

Unification of continuum mechanics and thermodynamics by means of Lagrange-formalism

Present status of the theory and presumable applications(*)

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BY MEANS of Lagrange-formalism it should be possible to find a unified description for continuum mechanics and thermodynamics. My aim is to take into account explicitly internal variables which are physically identified on the microlevel. The paper gives a summary of Lagrange-formalism with special regard to thermodynamics. The possible applications of the theory to defect dynamics in solids are discussed in some detail.

Formalizm lagranżowski powinien umożliwić ujednoczenie podejścia do mechaniki ośrodków ciągłych i termodynamiki. Celem rozważań jest wzięcie pod uwagę tych zmiennych wewnętrznych, które można zidentyfikować na poziomie mikro. W pracy przedstawiono zasady formalizmu Lagrange'a ze szczególnym uwzględnieniem termodynamiki. Bardziej szczegółowo omówiono możliwość zastosowania teorii do dynamiki defektów w ciałach stałych.

Лагранжевый формализм должен дать возможность унифицировать подход к механике сплошных сред и термодинамике. Целью рассуждений является обращение внимания на эти внутренние переменные, которые можно идентифицировать на микро уровне. В работе представлены принципы лагранжевого формализма, с особым учетом термодинамики. Более подробно обсуждена возможность применения теории к динамике дефектов в твердых телах.

1. Preliminaries

1.1. Why Lagrange-formalism in phenomenological thermodynamics of irreversible processes?

BY MEANS of Hamilton's Principle a given physical theory gets its formal closure. On the other hand, a physical theory can be completely deduced by means of Lagrange-formalism once its Hamilton's Principle is established. In the past this statement was especially true for theories of non-dissipative mechanical processes. However, there was a missing link concerning thermodynamics of irreversible processes which in the case of mechanical processes are associated with dissipation of mechanical energy. I have shown that thermodynamics of irreversible processes can indeed be included into Lagrange-formalism [1, 2, 3]. So far I have been successful in the particular processes of heat flow, diffusion and chemical reactions. It is the aim of this paper to outline how these investigations might be generalized in order to describe dissipative mechanical processes of material bodies.

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In thermodynamics of irreversible processes a lot of variation principles are discussed⁽¹⁾. However, Hamilton's Principle in its original sense and in the sense of Lagrange-formalism is distinguished by the fact that the set of fundamental process variables of a system is submitted to free and independent variations of all variables [6, 7]. Some remarkable facts concerning this principle and the associated Lagrange-formalism will be summarized in advance:

I. By means of Hamilton's variation principle, a complicated initial and boundary value problem can be solved numerically along the line of Ritz's method.

II. Universal structures involved in Hamilton's Principle and in Lagrange-formalism have fundamental significance in theoretical physics as well as in the practical use of the theory:

a. The universal structures apply for all systems subsumed under Lagrange-formalism, thus giving rise to a methodically unified description of all processes. In the case of dissipative deformation processes of material bodies, this means that mechanical and thermodynamical degrees of freedom are handled methodically in the same way, i.e., mechanics and thermodynamics are methodically unified and joined together within Lagrange-formalism.

b. The total information concerning the processes of a system is involved into a single function, namely into its Lagrangian. Thus Lagrange-formalism starts from the smallest possible entity to define a physical system.

c. In Lagrange-formalism all observables, e.g., mass, energy, momentum a.s.o. are defined by means of universal invariance requirements for the Lagrangian. These requirements apply in the same way to all physical systems thus giving rise to a universal, unique and straightforward derivation of the relevant balance equations and of the constitutive equations for the associated densities, fluxes and production rates.

The remarkable facts mentioned in II.b and II.c contrast with traditional theories of irreversible processes where a whole set of conceptual independent constitutive equations has to be established for the definition of a particular material behaviour [8, 9, 10]. In practical cases this set might be even very large. However, using Lagrange-formalism the methodical situation resembles that of thermostatics, where all information of a system is also comprised into one thermodynamical potential only, e.g., into the free energy function.

III. In principle, Lagrange-formalism allows for general dynamics of the system without any restrictions. This contrasts with traditional thermodynamics of irreversible processes, which is based on the Principle of Local Equilibrium [8, 9] and is an extrapolation of thermostatics into the neighbourhood of thermodynamical equilibrium. Therefore this theory has to be restricted to those irreversible processes which are locally sufficiently close to equilibrium states. Lagrange-formalism, however, does not suffer such a restriction. Having defined an appropriate Lagrangian, it also applies to processes far away from local equilibrium. For instance, this fact might be important for dislocation dynamics associated with plastic deformation of solids.

Rational thermodynamics has improved the situation insofar as the processes are no

⁽¹⁾ See e.g. GYARMATI [4], LEBON [5].

more restricted to the neighbourhood of local equilibrium [10]. However, the set of conceptually-independent constitutive equations is still left. I have shown that the definition of constitutive equations of the traditional formulations of thermodynamics of irreversible processes and especially those of rational thermodynamics can be unified within Lagrange-formalism.

IV. The dynamics of internal variables gives rise to after-effects of the external variables. In rational thermodynamics these effects are taken account of in the constitutive equations by means of memory functionals depending on the external variables only. I intend to include the dynamics of internal variables explicitly into Lagrange-formalism in order to get instantaneous constitutive relations. On the one hand, internal variables have to be identified on the microlevel with physical entities such as structure defects. On the other hand, essential features of its microdynamics will be taken over to the phenomenological level by modelling the Lagrangian properly.

1.2. Plasticity. Material manifold versus microdynamics of defects

Phenomenological plasticity of solids is associated with irreversible dislocation dynamics on the atomic level. When giving its phenomenological description by means of any thermodynamical theory of irreversible processes, the following facts should be kept in mind:

I. Because of its high creation energy, a dislocation network is far away from thermal equilibrium. In a stationary state it is but in a mechanical equilibrium state with respect to its associated elastic eigen-strains. From the thermodynamical point of view, this state is a metastable state which is far away from the absolute thermodynamical equilibrium.

II. Applying a plastic deformation to a body gives rise to a driven dislocation migration against internal forces which are due to the interaction with the dislocation network and

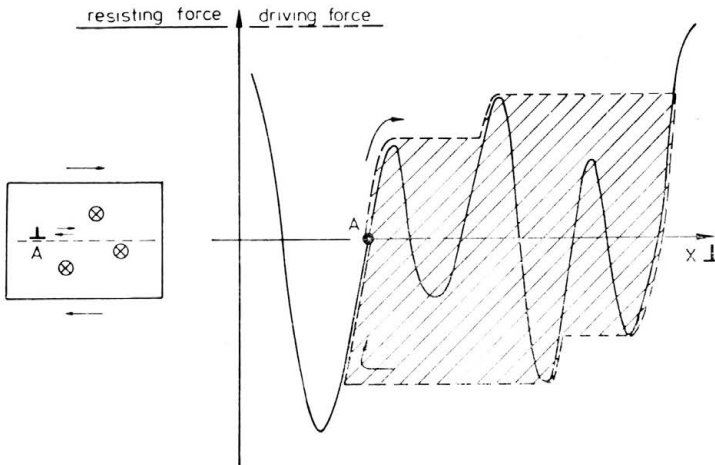


FIG. 1. Irreversible dislocation migration.

with various other obstacles. Figure 1 demonstrates the situation for the path of a dislocation back and forth, starting and ending at site *A*. The dashed line represents the driving force at the dislocation. It is balanced by the statistically-distributed resisting force (full

line). The dislocation gets unstable at each peak of the resisting force, what finally results in a microhysteresis⁽²⁾. The hatched area represents the mechanical energy dissipated during the cyclic dislocation migration.

These considerations show that plastic deformation is extremely dissipative due to the microdynamics of dislocations. The microhysteresis is even preserved if the plastic deformation velocity tends to zero, which means that a quasi-static plastic deformation process never tends towards a reversible process.

Ordinary thermostatics operates on the manifold⁽³⁾ of unconstrained thermal equilibrium states. A path in the manifold represents a reversible process which is physically realized by means of quasi-static experimental operations. Gibbs' fundamental form is associated with an infinitesimal path. Neither of these concepts holds for dislocation networks and its dynamics as is shown by topics I and II of the present chapter. There is neither a thermal equilibrium manifold including dislocation networks nor a reversible, quasi-static path which could be associated with a Gibbs' fundamental form including variations of the dislocation network. Thus, for plasticity, we have no thermostatics which could be extrapolated into the neighbourhood of equilibrium states by means of the traditional Principle of Local Equilibrium.

