Thermodynamics in finite time. II. Potentials for finite-time processes

Peter Salamon, Bjarne Andresen, and R. Stephen Berry

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

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Within the context of conventional time-independent thermodynamics, an algorithm is developed to construct potentials $\mathcal{P}$ that define the extremal values of work for processes with arbitrary constraints. An existence theorem is proved that demonstrates that such potentials $\mathcal{P}$ can be given for any quasistatic process. This theorem extends the capability of thermodynamics from reversible processes to one class of time-dependent processes. A corollary shows how such potentials can be constructed for systems whose time dependence is first order. A final theorem shows the equivalence of the extremal work derived by solution of an optimal control problem with the work derived as a change in the generalized potentials, $\Delta \mathcal{P}$. Examples are given to illustrate the constructions.

I. INTRODUCTION

The three laws of thermodynamics were conceived about irreversible processes. The subsequent development of the subject however turned away from irreversible processes and focused on equilibrium systems. This happened even though many questions which gave the subject its original impetus remained unanswered. Examples of such questions are, as follows: (1) What is the least energy ΔE required by a given machine, to produce a given work W in time t? (2) What is the most work W that can be produced by a given machine in time t, utilizing a given energy ΔE? (3) What is the most efficient way to run a given thermodynamic process in finite time?

Classical thermodynamics does not try to answer these questions, although it does give a fairly complete description of equilibrium states and reversible processes. The only facts it tells us about real processes is that they always produce less work and more entropy than the corresponding reversible processes.[1] Reversible processes, however, are possible only in the limit of infinite time. But no one wants to run a factory infinitely slowly, and in practice engines seldom attain more than 30–40% of the reversible efficiency.[1]

We should be capable of extending the classical theory to at least quasistatic processes. (We take a process to be quasistatic if the internal relaxation times of the system are much shorter than times characterizing interactions between system and surroundings.[1]) This would be a significant extension, since quasistatic processes happen in finite time, produce entropy, and provide an excellent approximation to many real processes. Conventional irreversible thermodynamics[2,3,4] has become increasingly powerful but its micro, dif-

ferential viewpoint does not lend itself to global questions such as those stated above.

The methods of optimum control theory[5] provide a natural way to attack the above questions for quasistatic processes. We can express the work as an integral and use the calculus of variations to find the process which optimizes that integral. This approach, although very useful in a precise formulation of problems, almost always results in cumbersome nonlinear differential equations. Analytic solutions have been found only for the simplest examples.[5,6] For this reason, we have examined several other approaches,[6,7] and results to date seem to indicate that much can be accomplished in the field.

Below, we present one such approach toward a theory of processes: the construction of thermodynamic potentials for finite-time processes. The word "potential" will be used to mean a function of state whose changes give (or bound) the value of a process variable such as heat or work.

In Sec. II we review the classical theory in the context of processes. We then proceed (in Sec. III) to examine the classical Legendre transform, and we extend it to the general reversibly coupled system. In Sec. IV we present an original theorem about the existence and uniqueness of potentials for quasistatic processes. We go on (Sec. V) to present the algorithm for the construction of potentials in some time dependent examples and conclude (Sec. VI) with the connection of the theory to a variational approach.

II. REVIEW OF THE CONCEPTUAL HISTORY (REF.8)

Thermodynamics started as a subject dealing with practical energy conversion, especially in the operation of steam engines.[9] The first law asserts that the process variables heat and work

can have identical effects on a system.[10] The second law asserts that heat flows spontaneously only from a body at a higher temperature to a body at a lower temperature. These two laws were used to construct two functions of state: the internal energy E and the entropy S. We will see in Sec. IV how the technique of using process variables to construct functions of state can be extended to a more general setting.

Gibbs used the state variables E and S to characterize equilibrium states.[11] The success of the equilibrium theory soon led to the development of statistical mechanics and a microscopic theory of equilibrium states. This evolution of the focus of the theory left the questions of optimality for irreversible processes to the engineers. The engineers in turn responded with the traditional techniques of experimental design,[12,13] specific to each device or process.

