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Variational Principles in Thermodynamics

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Instead of equations of motion, variational principles are often used for describing the dynamical behavior of a system. If the equations of motion are variational self-adjoint, the variational principle is equivalent to the equations of motion, because those are given by the Euler-Lagrange equations which belong to the variational principle. If the equations of motion are not variational self-adjoint –as it is the general case in thermodynamics– procedures are discussed to obtain also in these cases a variational problem. Because of lack of variational self-adjointness these variational problems cannot be true ones, they are non-Hamiltonian. By presupposing sufficient conditions an evolution criterion can be derived from the Second Law which results in a Hamiltonian variational principle, also in thermodynamics.

1 Introduction

Dynamic behavior in physics is mostly described by equations of motion which form a system of ordinary or partial differential equations describing the evolution of the physical system in consideration in space and time. If the state of the system is determined by F fields $\varphi^l(x^\mu)$ on space-time $(x^\mu) \in R^4$, equations of motion of second order are

$$\varepsilon_k[x^\mu, \varphi^l(x^\mu), \partial_{x^\nu}\varphi^l(x^\mu), \partial_{x^\nu}\partial_{x^\lambda}\varphi^l(x^\mu)] = 0 \qquad (1)$$
$$\mu, \nu, \lambda = 1,2,3,4 \qquad k, l = 1, 2, ..., F$$

Besides these equations of motion an other description of the dynamical behavior of systems is often used (Yourgau and Mandelstam, 1956; Lánczos, 1949): A variational principle from which the equations of motion follow by a special procedure. This special procedure is often a usual, so-called Hamiltonian action principle, a variational extremal problem for which the equations of motion are the Euler-Lagrange equations (Landau and Lifshitz, 1960) of the extremal problem

$$\int \mathcal{L}[x^\mu, \varphi^l(x^\mu), \partial_{x^\nu}\varphi^l(x^\mu), \partial_{x^\nu}\partial_{x^\lambda}\varphi^l(x^\mu)]dx^\mu \to \text{extremal} \qquad (2)$$

Here $\mathcal{L}[x^\mu, \varphi^l(x^\mu), \partial_{x^\nu}\varphi^l(x^\mu), \partial_{x^\nu}\partial_{x^\lambda}\varphi^l(x^\mu)]$ is the Lagrange density which is now replacing the equations of motion (1), because these follow from equation (2). Instead of a Hamiltonian variational problem a lot of different variational procedures are applied (Muschik and Trostel, 1983), some of which are also discussed in this paper.

The question now arises, why to formulate a variational problem by equation (2), if the equations of motion (1) are known? The answer to that question is manifold. There are people claiming that a variational principle is an elegant and esthetically satisfactory formulation of the system's dynamical problem, an answer which is irrelevant with respect to scientific procedures. More essential is that the variational problem represented by equation (2) can be treated numerically much better than the system of differential equations (1). Beyond that, the very effective tools provided by Noether's theorem can be applied, if a variational problem is formulated. An other field for applying variational principles is if the equations of motion are unknown, and –believing in the validity of a variational principle– one has to find them. Constructing along accepted lines the Lagrange density in equation (2), equation (1) can be derived. The belief in this procedure is represented by the fact that the system of differential equations (1) can only be derived from a variational principle, if they are variational self-adjoint. Consequently only variational self-adjoint systems of differential equations can be derived by variational principles. If the wanted equations of motion are not variational self-adjoint, one cannot find them by formulating a variational principle. Although this fact in mind, ad-hoc variational principles are formulated in several disciplines of physics, among them also thermodynamics (Anthony, 1990; Gambár et al., 1991; Gyarmati, 1969; Lambermont and Lebon, 1972; Lebon, 1980; Sieniutycz, 1984). A structural investigation of some of these principles can be found in Ván and Muschik (1995) and in this paper.