Dislocations are a most prominent example of microscopic objects which have to be described in phenomenological thermodynamics by means of internal variables. These objects cannot be manipulated from outside; nevertheless their dynamics is the main feature of plasticity which takes place far away from local thermal equilibrium⁽⁴⁾. So Lagrange-formalism might be an appropriate tool to describe this phenomenon.

Dislocation dynamics gives rise to a further difficulty which is usually suppressed in the phenomenological plasticity theory. However, this lack actually cancels the dislocation concept in the theory: The continuum theory of plastic deformation processes is traditionally based on the concept of the

III. Material manifold.

Here "manifold" is understood in the usual mathematical sense. This concept, which originally is due to pure elasticity, is a mathematical correlate not only of the continuously distributed matter in the body but also of a quite particular class of deformation modes of the body, namely of the compatible deformations. The points and the coordinate systems of the manifold correspond in the body with material elements and with material coordinate systems respectively. The n -times continuous differentiable transformations⁽⁵⁾ between different material coordinate systems are associated with compatible deformations. The situation is visualized by Fig. 2: the body is embedded into the three-dimensional Euclidean space R^3 . During a deformation process the spatial coordinate net Σ is taken over into the body at a particular state A in order to define a material coordinate system Σ_A which will substantially be dragged along with

⁽²⁾ Of course the closed microcycle of a dislocation does not correlate with a macroscopic plastic deformation cycle.

⁽³⁾ "Manifold" in the usual mathematical sense.

⁽⁴⁾ If dislocations were external variables, they could be manipulated reversibly from outside and the dashed curve of the driving force in Fig. 1 would join the full curve of the resistance force.

⁽⁵⁾ $n = 0, 1, 2, \dots$ is not specified here.

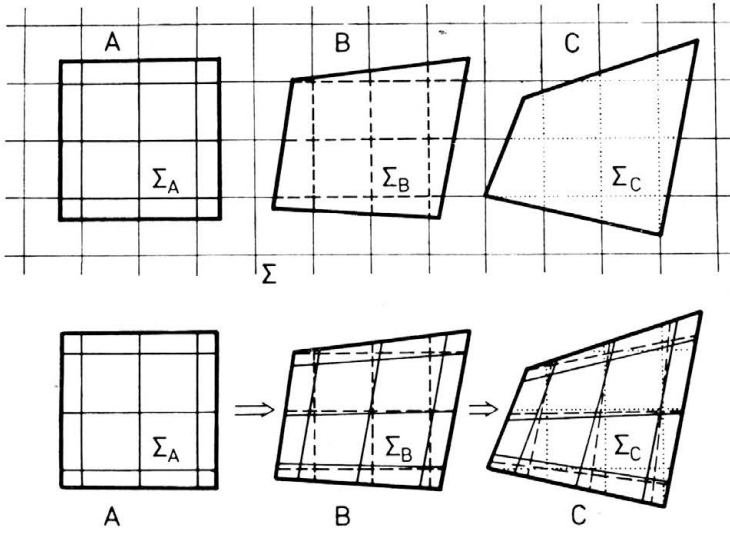


FIG. 2. Material manifold and material coordinate systems.

the body. Performing this procedure at each state A, B, C, \dots , we get a continuously varying set of material coordinate systems $\Sigma_A, \Sigma_B, \Sigma_C, \dots$ in the body. The transformations between these systems obviously describe the deformations of the body in ordinary space with respect to the spatial coordinate system Σ . The continuity properties of the transformations, i.e., the order n of the manifold defines the character of the compatible deformations: In any case $n \geq 0$ there is no tearing or material overlap in the body; for $n \geq 1$ each smooth material curve is deformed again in a smooth curve, a.s.o.

The concept of the material manifold has been taken over into the plasticity theory because of the empirical fact, that a plastically-deformed body is macroscopically not torn into pieces. In particular, the phenomenological plastic deformation, which subsequently will be called "total deformation", has been assumed to be a compatible one as in Fig. 2. However, to take account of the specifications of plasticity as compared with pure elasticity, the following supplementary assumption has been added:

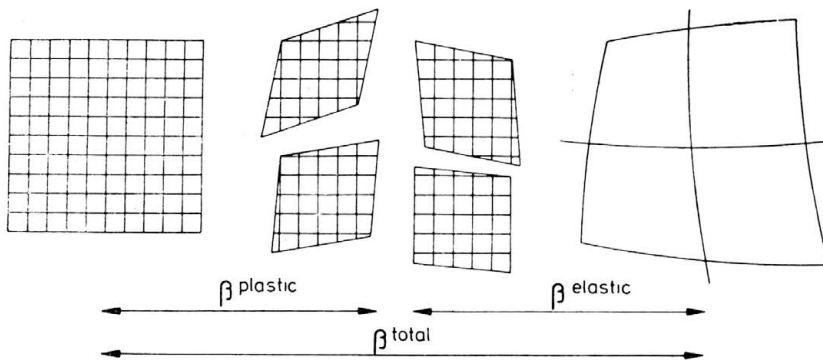


FIG. 3. Incompatibilities in plastic deformations.

IV. The total deformation of a plastically-deformed body is divided into a pure elastic and a pure plastic part which are both incompatible deformations (see Fig. 3). The incompatibility is associated with the dislocation density, whereas the total deformation is assumed to be a compatible one. In the case of the linear theory, these ideas are formally described by the equations [19]

$$(1.1) \quad \beta^{\text{total}} = \beta^{\text{elastic}} + \beta^{\text{plastic}},$$

$$(1.2) \quad \text{curl} \beta^{\text{elastic}} = \alpha,$$

$$(1.3) \quad \text{curl} \beta^{\text{plastic}} = -\alpha,$$

$$(1.4) \quad \text{curl} \beta^{\text{total}} = 0,$$

$$(1.5) \quad \beta^{\text{total}} = \text{grad } \mathbf{u}.$$

β^{total} , β^{elastic} , β^{plastic} and α are the total, elastic, plastic distortion tensors and the dislocation density tensor respectively. \mathbf{u} is the displacement vector of the total deformation.

Although these ideas concerning plasticity and the material manifold are commonly accepted, they nevertheless suffer from the fact that they completely disregard the dynamics of dislocations. Macroscopic plastic deformation is associated with dislocation migration on the microlevel and a smooth material line in the body will be torn by moving dislocations (see Fig. 4). Of course the final misfit of the line due to one dislocation is but one

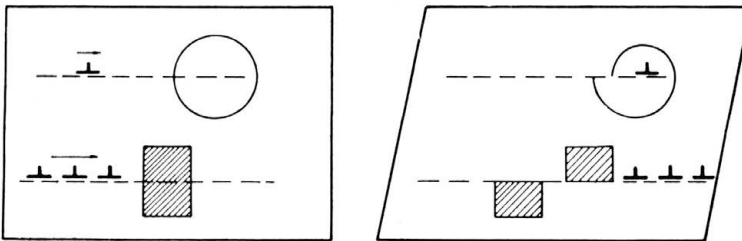


FIG. 4. A plastically-deformed material is no material manifold.

atomic distance across the slip plane of the dislocation. However, in reality a whole cascade of dislocation may run along the same slip plane and it finally may be the case that even domains of considerable size are torn into pieces. This can be confirmed experimentally by means of real macroscopic slip line cascades at the surface of strongly deformed single crystals [11]. So the total deformation of a plastically-deformed crystalline body can never be compatible and the dislocation dynamics contradicts the properties mentioned above of a material manifold:

V. A plastically-deformed body is no material manifold, though the continuity of mass distribution is preserved. Especially Eqs. (1.4) and (1.5) have to be omitted.

One might object to my arguments, that the concept of material manifold can be preserved if the microlevel is established at a larger scale than the atomic one in order to average the dislocation dynamics in some way. In my opinion, however, such a procedure would cancel dislocation dynamics completely and the physical interpretation

of internal thermodynamical variables due to plastic deformation would become quite vague. Furthermore, it should be carefully discussed, whether dislocation dynamics really can be averaged in such a way as to smooth down discontinuities of plastic deformations. Because of the existence of macroscopic surface slip lines, I think that dislocation dynamics is a macroscopic phenomenon as well.

