THERMODYNAMICS AND STABILITY (HOMOGENEOUS SYSTEMS)

P. VÁN

December 14, 1995

ABSTRACT. The interpretation of the Second Law is a central problem of every theory of thermodynamics. Here the possibilities of a dynamical interpretation are investigated in case of homogeneous bodies. Now the Second Law appears as a condition of the asymptotic stability.

1. Introduction

Classical phenomenological thermodynamics is a theory with a contradiction in its name. This is a theory of physics without any dynamics, we cannot give the time development of the thermodynamical state parameters, there are no true thermodynamical processes. With this property classical phenomenological thermodynamics is unlike any other physical theory and this fact is well reflected in some other widely used names of the theory: 'equilibrium thermodynamics', 'thermostatics' [1, 2]. However the thermodynamical parameters of the bodies in the reality changes in time, for example if we put a glass of water from the room into a refrigerator it get cool and in a lot of cases only little inhomogeneities accompanies the process. Furthermore the continuous details of the cooling are not important, we would need only the (average) temperature of the water as a function of time. 'Thermostatics' cannot give answer such questions, and the need for a dynamical model was the origin of 'non-equilibrium' or 'irreversible' thermodynamics. Now we have a well developed theory of continuous matter but only a static theory for homogeneous media. Let us imagine this paradox situation in mechanics: we have a well developed continuum mechanics but there is no dynamics of masspoints only statics. How strange and hard would be the understanding of such a theory! What kind of concepts we would need to explain a process! This is the main purpose of a real thermo-dynamics beyond the practical importance: to give a simple and easy understanding of the basic theoretical concepts of thermodynamics first of all the concept of entropy and the Second Law. The formulation and the content of these fundamental principles of physics should be in agreement with the previous formulations and should reflect our physical expectations.

This paper deals with the possibilities of such a dynamical description. Therefore we cannot use the name 'equilibrium thermodynamics' and for the sake of distinction we will call the realm of reality which is aimed to describe by the 'equilibrium' or 'classical' phenomenological theories as thermodynamics of homogeneous bodies

according to Landau [3]. We find that in case of a true dynamical description a natural formulation of the content of the Second Law is the requirement of the asymptotic stability of some thermodynamic processes, especially the equilibrium of some thermodynamical systems.

In the next chapters we restrict ourselves to the traditional description of dynamics like other theories of physics: we will give differential equations to describe thermodynamical processes. Of course there are other examples on the description of the dynamics too [4, 5]. It is quite straightforward to interpret the first law, or more properly the Gibbs relation as a differential equation in time like Landau or Truesdell and Bharatcha [3, 6]. However this results only one differential equation, so gives a dynamical description only for systems with one state variable. We need more equations, a whole dynamical law.

Two theories suggest enough differential equations to describe the time development: the non-equilibrium or irreversible thermodynamics for 'discrete systems' (which is the same as homogeneous bodies in our case) [7] and ordinary thermodynamics of Matolcsi [8]. The crucial question, like any other thermodynamical theory, the formulation of the Second Law. In case of differential equations the content of the Second Law is the asymptotic stability of the equilibrium of some special thermodynamical systems and a natural device of the investigation of the asymptotic stability is the first and second theorem of Liapunov. In the next chapters of this paper we will investigate these theories to give the relations of the concepts of stability theory and thermodynamics. For example we will give Liapunov functions for these systems, and we can see what is the relation of this Liapunov function, and the entropy of the system.

2. Entropy as a Liapunov function

Some formulations of the Second Law are directly connected to some properties and the existence of the entropy function. If we accept that this function exists (which is a crucial question of the problem set called Second Law) then we usually suppose that

- entropy is a concave function of its variables,
- along thermodynamical processes of some definite systems the entropy 'grows', it is an increasing function in time, as the system tend to equilibrium.

These two statements formulate independent properties of the entropy, and in the different phenomenological and statistical theories of thermodynamics sometimes the first property, sometimes the second and sometimes both together are accepted and postulated as the Second Law of thermodynamics.