2 Variational Self-Adjointness

Well-known is the following
Proposition:
If we define the Lagrange density by

$$\mathcal{L}[x^\mu, \varphi^l(x^\mu), \partial_{x^\nu}\varphi^l(x^\mu), \partial_{x^\nu}\partial_{x^\lambda}\varphi^l(x^\mu)] :=$$
$$:= \varphi^k(x^\mu)\int_0^1 d\tau \varepsilon_k[x^\mu, \tau\varphi^l(x^\mu), \tau\partial_{x^\nu}\varphi^l(x^\mu), \tau\partial_{x^\nu}\partial_{x^\lambda}\varphi^l(x^\mu)] \tag{3}$$

it satisfies the following identity

$$\frac{\partial\mathcal{L}}{\partial\varphi^k} - \partial_{x^\nu}\frac{\partial\mathcal{L}}{\partial\partial_{x^\nu}\varphi^k} + \partial_{x^\nu}\partial_{x^\mu}\frac{\partial\mathcal{L}}{\partial\partial_{x^\nu}\partial_{x^\mu}\varphi^k} \equiv$$
$$\equiv \varepsilon_k[x^\mu, \varphi^l(x^\mu), \partial_{x^\nu}\varphi^l(x^\mu), \partial_{x^\nu}\partial_{x^\lambda}\varphi^l(x^\mu)] \tag{4}$$

if $\varepsilon[\cdot]$ satisfies variational self-adjointness represented by the following system of partial differential equations

$$0 = \frac{\partial\varepsilon_k}{\partial\partial_{x^\nu}\partial_{x^\mu}\varphi^l} - \frac{\partial\varepsilon_l}{\partial\partial_{x^\nu}\partial_{x^\mu}\varphi^k} \tag{5}$$

$$0 = \frac{\partial\varepsilon_k}{\partial\partial_{x^\nu}\varphi^l} + \frac{\partial\varepsilon_l}{\partial\partial_{x^\nu}\varphi^k} - 2\partial_{x^\mu}\frac{\partial\varepsilon_l}{\partial\partial_{x^\mu}\partial_{x^\nu}\varphi^k} \tag{6}$$

$$0 = \frac{\partial\varepsilon_k}{\partial\varphi^l} - \frac{\partial\varepsilon_l}{\partial\varphi^k} + \partial_{x^\mu}\frac{\partial\varepsilon_l}{\partial\partial_{x^\mu}\varphi^k} - \partial_{x^\nu}\partial_{x^\mu}\frac{\partial\varepsilon_l}{\partial\partial_{x^\nu}\partial_{x^\mu}\varphi^k} \tag{7}$$

From this proposition there follows that variational self-adjointness, equation (5) to equation (7), induces Euler-Lagrange equations (4), if the equations of motion (1) are valid. Vice versa the equations of motion generate Euler-Lagrange equations according to equation (4), if variational self-adjointness is satisfied. Consequently variational self-adjointness is necessary and sufficient for the existence of a variational problem which belongs to the equations of motion.

Now the question arises, what to do if the equations of motion are not variational self-adjoint? According to the propositions it is evident that there does not exist a variational problem for a non-self-adjoint system of differential equations. But also in this case it may be possible to generate a variational problem, if certain presuppositions are valid, as we will discuss in the next sections.

3 If Variational Self-Adjointness Is not Valid

Here we investigate special cases in which the equations of motion are not variational self-adjoint, but in which by application of special procedures variational self-adjointness can be generated. For demonstrating these procedures we will consider special simple examples.

3.1 Integrating Factor

We consider the equation of motion of a damped harmonical oszillator

$$\varepsilon(\ddot{q}, \dot{q}, q) = \ddot{q} + a\dot{q} + bq = 0 \tag{8}$$

A comparison of equation (8) with equation (1) shows, that $\nu, \mu, \lambda = 1$ and $k, l = 1$, and the variational self-adjointness is not satisfied in general, as we can see easily from equation (6):

$$\varphi^l \longrightarrow q, \quad x^\nu \longrightarrow t, \quad \partial_{x^\nu}\varphi^l \longrightarrow \dot{q} \tag{9}$$

$$\frac{\partial\varepsilon_k}{\partial\partial_{x^\nu}\varphi^l} \longrightarrow \frac{\partial\varepsilon}{\partial\dot{q}} = a \tag{10}$$

