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Thermodynamic Length and Dissipated Availability

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New expressions for the availability dissipated in a finite-time endoreversible process are found by use of Weinhold's metric on equilibrium states of a thermodynamic system. In particular, the dissipated availability is given by the square of the length of the corresponding curve, times a mean relaxation time, divided by the total time of the process. The results extend to local thermodynamic equilibrium if instead of length one uses distance (length of the shortest curve) between initial and final states.

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The results presented below give an important tool for finding limits on the efficiency of operation of thermodynamic processes in finite time. We have been pursuing various approaches to this problem for several years,[1] but the results below give a new inroad for a remarkably general class of processes by providing expressions for the inherent irreversibility quantified by the loss of available work: the availability not transformed into work during the process. This *dissipated* availability is sometimes called "irreversibility."[2] The dissipated availability dA_u is related to the entropy production dS_u by $dA_u = TdS_u$.

We derive expressions for the availability dissipated when a thermodynamic system undergoes a process during which it may be assumed to be in internal equilibrium, though interacting with an environment, which is also in equilibrium. Since the dissipated availability is an extensive quantity, an extension of our expressions to local thermodynamic equilibrium is immediate. These expressions involve the thermodynamic length introduced by Weinhold[3,4] and hint at the existence of a temporal element in the classical formalism dealing only with equilibrium.

We assume that the time scales for internal relaxation of system and surroundings are much shorter than the time scale on which system and surroundings interact. This implies that we may consider both system and surroundings to be in equilibrium states at each instant of time. This assumption is already among the postulates for local thermodynamic equilibrium. The macroscopic form of this assumption was introduced by Rubin[5]: a process is *endoreversible* provided the subsystems participating in the process are in internal equilibrium at each instant. The expression given below for dissipation in a shock wave hints that our expressions for the dissipated availability are valid in a context wider than our derivations based on endoreversibility show.

Besides the total time for the process, our expressions for the dissipated availability include only one nonequilibrium parameter: the mean relaxation time. The interpretation of this relaxation time is straightforward for processes during which the system and its environment are close to equilibrium with each other. This automatically holds (except perhaps at the boundary) if the local thermodynamic equilibrium model is appropriate.

We now define the notion of thermodynamic length. The second-derivative matrix of the internal energy U with respect to extensive variables $X = (X_1, \ldots, X_n)$,

$$\eta_{ij} = \partial^2 U / \partial X_i \, \partial X_j , \tag{1}$$

was called the "stiffness tensor" by Tisza.[6] According to the traditional view,[6,7] $\eta = [\eta_{ij}]$ is the second fundamental form[8] of the equilibrium surface $U = U(X)$ and, for small displacements $\Delta X = X - X^0$, $\Delta X^t \eta \Delta X$ measures the vertical distance between the surface and its tangent plane at some point $X^0 = (X_1^0, \ldots, X_n^0)$. If $\tilde{U} = U^0 + \nabla U|_{X^0} \cdot \Delta X$ is the equation of the tangent plane, then

$$U - \tilde{U} = \tfrac{1}{2} \sum_{i,j} \eta_{ij} \Delta X_i \Delta X_j = \tfrac{1}{2} \Delta X^t \eta \Delta X . \tag{2}$$

Gibbs[7] identified this (2) as the available work, now called availability or energy, that may be obtained from a system that can return from its displaced state at X to the state of equilibrium with its environment at X^0. Denoting the intensive variables by $Y_i = \partial U/\partial X_i$, we note that, again for small displacements from equilibrium,

$$\Delta Y_i = \sum_j \eta_{ij} \Delta X_j \,. \tag{3}$$

Weinhold showed[3] that the first and second laws of thermodynamics endow η_{ij} with the positivity required to make it a metric, or first fundamental form, on the surface of thermodynamic states, wherever the matrix η is nonsingular.[9] Consider a path γ on the space of thermodynamic states. The length L of γ as measured by η is independent of parametrization, but may be written in terms of a parameter ξ, $0 \leqslant \xi \leqslant \xi^{\max}$, so that

$$\begin{aligned} L &\equiv \int \Big[\sum_{i,j} \eta_{ij}\, dX_i dX_j\Big]^{1/2} \\ &= \int_0^{\xi^{\max}} \left[\sum_{i,j} \eta_{ij} \frac{dX_i}{d\xi}\frac{dX_j}{d\xi}\right]^{1/2} d\xi \\ &= \int_0^{\xi^{\max}} \left(\frac{dX^t}{d\xi}\,\eta\,\frac{dX}{d\xi}\right)^{1/2} d\xi . \end{aligned} \tag{4}$$

The dimensions of L are those of $(\text{energy})^{1/2}$ or, if specific energy is used, L has the dimensions of speed. We call L the "thermodynamic length" of the path γ. This quantity may be evaluated easily for a variety of processes, from a knowledge of the equation of state of the working material. It was shown[10] that L corresponds to the change in a mean molecular velocity characterized by the particular nature of the process defining γ.