However, the second statement is problematic without a dynamical theory, because the second statement tell us something on the dynamics of the system: the processes are determined on such a way, that there is a function with the properties above. It follows, that almost all of the statistical and phenomenological theories of thermodynamics for homogeneous bodies are unable to give a correct postulation for the second statement: dynamics is out of the realm of these theories.

An other important remark that these properties of the entropy function resembles ourselves to the properties of a Liapunov function in the second method of Liapunov [9]. This fact was realized and applied long ago for continuum theories

[10], and for statistical theories as well [11]. However, the basic concepts of thermodynamics are originated in the phenomenological theory for homogeneous bodies. This is the most simple theory of thermodynamics for the most simple practical situations: any thermodynamical theory should be in agreement with it. Thus if we develop a continuum or statistical theory based on that kind of concept of the Second Law then we should be able to give a corresponding phenomenological theory for homogeneous bodies as well. Moreover, to deal with more complex theories can result inadequate understanding of the structure of the theory: eg. Glansdorff and Prigogine use a Liapunov function (in the so called 'general evolution criteria') only for the linearized continuum equations and does not realize that it is a Liapunov function for the whole nonlinear set of equations of some systems of continuum physics as well [12].

The concept of Liapunov function is meaningful in the light of a dynamical law, possibly a differential equation. Speaking on Liapunov functions without a differential equation, without a correct formulation of the problem is no more than the expression of a need of that kind of mathematical background: an intermediate state along the development of the theory. In the following chapters we investigate the possibility of that kind of interpretation of the Second Law in the theory of 'thermostatics' or more properly: thermodynamics of homogeneous bodies.

3. Background from thermostatics

Let us investigate a simple example system, the 'charge probe' of thermodynamics: a cylinder filled with some gas and closed by a piston. We suppose that this system can be characterized by four thermodynamical variable: the e internal energy, v specific volume, T temperature and p pressure. Let us suppose that the system is thermally and mechanically connected to its environment. The temperature and the pressure of the environment is given by T_a and p_a .

The material inside the cylinder, the gas is given by two state functions, the temperature and the pressure, as functions of the internal energy and the specific volume:

$$T = T(e, v), \qquad p = p(e, v).$$

Let us suppose, that these state functions are given in such a way, that there is an entropy function s with the following properties:

$$\frac{\partial s(e,v)}{\partial e} = \frac{1}{T(e,v)}, \qquad \frac{\partial s(e,v)}{\partial v} = \frac{p(e,v)}{T(e,v)}$$

In this case the usual formulation of the first law or Gibbs relation and the corresponding differential equation is the following [3, 6]:

$$(3.1) de = q - pdV \iff \dot{e} = q - p\dot{v},$$

where de is the differential of the internal energy and q is the heating which is equal Tds in our case, when the entropy function exist.

Remark 3.1. Sometimes the different forms of the First Law are distinguished from the Gibbs relation, but from our point of view it is not important, we can call it anyhow, the analogy is clear. A far more detailed treatment is given for example in [6, 8]

This is one equation for two variable, even in this simple case we would need an other one to pose a proper problem to determine the time development. However we do not find a clue in thermostatics for the additional equation, therefore we can see it in other theories.

4. Onsagerian Thermodynamics

The aim at the foundation and development of non-equilibrium thermodynamics, as it is reflected in its name, was to eliminate the contradiction mentioned in the introduction: to construct a thermodynamical theory which would give the time development of thermodynamical systems. This aim was fulfilled only partially, now we have a reasonable dynamical phenomenological theory of continuous systems, but for discrete systems, for homogeneous bodies the view suggested by non-equilibrium thermodynamics is ambiguous. Let us see the suggestions of Onsagerian irreversible thermodynamics for our example system.

