Interdiffusion and free-boundary problem for r-component $(r \ge 2)$ one-dimensional mixtures showing constant concentration

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The concept of separation of diffusional and drift flows, i.e., the postulate that the total mass flow is a sum of diffusion flux and translation only, is applied for the general case of diffusional transport in an rcomponent compound (process defined as interdiffusion in a one-dimensional mixture). The equations of local mass conservation (continuity equations), the appropriate expressions describing the fluxes (drift flux and diffusional flux), and momentum conservation equation (equation of motion) allow a complete quantitative description of diffusional transport process (in one-dimensional mixture showing constant concentration) to be formulated. The equations describing the interdiffusion process (mixing) in the general case where the components diffusivities vary with composition are derived. If certain regularity assumptions and a quantitative condition (concerning the diffusion coefficients-providing a parabolic type of the final equation) are fulfilled, then there exists the unique solution of the interdiffusion problem. Good agreement between the numerical solution obtained with the use of Faedo-Galerkin method and experimental data is shown. An effective algebraic criterion allows us to determine the parabolic type of a particular problem. A condition for the "up-hill diffusion" in the three component mixture is given and a universal example of such effect is demonstrated. The results extend the standard Darken approach. The phenomenology allows the quantitative data on the dynamics of the processes to be obtained within an interdiffusion zone.

I. INTRODUCTION

The majority of phenomenological models of the interdiffusion have neglected the effects due to variation of medium properties with the composition, neglected the effects of differences in the partial molar volumes of the diffusing species, and all of them ignored the possible reactions within the diffusion zone. For example, the fundamental Darken-Wagner equations assume that the partial molar volumes of the diffusing components are constant^{1,2} and equal.² The conservation of momentum is not included in all the models of interdiffusion.^{3,4} Thus, under these simplified assumptions, all the models of interdiffusion neglect the dynamics of the transport process.¹⁻⁴

This paper is an attempt to unify the interdiffusion phenomenology, to bridge the gap between the physicochemical statements of the processes (which are inherently coupled with the reactive, mutual, and interdiffusion processes, mass transport in general) and their reduction to diffusion problems. The essence of this attempt comprises (i) the postulate that the total mass flow is a sum of diffusion and translation fluxes only, and (ii) a rigorous use of the fundamental Darken concept, the concept of the drift velocity² (which is a common velocity of all the mixture components, e.g., the common translation velocity of the mixture components).

The medium expansion as a result of accumulation within the transport zone are inherent processes of the diffusional mass transport. The complete description of the transport may not neglect the local momentum conservation. Consequently, the Navier-Stokes equations are included in the presented analysis of the interdiffusion.

A more detailed analysis of the concepts of drift velocity, the choice of the proper reference frame for diffusion, as well as the other consequences of the proposed formalism have already been published.^{5,6} A general phenomenological treatment of the interdiffusion problem is given below.

II. THEORY

It is essential to state the common aspects of the already mentioned fundamental models of diffusional mass transport. $^{1-4}$

(i) The seemingly attractive choice of internal reference frame is *useless* in the direct description of transport processes in the external reference frame (it is termed often as an observer or laboratory frame of reference). However, because the laws of conservation does not depend on the choice of the reference frame, this frame of reference can be used as a source of information about the dynamics of the system (enables mathematical disjoining of dynamics and diffusion).

(ii) The reactions within the *diffusion zone*—e.g., medium (compound) production, and/or local accumulation—affect the local drift velocity of the medium in any fixed external reference frame.

50 13 336

(iii) A common, for all models, unified approach to the relation between the mobility, diffusivity and activity [the Darken's concept of the *variable* intrinsic diffusion coefficient Θ_i ;² to avoid collisions with other mathematical symbols, the intrinsic diffusion coefficients will be denoted as Θ_i ($=D_i$)].

When any compound (media) acts upon a field (e.g., chemical potential gradient), the different elements respond in different ways. In case of a multicomponent medium, the force arising from any concentration gradient causes the atoms of the particular component to move with a velocity (v_i) , which in general may differ from velocity of the atoms of some or all the other components. As the medium is common for all the transported species, all the fluxes are coupled and their local changes can affect the common compound drift velocity (v). The above phenomenon is called interdiffusion.

The *i*-component conservation in the external reference frame (the only reference frame available in the experimental conditions) is expressed by the equation-of-mass conservation (local continuity equation of an *i*th component):

$$\frac{\partial \rho_i}{\partial t} = -\operatorname{div} j_i , \qquad (1)$$

$$[\operatorname{accumulation}] = \begin{bmatrix} \operatorname{mass transport}, \\ \operatorname{local change of flux} \\ \operatorname{in the fixed external} \\ \operatorname{reference frame}(ERF) \end{bmatrix}.$$

where the reaction term (local sink-source of mass) is neglected (formation of the new compounds is not allowed in the course of the analyzed interdiffusion process).

The flux vector is a sum of the diffusional and drift (translation) flows:

$$j_i = j_i(\text{diff}) + j_i(\text{drift}) = \rho_i v_{d,i} + \rho_i v = \rho_i v_i .$$
(2)

Thus, upon substituting Eqs. (1) and (2), the equation describing the mass conservation of the *i*-component in the ERF takes the usual form of the continuity equation, where the physical sense of all the terms is given below the equation:

$$\begin{cases} \frac{\partial \rho_i}{\partial t} = -\operatorname{div} j_{d,i} - v \operatorname{grad} \rho_i - \rho_i \operatorname{div} v = -\operatorname{div} (\rho_i, v_i) , \\ \\ \left[\operatorname{accumulation}_{\mathbf{IRF} \neq \mathbf{ERF}} \right] = \left[\operatorname{diffusion}_{\mathbf{ERF} = \mathbf{IRF}} \right] + \left[\operatorname{drift}_{\mathbf{flow}, } \\ \operatorname{translation}_{\mathbf{ERF} \neq \mathbf{IRF}} \right] + \left[\operatorname{drift}_{\mathbf{generation}}_{\mathbf{ERF} = \mathbf{IRF}} \right] + \left[\operatorname{drift}_{\mathbf{generation}}_{\mathbf{ERF} = \mathbf{IRF}} \right] = \left[\operatorname{mass flow}_{\mathbf{ERF} \neq \mathbf{IRF}} \right] ,$$

$$(3)$$

where IRF is the internal reference frame.

