Chapter 10
On the Spectrum of Relaxation Times of Coupled Diffusion and Rheological Processes in Media with Microstructure

Dmitrii S. Dudin and Ilya E. Keller

Abstract The effective diffusion and viscous linear coefficients is studied for the coupled set of equations with incorporating the processes of interdiffusion in a binary alloy, viscoelastic deformations, and microstructure changes. The technique developed in works of G.B. Stephenson, Z. Suo, and L. Brassart is used, but to study abnormally fast processes of chemical composition changing in metal alloys under intensive plastic deformations, the presence of microstructure was consistently regarded in the model. The microstructure is described by a scalar internal variable being the concentration of grain boundaries, and by the intensity of deviatoric inelastic strains associated with dislocation density of the crystal lattice. The model, preferred by specialists in atomic diffusion and based on the experimental method for determining the Kirkendall – Darken interdiffusion coefficients, is adopted as the equations of interdiffusion in a medium experiencing elastic and viscous deformations. The model problem of free axial deformation of a rod, constrained on the sides, with torsion is considered. For this problem, effective diffusion and viscous linear coefficients are determined for perturbating a homogeneous stationary solution. The equations for perturbations are reduced to an eigenvalue problem, which is addressed through computer algebra. In the long-wave and short-wave approximations, the relaxation of perturbations is characterized by a spectrum of effective diffusion coefficients and viscosity. The sensitivity of diffusion coefficients to thermodynamic and kinetic coefficients associated with microstructure is established. One of the effective diffusion coefficients can drastically increase, when those parameters are changed, and it can explain the abnormally fast diffusion of the alloy components.

Key words: Interdiffusion · Metal alloys · Viscoelastic deformations · Microstructure evolution · Coupled processes · High pressure torsion · Effective coefficients · Fast diffusion

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Dmitrii S. Dudin · Ilya E. Keller
Institute of Continuous Media Mechanics of the Ural Branch of Russian Academy of Science, Academician Korolev St., 1, Perm 614013, Russian Federation,
e-mail: dudin.d@icmm.ru, kie@icmm.ru

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10.1 Introduction

The work is devoted to study the possibilities of describing the coupled processes of viscoelastic deformations and interdiffusion in metal alloys by an effective model with consisting of connected diffusion and viscous elements and having a certain spectrum of characteristic times. It is some phenomenological description of the quite complex physical process to understand some anomalies of mechanodiffusion processes during mechanical alloying and intensive plastic deformations of solid and powder metals. In particular, some observed processes of decomposition, stratification of metallic solid solutions may have a rate many orders of magnitude higher than the rate of concentration diffusion [1]. Therefore, it is necessary to find out to what extent the coupled diffusion and rheological processes can explain these anomalies. In addition, the processes are usually accompanied by the evolution of microstructure in the crystal lattice of metal, and the effective kinetic coefficients are very structurally sensitive. Therefore, the connectivity of diffusion processes with microstructural ones should also be considered in this study. The work continues the researches started in [2, 3, 4], and the methodology of these works is taken as a basis. Elastic and viscous deformations are regarded within the shear compression scheme, and the evolution and migration of microstructure is described by a scalar variable. The connectivity of processes is considered both by thermodynamic coefficients and by the kinematics of diffusion processes in a deformable body. The work is based on the theory [4], in which, to superimpose diffusion processes on deformation ones, the velocity of material markers, relative to which the laws of diffusion are determined, is identified with the convective velocity. Another approaches to study coupled mechanodiffusion processes were considered in our work [5], and we afford to give some of them [6]-[11].

10.2 Deformations

It is assumed that at the reference time instant $t = 0$ the position of the material element of the continuum is given by the radius vector $\boldsymbol{R}$, and the volume, occupied by the material element, is denoted by dV_0. For the current time respective values $\boldsymbol{r}$, dV are introduced along with the displacement $\boldsymbol{u} = \boldsymbol{r} - \boldsymbol{R}$ and the total volumetric strain $\varepsilon_V = (dV - dV_0)/dV_0$. The total strain of the material element is assumed to be small and described by a tensor

$$\boldsymbol{\varepsilon} = \frac{1}{2}\left(\nabla\boldsymbol{u} + \boldsymbol{u}\nabla\right), \tag{10.1}$$

where ∇ is the gradient operator in the current configuration. The total strain consists of elastic $\boldsymbol{\varepsilon}^e$, viscous $\boldsymbol{\varepsilon}^v$, and diffusive $\boldsymbol{\varepsilon}^d$ components

