MICROSCOPIC HEAT AND FIRST LAW OF THERMODYNAMICS

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ABSTRACT

Heat is defined in classical thermodynamics as an energy transfer mechanism, but its fundamental nature is not yet fully understood. After reviewing previous macroscopic, mesoscopic, and microscopic approaches to heat, we propose a fundamental definition of heat in terms of a fully detailed microscopic description and apply this definition to a one-component gas with constant composition for comparison with the usual macroscopic formulae. Using the new definition, we debunk common claims in the literature that associate heat with our ignorance of the microscopic details of a thermodynamic system.

1   INTRODUCTION

Thermodynamics was born with the concepts of temperature and heat. One could imagine that more than four hundred years after the invention of the thermometer, the concept of heat would be defined in a rigorous and complete way. This is not the case and we can even find some common misconceptions in the literature, as we will see in a moment.

Every scientist and engineer has an intuitive concept of heat as something related to the concepts of heating and cooling and, in fact, the textbook[1] by Greiner, Neise, and Stöcker, initially defines heat by the expression $đQ = C d\mathcal{T}$, in which C is a proportionality constant and $\mathcal{T}$ is the temperature. A similar characterization is provided by Guggenheim, for whom heat is "*determined by a temperature difference*".[2] However, in more advanced expositions

of thermodynamics we learn that bodies can exchange energy in the form of heat even when the temperature remains constant, the so-called isothermal heat.

Swendsen states that "*heat is a form of energy*".[3] Feynman, Leighton, and Sands[4] claim that "*heat energy*" is simply another form of energy, they inmediately add that "*it is not really a new form, it is just kinetic energy-internal motion*", and when discussing the crystalline structure of a piece of ice, the trio of authors claims that "*ice has heat*". Such statements are incorrect. Ice, like any other material, has no heat. As Landau, Lifshitz, and Pitaevskii correctly mention, "*we can therefore speak of the energy E in a given state, but not, for example, of the quantity of heat which a body possesses in a given state*".[5] We know from classical thermodynamics that heat and work are energy transfer mechanisms, and not forms of energy. Kinetic energy, internal energy, relativistic rest energy, and potential energy (gravitational, electromagnetic, nuclear, or any other kind) are properly forms of energy.

Heat is modernly understood as a mechanism of transfer of energy, but what is its fundamental nature? We will review previous attempts to answer this question in section 2 and provide a microscopic definition in section 3.

2   PREVIOUS DEFINITIONS OF HEAT

According to Haase,[6] the first scientist who attempted to answer the aforementioned question unequivocally was Max Born in 1921 who, with the help of the first law of classical thermodynamics, defined the heat $đQ$ as the change in energy $\mathcal{E}$ not caused by work

$$đQ = d\mathcal{E} - đ\mathcal{W}. \tag{1}$$

However, Bryan provided the same definition[7] in 1907. Accordingly, we will refer to (1) as Bryan's definition of heat. In the above formula, đ denotes an inexact differential.

Note: Bryan used a different sign criterion for work (his $\mathcal{W}$ is our $-\mathcal{W}$), but the physics described are the same.

Bryan's definition has two shortcomings. The first is that assigning heat to a remainder of the energy change implies that if we do not identify all sources of work, then all the work that has not been identified would be incorrectly characterized as heat. The distinction between work and heat is obvious in most typical situations, but becomes difficult in certain critical cases.

Neither Brian nor Bohr provided a general expression for work, which means that different concepts of heat will follow depending on the definition of work used in (1). For example, would the energy released by a chemical reaction be included as part of heat or not? And the changes in the kinetic energy of difussion? Do we count them as work or heat? Furthermore, (1) is only valid for closed systems, because for open system we must include an extra term related to the flow of matter into or out the system. The second deficiency of (1) is that the characterization of heat as residual does not provide a true insight into what heat really is. We only know from Bryan's definition that heat is distinct from thermodynamic work.

For systems at rest, all energy $\mathcal{E}$ is internal energy. This is the case tipically considered in standard textbooks and applications. In the remainder of this section, we will consider thermodynamic systems at rest.

Definition (1) and its integral version, $Q = \Delta\mathcal{E} - \mathcal{W}$, are used in main thermodynamics textbooks for physicists and chemists.[5, 8–11]

If we use $đW = -PdV$ for the work and $\mathcal{E} = \mathcal{E}(T, V)$ for the internal energy in (1), we obtain the following expression for the heat for a one-component gas with constant composition[7]

$$đQ = C_V dT + \left(P + \frac{\partial \mathcal{E}}{\partial V} \right) dV, \qquad (2)$$

with C_V being the so-called heat capacity at constant volume, and the term within parentheses is what they call the latent heat of expansion at constant temperature. We will derive a microscopic generalization of (2) in section 4.

Note: The terms "*heat capacity at constant volume*" and "*latent heat of expansion at constant temperature*" are two unfortunate names since heat is only an energy transfer mechanism. The historical origin of this inappropiate terminology is found in the ancient caloric theory, when it was believed that heat was an invisible, tasteless, odourless, and weightless fluid that could permeate bodies.

We have seen an attempt to define heat using the first law of classical thermodynamics. Another attempt to define heat is based on the second law; see for example section "*10.4.2 Heat*" in Swendsen's textbook.[3] The definition is

$$đQ = T dS. \qquad (3)$$

However, this definition is based on a version of the second law that is only valid for closed systems and reversible processes and therefore (3) does not define heat in more general situations, even if we limit ourselves to the realm of classical thermodynamics.