A solution to these problems might again be Lagrange-formalism. Within this theory the essential quantities should be densities and fluxes of dislocations and of mass, both being kinematically coupled. A material manifold will no more be involved.

2. Lagrange-formalism

2.1. Hamilton's principle. Lagrangian. Field equations

A process of a system is defined by a set

$$(2.1) \quad P = \{\psi_k(x, t), k = 1, \dots, N\}$$

of fundamental field variables in space and time. Let us consider an action integral with physical dimension (energy·time)

$$(2.2) \quad J_1 = \int_{t_1}^{t_2} \int_{V(t)} l(x, t; \psi(x, t), \partial\psi(x, t)) d^3x dt,$$

$$\psi = \{\psi_k, k = 1, \dots, N\}, \quad \partial = \left\{ \nabla, \partial_t = \frac{\partial}{\partial t} \right\},$$

which is based on a real-valued Lagrange-density-function l and which is associated once and for all with the processes of the system in a fixed but nevertheless arbitrary time interval $t_1 \leq t \leq t_2$. $V(t)$ is the instantaneous volume of the system. In the case of a first order theory, the Lagrangian l depends on the field variables ψ_k and on their first order derivatives with respect to space and time coordinates. In general, the Lagrangian may further depend explicitly on space and time coordinates due to an intervention of the outer world into the bulk of the system. In the following I shall skip such an influence. For simplicity and with regard to the examples in Sect. 5, I further restrict myself to processes in a rigid body, what implies

$$(2.3) \quad V(t) = V = \text{constant}.$$

The central and the only constitutive assumption in Lagrange-formalism is given by the Lagrangian: It contains the complete information concerning all processes P of the system. A particular function

$$(2.4) \quad l = l(\psi, \partial\psi)$$

defines a particular physical system, i.e., this single equation substitutes the set of constitutive equations of traditional thermodynamics of irreversible processes.

Hamilton's Variation Principle is exclusively based on the action integral (2.2)! On the basis of the Lagrangian it defines the dynamics of the system and reads as follows:

$$(2.5) \quad J_1 = \text{extremum} \quad \text{or} \quad \delta J_1 = 0$$

by free and independent variation of all fields ψ_k with fixed values at the beginning and at the end of the process:

$$\delta\psi_k(x, t_{1,2}) = 0.$$

Variations at the boundary ∂V are included depending on the specific boundary conditions of the system⁽⁶⁾.

Real processes are distinguished as solutions of Hamilton's Principle.

Performing the variation leads to N fundamental field equations for the real processes in the volume V (*Euler-Lagrange-equations*)

$$(2.6) \quad \partial_t \frac{\partial l}{\partial(\partial_t \psi_k)} + \nabla \cdot \frac{\partial l}{\partial(\nabla \psi_k)} - \frac{\partial l}{\partial \psi_k} = 0, \quad k = 1, \dots, N.$$

These are necessary conditions for an extremum of the action integral. By free variations at the boundary ∂V we get N *boundary conditions*

$$(2.7) \quad \mathbf{n} \cdot \frac{\partial l}{\partial(\nabla \psi_k)} = 0, \quad k = 1, \dots, N,$$

which belong to an *isolated system*. \mathbf{n} is the unit normal vector at the boundary surface. An isolated system is physically distinguished by unconstrained fields ψ_k at the boundary. This corresponds to the free variations $\delta\psi_k$ at ∂V . All fluxes have to vanish across ∂V which coincides with the conditions (2.7)⁽⁷⁾. For non-isolated systems the situation is more involved and the physics at the boundary has to be discussed in detail, e.g., continuity of mass and heat fluxes.

The Euler-Lagrange field equations (2.6) are a *set of self-adjoint partial differential equations* of the second order. They are derived from the Lagrangian only. On the other hand, for a given set of partial differential equations the property of self-adjointness is necessary and sufficient for the existence of a Lagrangian [12, 13]. Then the given set has the form (2.6). Physical consequences will be discussed in Sect. 3.

2.2. General structure of the theory. Lagrange-formalism

The scheme of Lagrange-formalism is illustrated in Fig. 5. For details the reader is referred to some other papers [1, 2, 3]. The theory is based on three pillars:

on *Hamilton's Principle* $\langle 1 \rangle$ ⁽⁸⁾ being a universal structure element;

on a *Lagrangian* $\langle 2 \rangle$ being a universal structure element as far as its existence is concerned and being at the same time an individual structure element of a particular system as far as its particular analytical form is concerned;

on a Lie-group of *universal invariance principles* $\langle 3 \rangle$ being again a universal structure element which applies to the Lagrangian. As a simple example I refer to the time shifting group

$$(2.8) \quad t' = t + \varepsilon, \quad -\infty < \varepsilon < \infty,$$

⁽⁶⁾ See the remarks concerning Eq. (2.7).

⁽⁷⁾ See Sect. 5.1: heat transport.

⁽⁸⁾ Numbers $\langle \dots \rangle$ are referred to Fig. 5.

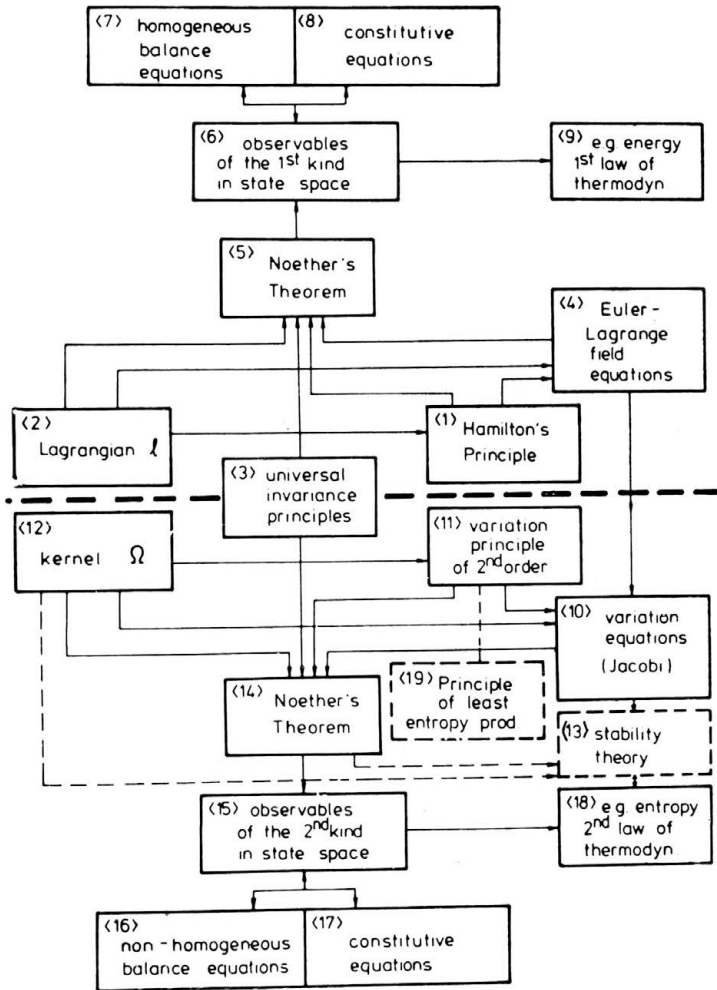


FIG. 5. Scheme of Lagrange-formalism.

which is associated with the methodical principle that each physical process can be reproduced at arbitrary different times. All the other invariance principles are also of methodical nature.

By “universal structure elements” I mean those structures which apply for each physical system. All structure elements above the dashed line in Fig. 5 operate in state space $P = \{\psi_k(x, t), k = 1, \dots, N\}$.

On the basis of a given Lagrangian $\langle 2 \rangle$, we get from Hamilton’s Principle $\langle 1 \rangle$ the fundamental field equations $\langle 4 \rangle$ of the system.