The one mathematical technique that the Gibbsian formalism provides for processes is the Legendre transform. This is a way of constructing thermodynamic potentials (free energies) for certain reversibly coupled processes. In the following sections, we discuss this classical construction and proceed to extend it to progressively larger classes of processes.

III. LEGENDRE TRANSFORM FOR REVERSIBLY COUPLED SYSTEMS

A. Classical Legendre transforms

Recall that the work for a reversible process bounds the work for all irreversible processes between the same states and with the same integrals of motion, e.g., the isobaric irreversible work done by a system is always less than the isobaric reversible work done by the same system. In a reversible process heat and work can be expressed as differential forms on the space of functions of state,[14] e.g.,

$$đQ = TdS, \quad đW = P\,dV. \tag{1}$$

Now given an integral of motion (e.g., constant pressure) we can make these differential forms exact by adding a zero. In the constant pressure case, this "zero" is the differential form $V\,dP$. If we add this form to $đW$ and $đQ$, we get (using the first law of thermodynamics in the form $dE = T\,dS - P\,dV$)

$$đW = P\,dV = P\,dV + V\,dP = d(PV),$$

$$đQ = T\,dS = dE + P\,dV = dE + P\,dV + V\,dP = d(E + PV).$$

The table below shows the results of this procedure for the classical examples.

Process type	Zero along process	Integrating form	Process variable	Potential
Isobaric	dP	$V\,dP$	$P\,dV$	PV
			$T\,dS$	$E + PV$
Isothermal	dT	$S\,dT$	$P\,dV$	$TS - E$
			$T\,dS$	TS
Isochoric	dV	$-P\,dV$	$P\,dV$	0
			$T\,dS$	E
Isentropic	dS	$-T\,dS$	$P\,dV$	$-E$
			$T\,dS$	0

The construction as described above can be readily generalized.[15] For example, we could calculate the work potential for an ideal gas in an adiabatic process by using the integral of motion $PV^\gamma = $ const:

$$đW = P\,dV = P\,dV + V^{1-\gamma}/(1-\gamma)\,d(PV^\gamma)$$

$$= d[PV/(1-\gamma)]. \tag{2}$$

This calculation yields the work potential $PV/(1-\gamma)$ whose differential is of course the same as dE, the previously calculated potential for an isentropic process, since in this case

$$dE = P\,dV - T\,dS = P\,dV.$$

The technique above does more than provide different ways to re-derive the classical potentials. It can calculate *new* potentials as well.

B. Nonclassical examples

1. Example 1: Spherical system with constant surface tension

Consider a spherical system in equilibrium with its elastic surface of constant surface tension. The actual system inside the surface can be any fluid. Even the amount of fluid inside the surface

can vary. Recall the well-known expression[16] for
the increase in pressure inside a spherical sys-
tem with radius r and surface tension $\hat{\gamma}$,

$$P = P_{ex} + 2\hat{\gamma}/r \ . \tag{3}$$

When rearranged, this becomes an equation in
pressure and volume,

$$V^{1/3}(P - P_{ex}) = (16\pi/3)^{1/3}\hat{\gamma} \ . \tag{4}$$

This equation says that $V^{1/3}(P - P_{ex})$ is an integral
of motion for the fluid inside the surface. Using
this integral of motion, we find a work potential
for a fluid in equilibrium with the surface,

$$dW = P\,dV = P\,dV + \tfrac{3}{2}V^{2/3}d\left[V^{1/3}(P - P_{ex})\right]$$

$$= d\left[(V/2)(3P - P_{ex})\right] \ . \tag{5}$$

The method of finding the zero form to be added
is described in Part C of this section. The work
potential for the coupled system: surface + fluid is
$\mathcal{P} = \tfrac{1}{2}V(3P - P_{ex})$. This means that the work done by
such a coupled system is given by the change in
the potential function $\mathcal{P}$.

