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Measures of dissipation

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The availability loss $-\Delta A^u$ in a process is equal to the flow of the extensive thermodynamic quantities multiplied by the respective intensity differences only if the degraded work, the "uncompensated heat" of Clausius, is disposed of into the environment. We define work deficiency as the above product in all situations and relate it to the dissipation bound based on thermodynamic length.

I. INTRODUCTION

While long recognized as important,[1] the problem of choosing appropriate measures for counting dissipation has gained new significance with the rise of interest in finite-time thermodynamics.[2-8] There is a range of interesting optima which present themselves once the constraint of finite time is imposed on a thermodynamic process. Minimizing dissipation is the conservationist's end of this range; maximizing power is the other.

Measuring dissipation amounts to measuring foregone work. Accordingly, different measures of dissipation may be appropriate provided that they are related to how much work was lost in a process. The two most common measures of dissipation are the total loss of available work $-\Delta A^u$ and the entropy production ΔS^u. The past decade has brought forward extensions and new relations for these measures. As one example, we cite finite-time availability[7] which counts only the work which could have been harvested in a finite time τ. Another example is the relation between the loss of availability and the thermodynamic length. Weinhold introduced a metric in the space of thermodynamic equilibrium states using the second derivatives of the internal energy with respect to the extensive variables entropy, volume, mole number, etc. This metric can be used to calculate a distance between two states or the length of a path in this space. Salamon and Berry[5] called this length "thermodynamic length" and they showed that this length can be used to construct a bound for the loss of availability. This bound applies to a class of thermodynamic processes in which all the dissipated energy is taken out of the system. The aim of this paper is to extend these studies to the case of thermodynamic processes in which part of the dissipated energy remains as heat in the system. As this is generally the case for real thermodynamic processes, this constitutes a considerable improvement over the previous studies. We investigate the relation between loss of availability, entropy production, and the bound given by thermodynamic length. The results of our study show that the bound provided by the thermodynamic length no longer exactly bounds the loss of availability but a new quantity which we term "work deficiency." On the other hand, total loss of availability and entropy production are proportional to each other with the constant of proportionality equal to the temperature of the reservoir that defines the scale of availability.

II. DEFINITIONS

As discussed by Tisza,[9] the work of Carnot set out to establish a temperature scale T and a quantity ΔS such that, in close analogy with a water wheel, the maximum work which may be produced when the entropy ΔS moves from T_1 to T_2 is $W^{\max}=(T_1-T_2)\Delta S$. In constructing the chemical potentials μ, Gibbs used this same criterion to again define them in such a way that $W^{\max}$ corresponding to a flow of Δn moles from μ_1 to μ_2 be given by $(\mu_1-\mu_2)\Delta n$. In other words, the thermodynamic intensities $Y^k=\partial U/\partial X^k$ corresponding to the extensities X^k in the energy picture are defined to make the available work from a flow of dX^k from Y_1^k to Y_2^k equal to

$$dW^{\max}=\sum_k (Y_1^k-Y_2^k)dX^k \; . \tag{1}$$

In vector notation, a combined flow from system 1 to system 2 of the quantities $d\mathbf{X}=(dS,dV,dN,\ldots,)$ across intensity differences $\mathbf{Y}_1-\mathbf{Y}_2=(T_1-T_2,p_2-p_1,\mu_1-\mu_2,\ldots,)$ is associated with the available work

$$dW^{\max}=(\mathbf{Y}_1-\mathbf{Y}_2)\cdot d\mathbf{X} \; . \tag{2}$$

If none of that work is captured as a result of the process, it is reasonable to take this sum as one measure of dissipation, representing the loss of available work associated with the flows $d\mathbf{X}$.[5,8]

