The Stability of Open Systems: A Thermodynamics Based Approach

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Abstract

The laws of thermodynamics are used to formulate a stability criterion based on the total internal entropy generation rate of an open system. These laws are also used to propose a method for monitoring systems stability that can be used when conventional approaches are not feasible. A simplified equation for evaluating the stability of open control volumes for large class of problems covering typical ambient conditions is derived using the stability criterion. An analysis is done to show that the stability of a wide variety of control volumes can be investigated using this equation when the internal details of the control volume are not well known. Further analysis also shows that random fluctuations that are always present in completely open environments will likely destabilize stable control volumes over time. Finally, the implications of the results on living organisms, particularly prebiotic systems and early life, are discussed.

Keywords

System stability, Second law, Entropy generation, Homeostasis, Prebiotic life

1. Introduction

The time evolution of systems exchanging mass and energy with its surroundings is governed by the principles of conservation of mass and energy and an increase in entropy following the fundamental laws of thermodynamics. Though these are based on equilibrium and stability considerations related to component, phase and chemical equilibria, concepts such as quasi-equilibrium states are applied to irreversible processes in order to expand the validity of the equations to non-equilibrium processes. The typical approach here includes an assumption of local equilibrium that is independent of variations within the larger system when it undergoes a perturbation or fluctuation. The thermodynamic laws are then supplemented by Onsager reciprocity relations, transport equations and empirical laws that are generally independent of underlying molecular models (e.g. Demirel and Gerbaud (2019)).

More recently, advanced thermodynamic theories that modify or do not make the assumption of local equilibrium have been developed (e.g. Muschik (2008), Martyushev (2021)). However, these are still mostly subjects of research and have found limited use, since research shows that methods based on local equilibrium assumptions are adequate for most situations encountered in practice. As a result, this assumption is normally used to study processes that are far from equilibrium including many that exhibit highly stable configurations referred to as dissipative structures. These studies show that unlike equilibrium processes where stability criteria are universal, the criteria for non-equilibrium processes depend on the process under consideration. Though these criteria can often be identified using common underlying mathematical techniques, their variability necessitates additional analysis when dealing with different processes.

For simple configurations, stability evaluations can be done using the theories of equilibrium and non-equilibrium thermodynamics. However, a different approach is typically used for the large fraction of engineering applications, particularly those involving complex open systems with continuous mass and energy transfer (i.e. “control volumes”). Since these often comprise large numbers of concurrent processes in series or parallel, a stable system design is typically developed by constraining individual processes to operate under conditions where localized perturbations are known to not have a destabilizing effect. The designs are then implemented in practice by incorporating sensors to monitor the various processes and provide data to local and system-wide control systems to maintain the operating conditions as required.

The above system design approaches are impractical in many modern applications that are under development today (e.g. autonomous microsystems, etc.). In these cases, it may not be feasible to incorporate sensors within individual processes and/or to monitor and control individual processes as is done in conventional systems. Local environments are inevitably more diverse and time-varying which also affects system controllability adversely. As a result, such systems can be difficult to design and implement, and further work is required in this area. This study is a step in that direction, and uses an integral approach to identify some fundamental aspects of stability as related to non-homogeneous control volumes.

2. Formulation of Problem and Analysis

A general model can be developed by considering an open system exchanging mass and energy with its surroundings. Unlike the infinitesimally small ("differential"), homogeneous case, its size is not constrained, and the control volume can incorporate an arbitrary number of irreversible process within it. The governing equations in this case, i.e. the laws of conservation of mass and the first and second laws of thermodynamics, can be written for the control volume as:

$$\frac{dN_I}{dt} = -\oiint \rho_I \bar{v}_I \cdot \bar{n}\, dA + \dot{N}_{S,I}\,; \quad I = 1,..,N \qquad (1)$$

$$\frac{dE}{dt} = -\oiint ([\bar{q} + \sum \rho_I (h + pe + ke)\bar{v}_I] \cdot \bar{n} - \dot{w})\, dA \qquad (2)$$

$$\frac{dS}{dt} = -\oiint (\frac{\bar{q}}{T} + \sum \rho_I s\, \bar{v}_I) \cdot \bar{n}\, dA + \dot{S}_G\,; \quad \dot{S}_G \geq 0 \qquad (3)$$

where
A is the surface area,
E is the total energy (including the internal, potential and kinetic energies) of the control volume,
h is the enthalpy, pe the potential energy and ke the kinetic energy associated with the mass transfer at the surface of the control volume
N is the mass of a specific component within a control volume
$\dot{N}_{S,I}$ is the rate at which a component is generated or utilized within the control volume due to internal reactions (equivalent to an internal source/sink)
$\bar{n}$ is the unit normal vector, taken positive facing outwards at the surface of the control volume,
$\bar{q}$ is the local heat flux (the heat transfer rate per unit surface area) vector, taken positive when heat is transferred to the control volume
S is the total entropy of the control volume
$\dot{S}_G$ is the total rate of entropy generation within the control volume (due to internal mass and heat flows, friction and viscous dissipation, chemical reactions, electromagnetic interactions, etc.),
s is the entropy associated with the mass transfer at the surface of the control volume,

T is the absolute temperature at which heat transfer occurs at the surface,
t is the time,
$\bar{v}$ is the local velocity (diffusion and/or convection) vector at the surface of the control volume,
$\dot{w}$ is the rate at which work is done at the surface per unit surface area, taken positive when done by the control volume, and
ρ is the density of a specific component crossing the surface of the control volume.

The summation (Σ) in the above equations refer to various components that are involved in the internal processes, and their evolution can be quantified using equations related to the various chemical reactions, if any. These are not explicitly stated here since details of the internal processes are not directly relevant to the present analysis. Additional equations describing the different heat transfer and work processes can also be used as appropriate. Eq. 1-3 apply to any general control volume (e.g. Tester and Modell (1997)) with arbitrary internal processes and energy transfer at the surface, i.e. heat transfer processes may include conduction and convection and radiation (with some limitations), and work interactions can include mechanical, electrical, chemical and other forms of energy transfer. The only requirement here is that the entropy values are based uniformly at zero absolute temperature and the heat of reactions, etc. are derived consistently accounting for different internal subsystems where necessary.

Before proceeding further, it is useful to define a reference temperature at this stage. Though this can be done in many different ways, it is preferable to use a control volume mass averaged temperature (T_{CV}) so that different subsystems within the overall control volume can be readily accommodated. After multiplying Eq. 3 by this reference temperature and simplifying, the following equation is obtained:

$$\frac{dT_{CV}S}{dt} = -\oiint \frac{T_{CV}}{T}(\bar{q} + \sum \rho_I Ts\,\bar{v}_I)\cdot\bar{n}\,dA + T_{CV}\dot{S}_G \qquad (4)$$

Eq. 2 and Eq. 4 are then combined, and written in a form that separate the terms related to the irreversible effects (i.e. the terms with T_{CV}/T and $\dot{S}_G$):

$$\frac{d\,(E - ST_{cv})}{dt} = -\oiint ([\Sigma\rho\,(h - Ts + pe + ke)\bar{v}_I + (1 - \frac{T_{cv}}{T})(\bar{q} + \Sigma\rho_I\,Ts\,\bar{v}_I)]\cdot\bar{n} - \dot{w})\,dA - T_{cv}\dot{S}_G \quad (5)$$

where $h - Ts$ corresponds to the Gibbs free energy per unit mass. Eq. 5 combines both the first and second laws of thermodynamics in a compact form and provides an overall energy balance for the control volume. Since it is based on Eq. 2-3, it is generally applicable for all open systems where the continuum assumptions are valid.

2.1. Evaluation of Control Volume Stability

Stability of a general control volume can be considered from two perspectives. In the first, a control volume can be considered to be stable if it reverts to a stable configuration over time regardless of its initial state. Given the infinite variations possible, this type of global thermodynamic equilibrium is not expected in heterogeneous, non-equilibrium systems. Instead, stability is defined based on steady-state considerations wherein a system at steady-state is considered to be stable if it maintains or returns to its initial steady condition when its external conditions change. For such steady-state conditions, the governing equations, i.e. Eq. 1-3 and 5, can be rewritten as:

$$\oiint \rho_I \bar{v}_I \cdot \bar{n}\, dA = \dot{N}_{S,I} \;=\; constant\,; \quad I=1,..,N \qquad (6)$$

$$\oiint ([\bar{q} + \Sigma\, \rho_I (h + pe + ke)\bar{v}_I] \cdot \bar{n} - \dot{w})\, dA \;=\; 0 \qquad (7)$$

$$\dot{S}_G \;=\; \oiint (\frac{\bar{q}}{T} + \Sigma \rho\, s\, \bar{v}_I) \cdot \bar{n}\, dA \;\geq\; 0 \qquad (8)$$

$$T_{cv} \dot{S}_G \;=\; -\oiint ([\Sigma \rho_I ((h - Ts) + pe + ke)\bar{v}_I - (1 - \frac{T_{cv}}{T})(\bar{q} + \Sigma \rho\, Ts\, \bar{v}_I)] \cdot \bar{n} - \dot{w})\, dA \;\geq\; 0 \qquad (9)$$

Eq. 5-7 show that for steady conditions, the net mass flow rate through the control volume surface is constant for individual components, the net energy flow through the control volume surface is equal to zero, and the net entropy flow through the control volume surfaces (i.e. the total entropy leaving the control volume) equals the rate of entropy generation within. The combined equation, Eq. 9, provides a similar insight into the net free energy flow to the control volume. In this case, the product on the left-hand-side is a measure of the irreversible internal heat generation rate within a control due to random dissipation and internal process inefficiencies. This wasted useful energy or “lost work” is balanced by free energy flows through the external surfaces of the control volume as given by the terms on the right-hand-side of the equation.

