Locally Equilibrium Diffusion Processes. I. Geometry of Local Thermodynamic Equilibrium States

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The geometric description of local thermodynamic equilibrium states in a locally homogeneous body is formulated. The considered geometry is defined on the basis of the condition that the gauge procedure of the partial derivative operations should preserve the form of the equations describing the local thermodynamic equilibrium state of the homogeneous body with diffusion, and be consistent with the description of diffusion as a Markovian diffusion process with different mean arriving and starting velocities. The statistical entropy of the diffusion process is examined.

1. INTRODUCTION

The classical diffusion theory is unsatisfactory for many reasons. The most important is the use of this theory for the description of diffusion processes for which the stationary distributions of diffusing matter appear only in the thermodynamic equilibrium state of a body with diffusion. The classical diffusion theory does not consider, for example, the possibility of formation, as a consequence of the diffusion, of so-called dissipative structures, that is, nonhomogeneous, nonequilibrium stationary states stable for small disturbances.

The sufficient condition for the applicability of thermodynamic methods for the description of dissipative structures is the assumption that in the considered system so-called local thermodynamic equilibrium states are being realized (Glansdorf and Prigogine, 1973).

The physical meaning of *local equilibrium* involves the postulate of the existence in each sufficiently large (but small from the macroscopic point of view) element of the medium volume of a thermodynamic equilibrium state with the remaining part of the medium (treated as the reservoir).

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Thermodynamic quantities for each such thermodynamic subsystem are expressed by the same functions as those corresponding to the whole system, replacing only equilibrium values of variables by their local values. As a whole, the considered thermodynamic system (e.g., the body with diffusion) may be not in the thermodynamic equilibrium state.

However, the thermodynamic theory of dissipative structures is often not sufficient for the description of macroscopic structure formation in media not in the thermodynamic equilibrium state. This makes it necessary to complement the thermodynamics (or sometimes replace it) by other methods (e.g., dynamic systems theory or information theory) (Haken, 1983). In this paper, as such a complement of the thermodynamics, a geometric version is accepted of the thermodynamic hypothesis that some properties of linear systems are preserved in states far from the thermodynamic equilibrium state (Glansdorf and Prigogine, 1973). Namely, if it is assumed that locally certain differential relations of the linear theory of the diffusion phenomenon are valid, then fields compensating the influence of the varying of the thermodynamic parameters (according to the concept of the local thermodynamic equilibrium state) on these relations should be introduced. In fact, this is an application (in the thermodynamic context) of the method known from field theory of the partial derivative operation gauge.

Thermodynamics, however, is not of field-theoretic character and this makes the choice of relations which should undergo the gauge procedure more difficult. This paper accepts, as the thermodynamic counterpart of "Lagrange background" in field theory, the stochastic model of the diffusion process considering the existence of different mean arriving and starting velocities of the diffusing particle (Section 2). This model is used to define which differential relations should undergo the gauge procedure (Sections 3 and 4).

Applying the procedures complementing the thermodynamics, it should be taken into account that some thermodynamic variables may change their primary sense by becoming so-called order parameters (Haken, 1983). The effective temperature of the local thermodynamic equilibrium state, introduced in Section 8, is an example of such an order parameter.

This paper also discusses the interpretation of the diffusion process as the realization of the statistical description of the dynamic system (Sections 5 and 6) and the statistical entropy of such an interpreted diffusion process is examined (Section 7).

Also considered are diffusion processes in a locally homogeneous crystalline body, which can be described as random motions of the particle (Trzęsowski and Kotowski, 1985). Here *local homogeneity* means that the considered crystalline body consists of a single material but its crystal lattice

is distorted by the defects (e.g., Trzęsowski, 1987). Formally, the consider-ations in Part I of this work can apply to the diffusion of particles possessing mass (e.g., interstitial atoms) as well as massless particles (e.g., lattice vacancies). However, because of the applications in Part II, the physical interpretations are formulated only for the case when the diffusing particle has mass.

2. ARRIVING AND STARTING DIFFUSION PROCESSES

Theories of diffusion usually ignore the possibility that the mean velocity of a diffusing particle arriving at a point may differ from the mean velocity of a particle starting from that point. In fact, these theories consider only the mean starting velocity of the particle from the point (see Section 3). The present section discusses the basic notions connected with the stochastic model of the diffusion processes permitting the existence of these two mean velocities.

I will use the following designations. Let $\varepsilon_A = (\delta_A^B; B \downarrow 1, 2, \ldots, n)$, $A = 1, 2, \ldots, n$, denote the standard base in R^n. If $X = X^A \varepsilon_A$ is a standard designation of a vector (identified with a point) in R^n, then let $X = (X^A)$ denote its coordinates in the base (ε_A), as well as the coordinate system on R^n corresponding to that base. The analogous convention will be used in the case of curvilinear coordinates in R^n. Although the mathematical formulations will concern arbitrary n, the physical interpretations will concern only the case when $n = 3$.

Call a *Wienerian process* on R^n the Markovian process $\mathbf{W}(t)$ with values in R^n,

$$\mathbf{w}(t) = w^a(t)\varepsilon_a$$
$$\varepsilon_a = \delta_a^A \varepsilon_A, \qquad t \in R_+ = [0, \infty) \tag{1}$$

whose infinitesimal generator has the form

$$W(\partial) = D^{ab} \frac{\partial^2}{\partial X^a \partial X^b}$$

$$D^{ab} = D^{ba} = \text{const}, \qquad X^a = \delta_A^a X^A \tag{2}$$

$$\mathbf{D} = D^{ab}\varepsilon_a \otimes \varepsilon_b = \left\| D^{ab} : \begin{array}{l} a \downarrow 1, 2, \ldots, n \\ b \rightarrow 1, 2, \ldots, n \end{array} \right\| \in GL^+(n)$$

where $\mathbf{D}$ is a constant, real, symmetric, positive-definite matrix. Then $\mathbf{w}_s(t) = \mathbf{w}(t) - \mathbf{w}(s)$, $0 \leq s \leq t$, is a Gaussian process and

$$E[\mathbf{w}_s(t)] = \mathbf{0}$$

$$E[\mathbf{w}_s(t) \otimes \mathbf{w}_s(t)] = 2\mathbf{D}(t - s) \tag{3}$$

Let

$$\mathbf{e}_a(X) = \mathbf{e}(X)\boldsymbol{\varepsilon}_a$$

$$= \underset{a}{e}^A(X)\boldsymbol{\varepsilon}_A, \qquad a = 1, 2, \ldots, n \tag{4}$$