It should be pointed out that the drift generation term can be the result of all local processes. Without external force fields, only the accumulation may affect locally the drift velocity, may generate the drift. The drift production term as well as a local drift velocity are always common for all the transported components.

In the general case of diffusion transport in the *r*-component mixture, *r*-continuity equations for all diffusing components must be fulfilled in any elementary volume within an open system. The continuity equation, Eq. (3), in the unidimensional mixture becomes

$$\frac{\partial \rho_i}{\partial t} = -\frac{\partial}{\partial x}(\rho_i v_i)$$

The important assumption of the local equilibrium in a mixture (nonexplicit assumption) is included in present analysis. This assumption is also a foundation of the majority of phenomenological models of transport (interdiffusion).^{1,2} Successful applications of these models in describing the mass transport justify the incorporation of this fundamental concept of nonequilibrium thermodynamics into the transport equations. The postulate of local equilibrium is as follows: "For a system in which

irreversible processes are taking place, all thermodynamic functions of state exist for each element of the system. These thermodynamic quantities for the nonequilibrium system are the same functions of local state variables as the corresponding equilibrium quantities."⁷

From this assumption it follows that (in the course of the analyzed processes of interdiffusion at constant temperature), the total concentration of the mixture is constant (as in the equilibrium state). In other words it is assumed, that the transport processes do not affect the local medium properties. Namely, it is assumed the transport processes do not affect the constant concentration of the mixture.

A. Formulation of the free-boundary value problem of interdiffusion in the *r*-component one-dimensional mixture

When we are not interested in the temperature effects (they can be neglected), the interdiffusion may be treated as a mixing (the process has low free energy of the reaction). In this section the interdiffusion in a r-component mixture will be formulated:

K. HOLLY AND M. DANIELEWSKI

13 338

Data

(1)	$M_i \in \left]0, \infty\right[$	Molecular mass of the <i>i</i> th component of the mixture $(i = 1, \ldots, r)$
(2)	Λ∈]0,∞[Right border of the segment occupied by the mixture at the beginning of the process $(t=0)$
(3)	$\dot{\rho}_i:[-\Lambda,\Lambda] \rightarrow \mathbb{R}_+$	Initial density distribution of the <i>i</i> th component in the mixture $(i = 1,, r)$. The initial global concentration of the mixture
		$c = \sum_{i=1}^{r} \frac{1}{M_i} \mathring{\rho}_i$
	of	initial procentration the mixture mol/vol $= \sum_{i=1}^{r} \begin{bmatrix} \text{initial} \\ \text{concentration} \\ \text{of the } i \text{th} \\ \text{component} \end{bmatrix}$
		is constant and positive
(4)	$\Theta_i: \underset{k=1}{\times} [0, cM_k] \rightarrow]0, \infty[$	Diffusion coefficient of <i>i</i> th component $(i = 1,, r)$, where \times denotes the Cartesian product
(5)	<i>T</i> ∈]0, ∞[The examination time (time at which measurements were carried out)
(6)	$\nu \in \mathbb{R}$	The viscosity coefficient of the mixture
(7)	$P \in \mathbb{R}$	Initial momentum of the mixture mass center
(8)	$D:[0,T] \rightarrow \mathbb{R}$	Time evolution of a force acting on the mixture boundary
(9)	$b:[0,T]\times\mathbb{R}\to\mathbb{R}$	Time evolution of a body force (e.g., of gravity force).

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The unknown:

(1)
$$\lambda_1, \lambda_2: [0,T] \rightarrow \mathbb{R}, \lambda_1 < \lambda_2$$
 Where λ_1 and λ_2 and
(2) $\rho_i: \bigcup_{\substack{0 \le t \le T \\ (\text{i.e., } \text{dom}\rho_i = \{(t,x): 0 \le t \le T, \lambda_1(t) \le x \le \lambda_2(t)\})} (i = 1, \ldots, r)$

(3)
$$v: \bigcup_{0 \le t \le T} \{t\} \times [\lambda_1(t), \lambda_2(t)] \to \mathbb{R}$$

(4)
$$p: \bigcup_{0 \le t \le T} \{t\} \times [\lambda_1(t), \lambda_2(t)] \to \mathbb{R}$$

Where λ_1 and λ_2 are the mixture boundaries Density of the *i*th component $(i = 1, \ldots, r)$ Drift velocity Pressure of the mixture.

Physical laws:

(1) The local mass conservation law for the ith component:

$$\frac{\partial \rho_i}{\partial t} + \frac{\partial}{\partial x} (\rho_i v_i) = 0 , \qquad (4)$$

where v_i is the *i*th component velocity, i.e.,

$$\rho_{i}v_{i} = -\Theta_{i}(\rho_{1}, \dots, \rho_{r})\frac{\partial\rho_{i}}{\partial x} + \rho_{i}v;$$
(5)
$$\begin{bmatrix} \text{total flux} \\ \text{of the ith} \\ \text{compon-} \\ \text{ent} \end{bmatrix} = \begin{bmatrix} \text{diffusional flux of the} \\ \text{ith component, where} \\ \text{diffusivities may depend} \\ \text{on mixture composition} \end{bmatrix} + \begin{bmatrix} \text{drift flux} \\ \text{of the ith} \\ \text{compon-} \\ \text{ent} \end{bmatrix}$$

13 339

(2) The postulate of constant concentration of the mixture:

$$\frac{1}{M_1}\rho_1 + \cdots + \frac{1}{M_r}\rho_r = c \quad . \tag{6}$$

Note that the mixture density, $\rho := \sum_{i=1}^{r} \rho_i$, assumes values in the interval

 $[c \min_{1 \leq i \leq r} M_i, c \max_{1 \leq i \leq r} M_i];$

(3) The local law of momentum conservation (equation of motion):

(1)
$$\lambda_1(0) = -\Lambda, \quad \lambda_2(0) = \Lambda$$

(2)
$$\rho_i(0,x) = \mathring{\rho}_i(x) \quad (i = 1, ..., r)$$

(3)
$$\frac{d}{dt}\int_{\lambda_1(t)}^{\lambda_2(t)}\rho(t,x)x\ dx\bigg|_{t=0}=P$$

Boundary conditions

(1)
$$\dot{\lambda}_i(t) = u(t, \lambda_i(t)) \quad (j=1,2)$$

(2)
$$[\rho_i(v_i - u)](t, \lambda_j(t)) = 0 \quad (1 \le i \le r, 1 \le j \le 2)$$

(3)
$$p(t,\lambda_1(t))-p(t,\lambda_2(t))=D(t)$$

B. Examples of possible modifications

Instead of the data (6) and (8) [or the data (7) and (8)], the initial condition (3) and the boundary condition (3), one can give an evolution $\lambda_1:[0,T] \rightarrow \mathbb{R}$ of the left boundary of the mixture. As an example, for the *r*-component alloy bar (mixture segment $[\lambda_1(t), \lambda_2(t)]$), which is placed vertically on a rigid immovable surface, one can put $\lambda_1 \equiv -\Lambda$.

