Negative internal entropy production

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The Second Law of thermodynamics requires positive internal entropy production (IEP) when a system evolves from one state to the next. IEP supposedly indicates that an isolated system equilibrates and is steady thereafter, and that a process is irreversible between two equilibrium states. Originally, Clausius postulated the entropy law based on his First Law of thermodynamics, which represents internal energy conservation. However, total energy conservation not only clarifies the sources of entropy but also reveals that negative IEP occurs, violating the Second Law. Entropy does not generally indicate spontaneous (irreversible) processes between equilibrium states.

Initial focus on heat engines set the path along which standard thermodynamics theory developed thereafter. The limited form of the First Law, derived by Rudolf Clausius, spawned a second postulate about entropy to account for the difference between outside heat exchange and system heat content. This indirect approach becomes transparent by recognizing macroscopic and formation energy, both of which are non-thermal, as the only possible internal sources of heat.

Standard theory assumes that entropy always increases to equilibrium (Josiah Gibbs postulate [1]) and that internal entropy is always produced in real processes between equilibrium states (Clausius postulate [2, p. 363]). The former assumption is found to be invalid in Ref. [3]. This article refutes the latter assumption.

Heat engines function by exchanging heat and doing mechanical work on an external load. Rudolf Clausius envisioned a steam engine operating in a closed circuit by directing effluent steam through a heat exchanger. Energy balance for an incremental process then is simply

$$\Delta U = \Delta Q^{\text{outside}} + \Delta W^{\text{outside}}\,, \tag{1}$$

known as the First Law, for some measure U called the internal energy of the system. He reasoned that U is an integration constant of a complete process and an equilibrium state function. However, he makes no attempt to compare U to the total energy contained in a system. Internal energy is generally understood to correspond to "energy of thermal agitation and short range molecular forces" [4], that is microscopic energy including heat and formation energy. There is no macroscopic energy in the context of heat engines; the only macroscopic motion occurs in mechanical coupling outside the working fluid.

Clausius makes cursory statements regarding the equivalence value of macroscopic transformations and formation energy but does not alter the First Law to reflect this knowledge. This omission must be compensated for in another way, by inventing internal entropy production (IEP) as the equivalence value of dissipation. He concluded that equivalence value indicates when a process is irreversible, i.e. can proceed spontaneously, which is a primary purpose of the theory. He proposed a second universal law governing evolution, independent of the First Law as stated in (1). Gibbs theory exclusively focuses on equilibrium conditions, given a maximum entropy condition, and does not address this issue. Nonequilibrium theory, such as presented in Ref. [4], blends these two approaches.

Clausius postulated that the accumulated equivalence value over a cyclic process cannot be positive, $\oint dQ^{\text{reservoir}}/T \leq 0$, due to "uncompensated" transformations converting heat from a reservoir $\Delta Q^{\text{reservoir}}$ into work and work into heat at temperature T. He defines entropy only in the reversible, quasi-static limiting case $\Delta S = \Delta Q^{\text{reservoir}}_{\text{reversible}}/T$. By doing so, he disassociates entropy from internal energy (1), which applies to all processes. These results combine to produce his entropy law

$$\Delta S \geq \Delta Q^{\text{reservoir}}/T \tag{2}$$

by assuming that any two equilibrium states are connected by a quasi-static process. The difference must be generated internally as IEP,

$$\Delta S^{\text{int}} = \Delta S - \Delta Q^{\text{reservoir}}/T \geq 0\,. \tag{3}$$

Entropy consequently must increase over a real, adiabatic, cyclic process $\oint dS > 0$. Yet entropy would then have multiple values in the final system state, and so would not be a state function. This confusion has inspired debate and uncertainty whether such processes are physically possible, what cyclic means, and whether entropy is a true state function. Discussion whether IEP may be negative is notably absent.