$$\mathbf{e}(X) = \underset{a}{e}^A(X)\boldsymbol{\varepsilon}_A \otimes \boldsymbol{\varepsilon}^a = \left\| \underset{a}{e}^A(X); \quad \begin{matrix} A \downarrow 1, \ldots, n \\ a \rightarrow 1, \ldots, n \end{matrix} \right\| \in GL^+(n)$$

be the local basis field in R^n, generally nonintegrable (Trzęsowski, 1987, Part I). If the appropriate assumptions concerning the smoothness of the matrix $\mathbf{e}(X)$ are fulfilled, then there exists exactly one stochastic process $\mathbf{W}(t)$ in R^n such that

$$\forall t \geq 0 \quad \mathbf{W}(t) = \mathbf{W}_0 + \int_0^t \mathbf{e}(W(t)) \, d\mathbf{w}(t)$$

$$= W^A(t)\boldsymbol{\varepsilon}_A \tag{5}$$

and having continuous trajectory with probability 1 (Girhman and Skorokhod, 1983). The integral in the formula (5) is the so-called stochastic integral (Girhman and Skorokhod, 1983). The representation (5) of the process $\mathbf{W}(t)$ is usually written in the form of the so-called stochastic Ito equation:

$$d\mathbf{W}(t) = dW^A(t)\boldsymbol{\varepsilon}_A$$

$$\tag{6}$$

$$dW^A(t) = \underset{a}{e}^A(W(t)) \, dw^a(t)$$

with the initial condition $\mathbf{W}(0) = \mathbf{W}_0$. Because equations (6) may be written in the form

$$d\mathbf{W}(t) = dw^a(t)\mathbf{e}_a(\mathbf{W}(t)) \tag{7}$$

the process $\mathbf{W}(t)$ will be called *locally Wienerian*. This process is a Markovian process with infinitesimal generator of the form

$$W(\partial) = D^{AB}(X)\partial_A\partial_B, \qquad \partial_A = \partial/\partial X^A \tag{8}$$

where

$$\mathbf{D}(X) = D^{AB}(X)\boldsymbol{\varepsilon}_A \otimes \boldsymbol{\varepsilon}_B$$

$$= \|D^{AB}(X)\| \in GL^+(n) \tag{9}$$

$$D^{AB}(X) = \underset{a}{e}^A(X)\underset{b}{e}^B(X)D^{ab} = D^{BA}(X)$$

For this process

$$E[d\mathbf{W}(t)|\mathbf{W}(t) = \mathbf{X}] = \mathbf{0}$$
$$E[d\mathbf{W}(t) \otimes d\mathbf{W}(t)|\mathbf{W}(t) = \mathbf{X}] = 2\mathbf{D}(\mathbf{X})\, dt \tag{10}$$

where, according to the formula (9), $\mathbf{D}(\mathbf{X})$ is a real, symmetric, positive-definite matrix.

If $\mathbf{b}(\mathbf{X}, t) = b^A(X, t)\boldsymbol{\varepsilon}_A$ is a vector function with values in R^n, then, with the appropriate assumptions about the smoothness of functions $\mathbf{b}$ and $\mathbf{e}$, there exists exactly one stochastic process $\mathbf{X}_s(t)$, $t \geq s \geq 0$, fulfilling the equation

$$\forall t \geq s \quad \mathbf{X}_s(t) = \mathbf{X} + \int_s^t \mathbf{b}(\mathbf{X}_s(\tau), \tau)\, d\tau + \int_s^t \mathbf{e}(\mathbf{X}_s(\tau))\, d\mathbf{w}(\tau) \tag{11}$$

and having a continuous trajectory with the probability 1 (Girhman and Skorokhod, 1983). Stochastic processes of the form (11) are called solutions of the stochastic Ito equation

$$d\mathbf{X}(t) = \mathbf{b}(\mathbf{X}(t), t)\, dt + d\mathbf{W}(\mathbf{X}(t); t)$$
$$d\mathbf{W}(\mathbf{X}(t); t) = \mathbf{e}(\mathbf{X}(t))\, d\mathbf{w}(t) \tag{12}$$

fulfilling the initial condition $\mathbf{X}(s) = \mathbf{X}$.

If functions $\mathbf{b}(\mathbf{X}, t)$ and $\mathbf{D}(\mathbf{X})$ fulfill the appropriate conditions of smoothness and behavior at infinity, then the stochastic process $\mathbf{X}(t)$, $t \geq 0$, fulfilling (12) is a special case of the so-called Markovian diffusion processes (Girhman and Skorokhod, 1983). Let us denote by $P(s, \mathbf{X}; t, U)$ the probability of arriving at the set $U \subset R^n$ at the moment t, under the condition of starting from the point $\mathbf{X}$ at the moment $s < t$, i.e.,

$$P(s, \mathbf{X}; t, U) = P(\mathbf{X}(t) \in U | \mathbf{X}(s) = \mathbf{X}), \qquad 0 \leq s < t \tag{13}$$

In the case when the solution of the stochastic Ito equation (12) is a Markovian process, the function $P(s, \mathbf{X}; t, U)$ of the "forward" conditional probability is of the form (Girhman and Skorokhod, 1983)

$$P(s, \mathbf{X}: t, U) = P(\mathbf{X}_s(t) \in U) \tag{14}$$

If $\mathbf{X}(t)$, $t \geq 0$, is a Markovian process, then changing the reading of the time direction leads to the function $P_*(s, \mathbf{X}; t, U)$ of the "backward" conditional probability, described as the probability of starting from the set $U \subset R^n$ at the moment t under the condition of arriving at the point $\mathbf{X}$ at the moment $s > t$ (Kovalenko *et al.*, 1983):

$$P_*(s, \mathbf{X}; t, U) = P(\mathbf{X}(t) \in U | \mathbf{X}(s) = \mathbf{X}], \qquad 0 \leq t < s \tag{15}$$