While some of the work terms in the sum of Eq. (1) may be negative, and hence the corresponding flows are driven by the positive ones, a spontaneous process can only occur, if the sum is positive. This point of view amounts to considering the work $dW^{\max}$ produced (reversibly) by the system and made available for use or disposal somewhere else. Whereas conceptually this is a convenient separation, in a spontaneous process some or all of this work must be degraded into heat: the so-called "uncompensated heat" of Clausius dQ^{Cl},

$$dW^{\max}=dW+dQ^{\mathrm{Cl}} , \tag{3}$$

with dW being that part of the work which is not degraded. If the subsystem in which this heat dQ^{Cl} appears is at a temperature T different from the temperature T_0 of the heat reservoir (the environment) which is used to define availability, then such heat carries a residual availability which represents the work that would result from running a heat engine while letting the heat dQ^{Cl} move to the environment. By this device we can in fact have partial compensation for this "uncompensated" heat. To determine the extent to which such heat is compensated through the residual availability which such heat represents, it becomes important to specify which fraction of $dW^{\max}$ moves to which subsystem at which temperature. We introduce a vector $\boldsymbol{\alpha}=(\alpha_0,\alpha_1,\ldots,\alpha_n,\alpha_\infty)$, $\sum_i \alpha_i=1$, as a convenient method for indicating which fraction of the available work $dW^{\max}$ is added to each of the subsystems participating in the process. For instance, for an actual finite time-thermodynamics optimization of a car engine it is necessary to know which fraction of the energy dissipated by friction at the cylinder rings goes into the working fluid and which fraction goes into the cylinderwalls and thus into the cooling system. Also, $\boldsymbol{\alpha}$ is similar to the heat addition function $h(T)$ used in rational thermodynamics.[10] Of course not all of the available work $dW^{\max}$ needs to be degraded to heat, some may be captured as work. This is accommodated within the formalism by an α_∞ which is the undegraded fraction of $dW^{\max}$. Since this energy has no associated transfer of entropy, we take (for convenience in the formula below[11]) the corresponding T_∞ to be infinite, making $dS_\infty=\alpha_\infty dW^{\max}/T_\infty=0$.

From this new perspective not all of the availability $dW^{\max}$ is (necessarily) lost, and we will modify previous praxis[5,8] in calling the right-hand side (rhs) of Eq. (2) the *work deficiency* dW^d as opposed to calling it the availability loss. This work deficiency dW^d is the total loss of availability which would have resulted if all the available work were lost to the environment. The remaining part includes the latent availability of storing $\alpha_i dW^d$ at $T_i, i=1,\ldots,n,\infty$. Thus the actual loss of availability $-dA^u$ is only $T_0 dW^d \sum_i \alpha_i/T_i$.

This approach counts availability loss by focusing on the flows. While it has the advantage of allowing the separation of the interesting terms in the dissipation, it requires the additional postulate of endoreversibility,[12] i.e., that the thermodynamic systems participating in a process are in internal equilibrium during the process and thus that they have well-defined intensities. While it does not allow focusing on the dissipation from the flows, the more general approach due to Gibbs is to define a state function for availability A. Changes in this function, summed over subsystems, give ΔA^u. We remind the reader that

$$A=U-T_0S+p_0V-\mu_0N,\ldots, \tag{4}$$

where the subscript zero indicates intensities associated with the environment.

In the simple systems primarily discussed in the literature so far it has been advantageous to consider the universe composed of a "system" in which the process proceeds and a "reservoir" or "environment" with fixed intensities with reference to which availability is defined according to Eq. (4). For composite systems, like the ones discussed below and in Ref. 13, summations become more natural if the environment is considered part of the system so that "universe" and "system" become synonymous. Different parts of the system are then termed "subsystems" and serve the same conceptual function as system in the simpler examples. In order to emphasize that environments are fully controllable[13] and at no cost to the process, we will generally call them "baths." Note that this definition includes the traditional notion of an environment having constant intensities. We will reserve the term environment exclusively for the subsystem, whose (constant) intensities define the availability scale.

III. AN EXAMPLE

Consider a system (see Fig. 1) consisting of two subsystems 1 and 2 and an environment 0, each having internal energy $U_i(S_i,V_i)$ with corresponding intensities $p_i=\partial U_i/\partial V_i$, $T_i=\partial U_i/\partial S_i$, in addition to a work reservoir ∞. The intensities of the environment T_0 and p_0 are not affected by any process taking place, and we assume $p_1>p_2$.

We now want to calculate the work deficiency, the loss of availability, and the entropy production resulting from an infinitesimal flow of volume dV from subsystem 2 to 1. This process becomes uniquely defined only after deciding what happens to the work $(p_1-p_2)dV$ gained. In this simple example $(p_1-p_2)dV$ is the entire work deficiency dW^d, and we have to specify which fraction α_∞ of dW^d goes to the work reservoir and which fractions are degraded and go as heat to each of the other three subsystems.

