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NON-LINEAR DYNAMICS OF THE GENERALIZED CARNOT PROBLEM: MAXIMUM WORK RECEIVED IN A FINITE TIME FROM A SYSTEM OF TWO CONTINUA WITH DIFFERENT TEMPERATURES

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Abstract

A finite time extension of the classical Carnot problem of maximum work extracted from a system of two continua with different temperatures is a good example of the problem where non-linear thermodynamic models are linked with ideas and methods of the optimal control. In this work we restrict ourselves to a somewhat special but important case when the amount or flow of continuum 2 is very large so that its intensive parameters (T_2, μ_{2i}, etc.) do not change (ambient or environmental fluid, $T_2 = T^e$). In this context we consider applications of the optimization theory based on a classical (energy- like) Hamiltonian for various active continuous and cascade processes associated with the theory of a body in a bath, when the indirect exchange of the energy occurs through the working fluid of the participating engine, refrigerator or heat pump. These applications refer in particular to extension of the classical thermodynamic problem of minimal work (exergy) supplied to the system of a finite area of heat (mass) exchange or with a finite contacting time.

Non-linear thermodynamic models are obtained for the purpose of work optimization. The optimal work functionals (continuous and discrete) are optimized by calculus of variations, dynamic programming and maximum principle methods. An extended exergy function can next be discussed in terms of the finite process intensity and finite duration. A discrete canonical formalism strongly analogous to those in analytical mechanics and the optimal control theory of continuous systems is an effective tool for thermodynamic optimization of cascade systems.

The optimality of a definite irreversible process for a finite-time transition of a controlled fluid is pointed out as well as the connection between the process duration, optimal dissipation and the optimal process intensity measured in terms of a hamiltonian. A decrease of the maximum work received from an engine system and an increase of work added to a heat pump system is revealed in the high-rate regimes and for short durations of thermodynamic processes. The results show that the criteria known from the classical availability theory should be replaced by limits obtained for finite time processes which are closer to reality. Hysteretic properties which arise as the difference between the work supplied and the work delivered are effective.

Keywords: Carnot engine, finite time thermodynamics, exergy, energy utilization.

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1. Introduction: Non-linear Properties of Thermodynamic Networks

Classical nonequilibrium thermodynamics is known as the theory of in-principle linear relations. In a state space where lumped parameter processes are described the linearity of this theory can be displayed in form of linear relations between the fluxes and driving forces (the entropy gradients in the state space). However, when the so-called active or work-producing thermodynamic systems are considered, the combination of linear dissipative resistors with the active reversible components (Carnot or work-producing parts) results in a non-linear reality. In effect, a very large majority of real thermal and chemical networks exhibits a non-linear dynamics. In this work we consider such non- linear dynamics for a network representation of an engine system in which a hot fluid supplies the pure heat to an engine at a high $T = T_1$ and releases the pure heat to an environment at a low $T = T_2$. The case on which we concentrate is that of an infinite environment, which corresponds to $T_2 = T^e$ where each of these temperatures is constant. The whole process is in the steady state. We start with the simplest case of the purely reversible (Carnot) system, which is the classical, active (work-producing) system without any production of the entropy. Next, two conductances are added, linking the heat sources with the working fluid of the engine at high and low T, as in the well-known Curzon–Ahlborn–Novikov engine or CAN engine; (NOVIKOV, 1984; CURZON – AHLBORN, 1975; DE VOS, 1992). Such a modest change preserves the generic nature of the system which means that its properties (while different from those of the Carnot engine) are still quite universal, i.e. independent of most details of the system construction. As an extension, a cascade composed of N such generic (CAN) engines is then analysed. This is again an active (work-producing) system. In a limiting continuous case, it describes the heat exchange between the two flowing fluids characterized by their own boundary layers as their dissipative properties. The differential Carnot engines are in this case located continuously between the two adjacent boundary layers of the fluids. and they work along their interface. This somewhat abstract model of the active energy exchange associated with the power production is a finite-rate generalization of the corresponding classical model of the available energy of the system composed of the body and bath (LANDAU – LIFSHITZ, 1975) in which there are neither boundary layers nor dissipation because the rate of the energy exchange is infinitely slow and the limiting power production is zero. In this paper we display non-linear properties of these generic cascades and their continuous limits and show that they constitute a suitable theoretical tool to obtain a finite-time available energy (exergy) of the driving fluid.

The classical availability is the function of the system state and the intense parameters of the environment (which plays the role of a bath). This function is well known from many textbooks (SZARGUT – PETELA, 1965;

KOTAS, 1985), and interesting unifying methodological schemes towards its derivation can be proposed (MUSCHIK, 1978). Classical exergy may be defined as the maximal work associated with the reversible transition of a system which is not in equilibrium with the environment to the state of its equilibrium with this environment. (For many subtleties associated with the applicability of this definition to reacting systems see, e.g., SZARGUT – PETELA, 1965). Since the reversible process is associated with an infinite duration and zero rates at each time instant the irreversibility of such a process is zero, and this vanishing irreversibility is, in fact, a minimal irreversibility corresponding to the infinite duration. In this work our interest is in the finite time transitions. They are associated with a minimum possible irreversibility as well, but this minimal irreversibility remains finite, due to the finite process rates necessary to accomplish a given change of state in a finite time.

A number of works towards the finite-time available energy (exergy) have already been published (SALAMON et al., 1977; ANDRESEN et al., 1983; D'ISEP – SERTORIO, 1983; MIRONOVA et al., 1994; RADCENCO, 1994). The common flaw of these works is the absence of explicit functionals which could show a link between the path properties of the process (through its rate properties) and the value of the work. Such functional is derived and discussed here for pure heat transfer processes. For quasistatic reversible processes with vanishing rates this functional simplifies to the (path independent) integral of the classical exergy $E_x = \Delta h - T^e \Delta s$. For any finite time duration, however, the optimal value of the work functional is duration dependent. Some additional issues related to this variational problem, as, e.g. its Hamilton-Jacobi equation, will be discussed in the forthcoming book (TSIRLIN et al., 1997). An economic analog of the present development may be constructed, through application of the recent economic model of DE VOS (1995) to the availability context.