If the evolution $\lambda_1:[0,T] \to \mathbb{R}$ is known, then one can bypass the determining of the pressure p, and eliminate the Navier-Stokes equation, data (6)-(9), initial condition (3), and boundary condition (3).

Instead of the data (7)-(9), one can give an evolution $F:[0,T] \rightarrow \mathbb{R}$ of the total force acting on the mixture as a whole. In such a case one can bypass the determining of the pressure and eliminate the boundary condition (3). Then, instead of the Navier-Stokes equation, it is postulated that

$$\frac{d^2}{dt^2}\int_{\lambda_1(t)}^{\lambda_2(t)}\rho(t,x)x\ dx=F(t)$$

$$\rho \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \right] = v \frac{\partial^2 u}{\partial x^2} - \frac{\partial p}{\partial x} + \rho b , \qquad (7)$$

where the velocity of the mixture is given by

$$u := \sum_{i=1}^{r} \frac{\rho_i}{\rho} v_i , \qquad (8)$$

more precisely it is a distribution of the velocities of the local mass centers.

Initial conditions:

Initial position of the mixture boundaries

Initial distribution of the mixture components

Initial momentum of the mixture

The velocities of the mixture boundaries

- Total flux of the *i*th component in the internal reference frame (i.e., mass flow through the mixture boundaries does not occur, the mixture is in a closed system)
- The resultant (the net) thrust force acting on the boundary of the mixture

In particular, if $F \equiv 0$, then the first law of dynamics results.

C. Plan of the procedure

First, we shall prove that $\lambda_2(t) = \lambda_1(t) + 2\Lambda$ for all $0 \le t \le T$. Second, disregarding the data (6)-(9), the spatially shifted density of the *i*th component will be found,

$$[-\Lambda,\Lambda] \ni z \mapsto \rho_i(t,\lambda_1(t)+z+\Lambda) \in \mathbb{R}_+$$
,

for all components, $1 \le i \le r$, and any fixed time $t \in [0, T]$. Third, with the use of the data (6)-(9), the Navier-Stokes equation, the initial condition (3) and the boundary condition (3), we shall determine the evolution $\lambda_1(t)$ of the left boundary of the mixture. Finally, we shall determine the local densities ρ_1, \ldots, ρ_r , the drift velocity v, and the pressure p.

D. Reformulating the problem

Upon using Eq. (4) and boundary conditions (1) and (2), one can calculate

$$\frac{d}{dt} \int_{\lambda_1(t)}^{\lambda_2(t)} \rho_i(t,x) dx = \int_{\lambda_1(t)}^{\lambda_2(t)} \frac{\partial \rho_i}{\partial t}(t,x) dx + \dot{\lambda}_2(t) \rho_i(t,\lambda_2(t)) - \dot{\lambda}_1(t) \rho_i(t,\lambda_1(t)) \\ = [\rho_i(v_i - u)](t,\lambda_1(t)) - [\rho_i(v_i - u)](t,\lambda_2(t)) = 0.$$

It is the law of mass conservation of the *i*th component in the mixture:

$$\frac{d}{dt}\int_{\lambda_1(t)}^{\lambda_2(t)}\rho_i(t,x)dx = 0 \quad (i=1,\ldots,r) \ . \tag{9}$$

Upon adding Eqs. (9) for all the components, i = 1, ..., r, one gets

$$\frac{d}{dt}\int_{\lambda_1(t)}^{\lambda_2(t)}\rho(t,x)dx=0, \qquad (10)$$

i.e., the total mass conservation law of the mixture.

Upon summing up the local mass conservation laws [continuity equations, Eqs. (4)] for all the components, one gets

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho u) = 0 , \qquad (11)$$

i.e., the local conservation law of the mass of the mixture (the local continuity equation for the mixture).

Upon multiplying by $1/M_i$ the *i*th component total mass conservation law, Eq. (9), and adding all the obtained equations, one gets $d/dt \int_{\lambda_1(t)}^{\lambda_2(t)} c \, dx = 0$. Hence

$$\lambda_2(t) = \lambda_1(t) + 2\Lambda$$
 for all $0 \le t \le T$.

Accordingly, the first part of our plan is accomplished. If $x_1, x_2:[0, T] \rightarrow \mathbb{R}$ are solutions of the differential equation: $\dot{x}(t) = u(t, x(t))$

(i.e., x_1, x_2 represent time evolution of position of two mixture particles). Then, providing that $x_1(0) < x_2(0)$, one has

$$x_1(t) < x_2(t)$$
 for all $0 \le t \le T$.

The above inequality, the boundary condition (1) and the Liouville theorem⁸ result in

$$\frac{d}{dt} \int_{\lambda_{1}(t)}^{\lambda_{2}(t)} \rho(t, x) x \, dx = \int_{\lambda_{1}(t)}^{\lambda_{2}(t)} (\rho u)(t, x) dx \tag{12}$$

$$\begin{vmatrix} momentum of the mass \\ center of the mixture \end{vmatrix} = \begin{vmatrix} sum of the moments of \\ the local mass centers \end{vmatrix}$$

Consequently, from Eq. (12) and the initial condition (3), it follows that

$$\int_{\lambda_{1}(t)}^{\lambda_{2}(t)} (\rho u)(t, x) dx \bigg|_{t=0} = P .$$
 (13)