Eq. 9 is well known in various forms, and is often used to justify the stability of complex natural structures and related phenomena in the presence of irreversible, dissipative effects. Thus, open systems are often assumed to be stable when the the net rate of free energy transfer through its boundaries equals the irreversible losses within. Though this is clearly the case for a homogeneous or differential control volume, the issue is more complex for the general case. This is evident when one considers non-homogeneous reversible, closed systems which have no mass or energy exchange with the surroundings. In such systems, stable conditions are not inevitable internally, and evolution to steady conditions occurs only for select combinations of processes. Thus, Eq. 6-9 will be satisfied (with both sides being equal to zero), but the overall control volume will not be stable from a steady-state perspective.

The above discussion shows that Eq. 9 (or Eq. 8) is a necessary, but not a sufficient condition for stability. Such a stability condition can be derived from Eq. 8-9 by noting that the irreversible losses associated with the internal processes do not change under steady state conditions. Thus, the total rate of entropy generation within the control volume remains constant in a stable control volume, which gives the following additional stability condition:

$$\left.\frac{d\,\dot{S}_{G,J}}{dt}\right|_{J=1,..,N} = \sum \frac{d\,\dot{S}_{G,J}}{dt} \;=\; \frac{d\,\dot{S}_G}{dt} \;=\; 0 \qquad (10)$$

where the subscript J is refers to the individual processes within the control volume.

The use of Eq. 10 as a stability condition above is quite different from most other applications of the

Second Law to stability analysis where the Second Law is typically used to identify a stable solution when the governing equations for a specific configuration (i.e. Eq. 1-2 and other relevant equations) have multiple solutions. An example of this is Bernard convection where a fluid between two horizontal plates (or a horizontal fluid layer) is heated from below. Stability analyses of this process focus on identifying the conditions under which different stable patterns form (e.g. Kawazura and Yoshida (2012)), and to illustrate the concepts of stability and "dissipative structures" in non-equilibrium thermodynamics. Unlike this common physical or structural view of stability, the thermodynamic perspective discussed above requires that the system return to its original state when external conditions change. The fact that the Bernard convection process is not stable in the thermodynamic sense can be confirmed by a simple Second Law analysis which shows that the total internal entropy generation rate does not remain constant or return to its original value when one of the boundary conditions is changed.

It is important to note that Eq. 10 is automatically satisfied when all processes are reversible and is not useful for the reversible situation. For a practical system in contrast, variations in one or more internal states will result in corresponding changes in related processes and their losses, and thus the overall internal entropy generation rate. Eq. 10 can therefore be used to evaluate/monitor the stability of not only the overall control volume, but also the stability of individual processes within. It is worth emphasizing however that overall control volume stability does not imply individual process stability in all cases. This is clear from a simple example where a control volume comprises two identical parallel processes that can run one-at-a-time. In this case, switching from one process to another will not result in any changes in the overall entropy generation rate, and the control volume will be essentially stable if the overall stability criterion is considered. This will not be the case if the control volume is analyzed from an individual process perspective. Thus, if individual process stability is important, this must be implemented via the more strict condition (on the left-hand-side) in Eq. 10.

Eq. 6-10 above show that a control volume in an open environment can be stable only when the net rate of mass and energy transfer at the surface is zero per Eq. 6-7, the net rate of free energy transfer at its surface equals the irreversible internal losses per Eq. 9, and the total internal entropy generation rate is constant per Eq. 8 and Eq. 10. Energy and entropy transfers at the system boundaries via heat transfer, mass transfer and work interactions must therefore remain unchanged with time to ensure stability. In a practical situation, this is not possible since external conditions are always susceptible to change, and changes in boundary conditions automatically affect one or more internal processes. Thus, the internal conditions of such control volumes (as given by local thermodynamic states) fluctuate with the external environment, and control volumes simultaneously affect the external environment on a continuous basis. The stability of open control volumes in arbitrary environments can therefore be defined only in terms of the level of internal fluctuations relative to their initial stable states and the fluctuations in the environment, i.e. by the stability of their internal processes.

The above discussion shows that (relatively) stable internal processes will result in (relatively) stable control volumes (though the converse is not always true). It also provides direct thermodynamic support for conventional methods for maintaining the stability of open systems which typically focus on controlling internal processes. However, when these methods are difficult to implement, as is the case in many modern systems, alternative methods are required to verify system stability. A control volume approach based on the above equations (Eq. 6-10) is one such option. In this method, properties measured at the interface between the control volume and the environment can be used to confirm stability in a two-step process as follows:

a. Verification of steady-state conditions is done by evaluating the different terms in the equations for conservation of mass and energy (Eq. 6-7). A control volume that satisfies Eq. 6-7 will also satisfy Eq. 8 when the rate of change in its internal properties (e.g. pressure, density, electric/magnetic field strength) are small (e.g. Tester and Modell (1997)). Since this is true in most applications (note that rate of change in E is already negligible per Eq. 7), steady-state conditions from mass and energy considerations generally implies steady-state conditions from entropy considerations. If necessary, additional control volume properties can be measured over time in order to verify that this is indeed the case.

b. The internal entropy generation rate $\dot{S}_G$ cannot be directly measured. However, process and control volume stability can be confirmed indirectly for steady-state conditions by evaluating the net rate of entropy transfer through the control volume surfaces (i.e. the right-hand-side of Eq. 8) to ensure that the total rate of internal entropy generation $\dot{S}_G$ does not change with time.

The control volume based method as described above can be used to study/monitor the stability of a control volumes in an uniform manner regardless of the type of internal processes (i.e. chemical, electrical, mechanical, etc.) since the technique is based on the fundamental laws of thermodynamics. This can have major benefits in systems development and analysis as illustrated by the following simple example:

Consider a control volume comprising of a two chip resistors in series that are supplied by a dc power source and connected to ground. From basic electrical engineering considerations, a constant voltage results in constant current flow and constant power consumption. Any fluctuations in voltage results in corresponding changes in current and a corresponding change in power consumption. Thus, the control volume in this case will be stable only when the external environment (i.e. the voltage source) is stable. This stability is typically monitored using simple electrical instrument(s) (i.e. a voltmeter, ammeter) by measuring the voltage drops between the resistors and the current flow through them.

The same configuration can be investigated using the method described above. Since there is no mass transfer to the control volume, Eq. 8 can be written as:

$$\dot{S}_G = \oiint \frac{1}{T} \bar{q} \cdot \bar{n} \, dA \geq 0 \quad (11)$$

Using Eq. 7, Eq.11 becomes:

$$\dot{S}_G = \sum \frac{\dot{Q}}{T} = \sum \frac{\dot{W}}{T} = \sum \frac{1}{T} I \Delta V \geq 0 \quad (12)$$

In the above equation, $\dot{Q}$ and $\dot{W}$ refer to the net heat transfer and work done for each resistor. Note that the electrical work is directly expressed as the product of the voltage drop (ΔV) and the current (I) since the internal circuit is known a priori (e.g. Demirel and Gerbaud (2019)). As expected, the above equation clearly identifies the two parameters relevant to stability, the voltage drop and the current flow. In addition, the effects of environmental conditions are automatically included through the $1/T$ term so that the temperature should also be monitored unless it can be assumed to be constant. This secondary temperature related effect is often missed in practice since it is not evident when the First Law is considered alone.

An alternative method of investigating the stability of the above configuration is to rewrite Eq. 12 directly as follows:

$$\dot{S}_G = \sum \frac{\dot{Q}}{T} = \Sigma \frac{C_I(T_J - T_\infty)}{T_J} \geq 0 \qquad (13)$$

where T_J are the temperatures of the individual components, and C_J are the associated conductances (i.e. the overall heat transfer coefficient times area). Thus, stability can now be studied by monitoring the temperature of the resistors (e.g by using a non-contact thermometer) and the temperature of the ambient air. Unlike the conventional approach, no direct access to the power source or resistors is required and the effects of ambient temperature are once again included automatically in the analysis. Any variation in conductance due to fluctuations in ambient air velocities can be accounted for by simultaneously measuring this parameter if necessary. A additional important point worth noting is the fact that no knowledge of the underlying electrical system is required to evaluate the stability of the given configuration when this approach is used.

The above discussion shows that the effects of voltage fluctuations (the driving force for the work interaction) in this type of configuration can studied indirectly through the fluctuations in temperature difference between the resistors and the ambient (the driving force for heat transfer). A temperature based method can therefore be used to investigate a modified configuration where the initial resistor is replaced by a voltage regulator chip. Eq. 12-13 still apply and the enhanced stability of this modified control volume will be immediately evident if the input voltage is known to be unstable. Furthermore, the stable region of operation can be identified empirically by measuring the input voltage and chip temperatures, and a model can be developed for this modified configuration. Note that neither the stability analysis nor the model development require access to the voltage regulator chip or a detailed knowledge of the electrical circuit associated with it.