All structure elements $\langle 1 \rangle$ to $\langle 4 \rangle$ are joined together in *Noether’s theorem* $\langle 5 \rangle$ in order to define those observables which I call *observables of the first kind* $\langle 6 \rangle$. Each of them is associated uniquely with a particular group parameter ϵ_x of the invariance group $\langle 3 \rangle$. By Noether’s theorem [6, 7] the observables are implicitly defined by *homogeneous balance*

equations <7>, the density and flux density functions of which are uniquely deduced from the Lagrangian (2.4):

$$(2.9) \quad \begin{aligned} &\text{group parameter } \varepsilon_{\kappa} \Rightarrow 1^{\text{st}} \text{ kind observable } \kappa 1, \\ &\kappa 1 \Rightarrow \text{balance equation} \quad \partial_t a_{\kappa 1} + \nabla \cdot \mathbf{J}_{\kappa 1} = 0, \end{aligned}$$

density of the observable $\kappa 1$

$$(2.10) \quad a_{\kappa 1} = a_{\kappa 1}(\psi, \partial\psi),$$

flux density of the observable $\kappa 1$

$$(2.11) \quad \mathbf{J}_{\kappa 1} = \mathbf{J}_{\kappa 1}(\psi, \partial\psi).$$

Of course the densities and fluxes depend on the same variables as the Lagrangian (2.4) does⁽⁹⁾. Taking Eqs. (2.10) and (2.11) together for all observables $\kappa 1$, I get the set of *constitutive equations* <8> which coincide with those of traditional thermodynamics of irreversible processes. However, instead of making a lot of constitutive assumptions, these equations (2.10), (2.11) are deduced from the single constitutive assumption (2.4) by straightforward mathematics.

Important observables of the first kind are the *energy*, *linear* and *angular momentum*, *mass* and *electric charge*. Especially the observable “energy” is due to the time shift parameter ε of the invariance transformation (2.8) and the associated balance equation (2.9) will be the *First Law of Thermodynamics* <9>. From this point of view, the First Law is but a correlate of the methodically-motivated homogeneity of time with respect to all physical processes⁽¹⁰⁾.

Let us consider a class of perturbations $Q = \{\eta_k(x, t), k = 1, \dots, N\}$ of a given process $P = \{\psi_k(x, t), k = 1, \dots, N\}$ ⁽¹¹⁾. Q is ruled by *Jacobi's equations* <10> which are deduced from the Euler-Lagrange field equations as *variation (or perturbation) equations* and which are therefore finally derived from the Lagrangian, too. Jacobi's equations have again the form of Euler-Lagrange equations:

$$(2.12) \quad \partial_t \frac{\partial \Omega}{\partial(\partial_t \eta_k)} + \nabla \cdot \frac{\partial \Omega}{\partial(\nabla \eta_k)} - \frac{\partial \Omega}{\partial \eta_k} = 0, \quad k = 1, \dots, N.$$

They are based on a new *kernel* Ω . <12> which depends on the unperturbed process P and on its perturbation Q :

$$(2.13) \quad (12) \quad 2\Omega = 2\Omega(\psi, \partial\psi; \eta, \partial\eta) = \sum_{i,j=1}^N \left(\frac{\partial^2 I(\psi, \partial\psi)}{\partial \psi_i \partial \psi_j} \eta_i \eta_j + \sum_{\alpha=0}^3 2 \frac{\partial^2 I(\psi, \partial\psi)}{\partial \psi_i \partial(\partial_\alpha \psi_j)} \eta_i \partial_\alpha \eta_j \right. \\ \left. + \sum_{\alpha,\beta=0}^3 \frac{\partial^2 I(\psi, \partial\psi)}{\partial(\partial_\alpha \psi_i) \partial(\partial_\beta \psi_j)} \partial_\alpha \eta_i \partial_\beta \eta_j \right),$$

⁽⁹⁾ The “Principle of Equipresence” used in rational thermodynamics [14] is a natural outcome in Lagrange-formalism.

⁽¹⁰⁾ The invariance group (2.8) is the mathematical correlate of time homogeneity.

⁽¹¹⁾ The reader should carefully distinguish between virtual variations in Hamilton's Principle and real physical perturbations.

⁽¹²⁾ The factor 2 in 2Ω is conventional.

$$(2.13) \quad \partial_\alpha = \{\partial_0 = \partial_t; \partial_1, \partial_2, \partial_3 = \nabla\}.$$

[cont.]

Following the last part of Sect. 2.1, it is obvious that Jacobi's equations are equivalent to a further variation principle which I call *variation principle of the second order* $\langle 11 \rangle^{(13)}$:

$$(2.14) \quad J_2 = \int_{t_1}^{t_2} \int_{V(t)} 2\Omega(\psi, \partial\psi; \eta, \partial\eta) d^3x dt,$$

$$(2.15) \quad J_2 = \text{extremum},$$

by free and independent variations of the perturbations η_k with fixed values at $t_{1,2}$

$$\delta\eta_k(x, t_{1,2}) = 0.$$

The functions ψ_k of the given unperturbed process are not affected by the variation.

One could call Eqs. (2.14), (2.15) Hamilton's Principle for the perturbations Q of a given process P .

The whole scheme in Fig. 5 is obviously symmetric with respect to the dashed line. The procedures above the line can be repeated analogously below the line and the whole structure thus obtained is primarily referred to the perturbation space $Q = \{\eta_k(x, t), k = 1, \dots, N\}$. In this way I get a structure which allows for a *stability theory* of dynamical processes in Ljapunov's sense $\langle 13 \rangle^{(14)}$.

However, this structure in perturbation space applies also to special perturbations Q which are obtained from the invariance group $\langle 3 \rangle$ and which are completely given by the unperturbed process variables $\psi_k(x, t)$ and its derivatives. As an example I refer to the time shift transformation (2.8) which, for each ε , transforms the real process P into another real process P' :

$$(2.16) \quad P = \{\psi_k(x, t)\} \Rightarrow P' = \{\psi'_k(x, t, \varepsilon) = \psi_k(x, t + \varepsilon)\}.$$

The transition from P to P' can be interpreted as a one-parameter perturbation, the main linear part of which is given by

$$(2.17) \quad Q = \left\{ \eta_k(x, t) = \left. \frac{\partial\psi'_k(x, t, \varepsilon)}{\partial\varepsilon} \right|_{\varepsilon=0} = \partial_t\psi_k(x, t) \right\}.$$

Another example are the gauge-transformations of complex-valued field variables which again transform real processes P into real processes $P'^{(15)}$:

$$(2.18) \quad P = \{\psi_k(x, t)\} \Rightarrow P' = \{\psi'_k(x, t, \varepsilon) = \psi_k(x, t)e^{i\varepsilon}\}.$$

The associated main part of the perturbation is given by

$$(2.19) \quad Q = \left\{ \eta_k(x, t) = \left. \frac{\partial\psi'_k(x, t, \varepsilon)}{\partial\varepsilon} \right|_{\varepsilon=0} = i\psi_k(x, t) \right\}.$$

⁽¹³⁾ In this context Hamilton's Principle will be regarded as the variation principle of the first order.

⁽¹⁴⁾ For illustration I refer again to Jacobi's equations (2.12), which describe the perturbations Q of the process P , and which therefore include inherently all information concerning the stability of a given process P . Noether's balance equations are the basis of a stability theory in Ljapunov's sense, which uses exclusively internal physical structures of the system. For details see [15].

⁽¹⁵⁾ See Sect. 5.

Along this line the whole invariance group can be dealt with, giving rise to the definition of *observables of the second kind* $\langle 15 \rangle$ in state space P . At this point *Noether's theorem* $\langle 14 \rangle$ is applied in two different ways: firstly, it is applied analogously to $\langle 5 \rangle$ defining observables in the usual way. Secondly, a slightly generalized Noether's theorem is applied to the kernel Ω with respect to scaling transformations of the perturbations

$$(2.20) \quad \eta \Rightarrow \eta' = \lambda \eta$$

which are correlated with scaling transformations of the set of group parameters of the invariance group $\langle 3 \rangle$:

$$(2.21) \quad \varepsilon \Rightarrow \varepsilon' = \frac{1}{\lambda} \varepsilon.$$

More easily the second application of Noether's theorem in $\langle 14 \rangle$ can be avoided by applying Euler's formula to the quadratic form Ω and using Jacobi's equations (2.12). However, the point in my arguments concerning Noether's theorem is to show that within Lagrange-formalism all constitutive equations are obtained in a methodical unified way, namely on the basis of universal invariance principles using Noether's theorem.