Another key issue is highlighted by a simple example. Internal energy is generally understood to omit overall macroscopic motion of the system, because transforming to the system rest frame should not alter thermodynamic conclusions. A system composed of two subsystems moving relative to each other presents a problem. Rubbing at their interface should generate heat, yet total system entropy is additive and therefore independent of this nonthermal motion. This heat would have to be exchanged with an outside reservoir in order to maintain constant temperature, implying an unaccounted for source of heat interpreted as IEP. The above scheme chosen by Clausius does not allow the analyst to discover the source and rectify the discrepancy.

Two other idealized cases were given by Clausius, and repeated since, to support his conclusions. First, when two isolated heat reservoirs make thermal contact, entropy always increases if heat only flows from hot to cold because $\Delta S = \Delta Q\,(1/T_1 - 1/T_2) \geq 0$. Second, when two isolated containers of different inert gases are connected through a conduit, entropy always increases as they mix because each particle ranges throughout a larger volume.

These cases are far from equilibrium immediately after contact is made and so cannot be part of a quasi-static process. No quasi-static process exists between states before and after contact, violating a key condition in Clausius' argument regarding cyclic processes. Therefore, it does not follow that entropy must increase more than equivalence value in these cases. Only dynamic particle analysis, directly deriving non-equilibrium particle, momentum and heat flux formulas [5], can answer the question whether entropy is maximum in equilibrium [3]. The following discussion considers processes initially in equilibrium.

In order to gain clarity, we need a more concrete expression than the equivalence value. Clausius formally defined entropy only through the equivalence value in reversible, quasi-static processes. Yet he made an alternative argument that the change in entropy equals internal thermal equivalence value plus disgregation (internal plus outside work), which is equivalent to the statistical definition $S = U/T + k_{\mathrm{B}} \ln Z$ for system partition function $Z(T, \{N_j\}, V) = \sum_s^{\text{states}} \exp[-E_s/k_{\mathrm{B}}T]/\prod_i N_i!$. This formula is inherently an equilibrium state function because each component is. Also, any system energy E_0 that is common to all particle configurations, i.e. $E_s = E_0 + E_s^{'}$, factors out of U and Z and cancels in entropy. Such energy in common is non-thermal. Entropy is a state function solely of thermal energy content Q^{system}.

Any quasi-equilibrium incremental process, reversible and irreversible, produces the Fundamental Equation by linear extrapolation:

$$T\Delta S = \Delta Q^{\text{system}} + p\,\Delta V - \sum_j^{\text{substance}} \mu_j'\,\Delta N_j\,, \tag{4}$$

for isotropic material. Parameter T is the system temperature. Chemical potential $\mu_j' = k_{\mathrm{B}} T \partial_{N_j} \ln[Z']$ represents the thermal part. Clausius actually derived an equivalent form $T\Delta S = \partial_T U\,\Delta T + (p + \partial_V U)\,\Delta V$ for a closed system. He identified disgregation as $(p + \partial_V U)\,\Delta V/T = \partial_T p\,\Delta V$ [2, 6th Memoir, pp. 215–250].

Clausius assumes that, "Increase in disgregation is the action by means of which heat does work" [2, p. 227], which again implies (2) for closed, inert systems by combining (4) and (1) with $\Delta U = \Delta Q^{\text{system}} + \Delta W^{\text{internal}}$.

Standard theory identifies only substances. Each stable configuration of particles is discrete, separated by ranges of unstable conditions. Species are independent material forms, with unique properties and interactivity. To be concrete, the substance and stable phase must be identified as a distinct species of particle.

There are two forms of non-thermal energy: formation and macroscopic. Generally, any system can be created by forming the constituent particles in their ground quantum state, boosting them in bulk and applying force fields, and finally heating them to the desired temperature. Total system energy may be expressed as

$$E^{\text{system}} = E^{\text{system}}_{\text{macro}} + Q^{\text{system}} + E^{\text{system}}_{\text{formation}}\,. \tag{5}$$

Formation energy ε_{0j} of a particle of species j can be computed from first principles. Measuring the number of particles N_j yields the system formation energy $E^{\text{system}}_{\text{formation}} = \sum_j^{\text{species}} N_j \varepsilon_{0j}$.