It is important to note that empirical and semi-empirical studies similar to the above example are often used in a variety of engineering applications (e.g. building and power plant inspections, electrical and electronic system evaluations, monitoring of manufacturing processes, etc.). However, these are typically limited in nature and do not consider the system as a whole. Unlike these approaches, the method presented in this paper provides a basis for systematic investigations of control volumes comprising vastly different types of internal processes. Since it focuses on the exterior of the control volume, it can also be used to monitor multiple control volumes encompassed in a larger open system, e.g. for studying a collection of small identical microsystems where averaged values can be monitored more easily than local values associated with an individual units.

2.2. Effects of Variations in the External Environment on Control Volume Stability

Given that Eq. 10 cannot be satisfied in open environments, it is useful to consider the effects of changes in external conditions on a general control volume. When the internal details of the controlled volume are known, the simplest approach is to solve Eq. 1-2 together with equations modeling the internal processes and suitable coupling functions (e.g. Stankovski et al. (2017)) using methods of network thermodynamics (e.g. Lewis (1995)). Alternatively, comprehensive multi-physics models can be used to obtain more details of the internal states throughout the control volume as functions of time. The stability of the control volume (and individual processes if necessary) can then be confirmed by (a) verifying that Eq. 6-7 are satisfied, (b) checking that the total entropy content of the control volume remains unchanged, and (c) ensuring that the total internal entropy generation rate (and the rates for individual processes if necessary) remain constant over time using Eq. 10.

The problem of control volume stability is more difficult to analyze when the internal processes are not well known. The best approach then is to consider the situation where an initially stable control volume (i.e. when $\dot{S}_G$ is constant) is subject to a change in external conditions. In this case, Eq. 1-3 still apply and Eq. 10 can be modified as:

$$\frac{d\,\dot{S}_G}{dt} = \frac{d\,\dot{S}_{G0}}{dt} + \frac{d\,\dot{S}_{GF}}{dt} \qquad (14)$$

where the subscript $_{G0}$ refers to the rate of entropy generation under stable conditions (= 0 since it is a constant) and $_{GF}$ to the time-varying fluctuating component that accounts for changes in the external and corresponding internal conditions.

In order to obtain an expression for the time-varying component of the total entropy generation rate, it is necessary to focus on the governing equations. Eq. 8 shows that the entropy transfers to/from the control volume are driven by the mass ($\rho\,\bar{v}\cdot\bar{n}$) and energy (in the form of heat ($\bar{q}\cdot\bar{n}$)) fluxes at its surfaces. Given the conservation laws at the interface, these can be evaluated using the gradients of different properties (pressure, concentration, electric/magnetic field strength, etc. for the velocity vector and temperature for heat flux vector) at either the interior or the exterior faces of the surfaces. When entropy transfers occur over discrete (as opposed to differential) surface areas, it is convenient to focus on the surface exterior, and replace these gradients by corresponding differences between the environmental value (subscript ∞) and the value at the control volume surface (subscript S) multiplied by surface conductances averaged over a specific surface area. Eq. 8 can now be rewritten as:

$$\dot{S}_G = \frac{dS}{dt} + \sum z_i C_i (x_S - x_\infty)_i = \dot{S}_{G0} + \dot{S}_{GF} = \dot{S}_{G0} + \frac{dS}{dt} + \sum z_i C_i (x_{SF} - x_{\infty F})_i \geq 0 \qquad (15)$$

In the above equation, C is the conductance (e.g. the product of the area and the heat or mass transfer coefficient, etc.), x refers to the specific variable driving the entropy transfer (temperature for heat flow, and pressure, concentration, electric/magnetic field strength, etc. for mass flow), z is the scalar variable associated with each entropy transfer mode (= $1/T$ for heat flow and = s for mass flow related entropy transfer), the subscript F refers to the fluctuating component and the subscript i refers to the entropy flow rate associated with each individual entropy transfer stream.

For unsteady conditions where the internal entropy generation rate is not constant, Eq. 14 can therefore be written as:

$$\frac{d\,\dot{S}_G}{dt} = \frac{d^2 S}{dt^2} + \sum z_i C_i (x_S - x_\infty)_i \left[\frac{1}{z}\frac{dz}{dt} + \frac{1}{C}\frac{dC}{dt} + \frac{1}{x_S - x_\infty}\left(\frac{dx_S}{dt} - \frac{dx_\infty}{dt}\right) \right]_i \qquad (16)$$

It is possible to simplify the above equation for typical conditions by comparing the three different terms on the right-hand-side above. In order to reduce unnecessary complications, this is best done by taking an arbitrarily driving force $x_S - x_\infty$, and then focusing on each term. When the first term is considered, for $z = 1/T$ corresponding to entropy transfer via heat flow, dz is proportional to $(1/T)^2$. Similarly, for $z = s$ corresponding to entropy transfer via mass flow, dz is proportional to $1/T$. dz/z is therefore proportional to $1/T$ in both cases. Thus, for typical ambient temperatures ($T \sim 300$K or for any $T >> 0$K) and changes in x_∞ such that $\Delta(x_S - x_\infty) \sim O(x_S - x_\infty)$, i.e. when environmental changes are not very large, the following condition will generally be true:

$$\left|\frac{1}{z}\frac{dz}{dt}\right|\Bigg|_i \ll \left|\frac{1}{x_S - x_\infty}\frac{d(x_S - x_\infty)}{dt}\right|\Bigg|_i \qquad (17)$$

The second term is considered next. It involves changes in conductances which depend on material properties and, in some cases, on the driving force $x_S - x_\infty$ itself. The effects of material properties can be neglected in most cases since these are relatively small unless there are large changes in thermodynamic properties. However, the effects of the driving forces must be accounted when appropriate. This is typically done by using power law models, i.e. C is taken to be proportional to $(x_S - x_\infty)^m$ where m is a constant. The second term can therefore be written as:

$$\frac{1}{C}\frac{dC}{dt}\bigg|_i = \frac{m}{x_S - x_\infty}\frac{d(x_S - x_\infty)}{dt}\bigg|_i \qquad (18)$$

Note that $m = 0$ in this equation corresponds automatically to the case where C is independent of the driving force. Eq. 16 can now be rewritten using Eq. 15, 17-18 as:

$$\frac{d\dot{S}_{GF}}{dt} = \frac{d^2S}{dt^2} + \sum (1+m)_i z_i C_i \left(\frac{dx_S}{dt} - \frac{dx_\infty}{dt}\right)_i = \frac{d^2S}{dt^2} + \sum (1+m)_i z_i C_i \left(\frac{dx_{SF}}{dt} - \frac{dx_{\infty F}}{dt}\right)_i \qquad (19)$$

where the conductances C_i can vary with external conditions in many cases.

Eq. 19 can be solved for the fluctuations in the entropy generation rate if the rates of change of dS/dt, x_{SF} and $x_{\infty F}$ are known. In a given physical situation, the term $dx_{\infty F}/dt$ depends on the external conditions. Thus, it can be taken as a known function of time representing different environmental scenarios. Also, since dx_{SF}/dt is driven by fluctuations in internal processes, and since both dx_{SF}/dt and $\dot{S}_{GF}$ are determined by the internal kinetics of a control volume, they are directly related to each other at any given time. In addition, since the total internal entropy generation rate depends on the entropy generation rate of the individual internal processes within the control volume, it is possible to write:

$$\frac{dx_{SF}}{dt}\bigg|_i = G_i(t, \dot{S}_{GF}) = H_i(t, \dot{S}_{GF,J}\big|_{J=1,\dots N}) \qquad (20)$$

where the functions G_i and H_i depend on the actual processes within a given control volume (see Appendix A.1), and the subscript J refers to the individual processes. Note that these functions may not be known a priori, but can be evaluated if the conditions within the control volume are known as a function of time. Using this equation, Eq. 19 can be written as:

$$\frac{d\dot{S}_{GF}}{dt} = \frac{d^2S}{dt^2} + \sum (1+m)_i z_i C_i \left[G_i(t, \dot{S}_{GF}) - \frac{dx_{i\infty F}(t)}{dt}\right] \qquad (21)$$

Process stability cannot be expected to occur independently of steady-state conditions. Though perfectly steady conditions cannot exist when boundary conditions change, near steady-state conditions occur when the terms on the left-hand-sides of Eq. 1-3 are significantly smaller than the corresponding terms on the right-hand-sides, so that Eq. 6-8 are (approximately) satisfied. Under these circumstances, control volume stability is possible in many cases. For control volumes that achieve steady conditions after being subject to changes in the external environment, the rate of change of entropy (*dS*/*dt*) is negligible, and Eq. 21 can be simplified further as:

$$\frac{d\,\dot{S}_{GF}}{dt} = \sum (1+m)_i z_i C_i \left[G_i(t,\dot{S}_{GF}) - \frac{dx_{i\infty F}(t)}{dt} \right] \quad (22)$$

Eq. 22 is noteworthy not only because it can be used to evaluate the fluctuations in the entropy generation rate of a control volume approaching steady state, but also due to the form of equation itself. Since such equations are widely associated with the study of dynamical systems (e.g. Haken (1977), Teschl (2012)), it shows that the stability of general open systems can be evaluated using similar techniques. Previous work done in dynamical systems also shows that the stability of dynamical systems is ultimately linked to a means of control in a general sense (e.g. Sontag (1998)). Thus, open control volumes must have some form of control based on the internal entropy generation rates if they are to be stable. This will be true for a wide range of applications since Eq. 22 is not based on a specific configuration, but has been developed by considering an arbitrary control volume.