The irreversible and hysteretic properties of our generalized exergy as a finite-time work potential are discussed in this paper. They are associated with different values of the work function obtained when the process of leaving the equilibrium is compared with the inverse processes of approaching the equilibrium. The first process corresponds to the so-called heat-pump mode, associated with the supply of work to the system, the second to the engine mode, characterized by the delivery of work from the system. While in classical reversible thermodynamics the two modes are accomplished with exactly the same absolute value of work, the works consumed and produced at a finite rate are no longer equal. A significant decrease in the maximal work received from an engine system and an increase in the minimal work added to a heat pump system is shown in the high-rate regimes and for short durations of thermodynamic processes.

The structure of the paper is as follows. The reversible (Carnot) engine is considered first (Section 2). Next its irreversible generalization, that is the Curzon–Ahlborn–Novikov engine (CAN), is analysed in Section 3.

The problem of maximum work in a cascade of CAN engines is stated in Section 4, and the related discrete optimization models are analysed in Section 5. Equations of continuous limit of these models, for infinite number of stages N, are derived in Section 6. Next, in Section 7, some important results of the work optimization following from the use of Pontryagin's principle are discussed. Formulae which describe the extremal work function as a generalized exergy are given in Section 8. In the concluding part of the paper (Section 9) the hysteretic, irreversible properties of this work function are discussed and their role in establishing the finite-rate limits for real processes is pointed out.

2. Reversible (Carnot) Engine System

The conservation of energy has the form

$$q_1 = w + q_2, \tag{1}$$

where q_1 is the input heat flow, q_2 is the output heat flow and w is the power produced. When combined with the conservation of the entropy

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \tag{2}$$

and the conversion efficiency definition

$$\eta = \frac{w}{q_1} \tag{3}$$

the result is the well-known Carnot efficiency formula

$$\eta_C = \left(\frac{w}{q_1}\right)_{\sigma_s=0} = \frac{q_1 - q_2}{q_1} = \frac{q_1 - q_1\frac{T_2}{T_1}}{q_1} = 1 - \frac{T_2}{T_1}. \tag{4}$$

3. Irreversible (Curzon–Ahlborn–Novikov) Engine

This is the system in which there are resistances between the Carnot cycle and the heat sources, *Fig. 1.*

Endoreversible efficiency of the power production,

$$\eta_\sigma = \frac{w}{q_1}, \tag{5}$$

is smaller than the efficiency of the Carnot cycle operating between T_1 and T_2. The entropy balance of the reversible part of the stage

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \tag{6}$$

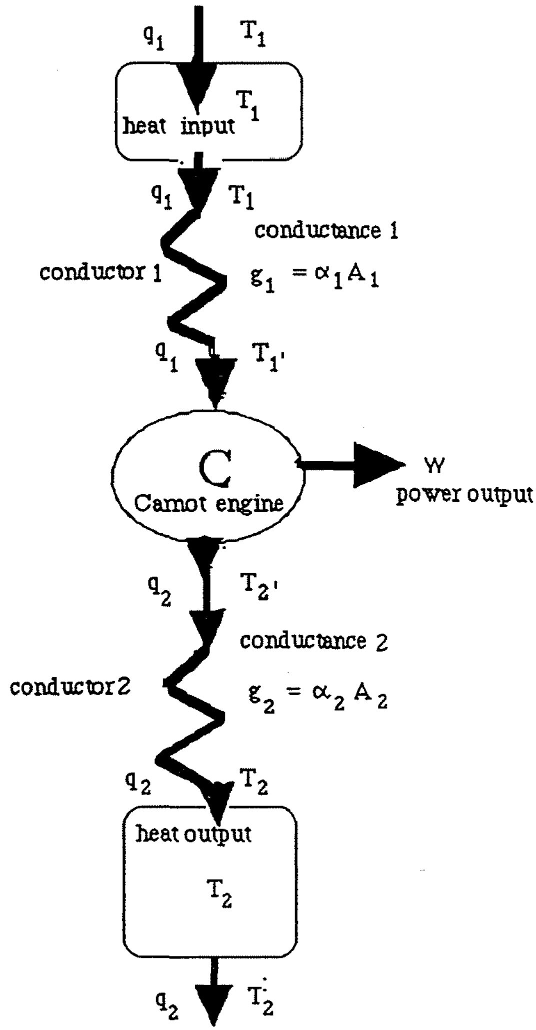

Fig. 1. Scheme of the Curzon–Ahlborn–Novikov engine (CAN engine)

and the energy balance $q_1 = q_2 + w$, yield the stage efficiency given again by the Carnot formula

$$\eta = 1 - \frac{T_{2'}}{T_{1'}}, \tag{7}$$

but η is now lower than that of *Eq.* (4) as it now applies to the intermediate temperatures $T_{1'}$ and $T_{2'}$. These temperatures are unknown, hence they should be expressed in terms of the boundary temperatures T_1 and T_2 and the stage efficiency, η. For this purpose one solves the reversible entropy balance

$$\frac{g_1 (T_1 - T_{1'})}{T_{1'}} = \frac{g_2 (T_{2'} - T_2)}{T_{2'}} \tag{8}$$

along with *Eq.* (7). Substitution of $T_{2'} = (1-\eta)T_{1'}$ into *Eq.* (9) yields

$$g_1 (T_1 - T_{1'}) (1-\eta) = g_2 [(1-\eta)T_{1'} - T_2], \tag{9}$$

whence

$$g_1 T_1 (1-\eta) - T_{1'}(1-\eta)(g_1 + g_2)(1-\eta) + g_2 T_2 = 0 \tag{10}$$

and one obtains for the intermediate temperatures $T_{1'}$ and $T_{2'}$

$$T_{1'} = \frac{g_1}{g_1+g_2} T_1 + \frac{g_2}{(1-\eta)(g_1+g_2)} T_2, \tag{11}$$

$$T_{2'} = \frac{g_1}{g_1+g_2}(1-\eta) T_1 + \frac{g_2}{g_1+g_2} T_2. \tag{12}$$

For $\eta = 1 - T_2/T_1 = \eta_C$ (Carnot efficiency) these equations give $T_{1'} = T_1$ and $T_{2'} = T_2$. The corresponding heat fluxes are

$$q_1 = g_1 (T_1 - T_{1'}) = \frac{g_1 g_2}{g_1+g_2}\left[T_1 - \frac{1}{(1-\eta)} T_2\right], \tag{13}$$

$$q_2 = g_2 (T_{2'} - T_2) = \frac{g_1 g_2}{g_1+g_2}[(1-\eta)T_1 - T_2] \tag{14}$$

and vanish for $\eta = 1 - T_2/T_1 = \eta_C$. The work flux (power) w equals $q_1\eta$ or the difference of the fluxes q_1 and q_2.

