Thermodynamics and Stability in Extended Irreversible Thermodynamics

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Abstract
An old pursuit is in thermodynamics to connect the second law to the stability of some processes. This paper gives an interpretation of the second law based on stability considerations. This approach answers some problems of the extended irreversible thermodynamics (wave approach to thermodynamics).

1 Stability and the second law in phenomenological thermodynamics

Every theory in thermodynamics uses the second law, the most important basic principle of this field of physics. However, the formulations and the meanings of the second law are loosely related in the different thermodynamical theories, moreover we can find different second laws even in a single theory.

There is a possibility for the unique formulation that seems to be generally acceptable. One of the most frequently used form of the second law can be written as follows:

"The entropy of a closed thermodynamical system grows."

An old conjecture in thermodynamics is that the content of this sentence can be grasped in a rigorous way with the help of some kind of Liapunov stability and Liapunov function. There are examples that try to connect this formulation of the second law to some concepts of stability in the continuum thermodynamical theory [1-5] and establish relation between the second law, entropy and asymptotic stability of the equilibrium.

The evolution of a thermodynamical system is given by a differential equation. Moreover some thermodynamical conditions and constitutive assumptions, which are sometimes considered in themselves as the second law, are
additional prescriptions for the differential equation. They will imply together that the equilibrium of a closed (and some open) thermodynamical system will be asymptotically stable, and the entropy function is closely connected to a Liapunov function of the equilibrium. Of course, the Liapunov function is related to the equilibrium of the original differential equation (not to the linearized one) resulting in non-linear stability in a definite neighbourhood of the equilibrium.

We can apply these considerations in thermostatics \cite{6,7} and in rational thermodynamics \cite{5}. In this paper we investigate some consequences of these ideas in extended irreversible thermodynamics.

Regarding the technical difficulties arisen on the application of Liapunov direct method to partial differential equations we refer to Walker \cite{8}.

2 The second law in classical irreversible thermodynamics

In this chapter we investigate one of the most simple continuum thermodynamical system which can be described by its density, velocity and specific internal energy.

We will consider a continuum in a classical spacetime, and in a given system of reference. In this case our quantities are defined on some connected open bounded set \( U \in \mathbb{R}^3 \) with a smooth boundary. \( \varphi := (\rho, u, \epsilon) : U \times \mathbb{R} \longrightarrow \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+ \), where \( \rho \) is the density, \( u \) is the velocity field and \( \epsilon \) is the specific internal energy as a function of space and time. It is possible to give a more general, reference frame independent (absolute) description, but it would require more mathematical tools \cite{9,10}.

In the present case the classical evolution equation of the continuum is given as follows

\[
\frac{\partial}{\partial t} \begin{pmatrix} \rho \\ u \\ \epsilon \end{pmatrix} = \begin{pmatrix} \frac{\partial^2}{\partial t^2} (\rho u) \\ -u \cdot \nabla \circ u - \frac{1}{\rho} \nabla \cdot P \\ -u \cdot \nabla \epsilon - \frac{1}{\rho} \nabla \cdot k - \frac{1}{\rho} P \cdot \nabla \circ u \end{pmatrix} = -u \cdot \nabla \varphi + F(\rho, u, \epsilon),
\]

where \( P, k \) are the pressure tensor and the heat flow (conductive current of the internal energy); \( \nabla, \nabla \cdot \) denotes well known differential operators; \( P \) is symmetric (the internal angular momentum is zero). To make this problem to a well determined Cauchy problem we should give how \( P \) and \( k \) depends on the independent variables, giving some constitutive functions (equations), and giving some initial and boundary conditions.

In this chapter we restrict ourself to the case of local equilibrium in the following manner:

The state functions (equations) of the temperature and pressure are defined as \( (T, p) : \mathbb{R}^+ \times \mathbb{R}^+ \longrightarrow \mathbb{R}^+ \times \mathbb{R} \), \( (\rho, \epsilon) \mapsto (T, p)(\rho, \epsilon) \). The specific entropy
function \( s : \mathbb{R}^+ \times \mathbb{R}^+ \rightarrow \mathbb{R}, (\rho, \epsilon) \mapsto s(\rho, \epsilon) \). has the properties

\[
\frac{\partial s}{\partial \epsilon}(\epsilon, \rho) = \frac{1}{T(\epsilon, \rho)}, \quad \frac{\partial s}{\partial \rho}(\epsilon, \rho) = -\frac{p}{T\rho^2(\epsilon, \rho)}.
\]