$$2\partial_{x^\mu}\frac{\partial\varepsilon_l}{\partial\partial_{x^\mu}\partial_{x^\nu}\varphi^k} \longrightarrow 2\partial_t\frac{\partial\varepsilon}{\partial\ddot{q}} = 0 \tag{11}$$

$$0 = \frac{\partial \varepsilon_k}{\partial \partial_{x^\nu} \varphi^l} + \frac{\partial \varepsilon_l}{\partial \partial_{x^\nu} \varphi^k} - 2\partial_{x^\mu} \frac{\partial \varepsilon_l}{\partial \partial_{x^\mu} \partial_{x^\nu} \varphi^k} = 2a \tag{12}$$

The self-adjointness is only satisfied, if the oscillator is undamped ($a = 0$). Consequently there is up to now no variational problem which generates the equation of motion (8) of the damped oscillator.

For generating such a variational problem we write equation (8) in a different way, so that the conditions of variational self-adjointness can be satisfied.

$$\varepsilon^*(t, \ddot{q}, \dot{q}, q) = F(t)[\ddot{q} + a\dot{q} + bq] = 0 \qquad F(t) \neq 0 \tag{13}$$

which results in

$$\frac{\partial \varepsilon^*}{\partial \dot{q}} = aF(t) \qquad 2\partial_t \frac{\partial \varepsilon^*}{\partial \ddot{q}} = 2F_t(t) \tag{14}$$

Therefore equation (6) yields

$$0 = \frac{\partial \varepsilon_k^*}{\partial \partial_{x^\nu} \varphi^l} + \frac{\partial \varepsilon_l^*}{\partial \partial_{x^\nu} \varphi^k} - 2\partial_{x^\mu} \frac{\partial \varepsilon_l^*}{\partial \partial_{x^\mu} \partial_{x^\nu} \varphi^k} = 2aF(t) - 2F_t(t) \tag{15}$$

which results in

$$F(t) = e^{at} \tag{16}$$

Because equation (5) is identical satisfied, we have to check equation (7)

$$0 = \frac{\partial \varepsilon_k^*}{\partial \varphi^l} - \frac{\partial \varepsilon_l^*}{\partial \varphi^k} + \partial_{x^\mu} \frac{\partial \varepsilon_l^*}{\partial \partial_{x^\mu} \varphi^k} - \partial_{x^\nu} \partial_{x^\mu} \frac{\partial \varepsilon_l^*}{\partial \partial_{x^\nu} \partial_{x^\mu} \varphi^k} = aF_t(t) - F_{tt}(t) \tag{17}$$

which is valid according to equation (16). Consequently

$$\varepsilon^*(t, \ddot{q}, \dot{q}, q) = e^{at}[\ddot{q} + a\dot{q} + bq] \tag{18}$$

is variational self-adjoint.

We introduce the Lagrange function according to equation (3)

$$L(t, q, \dot{q}, \ddot{q}) := q \int_0^1 d\tau \tau e^{at}[\ddot{q} + a\dot{q} + bq] = q\frac{1}{2}e^{at}[\ddot{q} + a\dot{q} + bq] \tag{19}$$

A short calculation yields

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} + \frac{d^2}{dt^2}\frac{\partial L}{\partial \ddot{q}} = e^{at}[\ddot{q} + a\dot{q} + bq] \tag{20}$$

which is the Euler-Lagrange equation (4), if the equation of motion (8) is valid.

3.2 Doubling of the Fields

We consider the equation of motion of a growth process

$$\varepsilon(q, \dot{q}) = \dot{q} + aq \tag{21}$$

From equation (6) follows, that equation (21) is not variational self-adjoint. To generate self-adjointness we double the fields. So we introduce two fields, one of them is the wanted field q in equation (21), the other one Q has first of all no interpretation. That is the reason why this field doubling in physics is questionable. In general the additional fields cannot be interpreted, although they appear in the Lagrange density, as we will see.

$$\varphi^1(x^\mu) \equiv q(t) \qquad \varphi^2(x^\mu) \equiv Q(t) \tag{22}$$

$$\varepsilon_2(q,\dot{q}) = \dot{q} + aq \qquad \varepsilon_1(Q,\dot{Q}) = -\dot{Q} + aQ \tag{23}$$