As a consequence, each group parameter ε_{κ} of the invariance group $\langle 3 \rangle$ is associated uniquely with two different observables of the 2nd kind in state space P . By Noether's theorem they are implicitly defined by *nonhomogeneous balance equations* $\langle 16 \rangle$:

$$(2.22) \quad \begin{array}{l} \text{group parameter } \varepsilon_{\kappa} \Rightarrow 2^{\text{nd}} \text{ kind observable } \kappa 2. \\ \kappa 2 \Rightarrow \text{balance equation: } \partial_t a_{\kappa 2} + \nabla \cdot \mathbf{J}_{\kappa 2} = \sigma_{\kappa 2}. \end{array}$$

Again the quantities involved in Eq. (2.22) are uniquely deduced from the kernel Ω (Eq. (2.13)) and thus from the Lagrangian. They give rise to another set of *constitutive equations* $\langle 17 \rangle$:

$$(2.23) \quad \begin{array}{l} \text{density of the observable } \kappa 2 \\ a_{\kappa 2} = a_{\kappa 2}(\psi, \partial\psi; \eta, \partial\eta)|_{\eta \Rightarrow \psi}, \end{array}$$

$$(2.24) \quad \begin{array}{l} \text{flux density of the observable } \kappa 2 \\ \mathbf{J}_{\kappa 2} = \mathbf{J}_{\kappa 2}(\psi, \partial\psi; \eta, \partial\eta)|_{\eta \Rightarrow \psi}, \end{array}$$

$$(2.25) \quad \begin{array}{l} \text{density of the production rate of } \kappa 2 \\ \sigma_{\kappa 2} = \sigma_{\kappa 2}(\psi, \partial\psi; \eta, \partial\eta)|_{\eta \Rightarrow \psi}. \end{array}$$

The substitution $\eta \Rightarrow \psi$ is meant in the sense of Eqs. (2.17), (2.19).

Among the observables of the second kind one finds the entropy $\langle 18 \rangle$. It is associated with gauge transformations of complex-valued field variables ψ_k $\langle 16 \rangle$. Its balance equation (2.22) has to be interpreted as the *first part of the Second Law of Thermodynamics*. It is a remarkable fact that the *second part of the Second Law*, namely

$$(2.26) \quad \sigma_{\text{entropy}} \geq 0,$$

can be *related with stability of the thermal processes*. Finally, from the second order variation principle $\langle 11 \rangle$ a *Principle of Least Entropy Production* $\langle 19 \rangle$ can be deduced, which applies

⁽¹⁶⁾ See Sect. 5.

to each thermal process without any restrictions. This contrasts with an analogous traditional principle [8] which is restricted to the linear theory of irreversible processes⁽¹⁷⁾ and to stationary processes and which — to my knowledge — has been proven only for the scalar phenomena of heat transport, diffusion and chemical reactions.

3. Traditional variables versus “fundamental” variables

3.1. Lagrange-formalism and thermodynamics, an unsolvable contradiction?

In traditional linear thermodynamics, heat conduction and diffusion are described by *Fourier’s Law*:

$$(3.1) \quad c\partial_t T - \lambda \Delta T = 0$$

and by *Fick’s Law*:

$$(3.2) \quad \partial_t \varrho - D \Delta \varrho = 0,$$

respectively, where c is the specific heat, λ the coefficient of heat conductivity and D the diffusion constant. T is the temperature and ϱ the mass density of the diffusing material.

Both equations are not self-adjoint. So it is impossible to find a Lagrangian of the form

$$(3.3) \quad l = l(T, \partial_t T, \nabla T)$$

or

$$(3.4) \quad l = l(\varrho, \partial_t \varrho, \nabla \varrho)$$

so that Eq. (3.1) or Eq. (3.2) were the respective Euler–Lagrange equation (2.6).

One could argue that Eqs. (3.1), (3.2) are the energy and mass balance equations respectively. So it might be that these equations differ from the yet unknown Euler–Lagrange equations. Such an assumption, however, can be put into a physical contradiction: let me assume the existence of respective Lagrangians of the form (3.3) and (3.4). Let me consider further a stationary heat or mass flow between two heat or material reservoirs (Fig. 6):

$$(3.5) \quad \partial_t T(x, t) = 0, \quad \partial_t \varrho(x, t) = 0.$$

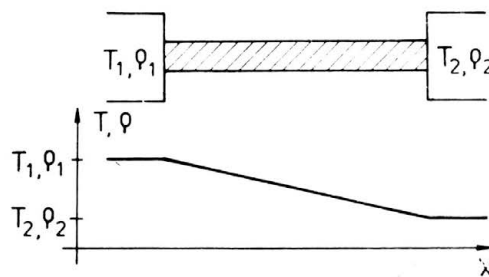


FIG. 6. Stationary heat flow or diffusion.

⁽¹⁷⁾ Linear constitutive relations between fluxes and thermodynamical forces.

These processes are associated with linear profiles of temperature or mass density according to Eqs. (3.1) or (3.2). There is no physical doubt that in both cases there is a non-vanishing energy flux \mathbf{J} from left to right, namely a heat flux and a flux of chemical energy respectively:

$$(3.6) \quad \mathbf{J} \neq 0.$$

Following, on the other hand, Lagrange-formalism, the Lagrangians (3.3) and (3.4) lead uniquely to the respective energy fluxes

$$(3.7) \quad \mathbf{J} = \frac{\partial l}{\partial(\nabla T)} \partial_t T \quad \text{and} \quad \mathbf{J} = \frac{\partial l}{\partial(\nabla \rho)} \partial_t \rho$$

which, according to the expressions (3.5), vanish in contradiction to our physical knowledge (Eq. (3.6)).

Two alternative conclusions can be drawn from this situation:

1. A Lagrangian does not exist in thermodynamics. That is the historical answer as a result of which the older linear thermodynamics or the modern rational thermodynamics have been established outside Lagrange-formalism.

2. A Lagrangian does exist in thermodynamics for methodical reasons. But the traditionally used set of process variables T, ρ, \dots is incomplete. It has to be replaced by an enlarged set of variables which I call the set of *fundamental variables*. This is my answer.

3.2. Complex-valued fundamental variables

Thermodynamics of *heat transport* can be included into Lagrange-formalism by introducing a *complex-valued field* $\psi(x, t)$ which I call *field of thermal excitation*. In Lagrange-formalism ψ is the most fundamental variable of phenomenological thermodynamics of irreversible processes. Together with its complex conjugate $\psi^*(x, t)$, the *absolute temperature* is defined by

$$(3.8) \quad \psi\psi^* = T > 0.$$

Obviously T is a positive definite quantity as it should be.

The complex variable ψ contains two real-valued degrees of freedom, thus giving rise to the enlargement of the set of variables which I mentioned at the end of Sect. 3.1. In addition to the temperature T , the real-valued phase function $\varphi(x, t)$ is taken into account:

$$(3.9) \quad \psi(x, t) = \sqrt{T(x, t)} \cdot e^{i\varphi(x, t)}.$$

By means of the additional quantity φ , the physical contradiction of Sect. 3.1 concerning the heat flux can be solved: The ansatz (3.3) for the Lagrangian is replaced by

$$(3.10) \quad l = l(\psi, \psi^*, \partial_t \psi, \partial_t \psi^*, \nabla \psi, \nabla \psi^*)$$

or, equivalently, by

$$(3.11) \quad l = l(T, \partial_t T, \partial_t \varphi, \nabla T, \nabla \varphi).$$

⁽¹⁸⁾ These equations are due to the box <8> of Fig. 5.

As a consequence, the heat flux (3.7)₁ is supplemented by a second term:

$$(3.12) \quad \mathbf{J} = \frac{\partial l}{\partial(\nabla T)} \partial_t T + \frac{\partial l}{\partial(\nabla \varphi)} \partial_t \varphi.$$

In the stationary case this gives rise to $\mathbf{J} \neq 0$ ⁽¹⁹⁾.

