PAPER

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Why is dissipative work insistently ignored? The case of heat capacities

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Abstract
Dissipative work is used to address some textbook definitions of heat capacity at constant volume C_V and at constant pressure C_P. It is shown that dissipative work should be accounted for when this topic is presented to the students, so that all C_V (and C_P) definitions are equivalent, instead of imposing unnecessary restrictions on thermodynamic processes. Finally, one simple but illustrative example is given. This work is also relevant from a didactic and pedagogical standpoint, since it helps dispel some misunderstandings related to the concepts outlined herein.

Keywords: heat capacity, heat, dissipative work

1. Introduction

Thermodynamics is an area of physics in which some issues remain unclear or even ignored. Despite publications addressing certain subtle aspects, aiming to clarify some concepts and/or correct some errors persistent in the literature, an integrated view of the basic concepts of thermodynamics is still lacking.

A key concept to which insufficient emphasis has been given is that of *dissipative work* [1, 2]. As explained in [2], dissipative work δW_{D} is the difference between *work* δW and *configuration work* δW_{C} (the part of work that is used to configure the system), i.e.

$$\delta W_{\mathrm{D}} = \delta W - \delta W_{\mathrm{C}}, \tag{1}$$

δW_{D} being converted into internal energy of the system or surroundings, so that it can no longer be used as work, being thus appropriately considered as lost work.

Together with heat, δW_{D} contributes to the entropy increase of the universe. δW_{D} is a *positive process-invariant*, i.e. for a given process δW_{D} is independent of what is labelled as system or surroundings [2], and the lack of sufficient attention given to it explains the persistence of misunderstandings regarding some definitions and concepts; therefore, it is never too much to ask to pay attention to dissipative work.

In this work, we are focused on the definition of heat capacities and how some inconsistencies in their definitions are eliminated by simply bearing in mind dissipative work. Our aim is to show that some definitions of heat capacities used in textbooks and in the classroom, which are based on process variables, should be improved to account for dissipative work, in order to acquire consistency with general definitions built from state variables.

2. Heat and dissipative work yield equivalent effects in the system

A thermodynamic process is a system−surroundings interaction which can be considered as a superposition of infinitesimal processes, each described by [2]

$$T\mathrm{d}S - P\mathrm{d}V = -T_{\mathrm{e}}\mathrm{d}S_{\mathrm{e}} + P_{\mathrm{e}}\mathrm{d}V_{\mathrm{e}}, \tag{2}$$

which contains system and surroundings variables, the latter ones denoted by the subscript 'e' (for external), and where T, S, P and V are, respectively, temperature, entropy, pressure and volume. The LHS of (2) is the variation of system internal energy, and this statement constitutes the *energetic fundamental relation* [3, 4]:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V. \tag{3}$$

Unlike (3), which appears often in the literature, equation (2) has received scant attention, in spite of its relevance in describing a thermodynamic process—see [2, 5]. Taking the energy entering the system as positive (and negative otherwise), the two terms in the RHS of (2) have precise meanings [2]: the first is the *heat*

$$\delta Q = -T_{\mathrm{e}}\mathrm{d}S_{\mathrm{e}}, \tag{4}$$

while the second is the *work*

$$\delta W = P_{\mathrm{e}}\mathrm{d}V_{\mathrm{e}}. \tag{5}$$

It is important to emphasize that heat and work, given by the above expressions, are defined *solely* by surroundings variables, which means that surroundings are considered to consist of heat and work reservoirs [5].