Furthermore, since entropy is often identified with "*ignorance*", more specifically with the lack of information we have about the system,[3,9] the use of expressions like (3) can generate all kinds of misconceptions about heat. An example is when Gell-Mann claims that the thermodynamic entropy would be zero for a perfectly

informed observer who knows all the microscopic details of the system. Consequently, Gell-Mann also states that:[12]

> "*Indeed, it is mathematically correct that the entropy of a system described in perfect detail would not increase; it would remain constant.*"

However, if $dS = 0$ then the heat would always be zero by virtue of (3). This is absurd because heat is a physical property of the system and therefore independent of the information acquired by an observer about the system; it is even independent of the existence of any observer. We will show in the next section how heat is not zero when the system is described in detail.

As an introduction, we have reviewed how heat is defined in classical thermodynamics texts, but classical thermodynamics ignores the structure of matter and instead treats it as a continuous material medium. Therefore, this discipline is not helpful for understanding the nature of heat at a fundamental level. However, statistical mechanics is generally considered to provide "*a foundation for thermodynamics and the ultimate justification of why thermodynamics works*".[3] We might therefore expect statistical mechanics to provide a fundamental definition of heat valid in arbitrary cases and, although most texts avoid this question, some provide the following line of reasoning.[9,14] The starting point is the ensemble average for the energy

$$\langle E \rangle = \sum_i P_i E_i, \tag{4}$$

in which, P_i is the probability that a member of the ensemble has the internal energy E_i. Differentiating the above expression, we obtain

$$d\langle E \rangle = \sum_i E_i dP_i + \sum_i P_i dE_i, \tag{5}$$

and heat is then identified with the variation of probabilities

$$\text{đ}\langle Q \rangle = \sum_i E_i \text{d}P_i. \tag{6}$$

Hill uses[14] the canonical ensemble to obtain a specific expression for the probabilities in the expression above, but (6) could be used, in principle, for arbitrary ensembles. Le Bellac, Mortessagne, and Batrouni provide a similar definition for heat, but they use operator methods from quantum statistical mechanics and propose $\text{đ}\langle Q \rangle = \text{Tr}\{\hat{H}\text{d}\hat{\rho}\} = \sum_i \sum_j \langle z_i|\hat{H}|z_j \rangle \text{d}\langle z_j|\hat{\rho}|z_i \rangle$, with $\hat{H}$ and $\hat{\rho}$ being the Hamiltonian and state operators, respectively and $|z_i\rangle$ a basis set. By choosing a diagonal basis, the evaluation of the trace matches expression (6).

Hill asserts that (6) provides us with the molecular interpretation of the thermodynamic concept of heat as the change in the energy of the system "*accomplished not by changing the energy levels of the system but rather by a shift in the fraction of time the system spends in the various energy states*".[14] Le Bellac and his coworkers make a similar assertion, for them heat is associated to "*a modification of […] the probabilities of energy level occupations*". We can find similar statements in the rest of the literature, but this molecular interpretation of the concept of heat is open to several objections.

The first objection is that (4) is not the energy of the thermodynamic system, but an ensemble average. But first we must introduce the concept of ensemble used in statistical mechanics:[14]

> "*An ensemble is simply a (mental) collection of a very large number $\mathcal{N}$ of systems, each constructed to be a replica on a thermodynamic (macroscopic) level of the actual thermodynamic system whose properties we are investigating.*"

A thermodynamic system will have an internal energy E at each instant and, in general, $E \neq \langle E \rangle$. In expression (4), E_i is the energy

of system i. Since (6) is obtained by differentiating (4), this implies that (6) does not provide a molecular interpretation of the heat exchanged by the system. At best, đ⟨Q⟩ would describe an average heat in the ensemble sense.

Another objetion to the alleged "*molecular interpretation*" is related to the interpretation of the probabilities that enter in expression (6). Gibbs introduced the concept of ensemble to deal with situations in which we do not know the molecular details of large systems. In this view, probabilities $(P_1, P_2, ... P_{\mathcal{N}})$ describe our lack of knowledge about the positions, velocities... of all the entities that make up the thermodynamic system, but if (6) were the fundamental definition of heat, then it would be a subjective or antrophomorphic quantity associated with changes in our ignorance, which is very difficult to accept. As mentioned at the beginning of the introduction, thermodynamic heat is a physical quantity that can be related to temperature changes in certain processes, and it is obvious that a thermometer provides the same readings regardless of our knowledge about the molecular details of the thermodynamic system under study. Even if we reinterpret the meaning of the probabilities that enter into definition (6), this only provides an characterization of the average heat đ⟨Q⟩ associated with the statistical ensemble and not the actual heat đQ for the system under study.

Note: So far, we have discussed the probabilities in (6) abstractly, without giving concrete values for specific physical situations. However, as mentioned above, Hill uses the canonical ensemble to obtain the following expression[14] for the probabilities $P_i = \exp(-E_i/k_\mathrm{B}\mathcal{T})/\sum_j \exp(-E_j/k_\mathrm{B}\mathcal{T})$. It would also be emphasized that the temperature appearing in this expression is not the current temperature of the thermodynamic system, but rather a statistical concept of temperature associated with the canonical ensemble. $\mathcal{T}$ in the above expression is a fixed parameter. Both temperatures only coincide in the limit of an

infinite system. This is another drawback of the "*molecular interpretation*" of heat.