A loose physical interpretation of the thermal excitation field $\varphi(x, t)$ is suggested by the definition (3.8): Wherever and whenever the system is thermally excited ($\varphi \neq 0$), it is found at a finite temperature $T > 0$, and vice versa. Furthermore the existence of the absolute zero point $T = 0$ is included. It is associated with a state of no thermal excitation⁽²⁰⁾.

An analogous procedure holds for diffusion. As a fundamental variable I introduce a classical⁽²¹⁾, *complex-valued matter field* $\Phi(x, t)$ which by

$$(3.13) \quad \Phi \Phi^* = \varrho \geq 0$$

defines the *mass density* of the diffusing matter. Again the “vacuum” is involved by $\Phi = 0$. By means of the real-valued phase function χ , the matter field can be represented by its two real-valued degrees of freedom:

$$(3.14) \quad \Phi(x, t) = \sqrt{\varrho(x, t)} e^{i\chi(x, t)}.$$

A multicomponent diffusion problem will be described by a *multicomponent matter field*

$$(3.15) \quad \Phi = \{\Phi_1(x, t), \Phi_2(x, t), \dots\}.$$

Each component Φ_k is associated with a particular diffusing constituent, the *partial mass density* of which is given by

$$(3.16) \quad \Phi_k \Phi_k^* = \varrho_k \geq 0.$$

Finally the *total mass density* is defined by the formula

$$(3.17) \quad \begin{aligned} \langle \Phi | \Phi \rangle &= \Phi_1 \Phi_1^* + \Phi_2 \Phi_2^* + \dots \\ &= \varrho_1 + \varrho_2 + \dots = \varrho \geq 0. \end{aligned}$$

At this point it is qualitatively quite clear how to proceed with chemical reactions: By properly coupling the partial matter fields Φ_k with each other and with the thermal excitation field φ , it is possible to describe the dynamics of chemical reactions.

Referring again to the box <3> of Fig. 5, one very important *invariance principle* should be mentioned. Obviously the definitions (3.8), (3.13), (3.17) for the temperature and the mass densities are invariant with respect to *gauge transformations* of the complex-valued fields:

$$(3.18) \quad \begin{aligned} \psi &\Rightarrow \psi' = \psi e^{i\varepsilon}, \\ \Phi_k &\Rightarrow \Phi'_k = \Phi_k e^{i\varepsilon_k}, \quad -\infty < \varepsilon, \varepsilon_k < \infty. \end{aligned}$$

⁽¹⁹⁾ The stationary heat flow is associated with $\partial_t T = 0$ and $\partial_t \varphi \neq 0$.

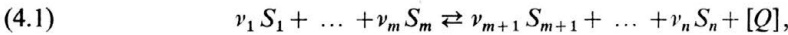
⁽²⁰⁾ Of course future investigations also should aim at giving a microscopic interpretation of the excitation field.

⁽²¹⁾ Φ has to be distinguished from the matter field of quantum mechanics.

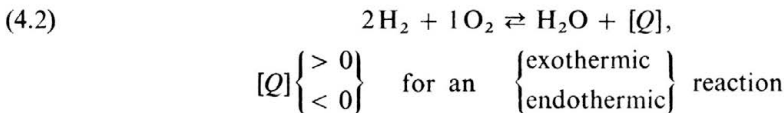
A group of *common gauge transformations* ($\varepsilon = \varepsilon_k$) of all fields ψ and Φ_k is taken as an *invariance principle for thermodynamics*. This principle is due to the idea that only phase differences of the various complex fields are physically relevant. The gauge invariance leads to *mass conservation* for diffusion processes and chemical reactions along the line of observables of the 1st kind. On the other hand, the *entropy is the associated observable of the 2nd kind*. Gauge invariance is the reason for the fact that the phase function φ of the excitation field does not appear among the variables of the Lagrangian (3.11).

4. Analogy between defect dynamics and the dynamics of material diffusion and chemical reactions

Let me consider a chemical reaction between the constituents S_1, \dots, S_n and let me add for convenience the heat release $[Q]$ of the gross reaction into the chemical reaction equation:



example



running from the left to the right-hand side.

The atomic structure of the constituents manifests itself by the *Principle of Multiple Proportions*

$$(4.3) \quad \sigma_1 : \sigma_2 : \dots : \sigma_n = M_1 \nu_1 : M_2 \nu_2 : \dots : M_n \nu_n$$

and by the *gross mass balance*

$$(4.4) \quad \sum_{k=1}^n M_k \nu_k = 0$$

of the gross reaction. M_k is the molecular mass of constituent S_k . In Eqs. (4.3), (4.4) the stoichiometric coefficients ν_k are chosen positive or negative according to their position on the left or right-hand side of the reaction equation (4.1). σ_k is the *mass production rate of the constituent S_k* due to the chemical reaction.

In Lagrange-formalism the constituents S_k are represented by n different matter fields ψ_k ⁽²²⁾. These are coupled in such a way as to take account of the relations (4.3) and (4.4) which are essential features of the microdynamics of the chemical process. Due to the gauge transformations (3.18), the *partial mass balance equations*

$$(4.5) \quad \partial_t \varrho_k + \nabla \cdot \mathbf{J}_k = \sigma_k$$

are defined for all constituents S_k , where the *mass production rates* are given by

$$(4.6) \quad \sigma_k = \xi(T, \varrho_i, \partial T, \partial \varrho_i, \partial \varphi, \partial \varphi_i) M_k \nu_k.$$

⁽²²⁾ The nomenclature is changed as compared with Sect. 3.2: $\Phi_k \Rightarrow \psi_k$.

\mathbf{J}_k , ξ are the *partial mass flux* and the *reaction velocity*. Equation (4.6) is a constitutive equation associated with the 1st kind observable "partial mass of constituent S_k ". Obviously it is a solution of Eq. (4.3). Summing up Eqs. (4.5) for $k = 1, \dots, n$, the *conservation of the total mass* is found on the basis of Eq. (4.4):

$$(4.7) \quad \sum_{k=1}^n \sigma_k = 0,$$

$$(4.8) \quad \partial_t \varrho + \nabla \cdot \mathbf{J}_{(\varrho)} = 0,$$

$$(4.9) \quad \varrho = \sum_{k=1}^n \varrho_k, \quad \mathbf{J}_{(\varrho)} = \sum_{k=1}^n \mathbf{J}_k.$$

A chemical reaction can be looked upon as a mass transfer between different material degrees of freedom ψ_k . Equation (4.7) is the mathematical correlate for this transfer. As to the energy transfer, we have further to take account of the heat release $[Q]$ of the chemical reaction. This will be done by properly coupling the matter fields ψ_k with the thermal excitation field ψ . From this point of view heat release is an energy transfer from the material degrees of freedom ψ_k to the thermal degree of freedom ψ , i.e., energy is transformed from chemical forms into the thermal form and *vice versa*.

These considerations show how microscopic structures can be transferred into Lagrange-formalism. However, it is not necessary to fix our attention exclusively on the mass. Instead, we can look equally well upon the *number of nuclei* (= atoms) in the constituents. Along this line the analogy between chemical dynamics and defect dynamics in solids becomes much wider: Let N_k be the number of atoms in the molecule of constituent S_k . Then, during a chemical reaction the total number of atoms is preserved and Eqs. (4.3), (4.4) have to be replaced by a *modified Principle of Multiple Proportions*:

$$(4.10) \quad \tau_1 : \tau_2 : \dots : \tau_n = N_1 \nu_1 : N_2 \nu_2 : \dots : N_n \nu_n$$

and by the gross balance of numbers of atoms:

$$(4.11) \quad \sum_{k=1}^n N_k \nu_k = 0.$$

τ_k is now the *production rate of the constituent S_k normalized to the number of atoms*. The rest concerning Eqs. (4.5)–(4.9) runs as before and is left to the reader.

The essential point of the analogy between chemical reactions and defect dynamics of solids is the existence of a large number of countable objects on the microlevel in both cases. In either case the objects might be composed of more than one elementary nucleus. The following examples are self-evident and can in principle be dealt with in the same formal way as diffusing and reacting chemical substances.