Let $\mathbf{X}(t)$, $t \geq 0$, be the Markovian diffusion process defined by conditions (10) and (12). We can assume (Nelson, 1967) that there exists a vector function $\mathbf{b}_*(\mathbf{X}, t)$ with values in R^n and there exists a stochastic process $\mathbf{W}_*(t)$, $t \geq 0$, with values in R^n, such that if $\mathbf{X}_{*s}(t)$, $0 \leq t \leq s$, is a solution of the stochastic Ito equation

$$d\mathbf{X}_*(t) = \mathbf{b}_*(\mathbf{X}_*(t), t)\, dt + d\mathbf{W}_*(t) \tag{16}$$

fulfilling the arriving condition $\mathbf{X}_{*s}(s) = \mathbf{X}$, then the function of backward conditional probability [formula (15)] is of the form

$$P_*(s, \mathbf{X}; t, U) = P(\mathbf{X}_{*s}(t) \in U) \tag{17}$$

We restrict our considerations to the case when

$$d\mathbf{X}_*(t) = \mathbf{b}_*(\mathbf{X}_*(t), t)\, dt - d\mathbf{W}(\mathbf{X}_*(t); t) \tag{18}$$

The Markovian diffusion processes $\mathbf{X}(t)$ and $\mathbf{X}_*(t)$, $t \geq 0$, defined by equations (12) and (18) will be called the *starting* and *arriving diffusion processes*, respectively. Infinitesimal generators of starting and arriving diffusion processes are of the form $T_s(\partial)$ and $T_{*s}(\partial)$, respectively, where (Dankel, 1971)

$$T_s(\partial) = b^A(X, s)\partial_A + W(\partial)$$
$$T_{*s}(\partial) = b^A_*(X, s)\partial_A - W(\partial) \tag{19}$$

where the operator $W(\partial)$ is of the form (8). Functions $\mathbf{b}$ and $\mathbf{b}_*$ will be called the *mean starting* and *arriving velocities*, respectively, because

$$E[d\mathbf{X}(t)\,|\,\mathbf{X}(t) = \mathbf{X}] = \mathbf{b}(\mathbf{X}, t)\, dt$$
$$E[d\mathbf{X}_*(t)\,|\,\mathbf{X}_*(t) = \mathbf{X}] = \mathbf{b}_*(\mathbf{X}, t)\, dt \tag{20}$$

Let us consider Markovian processes such that the functions of forward [formula (13)] and backward [formula (15)] conditional probability are defined by the starting and arriving diffusion processes [formulas (14) and (17)]. Moreover, let us assume the existence of the density function $p(X, t)$ of the absolute probability of localization, the same for the starting $[\mathbf{X}(t)]$ and arriving $[\mathbf{X}_*(t)]$ processes:

$$P(\mathbf{X}_*(t) \in U) = P(\mathbf{X}(t) \in U) = \int_U p(X, t)\, dV(X) \tag{21}$$

where $dV(X) = d^n X$ is the volume element in the Euclidean space R^n. Then the function $p(X, t)$ should fulfill two Fokker–Planck equations at the same time: the equation

$$\partial_t p + F_t p = 0 \tag{22a}$$
$$F_t = F_t(\partial) = \partial_A(b^A(X, t) \cdot) - \partial_A \partial_B(D^{AB}(X) \cdot) \tag{22b}$$

corresponding to the starting process and the equation

$$\partial_t p + F_{*t} p = 0 \tag{23a}$$

$$F_{*t} = F_{*t}(\partial) = \partial_A (b_*^A(X, t) \cdot) + \partial_A \partial_B (D^{AB}(X) \cdot) \tag{23b}$$

corresponding to the arriving process. Let us denote

$$\mathbf{v} = \tfrac{1}{2}(\mathbf{b}_* + \mathbf{b}) = v^A(X, t)\boldsymbol{\varepsilon}_A$$
$$\mathbf{u} = \tfrac{1}{2}(\mathbf{b}_* - \mathbf{b}) = u^A(X, t)\boldsymbol{\varepsilon}_A \tag{24}$$

Equations (22) and (23) will be fulfilled at the same time by the function $p = p(X, t)$ iff the following equation of continuity is fulfilled:

$$\partial_t p + \partial_A(p v^A) = 0 \tag{25}$$

the field $\mathbf{u}$ allows the representation

$$u^A = -\frac{1}{p} \partial_B(D^{AB} p) \tag{26}$$

and the flux

$$j^A = p u^A \tag{27}$$

where u^A is of the form (26), is defined with exactness by the transformation

$$j^A \to \hat{j}^A = j^A + \phi^A, \qquad \partial_A \phi^A = 0 \tag{28}$$

The vector field $\mathbf{v}$ is called *the diffusion peculiar velocity* and the vector field $\mathbf{u}$ is *the diffusion velocity* (Trzęsowski and Kotowski, 1985). The coefficients $D^{AB} = D^{AB}(X)$ appearing in the formula (26) are called *the diffusion coefficients*.

So, finally, we observe that the theory of Markovian processes allows processes which can be characterized by the existence of conjugate arriving and starting diffusion processes and for which equations (24)–(28) are valid.

3. GENERALIZATION OF CLASSICAL DESCRIPTION OF DIFFUSION PHENOMENON

Let us consider a diffusion process which may be described as a Markovian diffusion process and for which the density function $p(X, t)$ of the localization probability [formula (21)] equals the concentration of the diffusion particles [see further Section 5 and Trzęsowski and Kotowski (1985), i.e.,

$$p(X, t) = \frac{n(X, t)}{N(t)}$$

$$N(t) = \int_{R^3} n(X, t)\, dV(X) \tag{29}$$

where $n(X, t)$ is the number of diffusing particles per unit of volume. Then equation (25) may be written in the form of an equation of local balance of the number of diffusing particles:

$$\partial_t n + \partial_A(nv^A) = \beta(t)n$$
$$\beta(t) = \dot{N}(t)/N(t)$$
(30)

If the diffusion coefficients are constant, then in the formulas in Section 2 one can assume, without restricting the generality of considerations, that

$$e^A_a = \delta^A_a$$

and equation (26) takes the form

$$u^A = -\frac{1}{p} D^{AB}\partial_B p = -2D^{AB}\partial_B R$$
$$R = \ln(p/p_0)^{1/2}, \qquad D^{AB} = \text{const}$$
(31)

where p_0 is an arbitrary positive constant with the dimension of concentration p. Then the flux J^A defined by [cf. (27) and (29)]

$$J^A = nu^A = -D^{AB}\partial_B n$$
(32)

has the form of a diffusion flux in a homogeneous body caused by the nonuniform distribution of the diffusing particles close to the thermodynamic equilibrium state. In the case of the diffusion of atoms in a crystalline solid body, such a form of the diffusion flux may be accepted with the assumption that the lattice vacancies are everywhere in local thermal equilibrium or when their concentration is small in relation to the concentration of the diffusing atoms (Christian, 1975). With such identification, taking the direction of the diffusion flux (32) opposite to the concentration gradient direction (so-called Fick law) denotes the positive difiniteness of the diffusion coefficient matrix $\mathbf{D} = \|D^{AB}\|$. The symmetry of that matrix leads to the so-called Onsager relation. Since from equation (24)

$$\mathbf{v} = \mathbf{b} + \mathbf{u}$$
(33)

then in the case (31) the equation of balance (30) may be written in the form of the equation of diffusion with sources:

$$\partial_t n - D^{AB}\partial_A\partial_B n + \partial_A(nb^A) = \beta(t)n$$
(34)

Equation (34) is equivalent to the Fokker–Planck equation (22) for the starting process, having constant diffusion coefficients.