We now check the conditions for variational self-adjointness equation (5) to equation (7). Here equation (5) is identically satisfied, and both the other two equations become

$$0 = \frac{\partial \varepsilon_1}{\partial \dot{\varphi}_2} + \frac{\partial \varepsilon_2}{\partial \dot{\varphi}_1} = -1 + 1 \tag{24}$$

$$0 = \frac{\partial \varepsilon_1}{\partial \varphi_2} - \frac{\partial \varepsilon_2}{\partial \varphi_1} + \frac{d}{dt}\frac{\partial \varepsilon_1}{\partial \varphi_2} = a - a + 0 \tag{25}$$

By introducing the second field Q self-adjointness of equation (23) is enforced.

The Lagrange function in equation (3) is according to equation (23)

$$L = q\int_0^1 d\tau\tau[-\dot{Q} + aQ] + Q\int_0^1 d\tau\tau[\dot{q} + aq] = \frac{1}{2}Q[\dot{q} + 2aq] - \frac{1}{2}\dot{Q}q \tag{26}$$

from which the Euler-Lagrange equations (4) follow

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = aQ - \dot{Q} = \varepsilon_1 = 0 \tag{27}$$

$$\frac{\partial L}{\partial Q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{Q}} = aq + \dot{q} = \varepsilon_2 = 0 \tag{28}$$

3.3 Inexact Variational Principles

Again we start out with the equation (21) of motion of a growth process which does not satisfy the condition of variational self-adjointness. Irrespective of this fact we define a quasi-Lagrange function

$$L := Aq(t) + \frac{1}{2}aq^2(t) \tag{29}$$
$$A = const \quad \text{with respect to the variation}$$

The corresponding "Euler-Lagrange equation" is

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = A + aq \tag{30}$$

If now after the variation A is identified with $\dot{q}$

$$A \equiv \dot{q} \not\equiv const \tag{31}$$

an identication which is of course incompatible with the kind of variation before, therefore the name "inexact", equation (30) results by equation (21) in an Euler-Lagrange equation with vanishing right-hand side.

3.4 Quasi Variational Principles

Consider a space equipped with a real scalar product. The differential equation which we want to transform into a variational problem has the form

$$D\varphi = 0 \tag{32}$$

Introducing a linear, regular operator K on this space we obtain for an arbitrary $\delta\varphi$

$$< K\delta\varphi | D\varphi >= 0 \qquad < \delta\varphi | K^+ D\varphi >= \mathcal{F}(\varphi, \delta\varphi) = 0 \tag{33}$$

For application of an approximation procedure, such as that of Galerkin-Ritz, we have to take the variation δ out of the product. To achieve that, we presuppose that K^+D is self-adjoint

$$K^+D \doteq [K^+D]^+ = D^+K \tag{34}$$

Then equation $(33)_2$ results in

$$\frac{1}{2} < \delta\varphi|K^+D\varphi > + \frac{1}{2} < \delta\varphi|D^+K\varphi >= 0 \tag{35}$$

The second term can be transformed into

$$< \delta\varphi|D^+K\varphi >=< K^+D\delta\varphi|\varphi >=< \varphi|K^+D\delta\varphi > \tag{36}$$

By introducing the scalar product

$$S(\varphi) :=< \varphi|K^+D\varphi > \tag{37}$$

we obtain from the equations (35), (36) and $(33)_2$, the variational problem

$$\delta S(\varphi) = \delta < \varphi|K^+D\varphi >= 0 \tag{38}$$

The variation in equation (38) does not represent a real variational problem (therefore the name quasi), because the correct φ in equation (32) does not make $S(\varphi)$ to an extremal. Also the case that $K\varphi$ and $D\varphi$ are perpendicular to each other is not excluded. But despite these theoretical shortcomings, the procedure may be advantageous for practical approximations. Obvious is that the differential equation (32) is not an Euler-Lagrange equation which belongs to a Hamiltonian variational problem.