The starting point of the construction of dynamical equations is the the entropy production [7, 10, 13]. We suppose that the entropy production σ_s for two variables is

$$\sigma_s = \alpha_1 X_1 + \alpha_2 X_2 > 0,$$

where α_1, α_2 are alpha type thermodynamical variables so their derivatives are the thermodynamical currents and X_1, X_2 are the corresponding thermodynamical forces. It is supposed to a be a positive definite quadratic form of the forces and the currents, according to our second assumption on the Second Law. What are the forces and the currents in our specific case? The most straightforward answer is, that the α variables are the extensive quantities and the currents are the differences of the corresponding entropical intensive parameters:

$$\alpha_1 = e,$$
 $\alpha_2 = v;$ $X_1 = \left(\frac{1}{T} - \frac{1}{T_a}\right),$ $X_2 = \left(\frac{p}{T} - \frac{p_a}{T_a}\right).$

According to the supposed form of the entropy production (4.1) we can give the linear laws, as follows

$$\begin{pmatrix} \dot{e} \\ \dot{v} \end{pmatrix} = \begin{pmatrix} l_{00} & l_{01} \\ l_{10} & l_{11} \end{pmatrix} \cdot \begin{pmatrix} \frac{1}{T} - \frac{1}{T_a} \\ \frac{p}{T} - \frac{p_a}{T} \end{pmatrix} = F(e, v).$$

Now the linear phenomenological coefficients l_{00} , l_{01} , l_{10} , l_{11} are constants. This equation give us the dynamical law for the system considered. Let us investigate the stability properties of the equilibrium of these differential equations.

The equilibrium is given by the constant function (e_0, v_0) , where (e_0, v_0) is defined by the algebraic equations:

$$T_a = T(e_0, v_0), \qquad p_a = p(e_0, v_0).$$

This equilibrium is asymptotically stable as we can see after the linearization of equation (4.2). The linearization of F(e, v) around the equilibrium in (4.2) results

$$DF(e_0, v_0) \cdot (e - e_0, v - v_0) = L \cdot D^2 s(e_0, v_0) \cdot (e - e_0, v - v_0).$$

The matrix of the linear phenomenological coefficient is positive definite because the entropy production (4.1) is positive and the matrix of the second derivative of the entropy is negative definite according to the concave property of the entropy function. Therefore the whole matrix is negative definite, the real parts of its eigenvalues are negative. Then the equilibrium of (4.2) is asymptotically stable according to the first theorem of Liapunov [9].

On the other hand a bit stronger statement is also valid. Let us investigate the next function

(4.3)
$$L(e, v) = T_a s(e, v) - e - p_a v + T_a \mu_0,$$

where $\mu_0 = e_0 + p_a v_0 - T_a s_0$ is the chemical potential of the system in equilibrium. It is easy to prove that L is a Liapunov function of the equilibrium of (4.2):

- (i) L is negative definite, because $L(e_0, v_0) = 0$, $DL(e_0, v_0) = 0$ and $D^2L(e, v) = D^2s(e, v)$,
- (ii) the derivative of L along the differential equation (4.2) can be written as

$$D^{\square}L(e,v) = DL(e,v) \cdot F(e,v) = T_a \sigma_s;$$

which is the entropy production (4.1) times the equilibrium temperature. σ_s is a positive quantity according to our assumptions.

Thus the equilibrium of (4.2) is asymptotically stable according to the second theorem of Liapunov [9].

The stability properties seems to match to our suggested interpretation of the Second Law, but the presentation above suffers from some ambiguities:

- The first step in constructing the differential equations was the form of the entropy production. However, I did not mention the corresponding entropy function. for example de Groot and Mazur [7] introduce it according to some continuum analogies.
- The only fix point contributed to the dynamics from the theory of thermostatics is the form of the first law (3.1). The first equation of (4.2) seems to contradict to it.
- From a physical point of view our simple system (a gas closed in the piston)
 can oscillate mechanically. Our Onsagerian dynamical law does not make
 it possible.
- Neither the suggested form of the entropy production nor the dynamical law does not show an analogy to the corresponding equations of continuum physics: the momentum and the energy balance and the Clausius-Duhem inequality.

5. Continuum analogies: extended ordinary thermodynamics

Let us consider our simple system again. We know, that there is an other (phenomenological) possibility to give a quantitative description. The piston, closed by a cylinder and some gas inside has a continuum model, too. In this case we do not characterize the system with a uniform temperature and pressure, but we give the distribution of the corresponding quantities. This model is far more difficult than the homogeneous one. The two models should correspond to each other, at least some clear analogies should exist between them.