2. Example 2: Cylinder with a spring-loaded piston

Consider a fluid in a cylinder equipped with a
spring-loaded piston. (Again the amount of fluid
need not stay constant.) We examine the work
done by the fluid-spring system maintained in in-
ternal equilibrium, i.e., the pressure of the fluid
always balancing the force of the spring. If k is
the force constant of the spring and A is the sur-
face area of the piston, then in order to maintain
zero net force F_{net} on the piston during a change in
the pressure of the fluid, the spring must respond.
This response of the spring can be used to give a
zero along the path, and therefore an integral of
motion:

$$F_{net} = A\,dP - (k/A)\,dV = d(AP - kV/A) = 0 \ ,$$

therefore   (6)

$$AP - kV/A = \text{const.}$$

We can then use this integral of motion to find a
potential for work done by the fluid-spring system.

$$dW = P\,dV = P\,dV + (A/k)\,Pd(AP - kV/A)$$

$$= d(A^2P^2/2k) = d\mathcal{P} \ . \tag{7}$$

The general algorithm for finding the factor A/k
is given in the next section. Once again the work
done by the coupled system is bounded by the
change in the potential function $\mathcal{P} = A^2P^2/2k$.

C. General reversible coupling

We now examine the above construction of poten-
tial functions for reversibly coupled systems in

general. It is a tool for calculating the work or
heat extracted from a composite system in in-
ternal equilibrium. This composite system, for
the classical examples, is made up of the thermo-
dynamic system of interest, and one or more of
the following: constant pressure reservoir, con-
stant temperature reservoir, ideal rigid vessel
(constant volume reservoir), or ideal insulated
vessel (constant entropy reservoir). The two
examples above show how we can consider more
generally coupled systems, when equilibrium be-
tween the coupled systems exists. The potential
function is obtained by using the condition that
equilibrium be maintained to find an integral of
motion for one of the coupled systems. This in-
tegral of motion can then be used to integrate the
inexact differential forms dW and dQ to give po-
tentials for these flows. We thus get the work
(or heat) extracted from a coupled system ex-
pressed as a change in a function of state of one
of the coupled systems.

The actual construction is as follows. Given the
integral of motion $g(P, V) = \text{constant}$, we look for
a function $f(P, V)$ such that $P\,dV + f\,dg$ is an exact
differential. To this end we can expand and get

$$P\,dV + f\,dg = P\,dV + f\left(\frac{\partial g}{\partial P}dP + \frac{\partial g}{\partial V}dV\right)$$

$$= \left(P + f\frac{\partial g}{\partial V}\right)dV + \left(f\frac{\partial g}{\partial P}\right)dP \ . \tag{8}$$

We then equate cross derivatives giving

$$\frac{\partial(P + f\,\partial g/\partial V)}{\partial P} = 1 + \frac{\partial f}{\partial P}\frac{\partial g}{\partial V} + f\frac{\partial^2 g}{\partial P\partial V} = \frac{\partial(f\,\partial g/\partial P)}{\partial V}$$

$$= \frac{\partial f}{\partial V}\frac{\partial g}{\partial P} + f\frac{\partial^2 g}{\partial V\partial P} \ . \tag{9}$$

Rearrangement yields the partial differential equa-
tion

$$\left(\frac{\partial f}{\partial V}\right)_P\left(\frac{\partial g}{\partial P}\right)_V - \left(\frac{\partial f}{\partial P}\right)_V\left(\frac{\partial g}{\partial V}\right)_P = \{f,g\}_{P,V} = 1 \ ,$$

$$\tag{10}$$

where $\{\cdots\}$ denotes the Poisson bracket. Given a
solution f, we form the exact differential $P\,dV$
$+ f\,dg = d\mathcal{P}$ and obtain a potential function $\mathcal{P}$. We
shall refer to the construction of an exact differ-
ential for a reversible process by this technique
as a Legendre construction. The existence and
uniqueness of solutions is discussed in Theorem 1
below. We consider an example of the nonunique-
ness of solutions for the cylinder with a spring-
loaded piston before stating and proving the results
in general.

