_Q^{[3]} \nabla \left(\frac{1}{T} \right) - \sum_k \left(\frac{J_k}{T} \right) (\nabla \mu_k)_T$$ (11)

and the entropy flow as

$$J_S = \frac{J_Q^{[3]}}{T} + \sum_k s_k J_k,$$ (12)

for a heat flow $J_Q^{[3]} \equiv J_U - \sum_k (\mu_k + Ts_k)J_k$. This definition is preferred by KONDEPUDI & PRIGOGINE [1], by HAASE [2] and by SMITH [6]; and it is noted by DEGROOT & MAZUR in their study of alternative definitions [7].

The main advantages of this third definition are its non-redundancy and its distinction between closed and isolated systems. The main objections being the disagreement with the kinetic definition and that it is not defined in natural variables. Indeed, this definition explicitly involves $s_k = s_k(T, n)$.

Precisely KONDEPUDI & PRIGOGINE introduce $J_Q^{[3]}$ after changing the internal energy density from $u = u(s, n)$ to $u = u(T, n)$ in the energy balance equation [1]. Neither s nor u are thermodynamic potentials in a temperature-composition state space.

3   New definition of heat flow

We start by considering an element of volume that can interchange internal energy, matter, and other extensive thermodynamic quantities, whose densities are x_i. The local production of entropy (2) and the entropy flow (3) are generalized to

$$\sigma = J_U \nabla \left(\frac{1}{T} \right) - \sum_k J_k \nabla \left(\frac{\mu_k}{T} \right) + \sum_i J_i \nabla \left(\frac{\gamma_i}{T} \right) \tag{13}$$

and

$$J_S = \frac{1}{T} \left(J_U - \sum_k \mu_k J_k + \sum_i \gamma_i J_i \right), \tag{14}$$

where J_i and γ_i/T are the flow and intensive entropic parameters, respectively, associated to the quantity i. The production of entropy (13) continues showing the usual product of flows and thermodynamic forces.

The new definition of heat follows by separating the gradient of γ_i from the gradient of $(1/T)$ in (13). Using

$$\nabla \left(\frac{\gamma_i}{T} \right) = \gamma_i \nabla \left(\frac{1}{T} \right) + \left(\frac{1}{T} \right) \nabla \gamma_i, \tag{15}$$

the production of entropy can be rewritten as

$$\sigma = J_Q \nabla \left(\frac{1}{T} \right) - \sum_k J_k \nabla \left(\frac{\mu_k}{T} \right) + \sum_i \left(\frac{J_i}{T} \right) \nabla \gamma_i \tag{16}$$

and the entropy flow as

$$J_S = \frac{1}{T} \left(J_Q - \sum_k \mu_k J_k \right), \tag{17}$$

for a heat flow $J_Q \equiv J_U + \sum_i \gamma_i J_i$. This new definition has a number of advantages over the existent definitions, as showed next.

Unlike $J_Q^{[1]}$, the new definition is not redundant because it is not just J_U. However, J_Q correctly reduces to the heat flow used in the kinetic theory of gases, where the only local extensive variables are the energy and composition.

This new definition distinguishes closed from open systems, eliminating another main objection to $J_Q^{[2]}$. Using (17), the external variation of entropy is now

$$d_e S = \frac{1}{T} \left(dQ - \sum_k \mu_k dn_k \right),$$ (18)

instead of (9). The standard expression $d_e S = dQ/T$ is recovered from (18) for closed systems. Unlike $J_Q^{[2]}$, the use of the new J_Q does not obligate us to interpret as heat any transfer of entropy inside or outside a thermodynamic system.

Integrating the new heat flow J_Q over the area A of the whole system and over the time interval Δt needed to achieve a final equilibrium state, from an initial equilibrium state, gives a generalization of the BORN heat definition (1)

$$Q \equiv \Delta E - W + \sum_k \mu_k \Delta n_k,$$ (19)

with W being the total work.

The main advantages of J_Q over $J_Q^{[3]}$ are that the new definition retains the natural variables for the thermodynamic potentials and that correctly reduces to the kinetic definition. Comparison of (12) with (17) provides a relation between both flows

$$J_Q = J_Q^{[3]} + \sum_k u_k J_k,$$ (20)

where the partial molar internal energy, $u_k = \mu_k + T s_k$, of the component k has been used [1]. Precisely $\sum_k u_k J_k$ is the term that guarantees the compatibility of J_Q with kinetic theory.

Summarizing, the new definition of heat flow $J_Q \equiv J_U + \sum_i \gamma_i J_i$ is (i) non-redundant, (ii) agrees with the definition used in the kinetic theory of gases, (iii) uses natural variables for the thermodynamic potentials, and (iv) properly generalizes classical thermodynamic expressions –such as $dQ = TdS$ and BORN definition (1)– to open systems.

References

[1] Modern Thermodynamics **1998:** *John Wiley & Sons Ltd.; Chichester.* KONDEPUDI, D. K.; PRIGOGINE, I.

[2] Survey of fundamental laws **1971:** *In Physical Chemistry, An Advanced Treatise; Volume I Thermodynamics; Academic Press, Inc.; London; Wilhelm Jost (Editor).* HAASE, R.

[3] Thermodynamics and an Introduction to Thermostatistics; Second Edition **1985:** *John Wiley & Sons Inc.; New York.* CALLEN, HERBERT B.

[4] CALLEN uses the term «*closed*» instead of the more modern and accurate term «*isolated*» for referring to systems that cannot interchange energy or matter with the surrounds [1, 2].

[5] This is an excellent approximation for systems where there are not large gradients and/or fast processes. When the local approximation does not hold, the formalism of extended thermodynamics is needed. See [1] and references cited therein.

[6] Definition of Heat in Open Systems **1980:** *Aust. J. Phys.,33, 95–105.* SMITH, D. A.

[7] Non-equilibrium thermodynamics **1984:** *Courier Dover Publications.* DEGROOT, SYBREN RUURDS; MAZUR, PETER.

[8] Non-equilibrium thermodynamics **2001:** *In Encyclopedia of Chemical Physics and Physical Chemistry; Volume I Fundamentals; IOP Publishing, Ltd.; Bristol; John H. Moore; Nicholas D. Spencer (Editors).* FOX, RONALD F.

[9] Extended Irreversible Thermodynamics; fourth edition **2010:** *Springer.* JOU, DAVID; CASAS-VÁZQUEZ, JOSÉ; LEBON, GEORGY.

[10] Gravitation **1973:** *W. H. Freeman & Co.; San Francisco.* MISNER, C.; THORNE, K.; WHEELER, J.

[11] Statistical dynamics; matter out of equilibrium **1997:** *Imperial College Press.* BALESCU, RADU.