The structure of the existing continuum theory suggests some idea for the dynamical law, moreover there are more than one solutions [8]. Here our starting points are the balance equations of the extensive quantities of the corresponding system except the entropy balance which gives an additional, derived connection.

Now the mass density and the density of the specific internal energy characterizes the system therefore the corresponding continuum equations are the balance equations of the mass, momentum and the energy, as follows:

$$\dot{\varrho} = -\varrho \nabla \cdot \mathbf{u},$$

$$(5.2) \varrho \dot{\mathbf{u}} = -\nabla \cdot \mathbf{P} + \varrho \mathbf{f}.$$

(5.3)
$$\varrho \dot{e} = -\nabla \cdot \mathbf{J}_q + \mathbf{P} \cdot \nabla \cdot \mathbf{u},$$

Here ϱ is the mass density, e is the specific internal energy, \mathbf{J}_q is the heat current, \mathbf{P} is the pressure tensor, \mathbf{u} is the velocity of the continuum and \mathbf{f} is the force density. The corresponding entropy production is the following [7, 13]:

(5.4)
$$\sigma_s = -\mathbf{J}_q \cdot \nabla \frac{1}{T} - \frac{\mathbf{P}^v : \nabla \circ \mathbf{u}}{T} \ge 0,$$

where \mathbf{P}^v is the viscous part of the pressure. It supposed to be a positive quantity and forms the Clausius-Duhem inequality in our case. The continuum balance equations suggest the following homogeneous ones:

$$\begin{array}{rcl}
\dot{e} & = & q - p\dot{v}, \\
\ddot{v} & = & f.
\end{array}$$

where q is the heating, f is called forcing and they are functions of the intensive variables of the body and the environment and they vanish at the equilibrium. For example if α , β are constant numbers:

$$\dot{e} = \alpha (T - T_a) - p\dot{v},
\ddot{v} = \delta (p - p_a).$$

Let us observe that the analogy of the momentum balance is a second order equation, so we can introduce naturally the $u:=\dot{v}$ volume velocity. Furthermore we remark, that it is more than one possibility to introduce the second equation, for example we can investigate the possibility of a first order one [8]. This would satisfy all of our enumerated requirements at the end of the section 4 except the third, a first order equation would be a model of systems that cannot oscillate. In the next chapter we will clarify the exact meaning of the functions introduced and investigate the stability properties of this model. According to the traditions of thermodynamics it will be given in a more axiomatic way.

6. Stability: extended ordinary thermodynamics

A1 Requirements on the thermodynamical body

(i) Thermodynamical body

Definition 6.1. A simple *thermodynamical body* is given by its state functions (equations):

$$(\tilde{T}, \tilde{p}): \mathbb{R}^+ \times \mathbb{R}^+ \times \mathbb{R} \longrightarrow \mathbb{R}^+ \times \mathbb{R}^+; \qquad (e, v, u) \mapsto \left(\tilde{T}(e, v, u), \tilde{p}(e, v, u)\right)$$

Moreover we can split the pressure and the temperature into an 'equilibrium' and 'irreversible' part:

$$\tilde{p}(e, v, u) = p(e, v) + \hat{p}(e, v, u), \quad where \quad \hat{p}(e, v, 0) = 0,$$
 $\tilde{T}(e, v, u) = T(e, v) + \hat{T}(e, v, u), \quad where \quad \hat{T}(e, v, 0) = 0.$

Here u denotes the volume velocity (A2), p, T are the 'equilibrium' values and \hat{p}, \hat{T} are the 'irreversible' parts. The reason of the nomination must be clear from the definition.

(ii) The body is entropical. The vector field (1/T, p/T)(e, v) is conservative. In this case there exist a potential of this field, the entropy function $s : \mathbb{R}^+ \times \mathbb{R}^+ \longrightarrow \mathbb{R}$, $(e, v) \mapsto s(e, v)$, with the properties:

$$\frac{\partial s}{\partial e} = \frac{1}{T}(e, v); \qquad \frac{\partial s}{\partial v} = \frac{p}{T}(e, v).$$

(iii) Concave entropy. We suppose that the entropy function is concave:

$$\begin{array}{ccc} \frac{\partial T}{\partial e} & > & 0; \\ \\ \frac{\partial T}{\partial e} \frac{\partial p}{\partial p} - \frac{\partial T}{\partial v} \frac{\partial p}{\partial e} & < & 0 & \left(\frac{\partial p}{\partial v}(T,v)\right) < 0 \end{array}$$

Remark 6.1. We remark, that the second property, the existence of the entropy function is not necessary to the stability of the equilibrium of thermodynamical bodies.