3. Example 3: Nonuniqueness of solutions

We re-examine the cylinder with a spring-loaded piston example. For this example we have the integral of motion $g = AP - kV/A$. Substituting this g into Eq. (1) gives

$$A \left(\frac{\partial f}{\partial V} \right)_P + \frac{k}{A} \left(\frac{\partial f}{\partial P} \right)_V = 1 . \tag{11}$$

Recall that we are interested in *any* solution f of this equation and can therefore choose $\partial f/\partial V = 0$, giving $f = AP/k$. This was the f used in the solution of example 2 that give $\wp = A^2 P^2/2k$. We could as well have chosen $\partial f/\partial P = 0$, giving $f = V/A$. We now find

$$dW = P\,dV = P\,dV + (V/A)\,d(AP - kV/A)$$

$$= d(PV - kV^2/2A^2) = d\wp'$$

and a "different" potential $\wp' = PV - kV^2/2A^2$. Note however that the two potentials $\wp$ and $\wp'$ in this example have the property

$$\Delta(\wp - \wp') = \Delta\wp - \Delta\wp' = \Delta(A^2 P^2/2k) - \Delta(PV - kV^2/2A^2)$$

$$= (1/2k)\,\Delta(AP - kV/A)^2 = (1/2k)\,\Delta g^2 = 0 \tag{12}$$

that their difference is an integral of motion, so that the derived process variable remains the same. The fact that this is always the case is proved in Theorem 1 below.

Theorem 1

Suppose we are given a function $g(P, V)$, continuously differentiable on an open set U in P, V space. If the vector ∇g is zero on at most a finite number of points in U, then there exist continuously differentiable functions $f(P, V)$ and $\wp(P, V)$ such that $d\wp = P\,dV + f\,dg$. Furthermore if $f, \wp$ and $f', \wp'$ are any two pairs of functions with the above property, then $f - f'$ and $\wp - \wp'$ can be expressed as functions of g.

We pause before the proof of the theorem for a brief discussion of its assumptions. In stating this theorem, we deal with only two variables, for convenience only, because the argument can be made without recourse to techniques of differential geometry. The general case is covered in Corollary 3, below. The smoothness conditions on g are present so standard existence theorems from the theory of partial differential equations may be applied. The condition that the gradient be non-zero has an easy physical interpretation. We will be interested in a process for which g is a constant of motion. In that case the *directional* derivative of g along the process trajectory is zero. This condition assures that the gradient of g is locally

orthogonal to the trajectory of the process. We can think of this relation as the information content of the constraint g = constant on the trajectory. Whenever $\nabla g = 0$, the directional derivative of g is zero for every direction, not only in the direction of the process. Hence, if $\nabla g = 0$ at more than a finite number of points along the path, there is a region in which g cannot give information about the process.

Proof. If $\nabla g \neq 0$ then either $\partial g/\partial V \neq 0$ or $\partial g/\partial P \neq 0$. Recall that in order for $d\wp$ to equal $P\,dV + f\,dg$, we must have $\{f, g\} = 1$. If g satisfies our hypotheses, then this equation is a linear partial differential equation with continuous function coefficients not all of which vanish, and we can invoke the standard existence theorem from the theory of partial differential equations[17] to insure that f exists on the entire domain U.

As for uniqueness, consider any two solutions $f, \wp$ and $f', \wp'$. We first show that the function $\wp - \wp'$ can be expressed as a function of g. We have

$$d(\wp - \wp') = d\wp - d\wp' = (P\,dV + f\,dg) - (P\,dV + f'\,dg)$$

$$= (f - f')\,dg . \tag{13}$$

Since g is not a constant function either we can express $\wp - \wp'$ as a function of g, or the difference $\wp - \wp'$ and g form (at least locally) a coordinate system in P, V space. To show that the latter is not the case we show that the Jacobian of the coordinate transformation (P, V) into $(g, \wp - \wp')$ equals zero, which means that the two functions considered are not a good coordinate system. The Jacobian of the coordinate transformation is

$$\frac{\partial(\wp - \wp', g)}{\partial(P, V)} = \begin{vmatrix} \partial(\wp - \wp')/\partial P & \partial g/\partial P \\ \partial(\wp - \wp')/\partial V & \partial g/\partial V \end{vmatrix}$$

$$= \frac{\partial(\wp - \wp')}{\partial P} \frac{\partial g}{\partial V} - \frac{\partial(\wp - \wp')}{\partial V} \frac{\partial g}{\partial P} . \tag{14}$$