The relationships which describe the fluxes in terms of the efficiency and the boundary temperatures are called the characteristics of the system. These characteristics are presented in diagrams, see DE VOS, 1992.

The overall conductance of conventional heat transfer is defined as

$$g = \frac{g_1 g_2}{g_1+g_2}. \tag{15}$$

From now we will always mean the Carnot efficiency as that referred to the boundary temperatures

$$\eta_C (T_1, T_2) = 1 - \frac{T_2}{T_1}. \tag{16}$$

The heat flow q_1, *Eq.* (13), can be written in terms of g and the Carnot efficiency. They are three equivalent forms

$$q_1 = g\left(T_1 - \frac{T_2}{1-\eta}\right) = g\frac{(T_1 - T_2 - T_1\eta)}{1-\eta} = gT_1\frac{(\eta_C - \eta)}{1-\eta}. \tag{17}$$

The power produced $w = q_1 - q_2 = \eta q_1$ can be written in the form of the three equivalent expressions

$$\begin{aligned} w(T_1, T_2, g_1, g_2, \eta) &= g\eta\left(T_1 - \frac{T_2}{1-\eta}\right) \\ = \frac{g\eta(T_1 - T_2 - T_1\eta)}{1-\eta} &= \frac{g\eta T_1(\eta_C - \eta)}{1-\eta}. \end{aligned} \tag{18}$$

The power function w has an extremum with respect to the efficiency η whose location can be determined by the differential calculus. Setting the first derivative of w to zero

$$\begin{aligned} \frac{\partial w}{\partial \eta} &= g\left(T_1 - \frac{T_2}{1-\eta}\right) - g\frac{\eta T_2}{(1-\eta)^2} \\ &= g\frac{T_1(1-\eta)^2 - T_2(1-\eta) - \eta T_2}{(1-\eta)^2} = g\frac{T_1(1-\eta)^2 - T_2}{(1-\eta)^2} = 0 \end{aligned} \tag{19}$$

yields the extremal efficiency

$$\eta^0 = 1 - \sqrt{\frac{T_2}{T_1}}, \tag{20}$$

which we call the CAN efficiency. The second derivative of w at the extremal point is negative, hence the extremum is the maximum.

An improved insight can be gained when the power produced is considered in terms of diverse decisions. A suitable decision, which can be used in place of the efficiency, can be the driving heat q_1. From the first expression of *Eq.* (17)

$$\eta = 1 - \frac{T_2}{T_1 - g^{-1}q_1} \tag{21}$$

which shows that the effective temperature of the upper source $T^{\text{eff}} = T_1 - g^{-1}q_1$ is reduced due to the finite heat flux, hence the efficiency decreases with q_1. The corresponding power expression shows explicitly the deviation from the Carnot theory caused by a non-vanishing heat current

$$w = \left(1 - \frac{T_2}{T_1 - g^{-1}q_1}\right)q_1 \tag{22}$$

or

$$\frac{w}{g} = \frac{\left(g^{-1}q_1\right)^2 - \left(g^{-1}q_1\right)(T_1 - T_2)}{g^{-1}q_1 - T_1}. \tag{22'}$$

The Cărnot efficiency is achieved when the effect of the overall resistance g^{-1} is negligible or the flux q_1 is very low. The maximum power corresponds to q_1 satisfying

$$\frac{\partial w}{\partial q_1} = \frac{\left(T_1 - g^{-1}q_1\right)^2 - T_1T_2}{\left(T_1 - g^{-1}q_1\right)^2} = 0 \tag{23}$$

whence, the driving heat flux at the maximum power conditions

$$q_{1(\max\ w)} = g\left(T_1 - \sqrt{T_1 T_2}\right) . \tag{24}$$

When this result is substituted into *Eq.* (21), the CAN efficiency,

$$\eta^0 = 1 - \sqrt{\frac{T_2}{T_1}}$$

Eq. (21) is obtained again.

4. Maximum Work in a Cascade

We now consider the fluid cooling by a cascade of N engines of CAN type with the efficiency at each stage, η^n, or the local driving heat q_1^n as decision variables. The construction principle for such a cascade from the separate stages is illustrated in *Fig. 2.* To describe the cascade process, we will make the energy balance of the process. Let us introduce a cumulative driving heat Q^n over the first n stages of the cascade, $Q^n = \sum q_1^i$, where $i = 1, 2, \ldots, n$. The sequence of the local heats q_1^i, which are received at the upper temperatures T_1^n by the Carnot part of the n-th stage engine, describes the allocations of Q between the stages, for the n-th stage subprocess. In other words, each local heat q_1^n equals the change of the cumulative heat $Q^n - Q^{n-1}$.

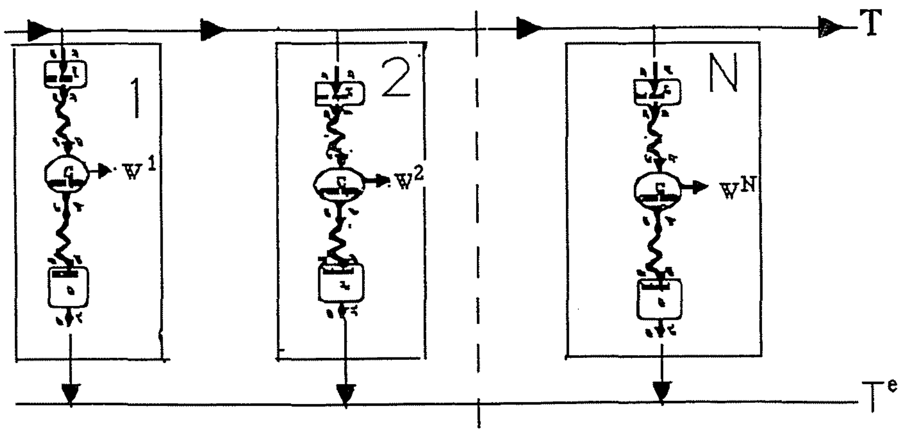

Fig. 2. Multistage Curzon–Ahlborn–Novikov engine (multistage CAN engine). Designations correspond to the forward algorithm with respect to the flow of the first fluid.