In the classical diffusion theory, equation (34) is complemented with the so-called Stokes relation:

$$\mathbf{F} = \zeta \mathbf{b} \tag{35}$$

which connects the force $\mathbf{F}$ acting on a point defect with its mean starting velocity $\mathbf{b}$; ζ is a friction coefficient and its inverse $1/\zeta$ is called the mobility of the defect. If, for example, we ignore the influence of the point defect on the interatomic forces in the crystal lattice, then in the external field of small elastic strains ε_{AB}

$$F_A = KV^{BC}\partial_A\varepsilon_{BC} \tag{36}$$

where V^{AB} is a constant with the dimension of volume and K is a constant with the dimension of stress (Kosevitch, 1972). In the isotropy approximation

$$D^{AB} = D\delta^{AB}, \qquad V^{AB} = V_0\delta^{AB} \tag{37}$$

and K is equal to the bulk modulus of the elastic medium and the formulas (31) and (36) take the following form:

$$\mathbf{u} = -2D\,\nabla R \tag{38a}$$

$$\mathbf{F} = -V_0\,\nabla\sigma \tag{38b}$$

where $\sigma = (1/3)\,\mathrm{tr}\,\boldsymbol{\sigma}$ is the hydrostatic pressure corresponding to the field of external stresses $\boldsymbol{\sigma}$, and V_0 is the volume of the material "transferred" by the diffusing atom. From (33), (35), and (38) it follows that in this case the peculiar velocity $\mathbf{v}$ of the diffusion process is an irrotational field:

$$\mathbf{v} = -2D\,\nabla S$$
$$S = (V_0/2D_\zeta)\sigma + R \tag{39}$$

The force $\mathbf{F}$ of the form (38b) is, in the linear approximation, the force with which the external field acts on the center of dilatation in the isotropic medium. It can be shown that in this approximation the point defects do not interact (Kosevitch, 1972). In this case, it is admissible to identify the density of distribution of the localization probability p with the concentration of the diffusing defects [formula (29)], though in general the centers of dilatation interact and in such cases the approximation (29) may be considered only for small concentrations of the diffusing particles (Trzęsowski and Kotowski, 1985).

If the number of diffusing particles does not change [$N(t) = N_0 = $ const in formula (29)] and the diffusion coefficient D is defined by the so-called Einstein relation

$$D = kT/\zeta \tag{40}$$

where k is Boltzmann's constant and T is an absolute temperature, then from (34)-(38) it follows that the concentration function $p(X)$ of the stationary distribution of the diffusing matter equals the density of the Boltzmann distribution probability (Trzęsowski and Kotowski, 1985):

$$p(X) = C \exp[-U(X)/kT]$$
$$U(X) = (V_0/\zeta)\sigma(X) \tag{41}$$

where the constant C is of the form

$$C = p_0 \exp(F/kT), \qquad F = -kT \ln Z$$
$$Z = p_0 \int_{R^3} \exp[-U(X)/kT]\, dV(X) \tag{42}$$

The constant F may be identified with the free energy for one particle of a particle system in the thermodynamic equilibrium state [in an external field with potential $U(X)$] and

$$F = E - TS \tag{43a}$$

$$E = \langle U \rangle = \int_{R^3} p(X) U(X)\, dV(X) \tag{43b}$$

$$S = -k \int_{R^3} p(X) \ln[p(X)/p_0]\, dV(X) = -2k\langle R \rangle \tag{43c}$$

where E and S may be identified, respectively, with the energy and thermodynamic entropy for one particle of a particle system in the thermodynamic equilibrium state (Trzęsowski and Kotowski, 1985).

The above result shows that if we want to consider stationary states of diffusing matter that are not thermodynamic equilibrium states, we have to give up the classical Stokes relation (35). Then, however, the mean starting velocity **b** loses its physical distinction and equation (34) can no longer be treated as the fundamental equation describing the phenomenon of diffusion. There is also no reason to distinguish the arriving diffusion process. Because of that, here we take as the basic fundamental kinematic variables of the diffusion process the diffusion velocity **u** and (in the place of the mean starting velocity **b**) the peculiar diffusion velocity **v**. The relation of these velocities to the concentration p of the diffusing matter is defined by formulas (25) and (26).

4. LOCAL THERMODYNAMIC EQUILIBRIUM

Let us consider the case when the stochastic character of the diffusion process is defined by random fluctuations around the stationary local

thermodynamic equilibrium states (cf. Section 1). Let us introduce, in order to describe such a process, "the thermodynamic observer" in the form of the vector basis stationary fields $e_a(X)$, $X \in R^3$, $a = 1, 2, 3$, defined by the formula (4). Because equations (12) and (18) may be written in the form [see equation (7)]

$$dX - b(X, t)\, dt = dw^a(t) e_a(X)$$
$$dX_* - b_*(X_*, t)\, dt = -dW^a(t) e_a(X_*)$$

(44)

and the diffusion coefficient matrix has the representation

$$D(X) = D^{ab} e_a(X) \otimes e_b(X)$$

(45)

then the thermodynamic observer (4) "sees" locally the diffusion process fluctuations as the random motion of a Brownian particle [which is characteristic for the thermodynamic equilibrium states of the diffusion process (Reif, 1965)]. The diffusion velocity u [equation (26)] will be locally observed as the diffusion velocity in a homogeneous body of the form (31) (we deal with a locally homogeneous body!), with the partial derivative ∂_A appearing in equations (26) and (31) changed for the covariant derivative ∇_A such that

$$\nabla_A D^{BC}(X) = 0$$

(46)