Upon applying the Liouville theorem, the equation of continuity for the mixture, the equation of motion, and the third boundary condition, one can calculate the total force acting on the center of mass (the mixture mass center) at a moment t:

$$\frac{d}{dt} \int_{\lambda_{1}(t)}^{\lambda_{2}(t)} (\rho u)(t,x) dx = \int_{\lambda_{1}(t)}^{\lambda_{2}(t)} \left[\rho \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \right] \right](t,x) dx$$

$$= \int_{\lambda_{1}(t)}^{\lambda_{2}(t)} \left[v \frac{\partial^{2} u}{\partial x^{2}} - \frac{\partial p}{\partial x} + \rho b \right](t,x) dx = v \frac{\partial u}{\partial x}(t,x) \left| \frac{\lambda_{2}(t)}{\lambda_{1}(t)} + D(t) + \int_{\lambda_{1}(t)}^{\lambda_{2}(t)} (\rho b)(t,x) dx \right|,$$
(14)

where

$$\frac{\partial u}{\partial x}(t,x)\Big|_{\lambda_1(t)}^{\lambda_2(t)} = \frac{\partial u}{\partial x}(t,\lambda_2(t)) - \frac{\partial u}{\partial x}(t,\lambda_1(t))$$

Equation (14), with the use of Eq. (13), can be integrated over the time interval [0,t]:

$$\int_{\lambda_1(t)}^{\lambda_2(t)} (\rho u)(t,x) dx = P + v \int_0^t \frac{\partial u}{\partial x}(\tau,x) \left|_{\lambda_1(\tau)}^{\lambda_2(\tau)} d\tau + \int_0^t D(\tau) d\tau + \int_0^t \int_{-\Lambda}^{\Lambda} (\rho b)(\tau,\lambda_1(\tau) + z + \Lambda) dz \, d\tau \right| .$$
(15)

Multiplying by $1/M_i$ the equations of continuity of the *i*th component, Eq. (4), and summing the all obtained formulas, one gets

$$\frac{\partial}{\partial x}\left[cv-\sum_{i=1}^{r}\frac{\Theta_{i}(\rho_{1},\ldots,\rho_{r})}{M_{i}}\frac{\partial\rho_{i}}{\partial x}\right]=0.$$

Consequently for any $t \in [0, T]$ there exists a unique $K(t) \in \mathbb{R}$ such that for all $x \in [\lambda_1(t), \lambda_2(t)]$,

$$v(t,x) = K(t) + \sum_{i=1}^{r} \left[\frac{\Theta_i(\rho_1, \dots, \rho_r)}{cM_i} \frac{\partial \rho_i}{\partial x} \right](t,x) .$$
(16)

Hence, from Eqs. (5) and (8),

$$\rho u = \rho K(t) - \sum_{i=1}^{r} \left[1 - \frac{\rho}{cM_i} \right] \Theta_i(\rho_1, \dots, \rho_r) \frac{\partial \rho_i}{\partial x} .$$
(17)

Upon integration of Eq. (17) over x range $|_{\lambda_1}^{\lambda_2}$, using the conclusion of preceding step, Eq. (15), and the mass conservation law from the first step, Eq. (10), one calculates:

$$mK(t) = \int_{\lambda_1(t)}^{\lambda_2(t)} \left[\sum_{i=1}^{r} \left[1 - \frac{\rho}{cM_i} \right] \Theta_i(\rho_1, \dots, \rho_r) \frac{\partial \rho_i}{\partial x} \right] (t, x) dx + P$$
$$+ \int_0^t D(\tau) d\tau + v \int_0^t \frac{\partial u}{\partial x} (\tau, x) \left|_{\lambda_1(\tau)}^{\lambda_2(\tau)} d\tau + \int_0^t \int_{-\Lambda}^{\Lambda} (\rho b)(\tau, \lambda_1(\tau) + z + \Lambda) dz d\tau \right]$$

where

$$m := \int_{\lambda_1(t)}^{\lambda_2(t)} \rho(t, x) dx = \int_{-\Lambda}^{\Lambda} \sum_{i=1}^{r} \mathring{\rho}_i(z) dz$$

is the total mass of the mixture.

Incorporation of Eq. (16) into the general flux formula, Eq. (5), yields:

$$\rho_{i}(v_{i}-u) = -\Theta_{i}(\rho_{1},\ldots,\rho_{r})\frac{\partial\rho_{i}}{\partial x} + \rho_{i}\left[K(t) + \sum_{l=1}^{r} \frac{\Theta_{l}(\rho_{1},\ldots,\rho_{r})}{cM_{l}}\frac{\partial\rho_{l}}{\partial x} - u\right].$$
(18)

Upon multiplying by $1/cM_i$ the Eq. (18) and, adding all the obtained formulas, one gets

$$K(t) = u(t, \lambda_i(t)) , \qquad (19)$$

which elucidates the physical interpretation of the integration constant K(t).

Upon combining Eqs. (18) and (19) (for fixed $j \in \{1,2\}$ and $t \in [0, T]$), one gets

$$\theta_i \frac{\partial \rho_i}{\partial x}(t, \lambda_j(t)) = \rho_i(t, \lambda_j(t)) S , \qquad (20)$$

where

$$\theta_i := [\Theta_i(\rho_1, \dots, \rho_r)](t, \lambda_j(t)) > 0 ,$$

$$S := \left[\sum_{l=1}^r \frac{\Theta_l(\rho_1, \dots, \rho_r)}{cM_l} \frac{\partial \rho_l}{\partial x} \right] (t, \lambda_j(t)) .$$

Upon writing Eq. (20) in the form

$$\frac{\partial \rho_i}{\partial x}(t,\lambda_j(t)) = \frac{\rho_i(t,\lambda_j(t))}{\theta_i} S .$$
(21)

multiplying by $1/M_i$ and adding all the obtained formu-

las with the use of the postulate (2), Eq. (6), one gets

$$\frac{\partial c}{\partial x}(t,\lambda_j(t)) = \left| \sum_{i=1}^r \frac{\rho_i(t,\lambda_j(t))}{M_i \theta_i} \right| S$$

Because $\partial c / \partial x \equiv 0$ and $\sum_{i=1}^{r} [\rho_i(t, \lambda_j(t)) / M_i \theta_i] > 0$, it is obvious that S=0. Thus, from Eq. (21) it follows that

$$\frac{\partial \rho_i}{\partial x}(t,\lambda_j(t))=0,$$

for $i \in \{1, \ldots, r\}$, $j \in \{1,2\}$, $t \in [0, T]$. In other words we have proved that, in the unidimensional mixture of constant composition, which does not exchange mass with the surrounding (which can be treated as a closed system), the gradients of all components at both boundaries of the mixture vanish (i.e., are equal zero).