For all the above reasons, we may abandon statistical mechanics and look for a fundamental definition of heat that does not use ensembles, averages, or probabilities. Sekimoto takes a step in this direction when, with the help of the theory of stochastic processes, he provides a mesoscopic definition of heat.[15]

Sekimoto first introduces a "*mesoscopic (or Landau) free energy*" $F = F(x, a, \beta)$, where x is the slow variable of interest –the position of the magnetic bead in the context of the example described in the introduction of his paper–, while a is an external control parameter and $\beta = 1/k_\mathrm{B}\mathcal{T}$, where again $\mathcal{T}$ is not the actual temperature of the thermodynamic system, but an ensemble temperature. Differentiating this mesoscopic free energy at constant temperature, we obtain

$$\mathrm{d}F = \frac{\partial F}{\partial x}\mathrm{d}x + \frac{\partial F}{\partial a}\mathrm{d}a. \tag{7}$$

Sekimoto then associates a mesoscopic heat to the first component of the differential

$$\mathrm{d}Q = \frac{\partial F}{\partial x}\mathrm{d}x, \tag{8}$$

and using a Langevin equation, he rewrites this heat as

$$\mathrm{d}Q = \left[-\gamma\frac{\mathrm{d}x}{\mathrm{d}t} + \xi(t)\right]\mathrm{d}x, \tag{9}$$

with γ the friction coefficient for x, and $\xi(t)$ a white Gaussian random force.

The first thing that I want to point out is that, contrary to the title of his paper,[15] expression (8) does not provide a microscopic definition of heat. Sekimoto's work is based on a Langevin-type

mesoscopic dynamics. However, the biggest concern with his approach is that (8) does not represent thermodynamic heat, as we will see in a moment.

Consider a system at rest. The position x of the system is constant and only the random force $\xi(t)$ contributes to (9). Now, for certain sufficiently large systems, fluctuations can be ignored, as is usually done in classical thermodynamics, and from definition (9) we would conclude that heat is always zero, which contradicts not only classical thermodynamics, but also our entire experience with those systems.

Note: Sekimoto makes a distinction between the heat that he defines in his paper and the heat that, in principle, can be measured experimentally using calorimetric techniques. However, the distinction between both is simply related to temperature changes and does not affect our criticism of (8) and (9).

The problem with Sekimoto's work and similar stochastic approaches to thermodynamics is that they identify the energy absorbed or released as heat with changes in the kinetic energy of the system, when heat is related to changes in internal energy. This is the reason why when we heat a tennis ball we increase its internal energy, but not its speed.

We must abandon the so-called stochastic approach to define heat, not only because it is actually a mesoscopic approach, but because it is incorrect. Expression (8) is, in fact, the standard definition of mechanical work, since it gives the variation in the energy of the system caused by a change in its position.

A truly microscopic attempt to define heat was recently made by Menon and Agrawal.[16] The two authors start with the Hamiltonian for the universe, extract the Hamiltonian H_a for the system of interest, and provide expressions for heat and work. Heat for

system a is defined as[16]

$$dQ_a = -\sum_{b \neq a} \left(\frac{\partial H_b}{\partial x_b} dx_b + \frac{\partial H_b}{\partial p_b} dp_b \right) - \sum_{b \neq a} \sum_c \left(\frac{\partial V_{bc}}{\partial x_c} dx_c + \frac{\partial V_{bc}}{\partial p_c} dp_c \right).$$
(10)

In the above definition, H_b is the Hamiltonian for all the systems that are not the system under study, p and x are momenta and position coordinates, respectively, and V_{bc} is the interaction between b and c; the index c runs over all the systems in the universe, while b runs over all the systems excluding the system of interest.

We cannot accept (10) as a microscopic definition of heat because it conflicts with classical thermodynamics and with experience. If, instead of starting with the Hamiltonian for the universe, we start with the Hamiltonian H_a for the system of interest and calculate its infinitesimal variation,

$$dH_a = -\sum_{b \neq a} \left(\frac{\partial V_{ba}}{\partial x_a} dx_a + \frac{\partial V_{ba}}{\partial p_a} dp_a \right),$$
(11)

we can see that this is just one of the components in (10). More specifically the terms with $c = a$, which implies that the rest of components in (10) cancel the term that Menon and Agrawal identify with work

$$dW_a = \sum_{b \neq a} \left(\frac{\partial V_{ba}}{\partial x_b} dx_b + \frac{\partial V_{ba}}{\partial p_b} dp_b \right).$$
(12)

We cannot accept (10), because it has been derived from an arbitrary split of the energy change of the system plus its surroundings. Note also that Menon and Agrawal identify work with a change in the coordinates of the environment, when work is traditionally associated to changes in the coordinates of the system under study. A similar criticism also applies to their heat definition, which contains a term that describes the variation in the energy of the bodies that are not the system under study. The two

authors have only provided a formal analogy of the first law of thermodynamics without any link to the true thermodynamic laws. In fact, they do not provide any derivation of known thermodynamic formulae or thermal phenomena.

A much more interesting approach is that developed by DeVoe,[17] who uses Newtonian mechanics to derive the total work done by the forces acting on all the entities of a system and then associates thermodynamic work and heat to the Newtonian work done on a thin outer layer of the system that is located next to the boundary surface of the system by contact forces exerted by the surroundings. DeVoe defines heat as

$$Q = \sum_\tau \sum_i \int \delta_{i\tau} \boldsymbol{F}_i^{\mathrm{cnt}} \cdot \mathrm{d}\boldsymbol{r}_{i\tau}. \tag{13}$$

In the definition above, $\delta_{i\tau}$ is a Kronecker-like delta, equal to one when the entitiy i is in segment τ of the boundary layer and equal to zero otherwise. $\boldsymbol{F}_i^{\mathrm{cnt}}$ is the net contact force exerted on the entity i by nearby particles in the surroundings, and $\boldsymbol{r}_{i\tau}$ is a vector from a point fixed on the outer face of the segment τ at the boundary to the entity i inside the segment (see figure 1 on ref. [17] for details). Besson developed a closely related approach.[18]

One objection to the Newtonian approaches of DeVoe and Besson is that they associate heat with short-range interactions at mesoscopic boundaries. There is no reason why heat should only be a local mechanism for energy transfer. In classical diffusive energy transfer, the heat flux can be calculated from Fourier's law, in terms of the local thermal conductivity and the local temperature gradient, but in more general situations the local quantities are not sufficient to calculate the heat and we must take into account the physical conditions of a larger part of the system or even the entire system. This show the general nonlocal nature of heat.