This is the determinant of the matrix whose columns are the components of the vectors dg and $d(\wp - \wp')$. Since a determinant is an anti-symmetric function of its column vectors, this Jacobian vanishes since by Eq. (13) dg and $d(\wp - \wp')$ are multiples of each other. Therefore $\wp - \wp'$ can be expressed as some function $F(g)$. Now we get using (13)

$$f - f' = d(\wp - \wp')/dg = dF(g)/dg = G(g) \tag{15}$$

for some function $G(g)$, which is *not* dependent on any other variables, and the theorem is proved.

In the event that g is an integral of motion, we call f its conjugate[18] and $\wp$ its potential. We can then express the result of the theorem above as follows.

Corollary 1

Given an integral of motion, any two conjugates, as well as any two potentials, of the integral of motion differ by some integral of motion.

Process type	Zero along process	Integrating form	Process variable	Potential
Constant g	dg	$f\,dg$	$P\,dV$	$\mathcal{P} = \int (P\,dV + f\,dg)$
			$T\,dS$	$\mathcal{P}^* = E + \mathcal{P}$

where the integral in the table is independent of path.

IV. EXISTENCE THEOREM FOR POTENTIALS OF QUASISTATIC PROCESSES

We proceed to extend the construction of potential functions to quasistatic processes. Since some variation exists in the usage of the term "quasistatic" we begin with a careful examination of the meaning of the term.

Description of most real processes is complicated by the fact that the uniformity of the system is disrupted during the process. Variables such as temperature and pressure cannot be assigned a single real value. The nonuniformity makes the number of degrees of freedom (independent observables) infinite. There are however real processes with only a finite number of degrees of freedom. A very important subset of the finite degree of freedom processes are quasistatic. Recall[1] that a process Π is quasistatic for a system Σ if and only if the relaxation times of the system Σ are negligibly short compared to the time scale of the process Π. A small displacement from equilibrium causes a spontaneous process to occur in Σ, in zero time compared with times of interaction with the outside. Hence Σ is in *internal* equilibrium after each displacement so that every state of Σ during the process Π is a state of internal equilibrium. We can consider the process Π as a time-parametrized sequence of equilibrium states of Σ. If we ignore what happens outside the system, then this time-parametrized curve in the space of equilibrium states is a complete description of the process. If we wish to distinguish between a quasistatic process that goes completely dissipatively and the "same" process proceeding with some nondissipative work exchange, we have to look outside Σ and specify more than just the sequence of its equilibrium states. We can, for example, insist that in order for two processes to be the same they must both produce the same amount of work (or power, entropy, etc.) as a function of time. We show below that such func-

Before we proceed to the irreversible constructions, note that we can now extend the table of Legendre transforms by adding the reversibly coupled case.

tions of time can be expressed (represented by) functions of the equilibrium states. For example, we can find a function of state whose changes are the values of the useful work delivered by the process. We again call such free energy-like functions *potentials*.

We emphasize that quasistatic processes provide a far more realistic model of real processes than do reversible ones, for which equilibrium between Σ and surroundings is required. In order to reverse a quasistatic process, we have to convert work to heat. Quasistatic processes also produce entropy and proceed in finite time.

Theorem 2

Suppose given a system Σ a quasistatic noncyclic process Π of Σ. (For cyclic processes, each branch must be treated separately.) The process Π is given by the time-parametrized curve $\sigma(t)$ of states of Σ and a function $W(t)$ of time that specifies (say) the work output of the system during the process. Then there exists a function of state $\mathcal{P}[\sigma]$ such that $\Delta\mathcal{P}[\sigma(t)] = W(t)$ for all t along the process Π. $\mathcal{P}$ is unique up to an integral of motion.