3.5 Transformation of Variables

Starting out with the differential equation (32) we can introduce new variables

$$\psi \;=\; K\varphi, \qquad \exists\, K^{-1} \tag{39}$$

Then equation (32) results in

$$DK^{-1}\psi \;=\; 0 \tag{40}$$

One is looking for such a K, that the operator DK^{-1} can be treated with one of the methods described above.

These five procedures discussed above, which can be helpful if the differential equations of the original problem are not variational self-adjoint, are not the only possibilities to overcome the non-self-adjointness. Other possibilities are described in Trostel (1982), Muschik and Trostel (1983), Ván and Muschik (1994), and Ván and Muschik (1995).

4 Evolution Criterion

In general the governing equations of non-equilibrium thermodynamics, that are the balance equations of mass, momentum, angular momentum, energy, entropy, and others for additional fields describing the system in consideration, are not variational self-adjoint. Consequently a Hamiltonian variational problem for non-equilibrium thermodynamics is not available. That is just the reason why people use procedures described in section 3. All these procedures are mathematically induced: One wants to formulate a non-Hamiltonian variational problem, whatever the reasons for that may be.

Here now we want to treat the more physically induced problem: Starting out with the Second Law, what are the physical presuppositions we have to make, so that we can formulate a variational problem?

We will see that this aim can be reached in two different steps. First of all we derive from the Second Law in form of the gobal balance for the entropy

$$\frac{d}{dt}\int_{G(t)} \varrho s dV + \oint_{\partial G(t)} \boldsymbol{\Phi}\cdot d\boldsymbol{f} - \int_{G(t)} \varrho\varphi dV \geq 0 \tag{41}$$

a so-called evolution criterion which is always of the form

$$\frac{d}{dt}\int_{G(t)} \mathcal{F}[\clubsuit(\boldsymbol{x},t), \heartsuit(\boldsymbol{x},t), \spadesuit(\boldsymbol{x},t)]dV \geq 0 \tag{42}$$

Here $G(t)$ is a body in non-equilibrium, $\partial G(t)$ its surface, ϱ the field of the mass density, s the specific entropy field, $\boldsymbol{\Phi}$ the entropy flux density field, and φ the entropy supply. By evolution criterion represented by equation (42) we see that the integral in equation (41) is maximal in equilibrium. This is a variational problem for the equilibrium fields in equation (41): They have to be determined, so that the integral is maximal. But first of all these fields $\clubsuit$ etc. are unknown and have to be derived, what we will report in this section (Muschik and Papenfuss, 1993).

The global entropy flux is

$$-\oint_{\partial G(t)} \boldsymbol{\Phi}\cdot d\boldsymbol{f} = \dot{Q}/\Theta \tag{43}$$

Here $\dot{Q}$ is the global net heat exchange between $G(t)$ and its environment

$$-\oint_{\partial G(t)} \boldsymbol{q}\cdot d\boldsymbol{f} = \dot{Q} \tag{44}$$

Θ is the contact temperature of $G(t)$, a non-equilibrium temperature which is defined by the inequality (Muschik, 1977; Muschik and Brunk, 1977)

$$\dot{Q}\left[\frac{1}{\Theta} - \frac{1}{T^*}\right] \geq 0 \tag{45}$$

Here T^* is the constant thermostatic temperature of the system's equilibrium environment. By use of the defining inequality (45) we obtain from equation (43)

$$-\oint_{\partial G(t)} T^*\boldsymbol{\Phi}\cdot d\boldsymbol{f} \geq -\oint_{\partial G(t)} \boldsymbol{q}\cdot d\boldsymbol{f} \tag{46}$$

Inserting this into $T^*\times$(41), this inequality becomes

$$\frac{d}{dt}\int_{G(t)} \varrho T^* s dV - \int_{G(t)} \varrho T^*\varphi dV \geq -\oint_{\partial G(t)} \boldsymbol{q}\cdot d\boldsymbol{f} \tag{47}$$

The global balance of internal energy and the local balance of momentum are

$$\frac{d}{dt}\int_{G(t)} \varrho\varepsilon dV = -\oint_{\partial G(t)} \boldsymbol{q}\cdot d\boldsymbol{f} + \int_{G(t)} [\mathbf{T}:\nabla\boldsymbol{v} + \varrho r]dV \tag{48}$$

$$\varrho\dot{\boldsymbol{v}} - \nabla\cdot\mathbf{T}^\top = \varrho\boldsymbol{f} \tag{49}$$