The above discussion clearly shows that open systems may be studied from a dynamical and control systems perspective when the functions G_i are known, i.e. when the processes within the control volume can be mathematically modeled. Though such systems must be initially analyzed using Eq. 6-7 together with equations governing the internal processes, a controls based approach may be preferable during systems design in some applications. More importantly, since Eq. 22 applies to arbitrary control volumes, it can also be used in situations when the internal details of a control volume are not known adequately. Under these circumstances, the functions G_i can be derived using Eq. 8 and a combination of experimental and computational methods (e.g. Ljung (2010), Daniels and Nemenman (2015), Brunton et. al (2016)). A stability analysis can then be done for such control volumes for different environmental conditions. Note that an analysis using functions G_i (as opposed to H_i (see Eq. 20)) cannot confirm that individual internal processes are stable when the overall control volume is stable. However, this may well be true in many cases.

A simple example using Eq. 22 is studied below in order to highlight some issues that are relevant to control volume stability. To ensure that the results are more widely applicable, the example is not directed towards a specific configuration but considers a general problem with the following assumptions:

a. The external fluctuations are related to only one entropy transfer stream in Eq. 22 (i.e. $i = 1$ only).

b. $\dot{S}_{GF}$ and dx_{SF}/dt are related through a power law model since such models are applicable for a wide variety of processes as long as their use is limited to specific parameter ranges (e.g. Clauset et al. (2009)).

Based on the above, the function G can be written as:

$$G = f(t)\dot{S}_{GF}^{n} \qquad (23)$$

where f(t) is an unknown function of time and n is a constant. Eq. 22 can then be written as:

$$\frac{d\,\dot{S}_{GF}}{dt} = (1+m)\,z\,C\left[f(t)\,\dot{S}_{GF}^{n} - \frac{dx_{i\infty F}}{dt}\right] \qquad (24)$$

Two different scenarios, viz. a step change and time-varying change in the environmental conditions, are considered below.

i) Effect of Step Changes in the External Environment

For time $t \geq 0$, a step change in the external environment is represented by:

$$x_{\infty} = x_{\infty 0} + x_{\infty F} \qquad (25)$$

where $x_{\infty 0}$ is the initial value corresponding to the stable condition and $x_{\infty F}$ is the step change which is a constant. Eq. 24 now reduces to the following:

$$\frac{d\,\dot{S}_{GF}}{dt} = (1+m)zC\,f(t)\dot{S}_{GF}^{n} \qquad (26)$$

When changes in z are small, this equation can be solved for constant conductance (i.e. C = constant, m = 0) with the following initial condition:

$$t = 0: \quad \dot{S}_{GF} = \dot{S}_{GF0} = zC(x_{S0} - x_{\infty F}) \qquad (27)$$

For $n \neq 1$, the solution is given by the following:

$$\dot{S}_{GF} = \left[\dot{S}_{GF0}^{1-n} + (1-n)(F(t) - F(0))\right]^{\frac{1}{1-n}}; \quad F(t) = zC\int f(t)dt \qquad (28)$$

For stability, fluctuations in the entropy generation rate must reduce to zero as the time t increases. This is possible for large class of functions $f(t)$, with the following being very simple examples:

$$n > 1: \quad f(t) = a\exp(ct) \qquad (29a)$$

$$n < 1: \quad f(t) = \frac{-c\,\dot{S}_{GF0}^{1-n}}{1-n}\exp(-ct) \qquad (29b)$$

where a and c are arbitrary constants ($c > 0$). When $n = 1$, i.e. the linear case, the solution is given by:

$$\dot{S}_{GF} = \dot{S}_{GF0}\exp(F(t)); \quad F(t) = zC\int f(t)dt \qquad (30)$$

In this case, stability is possible once again with a large class of functions for f(t) (e.g. polynomials with negative coefficients). The simplest option here is take f(t) as a negative constant for which Eq. 30 reduces to:

$$n = 1: \quad f(t) = -c, \quad c > 0; \quad \dot{S}_{GF} = \dot{S}_{GF0} \exp(-zC\,ct) \quad (31)$$

The above equations (Eq. 28-31) clearly show that are asymptotically stable solutions to step changes in boundary conditions exist for Eq. 26 for a large variety of power law functions, i.e. for many different types of control volumes.

From practical considerations, the most important conclusion of the above analysis is that a variety of open systems can be investigated using Eq 26. This is clear from the range of functions defined by Eq. 23 and Eq. 28-31. Thus, asymptotic stability to a step change in external conditions (where the control volume returns to its stable state as $t \rightarrow \infty$) is possible for a variety of control volumes as long as the total rate of internal entropy generation (resulting from various internal processes) meet specific functional criteria such as those given in Eq. 23-26. Such control volumes will be essentially stable as long as external changes occur sufficiently slowly such that internal processes can respond to it adequately (with the time constants being determined by the value of c in Eq. 29 and Eq. 31 for example). The problem where multiple entropy streams are involved can also be studied in a similar manner as above. Though analytical solutions can be obtained when the function $f(t)$ or the power function coefficients n in Eq. 23 are identical for all entropy streams, numerical methods must be used when this is not the case (as is more likely).

The situation where stability conditions are not satisfied, i.e. when the constant c is not positive, also provides some insight into the overall process. When $c = 0$, i.e. when the surface conditions are not influenced by internal processes, Eq. 26 shows that control volume jumps to a new state where the change in rate of entropy generation is driven directly by the external fluctuation. Thus, even though physical or structural stability may exist (i.e. Eq. 6-9 are satisfied), thermodynamic stability is no longer possible as the change in the rate of entropy generation does not reduce asymptotically to zero over time. Note that this change will be small only when the external changes are correspondingly small, and the control volume will remain approximately stable only under these circumstances. When $c < 0$ on the other hand, the control volume will tend to become unstable. In this case, Eq. 26 is no longer applicable as the control volume departs from its original state, and the Eq. 6-9 are unlikely to be satisfied over the long run.

It is important to emphasize that details of the individual processes within the control volume are not important from a broader perspective, but the critical factor is their combination that determines the stability criteria in terms of values of constants such as c in Eq. 29 and Eq. 31. At the same time, the critical nature of a single parameter such as c in Eq. 29 and Eq. 31 does not imply that a “centralized” control method is necessary, since equivalent effects can be obtained in a distributed configuration (e.g. by splitting Eq. 26 and evaluating the fluctuations in entropy generation rates for individual subsystems using a coupled set of equations). A linear stability criterion such as the one in Eq. 31 also does not suggest that the internal processes are linear since combinations of complex processes are known to result in simpler, sometimes linear, functional dependencies at a larger scale (e.g. Anderson (1972), Selvarajoo et al. (2009)).

It is also worth noting that the above conclusions hold even when the conductance depends on the driving forces, i.e. when $m \neq 0$. This situation can be studied qualitatively by considering a linearized form the equation that incorporates a modified (constant) value for C accounting for its varying magnitude in an approximate sense. Since the form of the governing equation and initial condition (Eq.

26-27) remain unchanged (as long as $m > -1$), the stable solutions will be identical in form to Eq. 26-31. Thus, a stable control volume will remain so under varying external fluctuations, with the only difference being the time required to approach the stable condition, i.e. the time constant for the process will change depending on the magnitude of the modified value of conductance. A similar conclusion can also be drawn when there are step changes in conductivity due to work done by other internal or external forces.

ii) Effect of Time-Varying Changes in the External Environment

A more general case that is particularly relevant from a practical perspective is the situation where there are continuous changes in the external environment. In order to highlight some important issues here, the effects of two types of external changes, viz. periodic fluctuations and random fluctuations, are compared for the linear case (i.e. constant conductance (C = constant, $m = 0$), and $n = 1$ with $f(t) = -c$ as in Eq. 31). For the first problem, i.e. when the fluctuations in the external environment are periodic, Eq. 25 can be replaced by the following:

$$x_\infty = x_{\infty 0} + x_{\infty A} \cos(\omega t) \qquad (32)$$

where $x_{\infty A}$ is the amplitude and ω is the angular velocity associated with the period of fluctuation. Eq. 24 can then be written as:

$$\frac{d\dot{S}_{GF}}{dt} = zC\left(-c\,\dot{S}_{GF} + x_{\infty A}\omega \sin(\omega t)\right) \qquad (33)$$