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^e + \boldsymbol{\varepsilon}^v + \boldsymbol{\varepsilon}^d,$$

which are decomposed into spherical and deviatoric parts

$$\boldsymbol{\varepsilon} = \frac{1}{3}\varepsilon_V \boldsymbol{I} + \boldsymbol{e},\ \boldsymbol{\varepsilon}^e = \frac{1}{3}\varepsilon_V^e \boldsymbol{I} + \boldsymbol{e}^e,\ \boldsymbol{\varepsilon}^d = \frac{1}{3}\varepsilon_V^d \boldsymbol{I},\ \varepsilon^v = \boldsymbol{e}^v,$$

$$\mathrm{sp}(\boldsymbol{e}) = \mathrm{sp}(\boldsymbol{e}^e) = \mathrm{sp}(\boldsymbol{e}^v) = 0. \tag{10.2}$$

The kinematics of the continuum, concurrently undergoing deformations of rheological and diffusive nature, was considered by a number of authors [2, 3, 4, 11, 12, 13, 14]. They regarded both elastic and diffusive, viscous and diffusive, or all three components. The diffusion component of deformation is caused by a change in the chemical composition of the material element. In our work [5] it is noted that consideration of deformations of diffusive and rheological nature, regardless of deformation magnitude, requires an additional hypothesis which is related to the method used for measuring diffusion coefficients (Boltzmann method relative to the Matano plane or Darken – Kirkendall method relative to the inert markers). A number of similar hypotheses were formulated in [5] and nonequivalence of the corresponding coupled models of diffusion and deformation processes was shown. In this paper, as in [4], the diffusion frame of reference is associated with the inert markers, but elastic deformations are also considered along with viscous and diffusive ones.

Here a binary system, consisting of A and B components, is considered. The material element contains dN_A and dN_B moles of the corresponding components and it is characterized by the molar concentrations $C_A = dN_A/dV_0$ and $C_B = dN_B/dV_0$ in the reference configuration, and $c_A = dN_A/dV$, $c_B = dN_B/dV$ in the current configuration. For the material element, the molecular incompressibility condition is assumed. It means that the material element is continuously filled with the molar volumes of components V_A and V_B

$$dV = V_A dN_A + V_B dN_B + \varepsilon_V^e dV_0,$$

and it is written in terms of the swelling ratio $\Omega = dV/dV_0$

$$\Omega = V_A(\xi)\, C_A + V_B(\xi)\, C_B + \varepsilon_V^e, \tag{10.3}$$

where $\xi = C_B/(C_A + C_B)$ is the composition variable. Supposing $\Omega = \Omega\left(C_A, C_B, \varepsilon_V^e\right)$ it is obtained

$$\dot{\Omega} = \frac{\partial \Omega}{\partial C_A}\dot{C}_A + \frac{\partial \Omega}{\partial C_B}\dot{C}_B + \frac{\partial \Omega}{\partial \varepsilon_V^e}\dot{\varepsilon}_V^e, \tag{10.4}$$

where

$$\dot{a} = \frac{da}{dt} = \frac{\partial a}{\partial t} + \boldsymbol{v} \cdot \nabla a$$

is the material derivative of some variable a and $\boldsymbol{v} = \dot{\boldsymbol{u}}$ is the velocity of the material element. On the other hand, the material derivative of (10.3) is

$$\dot{\Omega} = \dot{V}_A C_A + \dot{V}_B C_B + V_A \dot{C}_A + V_B \dot{C}_B + \dot{\varepsilon}_V^e. \tag{10.5}$$

Direct comparison of (10.4) with (10.5) allows for deducing the compatibility conditions

$$V_A = \frac{\partial \Omega}{\partial C_A}, \quad V_B = \frac{\partial \Omega}{\partial C_B}, \quad \dot{V}_A C_A + \dot{V}_B C_B = 0, \quad \frac{\partial \Omega}{\partial \varepsilon_V^e} = 1. \tag{10.6}$$

Because of weak dependence of molar volumes on the composition variable for solid deformable bodies [15, 16] it is assumed that V_A = const, V_B = const. Therefore, condition $(10.6)_3$ is fulfilled automatically.

In the current configuration, explicit expressions for the volumetric strains ε_V^e and ε_V^d are useful to write. To do that, the swelling ratio Ω is represented as

$$\Omega = 1 + \varepsilon_V,$$

and using decomposition (10.2) of volumetric strains $\varepsilon_V = \varepsilon_V^d + \varepsilon_V^e$, expressions (10.3) and the definition for the molar concentrations in the current configuration $c_A = dN_A/dV$, $c_B = dN_B/dV$ is deduced

$$\varepsilon_V^e = (1+\varepsilon_V)(1 - V_A c_A - V_B c_B), \; \varepsilon_V^d = V_A C_A + V_B C_B - 1. \tag{10.7}$$

According to the second equation in (10.7), the volume strain due to diffusion ε_V^d is a homogeneous function of the first order for C_A and C_B. Definitions (10.7) generalize the molecular incompressibility condition $c_A V_A + c_B V_B = 1$ in the case of elastic strains.