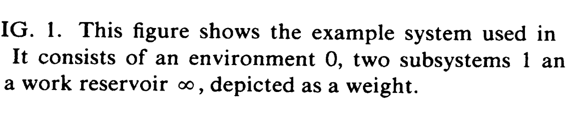

FIG. 1. This figure shows the example system used in Sec. III. It consists of an environment 0, two subsystems 1 and 2, and a work reservoir ∞, depicted as a weight.

For clarity we view the process as consisting of two distinct steps. Step 1 describes the gain of work which in step 2 is partially dissipated into heat at the temperatures of the three subsystems.

Step 1. This reversible step contains no heat flows, $dS_i=0$, but a small volume change $dV_1=dV$, $dV_2=-dV$. Recalling

$$dU_i=T_i dS_i-p_i dV_i \ , \tag{5}$$

$$\begin{aligned} dA_i&=dU_i-T_0 dS_i+p_0 dV_i \\ &=(T_i-T_0)dS_i-(p_i-p_0)dV_i \ , \end{aligned} \tag{6}$$

the availability changes then are

$$\begin{aligned} dA_0&=0 \ , \\ dA_1&=-p_1 dV+p_0 dV \ , \\ dA_2&=+p_2 dV-p_0 dV \ , \\ dA_\infty&=0 \ , \end{aligned} \tag{7}$$

and the work deficiency is

$$dW^d=(p_1-p_2)dV \ . \tag{8}$$

Step 2. Some of this work dW^d is now degraded into heat such that fractions α_i are put into each of the four subsystems resulting in the entropy changes

$$\begin{aligned} dS_0&=\alpha_0\frac{dW^d}{T_0} \ , \\ dS_1&=\alpha_1\frac{dW^d}{T_1} \ , \\ dS_2&=\alpha_2\frac{dW^d}{T_2} \ , \\ dS_\infty&=0 \ . \end{aligned} \tag{9}$$

The corresponding availability changes are

$$\begin{aligned} dA_0&=(T_0-T_0)dS_0=0 \ , \\ dA_1&=(T_1-T_0)dS_1=\left[1-\frac{T_0}{T_1}\right]\alpha_1 dW^d \ , \\ dA_2&=(T_2-T_0)dS_2=\left[1-\frac{T_0}{T_2}\right]\alpha_2 dW^d \ , \\ dA_\infty&=\left[1-\frac{T_0}{T_\infty}\right]\alpha_\infty dW^d=\alpha_\infty dW^d \ . \end{aligned} \tag{10}$$

As the changes in the intensities during steps 1 and 2 are infinitesimally small and were separated only for clarity, we can now combine these steps and calculate the net result of this process. The change of availability of the universe is

$$\begin{aligned} dA^u=\sum_i dA_i&=(p_2-p_1)dV+\left[1-\frac{T_0}{T_1}\right]\alpha_1 dW^d \\ &\quad+\left[1-\frac{T_0}{T_2}\right]\alpha_2 dW^d+\alpha_\infty dW^d \\ &=-dW^d\left[\alpha_0+\alpha_1\frac{T_0}{T_1}+\alpha_2\frac{T_0}{T_2}\right] \\ &=-dW^d\left[\frac{\alpha_0}{T_0}+\frac{\alpha_1}{T_1}+\frac{\alpha_2}{T_2}\right]T_0 \ , \end{aligned} \tag{11}$$

while the change in entropy is

$$dS^u=dW^d\left[\frac{\alpha_0}{T_0}+\frac{\alpha_1}{T_1}+\frac{\alpha_2}{T_2}\right] \ . \tag{12}$$

Equation (11) shows clearly the difference between the work deficiency and the loss of availability for this simple example.

An additional result, which can be easily gained from Eqs. (11) and (12) is

$$dA^u=-T_0 dS^u \ . \tag{13}$$

As this is true for every instant during a process, by integrating we find

$$\Delta A^u=-T_0\Delta S^u \ . \tag{14}$$

A similar relation between ΔA^u or ΔS^u and ΔW^d on the other hand cannot exist in general, as the α_i as well as the T_i of the different subsystem will change in time.