These properties can be considered as a definition of the entropy \([6,7]\). Furthermore we suppose that the entropy as a function of \((\epsilon, v)\) – where \(v := 1/\rho\) is the specific volume – is concave, its second derivative is negative definite. In our treatment it is more suitable to use the density as an independent variable. In this case the following inequalities means a necessary and sufficient condition for the concavity mentioned above, according to Sylvester criteria:

\[
\frac{\partial T}{\partial \epsilon} > 0, \quad \frac{\partial p}{\partial \epsilon} \frac{\partial T}{\partial p} - \frac{\partial p}{\partial \epsilon} \frac{\partial T}{\partial p} > 0.
\]

We can define the chemical potential function, as usual

\[
\mu(\epsilon, \rho): = \epsilon - T(\epsilon, \rho)s(\epsilon, \rho) + p(\epsilon, \rho)/\rho.
\]

The constitutive function (usually called constitutive equation) for \( P \):

\[
P(\rho, u, \epsilon) = p(\epsilon, \rho)I + P^v(\rho, u, \epsilon),
\]

where \( P^v \) is the viscous part of the pressure tensor, and \( I \) is the identity map of \( \mathbb{R}^3 \).

Our irreversible thermodynamical system is closed, internal energy and material cannot flow out, thus the boundary conditions are the followsings: the normal component of \( k \) and \( u \) on the boundary of \( U \) is zero. The remaining, not specified boundary conditions make our problem definite together with the initial conditions.

Our last assumption is the Clausius-Duhem inequality, that we should interpet as a prescription for the constitutive functions \( T, k \) and \( P^v \):

\[
-\int_U \frac{1}{T} \left( \nabla T \cdot k \frac{T}{T} + \nabla \circ u : P^v \right) dV \geq 0.
\]

We prescribe the remaining constitutive conditions for \( P^v \) and \( k \) so that the evolution equation (1) has an equilibrium solution \((\rho_0, 0, \epsilon_0)\), where \( \rho_0 \) and \( \epsilon_0 \) are constant functions, and we can determine them from the initial conditions. The functions \((\epsilon, u, \rho)\) are defined in the space region \( U \subset \mathbb{R}^3 \) and in time \( \mathbb{R} \) and satisfy the system of partial differential equations (1). In order to apply Liapunov’s method, we treat the space variable and the time variable in different ways.

Let \( \mathcal{H} \) be the Hilbert space of \( \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+ \) valued square integrable functions defined in \( U \subset \mathbb{R}^3 \) that is \( \mathcal{H} := \mathcal{L}^2(U, \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+) \). Then \( D := \mathcal{C}^2(U, \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+) \), the set of twice continuously differentiable \( \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+ \) valued functions defined in \( U \) is a dense linear subspace of \( \mathcal{H} \). We suppose that \((\epsilon, u, \rho) : U \times \mathbb{R} \rightarrow \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+ \)
\( \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+ \) is twice continuously differentiable. Thus for all \( t \in \mathbb{R}^+ \), \( \varphi(t) = (e, u, \rho)(e, t) \in \mathcal{D} \), i.e. we consider the function \( \varphi : \mathbb{R}^+ \to \mathcal{D} \), \( t \mapsto \varphi(t) \). Then we can write the evolution equation (1) in the form
\[
\dot{\varphi}(t) = F(\varphi(t)),
\]
where \( F : \mathcal{D} \to \mathcal{H} \).

Now we assume the non-specified conditions assure that this differential equation generates a dynamical system in \( \mathcal{H} \) [8].

**Theorem 2.1** The equilibrium solution of the evolution equation (1) (or (5)) is asymptotically stable with the conditions above.

**Proof:** We introduce some notations \( T_0 := T(e, \rho_0) \) and \( \mu_0 := \mu(e, \rho_0) \). Now we will prove, that the function
\[
L(\rho, u, e) = \int_U \left( \frac{\rho u^2}{2} + \rho e - T_0 \rho s(e, \rho) - \rho \mu_0 \right) dV
\]
is a Liapunov function of the equilibrium solution of the evolution equation (1) (or (5)) and this function satisfy the conditions of the theorem in [8, p157]

(i) \( L(\varphi) - L(\varphi_0) \geq f(d(\varphi, \varphi_0)) \), where \( d \) denotes the \( L^2 \) norm in \( L^2(U, \mathbb{R}^+ \times \mathbb{R}^3) \) and \( f : \mathbb{R}^+ \to \mathbb{R}^+ \), \( f(0) = 0 \) strictly monotone decreasing function.

To check this inequality we differentiate \( L \):
\[
DL(\varphi) = \begin{pmatrix}
\int_U \rho \left( 1 - \frac{T_0}{T} \right) dV; \\
\int_U \rho u dV; \\
\int_U \left( \frac{u^2}{2} + e - T_0 s - \rho s + \frac{\rho T_0}{\rho} \right) dV
\end{pmatrix}
\]

We can see, that \( DL(\varphi_0) \), the derivative of \( L \) at the equilibrium is zero, moreover its second derivative at the equilibrium is non-degenerate and strictly positive, then we verify, that the function \( L \) has a strict relative minimum at the equilibrium [11, p82].