Another objection is that both approaches are based on the *ad hoc* definition of an arbitrary-size subset of the system under study: the "*mesoscopic elements*"[18] or the "*segments of the interaction layer*".[17] Besson offers some qualitative arguments about the minimum and maximum sizes of those mesoscopic elements, but the split of energy transfer into heat and work remains subjective. Finally, both authors use Newtonian mechanics, while we look for the more general possible definition of heat.

3   MICROSCOPIC DEFINITION OF HEAT AND FIRST LAW

Before presenting a microscopic definition of heat, it is necessary to remember that thermodynamic relations are usually expressed in terms of differentials because most introductory texts describe all transformations of state as idealized, infinitely slow changes: the so-called quasistatic processes. With that restriction, heat and work cannot be defined in terms of a time interval dt in classical thermodynamics, since the transformations do not occur in a finite time.

Moreover, since heat and work are not state functions, these quantities cannot be uniquely specified by initial and final states and "*imperfect*"[8] or "*inexact*"[1,3,10] differentials đQ and đW are used to represent heat and work in classical thermodynamics. However, our approach is purely dynamical, contains time as a variable, and we can replace the classical expression (1) with the modern dQ = dE – dW, where the quantities dQ and dW are well defined. For example, the energy supplied in a time dt by a heating coil of resistance R carrying a current $\boldsymbol{J}$ is given by dQ = $(\boldsymbol{J}^2 R)$ dt.

Since we are looking for a fundamental concept of heat that is of general validity, we will consider an arbitrary system with N enti-

ties and energy E. The entities can be elementary particles, atoms, molecules, ions, macromolocules, stars, etc. This energy can be expressed in terms of different variables, such as the positions and velocities of the entities, momenta and positions, or others. For greater convenience, we will work with momenta $\boldsymbol{p}_i$ and positions $\boldsymbol{r}_i$, in which case the energy $E = E(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N)$ is just the Hamiltonian of the system. We make no assumptions about the equations of motion.

Using a dot notation $\dot{Z} \equiv (\mathrm{d}Z/\mathrm{d}t)$ for the rate of change of the quantity Z, the rate of change of the energy of the system is given by

$$\dot{E} = \sum_i^N \frac{\partial E}{\partial \boldsymbol{r}_i} \dot{\boldsymbol{r}}_i + \sum_i^N \frac{\partial E}{\partial \boldsymbol{p}_i} \dot{\boldsymbol{p}}_i. \tag{14}$$

The constituent entities of the thermodynamic system are moving and we intuitively associate thermodynamic work with a kind of 'ordered' motion that modifies some mechanical property that characterizes the system as a whole; for concreteness, we will consider the volume variations produced by a change in pressure. We also intuitively associate heat with a kind of 'disordered' motion. Greiner and coworkers offer an intuitive graphical distinction betwen heat and work[1] that we reproduce in figure 1.

Callen talks[8] about "*mechanical modes*" and "*hidden atomic modes*" of motion regarding work and heat. I think his terminology is misleading and the basis for a misinterpretation of heat as something associated with our ignorance. Besson talks about the coherence or incoherence of the interactions, which is much better terminology. We will discuss this topic in more depth below. As mentioned in the former section, Besson's approach is really mesoscopic; he also writes:[18]
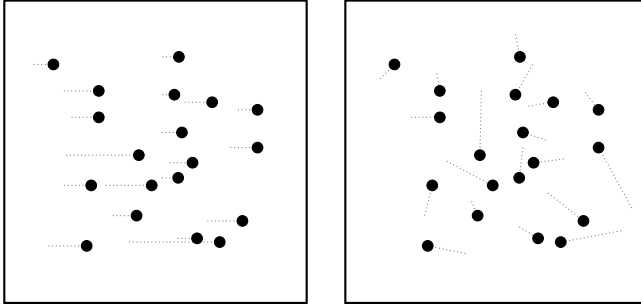
Figure 1: Collective movement of entities in the same direction and sense (left). Individual movement of each entity in random directions (right).

> "*The distinction between work and heat cannot be made at the microscopic level of molecules or atoms; on that scale, there is no difference between the two types of interaction. When one heats a glass by touching it or moves it by pushing it, the interaction between a molecule of the hand and a molecule of the glass is similar in kind.*"

We will show in this section how the distinction between thermodynamic work and heat can be made at the microscopic level.

Our goal will be to make this distinction rigorous and precise. To obtain a microscopic definition of heat, we want to characterize the total variation of energy of the system under study in terms of different microscopic modes of motion of the entities. To divide the total energy variation into different components, we must first reparametrize the position variables as $r_i = \lambda s_i$, where λ is a lineal scale parameter that characterizes the system as a whole and s_i are the new position variables. Considering that the system is enclosed in a cubic box of volume $V = \lambda^3$, then the result is $r_i = V^{1/3}s_i$. We have derived this expression assuming a cubic box for simplicity, but the reparametrization of the coordinates r_i into the collective parameter V and the individual remainders s_i can be done for any geometry of the volume.

This change of variables for the position coordinates must be done in a manner consistent with mechanics. Therefore, to preserve the conjugacy of positions and momenta

$$\mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N = \left[V^{1/3}\mathrm{d}\boldsymbol{s}\right]^N \mathrm{d}\boldsymbol{p}^N = \mathrm{d}\boldsymbol{s}^N \left[V^{1/3}\mathrm{d}\boldsymbol{p}\right]^N = \mathrm{d}\boldsymbol{s}^N \mathrm{d}\boldsymbol{g}^N, \quad (15)$$

and we can infer the expression $\boldsymbol{p}_i = V^{-1/3}\boldsymbol{g}_i$ from the phase space structure, with $\boldsymbol{g}_i$ the new momentum variables.