Figure 7a shows a crystal lattice with several eigen-defects: Single vacancies V_1 (\square), double vacancies V_2 ($\square\square$) composed of two single vacancies, eigen-interstitial atoms J_1 (\bullet). From solid state physics [16] we know that these defects migrate through the solid. Depending on temperature, there is a tendency of single vacancies to form bigger vacancy

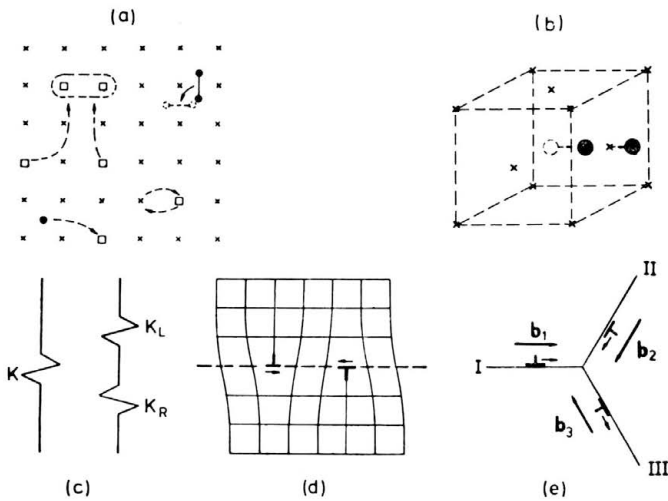


FIG. 7. a) Point-like lattice defects, b) formation of an interstitial dumbbell, c) kinks on a macromolecule, d) annihilation of dislocations, e) dislocation reaction.

clusters. On the other hand, these may decay again. Thus we get a reaction equation of the form



where $[Q]$ is the formation energy of the double vacancy.

A single vacancy and a single interstitial may annihilate each other or they may be created pairwise by thermal activation. The associated reaction equation reads



where $[Q]$ stands for the creation energy of a vacancy-interstitial pair. 0 stands for the unperturbed crystal lattice, which plays the role of a "vacuum state".

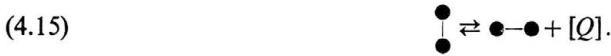
With respect to Eqs. (4.10), (4.11), interstitials and vacancies are endowed with the following nuclei-numbers:



The minus sign in the case of vacancies is due to the missing atomic mass. Obviously Eq. (4.11) is fulfilled by Eqs. (4.13), (4.14).

The Snoek-effect which gives rise to elastic relaxation is microscopically due to the directional relaxation of interstitial dumbbells (●—●). In a face-centered cubic lattice an interstitial atom may be unstable at the central site of the elementary cell. Shifting the interstitial towards its next neighbour in the face-center (Fig. 7b) gives rise to a symmetrically lying dumbbell. Of course, in thermal equilibrium and in a state, which is free of external stresses, the dumbbells are equally distributed the into three cubic directions. However, the dumbbell being an eigenstress center in the crystal interacts elastically with an external stress field. The result is a tendency of the dumbbells to switch over into a preferred direction

which is defined by the external stress field. This process gives rise to an elastic after-effect on the phenomenological level. The dumbbells are divided into three different classes according to the three cubic directions. Then the switching over from one direction to the other may again be associated with reaction equations of the form

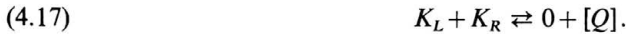


Here the energy release $[Q]$ is due to elastic interactions.

In polymer physics the "kink" on an otherwise stretched macromolecule is an important defect (Fig. 7c) [17]. It is formed and annihilated as a single defect by thermal activation



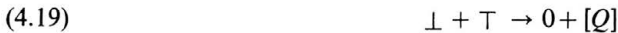
Because there are two different sorts of kinks involved, namely the left-handed and the right-handed kinks, they can be created and annihilated pairwise, too



As a final example of point-like defects, I mention electronically-excited atoms. Regarding different excitation states A_k as different "constituents", we have again reaction equations of the type (4.15):



In contrast with the examples given so far, the dislocation dynamics is much more complicated. In principle a lot of reaction equations can be discussed, e.g., see (Fig. 7d, e)



or



Equation (4.19) describes a pairwise annihilation of edge dislocations of opposite sign lying on the same slip plane (Fig. 7d). Equation (4.20) describes the combination of two edge dislocations along the intersection line of their slip planes I and II, thus producing a third dislocation which runs away on its slip plane III (Fig. 7e). All dislocation reactions have to follow a "gross balance equation"



for the Burgers-vectors of the reacting dislocations. Equation (4.21) is analogous to Eq. (4.4) or (4.11). All these dislocation processes are highly idealized. We should rather keep in mind that dislocations are line-shaped objects. Thus in reality we find a complicated three-dimensional network which cannot be described by means of point-like objects as is done in the simplified, two-dimensional models of Fig. 7d, e. I think, however, that the situation for future efforts is not completely hopeless because of the fact that in a real crystal only a few slip systems are activated.

5. The Lagrangian for special irreversible processes

Let me consider *heat transport, diffusion and one chemical reaction* in a n -component system. The processes take place in a *rigid material medium*, i.e., mechanical degrees of freedom for deformation are not yet taken into account. As compared with Sect. 3.2, the mass densities ρ are replaced by particle densities n . The Lagrangians are written down in terms of the *absolute temperature* $T(x, t)$, the *particle densities* $n_k(x, t)$ of the chemical constituents S_k and of the *phase functions* $\varphi(x, t)$ and $\varphi_k(x, t)$ of the *thermal excitation field*

$$(5.1) \quad \psi(x, t) = \sqrt{T(x, t)} e^{i\varphi(x, t)}$$

and of the matter fields

$$(5.2) \quad \psi_k(x, t) = \sqrt{n_k(x, t)} e^{i\varphi_k(x, t)}, \quad k = 1, \dots, n,$$

respectively.

Fourier's linear theory of heat transport can completely be deduced from the Lagrangian⁽²⁴⁾ [1, 2]

$$(5.3) \quad I = I(T, \partial T, \partial \varphi) = -\frac{1}{\omega} [cT \partial_t (\varphi - \varphi_0(t, T)) + (-\lambda \nabla T) \cdot \nabla (\varphi - \varphi_0(t, T)) + \partial_t G(T)]$$

with the abbreviations

$$(5.4) \quad \varphi_0(x, T) = -\omega t + \frac{T_0}{2T}$$

and

$$(5.5) \quad G(T) = \frac{T_0}{2T} \cdot \int_{T_0/T}^1 \frac{p(\xi T)}{\xi^2} d\xi.$$

The specific heat c and the coefficient λ of heat conductivity are assumed to be constant. T_0 is a reference temperature. The quantity $p(T)$ in the integrand of Eq. (5.5) is the pressure of the system which, because of the embedding into a rigid medium, has to be interpreted as a rigid body response. The frequency ω is not specified at this stage of the theory. However, it is necessary because of the physical dimension of the Lagrangian. It is physically associated with the rigid material background and will become relevant not before the system is liberated from its mechanical constraints.

The Euler-Lagrange field equations (2.6) for the variations $\delta\varphi$ and δT read as follows:

$$(5.6) \quad \delta\varphi: \quad c \partial_t T - \lambda \Delta T = 0,$$

$$(5.7) \quad \delta T: \quad c \partial_t (\varphi - \varphi_0(t, T)) + \lambda \Delta (\varphi - \varphi_0(t, T)) = 0.$$

In Eq. (5.7) I have already taken account of Eq. (5.6). By Eq. (5.6) obviously Fourier's law (3.1) of heat transport is rediscovered. Equation (5.7) has a particular solution,

$$(5.8) \quad \varphi = \varphi_0(x, t) = -\omega t + \frac{T_0}{2T(x, t)}$$

⁽²³⁾ As compared with Eqs. (3.13)–(3.17) the nomenclature for the matter fields has been changed.

⁽²⁴⁾ See Eqs. (3.10), (3.11).

which is associated with the *Principle of Local Equilibrium*. This interpretation is due to the fact that on the ground of the solution (5.8), all constitutive equations of Fourier's theory can be derived⁽²⁵⁾ and Fourier's theory itself is essentially based on that principle.