E. Mathematical disjoining of dynamics and diffusion

For a moment $t \in [0, T]$ the following natural parametrization of the interval $[\lambda_1(t), \lambda_2(t)]$,

$$a_t: [-\Lambda, \Lambda] \ni z \mapsto \lambda_1(t) + z + \Lambda \in [\lambda_1(t), \lambda_2(t)], \qquad (22)$$

will be useful. Note that for every differentiable function $f:[\lambda_1(t),\lambda_2(t)] \rightarrow \mathbb{R}$, it is

$$\frac{\partial}{\partial z}(f \circ a_t) = \frac{\partial f}{\partial x} \circ a_t .$$
(23)

We denote

$$m_i:=\frac{m_i}{2\Lambda cM_i}$$

(mean mole fraction of the *i*th component), where

$$m_i := \int_{\lambda_1(t)}^{\lambda_2(t)} \rho_i(t, x) dx = \int_{-\Lambda}^{\Lambda} \mathring{\rho}_i dx \quad ; \tag{24}$$

obviously m_i is the total mass of the *i*th component of the mixture. Moreover, for $t \in [0,T]$ and $z \in [-\Lambda,\Lambda]$ we denote

13 341

$$w_i(t,z) := \frac{1}{cM_i} \rho_i(t,a_t(z)) - m_i$$
(25)

(spatially shifted deviation of the mole fraction from its average). Consequently,

$$\rho_i(t,a_t(z)) = cM_i[w_i(t,z) + m_i] . \qquad (26)$$

From the Eqs. (6) and (24) one gets

$$\sum_{i=1}^{r} m_i = 1 . (27)$$

Hence

$$\sum_{i=1}^{r} w_i \equiv 0 . (28)$$

i=1Moreover,

$$\int_{-\Lambda}^{\Lambda} w_i(t,z) dz = 0 \quad (\text{for all } 1 \le i \le r)$$

For a vector $\kappa \in \mathbb{R}^r$, $\sum_i \kappa_i > 0$, let us denote

$$\widetilde{\Theta}_i(\kappa) := \Theta_i(cM_1\mathcal{P}_1(\kappa), \ldots, cM_r\mathcal{P}_r(\kappa))$$

(rescaled diffusion coefficients), where

$$\mathcal{P}_{k}(\boldsymbol{\kappa}) := \frac{\mathcal{H}_{0}(\boldsymbol{\kappa}_{k})}{\sum_{i=1}^{r} \mathcal{H}_{0}(\boldsymbol{\kappa}_{i})} , \qquad (29)$$

and $\mathcal{H}_0: \mathbb{R} \to \mathbb{R}$ is an antiderivative of the Heaviside function, i.e.,

$$\mathcal{H}_0(s) = \begin{cases} s, & \text{when } s \ge 0, \\ 0, & \text{when } s < 0. \end{cases}$$

By this denotation we have

$$[\Theta_i(\rho_1,\ldots,\rho_r)](t,a_i(z)) = \widetilde{\Theta}_i[w(t,z)+m], \qquad (30)$$

where

$$w(t,z):=(w_1(t,z),\ldots,w_r(t,z)),$$

(statement of the shifted deviations),

$$m := (m_1, \ldots, m_r)$$

(statement of the mean mole fractions). Apparently, by Eq. (23),

$$\frac{\partial w_i}{\partial z}(t,z) = \frac{1}{cM_i} \frac{\partial \rho_i}{\partial x}(t,a_t(z)) \; .$$

The initial and boundary conditions become, respectively,

$$w_i(0,z) = \frac{1}{cM_i} \left| \mathring{\rho}_i(z) - \frac{m_i}{2\Lambda} \right| = : \mathring{w}_i(z)$$
(31)

(initial deviation of the *i*th component),

$$\frac{\partial w_i}{\partial z}(t, -\Lambda) = \frac{\partial w_i}{\partial z}(t, \Lambda) = 0.$$
(32)

In addition,

$$\rho(t, a_t(z)) = \frac{m}{2\Lambda} + c \mathbf{M} \cdot w(t, z) , \qquad (33)$$

$$v(t,a_t(z)) = K(t) + \widetilde{\Theta}(w(t,z) + m) \frac{\partial w}{\partial z}(t,z) , \qquad (34)$$

where $\mathbf{M}:=(M_1,\ldots,M_r)$, $\tilde{\Theta}:=(\tilde{\Theta}_1,\ldots,\tilde{\Theta}_r)$, \cdot denotes the standard scalar product in \mathbb{R}^r and

$$u(t,a_{t}(z)) = K(t) + \sum_{j=1}^{r} \left[1 - \frac{2\Lambda cM_{j}}{m + 2\Lambda c\,\mathbf{M} \cdot w(t,z)} \right] \widetilde{\Theta}_{j}(w(t,z) + m) \frac{\partial w_{j}}{\partial z}(t,z) , \qquad (35)$$
$$mK(t) = P - c \sum_{j=1}^{r} \int_{-\Lambda}^{\Lambda} \left[\frac{m}{2\Lambda c} + \mathbf{M} \cdot w(t,z) - M_{j} \right] \widetilde{\Theta}_{j}(w(t,z) + m) \frac{\partial w_{j}}{\partial z}(t,z) dz + \int_{0}^{t} D(\tau) d\tau + v \int_{0}^{t} \frac{\partial u}{\partial x}(\tau,x) \Big|_{\lambda_{1}(\tau)}^{\lambda_{2}(\tau)} d\tau + \int_{0}^{t} \int_{-\Lambda}^{\Lambda} (\rho b)(\tau,\lambda_{1}(\tau) + z + \Lambda) dz d\tau . \qquad (36)$$

The last two terms on the right-hand side (rhs) of Eq. (36) can be rearranged to minimize their visual dependence on λ_1 . Namely, in the following way we eliminate the unknown $\lambda_1(t)$ term (in the last term on the rhs):

$$\rho(\tau,\lambda_1(\tau)+z+\Lambda) = \rho(\tau,a_{\tau}(z)) = \frac{m}{2\Lambda} + c \mathbf{M} \cdot w(\tau,z) .$$
(37)

The fourth term on the rhs of Eq. (36) can be rearranged using the local mass conservation law of the mixture, $(\partial \rho / \partial t) + (\partial / \partial x)(\rho u) = 0$. We calculate

$$\frac{\partial u}{\partial x} = -\frac{1}{\rho} \left| \frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} \right| .$$