Proof. For the existence part of the theorem, we need to find a function of state $\mathcal{P}[\sigma]$ such that

$$\mathcal{P}[\sigma(t)] - \mathcal{P}[\sigma(0)] = W(t). \tag{16}$$

If we take $\mathcal{P}[\sigma(0)] = 0$, then we can let Eq. (16) define $\mathcal{P}$ on the equilibrium states of Σ that lie on the curve representing the process Π. This definition can be extended to all equilibrium states of Σ by Tietze's extension theorem.[19] This theorem guarantees that any continuous function on a compact set in a manifold has a continuous extension to the entire manifold. Since the time-parametrized curve of equilibrium states is a compact set, our proof of existence is complete.

To show uniqueness, suppose we have two functions $\mathcal{P}$ and $\mathcal{P}'$ with the above property. Then

$$\Delta(\mathcal{P} - \mathcal{P}') = \Delta\mathcal{P} - \Delta\mathcal{P}' = W(t) - W(t) = 0.$$

Therefore, $\mathcal{P} - \mathcal{P}'$ is constant on all states along Π.

V. POTENTIALS FOR SOME QUASISTATIC PROCESSES

In the preceding section we showed the existence and uniqueness of potentials for quasistatic processes. The next step is to show how these potential functions can be computed. Below we present a computational scheme for a class of quasistatic processes. The technique as presented is limited, particularly by assumption 2, but other approaches permit one to extend the calculation to more general cases.[7]

Our knowledge of a process is frequently stated in the form of a system of differential equations. For example we might know that heat is flowing between systems Σ_1 and Σ_2 due to conduction through a wall with heat conductance κ. Newton's law of heat conduction implies that

$$-T_1 dS_1 = T_2 dS_2 = \kappa(T_1 - T_2) dt, \tag{17}$$

where T_i and S_i refer to the temperature and the entropy of systems Σ_i on either side of the wall, and the boundary conditions are the initial states of Σ_i. This example points out quite clearly the difficulties in integrating such differential equations. The equation itself involves variables of both systems and of the wall that connects them. We now make two simplifying assumptions which serve to eliminate such difficulties and allow the computation of potential functions.

Assumption 1. All variables appearing in the differential equations describing the process are either constant or expressible in terms of state function of Σ_1 and time. Note that if any intensities appear, the process is quasistatic in that degree of freedom.

Assumption 2. The differential equations describing the process are first order. This means that no second derivatives appear in the equations. This does not imply that the second derivatives are zero or that the equations are linear.

We now present an example to show the utility of these assumptions.

Example 4: Quasistatic expansion

Consider a gas inside a cylinder equipped with a piston. We denote the usual state functions of the gas by P, V, T, and S. The temperature of the environment is denoted by T_{ex}. For the boundary variables we use α for the coefficient of friction against the walls and κ for the heat conductance of the wall.

It is assumed that all the heat created by friction is absorbed by the environment. We also assume that the system obeys Newton's law of heat conduction to the environment and that the gas is expanding according to the equations

$$dS/dt = \kappa(T - T_{ex})/T, \quad dV/dt = aV. \tag{18}$$

Volume-dependent rates are typical of many engines.[20] The above equations satisfy our assumptions 1 and 2 only if T_{ex} and κ are constant. We now combine the equations to eliminate time and get

$$dS/dV = (\kappa/a)(T - T_{ex})/TV, \tag{19}$$

$$(TV) dS - (\kappa/a)(T - T_{ex}) dV = 0 = d\theta. \tag{20}$$

The differential $d\theta$ of Eq. (20) generates an integral of motion in the sense of Cartan.[21,22] If we reexamine Sec. III, we notice that state function integrals of motion are not necessary for the construction of potential functions. It is sufficient to have differential forms that vanish during the process. The useful work is given by

$$dW = P dV - \alpha(dV/dt) dV = (P - a\alpha V) dV, \tag{21}$$

and we look for a state function f such that the differential form

$$(P - a\alpha V) dV + f[(TV) dS - (\kappa/a)(T - T_{ex}) dV] = d\mathcal{P} \tag{22}$$

is exact.