10.3 Balance Equations

The system of coupled equations of diffusion and rheological processes with changes in microstructure includes the balance equations for variables describing the local chemical composition of a binary alloy, the momentum and microstructure density, and equations of state. As variables characterizing the chemical composition of a two-component mixture, the molar concentrations c_k, $k = A, B$ are taken and the diffusion fluxes relative to the material velocity $\boldsymbol{v}$ are introduced

$$\boldsymbol{j}_k = c_k (\boldsymbol{v}_k - \boldsymbol{v}),$$

where $\boldsymbol{v}_k$, $k = A, B$ are the velocities of the components in the current configuration. These diffusion fluxes are not coupled ($\boldsymbol{j}_A + \boldsymbol{j}_B \neq 0$), since the material velocity is not identified with the average velocity of multicomponent medium. For the same reason the balance equations for molar concentrations written without the volume production of components induced by chemical reactions

$$\frac{dc_k}{dt} + c_k \nabla \cdot \boldsymbol{v} = -\nabla \cdot \boldsymbol{j}_k, \; k = A, B \tag{10.8}$$

are independent. Similarly, the diffusion flux of microstructure is written relative to the material velocity

$$\boldsymbol{j}_H = h\left(\boldsymbol{v}_H - \boldsymbol{v}\right),$$

where h is the volume concentration of microstructure (the area of grain boundaries per unit volume of the material element in the current configuration), $\boldsymbol{v}_H$ is the migration rate of microstructure. The variable h satisfies the balance equation

$$\frac{dh}{dt} + h\nabla\cdot\boldsymbol{v} = -\nabla\cdot\boldsymbol{j}_H + p_H, \tag{10.9}$$

which includes the volume production of microstructure p_H. It is assumed that mechanical processes are much faster than diffusion ones, therefore the equilibrium equation is used

$$\nabla\cdot\boldsymbol{\sigma} = 0, \tag{10.10}$$

where $\boldsymbol{\sigma}$ is the Cauchy stress tensor.

During the derivation of the thermodynamic inequality, Eqs. (10.8) and (10.9), written in terms of the reference configuration, will be needed

$$\frac{dC_k}{dt} = -\overset{0}{\nabla}\cdot\boldsymbol{J}_k, \quad \frac{dH}{dt} = -\overset{0}{\nabla}\cdot\boldsymbol{J}_H + P_H, \quad \overset{0}{\nabla} = \frac{\partial}{\partial\boldsymbol{R}}, \quad k = A, B, \tag{10.11}$$

where $H = \Omega h$ is the microstructure concentration in the reference configuration, $P_H = \Omega p_H$ is the volumetric production of microstructure, and for the diffusion fluxes $\boldsymbol{J}_k$ and microstructure flux $\boldsymbol{J}_H$ in the reference configuration the connections $\overset{0}{\nabla}\cdot\boldsymbol{J}_k = \Omega\nabla\cdot\boldsymbol{j}_k$, $k = A, B$ and $\overset{0}{\nabla}\cdot\boldsymbol{J}_H = \Omega\nabla\cdot\boldsymbol{j}_H$ are valid [17].

10.4 The Helmholtz Free Energy

The Helmholtz free energy is key in the construction of constitutive relations, which will be derived in Sect. 10.6, and it affects the nature of the connectivity of the processes in question. In addition to the energy of grain boundaries, it is desirable to consider the dislocation energy, which is assumed to be proportional to the intensity of deviatoric viscous strains. It is supposed that for an isotropic material the density of free energy, assigned per unit volume of the reference configuration, is represented as

$$\psi = \psi\left(C_A, C_B, H, \varepsilon_V^e, I_2^e, I_2^v\right), \tag{10.12}$$

where H is the microstructure concentration, defined per unit volume of the reference configuration, $I_2^e = \boldsymbol{e}^e : \boldsymbol{e}^e$ is the second invariant of elastic deviatoric strain, $I_2^v = \boldsymbol{e}^v : \boldsymbol{e}^v$ is the second invariant of viscous deviatoric strain. The material derivative of (10.12) allows for getting