Macroscopic energy is the energy associated with the smooth, mean trajectory of all particles of a species. The macroscopic position of species j is the mean expectation value $\mathbf{r}_j^{\text{macro}} = \sum_i^{N_j} \langle \mathbf{r}_{ji} \rangle / \langle N_j \rangle$, equal to its center of mass because they have the same mass. Each particle deviates from this mean position by $\delta\langle \mathbf{r}_{ji} \rangle = \langle \mathbf{r}_{ji} \rangle - \mathbf{r}_j^{\text{macro}}$ such that the sum of deviations is zero. In the thermodynamic limit, when measurement time and sampling volume is larger than the correlation time and length, the macroscopic value varies smoothly and the deviation represents heat. (Mean value represents one particle and deviation is zero at the other extreme limit. These parts are inseparably mixed in the intermediate "emergent" regime.) The system kinetic energy then splits into macroscopic and microscopic parts, $\langle \text{KE} \rangle = \sum_j^{\text{Species}} \sum_i^{N_j} \frac{1}{2} m_j \left(\langle |\mathbf{v}_{ji}^{\text{macro}}|^2 \rangle + \langle |\delta \mathbf{v}_{ji}|^2 \rangle \right)$, because the cross term cancels out. Potential energy splits in a similar manner, with terms linear in position and velocity being purely macroscopic.

System energy can be computed directly another way. All particles exist in modes of motion. Particle trajectories fluctuate as they jump from mode to mode. The mean transition rate is determined by quantum mechanics but the timing of a transition is unpredictable. Let τ_{jik} be the residence time of particle i of species j in mode k during a measurement. The mean particle position over the duration of a measurement τ_{meas} is the weighted average $\langle \mathbf{r}_{ji} \rangle = \sum_k^{\text{Modes}} \mathbf{r}_{jk} \tau_{jik} / \tau_{\text{meas}}$. The mode spectrum is stable near equilibrium and the mean occupancy is $\langle N_{jk} \rangle = \sum_i^{N_j} \tau_{jik} / \tau_{\text{meas}}$. The total system energy may be computed similarly through the mode energy ε_{jk} to be $E^{\text{system}} = \sum_j^{\text{Species}} \sum_k^{\text{Modes}} \epsilon_{jk} \langle N_{jk} \rangle$. The system heat content can then be deduced by subtracting formation and macroscopic components from total system energy.

Total system energy may change generally by work, conduction of heat, and convection of particles from the outside environment:

$$\Delta E^{\text{system}} = W^{\text{outside}} + \Delta Q^{\text{conduction}} + \sum_j^{\text{species}} \varepsilon_j \Delta N_j^{\text{outside}}\,. \tag{6}$$

Mean measured values are implied for all parameters and properties from here on. Work may change the system macroscopic energy through shaft work, for example, and microscopic energy by pressure applied to internal fluids: $W^{\text{outside}} = W^{\text{macro}} - p\Delta V$. Total outside heat exchange includes conductive flow and heat carried by particles: $\Delta Q^{\text{outside}} = \Delta Q^{\text{conduction}} + \sum_j^{\text{species}} \left(\varepsilon_j - \varepsilon_j^{\text{macro}} - \varepsilon_{0j}\right) \Delta N_j^{\text{outside}}$. The change in constituents includes internal transformations as well as outside exchange: $\Delta N_j = \Delta N_j^{\text{trans}} + \Delta N_j^{\text{outside}}$.