Using this reparametrization of the position and momenta variables in (17), we obtain for the rate of change of the energy of the system the following expression

$$\dot{E} = \sum_i^N \frac{\partial E}{\partial \boldsymbol{r}_i}\left[\frac{\partial \boldsymbol{r}_i}{\partial \boldsymbol{s}_i}\dot{\boldsymbol{s}}_i + \frac{\partial \boldsymbol{r}_i}{\partial V}\dot{V}\right] + \sum_i^N \frac{\partial E}{\partial \boldsymbol{p}_i}\left[\frac{\partial \boldsymbol{p}_i}{\partial \boldsymbol{g}_i}\dot{\boldsymbol{g}}_i + \frac{\partial \boldsymbol{p}_i}{\partial V}\dot{V}\right]. \quad (16)$$

The partial derivations on the volume are easy to calculate, $(\partial \boldsymbol{r}_i/\partial V) = (\boldsymbol{r}_i/3V)$ and $(\partial \boldsymbol{p}_i/\partial V) = -(\boldsymbol{p}_i/3V)$, which yields

$$\dot{E} = \sum_i^N \left[\frac{\partial E}{\partial \boldsymbol{s}_i}\dot{\boldsymbol{s}}_i + \frac{\partial E}{\partial \boldsymbol{g}_i}\dot{\boldsymbol{g}}_i\right] - \frac{1}{3V}\sum_i^N \left[\frac{\partial E}{\partial \boldsymbol{p}_i}\boldsymbol{p}_i - \frac{\partial E}{\partial \boldsymbol{r}_i}\boldsymbol{r}_i\right]\dot{V}. \quad (17)$$

We have finally expressed the rate of change of the energy of the system as the sum of a collective term associated to the rate of change of the volume of the system and individual terms associated with each $\dot{\boldsymbol{s}}_i$ and $\dot{\boldsymbol{g}}_i$. However, we have not simplified the description, because we need $6N$ scalar variables plus the volume to calculate the rate of change of the energy. That is, our approach remains microscopic.

In the low velocity regime, the energy of a system of N entities can be divided into the kinetic energy of the center of mass and the internal energy of the system, $E = (\boldsymbol{P}^2/2M) + U$, with $\boldsymbol{P} \equiv \sum_i^N \boldsymbol{p}_i$ the total momentum, $M \equiv \sum_i^N m_i$ the total mass of the system, and U the internal energy. The concept of internal energy is necessary to adequately define heat, since the motion of the system as a

whole is exclusively associated with work. However, there are difficulties in defining the center of mass in the high-speed regime and in introducing an adequate generalization of the concept of internal energy used in classical thermodynamics. We will explore those difficulties elsewhere.[19] For the purposes of this article, we will consider a reference system for which $\boldsymbol{P} = \boldsymbol{0}$, in which case $E = U$ and we can continue using previous expressions such as (17) without worrying about the distinction between total energy and internal energy.

To make contact with thermodynamics, we first define the heat rate as

$$\dot{Q} \equiv \sum_i^N \left[\frac{\partial E}{\partial \boldsymbol{s}_i} \dot{\boldsymbol{s}}_i + \frac{\partial E}{\partial \boldsymbol{g}_i} \dot{\boldsymbol{g}}_i \right] \tag{18}$$

and next define the system pressure as

$$p \equiv \frac{1}{3V} \sum_i^N \left[\frac{\partial E}{\partial \boldsymbol{p}_i} \boldsymbol{p}_i - \frac{\partial E}{\partial \boldsymbol{r}_i} \boldsymbol{r}_i \right], \tag{19}$$

finally obtaining from (17) a very compact expression for the rate of change of internal energy

$$\dot{E} = \dot{Q} - p\dot{V}. \tag{20}$$

This is a microscopic generalization of the first law of classical thermodynamics, and the physical interpretation of each quantity is now evident. The $-p\dot{V}$ term describes the change in internal energy due to microscopic modes of motion that affect to all the particles at once through a change in volume, with the pressure measuring the sensitivity of the energy to such changes since $p = -(\partial E/\partial V)$ in (20). We call those modes collective. The heat rate $\dot{Q}$ describes the change in internal energy due to noncollective microscopic modes of motion. Heat is a total differential defined in the microscopic state space $(\boldsymbol{s}_1, \boldsymbol{g}_1, \boldsymbol{s}_2, \boldsymbol{g}_2, \dots, \boldsymbol{s}_N, \boldsymbol{g}_N)$. Contrary to

conventional wisdom, heat is not associated with our ignorance, since we are using a complete description of microscopic motion to define heat. We will see in section 4 that the conventional heat used in classical thermodynamics corresponds to an average of this microscopic concept of heat, but even after averaging heat cannot be associated with ignorance. Heat is a physical property as velocity or energy are.

Note: The minus sign in (20) is a historical consequence of the way that pressure was first defined in physics. We could absorb the sign into the definition of pressure and describe exactly the same phenomena, but our pressure values would be different from those found in tables and measured with standard apparatus.