$$
\begin{gathered}
\dot{\psi} = \sum_{k=A,B} F_k \dot{C}_k + F_H \dot{H} + F^e_V \dot{\varepsilon}^e_V + F^e_I \dot{I}^e_2 + F_v \dot{I}^v_2, \\
F_k = \frac{\partial \psi}{\partial C_k},\ k = A,B,\ F_H = \frac{\partial \psi}{\partial H},\ F^e_V = \frac{\partial \psi}{\partial \varepsilon^e_V},\ F^e_I = \frac{\partial \psi}{\partial I^e_2},\ F_v = \frac{\partial \psi}{\partial I^v_2}
\end{gathered}
\tag{10.13}
$$

where $F_k,\ k = A,B$ are the partial mixing energies, F_H is the microstructure energy, F^e_V and F^e_I are the constituents of elastic deformation energies, F_v is the dislocation energy. In the study of linearized problems, the following expansion of the function ψ is accepted

$$
\begin{aligned}
\psi \approx{}& f_A \frac{(\Delta C_A)^2}{2} + f_B \frac{(\Delta C_B)^2}{2} + f_H \frac{(\Delta H)^2}{2} + K \frac{\left(\Delta \varepsilon^e_V\right)^2}{2} + f_v \frac{\left(\Delta I^v_2\right)^2}{2} + G I^e_2 \\
&+ f_{AH} \Delta C_A \Delta H + f_{BH} \Delta C_B \Delta H + f_{Hv} \Delta H \Delta I^v_2 + L(C_A, C_B, H, \varepsilon^e_V, I^v_2),
\end{aligned}
\tag{10.14}
$$

up to quadratic terms near the perturbed state $C_A \equiv C^0_A,\ C_B \equiv C^0_B,\ H \equiv H_0,\ \varepsilon^e_V \equiv \varepsilon^{e0}_V,\ I^e_2 \equiv I^{e0}_2 = 0$ and $I^v_2 \equiv I^{v0}_2$. Expansion (10.14) contains the most significant thermodynamic coefficients describing the coupled processes. In the derivation of (10.14) Eq. (10.12) is used, and the following designations are introduced: L is the linear function of its arguments, $\Delta(\cdot) = (\cdot) - (\cdot)_0$ is the increment of a variable, K is the bulk modulus, and G is the shear modulus. The quadratic terms considered significantly affect the type of physical relations discussed in Sect. 10.6. Components of the Helmholtz free energy (10.13), given (10.14), have the form

$$
\begin{aligned}
F_A &= f_A \Delta C_A + f_{AH} \Delta H + F^0_A,\ F_B = f_B \Delta C_B + f_{BH} \Delta H + F^0_B, \\
F_H &= f_H \Delta H + f_{AH} \Delta C_A + f_{BH} \Delta C_B + f_{Hv} \Delta I^v_2 + F^0_H, \\
F^e_V &= K \Delta \varepsilon^e_V + F^0_e,\ F^e_I = G,\ F_v = f_v \Delta I^v_2 + f_{Hv} \Delta H + G^0_v,
\end{aligned}
\tag{10.15}
$$

All coefficients, situated on the right side of expressions (10.16), are functions of the variables at the perturbed state $f = f\left(C^0_A, C^0_B, H_0, \varepsilon^{e0}_V, I^{v0}_2\right)$.

10.5 Thermodynamic Inequality

To derive a restriction on the form of constitutive relations the theory of classical thermodynamics of irreversible processes is employed. Quasi-static processes occurring under isothermal conditions are considered. For them the second law of thermodynamics is written as a requirement that the power supplying the system does not exceed the rate of change of free energy

$$
\int_{V_0} \dot{\psi} dV_0 + \int_{S_0} \left(\mu_A \boldsymbol{J}_A + \mu_B \boldsymbol{J}_B + \mu_H \boldsymbol{J}_H\right) \cdot N dS_0 - \int_{V_0} \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} \Omega dV_0 \leq 0,
\tag{10.16}
$$

where $\mu_k,\ k = A,B$ are the chemical potentials, $\boldsymbol{J}_k,\ k = A,B$ are the diffusion fluxes at the reference configuration, $\boldsymbol{\sigma}$ is the Cauchy stress tensor, $S_0 = \partial V_0$ and V_0 are the surface and volume of body at the reference configuration. Using the divergence theorem and Eqs. (10.11) it can be obtained that

$$\int\limits_{V_0} \left(\Omega\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \dot{\psi} + \sum_{k=A,B} \left(\mu_k \dot{C}_k - \boldsymbol{J}_k \cdot \overset{0}{\nabla} \mu_k \right) + \mu_H \dot{H} \right.$$
$$\left. - \boldsymbol{J}_H \cdot \overset{0}{\nabla} \mu_H - P_H \mu_H \right) dV_0 \geq 0. \qquad (10.17)$$