The solution to the above equation is given by:

$$\dot{S}_{GF} = \left[\dot{S}_{SGF0} + \frac{(\omega / zCc)^2 zCx_{\infty A}}{1 + (\omega / zCc)^2}\right]\exp(-zCct) - \frac{(\omega / zCc)}{\sqrt{1 + (\omega / zCc)^2}}\, zCx_{\infty A} \sin(\omega t - \gamma) \qquad (34)$$

$$\tan\gamma = -\omega / zCc$$

For $c > 0$, the exponential term in the above equation decreases with time and becomes negligible for $t \gg 0$. Beyond this point, the rate of internal entropy generation fluctuates indefinitely with an amplitude that is a function of various parameters associated with the external disturbance, i.e. unlike the previous case where there was a step change in external conditions, asymptotic stability is not possible in this situation. However, a closer analysis of Eq. 34 shows that the amplitude reduces with the ratio ω/zCc, so that for $\omega/zCc \ll 1$ and $t \gg 0$, a simple solution is obtained:

$$\dot{S}_{GF} = -\left(\frac{\omega}{zCc}\right) zCx_{\infty A} \sin(\omega t) \qquad (35)$$

This shows that the amplitude of the fluctuation can be arbitrarily small as long as the ratio ω/zCc is sufficiently low to mitigate the effects of the external changes. This ratio can vary widely depending on the processes within the control volume and the environmental changes since it corresponds to the ratio of the time constant associated with the indirect internal (damping) effect (~ $1/zCc$) relative to the period of the external fluctuation (~ $1/\omega$). Thus, even though asymptotic stability is not possible when there are periodic changes in external conditions, the corresponding fluctuations in the total entropy generation rate can be reduced to very small values under certain conditions, i.e. Lyapunov stability is possible. A stability criterion can then be defined based on the ratio of the amplitude of a given fluctuation to the entropy generation rate under stable conditions as:

$$\frac{(\omega / zCc)}{\sqrt{1+(\omega / zCc)^2}} \; \frac{x_{\infty A}}{x_{S0} - x_{\infty 0}} \leq \varepsilon, \quad \varepsilon \ll 1 \qquad (36)$$

where the value of ε will depend on the control volume, and is typically selected during systems design.

It is important to note that though the above results have been derived by assuming that the external fluctuations can be modeled using a simple harmonic function, they can be readily extended to cover all other periodic effects that can be represented by a Fourier series. A similar analysis can also be done when the external fluctuations are represented by a more general time-series.

In addition to periodic changes, another factor comes into play when one considers a control volume in a completely open environment where the external processes are very large in number and independent of each other. In this situation, the external conditions will be affected by additional fluctuations that are effectively random, with a normal (Gaussian) distribution per the Central Limit Theorem. In order to study the effects of random fluctuations in the environment, the sinusoidal function in Eq. 32 is replaced by a random fluctuation given by $x_{\infty R}(t)$ that is a function of time:

$$x_{\infty} = x_{\infty 0} + x_{\infty R}(t) \qquad (37)$$

This fluctuation is taken as a random (Gaussian) process where all values of $x_{\infty R}(t_j) \quad (j = 1, \ldots, \infty)$, are independent of each other and previous values of $x_{\infty R}(t_j)$. In addition, it is assumed that the process is continuous and the fluctuations are finite at all times. Since the time derivative of such a random function almost never exists, the governing equation equivalent to Eq. 33 (i.e. the linear case with *f(t) = -c*, *c* > 0) is now written as:

$$d\dot{S}_{GF} = zC(-c\dot{S}_{GF}\,dt - dx_{\infty R}) = zC(-c\,\dot{S}_{GF}\,dt - \sigma\, d\mathrm{W}) \qquad (38)$$

where $\sigma^2 t$ is the variance of $x_{\infty R}(t)$ (note that this variance is initially zero when the control volume is stable, but increases with time due to random external effects), and W(*t*) is the Wiener function. Eq. 38 is a well-known stochastic differential equation, the Ornstein-Uhlenbeck equation, and individual solutions for $\dot{S}_{GF}$ can be obtained numerically for a specific random process $x_{\infty R}(t)$. For a given (i.e. measured or known) value of σ^2, these solutions have a Gaussian distribution (e.g. Doob (1954)) whose mean and variance are given by the following equations:

$$Mean(\dot{S}_{GF}) = \dot{S}_{GF0}\exp(-zCct) = 0 \quad for \quad \dot{S}_{GF0} = 0 \qquad (39)$$

$$Variance(\dot{S}_{GF}) = \sigma^2 \frac{zC}{2c}(1 - \exp(-2zCct)) = \sigma^2 \frac{ZC}{2c} \quad @ \quad t \to \infty \qquad (40)$$

Using the above, it is now possible to define a stability criterion similar to the one for the sinusoidal case based on a single standard deviation in $\dot{S}_{GF}$ (instead of the amplitude of fluctuation) as:

$$\frac{1}{x_{S0} - x_{\infty 0}} \sqrt{\frac{\sigma^2}{2zCc}} \leq \varepsilon, \quad \varepsilon \ll 1 \qquad (41)$$

This equation is superficially very similar to Eq. 36, but it masks a very important difference due to the fact that the actual fluctuation in a specific random sequence can be extremely large regardless of the finite value of σ^2. Though this suggests that Eq. 41 is not really useful, that assumption is incorrect since the probability of a control volume encountering an infinitely large external fluctuation can be infinitely remote. Thus, it is necessary to consider a secondary parameter together with Eq. 41, viz. the "first passage time" which corresponds the to the time required for the magnitude of the fluctuation to be greater than a selected value.

The first passage time with two symmetric bounds (+ve and -ve) has been evaluated for the Ornstein-Uhlenbeck equation by various researchers in the past. The mean first passage times t_{MFP} are presented in a normalized form (i.e. relative to the time constant (= $1/zCc$))) as a function of different fluctuation levels (magnitude of the fluctuation (= $\dot{S}_{GF}$) relative to the standard deviation of the fluctuation (= $\sigma(ZC/2c)^{1/2}$) in Table 1.

Normalized fluctuation	Normalized mean first passage time	Standard deviation of normalized mean first passage time
($\dot{S}_{GF}$ /($\sigma(ZC/2c)^{1/2}$))	($t_{MFP}\, zCc$)	
1	0.595749E00	0.502488E00
2	0.450160E01	0.412032E01
3	0.425745E02	0.417620E02
4	0.100817E04	0.100697E04
5	0.703694E05	0.703679E05
6	0.141338E08	0.141337E08
7	0.798998E10	0.798998E10

Table 1: Mean first passage times and its standard deviation for different magnitudes of fluctuations in entropy generation rates (Data from (Keilson and Ross (1975))

It is useful to focus on a specific example to highlight an important issue relevant to random external fluctuations. Thus, consider the normalized fluctuation level of 3 in the above table, for which the normalized mean first passage time is 42.57. This implies that a fluctuation level equal to 3 times the standard deviation of the fluctuation (3SD) will be reached within ~43 s on an average when the time constant associated with the internal changes in entropy generation rate is of the order of 1s (i.e. $1/zCc$ = 1s). Even higher fluctuation levels are also likely to occur in time-frames that are relatively short (~ 19-20 hours for 5SD), though extreme fluctuation levels are increasingly less likely (~5-6 months for 6SD, etc. Thus, random external fluctuations can be expected to have significant effects on a control volume when the variance of $x_{\infty R}(t)$ changes rapidly (i.e. in highly variable environments where σ is large) unless the time constants driving the changes in internal entropy generation rates are very small. Also, if the effects of random and sinusoidal (or other periodic) fluctuations are compared for a given control volume, these results show that random fluctuations will have much greater effects over realistic time periods even if the standard deviations of the resulting internal processes are similar.

High fluctuation levels resulting from large random changes in the environment, however infrequent, can have unpredictable effects. These may be destabilizing or stabilizing depending on the nature of the fluctuations and the internal processes, and must be considered on a case-by-case basis. If they result in new or modified internal processes that do not affect existing stability criteria or meet modified stability criteria, a new type of stable control volume may also result. On balance however, given the above results and the fact that systems subject to random noise must meet specific stability related conditions (e.g. Arnold et al. (1983)), it is more likely than not that stable control volumes will be destabilized by random external fluctuations over the long-term.

3. Discussion of Results

This study has focused on the influence of changes on the external environment on open systems. Unlike other current approaches, it emphasizes the importance of irreversible losses in determining control volume stability and explicitly proposes that internal losses and entropy generation rates remain constant in a truly stable system. This makes it possible to differentiate completely stable control volumes from partially stable ones that may be physically or structurally stable from a First Law perspective (e.g. Bernard convection), but are not thermodynamically stable to changes in boundary conditions. By focusing on the internal changes in a control volume when it interacts with an open environment, it also shows that stability can be best defined by the relative stability of its internal processes. This last conclusion is implicitly assumed in many current studies though questions regarding this issue continue to be raised (e.g. Pascal and Pross (2015)).

The stability condition given by Eq. 10 also highlights an important point, viz. different levels of stability are possible. This is understood in many applications, for example, many “steady” fluid-thermal processes comprise unsteady internal flow structures when the boundary conditions are essentially constant, i.e. some internal processes are “unstable” even when the overall control volume is essentially “stable” from an external perspective. Thus, in its simplest form, a control volume can be considered to be stable as long as its total irreversible entropy generation rate is limited to an acceptable values as in Eq. 36 or Eq. 41. When this is the case, internal processes are not separately constrained, and the only condition that these processes have to satisfy is that their individual irreversible losses remain bounded at all times. On the other hand, if it is necessary for internal processes to individually controlled, this must be explicitly imposed via the first form of Eq. 10 (see also Eq. 20). Engineered systems typically take this second approach, whereas the less strict version of stability is more often seen in natural settings.