Recall that we derived the $-p\dot{V}$ term by associating a lineal scale parameter λ to the volume $V = \lambda^3$ of the system. If, instead, we had related the parameter to the area A of the system or to its length L, using $A = \lambda^2$ or $L = \lambda$ respectively, we should have obtained alternative expressions for the energy rate, with the area or the length of the system being the new collective parameter. It is not necessary to repeat the entire derivation for such cases, we can simply take the $-p\dot{V}$ term, and use the geometric relation $V = AL$ to obtain

$$p\dot{V} = (pA)\,\dot{L} + (pL)\,\dot{A}. \tag{21}$$

This can be simplified to

$$p\dot{V} = -\tau\dot{L} - \gamma\dot{A} \tag{22}$$

by introducing two new concepts: the *linear tension* $\tau \equiv -pA$ and the *surface tension* $\gamma \equiv -pL$. Once again, the pressence of the minus signs is a historical artifact.

4   CLASSICAL THERMODYNAMICS AND THE THERMODYNAMIC LIMIT

If we multiply both sides of (20) by dt and define the infinitesimal work as $dW = -pdV$, we obtain

$$dE = dQ + dW. \tag{23}$$

This differential version of the first law is more like that found in classical thermodynamics textbooks.[1,2,8,10] The difference is that all the differentials in (23) are exact, while those textbooks must use inexact differentials because they do not consider the time variable as we will show in a moment (see also the comments made at the beginning of section 3).

We can obtain alternative expressions for heat by writing explicit expressions for the internal energy E. We mentioned before that there are difficulties in defining the center of mass of a system of entities in the high-speed regime. There are also related difficulties in relation to the generalization of the concept of temperature used in classical thermodynamics.[19] However, when the speeds are small compared to the speed of light, the internal energy is given by

$$E = C_V T + \Phi, \tag{24}$$

in which Φ is the interaction energy of the system and the microscopic temperature T is defined by

$$T \equiv \frac{1}{k_B 3N} \sum_i^N \frac{\boldsymbol{p}_i^2}{m_i}, \tag{25}$$

with k_B the Boltzmann constant.

Expression (24) for the energy is exact in the low-speed regime. Differentiating it and putting it in (23) yields

$$dQ = C_V dT + \left(p + \frac{\partial E}{\partial V} \right) dV + \sum_i^N \frac{\partial \Phi}{\partial \boldsymbol{s}_i} d\boldsymbol{s}_i, \qquad (26)$$

which is a microscopic generalization of the classical thermodynamics expression (2).

Our new formulation is more general than that of classical thermodynamics, but not only because all the quantities in our expressions are microscopic and instantaneous, and therefore include fluctuations and size effects, but because our expressions include adittional terms like the last term in (26), which does not appear in (2). For an isothermal system at constant volume, the classical expression (2) predicts there is no heat, but (26) predicts heat associated to noncollective changes in the internal potential energy.

In the remainder of this section, we will discuss the relationship of (23) to classical thermodynamics. First of all, we must eliminate fluctuations and size effects. To do this we must take time averages and the limit of an infinite system without gravitation: $G \to 0$, $N \to \infty$, and $V \to \infty$. Classical thermodynamics works in the quasistatic approximation and we can take the averages over an infinite time span $[0, \infty]$, defining the following quantities

$$\mathcal{E} \equiv \lim_{\substack{G \to 0}} \lim_{\substack{N \to \infty \\ V \to \infty}} \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau E(t)\, dt, \qquad (27)$$

$$đ\mathcal{Q} \equiv \lim_{\substack{G \to 0}} \lim_{\substack{N \to \infty \\ V \to \infty}} \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dQ(t)\, dt, \qquad (28)$$

and

$$đ\mathcal{W} \equiv \lim_{\substack{G \to 0}} \lim_{\substack{N \to \infty \\ V \to \infty}} \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dW(t)\, dt, \qquad (29)$$

results in the classical thermodynamics expression found in text-books[1, 2, 8, 10]

$$d\mathcal{E} = đQ + đ\mathcal{W}. \tag{30}$$

We can see now explicitly how time averaging removes the time variable from all classical thermodynamics quantities, forcing the formalism of classical thermodynamics to use inexact differentials for heat and work.

In the textbook-like expression (30), the thermodynamic work is given by $đ\mathcal{W} = -\mathcal{P}d\mathcal{V}$. We have mentioned before that (23) uses exact differentials and the time variable, while (30) does not. Other fundamental differences between (23) and (30) are that the energy in (23) is not an extensive quantity and the pressure is not intensive.

Note: Classical thermodynamics distinguishes between variables that are independent of the quantity of matter in a system, the intensive variables, and variables that depend on the quantity of matter, which are called extensive variables. Temperature, pressure, viscosity, concentration, and molar heat capacity are examples of intensive variables in classical thermodynamics because they do not depend on the number of particles, whereas volume and heat capacity are typical examples of extensive variables. For example, if we divide an infinite system without gravitation in half, $N \rightarrow (N/2)$, its energy decreases by the same proportion $\mathcal{E} \rightarrow (\mathcal{E}/2)$, but pressure remains unchanged $\mathcal{P} \rightarrow \mathcal{P}$.

Our new thermodynamics is valid for any classical system enclosed in a volume. If we divide the system into two subsystems A and B, the total energy is not the sum of the energy of each subsystem but it is given by $E = E_A + E_B + \Phi_{AB}$, where Φ_{AB} is the energy of the interaction between A and B. If we introduce this split of the energy into the definition of pressure (19), we obtain

$$p = \frac{V_A}{V}p_A + \frac{V_B}{V}p_B + \frac{1}{3V} \sum_i^N \left[\frac{\partial \Phi_{AB}}{\partial \boldsymbol{p}_i} \boldsymbol{p}_i - \frac{\partial \Phi_{AB}}{\partial \boldsymbol{r}_i} \boldsymbol{r}_i \right], \tag{31}$$

where we have recursively applied the definition (19) to each subsystem to obtain p_A and p_B. If we multiply both sides of the above expresion by the total volume $V = V_A + V_B$, we obtain

$$pV_A + pV_B = p_AV_A + p_BV_B + \mathcal{O}(\Phi_{AB}). \qquad (32)$$

We can now easily check that the identity $p = p_A = p_B$ is only possible if we ignore the interaction between systems A and B. Therefore, thermodynamic presure is not an intensive quantity in the general case.