Then the local form of thermodynamic inequality (10.16) is deduced

$$\Omega\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} + \sum_{k=A,B} \left((\mu_k - F_k)\, \dot{C}_k - \boldsymbol{J}_k \cdot \overset{0}{\nabla} \mu_k \right) + (\mu_H - F_H)\, \dot{H} - \boldsymbol{J}_H \cdot \overset{0}{\nabla} \mu_H$$
$$- \mu_H P_H - F_V^e \dot{\varepsilon}_V^e - F_I^e \dot{I}_2^e - F_v \dot{I}_2^v \geq 0. \quad (10.18)$$

In (10.18) expressions (10.13) and (10.14) are used. Applying to (10.18) a decomposition $\boldsymbol{\sigma} = \sigma_m \boldsymbol{I} + \boldsymbol{s}$, its consequence $\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} = \sigma_m \dot{\varepsilon}_V + \boldsymbol{s} : \dot{\boldsymbol{e}}$, Eq. (10.2), and definitions $I_2^v = \boldsymbol{e}^v : \boldsymbol{e}^v$, $I_2^e = \boldsymbol{e}^e : \boldsymbol{e}^e$, inequality (10.18) takes the form:

$$\sum_{k=A,B} \left(\left(\frac{\mu_k - F_k}{V_k} + \sigma_m \right) \frac{V_k \dot{C}_k}{\Omega} - \frac{\boldsymbol{J}_k \cdot \overset{0}{\nabla} \mu_k}{\Omega} \right) + (\mu_H - F_H)\, \frac{\dot{H}}{\Omega} - \frac{\boldsymbol{J}_H \cdot \overset{0}{\nabla} \mu_H}{\Omega}$$
$$- \mu_H \frac{P_H}{\Omega} + \left(\boldsymbol{s} - \frac{2F_v \boldsymbol{e}^v}{\Omega} \right) : \dot{\boldsymbol{e}}^v + \left(\boldsymbol{s} - \frac{2F_I^e \boldsymbol{e}^e}{\Omega} \right) : \dot{\boldsymbol{e}}^e + \left(\sigma_m - \frac{F_V^e}{\Omega} \right) \dot{\varepsilon}_V^e \geq 0. \, (10.19)$$

To write the constitutive equations in the actual configuration, the relations between the state variables, specified per unit volume in the actual and reference configurations, are used: the molar concentrations $c_k = C_k/\Omega$, $k = A,B$; the true volumetric penetration rates $i_k = V_k \dot{C}_k/\Omega = V_k \dot{c}_k + c_k V_k \nabla \cdot \boldsymbol{v}$, $k = A,B$ [4]; the diffusion fluxes $\boldsymbol{J}_k \cdot \overset{0}{\nabla} \mu_k = \Omega \boldsymbol{j}_k \cdot \nabla \mu_k$, $k = A,B$; the true rate of microstructure change $i_H = \dot{H}/\Omega = \dot{h} + h \nabla \cdot \boldsymbol{v}$; the microstructure flux $\boldsymbol{J}_H \cdot \overset{0}{\nabla} \mu_H = \Omega \boldsymbol{j}_H \cdot \nabla \mu_H$; the microstructure production $p_H = P_H/\Omega$. Finally, thermodynamic inequality (10.19) takes the form:

$$\sum_{k=A,B} \left(\left(\frac{\mu_k - F_k}{V_k} + \sigma_m \right) i_k - \boldsymbol{j}_k \cdot \nabla \mu_k \right) + (\mu_H - F_H)\, i_H - \boldsymbol{j}_H \cdot \nabla \mu_H$$
$$- \mu_H p_H + \left(\boldsymbol{s} - \frac{2F_v \boldsymbol{e}^v}{\Omega} \right) : \dot{\boldsymbol{e}}^v + \left(\boldsymbol{s} - \frac{2F_I^e \boldsymbol{e}^e}{\Omega} \right) : \dot{\boldsymbol{e}}^e + \left(\sigma_m - \frac{F_V^e}{\Omega} \right) \dot{\varepsilon}_V^e \geq 0. \quad (10.20)$$

The equality sign in (10.20) corresponds to the course of reversible elastic deformation processes. Microstructure changes, viscous deformations, and diffusive mass transfer are dissipative processes and they correspond to a strict inequality in (10.20).