Then

$$u^A = -\frac{1}{p} \nabla_B [D^{AB}(X) p]$$
$$= -\frac{1}{p} D^{AB}(X) \nabla_B p$$

(47)

In this paper consideration is restricted to the case when the covariant derivative ∇ is univocally defined by the diffusive properties of the medium [i.e., by the diffusion coefficients $D^{AB}(X)$]. Then ∇ is a symmetric metric covariant derivative (Levi-Civita covariant derivative) for the tensor $D(X)$. The diffusion coefficient tensor is not a convenient measure of length, because from (47) it follows that its absolute dimension equals the absolute dimension of velocity, i.e., $[D] = [u] = [t^{-1}]$ (Schouten, 1951). Because of that, we will assume that ∇ is a covariant Levi-Civita derivative corresponding to the metric tensor $G(X)$, $X \in R^3$, defined by

$$D(X) = DG(X)^{-1}, \qquad D > 0$$
$$[D] = [l^2 t^{-1}], \qquad [G] = [l^2], \qquad [D] = [t^{-1}]$$

(48)

where D is a certain constant characterizing the diffusion process. It follows from the form of the connection coefficients $\Gamma^A_{BC}(\mathbf{G})$ of that covariant derivative

$$\Gamma^A_{BC}(\mathbf{G}) = \tfrac{1}{2}G^{AD}(\partial_C G_{BD} + \partial_B G_{CD} - \partial_D G_{BC}) \tag{49}$$

that tensors $\mathbf{D}$ and $\mathbf{G}$ define the same covariant derivative. If $X = (X^A)$ is the so-called geometric dimensional frame reference characterized by (Post, 1982)

$$[X^A] = [l], \qquad [dX^A] = [l], \qquad [\partial/\partial X^A] = [l^{-1}] \tag{50}$$

then

$$\mathbf{D}(X) = D^{AB}(X)\partial_A \otimes \partial_B$$

$$\mathbf{G}(X) = G_{AB}(X)dX^A \otimes dX^B$$

$$D^{AB}(X) = DG^{AB}(X), \qquad \partial_A = \partial/\partial X^A \tag{51}$$

$$[D^{AB}(X)] = [l^2 t^{-1}], \qquad [G_{AB}(X)] = [G^{AB}(X)] = [1]$$

The existence of the constant D with the dimension of diffusion coefficient is not connected with whether we consider the diffusion of defects possessing mass (i.e., interstitial atoms) or massless defects (i.e., lattice vacancies). In Part II of this work it will turn out that only a second constant characterizing the diffusion process (in the form of the diffusive counterpart of Planck's constant) will allow the distinction of what sort of diffusing defect we deal with.

The diffusion process which can be described by equations (25)–(28) in which the partial derivative ∂_A is replaced by the covariant derivative ∇_A with the connection coefficients (49) will be called a *locally equilibrium diffusion process* (in a locally homogeneous body). In order to formulate the stochastic description of such a diffusion process, we have to modify the definition of the arriving and starting diffusion processes formulated in Section 2. It resolves itself into replacing the locally Wienerian process in R^3 by Brownian motion $\mathbf{W}(t)$, with the values in the Riemannian manifold $M = (R^3, \mathbf{G})$, where the metric tensor $\mathbf{G}$ is defined by (48). That process in M is defined, in the arbitrary coordinate system $X = (X^A)$ on M, by the condition that its infinitesimal generator should have the form $W(\nabla)$, i.e., [cf. (8)]

$$W(\nabla) = D^{AB}(X)\nabla_A \nabla_B = D\Delta \tag{52}$$

where Δ is the Laplace–Beltrami operator on M:

$$\Delta f = G^{AB}(X)\nabla_A \nabla_B f$$

$$= G(X)^{-1/2}\partial_A(G(X)^{1/2}G^{AB}(X)\partial_B f) \tag{53}$$

$$G(X) = \det\|G_{AB}(X)\|, \qquad f \in C^\infty(M)$$

Because

$$W(\nabla) = m^A(X)\partial_A + D^{AB}(X)\partial_A\partial_B$$
$$m^A(X) = -D^{BC}(X)\Gamma^A_{BC}(\mathbf{G})(X) \tag{54}$$

we can assume that the Brownian process in M fulfills the following stochastic Ito equation [cf. equation (6)]:

$$dW^A(t) = m^A(W(t))\, dt + e^A_a(W(t))\, dw^a(t) \tag{55}$$

The starting $[X(t)]$ and arriving $[X_*(t)]$ diffusion processes in M can be defined, in the arbitrary coordinate system $X = (X^A)$ on M, by [cf. (12) and (18)]

$$dX^A(t) = b^A(X(t), t)\, dt + dW^A(X(t); t)$$
$$dX^A_*(t) = b^A_*(X_*(t), t)\, dt - dW^A(X_*(t); t) \tag{56}$$
$$dW^A(Z; t) = m^A(Z)\, dt + e^A_a(Z)\, dw^a(t)$$

The infinitesimal generating operators of the considered diffusion processes are then of the following form [cf. (19)]:

$$T_s = (b^A + m^A)\partial_A + D^{AB}\partial_A\partial_B$$
$$= b^A\nabla_A + W(\nabla) = T_s(\nabla) \tag{57}$$

for the starting process and

$$T_{*s} = (b^A_* - m^A)\partial_A - D^{AB}\partial_A\partial_B$$
$$= b^A_*\nabla_A - W(\nabla) = T_{*s}(\nabla) \tag{58}$$

for the arriving process. If the covariant derivative ∇ has a vanishing curvature tensor, then there exists a coordinate system $X = (X^A)$ on M such that $\Gamma^A_{BC}(\mathbf{G}) \doteq 0$ and

$$m^A(X) \doteq 0 \tag{59}$$

and the considered diffusion processes are reduced to the processes discussed in Section 2. Now the mean starting and arriving velocities do not equal, respectively, the functions $\mathbf{b}$ and $\mathbf{b}_*$ appearing in equations (56) because

$$E[dX^A(t)|X(t) = \mathbf{X}] = B^A(X, t)\, dt$$
$$E[dX^A_*(t)|X_*(t) = \mathbf{X}] = B^A_*(X, t)\, dt \tag{60}$$

where $X(t)$ and $X_*(t)$ denote, respectively, the starting and arriving diffusion processes in M and where