Assume that the ratio of the surface areas a_1 and a_2 to the total surface area $a = a_1 + a_2$ is a constant $k = a_1/a$ (and hence $1 - k = a_2/a$) which is independent of the contact time. Then a modified overall transfer coefficient α' can be defined whose product with the total area at a stage is equal to the conductance g at this stage

$$\begin{aligned} g = \frac{g_1 g_2}{g_1 + g_2} &= \frac{\alpha_1 a_1 \alpha_2 a_2}{\alpha_1 a_1 + \alpha_2 a_2} = \frac{\alpha_1 k a \alpha_2 (1-k) a}{\alpha_1 k a + \alpha_2 (1-k) a} \\ &= \frac{\alpha_1 k \alpha_2 (1-k)}{\alpha_1 k + \alpha_2 (1-k)} a = \frac{\alpha_1' \alpha_2'}{\alpha_1' + \alpha_2'} a = \alpha' \Delta A \; . \end{aligned} \tag{25}$$

Therefore, the overall conductance at the n-th stage g^n can be measured in terms of the change of the total cumulative area A^n, such that $a^n = A^n - A^{n-1}$, and

$$g^n = \alpha'^n \left(A^n - A^{n-1}\right) \; . \tag{26}$$

The modified total heat transfer coefficient α'^n refers to the sum of the exchange areas $a^n = a_1^n + a_2^n$ by definition. From *Eq.* (22$'$) and the heat balance at the stage n

$$q_1^n \equiv Q_1^n - Q_1^{n-1} = -G_1 c_1 \left(T_1^n - T_1^{n-1}\right) \tag{27}$$

the coordinate of cumulative heat is simply the flux of the enthalpy. In the case of pure heat exchange any change in the cumulative heat coordinate can be measured by the fluid temperature. The power delivered at the stage n follows from *Eqs.* (22) or (22$'$), and *Eqs.* (26) and (27)

$$\frac{w^n}{G_1} = -c_1 \left(1 - \frac{T_2^n}{T_1^n + \frac{G_1 c_1 (T_1^n - T_1^{n-1})}{\alpha'^n (A^n - A^{n-1})}}\right) \left(T_1^n - T_1^{n-1}\right) \; . \tag{28}$$

For the majority of devices of this sort it is convenient to introduce the specific area $a_v^n = \mathrm{d}A^n/\mathrm{d}V^n$, where $\mathrm{d}V$ is the infinitesimal change in the system volume associated with the change in the total area by $\mathrm{d}A$ and F is the constant cross-sectional area of the system. Since $\mathrm{d}V = F\mathrm{d}x$, where x is the geometric coordinate in the direction of the increase of V or A, the difference $A^n - A^{n-1}$ can be evaluated as

$$A^n - A^{n-1} = a_v^n F^n \left(x^n - x^{n-1}\right) \tag{29}$$

and the power delivered from the stage n per unit flow of the fluid 1 is

$$\frac{w^n}{G_1} = -c_1 \left(1 - \frac{T_2^n}{T_1^n + \frac{G_1 c_1 (T_1^n - T_1^{n-1})}{\alpha'^n a_v^n F^n (x^n - x^{n-1})}}\right) \left(T_1^n - T_1^{n-1}\right) \; . \tag{30}$$

The sum of this power over the stages is a discrete functional which is maximized by the suitable choice of the interstage temperature and allocation of the total exchange area A^n or the distance x^n between the stages.

Since for the engine mode of the stage the temperature of the (hotter) fluid 1 can only decrease along a path, the term with a discrete slope of $\Delta T^n/\Delta x^n$ in *Eq.* (30) is negative, and, consequently, the efficiency of the stage which works in the engine mode is lower than the Carnot efficiency. The quantity

$$\frac{G_1 c_1}{\alpha' a_v F} = \mathrm{HTU}_1 \tag{31}$$

has the length dimension and is known from the heat transfer theory as the so-called 'height of the heat transfer unit' (HTU). In *Eq.* (31) it is referred to fluid 1, but an analogous quantity can be defined for fluid 2. The non-dimensional length x/HTU is known as the 'number of transfer units'. Since it is proportional to the extent of the system x and hence to the contact time of the fluid with the energy exchange area, it plays the role of a non-dimensional time and it is designated by τ_1

$$\tau_1 \equiv \frac{x}{\mathrm{HTU}_1} = \frac{\alpha' a_v F}{G_1 c_1} x \,. \tag{32}$$

Moreover, it follows from the efficiency definition and from *Eqs.* (27) and (30) that the first term in parentheses on the RHS of *Eq.* (30) represents the stage efficiency

$$\begin{aligned} \eta^n &= -\frac{w^n}{G_1 c_1 \left(T_1^n - T_1^{n-1}\right)} = 1 - \frac{T_2^n}{T_1^n + \frac{G_1 c_1 (T_1^n - T_1^{n-1})}{\alpha'^n a_v^n F^n (x^n - x^{n-1})}} \\ &= 1 - \frac{T_2^n}{T_1^n + \frac{T_1^n - T_1^{n-1}}{\tau^n - \tau^{n-1}}} = 1 - \frac{T_2^n}{T_1^n + u^n}, \end{aligned} \tag{33}$$

where the discrete slope $u^n = \Delta T_1^n/\Delta\tau^n$ is a measure of the heat power transferred from the driving fluid to the engine. In terms of the nondimensional time τ_1 the total power per unit flow of the fluid G_1 (the quantity W, of dimension of work per unit mass) is represented by the following sum

$$W^N \equiv G^{-1} \sum_{n=1}^{N} w^n$$

$$= -\sum_{n=1}^{N} c_1 \left(1 - \frac{T_2^n}{T_1^n + \frac{T_1^n - T_1^{n-1}}{\tau_1^n - \tau_1^{n-1}}}\right) \left(\frac{T_1^n - T_1^{n-1}}{\tau_1^n - \tau_1^{n-1}}\right) \left(\tau_1^n - \tau_1^{n-1}\right) \,. \tag{34}$$

When $T_2^n = T^e$ is constant (the case of infinite flow or stock of the second fluid), *Eq.* (34) represents a discrete functional of the Lagrange type with a single state variable T_1. The functional is dependent on the process tate and the discrete slope $\Delta T^n/\Delta x^n$.