Following Eq. (2.7), the Lagrangian (5.3) leads to the boundary conditions of a thermally-isolated system:

$$(5.9) \quad \delta\varphi: \quad \mathbf{n} \cdot \frac{\partial l}{\partial(\nabla\varphi)} = -\frac{1}{\omega} \mathbf{n} \cdot (-\lambda\nabla T) = 0,$$

$$(5.10) \quad \delta T: \quad \mathbf{n} \cdot \frac{\partial l}{\partial(\nabla T)} = -\frac{1}{\omega} \mathbf{n} \cdot \left[-\lambda\nabla(\varphi - \varphi_0) + (-\lambda\nabla T) \cdot \frac{T_0}{2T} \right] = 0.$$

From Eqs. (3.12) and (5.3), (5.8) we find the heat flux in the form

$$(5.11) \quad \mathbf{J} = -\lambda\nabla T.$$

Using Eq. (5.8) this means that the boundary conditions are fulfilled simultaneously if the heat flux vanishes across the boundary, as it should be for the isolated system.

The *combined process of heat transport, diffusion and one chemical reaction* is described by the Lagrangian

$$(5.12) \quad (26) \quad l = l(T, n_k, \partial T; \partial n_k, \partial\varphi, \partial\varphi_k)$$

$$\Rightarrow \quad = -\frac{1}{\omega} \{ u(T, n) \cdot \partial_t(\varphi - \varphi_0)$$

$$\bullet \quad + \sum_{i=1}^n n_i \partial_t [\mu_i(T, n) \cdot \alpha_i]$$

$$\Rightarrow \quad + \mathbf{J}(T, n, \nabla T, \nabla n) \cdot \nabla(\varphi - \varphi_0)$$

$$\bullet \quad + \sum_{i=1}^n \mathbf{J}_i(T, n, \nabla T, \nabla n) \cdot \nabla [\mu_i(T, n) \cdot \alpha_i]$$

$$+ R(T, n, \alpha)$$

$$\Rightarrow \quad + \partial_t G(T, n) \}.$$

The meaning of the symbols is as follows:

the arguments n, α represent all n_k, α_k for $k = 1, \dots, n$.

Abbreviations:

$$(5.13) \quad \varphi_0(t, T) = -\omega t + \frac{T_0}{2T},$$

$$(5.14) \quad \alpha_k = (\varphi_k - \varphi) - (\varphi_{k0}(t, T, n_k) - \varphi_0(t, T)),$$

$$(5.15) \quad \varphi_{k0}(t, T, n_k) = -\omega t + \gamma \frac{n_k}{2T},$$

$$(5.16) \quad G(T, n) = \frac{T_0}{2T} \cdot \int_{T_0/T}^1 \frac{p(\xi T, \xi n)}{\xi^2} d\xi,$$

⁽²⁵⁾ For details see references [1, 2, 3].

⁽²⁶⁾ For a detailed discussion of this Lagrangian the reader is referred to a forthcoming paper [18].

ω , T_0 , $p(T, n)$: as before in Eqs. (5.3)–(5.5). The pressure now depends on the particle densities, too. γ — a dimensional factor.

Constitutive functions:

$$\begin{aligned}
 & u(T, n) \quad \text{energy density,} \\
 & \mu_i(T, n) \quad \text{chemical potential of the constituent } S_i, \\
 \mathbf{J}(T, n, \nabla T, \nabla n) & \quad \text{energy flux density,} \\
 \mathbf{J}_i(\dots\dots\dots) & \quad \text{diffusion flux density of the constituent } S_i, \\
 R(T, n, \alpha) & \quad \text{a reaction potential with the property} \\
 (5.17) \quad & R(\dots, \alpha) = 0 \quad \text{for} \quad \alpha_k = 0, \quad k = 1, \dots, n.
 \end{aligned}$$

Terms marked by arrows are those already known from pure heat conduction. As compared with the Lagrangian (5.3), I have only substituted the special linear expressions for the energy density and for the energy flux by more general ones:

$$\begin{aligned}
 (5.18) \quad & cT \Rightarrow u(T, \dots), \\
 & -\lambda \nabla T \Rightarrow \mathbf{J}(T, \nabla T, \dots).
 \end{aligned}$$

The terms marked by dots are due to diffusion. Of course there is in general a coupling between the thermal and the material degrees of freedom ψ and ψ_k , which is taken into account by the mixed arguments T, n, \dots in the functions u , μ_i , \mathbf{J} and \mathbf{J}_i .

Finally the function R is a *reaction potential* which describes completely the dynamics of a chemical reaction⁽²⁷⁾. For instance the *particle production rates*⁽²⁸⁾ are derived from R by means of the formula

$$(5.19) \quad \sigma_k = \frac{1}{\mu_k} \frac{\partial R(\dots, \alpha)}{\partial \alpha_k}.$$

Especially the ansatz

$$(5.20) \quad R = -L \frac{1}{T} \left(\sum_{i=1}^n \mu_i \nu_i \alpha_i \right) \left(\sum_{j=1}^n \mu_j \nu_j \right)$$

leads to the well-known linear theory of chemical reactions [8, 9]:

$$(5.21) \quad \sigma_k = L \cdot \left(-\frac{A}{T} \right) \nu_k.$$

Comparing with Eq. (4.6), we find for the *reaction velocity* the constitutive relation

$$(5.22) \quad \xi = L \cdot \left(-\frac{A}{T} \right),$$

where L is a material parameter and A the affinity of the chemical reaction:

$$(5.23) \quad A = \sum_{j=1}^n \mu_j(T, n) \cdot \nu_j.$$

⁽²⁷⁾ The formalism can easily be generalized for an arbitrary number of reactions.

⁽²⁸⁾ See Eqs. (4.3), (4.5), (4.6). Keep in mind that I am dealing now with particle densities instead of mass densities.

Again the Lagrange (5.12) is associated with the *Principle of Local Equilibrium*. This holds on the ground of the particular solution

$$(5.24) \quad \varphi = \varphi_0(x, t) = -\omega t + \frac{T_0}{2T(x, t)},$$

$$(5.25) \quad \varphi_k = \varphi_{k_0}(x, t) = -\omega t + \gamma \frac{n_k(x, t)}{2T(x, t)}$$

for the phase functions. These solutions are universal insofar as they are independent of constitutive relations.

It is a remarkable fact that by the stepwise extension of the Lagrangian along the sequence “heat transport, diffusion, chemical reaction”, the preceding structures are preserved: this holds, for example, for the function φ_0 and G .

The Lagrangian (5.12) is obviously invariant with respect to a common gauge transformation of the thermal excitation field ψ and of the matter fields ψ_k ⁽²⁹⁾:

$$(5.26) \quad \varphi \Rightarrow \varphi' = \varphi + \varepsilon, \quad \varphi_k \Rightarrow \varphi'_k = \varphi_k + \varepsilon.$$

This is especially true for the phase difference $\varphi_k - \varphi$ in the quantity α_k . The gauge invariance leads to the entropy concept of the combined process.

The denominators in the functions φ_0 and φ_{k_0} (see Eqs. (5.13), (5.15)) indicate singularities at the absolute zero point $T = 0$. In the Lagrangian, the singularities can be removed by a proper behaviour of the constitutive quantities u , μ_i , \mathbf{J} and \mathbf{J}_i at the zero point. However, in the particular solutions (5.24), (5.25) they are still preserved. It might be so that this fact is related with the *Third Law of Thermodynamics* which asserts that it is impossible to get to the absolute zero-temperature by any experimental means.

6. Concluding remarks

According to the analogies shown in Sect. 4, the Lagrangian (5.12) can be transferred to the case of defect dynamics. However, one should keep in mind that its range of application is restricted by the Principle of Local Equilibrium. This means that the defect densities have to be locally in thermal equilibrium. In solid state physics this situation is found, e.g., for vacancies, interstitials and interstitial dumbbells in annealed materials. However, if we look, for example at a high vacancy density frozen in at low temperatures, the dynamics will initially run outside local equilibrium. In such cases the Lagrangian can be generalized in order to take account of those processes which run outside of local equilibrium [3]. Unfortunately this generalization is impossible for dislocation dynamics because of the lack of an appropriate thermostatics. The Lagrangian for dislocation dynamics has to be defined far away from equilibrium without reference to thermostatics.

The mechanical degrees of freedom are not yet taken into account. I think it should be possible to liberate the Lagrangian (5.12) from its constraints concerning the rigid material background. This will be done formally along the line of the gauge field theory or on the ground of more physical and heuristic ideas.

⁽²⁹⁾ See Eq. (3.18).

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