Regardless of the above, it is important to note that complete stability at “all” levels is impossible from a probabilistic viewpoint. This is based on the Second Law itself which arises from the fact that large numbers of particles cannot be individually stable due to continuing interactions between them. Instead, stability at different levels arise due to continuing two-way interactions between the external environment and “higher” and “lower” level processes within the control volume (e.g. Simon (1962)), and the problem must therefore be considered at the appropriate level for any given situation (e.g. Anderson (1972), Goldenfeld and Kadanoff (1999)). Thus, a preferred design approach for a given problem may be to identify combinations of processes that can lead to a simple forms of Eq. 20 (i.e. involving small numbers of internal processes) and a robust control volume. This issue has broad implications for future applications since the relative importance of individual process stability and overall control volume stability can vary from situation-to-situation, and unnecessarily strict design requirements can have a significant impact on costs.

The study also proposes a general method for studying/monitoring the thermodynamic stability of systems using the fundamental laws of thermodynamics. Since the method is based on measurements made at the external surfaces of the control volume, it can expected to be particularly useful where internal measurements are impractical. The simple example illustrating the method also shows that it has a number of advantages over other approaches. Most important of these is the fact that parameters relevant to control volume stability can be easily identified using this method so that appropriate approximations relevant to a given problem can be made in a systematic manner. At the same time, it can also be used to identify alternative parameters for evaluating stability if necessary. Model development can then be done using these secondary parameters without a detailed knowledge of the internal processes involved.

Entropy based stability analysis targeting specific problems in engineering have been undertaken by previous researchers (e.g. Robinett III et al. (2006), Ozkan and Ydstie (2019)). However, the present approach is broader in scope since it considers a general model that potentially covers a wide range of applications. It shows that the general nonlinear problem of stability can be simplified for large class of problems covering typical ambient conditions as long as environmental fluctuations are not very large. The stability of a such control volumes can then be studied using the methods of dynamical systems analysis and control systems. Thus, this study provides a bridge to the areas of Second Law analysis of systems and exergy based controls which have so far focused on identifying and minimizing irreversible losses in large integrated systems (e.g. James et al. (2020)).

Simple examples show that stability is possible for a wide variety of control volumes in open environments as long as the total rates of internal entropy generation meet specific criteria that depend on the nature of the internal processes. Random fluctuations that are present in completely open environments can also be expected to have a small effect as long as the time constants associated with the internal processes are very small. Over the long term however, random fluctuations will likely have large destabilizing effects which will limit the life of otherwise stable control volumes. Control volumes must therefore be able to duplicate themselves within this limited period if a stable population of similar control volumes is to be viable. In any case, "perfect" long-term stability is impossible in practice since continuing interactions between various control volumes and an uncontrolled environment make internal (i.e. "evolutionary") changes inevitable.

Two issues relevant to real-life systems have not been considered in this study. The first is related to energy storage within the control volume which is inevitable when a system interacts with a changing environment. In practice, the assumption of steady-state is only approximate as noted before, i.e. the terms on the left-hand-sides of Eq. 1-3 are significantly smaller than the corresponding terms on the right-hand-sides. Thus, the stability criteria such as those developed in previous sections can only be considered to be approximate. However, if storage effects are important from a physical perspective, energy transfer within the control volume through energy storage processes can be considered in a similar manner as energy transfer to/from the environment at its external boundaries. The fundamental difference here is that the process occurs internally and must therefore be considered in a stability analysis. In general however, better control is possible because these processes are internal, and energy storage more often than not results in increased stability for a control volume.

The second issue is related to the fact that the present study has focused entirely on the effects of external fluctuations based on the assumption that these changes do not affect the internal processes adversely in a permanent manner. In practice, internal changes are inevitable consequences of the Second Law of Thermodynamics whether there are external fluctuations or not. In the absence of suitable repair processes, these can lead to process as well as structural changes that can have adverse consequences in the long-term. Instabilities due to internal failures is therefore entirely possible, but this requires a detailed internal analysis of the control volume itself. Stability to external fluctuations beyond an internal failure related lifespan is therefore not likely to be very useful for a general control volume.

3.1. Implications for Living Organisms

The results of the present study have a number of implications of life, particularly early prebiotic forms. These are summarized below:

i) The idea that homeostasis exists not just for select internal processes within an organism, but at the level of the organism itself, continues to be an unsettled matter since researchers have linked the presence of systemic control to other higher level characteristics such as cognition (e.g. Baluska and Levin (2016)). This study shows that systemic control in stable control volumes has its roots in the fundamental thermodynamic principles. Thus, its presence should be expected in the most primitive forms of life, since without it, approximate stability is possible only if the changes in the external conditions are small. This study also shows that this control is not limited to internal processes only, but also involves continuing interactions with the environment which, in principle, can include neighboring control volumes. This supports the hypothesis that cellular communication may play an important role in evolution and development (Torday (2015)).

ii) The present study shows that a control volume can be thermodynamically stable only when it implements internal processes that provide control over energy and entropy transfer from/to the external environment. In addition, since this stability is often limited to relatively short durations due to destabilizing effects of random external fluctuations, long-term population stability is possible only if a control volume can duplicate itself prior to its failure. These results suggest that early life likely comprised a combination of all three primary forms that have been proposed (e.g. Dyson (2008)): (a) self-sustaining chemical reaction systems that extract energy from the surroundings, (b) enclosure type systems based on structures enclosed by lipid bilayers that can control mass and energy flows, and (c) replicative systems that are driven by RNA or mineral based processes. This has also been concluded by Lanier and Williams (2017) based on entirely different arguments related to fundamental biochemical and genetic characteristics of current living organisms.

iii) Research increasingly shows that stability and control is a two-way process in living organisms with high-level subsystems affecting lower-level subsystems and vice-versa (e.g. Noble (2012)). This is supported by this study which shows that system stability is ultimately determined by process stability and results from continuing interactions between internal processes. The fact that overall system stability does not imply similar stability at all levels in living organisms is also supported by the present study which shows that stability levels at different levels can be highly variable even when the overall control volume is generally stable. In addition, the result that relatively large random fluctuations can affect many stable control volumes within reasonable periods of time also supports the observation that new stable organisms sometimes develop due to random interactions with other organisms (e.g. Kapsetaki et al. (2024)).

4. Summary and Conclusions

The laws of thermodynamics have been used to show that the stability of open systems is best defined not by steady-state conditions, but by the stability of their internal processes. In addition, since changes in internal processes affects the rate of total internal entropy generation rate, a fundamental stability criterion can be defined based on this parameter. An advantage of using this criterion is that it can be used to evaluate the overall stability of control volumes using external measurements when internal processes cannot be directly monitored. The stability criterion can also be imposed at various levels based on the stability of individual internal processes so that different levels of stability are possible for a given control volume. However, this is subject to fundamental limits placed by the Second Law.

The study also shows that the general equations governing control volume stability can be simplified for large class of problems covering typical ambient conditions as long as environmental fluctuations are not very large. This equation is of a form that is commonly encountered in the study of dynamical systems so that open systems can be expected to be stable only if they have some form of internal control. This has been illustrated by simple examples which also show that random fluctuations in completely open environments will likely destabilize otherwise stable control volumes over the long-term. The overall results also provide some useful insights into some essential characteristics of early prebiotic systems, viz. the presence of system-level homeostasis, a controlled internal environment, steady energy flows and an ability to replicate in a relatively short period of time.

Data Availability Statement: No additional data is required to support this work or is available.

Conflict of Interest Disclosure: The authors have no conflicts of interests related to this work.

Funding Statement: This work was not supported by any organization or institution.

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APPENDIX

A.1. The function G_i (Eq. 20)

For a general control volume with time-dependent boundary conditions, a multi-physics or network thermodynamics formulation of the governing equations (i.e. the equations related to mass, energy, force/momentum conservation, external electromagnetic fields, etc.) can be used to determine changes at different locations as functions of time. At its surface, fluctuations will be given by an equation of the form:

$$x_{SF} = x_S(t) - x_{S0} = F(t, r) \quad ..(A.1)$$

where r refers to the coordinate/location and the function F will depend on the control volume and its initial and boundary conditions. Note that terms related to the various material properties are not shown explicitly in the above equation for convenience.

The rate of change of these surface conditions at a location r_i associated with a specific mass/energy/ entropy flow stream can therefore be obtained using the following equation:

$$\frac{dx_{SF,i}}{dt} = \frac{dF_i}{dt} = F_i'(t) \quad ..(A.2)$$

The term related to the location r_i is not retained explicitly on the right-hand-side of Eq. A.2 since it corresponds to a known fixed location.

An equation for the change in total entropy generation rate (or the entropy generation rates for select processes) within the control volume can also be obtained as a function of time in a similar manner using the solution to the governing equations together with Eq. 3. This equation can be written as:

$$\dot{S}_{GF} = \dot{S}_G(t) - \dot{S}_{G0} \quad ..(A.3)$$

After interchanging the dependent variable $\dot{S}_{GF}$ and the independent variable t in Eq. A.3, and substituting in Eq. A.2, the following equation is obtained:

$$\frac{dx_{SF,i}}{dt} = f_i(\dot{S}_{GF}) \quad ..(A.4)$$

where the function f_i depends on functions F_i' and $\dot{S}_G$ in Eq. A.2-A.3.