(ii) \( \dot{L}(\varphi) \leq -g(d(\varphi, \varphi_0)) \), where \( g : \mathbb{R} \to \mathbb{R}, g(0) = 0 \) strictly monotone decreasing like \( f \). With the help of the evolution equation we can calculate \( \dot{L}(\varphi) \) "the derivative of \( L \) along the motion".
\[
\dot{L}(\varphi) = \int_U \left( \frac{\partial}{\partial t} \left( \frac{\rho u^2}{2} \right) + \frac{\partial}{\partial t} (\rho e) - T_0 \frac{\partial}{\partial t} (\rho s) - \mu_0 \frac{\partial}{\partial t} (\rho) \right) dV
\]

After some transformations we get the final result:
\[
\dot{L}(\varphi) = -\int_{\partial U} \left( -\rho u - \rho T_0 s + \rho e + \frac{\rho u^2}{2} \right) u + P \cdot u + \left( 1 - \frac{T_0}{T} \right) k \right) dA(\mathcal{F})
\]

Here the first integral vanishes because of the boundary conditions, and the second integral is a negative quantity because of the Clausius-Duhem inequality.
(4). Thus $\dot{L}(\varphi) \leq 0$ and zero only, if $\varphi = \varphi_0$. Therefore the equilibrium state of our closed continuum thermodynamical system described by the evolution equations (1) is asymptotically stable. ■

Remark: If we modify our boundary conditions, that the temperature and/or the pressure (??) are uniform at the boundary, then the equilibrium of this modified system will be asymptotically stable as we can see with the help of the same Liapunov function.

3 Stability and the second law in extended irreversible thermodynamics (wave approach of thermodynamics)

In the wave approach of thermodynamics [12], or in extended irreversible thermodynamics [13,14], which are essentially equivalent theories, the second law is considered as a natural generalization of the second law in classical irreversible thermodynamics. These theories require that the production of the extended, generalized entropy will be positive. However, this requirement is based only on the analogy with the classical case. In addition there is some uncertainty in this respect, because Woods have the opinion that we should require only the positivity of the classical part of the entropy production [15].

If we take into account the second law in the form given above, we should require the asymptotic stability of the equilibrium of a differential equation describing a closed extended irreversible thermodynamical system. Furthermore, we expect that the generalized entropy will be closely connected to a Liapunov function ensuring stability.

In this chapter we generalize the evolution equation (1) and the constitutive and state functions /equations/, that they will be the extended /wave/ equivalent of the classical continuum physical system described in the chapters above, and we perform the stability investigations as previously.

Now we suppose that the equation (1) is formally valid, but with a different interpretation. We suppose, that our independent variables are $(\epsilon, u, p, k, P^v)$, thus we take current densities of the balance equations, in this particular case the heat current and the viscous part of the pressure tensor, as independent variables for which differential equations must be given as well. Usually the viscous part of the pressure tensor is split into two parts according to thermodynamical considerations

$$\dot{p}^v = p^v + \ddot{p}^v$$

where $\dot{p}^v = Tr(P^v)$, and $\ddot{p}^v = P^v - p^v$. Let us suppose, that the evolution equation of $\varphi_{ee} = (k, \dot{p}^v, \ddot{p}^v) : U \times \mathbb{R} \rightarrow \mathbb{R}^3 \times \mathbb{R} \times \mathbb{R}^5$ is given by:
\[
\frac{\partial \varphi_{ex}}{\partial t} = \frac{\partial}{\partial t} \left( \frac{k}{P^e} \right) = -u \cdot \nabla \varphi_{ex} + F(\varphi, \varphi_{ex}). \quad (8)
\]

According to the standard procedure, the particular form of \( F \) (which is a differential operator actually, like \( F \)) comes from the entropy production, introducing some thermodynamical forces and currents, and for example supposing a linear relationship between them. Now we do not specify the particular form of \( F \), but this notation indicates that we will interpret it as a part of the evolution equation of our independent variables \((e, u, \rho, k, P^e, \dot{P}^e)\):

\[
\frac{\partial \varphi}{\partial t} \left( \varphi_{ex} \right) = \begin{pmatrix} \nabla \cdot (\rho u) \\ -u \cdot \nabla \circ u - 1/\rho \nabla \cdot P \\ -u \cdot \nabla \varepsilon - 1/\rho \nabla \cdot k - P \nabla \circ u \\ -u \cdot \nabla \varphi_{ex} + F(\varphi, \varphi_{ex}) \\ -u \cdot \nabla \varphi_{ex} + F(\varphi, \varphi_{ex}) \end{pmatrix} = \begin{pmatrix} -u \cdot \nabla \varphi + F(\varphi, \varphi_{ex}) \\ -u \cdot \nabla \varphi_{ex} + F(\varphi, \varphi_{ex}) \end{pmatrix}. \quad (9)
\]

In this case we left the realm of local equilibrium because of our new dynamical variables, so we modify the state functions (equations) as follows.