It is often stated in textbooks that ordinary thermodynamics is valid for any macroscopic system:[8]

> "*In contrast to the specificity of mechanics and electromagnetism, the hallmark of thermodynamics is generality. Generality first in the sense that thermodynamics applies to all types of systems in macroscopic aggregation, and second in the sense that thermodynamics does not predict specific numerical values for observable quantities.*"

However, we have just shown that ordinary thermodynamic quantities such as pressure are intensive only when interactions are weak and energy is additive $E = E_A + E_B$. We must conclude that the thermodynamic formalism described in ordinary textbooks[1,2,8,10] is only valid for systems that are not too small to make electromagnetic or nuclear interactions important and, at the same time, the systems cannot be too big as to do gravitational interactions relevant. This is the meaning of the limits $G \to 0$ and of $N \to \infty$, $V \to \infty$ in (27), (28), and (29). The formalism described in the cited textbooks does not apply "*to all types of systems in macroscopic aggregation*", as Callen pretends, but only to macroscopic systems in which gravitation and fluctuations can be neglected.

Note: Scaling a material system to an infinitely large size implies that the gravitational potential energy grows more rapidly than linearly with the mass of the system, since the potential energy increases as the five-thirds power of the mass. What happens when we scale the size of a self-gravitating system while keeping the temperature and density constant is that it begins to fall apart into separate groups as soon as the systems exceed a critical mass, called the Jeans mass in astrophysics.

On the other hand, our thermodynamic expressions are completely general, because they have been derived from first principles without limiting the number of particles or the type of interactions.

The $N \to \infty$ and $V \to \infty$ limit deserves adittional comments. This limit is called the thermodynamic limit[3,9] and it is sometimes said that thermodynamics is only valid in the limit of infinite system sizes. But an obvious difficulty with this view is that we only carry out experiments on finite systems, which would imply that thermodynamics could never be applied to the real world.

$N \to \infty$ and $V \to \infty$ would be taken in thermodynamics in the same sense as the limit $c \to \infty$ in mechanics. If we take $c \to \infty$ literally, then Newtonian mechanics could never be applied to the real world since c has a finite value in our universe. For an entity i with velocity $\mathbf{v}_i$, we recover the Newtonian expressions when $(\mathbf{v}_i^2/c^2) \to 0$. Being rigorous, we would take N limits, one per entity $(\mathbf{v}_i^2/c^2) \to 0$, if we want to recover the Newtonian mechanics of a system of N entities; however, since c is common to all the entities, we formally apply a single $c \to \infty$ limit to the whole mechanical system.

To recover classical thermodynamics, we cannot take $N \to \infty$ and $V \to \infty$ literally. Readers might object that our remarks about this limit are trivial, but I want to emphasize that in the physics litera-

ture we can find statements such as *"thermodynamics is a special case of statistical mechanics for very many particles (N → ∞)"*[1] or that statistical mechanics presents paradoxes *"that can be resolved only by acknowledging the thermodynamic limit"*.[20,21] LeBellac, Mortessagne, and Batrouni mention the thermodynamic limit in their discussion of the physical basis of irreversibility and the problem of the Poincaré recurrences, and state that *"in rigorous arguments, we take the thermodynamic limit in order to avoid such recurrences"*.[3,9] There is nothing rigorous in these arguments because it can be demonstrated that the laws of classical thermodynamics stop working at that limit, in such a way that not only can we not explain irreversibility, but we could not explain any thermodynamic process. By considering the thermodynamic limit we can resolve several paradoxes of statistical mechanics, but at the cost of introducing paradoxes and inconsistencies in the thermodynamic formalism.

A simple way to understand why thermodynamics stops working in the thermodynamic limit is by calculating the second derivatives of the thermodynamic entropy in classical thermodynamics. Differentiating entropy twice with respect to the internal energy, we obtain

$$\frac{\partial^2 S}{\partial \mathcal{E}^2} = \frac{\partial}{\partial \mathcal{E}}\left(\frac{1}{\mathcal{T}}\right) = -\frac{1}{\mathcal{T}^2}\frac{\partial \mathcal{T}}{\partial \mathcal{E}} = -\frac{1}{\mathcal{T}^2 C_{\mathcal{V}}}. \tag{33}$$

The so-called heat capacity $C_{\mathcal{V}}$ is proportional to the number of entities, so taking the $N \to \infty$ limit implies that the temperature of the system cannot vary when the system absorbs or releases energy since $(\partial \mathcal{T}/\partial \mathcal{E}) = 0$.

Additionally, differentiating the thermodynamic entropy twice with respect to the volume gives

$$\frac{\partial^2 S}{\partial \mathcal{V}^2} = \frac{\partial}{\partial \mathcal{V}}\left(\frac{\mathcal{P}}{\mathcal{T}}\right) = -\frac{\mathcal{P}}{\mathcal{T}^2}\frac{\partial \mathcal{T}}{\partial \mathcal{V}} + \frac{1}{\mathcal{T}}\frac{\partial \mathcal{P}}{\partial \mathcal{V}} = -\frac{\mathcal{P}}{\mathcal{V}\mathcal{T}^2\alpha} - \frac{1}{\mathcal{V}\mathcal{T}\kappa} \tag{34}$$

with α the coefficient of thermal expansion and κ the isothermal compressibility. Taking the $\mathcal{V} \to \infty$ limit, we conclude that the temperature and pressure of the system remain constant with changes in the volume.