5. Discrete Optimization Models

n the format of the discrete Pontryagin's maximum principle one has to naximize the functional

$$W^N = -\sum_{n=1}^{N} c_1 \left(1 - \frac{T_2^n}{T_1^n + u^n}\right) u^n \Theta^n \tag{35}$$

subject to the difference constraints

$$\frac{T_1^n - T_1^{n-1}}{\tau_1^n - \tau_1^{n-1}} = u^n \tag{36}$$

and

$$\frac{\tau_1^n - \tau_1^{n-1}}{\Theta^n} = 1 \; . \tag{37}$$

Eq. (36) is in fact a form of the energy balance which links the transferred heat to the Carnot engine, *Eq.* (13), with the enthalpy change of the first fluid, *Eq.* (27).

The above model is sufficient whenever the flow or amount of the second fluid is very large so that its temperature T_2 can be assumed as a constant parameter of the problem. If this condition is not satisfied the explicit energy balance of the second fluid should be considered. This issue is ignored here.

Representation (35)-(37) uses the rate $(\Delta T_1/\Delta t)^n = u^n$ as the control variable. This rate is also the measure of the transferred driving heat q_1^n. *Fig. 3* shows the CAN cascade system working with these controls and the principle of the computational scheme by the forward discrete algorithm of the dynamic programming method.

In another representation, which deals with the efficiency η^n as the decision at the n-th stage, such that

$$u = \frac{T_2}{1-\eta} - T_1 \tag{38}$$

[see *Eq.* (33)] the above optimization model takes the form in which one has to maximize the work performance index

$$W^N = \sum_{n=1}^{N} c_1 \eta^n \left(T_1^n - \frac{T_2^0}{1-\eta^n}\right) \Theta^n \; . \tag{39}$$

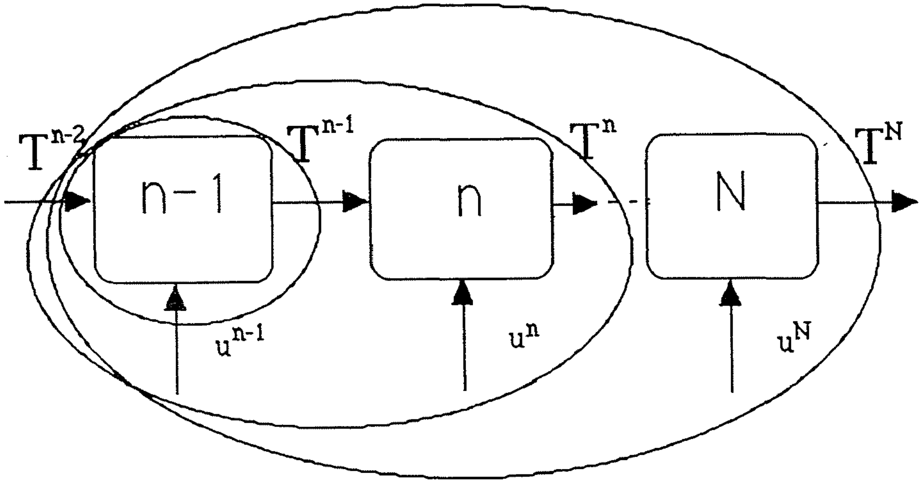

Fig. 3. Application of Bellman's principle of optimality to the CAN cascade. Forward algorithm of the dynamic programming method. Ellipse-shaped balance areas pertain to sequential subprocesses which grow by inclusion of remaining stages. The accepted controls are the discrete rates u^n

Equation (39) is extremized subject to the difference constraints

$$\frac{T_1^n - T_1^{n-1}}{\tau_1^n - \tau_1^{n-1}} = \frac{T_2^0}{1 - \eta^n} - T_1^n \tag{40}$$

$$\frac{\tau_1^n - \tau_1^{n-1}}{\Theta^n} = 1 \ . \tag{41}$$

Equations (39)-(41) still correspond to the forward algorithm of the dynamic programming illustrated in *Fig. 3,* in which the optimal work is considered in terms of the final states. Should one use the popular backward algorithm, in which the initial state is varied as in *Fig. 4,* the indices n and $n-1$ in the state equations considered had to be changed. Yet it is immaterial which set of the decisions (u^n or η^n) is accepted as the process controls. For the CAN cascade system in *Fig. 4* the controls are the stage efficiencies η^n.

Note that in the considered case (constant $T_2^0 = T^e$) the extremal work function describes a generalized exergy of the first fluid.

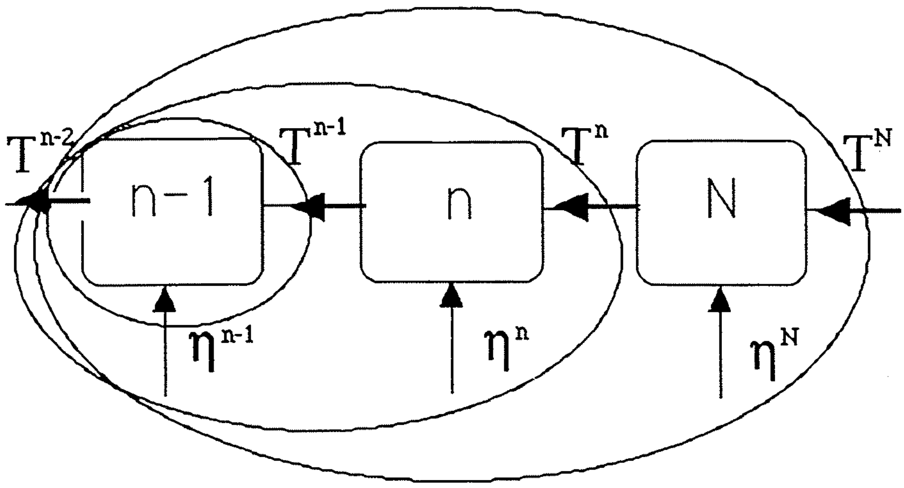

Fig. 4. Application of Bellman's principle of optimality to the CAN cascade. Backward algorithm of the dynamic programming method. Ellipse-shaped balance areas pertain to sequential subprocesses which grow by inclusion of remaining stages. The accepted controls are the stage efficiencies $\eta^n = w^n/q_1^n$.