10.6 Constitutive Equations

Thermodynamic inequality (10.20) is split into reversible and irreversible parts

$$\begin{aligned}
&\sum_{k=A,B}\left(\left(\frac{\mu_k - F_k}{V_k} + \sigma_m\right) i_k\right) + (\mu_H - F_H)\, i_H + \left(\boldsymbol{s} - \frac{2F_I^e \boldsymbol{e}^e}{\Omega}\right) : \dot{\boldsymbol{e}}^e \\
&\qquad\qquad + \left(\sigma_m - \frac{F_V^e}{\Omega}\right)\dot{\varepsilon}_V^e = 0, \\
&-\sum_{k=A,B} \boldsymbol{j}_k \cdot \nabla\mu_k - \boldsymbol{j}_H \cdot \nabla\mu_H - \mu_H p_H + \left(\boldsymbol{s} - \frac{2F_v \boldsymbol{e}^v}{\Omega}\right) : \dot{\boldsymbol{e}}^v \geq 0.
\end{aligned} \tag{10.21}$$

In [4] the terms with $i_k,\ k = A,B$ are assumed dissipative; here $i_k,\ k = A,B$ and i_H are assumed as conservative because of their weak effect on the relaxation times presented in Sect. 10.8. Since the velocities $i_k,\ k = A,B,\ i_H,\ \dot{\boldsymbol{e}}^e$ and $\dot{\varepsilon}_V^e$ are independent, the solution of the first equation of system (10.21) is given by the relations

$$\mu_k = F_k - \sigma_m V_k,\ k = A,B, \quad \mu_H = F_H, \quad \boldsymbol{s} = \frac{2F_I^e \boldsymbol{e}^e}{\Omega}, \quad \sigma_m = \frac{F_V^e}{\Omega}. \tag{10.22}$$

Applying the molecular incompressibility condition leads to appearing the term σ_m in expressions for chemical potentials μ_k [4]. The last two equations in (10.22), given F_V^e, F_I^e from (10.16) and the smallness of deformations $\Omega \approx 1$, are reduced to Hooke's law

$$\boldsymbol{s} = 2G\boldsymbol{e}^e,\ \sigma_m = K\varepsilon_V^e. \tag{10.23}$$

Particular solution of inequality (10.21) without cross terms is written in the form of quasi-linear relations

$$\begin{aligned}
&\boldsymbol{j}_k = -c_k M_k \nabla\mu_k, \boldsymbol{j}_H = -h M_H \nabla\mu_H,\ p_H = -\beta_H \mu_H,\ \boldsymbol{s} = \frac{2F_v \boldsymbol{e}^v}{\Omega} + 2\eta\dot{\boldsymbol{e}}^v, \\
&M_k > 0,\ M_H > 0,\ \beta_H > 0,\ \eta > 0,\ k = A,B
\end{aligned} \tag{10.24}$$

Using expressions for potentials μ_k, μ_H from (10.22), components of the Helmholtz free energy (10.16), and the definition of variables in the current configuration $C_A = \Omega c_A,\ C_B = \Omega c_B,\ H = \Omega h$ with $\Omega \approx 1$, the following expressions are obtained

$$\begin{aligned}\boldsymbol{j}_k &= -c_k M_k \left(f_k \nabla c_k + f_{kH} \nabla h - V_k \nabla \sigma_m\right), \ k = A, B, \\ \boldsymbol{j}_H &= -h M_H \left(f_H \nabla h + f_{AH} \nabla c_A + f_{BH} \nabla c_B + f_{Hv} \nabla I_2^v\right), \\ p_H &= -\beta_H \left(f_H \Delta h + f_{AH} \Delta c_A + f_{BH} \Delta c_B + f_{Hv} \Delta I_2^v + F_H^0\right), \\ \boldsymbol{s} &= 2\eta \dot{\boldsymbol{e}}^v + 2\left(f_v \Delta I_2^v + f_{Hv} \Delta H + G_v^0\right) \boldsymbol{e}^v\end{aligned} \tag{10.25}$$

To describe the effect of abnormally fast diffusion of components under intensive plastic deformations, in equations for diffusion fluxes (10.25) the gradients of microstructural variable and average stresses are provided, which are capable of both accelerating and decelerating diffusion process. The nonzero flux of microstructural variable $\boldsymbol{j}_H$ due to the connectivity of the equations also affect the diffusion fluxes. Constitutive relations (10.23), (10.25), approximations (10.1), (10.7), and balance equations (10.8) — (10.10) are the system of coupled equations of diffusion and deformation spatial problem with microstructural changes in an isotropic media.