A2 Dynamical law

We suppose the validity of the next system of differential equations for our variables:

(6.1)
$$\begin{aligned}
\dot{e} &= q(\tilde{T}, T_a, \tilde{p}, p_a, u) - \tilde{p}u, \\
\dot{v} &= u, \\
\dot{u} &= f(\tilde{T}, T_a, \tilde{p}, p_a, u).
\end{aligned}$$

Here the functions q and f are called *heating* and *forcing* and are the functions of the intensive variables of the body T, p and its environment T_a , p_a , and the volume velocity u of the body.

A3 Equilibrium

We suppose that the constitutive functions q and f are given in such a way that there exist an equilibrium of the differential equation (6.2):

$$q(T_a, T_a, p_a, p_a, 0) = 0,$$
 $p(T_a, T_a, p_a, p_a, 0) = 0$

In this case the equilibrium is not a basic concept of the theory: it has a clear definition concerning the differential equation (6.2), like the mechanical equilibrium: a specific solution of the differential equation when the state parameters do not change. According to these conditions the equilibrium of our dynamical law $(e_0, v_0, 0)$ is characterized by the following algebraic equations, like in the section 4:

$$T(e_0, v_0) = T_a, \qquad p(e_0, v_0) = p_a$$

A4 Positive mass

(6.2)
$$f(\tilde{T}, T_a, \tilde{p}, p_a, u)(\tilde{p} - p_a) \ge 0.$$

This requirement has a pure mechanical counterpart, which is rooted in the mechanical definition of the pressure and force. Therefore it has a clear physical meaning and it is necessary to the stability of the equilibrium of our system.

A5 Second Law

In our case the Second Law has the following form:

$$-\frac{\tilde{p}u}{T} - q\left(\frac{1}{T_a} - \frac{1}{T}\right) \ge 0,$$

The inequality above is clearly analogous with the Clausius-Duhem (5.4) inequality of continuum physics.

The thermodynamical system satisfying the properties A1-A5 is called *extended* ordinary thermodynamical system.

A bit specialization of our system helps to formulate the corresponding stability theorem in a very elegant form. The following definition contains the required specialization:

Definition 6.2. A thermodynamical system is *classical* if its forcing has the following form:

$$f(\tilde{T}, T_a, \tilde{p}, p_a, u) = \gamma(\tilde{p} - p_a),$$

where $\gamma \in \mathbb{R}^+$, is a positive number according to A4.

This definition is straightforward if we consider the mechanical definition of the pressure.

Now every condition is written, we are ready to characterize the stability properties of the system:

Theorem 6.1. The equilibrium of a classical extended ordinary thermodynamical system is asymptotically stable.

Proof: We will prove that the following function is a Liapunov function of the equilibrium of the system:

$$L(e, v, u) = T_a s(e, v) - e - p_a v - \frac{u^2}{2\gamma} + \mu_0,$$

where $\mu_0 = e_0 + p_a v_0 - T_a s(e_0, v_0)$ is the chemical potential of the body in equilibrium. According to the second theorem of Liapunov we should see, that the corresponding function has a maximum and increasing along the solutions of the differential equation (6.2).