By combining equations (2)–(5) we obtain the *first law*

$$\mathrm{d}U = \delta Q + \delta W, \tag{6}$$

which should not be confused with (3) because the terms on both right-hand sides are, in general, not equal, i.e. $\delta Q \neq T\mathrm{d}S$ and $\delta W \neq -P\mathrm{d}V$, $-P\mathrm{d}V$ being the configuration work δW_{C} [1, 2]

$$\delta W_{\mathrm{C}} = -P\mathrm{d}V. \tag{7}$$

Equation (6) shows that while heat and work depend on the process, their sum does not, being instead a state function; therefore, δQ and δW are *indistinguishable* with respect to the variation of the system internal energy. The latter sentence can be written, *mutatis mutandis*,

in relation to surroundings, since conservation of energy requires that

$$dU = -dU_e. \tag{8}$$

So, how can we distinguish *heat* from *work* and *dissipative work* from *configuration work*? To answer this question, we start from equation (3) and use equations (1), (6) and (7) to get

$$dS = \frac{\delta Q + \delta W_D}{T}, \tag{9}$$

and rewrite (4) as

$$dS_e = -\frac{\delta Q}{T_e}. \tag{10}$$

Equation (10) shows that heat and work are distinguished by their effects on surroundings entropy: while heat causes variation in surroundings entropy, work does not. On the other hand, (9) allows us to distinguish dissipative work from configuration work: while the former causes variation in system entropy, the latter does not.

It is important to point out that, unlike energy, it is entropy that allows the aforementioned distinctions to be made, it being necessary to look at both system and surroundings because, by contrast to (8),

$$dS \geqslant -dS_e; \tag{11}$$

it is important to highlight that by inserting (10) into (11) we get the famous Clausius relation [3]

$$dS \geqslant \frac{\delta Q}{T_e}. \tag{12}$$

Equation (9) shows that from the system standpoint alone δQ and δW_D are equivalent, i.e. they contribute indistinguishably to the system entropy variation, and thus *any system property that includes δQ in its definition should also include δW_D, and vice versa.*

3. Heat capacity: a system or a process property?

Thermal (or heat) capacities are important concepts in thermodynamics. For processes developing at constant volume or at constant pressure, they are often defined respectively as [e.g. 3, 4, 6–8]

$$C_V = \left(\frac{\delta Q}{dT}\right)_V, \tag{13a}$$

$$C_P = \left(\frac{\delta Q}{dT}\right)_P. \tag{13b}$$

We also find C_V and C_P defined *exclusively* in terms of system properties by [e.g. 4, 9]

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \tag{14a}$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P, \tag{14b}$$

or alternatively by [e.g. 10–14]

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V,$$ (15a)

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P,$$ (15b)

where the enthalpy H is defined as [3]

$$H = U + PV.$$ (16)

How do the three C_V and C_P definitions presented above compare?

Dividing (3) by dT and imposing the constant volume condition, we get

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V,$$ (17)

and inserting (3) into the differential of (16), dividing the resulting expression by dT and imposing the constant pressure condition, we get

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P,$$ (18)

which shows the equivalence of (14) and (15).

Regarding (13), to what extent is it equivalent to (14) and (15)? As far as we know, the discussion of this issue is virtually absent from the literature and textbooks. Strictly, there is no equivalence, because (13) includes heat, which is a process property, whereas (14) and (15) express relations among thermodynamic variables that are independent of the particular process taking place and thus originate definitions of C_V and C_P that are *system* properties, being thus independent of any process.

As previously discussed, since δQ is the only process property appearing in (13), for these expressions to constitute system properties, δQ must be replaced by $\delta Q + \delta W_\mathrm{D}$. Indeed, using (9) and (14) and considering $S(T, V)$ and $S(T, P)$, we have

$$\delta Q + \delta W_\mathrm{D} = C_V\,\mathrm{d}T + T\left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V,$$ (19a)

$$\delta Q + \delta W_\mathrm{D} = C_P\,\mathrm{d}T + T\left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P.$$ (19b)

Therefore, at constant volume and at constant pressure, we get

$$C_V = \left(\frac{\delta Q + \delta W_\mathrm{D}}{\mathrm{d}T}\right)_V,$$ (20a)

$$C_P = \left(\frac{\delta Q + \delta W_\mathrm{D}}{\mathrm{d}T}\right)_P.$$ (20b)