IV. THE GENERAL RELATION BETWEEN ΔA^u AND ΔS^u

Equation (14) has been proved previously for thermal subsystems.[14] We now proceed to prove it in general for an arbitrary number of subsystems interacting with one another, with an environment whose intensities are fixed, and with a work reservoir. We remind the reader that availability is defined with respect to the environment. Each of the subsystems i has an internal energy $U_i(\mathbf{X}_i)$ with $\mathbf{X}_i$ being the extensive variables of subsystem i and $\mathbf{Y}_i=\partial U_i/\partial\mathbf{X}_i$ being the corresponding intensities. Note that $\mathbf{X}_i$ may contain variables such as surface area which are not truly extensive.

For processes in an isolated system, i.e., those which have the property that the changes of all extensities, including U but excluding S, summed over the subsystems, balance,

$$\sum_i d\mathbf{X}_i=\mathbf{0} \ , \tag{15}$$

we have

$$dA^u=-T_0 dS^u \ . \tag{16}$$

Proof. We sum the loss of availability of all subsystems [cf. Eq. (6)],

$$\begin{aligned} dA^u &= \sum_i dU_i - \sum_i \mathbf{Y}_0 \cdot d\mathbf{X}_i \\ &= 0 - T_0 \sum_i dS_i \\ &= -T_0 dS^u \ . \end{aligned} \tag{17}$$

We note the following consequences of Eq. (16).

(i) Equation (16) is independent of the fate of the work lost, i.e., $\boldsymbol{\alpha}$.

(ii) As Eq. (16) is true for every instant of a process, we find by integration,

$$\Delta A^u = -T_0 \Delta S^u \ . \tag{18}$$

(iii) Equation (18) remains true even for *time-dependent* $\boldsymbol{\alpha}(t)$, that is the distribution of the lost work into the different heat baths may change.

(iv) The actual values of ΔA^u and ΔS^u for a given process do depend on $\boldsymbol{\alpha}(t)$.

V. WORK DEFICIENCY

For processes in which flows of extensities $d\mathbf{X}_{ji}$ occur from subsystem j to i,

$$dW^d = \tfrac{1}{2} \sum_{ij} (\mathbf{Y}_i - \mathbf{Y}_j) \cdot d\mathbf{X}_{ji} \ . \tag{19}$$

As a generalization of Eq. (2) this has been referred to in the literature as loss of availability.[5] However, this concurs with the definition of availability as given in Eq. (4) only in the case where this quantity of energy is degraded to heat and put into the environment with respect to which availability is defined. Only for $\alpha_0 = 1$ and $\alpha_i = 0$, $i > 0$ do they coincide. In order to avoid any ambiguity we term Eq. (19) the *work deficiency*, as it is the work which in principle could have been extracted from the process.

This distinction becomes particularly important when we realize that the bound on dissipation derived from thermodynamic length[5]

$$W^d \geq \varepsilon L_U^2 / \tau \tag{20}$$

was derived on the basis of Eq. (2) and thus properly is a bound on work deficiency rather than availability loss.

The bound in Eq. (20) is a statement about losses necessarily incurred in bringing the thermodynamic system along the path having the thermodynamic length L. The associated argument begins with Eq. (2) for one subsystem and one bath and uses as flows the vector $d\mathbf{X}$ of changes in extensities required by the condition that the given path be followed. As such, any uncompensated heat can only appear in the bath or in the environment, i.e., $\alpha_0 + \alpha_1 = 1$, $\alpha_2 = 0$. In many applications W^d is the quantity of interest since there is no (reasonable) possibility of recovering the availability $\alpha_1 W^d$ associated with extra heat content of our bath. One example is the cooling water of a car engine, which by its high temperature possesses some availability which, however, is not used. Thus $W^d > -\Delta A^u$. The analogous expression to Eq. (20),

$$\Delta S^u \geq \varepsilon L_S^2 / \tau \ , \tag{21}$$

for entropy production needs no such qualifications and gives a general bound for the entropy produced in using a bath to cause a system to traverse a given sequence of states.

One property of the work deficiency is that it does not in all cases bound the loss of availability. Consider for example the somewhat unusual situation of a system which degrades its work deficiency to heat in a subsystem with a temperature lower than that of the environment. If in Eq. (11) there would be a T_j with $T_j < T_0$ and $\alpha_j = 1$, $\alpha_{i \neq j} = 0$, then the loss of availability $-\Delta A^u$ would be greater than W^d. This comes about by the fact that one has forgone a possible work gain from transporting that energy from T_0 to the lower T_j.

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