- Maximum: The first derivative of L is:

$$DL(e, v, u) = \left(\frac{T_a}{T} - 1, \frac{T_a p}{T} - p_a, -\frac{u}{\gamma}\right).$$

It is easy to check that $DL(e_0, v_0, 0) = 0$. Then the concavity of the entropy function that is the inequalities (6.1) and **A4** require that the second derivative of L is negative definite:

$$D^{2}L(e, v, u) = \begin{pmatrix} T_{a}D^{2}s(e, v) & 0\\ 0 & -\frac{1}{\gamma} \end{pmatrix}$$

- Increasing L: The derivative of L along the differential equation 6.2 is positive according to the Second Law A5:

$$D^{\square}L(e, v, u) = T_a \left(\frac{\partial s}{\partial e} \dot{e} - \frac{\dot{e}}{T_a} + \frac{\partial s}{\partial v} \dot{v} - \frac{p_a}{T_a} \dot{v} - \frac{u\dot{u}}{\gamma T_a} \right)$$

$$= T_a \left((q - \tilde{p}u) \left(\frac{1}{T} - \frac{1}{T_a} \right) + u \left(\frac{p}{T} - \frac{p_a}{T_a} \right) - \frac{(\tilde{p} - p_a)u}{T_a} \right)$$

$$= T_a \left(q \left(\frac{1}{T} - \frac{1}{T_a} \right) - \frac{\hat{p}u}{T} \right) \ge 0.$$

It is worth a paragraph the physical meaning of the Liapunov function (6). The negative first three terms form the maximum available work of our open system:

$$W_{max}(e, v) = e + p_a v - T_a s(e, v).$$

The fourth term containing the volume velocity u gives the clear possibility to define a 'non-equilibrium entropy':

$$\tilde{s}(e, v, u) = s(e, v) - \frac{u^2}{2\gamma T_a},$$

like the modern thermodynamical theories containing internal dynamical variables (eg. extended irreversible thermodynamics). With this notation our Liapunov function is nothing more than the negative maximum available work in this general sense

$$L(e, v, u) = T_a \tilde{s}(e, v, u) - e - p_a v + \mu_0 = -\tilde{W}_{max}(e, v, u) + \mu_0.$$

The last term μ_0 translates the maximum to the equilibrium of the system, it has no role in the stability.

You can see clearly the most important backward of the 'non-equilibrium entropy' as well: it is not a state function, the 'non-equilibrium entropy' depends on the environment (T_a) , and the interaction (γ) . This property is essentially valid for the continuum theories as well and questions the possibility of the introduction of such an entropy concept at all.

7. Carnot-Clausius theorem

In this chapter we show some correspondence between the continuum concepts and the homogeneous ones. In this respect a special form of the Second Law, the Carnot-Clausius theorem gives the best example [7, 10, 13]. This is essentially a convenient form of the entropy balance for homogeneous systems. In this equation the total change of the entropy for a homogeneous thermodynamical system is divided into two parts:

$$ds = d_{e}s + d_{i}s$$

where $d_e s$ is the 'reversible part' of the entropy change, the entropy from the environment, and $d_i s$ is the 'irreversible part' of the entropy change due to the internal irreversibilities. This later part is supposed to be a positive quantity. With continuum terminology we guess that $d_e s$ is like the flow part of the balance and $d_i s$ is the source of the entropy.

This has a more transparent particular form in our case, with the help of the dynamical law we can derive the explicit form of the entropy change, the time derivative of the entropy function:

$$(7.1) \quad \dot{s}(e,v) = \frac{\partial s}{\partial e}\dot{e} + \frac{\partial s}{\partial v}\dot{v} = \frac{1}{T}(q - \tilde{p}u) + \frac{p}{T}u = \frac{q}{T} - \frac{\tilde{p}u}{T} + \frac{pu}{T} = \frac{q}{T} - \frac{\hat{p}u}{T}.$$

The last form suggest an interpretation of the Carnot-Clausius theorem for our special system: q/T is the 'reversible part', and $\hat{p}u/T$ is the 'irreversible part' of the entropy change. This later one is a positive quantity if we are a bit more rigorous than A5, requiring the positivity of both terms. This strict analogy suggest us a clear interpretation of the ambiguous concept 'quasystatic process'. It is said that d_is is zero for such kind of processes, and strictly positive for irreversible ones. Using our particular form we can say that this property is not the property of the process but more properly the property of the thermodynamical body (however it can depend on the speed of the processes of course [14]): if the pressure of the body does not depend on the volume velocity $\hat{p} \equiv 0$ then the process (body) 'quasystatic' in the other case 'irreversible'. Here we should remark, that according to our model the 'quasystatic processes' tend to the equilibrium as well, the asymptotic stability fulfills in this case, too.