We can repeat the calculation for the rest of second-order derivatives of the thermodynamic entropy and the result is the same. This has an easy explanation: the first-order derivatives of the entropy are intensive quantities in classical thermodynamics and the second-order derivatives are proportional to $(1/N)$ or $(1/\mathcal{V})$ and, consequently, they vanish in the thermodynamic limit. The laws of thermodynamics do not apply in the limit of infinitely large systems since, for example, heating an infinite system would not increase its temperature, contrary to what experimentation and observation in real systems shows.

Popular claims that thermodynamics is rigorously derived from statistical mechanics in the thermodynamic limit and that the behavior of matter is governed by the laws of thermodynamics only in this limit are common misconceptions. The thermodynamic limit must be interpreted physically in the same sense as the low-velocity limit in mechanics.

5   OPEN SYSTEMS

Traditional definitions of heat such as (1) and (3) are only valid when the total amount of matter in the system remains constant. The same is true for most classical thermodynamics formulae. For open systems, the macroscopic first law (30) must be generalized to

$$\mathrm{d}\mathcal{E} = \mathrm{d}\mathcal{Q} + \mathrm{d}\mathcal{W} + \mathrm{d}\mathcal{R}, \tag{35}$$

with đ$\mathcal{R}$ describing the variation in energy caused by matter entering or leaving the system. Experts disagree on how to define this new term.[6,8,13] Different definitions of heat for open systems are reviewed in ref **22**, in which a new definition for đ$\mathcal{R}$ was also proposed. The aforementioned authors use moles as unit for amount of matter, but we can use the number of entities instead, in which case đ$\mathcal{R} = \sum_k \mathcal{R}_k \, d_e N_k$, where $d_e N_k$ is the variation of the number of entities of substance k due to exchanges with the environment. Obviously, the physical meaning of the new quantity $\mathcal{R}_k$ depends of the definition of heat used.[22]

The macroscopic differential law (35) assumes that matter has a continuous nature. We could replace it with a macroscopic integral law $\Delta\mathcal{E} = Q + \mathcal{W} + \mathcal{R}$, in which $\mathcal{R}$ is defined in terms of discrete variations of matter $\Delta_e N_k$, but we will not be able to find a microscopic analogue of any of these laws. The difficulty here lies in the fact that the macroscopic laws assume the existence of three independent energy transfer mechanisms (heat, work, and matter), when only two of them are microscopically independent, as we will show in a moment.

For simplicity, consider an adiabatic process with no chemical, electromagnetic, or interfacial work. In this case (35) reduces to

$$d\mathcal{E} = -\mathcal{P}d\mathcal{V} + đ\mathcal{R}. \tag{36}$$

The work term is the product of an intensive quantity, the macroscopic pressure, and the change in volume. This product does not depend on the number of entities N_k and this is the reason why the term đ$\mathcal{R}$ is necessary to describe energy variations due to changes in N_k caused by surrounding flows of matter.

However, the microscopic pressure (19) is not an intensive quantity, since it depends on the number of entities, and if this number

changes from N to $(N + A)$ as a consequence of matter flows, then the microscopic law (23) applied to the same adiabatic process, with no chemical, electromagnetic, or interfacial work, changes from

$$dE_N = -p_N dV \tag{37}$$

to

$$dE_{N+A} = -p_{N+A} dV, \tag{38}$$

making it unnecessary to include an additional term to account for the energy change caused by matter entering or leaving the system.

Of course, we could *formally* write the last microscopic law as

$$dE_{N+A} = -p_N dV + dR_A, \tag{39}$$

with $dR_A \equiv (dE_{N+A} - dE_N)$, but in general $-p_N dV$ is not the work in the system with $(N + A)$ entities. Only in the limit of a very large system, $N \to \infty$, do we find that $p_{N+A} \approx p_N$ and recover an analogue of the classical law (36).

6 CONCLUDING REMARKS

Many conventional textbooks[1, 8, 9, 14, 23] identify the entropy of classical thermodynamics with ignorance –more explicitly with the lack of information about *"the exact microscopic state of a many-body system"*[3] and, by means of Clausius law $đQ = \mathcal{T} d\mathcal{S}$, they also associate heat with ignorance. Gell-Mann even claims that the entropy of a system described in perfect detail would remain constant,[12] but this would imply that the system cannot be heated or cooled, which is absurd.

This modern association of the thermodynamic concept of heat with ignorance can also be found in the usual statistical mechan-

ics approach, in which the molecular interpretation of heat is explicitly associated with modifications of our knowledge about the microstate. In fact, authors like Hill consider that thermodynamic variables such as temperature and entropy are instances of "*nonmechanical properties*",[14] while by mechanical properties he refers to pressure, energy, volume, number of molecules, etc. For Hill, mechanical properties can be defined in purely mechanical terms "*without, for example, introducing the concept of temperature*".

However, this dominant academic view on the nature of heat does not stand up to critical scrutiny, and some authors have attempted to offer a purely mechanistic, probability-free definition of heat. After reviewing previous attempts to define heat, we provide a fundamental microscopic definition of heat and of the first law valid for both closed and open systems. This definition makes no assumptions about sizes, extensivity, the type of interactions, or velocity regimes, and is completely general. We then apply the definition to a simple system, a one-component gas with constant composition, to make explicit contact with classical thermodynamics and show that our approach not only provides a nonstatistical foundation for classical thermodynamics but also offers generalized formulae.

We have shown that heat is the energy transfer mechanism resulting from the incoherent movement of the entities that constitute the system. We can also define temperature microscopically, and this opens the possibility of a future microscopic definition of entropy in terms of mechanical quantities. This paper is the first in a research program to redefine thermodynamics from a real microscopic basis, without ensembles or probabilities.

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