In practice, the independent variable t can be completely eliminated only when $\dot{S}_{GF}$ is a monotonic function of time, i.e. when it converges smoothly to a constant value or diverges. When this is not the case as is more likely, different functions for $\dot{S}_{GF}$ can be used whenever $d\dot{S}_{GF}/dt$ changes sign. Thus, the above equation can be replaced by the following:

$$\frac{dx_{SF,i}}{dt} = G_i(\dot{S}_{GF}(t)) = G_i(t, \dot{S}_{GF}) \quad ..(A.5)$$

Alternatively, since F_i' and $\dot{S}_{GF}$ are both functions of time, the two can be related using an implicit function g_i as follows:

$$g_i\left(\dot{S}_{GF}, F_i'\right) = 0 \quad ..(A.6)$$

Eq. A.6 can then be used to obtain F_i' as a function of $\dot{S}_{GF}$ at any given time, and Eq. A.5 (i.e. Eq. 20) is still applicable. Note that Eq. A.5 is simply a mathematical relation, and its validity does not by itself imply the existence of a stable condition since stability of a control volume depends on interactions between environmental fluctuations and internal processes. Thus, the simplest approach to stability analysis is to consider a stable control volume responding to a single such fluctuation (see example with a step-change in external condition earlier in the paper where both time dependent and time independent functions for G_i have been considered). For more general cases involving time-dependent environmental changes, the situation can be more complex (see other examples). Under these circumstances, three different methods can be used to evaluate the thermodynamic stability of a control volume as pointed out in the paper.

a. A fundamental approach involves the solution of the underlying governing equations with its time-varying boundary conditions. Stability of internal processes can then be evaluated individually, or the overall stability of the control volume can be determined from the fluctuations in total entropy generation rate.

b. The stability of a control volume when perturbed from steady conditions by external fluctuations can also be investigated by developing a dynamical model of the system. This is accomplished by using Eq. A.2-A.5 to identify the different functions G_i from select solutions of the governing equations (as in (a) above). The general stability of such control volumes can then be evaluated using Eq. A.5/Eq. 22. Note that combined functions $\boldsymbol{G}(t, \dot{S}_{GF})$ that simultaneously account for the effects of some or all of the individual functions G_i may be more appropriate in many cases.

c. For systems where the internal processes are not fully known, the functions G_i (or combined function(s) $\boldsymbol{G}(t, \dot{S}_{GF})$) can be evaluated experimentally. Stability can then be investigated using Eq. 22 as in (b) above.

Of the three, the dynamical systems approach proposed in this paper (i.e. b-c above) may be more practical for design and stability analysis of complex control volumes since it can be used when internal processes are not well characterized and is likely to be computationally less intensive.

A.2. Design Considerations for Control Systems of Autonomous Control Volumes

From a design perspective, the stability criteria for a general control volume can involve a large number of control parameters due to the high variability of an uncontrolled external environment (regardless of whether they are based on combined functions $\boldsymbol{G}(t, \dot{S}_{GF})$ or a number of individual functions G_i). The only exceptions to this are special situations where the external fluctuations and/or the surface conductances (C) for mass, and energy flows are small (see for example, Eq. 36, 41). In more general cases, methods for achieving stability can be identified from Eq.14-41 together with Eq. 8, or when temperature changes are small, a simplified version of Eq. 9:

$$\dot{S}_G = -\frac{1}{T}\oiint\left(\left[\Sigma\rho_I\left(\left(h - Ts\right) + pe + ke\right)\bar{v}_I\right]\cdot\bar{n} - \dot{w}\right)dA \qquad (A.7)$$

Note that unlike Eq. 8, Eq. A.7 relates the internal entropy generation rate to the free energy transport and work interactions at the control volume surface, so that *z* in Eq. 14-41 now refers to the scalar variables associated with these energy transfer modes. In either case, Eq. 14-41 show that stability of independent control volumes can be achieved by the following:

a. Selecting appropriate internal control parameters (e.g. *a* and *c* in Eq. 29, 31, 36, 41) to minimize the effects of the external fluctuations, and/or

b. Modifying or controlling environmental conditions (e.g. magnitudes and frequencies as given by $x_{\infty F}$, $x_{\infty A}$, $x_{\infty R}(t)$, ω, σ^2, etc. in Eq. 25, 32, 37) or the external conductances (C_i in Eq. 22) to minimize the external fluctuations and/or their effects on the control volume.

These options show that internal work and/or work interactions with the external environment are required in order to maintain thermodynamic stability. Most engineered systems use the first approach since it is relatively simple and can account for effects of long-term structural and functional changes resulting from internal dissipative effects. Such systems are then used in locations where external conditions remain within an acceptable range.

Autonomous control volumes that can be used in completely open, uncontrolled environments are far more complex since they must be able to manage the effects of constant external fluctuations and do additional work to move to more favorable locations, modify the surroundings, etc. As a result, they typically have the ability to maintain multiple stable configurations (e.g. a low-energy or dormant state) and include some energy/materials storage capacity in order to accommodate large environmental changes. In addition, systems with long lifespans often incorporate some form of adaptability within their control algorithms since variations in external conditions cannot be completely predicted over extended periods (e.g. $x_{\infty F}$, $x_{\infty A}$, $x_{\infty R}(t)$, ω, σ^2, etc. in Eq. 25, 32, 37 may change greatly over time). The stability criteria (e.g. *a* and *c* in Eq. 29, 31, 36, 41) and work parameters can then be adjusted when conditions change beyond a certain point.

The approaches described above are adequate for environments that vary slowly and unpredictably over time. For other general environments, more complex techniques are required. For example, when the frequencies of external fluctuations cycle over larger time-scales, the above methods can involve repeated adaptations which ultimately results in poor overall performance. Control systems that combine adaptability with memory (i.e. methods using some form of learning) are then preferable since these can preemptively adapt to changing conditions based on knowledge of past fluctuations. Their performances can be further improved by fine-tuning the learning algorithms by systematically simulating the effects of one or more external fluctuations iteratively via related internal (physical and/or computational) processes (e.g. Dayan et al. (1995)).

Control volumes that are subject to changes in a large number of environmental parameters require complex control systems to simultaneously manage the effects of all the different fluctuations. Combining adaptation, learning and system-wide simulations that model the control volume and its external environment is advantageous in this case since consistent internal models of the joint system can be obtained. Such models are particularly useful since they can help overcome time and resource constraints that can otherwise limit the ability of control volumes to successfully respond to multiple fluctuations in a timely manner. They can also incorporate self-protection (or self-preservation) algorithms that can further enhance stability. Note that this approach is widely used in living organisms, and some of their subconscious activities and their "consciousness" may be internal manifestations of such ongoing systemwide simulations.

The stability of an autonomous control volume can also be enhanced if it collaborates with other control volumes instead of simply controlling their effects as it does with other environmental fluctuations. Though this can be mutually beneficial for control volumes with similar or complementary stability requirements, it adds another layer of complexity since the control volumes must have the ability to communicate between each other. In addition, though decentralized communication and control may be adequate for less capable systems, centralized controls may become necessary under certain circumstances. Both approaches have additional energy requirements for information transmission, reception and storage that must be considered relative to the energy savings. Note that in all such cases, an entire group can often be evaluated as a single control volume using the concepts developed in this paper as long as the rules of collaboration are included as part of internal processes (e.g. by using active matter models).

Stable control volumes comprising groups of smaller individual control volumes can have capabilities well beyond that of a single individual control volume (e.g. Couzin (2025)). However, since the stability of a collective is driven by interactions between the individuals, its fundamental characteristics will ultimately be determined (and limited) to a certain extent by the characteristics of these individuals. The same can be expected to be true in reverse, i.e. some aspects of learning and adaptability associated with the collaboration can be imparted to individual control volumes. Thus, control volumes that leave a collective will likely differ from their pre-collaboration configuration. These factors are relevant for control volumes in open environments, and their effects can be quantified during design and testing phases.

Natural systems composed of individual elements routinely exhibit many of the above characteristics. For example, studies show that elaborate collective actions involving large groups of organisms often result from local interactions between individuals (e.g. Berdahl (2013)). Similarly, even though centralized control is common in complex multicellular organisms, the biology (i.e. genetics) of individual cells constrain both the structure of their control systems as well as their behavioral characteristics (e.g. Zwir et al. (2021)) at all times. Lower level control systems also continue to influence the responses of such organisms since communication networks, cognitive abilities and memories can be widely distributed at tissue/cellular levels (e.g. Levin (2021), Flores and Liester (2024)).

Studies also show that significant information exchanges occur between cells of multicellular organisms and other organisms directly or via the environment (e.g. Dinan et al. (2015), Moore et al. (2021)). Since individual (or collections of) cells can survive independently of a parent organism, it is also possible that such exchanges may continue to occur even after their separation from them. Given that all life, including unicellular organisms, have considerable learning capacities and cognitive abilities (e.g. Ramanathan and Broach (2007)), it is clear that communications and control systems networks in nature are extremely complex, and various cells can influence the behavior of complex organisms, either individually or in groups, in many different ways. The extent of this is currently unknown since the fundamental capabilities of cells are still under investigation. Ongoing work in this area may clarify this matter and help settle some longstanding philosophical and religious debates (e.g. Chalmers (2016), Crane (2001)).