$$B^A = b^A + m^A$$
$$B_*^A = b_*^A - m^A \tag{61}$$

So, for the considered diffusion processes, equations of the form (44) are valid, but with $\mathbf{b}$ and $\mathbf{b}_*$ replaced by $\mathbf{B}$ and $\mathbf{B}_*$, respectively. But this does not cause a change of the peculiar velocity of diffusion, because from (61) it follows that [cf. (24)]:

$$\tfrac{1}{2}(B_*^A + B^A) = \tfrac{1}{2}(b_*^A + b^A) = v^A \tag{62}$$

Let us denote by $\omega(\mathbf{X})$ the volume 3-form of the Riemannian manifold $M = (R^3, \mathbf{G})$, i.e.,

$$\omega(\mathbf{X}) = V_e \mathbf{e}^1(\mathbf{X}) \wedge \mathbf{e}^2(\mathbf{X}) \wedge \mathbf{e}^3(\mathbf{X})$$
$$= G(X)^{1/2} dx^1 \wedge dX^2 \wedge dX^3 \tag{63}$$

$$G(X)^{1/2} = V_0 e(X), \qquad e(X) = \det \mathbf{e}(X)$$

$$V_0 = (\det \| G_{ab} \|)^{1/2}$$

where $\mathbf{e}(X)$ is a matrix defined in (4), $G(X)$ is defined in (53), and $\{\mathbf{e}^a(\mathbf{X}), a = 1, 2, 3\}$ is a dual base to the base (4):

$$\mathbf{e}_a(\mathbf{X}) \cdot \mathbf{e}^b(\mathbf{X}) = \delta_a^b \tag{64}$$

Because the 3-form $\omega(\mathbf{X})$ is defined by the thermodynamic observer (4) and a certain characteristic dimensionless constant volume V_0, the volume element in M corresponding to it,

$$dV(\mathbf{X}) = G(X)^{1/2} d^3 X \tag{65}$$

where $d^3 X$ is an element of Euclidean volume in R^3, we will call this the *diffusive volume* and we will interpret $dV(X)$ as the volume of the physically infinitesimal neighborhood of a point $\mathbf{X}$ in the (local) equilibrium state. Defining the density function $p(X, t)$ of the absolute probability of localization by (21) with the condition that $dV(X)$ is the diffusive volume, we obtain that this function should at the same time fulfill Fokker–Planck equations of the form (22a) and (23a), with the change of ∂ for ∇, i.e., that (Dankel, 1971; Dohrn and Guerra, 1978)

$$F_t = F_t(\nabla) = \nabla_A (b^A(X, t) \cdot) - D\Delta$$
$$F_{*t} = F_{*t}(\nabla) = \nabla_A (b_*^A(X, t) \cdot) + D\Delta \tag{66}$$

Hence, in analogy to Section 2, it follows that the probability density p and peculiar diffusion velocity $\mathbf{v} = v^a \partial_A$ [equation (62)] should fulfill a continuity equation of the form

$$\partial_t p + \nabla_A (pv^A) = 0 \tag{67}$$

the diffusion velocity $\mathbf{u} = u^A \partial_A$, defined by [cf. (24)]

$$u^A = \tfrac{1}{2}(b^A_* - b^A) \tag{68}$$

should be of the form

$$u^A = -\frac{1}{p} D^{AB}(X)\partial_B p \tag{69}$$

and the flux (27) is defined with exactness by the transformation (28), with the partial derivative ∂_A replaced by the covariant derivative ∇_A. Let us observe that because here p is a scalar, so the formula (47) takes the form (69) analogous to the form (31) of the diffusion velocity in a homogeneous body. So locally the Fick law (32) is valid [with $D^{AB} = D^{AB}(X)$ and p of the form (29)].

In the case (29) [with $dV(X)$ of the form (65)—see Section 5], equation (67) can be written in the form

$$\partial_t n + \partial_A (nv^A) = \alpha(X, t)n$$
$$\alpha(X, t) = \beta(t) - \gamma(X, t)$$
$$\gamma = \partial_v G^{1/2} = \gamma_A v^A, \qquad \beta(t) = \dot{N}(t)/N(t) \tag{70}$$
$$\gamma_A = \Gamma^B_{AB}(G) = \partial_A G^{1/2}$$

From a comparison of the forms of equations (30) and (70) it follows that the nonintegrability of the diffusive volume $dV(\mathbf{X})$ distribution is one of the reasons for point defect creation (or annihiliation) in a body with diffusion.

So, finally, the locally equilibrium diffusion process can be described as a Markovian process in the Riemannian manifold $M = (R^3, \mathbf{G})$ characterized by the existence of conjugate arriving and starting diffusion processes. This differential manifold is the geometric model of the material structure of a locally homogeneous body with local thermodynamic equilibrium states of diffusion process and will be called the *material space* of the (locally homogeneous) body with diffusion.

5. DYNAMICAL SYSTEM ASSOCIATED WITH DIFFUSION PROCESS

Let us consider the microstate of the locally equilibrium diffusion process, i.e., $N(t)$-element subset $\Omega_t \subset M$ defined as the set of positions

of all diffusing particles at the moment $t \geq 0$. The probability $dp_t(\mathbf{X})$ of observing at the moment t the diffusing particle in the neighborhood of the point $\mathbf{X} \in M$ with the diffusive volume $dV(\mathbf{X})$ is

$$dp_t(\mathbf{X}) = p(\mathbf{X}, t)\, dV(\mathbf{X}) \tag{71}$$

Because we consider identical, but distinguishable particles with negligible interactions (Section 3), the microstate Ω_t may be identified with an $N(t)$-element statistical ensemble for the random variable $\mathbf{X}: R_+ \to M$, defined as the position of one of the diffusing particles (arbitrarily distinguished) at the moment $t \geq 0$. As a consequence, the probability $dp_t(\mathbf{X})$ may be calculated from the formula (Klimontovitch, 1982)

$$dp_t(\mathbf{X}) = \lim_{N(t) \to \infty} n(\mathbf{X}, t) dV(\mathbf{X}) / N(t) \tag{72}$$

and the approximation (29) is the better, the greater $N(t)$ is.