The physical interpretation of the thermodynamic length turns out to be much richer and more important than we had recognized. We show here that it is intimately connected with expressions for the dissipated availability in a thermodynamic process. To be more precise, we recall the term "endoreversible," introduced by Rubin[5]: an *endoreversible* process is a process in which the system itself undergoes only quasireversible transformations and all irreversibilities occur at the boundary between the system and its environment. Formally, we assume that such a process is defined by $X(t)$, the associated $Y(t)$, and the intensities $Y^e(t)$ of the environment, where $0 \leqslant t \leqslant \tau$ may be time or just a convenient parameter for the process. The best way to imagine the variation of $Y^e(t)$ is as a succession of reservoirs that the observer can put into contact with the system in order to drive it along the desired path $X(t)$. The availability dissipated by such a process is given by

$$\begin{aligned} \Delta A_u &= \int_0^\tau \Big\{\sum\nolimits_i [Y_i^e(t) - Y_i(t)]\, dX_i/dt\Big\}\, dt \\ &= \int (Y^e - Y)\cdot dX . \end{aligned} \tag{5}$$

Note that this integral is also independent of parametrization. ΔA_u is the change in the availability of this two-system universe. Such availability changes typically represent losses, although, for example, part of the energy in the $(P^e - P)dV$ term (where P and V represent pressure and volume, respectively) may go into the kinetic energy of a piston which may be recovered. The assumption inherent in calling ΔA_u the dissipated availability is that all work extracted from the process be counted as part of the change in internal energy of a work reservoir in the environment.

We now define $X^e(t)$ by requiring

$$Y^e(t) - Y(t) = \eta\,|_{X(t)} \cdot [X^e(t) - X(t)] \tag{6}$$

to hold. Since η is nonsingular,[9] $X^e(t)$ is well defined. For Y^e near Y, X^e is the state of our system which would be in equilibrium with the environment at Y^e; see Eq. (3). Substituting (6) into (5) and changing to arc length S as our parameter, we get

$$\Delta A_u = \int_0^L (dX/dS)^t\, \eta (X^e - X)\, dS . \tag{7}$$

Since S is arc length along $\gamma = X(t)$, dX/dS is a unit vector. The integrand is just the dot product of $X^e - X$ and dX/dS, relative to the metric η. Therefore the integrand is just the length of the projection of $X^e - X$ onto the direction dX/dS tangent to γ (see Fig. 1). We call this projected distance the *lag distance*, and denote it by D. Equation (7) can be interpreted in differential form to say that the rate of change of ΔA_u per unit distance moved in any direction is the length D of the projection of $X^e - X$ along that direction. A convenient form of (7) may be obtained by multiplying and dividing by L:

$$\Delta A_u = \bar{D} L , \tag{8}$$

where $\bar{D}$ is the average lag distance along the path γ.

Since D, and hence ΔA_u, depends only on the component of $X^e - X$ along $\dot{X}$ but is otherwise independent of the exact location of X^e, we may replace $X^e(t)$ in (7) by (see Fig. 1)

$$\tilde{X}^e = X + D\, dX/dS . \tag{9}$$

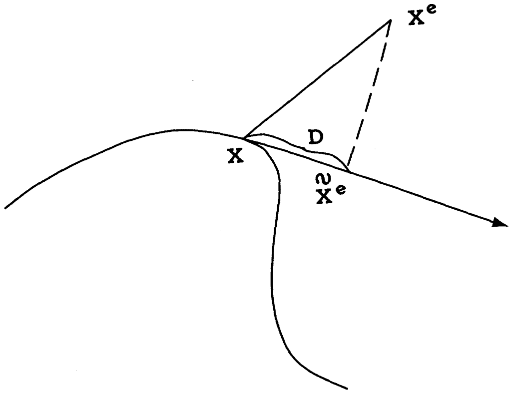

FIG. 1. The path $\gamma = X(t)$ in the space of extensive variables of the system. dX/dS is the unit tangent and $\tilde{X}^e$ is the projected state of the environment. D is the lag distance.

Though all the formulas remain valid generally, for the sake of interpretations it is convenient to assume that η is constant, an approximation which is good only for $\tilde{X}^e$ near X. Then we can identify D with the distance from X to $\tilde{X}^e$. We can also interpret $\tilde{X}^e$ as the state of equilibrium of our system in contact with an environment Y^e provided displacements from X are constrained to be tangential to γ at X. This follows since the availability for the system at state X is $(X^e - X)^t \times \eta(X^e - X)$, which is minimum for $X = \tilde{X}^e$. In this sense we interpret D as the distance between the state of our system and its state of equilibrium with the environment.

We now define the *lag time* $\epsilon = D/(dS/dt)$. Then

$$\tilde{X}^e = X + \epsilon\, dX/dt \tag{10}$$

and if we take ϵ small (again only for the sake of interpretation), we get

$$\tilde{X}^e \simeq X(t+\epsilon), \tag{11}$$

explaining our choice of a name for ϵ.

For $\tilde{X}^e$ near X, our system is near equilibrium for the aforementioned equilibration process with ΔX constrained to be parallel to $\dot{X}$. In such an equilibration process D decays exponentially with rate constant $-\epsilon^{-1} = (dD/dt)/D$, i.e., with relaxation time ϵ.