6. Continuous Limit for Infinite N

When the rate of the temperature change $u = \dot{T}$ is the control variable the limiting continuous process can be described by a system of two equations in which one has to maximize

$$W = -\int_0^{\tau_f} c\left(1 - \frac{T^e}{T+u}\right) u \mathrm{d}\tau \tag{42}$$

subject to

$$\frac{\mathrm{d}T}{\mathrm{d}\tau} = u \ . \tag{43}$$

The state variables are W and T. One may work simultaneously with the representation of the same problem in terms of the efficiency η as an alternative control variable. Then one has to maximize

$$W = \int_0^{\tau_f} c\eta \left(T - \frac{T^e}{1-\eta}\right) \mathrm{d}\tau \tag{44}$$

subject to

$$\frac{\mathrm{d}T}{\mathrm{d}\tau} = \frac{T^e}{1-\eta} - T \,. \tag{45}$$

However the simplest formulation of the problem is that of the variational calculus. It is obtained by substitution of the rate $u = \mathrm{d}T/\mathrm{d}\tau$ in place of u in *Eq.* (42). Then one has to maximize the functional

$$W = -\int_0^{\tau_f} c\left(1 - \frac{T^e}{T+\dot{T}}\right)\dot{T}\mathrm{d}\tau \,. \tag{46}$$

In the Pontryagin's type formulations, *Eqs* (42)–(45), we occasionally exploit the relations between the two control variables

$$u = \frac{T^e}{1-\eta} - T \,, \qquad \eta = 1 - \frac{T^e}{T+u} \tag{47}$$

[c.f. *Eqs*. (33) and (38)]. As the differential constraints remain unchanged, the adjoint system is the same in both cases considered.

7. Some Optimization Results Following from the Use of Pontryagin's Principle

Let us attack the continuous problem by the standard algorithm of Pontryagin's maximum principle. Both decisions u and η are briefly discussed.

The Hamiltonian function in terms of the variables u or η is

$$H = zu - c\left(1 - \frac{T^e}{T+u}\right)u = (z - c\eta)\left(\frac{T^e}{1-\eta} - T\right) \tag{48}$$

This function has to be a maximum with respect to u or η, *Fig. 5*.

For a stationary maximum point

$$\frac{\partial H}{\partial u} = z - c\left(1 - \frac{T^e T}{(T+u)^2}\right) = 0 \tag{49}$$

and

$$\frac{\partial H}{\partial \eta} = c\frac{T(1-\eta)^2 - T^e\left(1 - \frac{z}{c}\right)}{(1-\eta)^2} = 0 \,. \tag{50}$$

The first of these equations defines the adjoint variable z in terms of the process rate $u = \mathrm{d}T/\mathrm{d}\tau$. As for the extremal $z = \partial L/\partial u$, it is nothing but the momentum-like variable or the derivative of the integrand of *Eq.* (46)

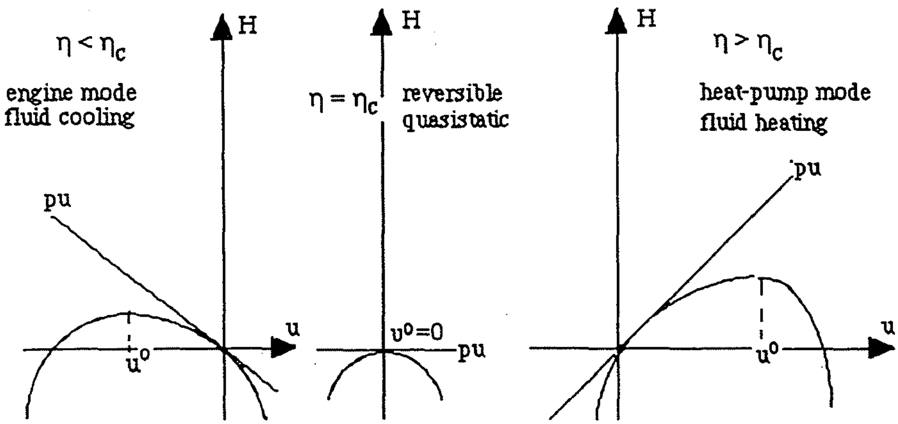

Fig. 5. Hamiltonian H as a function of intensity $u = \mathrm{d}T/\mathrm{d}\tau$ for three cases of $p = z/c - \eta_C$

with respect to $u = \mathrm{d}T/\mathrm{d}\tau$. The extremal control u follows from *Eq.* (49) in the form

$$u = \sqrt{\frac{T^e T}{1-\frac{z}{c}}} - T \; . \tag{51}$$

The second equation, *Eq.* (50), which may be obtained equally well by use of the first expression of *Eq.* (47) in *Eq.* (49), constitutes the generalized CAN condition

$$\eta = 1 - \sqrt{\left(1-\frac{z}{c}\right)\frac{T^e}{T}} \, , \qquad \left(= 1 - \frac{T^e}{T+u}\right) \, . \tag{52}$$

The expression in parentheses is the familiar u-representation of the same optimal efficiency. The original CAN condition holds only for free end points of the extremal path, which are optimal with respect to the free final or initial temperature and hence satisfy $z = 0$.

Substituting *Eqs.* (51) and (52) into the two expressions for H in *Eq.* (48) yields the common extremum Hamiltonian

$$H(T,z) = c\left(\sqrt{T^e} - \sqrt{T\left(1-\frac{z}{c}\right)^2}\right) \, . \tag{53}$$

It may also be verified that the energy function E which is obtained from the variational calculus approach to *Eq.* (46) represents the same Hamiltonian function.

The canonical equations are

$$\dot{T} = \frac{\partial H}{\partial z} = \frac{\left(\sqrt{T^e} - \sqrt{T\left(1 - \frac{z}{c}\right)}\right) T}{\sqrt{T\left(1 - \frac{z}{c}\right)}} = \sqrt{\frac{T^e T}{1 - \frac{z}{c}}} - T \tag{54}$$

[in agreement with *Eq.* (51)] and

$$\begin{aligned} \dot{z} &= -\frac{\partial H}{\partial T} = \frac{c\left(\sqrt{T^e} - \sqrt{T\left(1 - \frac{z}{c}\right)}\right)\left(1 - \frac{z}{c}\right)}{\sqrt{T\left(1 - \frac{z}{c}\right)}} \\ &= c\left(\sqrt{\frac{T^e\left(1 - \frac{z}{c}\right)}{T}} - \left(1 - \frac{z}{c}\right)\right) . \end{aligned} \tag{55}$$

The simplest way to solve these canonical equations is to eliminate z from *Eq.* (54) and substitute the result into *Eq.* (55). In this way a second order differential equation is obtained for T which should next be solved by standard methods. But the result of such elimination is z in terms of the variables T and $\mathrm{d}T/\mathrm{d}\tau$. i.e., the momentum variable of the variational calculus, and the resulting second order differential equation for T is

$$T\ddot{T} - \dot{T}^2 = 0 . \tag{56}$$

(The same result can be obtained from the variational calculus.)