Upon substituting the argument $(t, \lambda_j(t))$ and, using the relation

$$\frac{d}{dt}\rho(t,\lambda_j(t)) = \frac{\partial\rho}{\partial t}(t,\lambda_j(t)) + \dot{\lambda}_j(t)\frac{\partial\rho}{\partial x}(t,\lambda_j(t)) ,$$

we calculate

$$\frac{\partial u}{\partial x}(t,\lambda_j(t)) = -\frac{1}{\rho(t,\lambda_j(t))} \frac{d}{dt} \rho(t,\lambda_j(t)) = -\frac{d}{dt} \ln \rho(t,\lambda_j(t))$$

Consequently, using the Eq. (33) and, upon introducing denotation,

$$w_L(t):=w(t,-\Lambda), \quad w_R(t):=w(t,\Lambda)$$

 $\dot{\rho}:=\dot{\rho}_1+\cdots+\dot{\rho}_r$,

we calculate

$$\int_{0}^{t} \frac{\partial u}{\partial x}(\tau, x) \left| \begin{array}{c} \lambda_{2}(\tau) \\ \lambda_{1}(\tau) \end{array} \right|^{\lambda_{2}(\tau)} d\tau = -\int_{0}^{t} \frac{d}{d\tau} \ln \rho(\tau, \lambda_{2}(\tau)) d\tau + \int_{0}^{t} \frac{d}{d\tau} \ln \rho(\tau, \lambda_{1}(\tau)) d\tau = \ln \left[\frac{\dot{\rho}(\Lambda)}{\dot{\rho}(-\Lambda)} \frac{m + 2\Lambda c \,\mathbf{M} \cdot w_{L}(t)}{m + 2\Lambda c \,\mathbf{M} \cdot w_{R}(t)} \right].$$
(38)

Substitution of the Eqs. (37) and (38) into Eq. (36), results in

$$mK(t) = P - c \sum_{i=1}^{r} \int_{-\Lambda}^{\Lambda} \left[\frac{m}{2\Lambda c} + \mathbf{M} \cdot w(t,z) - M_i \right] \widetilde{\Theta}_i(w(t,z) + m) \frac{\partial w_i}{\partial z}(t,z) dz + \int_{0}^{t} D(\tau) d\tau + \nu \ln \left[\frac{\mathring{\rho}(\Lambda)}{\mathring{\rho}(-\Lambda)} \frac{m + 2\Lambda c \mathbf{M} \cdot w_L(t)}{m + 2\Lambda c \mathbf{M} \cdot w_R(t)} \right] + \int_{0}^{t} \int_{-\Lambda}^{\Lambda} \left[\frac{m}{2\Lambda} + c \mathbf{M} \cdot w(\tau,z) \right] b(\tau,\lambda_1(\tau) + z + \Lambda) dz d\tau .$$
(39)

Obviously, on the base of Eq. (19), the boundary condition (1) and the initial condition (1), the evolution $\lambda_1(t)$ of the left boundary of the mixture is a solution of the following Cauchy problem:

$$\hat{\lambda}_1(t) = K(t) , \qquad (40)$$

$$\lambda_1(0) = -\Lambda . \tag{41}$$

Using Eqs. (23), (30), (34), and (40), we get

$$\frac{\partial w_i}{\partial t}(t,z) = \frac{d}{dz} \left[\tilde{\Theta}_i(w(t,z)+m) \frac{\partial w_i}{\partial z}(t,z) - (w_i(t,z)+m_i) \tilde{\Theta}(w(t,z)+m) \frac{\partial w}{\partial z}(t,z) \right].$$
(42)

With a vector $\kappa \in \mathbb{R}^r$, $\sum_{i=1}^r \kappa_i > 0$, we may associate the linear operator

 $\mathcal{A}_{r}:\mathbb{I}^{1}\to\mathbb{I}^{1}$

given by the formula

$$\mathcal{A}_{\kappa}(\xi) := \sum_{i=1}^{r} \widetilde{\Theta}_{i}(\kappa) \xi_{i} e_{i} - [\widetilde{\Theta}(\kappa) \xi] \mathcal{P}(\kappa) , \qquad (43)$$

where

$$\mathbf{I}^{\perp} := \left\{ \boldsymbol{\xi} \in \mathbf{R}^{r} : \sum_{i=1}^{r} \boldsymbol{\xi}_{i} = 0 \right\}$$

(space of deviations), (e_1, \ldots, e_r) is the standard basis in \mathbf{R}^r , and

$$\mathcal{P}(\kappa):=(\mathcal{P}_1(\kappa),\ldots,\mathcal{P}_r(\kappa)),$$

where $\mathcal{P}_k(\kappa)$ is given by Eq. (29).

Finally, according to Eqs. (42), (31), and (32), the statement

$$w = (w_1, \ldots, w_r): [0, T] \times [-\Lambda, \Lambda] \rightarrow \mathbf{1}^{\perp}$$

(of the shifted deviations) is a solution of the following initial-boundary-value problem:

$$\frac{\partial w}{\partial t}(t,z) = \frac{d}{dz} \left[\mathcal{A}_{[w(t,z)+m]} \frac{\partial w}{\partial z}(t,z) \right], \qquad (44)$$

$$w(0,z) = \hat{w}(z) , \qquad (45)$$

$$\frac{\partial w}{\partial z}(t, -\Lambda) = \frac{\partial w}{\partial z}(t, \Lambda) = 0 .$$
(46)

The data (1)-(5) are sufficient for the solving of the problem (44)-(46). Thus the second part of our plan is accomplished.

Consequently, knowing the shifted deviations $w_1, ..., w_r$, we can find (e.g., by the Banach method of contraction mapping) the position $\lambda_1:[0,T] \rightarrow \mathbb{R}$ of the left boundary, as a solution of the Cauchy problem (40)-(41). It has to be memorized that the rhs of the integrodifferential Eq. (40) is given by the formula (39). Thus the third part of our plan is concluded.

Knowing w and λ_1 , one can calculate ρ_1, \ldots, ρ_r from the relations (26) and (22), the drift velocity v from Eqs. (34) and (39), and the pressure p from the following explicit formula:

$$p(t,x) = \operatorname{const}(t) + v \frac{\partial u}{\partial x}(t,x) + \int_{\lambda_1(t)}^{x} \left[\rho \left[b - \frac{\partial u}{\partial t} - u \frac{\partial u}{\partial x} \right] \right](t,y) dy , \quad (47)$$

where the mixture density ρ is given by Eq. (33), and where Eqs. (35) and (39) allow to calculate the velocity uof the local mass centers. Thus, the entire plan is concluded.