Using ϵ in (7) and switching to time t as the parameter gives

$$\Delta A_u = \int_0^\tau \frac{dX^t}{dt}\, \eta \frac{dX}{dt}\, \epsilon\, dt\,, \tag{12}$$

which gives

$$\Delta A_u = \bar{\epsilon} \int_0^\tau \dot{X}^t \eta \dot{X}\, dt\,, \tag{13}$$

where $\bar{\epsilon}$ is mean lag time. Note that the average of ϵ is taken over time and hence is dependent on parametrization, while the average of D is taken over arc length and is independent of parametrization. The parametrization along γ also affects the integral in (13). Its range of possible values is indicated by[11]

$$\int_0^\tau \dot{X}^t \eta \dot{X}\, dt \geqslant \left[\int_0^\tau (\dot{X}^t \eta \dot{X})^{1/2} dt \right]^2/\tau = L^2/\tau. \tag{14}$$

This inequality can be deduced either by minimizing the integral on the left over possible parametrizations on $[0, \tau]$, or by the Cauchy-Schwartz inequality.[12] Using inequality (14) in (13) we arrive at our central result,

$$\Delta A_u \geqslant \bar{\epsilon} L^2/\tau, \tag{15}$$

with equality only for the most favorable time parametrization of γ, i.e., the one for which

$$|\dot{X}| = (\dot{X} \eta \dot{X})^{1/2} = \text{const} = L/\tau. \tag{16}$$

This shows that for processes with given mean lag time $\bar{\epsilon}$, the process dissipates minimum availability when it proceeds at constant speed. We may also interpret (15) to say that for an endoreversible process, the dissipated availability is bounded by the mean lag time times the square of the Weinhold length L divided by the total time of the process.

Bounds on ϵ or $\bar{\epsilon}$ obtained from a detailed knowledge of the relaxation times during a process can further be used to bound ΔA_u. For example, suppose that each degree of freedom X_i has an associated constant relaxation time ϵ_i. Then $\bar{\epsilon}$ is the weighted average of the ϵ_i, where the weight of ϵ_i is given by the dissipation $\int_\gamma (Y_i^e - Y_i) dX_i$ in the ith degree of freedom. In particular the smallest relaxation time $\min_i\{\epsilon_i\}$ can be used as a bound for $\bar{\epsilon}$.

A general bound can be given for ΔA_u even when the ϵ_i are not constant, but a bound is known for the states along γ (or for a region containing γ). In fact the use of any such bound can be extended to a process which proceeds via states of local equilibrium. Let $\underset{\sim}{\epsilon}$ be such a bound. Assume that the paths followed by different elements of the fluid all begin and end at the same equilibrium states X_0 and X_1. Then L^2 for any such path is greater than or equal to $[d(X_0, X_1)]^2$, the square of the length of the shortest such path, and using the fact that L^2 is extensive we have

$$\Delta A_u \geqslant \underset{\sim}{\epsilon} [d(X_0, X_1)]^2/\tau. \tag{17}$$

A slightly different lag time

$$\epsilon' = D\tau/L \qquad (18)$$

is obtained on dividing D by the average speed L/τ rather than the instantaneous speed dS/dt. ϵ' has the advantage that we get an equality version of (15),

$$\Delta A_u = \bar{\epsilon}' L^2/\tau . \qquad (19)$$

It follows from (14) that

$$\bar{\epsilon}' \geqslant \bar{\epsilon} \qquad (20)$$

with equality only for a constant-speed process.

We consider two examples. The availability transferred to flow velocity during the passage of a shock wave was seen in Ref. 10 to be L^2. This implies that if an endoreversible model may be used for such a process, it must have $\bar{D} = L$ and $\epsilon' = \tau$, i.e., a mean lag distance equal to the length of the process and a mean lag time equal to the time of the process. Next consider a very different example provided by the endoreversible isothermal heating of an ideal gas. If we assume very fast pressure equilibration, i.e., $p^e = p$, and Newton's law heat transfer to the gas through conductance K, we find $\bar{\epsilon}' = \bar{\epsilon} = R/K$ for heating at constant speed ($\epsilon = 0$).

Above we found bounds for the inherent irreversibility as measured by the dissipated availability in a thermodynamic process. Except for one parameter—the mean relaxation time—the bounds involve only equilibrium properties of the system. If the process proceeds via states of equilibrium of the system, the bounds involve L^2, the square of the thermodynamic length of the process. If the process proceeds via states of local thermodynamic equilibrium, the bounds involve d^2, the square of the thermodynamic distance (length of the shortest path) between initial and final states. Although the above arguments apply only in these two cases, some evidence points to their validity in an even wider context and reveals a hitherto unrecognized temporal element within the formalism of equilibrium thermodynamics.

The extension of these lines of reasoning to local thermodynamic equilibrium as well as further examples and connections between Weinhold's metric and other useful metrics in thermodynamics will be discussed elsewhere.[13]

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