A.3. Population Dynamics of Replicating Thermodynamically Stable Control Volumes

Many types of autonomous systems are currently being developed for applications in engineering (e.g. defense, manufacturing, transportation) and the life sciences (e.g. healthcare, synthetic biology). Though replication is not currently under consideration in most cases, it may well occur in many synthetic biology and bio-robotic systems (the term “replication” is used synonymously with “reproduction” in this paper, unlike more specific definitions used in some literature). If replicating autonomous systems enter the general environment, they will interact with existing life-forms, and different populations will develop and evolve. This can have significant consequences on the environment which may not always be beneficial. An understanding of the origins of existing stable control volumes and their population dynamics in the physical universe is extremely useful in this regard since it can provide some valuable insights into the relevant processes.

From a fundamental perspective, the evolution of physical systems is determined by the conservation laws related to mass, momentum/forces and energy. These equations in their differential forms result from Boltzmann's equation and Newton's and Maxwell's Laws under certain conditions. They are known to have stable solutions for specific local (boundary) conditions, and the effects of short range forces tend to further enhance stability in many circumstances. As a result, stable (structural, chemical, thermal, etc.) configurations ranging from planetary systems to microscopic vesicles to complex chemical gardens and networks of autocatalytic reactions form entirely due to physical and chemical processes. Though their stability is restricted to specific physical characteristics in most cases, some can also exhibit thermodynamically stability as shown in this paper.

Given the finite lifespan of stable control volumes, their numbers are generally limited by their rate of creation relative to their failure rate. This changes in rare cases when continuing interactions with the environment result in modifications to the internal processes such that a few control volumes gain the ability to replicate themselves. Details of the mechanisms associated with such changes are still unclear, though investigations of physical and chemical replication processes (e.g. Ashkenasy et al. (2017)) suggest that there are no fundamental barriers to the replication of thermodynamically stable control volumes. Once this occurs, the number of stable control volumes can increase substantially since their creation rate increases. As their internal processes vary over generations, populations of different control volumes with different levels of stability exist in the environment.

The dynamics of populations depends on their interactions with the environment which includes other control volumes (e.g. Hofbauer and Sigmund (2003)). All interactions (and imperfect replications) have some effect on individual control volumes, and the resulting changes in internal processes can improve or degrade their control parameters thereby affecting their stability. When stability is enhanced (i.e. when the ability to respond to environmental fluctuations and other control volumes improves), control volumes have lower failure rates and survive better in changing conditions. This automatically results in the evolution of increasingly complex control systems and control volumes over time. Assuming that replication rates remain unchanged and most changes are passed on during the replication processes, populations comprising such control volumes then increase in number and expand more readily into new environments.

The general population growth processes discussed above can continue as long as free energy and appropriate materials are available. Thus, non-equilibrium conditions must always exist in the environment, which is not an issue in an infinite universe. However, many simple closed systems, such as those involving ideal gases, always achieve equilibrium over time (i.e. their entropy reach a maximum), so that stable control volumes will cease to exist at some point in such environments. In contrast, theoretical considerations and real-world experience suggest that large complex systems will probably never reach equilibrium even if they are closed because of interactions between independent energy fields and the degrees of freedom involved (e.g. Jaynes (1965)). A cosmological model also concludes that equilibrium conditions may never be attained in a closed universe (Frautschi (1982)), and its entropy never reaches a maximum. The constraints to population growth in a general case are therefore local, and related to energy/materials availability and process kinetics, i.e. different stable control volumes and processes will develop and evolve at different rates depending on available materials and local environmental conditions.

Control volumes that are stable to a larger variety of fluctuations are more likely to survive in changing conditions. More capable control systems require complex control volumes which are unlikely to develop naturally via single-step processes since the probability of a specific combination occurring randomly reduces exponentially with the number of its components. However, increasingly complex volumes can self-assemble from simpler control volumes in a hierarchical manner, particularly when aided by short range forces that are important at smaller scales (e.g. Whitesides and Grzybowski (2002), Whitelam and Jack (2014)). Thus, major control systems enhancements resulting from rare combinations or reconfigurations of simpler control volumes can intermittently supplement smaller changes that occur over generations via random internal variations. Diverse populations of control volumes with increasingly complex control systems can therefore develop in multi-step processes over time.

Even as multiple populations grow, unpredictable external fluctuations will destroy individual control volumes and entire populations in some locations. This is inevitable since perfect stability requires that the external environment be completely defined or predictable (e.g. Conant and Ashby (1981), see also previous analysis in paper), and this is never the case. Typically, individual control volumes survive extreme changes (e.g. by entering a dormant state) or recur, and new populations evolve. The worst case scenario where all populations are eliminated and no new populations occur again is highly unlikely since this is possible only if the entire environment is in equilibrium. Instead, it is far more probable that some populations will always exist with their sizes and complexities varying with time. In rare cases, select populations of stable control volumes may become so capable that they can expand into multiple environments and engage in significant environmental modifications such that overall equilibrium becomes even less likely.

The above discussion shows that population dynamics of replicating control volumes is determined by the underlying conservation laws <u>that govern process kinetics and resulting control functions</u>. It is driven by two competing forces, one that is primarily local and the other that is more global, viz. (i) increasingly capable control systems and stable control volumes that result from continuing interactions of generations of control volumes with their environments, and (ii) constant destabilization of individual control volumes by unpredictable changes in external conditions. The resulting interacting processes are then so complex that their dynamics cannot be predicted over extended periods of time. Thus, the long-term effects of uncontrolled releases of replicating, autonomous engineered systems into the environment cannot be known a priori, and can be dangerous if such systems are (or become) so stable that they successfully compete for or damage/destroy resources required by existing living organisms.

The parallels between the population dynamics of control volumes and the trajectory of life on earth are clearly evident above. This is to be expected since living organisms are essentially open control volumes with thermodynamic stability and the ability to replicate being two of their defining characteristics. Thus, the evolution of species and the growth of populations can be seen to result from the fundamental laws of physics since stability (i.e. "fitness") and its evolution are direct consequences of these laws. The observed increases in energy requirements and complexity of life over time are also inevitable since increased fitness/stability is only possible with more capable control systems that have higher energy requirements and involve more complex internal processes. Corresponding increases in internal entropy generation and environmental dissipation rates (Ulanowicz and Hannon (1987)) are then a product of this increased energy use.

A.4. Thermodynamic Stability of Control Volumes and Information Dynamics

Information is another important issue related to thermodynamic stability which arises from the fact that processes within stable control volumes (and in many cases, their environment) are driven by their control systems. Regardless of whether they are created through natural processes or engineered like autonomous systems, stable control volumes execute internal algorithms (e.g. MacLennan (2004)), and can be considered as heat engines that do "mathematical work" in addition to other types of internal and external work. Like all physical processes, information processing associated with control systems requires energy, and results in entropy generation per the Second Law unless all steps are reversible (e.g. Bennett (1982)). Similarly, information storage and exchange with other control volumes also involve energy use and entropy generation. Thus, information and its evolution are clearly interlinked with control volume stability and population dynamics.

From a physical perspective, the difference between a thermodynamically stable control volume and an arbitrary region is that the first is governed by specific (control) rules that do not apply to the second even though both are governed by the same underlying physical laws. As a result, the creation and replication of stable control volumes automatically involves the creation of information comprising the control algorithms and related data (parametric information, simulation models, etc.). These algorithms evolve and information grows within individual control volumes as they interact with each other (e.g. Boyd and Richerson (2005)) and the environment. Some of this information may also be stored externally by the control volumes and transmitted via these interactions. These processes continue indefinitely with the populations and information content evolving over time and the total entropy continuing to increase.

The results of this study provide a basis for identifying the algorithms (i.e. the control rules that result from the underlying thermodynamic processes) and relevant data generated within stable control volumes over time. Thus, the creation and evolution of information (i.e. the algorithms and data which by themselves are not physical) can be investigated simultaneously with the evolution of the physical universe via the underlying conservation laws. However, since this is feasible only for very simple configurations, focusing on more practical problems related to control systems and information dynamics may be preferable. One such option may be to study the evolution of control systems with constraints on energy use that change as a function of their capabilities over time. Another may be to simultaneously study the evolution of populations and their control systems by combining higher level population dynamics models together with evolutionary algorithms for control systems.

It is important to note that neither of the two simpler approaches proposed above involve simulations of the underlying physical processes. Thus, they must be appropriately constrained by physical laws (via limits on work interactions, power consumption, energy storage, memory, communication/processing speeds, etc.) if realistic evolutionary processes are to be investigated. Results of these studies can then help clarify the mechanisms of information creation, storage and transfer in interacting populations of thermodynamically stable control volumes, the effects of such populations and their information on long-term equilibrium of closed systems, and the relationships between different forms of information and a "physical observer". They may also help define life itself (on the basis of its information content (Bartlett et al. (2025))), provide important insights into the nature of control system networks and information transmission in living systems, and possibly explain various anomalous phenomena (e.g. Cardena et al. (2000)).

Statement Related to AI Usage: No AI assistance has been used in this work (Original paper and Appendix).

A.5. Additional References

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