III. DISCUSSION

Theorem. If certain regularity assumptions [concerning the data (3) and (4)] and the quantitative condition (49) (concerning the diffusion coefficients $\Theta_1, \ldots, \Theta_r$) are fulfilled, then there exists the unique solution $w = (w_1, \ldots, w_r)$ of the problem (44)-(46). Moreover, the densities ρ_1, \ldots, ρ_r [relevant to the shifted deviations w_1, \ldots, w_r by the formula (25)] take non-negative values only.

Numerical solution of the above problem can be obtained by the Faedo-Galerkin method. The calculations were made for β phase of Cu-Al system. For the calculations the following data were applied:⁹ (1) boundaries of the sample, $\Lambda = 0.2$ cm; (2) initial concentration profiles, $c_{\rm Cu}(0,x) = 87$ wt %, $x \in [-\Lambda, 0]$ and $c_{\rm Cu}(0,x) = 89$ wt %, $x \in [0,\Lambda]$; (3) diffusion coefficients, $\Theta_{\rm Cu} = 3.8 \times 10^{-8}$ cm² s⁻¹ and $\Theta_{\rm Al} = 1.4 \times 10^{-8}$ cm² s⁻¹; (4) time of the process duration, T = 18 h; and (5) standard atomic masses of Cu and Al. In the Fig. 1, the aluminum profile concentration for time T = 18 h is shown. The reliable agreement between the calculated and experimental results can be seen.

An effective algebraic criterion for parabolicity (concerning the components diffusivities, i.e., $\Theta_1, \ldots, \Theta_r$) can be demonstrated. For simplicity let us regard the situation of constant diffusivities $\Theta_1, \ldots, \Theta_r$. Consider the following condition:

$$\delta + h \sum_{k=1}^{r} (\Theta_k - \delta) > 0 , \qquad (48)$$

where

$$\delta := \min_{1 \le i \le r} \Theta_i ,$$

 $h := 0$, when $\{\Theta_1 = \cdots = \Theta_r \text{ or } r = 2\}$,

and otherwise



FIG. 1. The distribution of aluminum in β Cu-Al binary diffusional couple shown for fixed, 18-h, time period.

$$h := \min \left\{ y < 0:4r + \sum_{k \neq j} \frac{\alpha_j + (r-1)\alpha_k - 1}{\alpha_k - y} = 0 \right\}$$

for some $j \in \{1, \dots, r\}$

where

$$\alpha_i := \frac{\Theta_i - \delta}{\sum_{k=1}^r (\Theta_k - \delta)} \; .$$

One can prove that for all $r \ge 2$:

$$h \ge -\left[\left(\frac{r-1}{2r}\right)^{1/2} - \frac{1}{2}\right]$$

and

$$h = -\left[\frac{1}{\sqrt{3}} - \frac{1}{2}\right] \max_{1 \le i \le 3} \alpha_i \quad \text{for } r = 3$$

If the condition (48) is satisfied, then the Eq. (44) is *parabolic* in the following sense:

$$\exists \mu \in]0, \infty [\forall \begin{cases} \Phi, \Psi \in H^{1}(-\Lambda, \Lambda; \mathbb{R}^{r}) ,\\ \sum_{i=1}^{r} \Phi_{i} = 1, \quad \sum_{i=1}^{r} \frac{\partial \Psi_{i}}{\partial z} = 0 , \end{cases}$$

$$(49)$$

$$\int_{-\Lambda}^{\Lambda} \left[\mathcal{A}_{\Phi(z)} \frac{\partial \Psi}{\partial z}(z) \right] \frac{\partial \Psi}{\partial z}(z) dz \ge \mu \int_{-\Lambda}^{\Lambda} \sum_{i=1}^{r} \left[\frac{\partial \Psi_{i}}{\partial z}(z) \right]^{2} dz ,$$

where $H^{1}(-\Lambda,\Lambda;\mathbb{R}^{r})$ denotes the Sobolev space of all absolutely continuous \mathbb{R}^{r} -valued curves having square integrable derivatives, and the operator

$$\mathcal{A}_{r}: \mathbb{1}^{\perp} \to \mathbb{1}^{\perp}$$

was defined by (43) for any $\kappa \in \mathbb{R}^r$, $\sum_{i=1}^r \kappa_i > 0$. The condition (49) provides a "regular diffusion" [compare implication (50) in this section]. In the case of the binary mixture (r=2), since h=0, the condition (48) holds and consequently, the condition (49) is satisfied.

In the case of multicomponent mixture $(r \ge 3)$ one can demonstrate an example of diffusivities $\Theta_1, \ldots, \Theta_r$, which does not satisfy the condition (48). In such a case the condition (49) may be not satisfied. Then one can speculate on the possibility of a gradient "blow-up" of the solution.

In the case of $T = \infty$ one can show the following asymptotical behavior of the solution: if (49) holds, then

$$\lim_{t \to \infty} \int_{-\Lambda}^{\Lambda} \sum_{i=1}^{r} [w_i(t,z)]^2 dz = 0 .$$
 (50)

Furthermore, $(d/dt) \int_{-\Lambda}^{\Lambda} \sum_{i=1}^{r} w_i(t,z)^2 dz \leq 0$ for all $t \in \mathbb{R}_+$. In the other words, if $t \to \infty$, then the variance of the random vector

(represents the concentrations at the moment t) converges to zero.