Applying the ideal gas law, with C_v the molar heat capacity at constant volume and n the number of moles of gas, we have

$$d\mathcal{P} = [nRTV^{-1} - \alpha a V + nRTf - a^{-1}\kappa(T - T_{ex})f] dV$$
$$+ nf VC_v dT. \tag{23}$$

The condition that cross-partial derivatives be equal gives

$$nfC_v + nVC_v \frac{\partial f}{\partial V} = nRV^{-1} + nRf + nRT \frac{\partial f}{\partial T}$$
$$- a^{-1}\kappa f - a^{-1}\kappa(T - T_{ex}) \frac{\partial f}{\partial T}. \tag{24}$$

Using one arbitrary condition, we set $\partial f/\partial T = 0$ to obtain

$$f = \frac{nR}{V} \frac{1}{(a^{-1}\kappa - nR)}. \tag{25}$$

When (25) is substituted into (23), the exact differential becomes

$$d\mathcal{P} = A dT - 2BV dV + C V^{-1} dV, \tag{26}$$

where

$$A = \frac{n^2 RC_v}{a^{-1}\kappa - nR}, \quad B = \tfrac{1}{2}\alpha a,$$

and

$$C = T_{ex}\left(\frac{1}{nR} - \frac{a}{\kappa}\right)^{-1}$$
$$= \frac{T_{ex}}{nC_v} \frac{\kappa}{a} A.$$

By integrating (26), we obtain the potential

$$\varphi = AT - BV^2 + C \ln V.$$

$$= A\left(\frac{T_{\text{ex}}}{nC_v}\frac{\kappa}{a}\ln V + T\right) - BV^2. \qquad (27)$$

This potential φ has the property that $\Delta\varphi$ is the value of the useful work delivered in a quasistatic process which proceeds according to Eq. (18).

The calculation involved in the above example is considerably easier than actual integration of the equations of motion. It requires finding any solution of a partial differential equation in which one can choose some terms equal to zero.

The technique in the example above can be used only when it is possible to eliminate explicit time dependence from the equations of motion. Otherwise we must resign ourselves to including time in the set of thermodynamic variables. This yields a potential explicitly dependent on time. We can extend the construction of Theorem 1 to deal with processes that satisfy Assumptions 1 and 2.

Corollary 2

If a process satisfies assumptions 1 and 2, and the pressure P and volume V are described by the differential equations[23]

$$dP/dt = F(P, V, t) \text{ and } dV/dt = G(P, V, t), \qquad (28)$$

then a time-dependent potential $\varphi(t)$ can be constructed for the process, such that φ is a potential for the work done in the process.

Proof. We construct the invariant differential forms

$$đ\theta_1 = dP - Fdt \text{ and } đ\theta_2 = dV - Gdt, \qquad (29)$$

and make the work form exact by adding functional multiples of these Cartan integrals of motion:

$$d\varphi = đW + f_1 đ\theta_1 + f_2 đ\theta_2. \qquad (30)$$

The resulting potential φ is a function of state and time whose changes are the work done during a process proceeding according to the differential equations

$$đ\theta_1/dt = 0, \quad đ\theta_2/dt = 0. \qquad (31)$$

We now extend Corollary 2 to an arbitrary number of coordinates.

Corollary 3

Suppose a given process satisfying Assumption 1 and 2, and a complete set of coordinate X_i, $i = 1 \ldots n$, where n is the number of degrees of freedom of a system. If the time evolution of the X_i's is described by the differential equations

$$\frac{dX_i}{dt} = F^i(X_1 \ldots X_n, t),$$

then a potential $\varphi(X_1 \ldots X_n, t)$ can be constructed for the process.