We introduce a non-equilibrium entropy function as \( s : \mathbb{R}^+ \times \mathbb{R}^+ \times \mathbb{R}^3 \times \mathbb{R}^+ \times \mathbb{R}^5 \to \mathbb{R} \)

\[
(e, \rho, k, P^e, \dot{P}^e) \mapsto s(e, \rho) - m_1 \frac{k^2}{2} - m_2 \frac{P^e}{2} - m_3 \frac{\dot{P}^e}{2}, \quad (10)
\]

where \( s \) is the entropy function in the local equilibrium, \( m_1, m_2, m_3 \) are positive constants. We suppose the same boundary conditions as in the chapter 1, thus our system is closed, which means that the normal components of \( \mathbf{k} \) and \( \mathbf{u} \) on the boundary of \( U \) are zero. The remaining, not specified boundary conditions make our problem definit together with the initial conditions. Moreover we prescribe, that the constitutive functions and the boundary conditions are given so, that there is an equilibrium of the system in the form \( (\varphi, \varphi_{ex})_e = (\varepsilon_0, 0, \rho_0, 0, 0, 0) \) and the appropriate solutions of our differential equation constitute a dynamical system. Furthermore we modify the definition of the chemical potential according to our new entropy function.

\[
\mu(e, \rho, k, P^e, \dot{P}^e) = e - T(e, \rho) s(e, \rho, k, P^e, \dot{P}^e) + p(e, \rho)/\rho.
\]

Now we are ready to formulate the stability theorem in this special extended irreversible thermodynamical system.

**Theorem 3.1** The equilibrium solution \((e, 0, \rho_0, 0, 0, 0)\) of the evolution equation (9) is asymptotically stable, if
(i) \( m_1 \geq 0, \ m_2 \geq 0, \ m_3 \geq 0 \), and for the function \( s(\epsilon, \rho) \) the inequalities (3) are valid.

(ii)

\[
\int_{\mathcal{U}} \left( \frac{1}{T} \left( \frac{\nabla T}{T} + \nabla \circ u; P^w \right) + \left( m_1 \rho k, \ m_2 \rho p^w, \ m_3 \rho P^w \right) : F \right) \, dV \geq 0.
\]

and the equality is valid only for the equilibrium values of the variables.

**Proof:** The proof is based on the fact that the function

\[
L(\epsilon, u, \rho, k, p^w, P^w) = \int_{\mathcal{U}} \left( \frac{\rho u^2}{2} + \rho \epsilon - T_0 s(\epsilon, \rho, k, p^w, P^w) - \rho \mu_0 \right) \, dV
\]

is a Liapunov function of the equilibrium solution of the evolution equation (9) and this function satisfies the conditions of [11, p82].

**Remarks:**

1. We have got that we should require the positivity of the whole entropy production, and it is evident that the positivity of the classical part is not enough for the required stability.
2. Here the considered extended irreversible thermodynamical system is quite simple. It is easy to consider more general models, for example additional terms in the entropy current. The essence of the treatment and the Liapunov function itself does not change.
3. Sometimes equations (8) are considered as constitutive functions.

4 **Discussion**

1. We can compare this interpretation of the second law with the interpretation of Glansdorff and Prigogine and we can see that
   - it relates to nonlinear stability, not to the linearised equations, and
   - it propose another Liapunov function than Glansdorff and Prigogine.

   They investigate the stability of some steady states too. It would be interesting to investigate the role of this Liapunov function in the stability of steady states as well.

2. The stability structure of thermodynamics (the way of construction of Liapunov functions) can give some clue for construction Liapunov functions in purely mathematical problems as well.

3. The Liapunov function \( L \) of this paper is the same for some closed classical irreversible thermodynamical systems, for some open classical thermodynamical systems and closely related to the classical one for some extended thermodynamical systems. This universal property of \( L \) makes clear the way and the direction of the generalization of the given theorems for more general systems, too.
4. We usually think that the thermodynamical stability conditions (the Gibbs type stability for homogeneous systems) give only a first look of the dynamical stability of an irreversible thermodynamical system and we should use a 'dynamical' stability investigation (linearization and spectral analysis) to get applicable results. Now this paper suggest a dynamical and thermodynamical method for the stability investigations.

5. The solutions of the differential equations generally do not constitute a dynamical system, there are important non-continuous solutions (for example shock waves).

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6 References


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