Eq. (56) is satisfied by the function $T(\tau)$ which is solution of the following first order differential equation

$$\dot{T} = \xi T \tag{57}$$

where ξ is an arbitrary constant which may be positive or negative.

Equations (56) and (57) can describe the minimum of the work functional (46) only when the Legendre necessary condition

$$\frac{\partial^2 L}{\partial \dot{T}^2} = 2cT^e \frac{T}{\left(\dot{T} + T\right)^3} > 0 , \qquad \text{or} \qquad \dot{T} + T > 0 \tag{58}$$

is satisfied. In terms of η, the condition means that $T_2(1 - \eta)^{-1}$ must be positive or that η cannot be greater than unity. From the characteristic $q(\eta)$ we conclude that the necessary condition for minimum can be satisfied by only physical efficiencies η.

For a given duration and end temperatures the extremal function $T(\tau)$ is described by *Eq.* (59)

$$T\left(\tau, \tau^f, T^i, T^f\right) = T^i \left(\frac{T^f}{T^i}\right)^{\tau/\tau^f} \tag{59}$$

which shows that the extremal trajectories constitute the family of exponential curves. An equation which describes the function $z(\tau)$ can be obtained by substitution of the above equation into *Eq.* (55) and the subsequent integration,

$$
\begin{aligned}
z\left(\tau, \tau^f, T^i, T^f\right) &= c\left(1 - \frac{T^e}{T(\tau)(\xi+1)^2}\right) \\
&= c\left(1 - \frac{T^e}{T^i\left(\frac{T^f}{T^i}\right)^{\tau/\tau^f}\left(\frac{\ln\frac{T^f}{T^i}}{\tau^f}+1\right)^2}\right). \qquad (60)
\end{aligned}
$$

We stress that ξ is the proportionality constant between the rate and state in an extremal process, or a process intensity index. The constant ξ may also be called the logarithmic intensity of the extremal process.

The existence of the logarithmic intensity (57) may also be deduced from the known theorem of the variational calculus which states the energy-like quantity

$$
\begin{aligned}
E &\equiv \frac{\partial L}{\partial \dot{T}}\dot{T} - L = c\left(1 - \frac{T^e T}{\left(\dot{T}+T\right)^2}\right)\dot{T} - c\left(1 - \frac{T^e}{\dot{T}+T}\right)\dot{T} \\
&= cT^e\frac{\dot{T}}{\dot{T}+T}\left(1 - \frac{T}{\dot{T}+T}\right) = cT^e\frac{\dot{T}^2}{\left(\dot{T}+T\right)^2} \qquad (61)
\end{aligned}
$$

is a first integral of the Euler-Lagrange equation. For a constant $E = h$, *Eq.* (61) implies

$$
\frac{\dot{T}^2}{\left(\dot{T}+T\right)^2} = \left(1 - \frac{T}{T^e}(1-\eta)\right)^2 = \frac{h}{cT^e} \equiv h' \qquad (62)
$$

which proves that E vanishes at the Carnot point. From *Eq.* (62) one concludes that

$$
\dot{T} = \frac{\pm\sqrt{\frac{h}{cT^e}}}{1 - \pm\sqrt{\frac{h}{cT^e}}}T \equiv \xi T \qquad (63)
$$

where

$$
\xi \equiv \frac{\pm\sqrt{\frac{h}{cT^e}}}{1 - \pm\sqrt{\frac{h}{cT^e}}} \qquad (64)
$$

which agrees with *Eq.* (57). *Eq.* (64) determines ξ in terms of h. The upper sign refers to processes of fluid heating in a heat pump system ($u > 0$) whereas the lower sign to cooling processes by the engine system.

8. Extremal Work Function as a Generalized Exergy

By integration of the work integral with the extremal rate $\dot{T} = \xi T$ one obtains the extremal work function for a finite rate transition

$$W^0 = c\left(T^i - T^f\right) - \frac{T^e}{1+\xi(h)} c \ln \frac{T^i}{T^f} \, . \tag{65}$$

Under appropriate boundary conditions *Eq.* (65) can be transformed to a form in which the classical exergy function is explicit

$$E_x(T, T^e, \tau^f) = c(T - T^e) - cT^e \ln \frac{T}{T^e} + cT^e \frac{\pm\left(\tau^f\right)^{-1}\left(\ln \frac{T}{T^e}\right)^2}{1 + \pm(\tau^f)^{-1} \ln \frac{T}{T^e}} \tag{66}$$

where the sum of the first two terms is the classical exergy $E_x(T, T^e)$ of the flowing fluid. A hysteretic effect of dissipation, i.e.. an increase in the exergy supplied to the pump mode heating and a decrease in the exergy released in the engine mode cooling is seen from *Eq.* (66). The same hysteretic effect E_x is seen when the intensity ξ of *Eq.* (65) is eliminated on account of the hamiltonian (which is another intensity index)

$$\begin{aligned} E_x(T, T^e, h) &= E_x(T, T^e, 0) + cT^e \ln \frac{T}{T^e} \frac{\xi(h)}{1+\xi(h)} \\ &= c(T - T^e) - cT^e \ln \frac{T}{T^e} \pm cT^e \ln \frac{T}{T^e} \sqrt{\frac{h}{cT^e}} \, . \end{aligned} \tag{67}$$

Since the hamiltonian h is a constant of motion of any autonomous optimal process, an extremal is characterized by a single value of h. This makes the constant h a natural parameter of various finite time paths. The classical reversible paths, of infinite duration, are those of vanishing h. The finite time paths are those of nonvanishing h.