Ternary "up-hill diffusion." Let us assume a ternary mixture (r=3) showing the composition-independent diffusion coefficients, $\Theta_1, \Theta_2, \Theta_3$ (i.e., constant diffusivities). The function

$$\eta_i:=w_i+m_i:[0,T]\times[-\Lambda,\Lambda]\to\mathbb{R}_+$$

represents the spatially shifted molar ratio of the *i*th component. According to (44)-(46), the statement (η_1, η_2, η_3) is a solution of the initial-boundary-value problem:

$$\frac{\partial \eta_i}{\partial t} = \frac{\partial}{\partial z} \left[\Theta_i \frac{\partial \eta_i}{\partial z} - \eta_i \sum_{j=1}^3 \Theta_j \frac{\partial \eta_j}{\partial z} \right], \qquad (51)$$

$$\eta_i(0,z) = \frac{1}{cM_i} \mathring{\rho}_i(z) ,$$
 (52)

$$\frac{\partial \eta_i}{\partial z}(t,\pm\Lambda)=0.$$
(53)

In addition, from relations (27) and (28) it follows that $\eta_1 + \eta_2 + \eta_3 \equiv 1$. Let us assume that the spatial distribution of the shifted molar ratio of the third component, $\eta_3(t_*, \cdot)$ (at a moment $t_* \in [0, T]$) attains the maximal value at certain position $z_* \in [-\Lambda, \Lambda]$. In such a circumstance it is evident that

$$\eta_{3}(t_{*}, z_{*}) \ge m_{3} ,$$

$$0 = \frac{d}{dz} \eta_{3}(t_{*}, z) \bigg|_{z=z_{*}} = \frac{\partial \eta_{3}}{\partial z}(t_{*}, z_{*}) ,$$

$$0 \ge \frac{d^{2}}{dz^{2}} \eta_{3}(t_{*}, z) \bigg|_{z=z_{*}} = \frac{\partial^{2} \eta_{3}}{\partial z^{2}}(t_{*}, z_{*}) .$$
(54)

Thus, the differential equations (51) result in the following equality at the argument (t_*, z_*) :

$$\frac{\partial \eta_3}{\partial t} = \left[\Theta_2 \eta_3 + \Theta_3 (1 - \eta_3)\right] \frac{\partial^2 \eta_3}{\partial z^2} - \left(\Theta_1 - \Theta_2\right) \eta_3 \frac{\partial^2 \eta_1}{\partial z^2} .$$

From the above relation and the inequality (54) it results that the following conditions are equivalent:

$$\left[\Theta_2\eta_3 + \Theta_3(1-\eta_3)\right] \left| \frac{\partial^2 \eta_3}{\partial z^2} \right| < (\Theta_2 - \Theta_1)\eta_3 \frac{\partial^2 \eta_1}{\partial z^2} \quad (55)$$

at the argument (t_*, z_*) ;

$$\frac{\partial \eta_3}{\partial t}(t_*, z_*) > 0 .$$
(56)

Inequality (56) indicates up-hill diffusion of the third component at the moment t_* and at the position z_* . Indeed, then

$$\frac{d}{dt}\eta_3(t,z_*)\Big|_{t=t_*}>0$$

and consequently, there exists $\varepsilon > 0$ such that

$$\frac{\partial \eta_3}{\partial t}(t,z_*) > 0, \quad \eta_3(t,z_*) > \eta_3(t_*,z_*)$$

$$\frac{\partial w_3}{\partial t}(t,z_*) > 0, \quad w_3(t,z_*) > w_3(t_*,z_*)$$

for every $t \in]t_*, t_* + \varepsilon[$.

for every $t \in]t_*, t_* + \varepsilon[$

In other words, the deviations of the molar ratio of the third component from its average value increases during the period $]t_*, t_* + \varepsilon[$ of time, in particular, the maximal density of the third component in the mixture, increases.

Example. In order to generate the up-hill diffusion effect for the third component-the exact information on the Θ_1 , Θ_2 , and Θ_3 is not a prerequisite—it is sufficient to know that

$$\Theta_2 > \Theta_1 . \tag{57}$$

Let us put $t_*=0(\in[0,T])$, $z_*=0(\in[-\Lambda,\Lambda])$ and assume the following initial conditions in the relations (52):

$$\frac{1}{cM_1}\dot{\rho}_1(z) := \frac{1-\gamma}{3} - \gamma \cos\frac{\pi}{\Lambda}z ,$$
$$\frac{1}{cM_2}\dot{\rho}_2(z) := \frac{1-\gamma}{3} + \gamma \cos\frac{\pi}{\Lambda}z ,$$
$$\frac{1}{cM_3}\dot{\rho}_3 \equiv \frac{1+2\gamma}{3} \quad (\text{constant function}) ,$$

for an arbitrary fixed parameter $\gamma \in]0, \frac{1}{4}[$. Remark that all the initial mole fractions $\mathring{\eta}_i := (1/cM_i)\mathring{\rho}_i$ (i=1,2,3) attain the same maximum in the mixture, Fig. 2. Since

$$\frac{\partial^2 \eta_1}{\partial z^2}(t_*, z_*) = \frac{d^2}{dz^2} \hat{\eta}_1(z) \bigg|_{z=z_*}$$
$$= \gamma \left[\frac{\pi}{\Lambda} \right]^2 \cos \frac{\pi}{\Lambda} z \bigg|_{z=0} > 0$$

and inequality (57) holds, the inequality (55) is satisfied. Thereby, the condition (56) is satisfied and consequently, the maximum of the density of the third component increases in the period $]0, \varepsilon[$ of time for some positive ε .

Presented theory can be adapted to a more general case



FIG. 2. Up-hill diffusion in the ternary mixture; initial distribution of the molar ratios of components when $\Theta_2 > \Theta_1$.

or

of the variable viscosity coefficient:

$$v = v(\rho_1, \ldots, \rho_r),$$

i.e., to a case of the mixture in which viscosity is a function of all components densities. Moreover, the Navier-Stokes equation, Eq. (7), can be substituted for any other formula of local momentum conservation (e.g., Ref. 6). In such a case the formulated method of mathematical *disjoining* of dynamics and diffusion will be not violated.

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- ¹C. Wagner, in *Atom Movements* (American Society for Metals, Cleveland, Ohio, 1951).
- ²L. S. Darken, Trans. AIME 174, 184 (1948).
- ³R. W. Balluffi, Acta Metall. 8, 871 (1960).
- ⁴S. J. Prager, Chem. Phys. 21, 1344 (1953).
- ⁵M. Danielewski, Netsu Sokutei 20, 7 (1993).

- ⁶M. Danielewski, Defect Diffusion Forum 95-98, 125 (1993).
- ⁷D. D. Fitts, *Nonequilibrium Thermodynamics* (McGraw-Hill, New York, 1962), pp. 21, 44, and 88.
- ⁸A. J. Chorin and J. E. Marsden, A Mathematical Introduction to Fluid Mechanics (Springer-Verlag, New York, 1990), p. 10.
 ⁹A. D. Romig, J. Appl. Phys. 21, 3172 (1983).