Comparing (13) to (20) leads to the obvious conclusion that the latter has an additional term, i.e. (20), or equivalently (14) and (15), are more general C_V and C_P definitions than (13). As far as we know, equations (20), which define C_V and C_P in terms of heat and dissipative work, are virtually absent from the literature, as is their equivalence with equations (14) and (15)—an omission which might cause conceptual difficulties, the most critical being the tendency to identify δQ with $T\mathrm{d}S$ when comparing (13) with (14). In contrast, when comparing (20) with (14), we get the general relation $\delta Q + \delta W_\mathrm{D} = T\mathrm{d}S$.
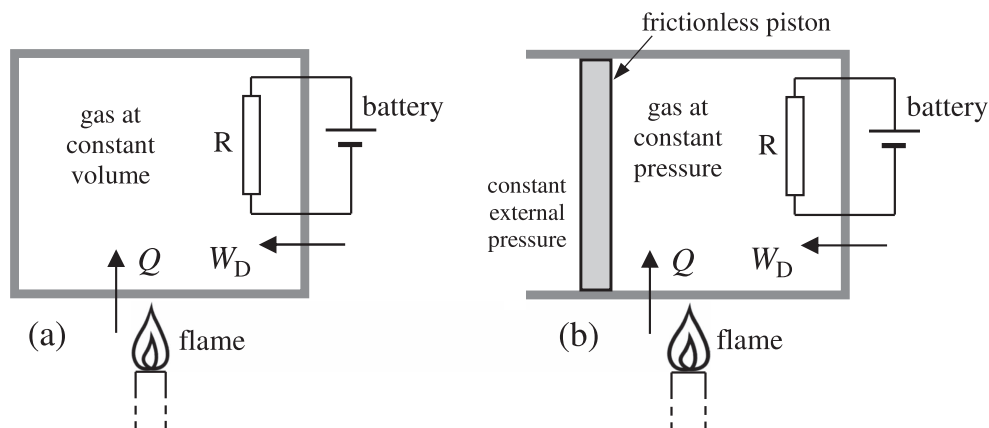
Figure 1. Heating a gas from T to $T + \Delta T$ at (a) constant volume and (b) constant pressure. In both cases, the gas is supplied with heat Q and/or dissipative work W_D, which are indistinguishable to the system.

Of course (20) reduces to (13) when $\delta W_D = 0$. However, even this is often incorrectly explained in the literature, where what is usually done is to consider the process reversible—a restriction which is excessive, because for (13) to be valid it is sufficient that $\delta W_D = 0$. For a process to be reversible, in addition to $\delta W_D = 0$, δQ must occur with T infinitely close to T_e, i.e. $T_e = T$.

System-based definitions (14) and (15) are general, as they implicitly incorporate dissipative work, and must therefore remain unchanged in textbooks. By contrast, process-based definitions (13) should be replaced by (20) to account for dissipative work and become valid for any process, rather than be restricted to processes without dissipative effects.

Why omit dissipative work from definitions when this concept is perfectly defined by (1)? To the contrary, including it makes formalism more consistent, and particular cases can be obtained clearly and naturally. We believe that restrictions should only be used if they simplify the formalism without obscuring the concepts.

4. An illustrative example

Before concluding, we give an illustrative example. Consider heating a gas from T to $T + \Delta T$, at constant volume (figure 1(a)) or at constant pressure (figure 1(b)). In both cases, the gas is supplied with heat Q (by means of a flame) and/or dissipative work W_D (by means of a battery connected to a resistor), as shown in figure 1. For a given ΔT, the system attains the same final state regardless of whether the energy is being supplied through the battery or the flame. In other words, from the system standpoint, dissipative work is undistinguishable from heat, and therefore, to define C_V and C_P, the former has to be accounted for in exactly the same way as heat is; contrary to (13), (20) clearly meets this requirement.

5. Conclusion

The little relevance that has been given to dissipative work is at the root of some difficulties in understanding certain concepts in thermodynamics. In this work, heat capacities at constant

volume and at constant pressure are addressed. Instead of presenting a heat capacity definition that is only valid for restricted processes, a dissipative work term must be added to the heat term in order to obtain equivalence between heat capacity definitions in the literature.

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