Equation (6) can be rearranged into a form similar to the First Law by separating the macroscopic and formation components:

$$\Delta Q^{\text{system}} = \Delta Q^{\text{outside}} - p\,\Delta V - \sum_j^{\text{species}} \varepsilon_{0j} \Delta N_j^{\text{trans}} + \left(W^{\text{macro}} - \Delta E_{\text{macro}}^{\text{system}} + \sum_j^{\text{species}} \varepsilon_j^{\text{macro}} \Delta N_j^{\text{outside}}\right). \tag{7}$$

The first two terms on the right hand side appear in (1). The third term represents conversion of latent heat. The last term, in parentheses, equals frictional heat generated $W^{\text{friction}} \geq 0$. In the absence of friction, macroscopic work and convective inflow produces an equal change in system macroscopic energy and this term is zero. It is positive, otherwise, because transitions from a less correlated configuration to one more correlated becomes extremely unlikely in the thermodynamic limit; at any time, the current state is coupled to far more mode configurations with a lower proportion of macroscopic energy [5].

The change in internal energy, as envisioned by Clausius in (1), *subtracts* friction and latent heat contribution from the actual gain in heat content,

$$\Delta U = \Delta Q^{\text{system}} - W^{\text{friction}} + \sum_j^{\text{species}} \varepsilon_{0j} \Delta N_j^{\text{trans}}. \tag{8}$$

Consequently, less outside heat need be supplied than in the frictionless case, allowing Clausius to conclude (2). Internal energy U is not equal to system microscopic energy content and the First Law does not represent conservation of microscopic energy.

Note also that the sums in (8) are over species, whereas standard theory only distinguishes substances, so that U is a function of the constituent number of each substance. To conform to this standard, the sum in (8) must refer to substance. Internal energy tracks reactions between different substances but not phase transitions because the number of particles of each substance does not change in that case. Phase transitions are indicated indirectly by the subsequent work and exchanged heat. but this omission regarding internal energy must be accounted for by some other change, namely entropy.

Now construe these general results in the standard structure. First differentiate phase transitions from reactions among substances, $\Delta N_j^{\text{trans}} = \Delta N_j^{\text{phase}} + \Delta N_j^{\text{reaction}}$. The phase of incoming particles must be known for concrete analysis. The latent heat of phase transitions is absorbed into the unknown internal heat content,

$$\Delta U = \left[\Delta Q^{\text{system}} - W^{\text{friction}} + \sum_j^{\text{species}} \varepsilon_{0j} \Delta N_j^{\text{phase}}\right] + \sum_j^{\text{substance}} \varepsilon_{0j} \Delta N_j^{\text{reaction}}. \tag{9}$$

Alternatively, (7) may be substituted into (4) to produce

$$T\Delta S = \Delta Q^{\text{eff}} \tag{10}$$

where the total contribution from all sources of heat is

$$\Delta Q^{\text{eff}} = \Delta Q^{\text{conduction}} + W^{\text{friction}} - \sum_j^{\text{species}} \varepsilon_{0j} \Delta N_j^{\text{phase}} - \sum_j^{\text{substance}} \left(\varepsilon_{0j} + \mu_j'\right) \Delta N_j^{\text{reaction}} + \sum_j^{\text{substance}} \left(\varepsilon_j - \varepsilon_j^{\text{macro}} - \varepsilon_{0j} - \mu_j'\right) \Delta N_j^{\text{outside}}. \tag{11}$$

Reactions consume or produce substances in strict ratios represented by stoichiometric coefficients x_j such that $\Delta N_j^{\text{reaction}} = x_j \Delta N^{\text{reaction}}$ for each unit of reaction. Kinetic balance in equilibrium requires $\sum_j x_j \mu_j = \ln[K]$ where $\mu_j = \varepsilon_{0j} + \mu_j'$ is the standard chemical potential [3]. Reaction rate quotient K is not equal to one. Allowing for multiple reactions to occur simultaneously,

$$\Delta Q^{\text{eff}} = \Delta Q^{\text{conduction}} + W^{\text{friction}} + \Delta E^{\text{latent}} - \sum_i^{\text{reactions}} \ln[K_i]\, \Delta N_i^{\text{reaction}} + \sum_j^{\text{substance}} \left(\varepsilon_j - \varepsilon_j^{\text{macro}} - \mu_j\right) \Delta N_j^{\text{outside}}. \tag{12}$$

IEP is $\Delta Q^{\text{eff}}/T$ omitting outside exchange ($\Delta Q^{\text{conduction}} = \Delta N_j^{\text{outside}} = 0$). The latent energy $\Delta E^{\text{latent}} = -\sum_j^{\text{species}} \varepsilon_{0j} \Delta N_j^{\text{phase}}$ does not appear in the standard theory because substance population doesn't change in phase transitions. A separate term must be inserted manually instead and determined from exchanged heat and pressure work.