10.7 Model Problem and its Equations

The influence of rheological processes and microstructure evolution on diffusion under the formulated coupled set of equations will be investigated using the simplest one-dimensional problem, which is expressed by the following assumptions:

- Components are able to diffuse only along one coordinate

$$c_A = c_A(x,t), \ c_B = c_B(x,t) \tag{10.26}$$

- All components of the total strain tensor are equal to zero except for

$$\varepsilon_{xx} = \varepsilon(x,t) \neq 0, \ \varepsilon_{yz} \equiv \gamma_0 \neq 0 \tag{10.27}$$

- All components of the stress tensor are zero except for

$$\sigma_{yy} = \sigma_{zz} = \sigma(x,t) \neq 0, \ \sigma_{yz} = \tau(x,t) \neq 0 \tag{10.28}$$

- Microstructural changes occur only along the considered coordinate

$$h = h(x,t) \tag{10.29}$$

The examined type of stress and strain fields satisfies by default the equilibrium equation and the deformation compatibility conditions. Applying hypotheses (10.26) — (10.29) to model equations (10.1), (10.7), (10.23) and (10.25) — (10.10) gives a nonlinear system of one-dimensional partial differential equations having a homogeneous stationary solution

$$\sigma_m(x,t) \equiv \sigma_m^0, \ \tau(x,t) \equiv \tau_0, \ h(x,t) \equiv h_0, \ c_A(x,t) \equiv c_A^0, \ c_B(x,t) \equiv c_B^0. \tag{10.30}$$

In the vicinity of solution (10.30) the behavior of small perturbations is investigated in Sect. 10.8.

To obtain the set of equations, the certain treatment is conducted. First, in Eqs. (10.24) the hypothesis $\eta = 0$ is accepted, which is justified by the fact that the shear viscosity does not affect the diffusion processes in the perturbed state [13].

Then the expressions for ε_V and σ_m are deduced. For that it is derived $\boldsymbol{e}^e = \boldsymbol{s}/(2G)$, $\boldsymbol{e}^v = \boldsymbol{s}/(2F_v)$, therefore the total deviatoric strain is defined by $\boldsymbol{e} = \boldsymbol{e}^e + \boldsymbol{e}^v = (1/G + 1/F_v)\boldsymbol{s}/2 = \boldsymbol{s}/(2G_{ev})$. The components of deviatoric tensors are determined $s_{xx} = -2\sigma/3 = -\sigma_m$, $e_{xx} = 2\varepsilon_V/3$, which, given the constitutive relation $s_{xx} = 2G_{ev}e_{xx}$, provide $\sigma_m = -4G_{ev}\varepsilon_V/3$ (other diagonal components give the same expression). Because of $\varepsilon_V = \varepsilon_{xx}$ and $\varepsilon_{xx} \ll 1$, G_{ev} can be considered as constant in linear approximation of σ_m, thus the relation $\sigma_m = -4G_0\varepsilon_V/3$ with $1/G_0 = 1/G + 1/G_v^0$ is valid. Eventually, the system of three equations is solved: $\sigma_m = -4G_0\varepsilon_V/3, \sigma_m = K\varepsilon_V^e$, $\varepsilon_V^e = (1+\varepsilon_V)(1 - c_A V_A - c_B V_B) \approx \varepsilon_V^{e0}(1+\varepsilon_V) - V_A\Delta c_A - V_B\Delta c_B$ at $1 - V_A c_A^0 - V_B c_B^0 = \varepsilon_V^{e0}/(1+\varepsilon_V^{e0}) \approx \varepsilon_V^{e0}$, $\varepsilon_V^{e0} \ll 1$. The solution is the following:

$$\varepsilon_V = \frac{V_A\Delta c_A + V_B\Delta c_B - \varepsilon_V^{e0}}{k_G + \varepsilon_V^{e0}}, \sigma_m = -\frac{4G_0}{3}\varepsilon_V, k_G = \frac{4G_0}{3K}, G_0 = \frac{GG_v^0}{G+G_v^0}. \quad (10.31)$$

The above variables and coefficients with the upper index 0 correspond to the perturbed state and they coincide with the designations in Sect. 10.4.

A relation for perturbation of the second invariant of viscous strains is also required. For that purpose, I_2^v is expanded in series up to linear terms by the components of viscous deviatoric strains $e_{xx}^v = \varepsilon_v$, $e_{yy}^v = \varepsilon_{v\perp}$, $e_{yz}^p = \gamma_v/2$ (the rest equal to zero) that gives $\Delta I_2^v = 2\varepsilon_v^0\Delta\varepsilon_v + 2\varepsilon_{v\perp}^0\Delta\varepsilon_{v\perp} + \gamma_v^0\Delta\gamma_v$. Further, the relation $\gamma_v^0 \gg \varepsilon_v^0, \varepsilon_{v\perp}^0$ is taken, which provides $\Delta I_2^v = \gamma_v^0\Delta\gamma_v$. The expression for $\Delta\gamma_v$ follows from $\gamma_v = \gamma_0 - \gamma_e = \gamma_0 - \tau/G$, where γ_0 is the shear strain in the perturbed state, and it gives $\Delta\gamma_v = -\Delta\tau/G$ with $\Delta\tau = \Delta G_{ev}\gamma_0 = \tau_0\Delta G/G_0 = \tau_0 G/(2G_v^0(G+G_v^0))\left(f_{Hv}\Delta h + f_v\Delta I_2^v\right)$. Solving the equation $\Delta I_2^v = \gamma_v^0\Delta\gamma_v(\Delta I_2^v)$ relative to ΔI_2^v with $\Delta\gamma_v = -\Delta\tau/G$ and $\gamma_v^0 = \tau_0/F_v^0 = \gamma_0 - \tau_0/G$ it is finally received