Again we choose f_i's such that

$$đW + f_i(F^i dt - dX_i)$$

is exact. We have now completed the extension of the development of a potential φ by the Legendre transform method to all processes satisfying assumptions 1 and 2. We shall refer to this generalization of the Legendre construction to time-dependent processes as the Legendre-Cartan construction.

We have in mind for Eqs. (28), Euler-Lagrange equations as well as equations of external constraint.

VI. CONNECTION TO A VARIATIONAL APPROACH

We now examine the connection of the potential formalism developed above to the optimal control theory mentioned in the introduction.[5,6] The optimal control theory approach proceeds briefly as follows. We have part of the process determined, and we adjust the remaining "free part" of the process to optimize a given process variable. Consider for example a slight variant of example 4 above in which we retain the equation for heat conduction through the walls, and adjust the rate of motion of the piston to maximize work output. In terms of the mathematical formalism employed, the determined part of the process is an incomplete system of differential equations. Since the process must satisfy these equations, they are called the constraint equations. The process variable to be optimized is expressed as an integral. The Euler-Lagrange equations that result from the requirement that this integral be stationary, complete our system of differential equations. Then together with the initial and final states of the process we have the optimal process completely determined.

As mentioned in the Introduction, the explicit solution of the equations of motion for such optimal processes is possible only for the simplest examples.[24] We can however settle for less information and ask only for the value of the optimized process variable for the optimally running process.

Theorem 3

If we can construct a potential for a process variable by using the Legendre-Cartan construction based on constraint equations and Euler-

Lagrange differential equations, then changes in this potential tell us the value of the process variable for that process satisfying the condition of optimal control. The process variable plays the role of object function, and the variations leading to the Euler-Lagrange equations are taken with respect to the control variables.

Proof. The potential is constructed by making an exact differential from the integrand that gives rise to the process variable. To the integrand we add precisely those differential forms that vanish along the path for the process. The path is either completely fixed by external constraints (and thus trivially optimal) or is nontrivially optimal because it is required to satisfy a variational condition. Since these forms are zero along the optimal path, they do not alter the value of the integral on that path. We thereby evaluate the optimized process variable without having to solve the Euler-Lagrange equations and find the path explicitly.

The Legendre-Cartan differential forms must be found from either the constraint or the Euler-Lagrange equations. Unfortunately the computation schemes discussed in the previous sections

apply only if the equations of motion for the process satisfy the stringent conditions of Assumptions 1 and 2 of Sec. V. Further work is needed to extend the construction to less restrictive assumptions.[25] Potentials for realistic processes ought to provide a valuable tool for thermodynamic design.

VII. CONCLUSION

The above results show a step-by-step extension of the thermodynamic Legendre transform—the assignment of state functions to limiting values of process variables—to progressively larger classes of processes. Similar work on extending the other standard constructions of classical thermodynamics to encompass real time processes is needed. We will discuss these other extensions in forthcoming articles.

ACKNOWLEDGMENTS

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[18]"Conjugate" is defined here by $\{f,g\} = 1$ as in classical mechanics, and not by $(\partial E/\partial g)_V = f$, as is customarily done in thermodynamics.

[19]See for example C. T. C. Wall, *A Geometric Introduction to Topology* (Addison-Wesley, Reading, Mass. 1972), p. 79; or I. Singer and A. Thorpe, *Lecture Notes on Elementary Topology and Geometry* (Scott Foresman, Glenview, Ill., 1967). The space of internal equilibrium states defines a manifold, which therefore guarantees the T_4 topology necessary for Tietze's theorem.

[20]An internal combustion engine with constant crankshaft velocity for example.

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[23]The choice of the variables P, V here is arbitrary.

[24]The Euler-Lagrange equation for the presently available examples are very nonlinear and often include nonconstant parameters from the environment. Even the

formulation of these variational problems required great care as they are very easily over or under determined.

[25] A weaker form of this restriction is possible. If the relaxation time to some degrees of freedom is so long compared to the time scale of the process that the corresponding degrees of freedom is frozen out, the active system can be defined to exclude these modes.