Here ε is the specific internal energy, $\mathbf{T}$ the Cauchy stress tensor, $\boldsymbol{v}$ the material velocity, r the energy supply, and $\boldsymbol{f}$ the external force density. Inserting equation (48) into equation (47) we obtain

$$\frac{d}{dt}\int_{G(t)} (\varrho T^* s - \varrho\varepsilon)dV - \int_{G(t)} [\varrho T^*\varphi - \mathbf{T}:\nabla\boldsymbol{v} - \varrho r]dV \geq 0 \tag{50}$$

The first term of this inequality has already the form of equation (42). To transform also the second term into a time derivative of a volume integral, we now make assumptions which are sufficient for achieving

this transformation. First of all we set the entropy supply and the energy supply to zero. The remaining term in the second part of the left-hand side of equation (50) is transformed by use of equation (49). Two further assumptions bring it into the wanted shape (Muschik and Papenfuss, 1993): The forces are conservative

$$\boldsymbol{f}(\boldsymbol{x}) \;=\; \nabla\gamma(\boldsymbol{x}) \tag{51}$$

and the equilibrium environment is an ideal fluid

$$\mathbf{T} \;=\; -p^*\mathbf{1}, \qquad p^* \;=\; const \tag{52}$$

By these sufficient assumptions we obtain the wanted evolution criterion

$$\frac{d}{dt}\int_{G(t)}\left[\varrho T^* s \;-\; \varrho\varepsilon \;-\; \varrho\gamma \;-\; p^* \;-\; \frac{1}{2}\varrho\boldsymbol{v}^2\right] dV \;\geq\; 0 \tag{53}$$

The unknown fields in equation (42) are now determined. The integrand in equation (53) is a special kind of negative free energy modified by the kinetic energy and the equilibrium pressure of the environment. Because both these fields are not negative, we obtain a weaker formulation of the evolution criterion by

$$\frac{d}{dt}\int_{G(t)}\left[\varrho T^* s \;-\; \varrho\varepsilon \;-\; \varrho\gamma\right] dV \;\geq\; 0 \tag{54}$$

In contrast to the usual procedures the evolution criterion in equation (53) does not need the hypothesis of local equilibrium (no Gibbs fundamental equation was used) and no additional stability criteria (Glansdorff and Prigogine, 1971). It is here written down for materials without internal angular momentum. But the spin can be included, and the evolution criterion can be applied to liquid crystals (Papenfuss and Muschik, 1997). The evolution criterion is valid during the whole non-equilibrium process and not only near equilibrium. Of course the evolution criterion represented by equation (53) is not totally general because its validity depends on the sufficient assumptions made on the material and on the system's environment controlling it. For completeness we will make up again the sufficient conditions which we need for deriving the evolution criterion:

- There are no entropy- and energy-supply,
- the entropy flux density through $\partial G(t)$ is purely thermal (see equations (45) and (46)),
- the force density is conservative,
- the environment of the system has reservoir properties, that means it is always in equilibrium and its state is time independent ($T^* = const, p^* = const$),
- the vicinity consists of a perfect fluid.

Presupposing these five conditions we obtain the evolution criterion in equation (53). The integral in the evolution criterion in equation (53) is maximal in equilibrium and consequently constitutes a variational principle.

$$\delta\int_{G(t)}\mathcal{F}(\boldsymbol{x}, t\to\infty)dV \;=\; 0 \tag{55}$$

$$\mathcal{F} \;\equiv \varrho T^* s \;-\; \varrho\varepsilon \;-\; \varrho\gamma \;-\; p^* \;-\; \frac{1}{2}\varrho\boldsymbol{v}^2$$

The integral represents a modified negative free energy of the system $G(t)$. An essential point is that this evolution criterion can be derived from the Second Law by sufficient assumptions without any additional constraints. A remaining task is to weaken the made assumptions and to include additional field for complex materials.

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