Let $\mathbf{v}(\mathbf{X}, t) = v^A(X, t)\partial_A$ be a peculiar velocity of the diffusion process defined by equations (67) and (69). Let us consider equation (67) as the generalized Liouville equation, corresponding to the dynamical system on the manifold M defined by the equation

$$\dot{\mathbf{X}} = \mathbf{v}(\mathbf{X}, t) \tag{73}$$

We will call this the dynamical system *associated* with the diffusion process. The function $p = p(\mathbf{X}, t)$ defined by equations (71) and (72) is the probability distribution function for the ensemble of systems each of which is governed by equation (73), but which differ in their initial conditions according to a certain arbitrarily chosen initial probability distribution function $p_0(X) = p(\mathbf{X}, 0)$ (Klimontovitch, 1982; Ramshaw, 1986). This means that a locally equilibrium process may be considered as one realizing the statistical description of its associated dynamical system, i.e., that diffusion process can be interpreted as the flow of "gas" of ensemble systems in the space M.

We can observe, then, that in the case (29) the description of the state of a locally homogeneous body with locally equilibrium diffusion process can be formulated in terms of the statistical description of the dynamical system associated with that diffusion process. In this paper we will restrict ourselves to considering, as the state function for the locally equilibrium diffusion process, the measure of indetermination of that statistical description in the form of the so-called statistical entropy (Section 7).

6. DIFFUSION PROCESS CONCENTRATED IN DOMAIN

In this section we consider the locally equilibrium diffusion process concentrated in the regular domain $\Omega \subset M$, with the boundary $\partial\Omega$ (Westenholz, 1978), i.e., a process whose concentration function $p(\mathbf{X}, t)$ fulfills the

condition

$$\forall t \in I \quad p(\mathbf{X}, t) \begin{cases} \geq 0 & \text{for} \quad \mathbf{X} \in \Omega \\ = 0 & \text{for} \quad \mathbf{X} \in M - \Omega \end{cases} \tag{74}$$

where $I \subset R_+$ is a certain time interval. From (74) it follows that

$$\forall t \in I \quad \int_\Omega p(\mathbf{X}, t) \, dV(\mathbf{X}) = 1 \tag{75}$$

and in the formula (29) [with the volume element $dV(X)$ of the form (65)]

$$N(t) = \int_\Omega n(\mathbf{X}, t) \, dV(\mathbf{X}) \tag{76}$$

From (74) it also follows that the function $p: \Omega \times I \to R_+$ should fulfill the equation [see equation (67)]

$$\partial_t p + \operatorname{div}(p\mathbf{v}) = 0 \quad \text{in } \Omega \times I$$
$$p = 0 \quad \text{on } \partial\Omega \times I \tag{77}$$

where $\mathbf{v}$ is the peculiar diffusion velocity and div denotes the divergence operator, based on the covariant derivative ∇ defined in Section 4. The diffusion velocity $\mathbf{u}$ is defined by (69) and may be represented in the form [cf. (31)]

$$u^A = G^{AB} u_B$$

$$u_B = -\frac{1}{p} D \, \partial_B p = -2D \, \partial_B R \tag{78}$$

$$R = \ln(p/p_0)^{1/2}$$

The Riemannian submanifold $M|\Omega = (\Omega, \mathbf{G})$ of the material space M of a body with diffusion, in which equations (75)-(78) induced from M are valid, is the material space describing the diffusion process concentrated in Ω. The dynamical system associated with that diffusion process (Section 5) is defined by equation (73) considered on $\Omega \times I$, and equation (77) is then the generalized Liouville equation corresponding to it. Let us observe that because $\Omega \neq R^3$, the concentration function $p(\mathbf{X}, t)$ fulfilling conditions (71) and (77) with the change of M for $M|\Omega$ cannot be connected in the way discussed in Sections 2 and 4 with the Markovian diffusion processes in Ω. However, this function can be treated as the one defining the distribution of probability for the ensemble of systems governed by equation (73) [see the commentary after equation (73)]. We can observe, then, that the notion of dynamical system associated with a diffusion process can be treated as a generalization of the description of that process based on the

consideration of the Markovian diffusion processes. The further part of the paper will be based on that generalization rather than on the theory of Markovian processes.

7. STATISTICAL ENTROPY OF DIFFUSION PROCESS

By the statistical entropy of the diffusion process we will call the integral $S_t(p)$ defined by Ciesielski, 1971; Klimontovitch, 1982)

$$S_t(p) = \int_{R^3} \Theta(p_t(\mathbf{X}))$$

$$\Theta(p_t(\mathbf{X})) = p_0 s(p_t/p_0)\, dV(\mathbf{X}), \qquad p_t(\mathbf{X}) = p(\mathbf{X}, t)$$

$$s(x) = \begin{cases} -kx \ln x & \text{for} \quad x > 0 \\ 0 & \text{for} \quad x = 0 \end{cases}$$

(79)

where k is Boltzmann's constant and p_0 is an arbitrary homogeneous concentration. The statistical entropy differs from the so-called information entropy only in the multiplier kp_0 (e.g., Ramshaw, 1986). For the diffusion process concentrated in the regular domain Ω(Section 6), we may assume, without restricting the generality of further considerations, that Ω is a support of the function p defined by the condition (74); in that case we will additionally assume that

$$V(\Omega) = \int_{\Omega} dV(\mathbf{X}) < \infty$$

(80)

From (78) and (79) it follows that for such a diffusion process

$$S_t(p) = -\int_{\Omega} kp_t \ln(p_t/p_0)\, dV$$

$$= -2k\langle R \rangle_t$$

(81)

where

$$\langle f \rangle_t = \int_{R^3} p_t(\mathbf{X}) f(\mathbf{X})\, dV(\mathbf{X})$$

$$= \int_{\Omega} p_t(\mathbf{X}) f(\mathbf{X})\, dV(\mathbf{X})$$

(82)

From a comparison of the equations (31) and (43c) with equations (78)–(82) it follows that the statistical entropy of the locally equilibrium diffusion process concentrated in the domain Ω is the generalization of the thermodynamic entropy on one particle of the diffusing particle system in the thermodynamic equilibrium state. Thus, (Ciesielski, 1971)

$$S_t(p) \le k \ln[p_0 V(\Omega)]$$

(83)

which means that the statistical entropy of the considered diffusion process has an upper bound corresponding to the chaotic equilibrium distribution in Ω of diffusing particles (Reif, 1965).