Clausius does recognize that phase transition is similar to chemical reaction: "The separation of chemically combined substances is likewise an increase of the disgregation, and the chemical combination of previously isolated substances is a diminution of their disgregation; and consequently these processes may be brought under considerations of the same class as the formation or precipitation of vapour" [2, p. 240]. He uses parameters to represent the fraction of a substance in each phase, but has no direct means to determine the parameter value in a given equilibrium state of coexisting phases. This requires an expression for diffusive flows. Modal analysis yields varying rate quotients specific to each transformation [5].

Consider adapting standard theory to recognize species consistently. If (4) is summed over species rather than only substances, IEP becomes

$$\Delta S^{\mathrm{int}} = W^{\mathrm{friction}} - \sum_{i}^{\mathrm{transformations}} \ln[K_i]\,\Delta N_i^{\mathrm{trans}}\,, \quad (13)$$

including reactions and phase transitions as particle transformations. The rate quotients are not equal to one and so contribute negatively as well as positively, depending on the direction each transformation progresses.

Apart from a possible adiabatic cyclic contradiction, the Second Law appears to be self-consistent in the standard theory, when reaction dynamics are governed by a minimum free energy condition, assuming maximum entropy in equilibrium. Empirical activity coefficients mistakenly subsume all rate quotients and all rate quotients are effectively set to one as a result [3]. Friction remains as the only source of IEP in standard theory and is always positive in the thermodynamic limit.

Negative IEP appears when particle transformations are analyzed rigorously. This result directly contradicts Clausius' entropy law (2). There is no inequality condition in (10) to motivate the Second Law as an indicator of irreversible processes. All energy sources are accounted for in a true energy conservation equation (6). System entropy change simply measures total input heat (11). In any real cyclic processes, there is zero IEP over an cyclic process in which the microscopic state is restored; any production during one stage of such a process then is compensated by reduction in other stages. Where, then, is the weak logical link in standard theory?

Clausius argues convincingly that entropy should not change over adiabatic processes in ideal gas systems, but is far from justified in extending this reasoning to all particle interaction. His proof ultimately rests on the following statements after describing several special cases: "…relying simply on the law established by myself in relation to the working force of heat, it appears to me that but one of the following cases can be possible. Either the above law is correct, in which case the real [capacity for heat] remains the same, not only for the same state of aggregation, but for the different states of aggregation, or the law is not correct, and in this case we have no definite knowledge whatever concerning the real [capacity for heat], and it may equally well be variable within the same state of aggregation as in different states of aggregation. [Section] 9. I believe, indeed, that we must extend the application of this law, supposing it to be correct, still further, and especially to chemical combinations and decompositions. … Heat itself can never, in my opinion, tend to produce [chemical] combination, but only, and in every case, decomposition. … it will be apparent what enormous simplifications the law which we have established is capable, supposing it to be true, of introducing into the doctrine of heat" [2, p. 240].

What an enticing appeal! His entropy law seems to be arguably true under many analyzable cases, revealing a symmetry of the world that makes intuitive sense. Extrapolating to all cases is utterly powerful compared to "having no definite knowledge." Despite criticism and confusion about the Second Law [7], the principle of ever increasing total entropy quickly became the foundation adopted by all later researchers in the field. Investigation has focused on formulating IEP, with ambiguous results after 170 years [8], rather than considering whether the Clausius growth condition is true. This issue is resolved by rigorous dynamic analysis in which transport equations, not entropy, determine spontaneous evolution. [5].

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