An other rearrangement at the end:

$$\dot{s} - \frac{q}{T_a} = q \left(\frac{1}{T_a} - \frac{1}{T} \right) - \frac{\hat{p}u}{T} \ge 0.$$

This is the entropy balance clearly. We see, that the a positive source is the requirement of A5. This form cannot be the counterpart of the Carnot-Clausius theorem because the first term of the entropy production concerns to the entropy change and not the internal irreversibilities.

8. Conclusions

In the preceding chapters we gave a frame of a new approach to the classical thermodynamics where we considered real processes in time that are governed by a system of ordinary differential equations. We required that the Second Law should result the asymptotic stability of the equilibrium of thermodynamical systems and investigated the conditions of such kind of stability for our simple example system. Our results are in full agreement with the usual requirements on the thermodynamical systems, and we have seen that several, independently required conditions will give the expected stability properties. For entropical bodies (A1/ii) the concavity of the entropy function and the homogeneous counterpart of the Clausius-Duhem inequality played the key role.

Furthermore we investigated several possibilities to introduce a dynamics into the theory and concluded that the old examples (classical, Onsagerian) does not fulfill all of our requirements. Therefore a new dynamical law was suggested, which corresponds all of our expectations and gives a clear view on the classical equilibrium theory.

As a final remark I call the attention to the application of these concepts to some more difficult system. We can treat more coupled bodies in more than one environment, phase transitions, the role of the reservoirs, etc...

References

- H. B. Callen. Thermodynamics and an Introduction to Thermostatistics. John Wiley & Sons, New York - etc.., 1985.
- 2. P. T. Landsberg. Thermodynamics. Interscience, N.Y., 1961.
- L. D. Landau and E. M. Lifsic. Course of Theoretical Physics V. /Statistical Physics I./. Pergamon Press, Oxford-etc.., 1980.
- D. R. Owen. A First Course in the Mathematical Foundations of Thermodynamics. Springer Verlag, 1984.
- H. J. Keuzer. Non-equilibrium Thermodynamics and its Statistical Foundations. Clarendon Press, Oxford, 1981.
- C. Truesdell and S. Bharatha. Classical Thermodynamics as a Theory of Heat Engines. Springer Verlag, 1977.
- S. R. de Groot and P. Mazur. Non-equilibrium Thermodynamics. North-Holland Publ. Company, Amsterdam, 1962.
- 8. T. Matolcsi. Dynamical laws in thermodynamics. Physics Essays, 5/3:320-327, 1992.
- N. Rouche, P. Habets, and M. Laloy. Stability Theory by Liapunov's Direct Method. Springer Verlag, New York Inc., 1977.
- P. Glansdorff and I. Prigogine. Thermodynamic Theory of Structure, Stability and Fluctuations. Wiley-Interscience, London-etc.., 1971.
- G. P. Beretta. A theorem on lyapunov stability for dynamical systems and a conjecture on a property of entropy. *Journal of Mathematical Physics*, 27/1:305-308, 1986.
- 12. P. Ván. Asymptotic stability and the Second Law in Extended Irreversible Thermodynamics. In Salvatore Rionero and Tommaso Ruggeri, editors, 7th Conference on Waves and Stability in Continuous Media, Bologna, Italy October 4-9. 1993, volume 23 of Series on Advances in Mathematics for Applied Sciences, pages 384-389, Singapore-New Jersey-London-Hong Kong, Oktober 1994. Quaderno CNR Gruppo nazionale per la Fisica Matematica, World Scientific.
- I. Gyarmati. Non-equilibrium Thermodynamics / Field Theory and Variational Principles/. Springer Verlag, 1970.
- 14. T. Matolcsi. Reservoirs in thermodynamics. Physics Essays, 8/1, 1995.

TECHNICAL UNIVERSITY OF BUDAPEST, DEPARTMENT OF CHEMICAL PHYSICS, 1521 BUDAPEST, BUDAFOKI ÚT 8., (GROUP OF CLEAN CONCEPT PHYSICS)

E- $mail\ address$: van@phy.bme.hu