9. Concluding Remarks

For processes which are infinitely long or are characterized by an infinite number of the transfer units the minimum work reduces to the classical exergy of a continuous process

$$E_x = \int_{T^e}^{T} c\left(1 - \frac{T^e}{T}\right) \mathrm{d}T = c(T - T^e) - cT^e \ln \frac{T}{T^e} . \tag{68}$$

The environmental temperature T^e is a constant parameter. The above formula is an idealized abstract as it pertains to an equipment of infinite size. It may be derived as the work necessary to accomplish a production process in which a final nonequilibrium state of a body is obtained form its state of equilibrium with the environment, by using a model of infinite number of differential Carnot heat-pump (reversible) cycles which supply this minimal work. The process goes with continuous change of T from an equilibrium state (when the fluid has a temperature of T^e) to an actual state of nonequilibrium, represented by the temperature T, while a fluid is heated along an isobar.

With the classical exergy, thermostatics simultaneously provides the lower bound to the real work which should be supplied to the system and the upper bound to the work which can be released by the system. The second process is inversion of the first one (the final state of the second process is the initial state of the first one and conversely), and the duration of each process is infinitely long. In thermostatics the two bounds mentioned above coincide.

However, such limits are too far from reality to be very useful. Whenever one takes into account the necessity of termination of the process in a finite time and the inherent role of resistances as dissipative parts of the system (in boundary layers in particular) the finite- rate exergy provides a lower bound to the real work which should be supplied to the system. This lower bound is higher and hence more realistic than the quasistatic lower bound obtained from classical thermostatics. The generalized exergy describing this bound as a finite rate effect (per unit mass of the flowing fluid) is defined as the minimum of the path-dependent work functional (46).

In a concrete practical process (with the same boundary states and duration as in the optimal CAN process) the real work of the heat-pump mode can be only larger that the above mentioned finite-rate limit, *Fig. 6*. This is so because the state transition occurs generally under a control which can only be worse than the optimal control. Similarly the finite-rate exergy provides a more realistic (lower) upper bound to the real work which can be delivered by a nonequilibrium system producing work. A real work received from a concrete process, with the CAN boundary states and duration but with a suboptimal control, can only be lower than the above mentioned finite-rate limit.

Consequently, *Fig. 6*, for a process and its inversion, the two bounds which coincide in thermostatics diverge in thermokinetics and the divergence grows with the rate indices (x or h). This means that for sufficiently high

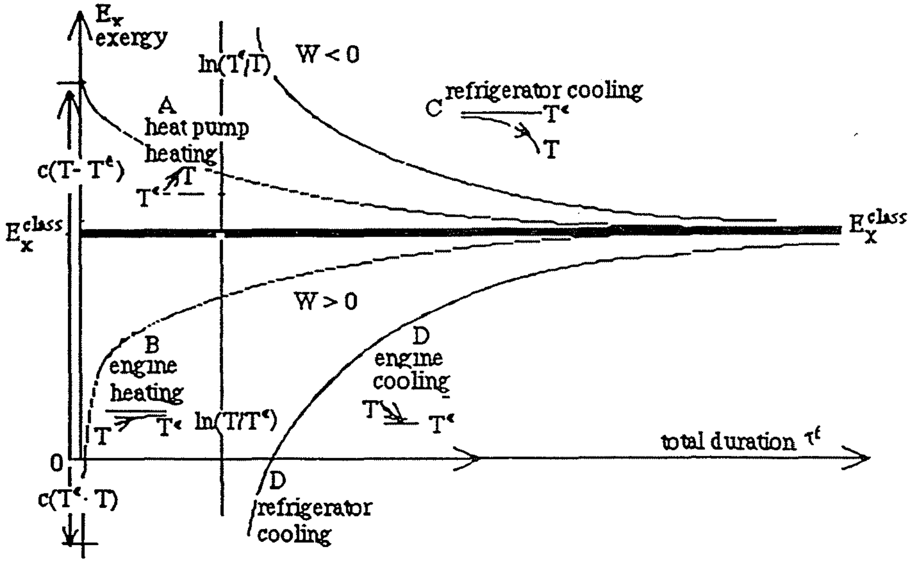

Fig. 6. Generalized exergy E_x as function of the duration for various modes

rate indices one can obtain quite high lower bounds to the supplied work and even vanishing upper bounds to the released work. By taking $E_x = 0$ in *Eq.* (67) one can evaluate the critical value of the hamiltonian intensity h associated with vanishing generalized exergy for a given temperature T

$$h = cT^{\epsilon}\left(\frac{T - T^{\epsilon}}{T^{\epsilon}\ln\frac{T}{T^{\epsilon}}} - 1\right)^2 . \tag{69}$$

The classical exergy provides the accurate evaluation of the extremal work in the case of small HTU, that is in the case of excellent transfer conditions. Another situation when the bounds of the classical exergy are justified is the case of sufficiently long contact times or large total lengths L. This case occurs in quasistatic or quasiequilibrium processes. Otherwise, for a finite h, the contribution of the finite-time term plays a role. The finite rate processes close to equilibrium always increase the absolute value of the extremal work supplied in a heat pump mode and decrease the corresponding work produced in the engine mode. A general statement summarizing these effects is valid:

Real finite rate processes approaching equilibrium with an environment can release a work which is not larger than the generalized exergy of the engine mode (lower sign) whereas those leaving this equilibrium require the supply of work which is not smaller than the generalized exergy of the pump mode (upper sign).

This statement, along with the quantitative analysis presented above, provide a means for improved evaluation of the limits of the energy consumption in practical systems. While the analysis presented here has been made only for the processes of pure heat exchange and a similar quantitative analysis for mass transfer processes has still to be done, the extension of the above statement for those with mass exchange is obvious. Consistently the finite rate limits for high-rate separation processes can be shown to lie much above the well known classical thermostatic limits (KING, 1971). Especially important are systems involving chemical reaction systems, in particular combustion systems or rocket engines, in which the residence time of the reactants and products in the system for a fixed state change can be very short. While the FTT treatments of such systems have already been initiated (ONDRECHEN et al., 1981; HOFFMAN, 1990) yet much has to be done as regard the extended availability properties for such processes. In this case the kinetic limit of the work released by the engine lies much below its thermostatic (reversible) limit, so that one can be ascertained that the real power released per unit time is much below that of the classical thermodynamics evaluation. In this case the classical limit evaluations based on chemical thermodynamics (DENBIGH, 1956; RATKJE – SWAAN ARONS, 1995) are insufficient, and the progress in terms of the power production can be made only through innovations and improvements acting on the kinetic parameters and the size (topology) of the system.

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