From equations (77), (81), and (82) and from the divergence theorem of Gauss for Riemannian manifolds (Westenholz, 1978), it follows that

$$\dot{S}_t(p) = \frac{d}{dt} S_t(p) = k\langle \text{div } \mathbf{v}\rangle_t \tag{84}$$

Because for the 3-form volume ω [equation (63)]

$$L_\mathbf{v}\omega = (\text{div } \mathbf{v})\omega \tag{85}$$

where $L_\mathbf{v}$ is the Lie derivative (Westenholz, 1978), then from (82) and (84) it follows that the sign of the derivative $\dot{S}_t(p)$ depends on the field of infinitesimal changes of the diffusive volumes $dV(\mathbf{X})$, $\mathbf{X} \in \Omega$, defined by the peculiar diffusion velocity $\mathbf{v}$. In particular, if in almost every point $\mathbf{X} \in \Omega$:

(a) $\text{div } \mathbf{v} > 0$ (local expansion), then $\dot{S}_t(p) > 0$ (increase of entropy)
(b) $\text{div } \mathbf{v} < 0$ (local compression), then $\dot{S}_t(p) < 0$ (decrease of entropy)
(c) $\text{div } \mathbf{v} = 0$ (local volume preservation), then $\dot{S}_t(p) = 0$ (the constancy of entropy).

From (83) it follows that an increase of the statistical entropy indicates a change toward a decrease of ordering in the distribution of the diffusing matter. From the point of view of information theory, the entropy of the nonequilibrium thermodynamic system increases because the information about its internal configuration is lost upon its evolution with the passage of time. In fact, this is the basic sense of the second law of thermodynamics, which says that in an isolated system the entropy does not decrease (Andrew, 1984). Hence, it follows that a decrease of the statistical entropy is possible only in a thermodynamically open system. It should be remembered that the thermodynamic openess of the system can be connected not only with its contact with the neighborhood in the topological sense, but can also, e.g., denote the interaction with the internal degrees of freedom of the system, not included in the variables describing its thermodynamic state (Ramshaw, 1986). From the point of view of information theory, the decrease of entropy is the effect of the supply of new information to the system (Andrew, 1984).

From the above remarks it follows that cases (a) and (b) have the clear thermodynamic sense, consistent with their informational sense. In case (c) the volume is preserved in the configuration space of the dynamical system associated with the considered diffusion process. This suggests that this

case can be connected with the Poincaré recurrence theorem for the dynamical system. In that sense, in case (c) we may talk about the reversibility of the process (cf. Ramshaw, 1986). The lack of a direct relation between the statistical and thermodynamic entropy makes the discussion of such reversibility impossible in terms of the dissipation of energy. It may be admitted that the case $\dot{S}_t(p) \neq 0$ denotes the existence of dissipation, but it cannot be expected that $\dot{S}_t(p) = 0$ always denotes its lack.

8. REMARKS

The proposed geometric method of description of the local thermodynamic equilibrium states does not require considering all thermodynamic parameters and functions of state appearing in the description of the global thermodynamic equilibrium state, though it does not exclude the possibility that some of them appear in a hidden way in that description. In order to convince oneself of this, one should consider the case when the material space of the body with diffusion (Sections 4 and 6) is conformally Euclidean, i.e., the case when in the formula (48)

$$\mathbf{G}(\mathbf{X}) = \lambda(\mathbf{X})\mathbf{C}(\mathbf{X})$$
$$\lambda(\mathbf{X}) > 0, \qquad \lambda \in C^\infty(M), \qquad [\lambda] = [1] \tag{86}$$

where $\mathbf{C}$ is a metric tensor on R^3, to which corresponds the Levi-Civita covariant derivative with vanishing curvature tensor. The tensor $\mathbf{C}$ can be regarded as the right Cauchy–Green tensor induced in the body by the elastic deformation of its solid figure (Trzęsowski, 1987, Part I). In that case, the tensor of the diffusion coefficients is of the form

$$\mathbf{D}(\mathbf{X}) = D(\mathbf{X})\mathbf{C}(\mathbf{X})^{-1}$$
$$D(\mathbf{X}) = \lambda(\mathbf{X})^{-1}D \tag{87}$$

Taking the constant D in the form (40) and assuming additionally that in the considered local thermodynamic equilibrium state the friction coefficient ζ is equal to its (constant) equilibrium value, we obtain

$$D(\mathbf{X}) = kT(\mathbf{X})/\zeta$$
$$\lambda(\mathbf{X}) = T/T(\mathbf{X}), \qquad T = \text{const} \tag{88}$$

Thus, in the considered case the property that (in general) the material space of the body with diffusion is non-Euclidean can be characterized by the existence of a field of effective temperatures describing the local thermodynamic equilibrium steady state in the diffusive volumes $dV(\mathbf{X})$ of the

body. The diffusive volume of the body is in that case defined by [see equation (65)]

$$dV(\mathbf{X}) = \lambda(\mathbf{X})^{3/2} \, dV_0(\mathbf{X})$$

$$dV_0(\mathbf{X}) = C(X)^{1/2} \, d^3X \qquad (89)$$

$$C(X) = \det\|C_{AB}(X)\|$$

where $dV_0(\mathbf{X})$ is a volume element in the elastically deformed body, i.e., there exists a coordinate system $X = (X^A)$ such that in this system $C_{AB}(X) \overset{\pm}{=} \delta_{AB}$ and $dV_0(\mathbf{X}) \overset{\pm}{=} d^3X$.

From (88) and (89) it follows that the diffusive volume is inversely proportional to the effective temperature of that domain. It denotes, according to the formula (71), that for the stationary locally equilibrium distribution of the diffusing matter (see the beginning of Section 4 and the Introduction) the probability of the localization of the particle in the local thermodynamic equilibrium domain is inversely proportional to the effective temperature of that domain. The formula (89) is then consistent with the statements concerning the influence of the temperature on the amplitude of vibrations of particles around their equilibrium positions (Ashcroft and Mermin, 1986).

In the considered case, the source term γ in equation (70) is defined by functions γ_A, $A = 1, 2, 3$, of the form

$$\gamma_A(X) \overset{\pm}{=} \tfrac{3}{2}\lambda(X)^{3/2}\partial_A \ln \lambda(X)$$

$$\overset{\pm}{=} -\tfrac{3}{2}[T/T(X)]^{3/2}T(X)^{-1}\partial_A T(X) \qquad (90)$$

This means that the "thermodynamic impulse" describing the creation (or annihilation) of point defects which accompanies the locally equilibrium diffusion process is proportional to the effective temperature gradient.

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