$$\Delta I_2^v = -\frac{f_{Hv}}{f_v + \frac{2(G_v^0+G)}{\gamma_0^2}\left(1+\frac{G_v^0}{G}\right)^2}\Delta h, \ \tau_0 = G_0\gamma_0. \quad (10.32)$$

From (10.25) expressions for the diffusion fluxes and microstructure flux are defined. They are written in a linearized form

$$\begin{aligned} j_k &= -D_k\left(\frac{\partial c_k}{\partial x} + \frac{f_{kH}}{f_k}\frac{\partial h}{\partial x} - \frac{V_k}{f_k}\frac{\partial \sigma_m}{\partial x}\right), \ k = A, B, \\ j_H &= -D_H\left(\frac{\partial h}{\partial x} + \frac{f_{AH}}{f_H}\frac{\partial c_A}{\partial x} + \frac{f_{BH}}{f_H}\frac{\partial c_B}{\partial x} + \frac{f_{Hv}}{f_H}\frac{\partial I_2^v}{\partial x}\right), \end{aligned} \quad (10.33)$$

where $D_k \equiv c_k^0 M_k f_k$ is the diffusion coefficients of components k, $D_H \equiv h_0 M_H f_H$ is the coefficient determining microstructure mobility.

Linearized balance equations of components (10.8) and microstructure (10.9)

$$\begin{gathered}\frac{\partial c_k}{\partial t}+c_k^0\frac{\partial \varepsilon_V}{\partial t}=-\frac{\partial j_k}{\partial x},\ \frac{\partial h}{\partial t}+h_0\frac{\partial \varepsilon_V}{\partial t}=-\frac{\partial j_H}{\partial x}+p_H,\ k=A,B,\\ p_H=-\beta_H\left(f_H\Delta h+f_{AH}\Delta c_A+f_{BH}\Delta c_B+f_{Hv}\Delta I_2^v+F_H^0\right)\end{gathered} \tag{10.34}$$

along with (10.31) — (10.33) are the system of linear coupled differential equations of the model problem.

10.8 Diffusion Coefficients in Coupled System

For a set of equations (10.31) — (10.34) linearized in the vicinity of a homogeneous stationary solution (10.30) the perturbed solutions are considered

$$\begin{aligned}c_k(x,t)&=c_k^0+\hat{c}_k\exp\left(-\frac{t}{\tau}\right)\sin\left(\frac{2\pi x}{\lambda}\right),\ k=A,B\\ h(x,t)&=h_0+\hat{h}\exp\left(-\frac{t}{\tau}\right)\sin\left(\frac{2\pi x}{\lambda}\right)\end{aligned} \tag{10.35}$$

where $\hat{c}_A,\ \hat{c}_B,\ \hat{h}\in R, |\hat{c}_A|,\ |\hat{c}_B|,\ |\hat{h}|\ll 1, \tau$ is the relaxation time, λ is the perturbation wavelength.

Solution (10.35) must satisfy the linearized system of equations, which is equivalent to solving an eigenvalue problem with a third-order eigenvalue equation for τ. Positive solutions of the equation $\tau=\tau_k(\lambda),\ k=1,2,3$ and the corresponding eigenvectors $\hat{\boldsymbol{u}}_k=\left(\hat{c}_{Ak},\hat{c}_{Bk},\hat{h}_k\right),\ k=1,2,3$ are determined. If for a particular branch $\tau=\tau_{k0}(\lambda)$ the eigenvector has the form $\hat{\boldsymbol{u}}_{k0}=\left(0,0,\hat{h}_{k0}\right)$, then relaxation processes are controlled by microstructure changes. Otherwise, at $\hat{\boldsymbol{u}}_{k0}=(\hat{c}_{Ak0},\hat{c}_{Bk0},0)$ the relaxation is determined by diffusive mass transfer and stresses, inextricably associated with changes in c_A and c_B (10.31). Finally, if $\hat{\boldsymbol{u}}_{k0}=\left(\hat{c}_{Ak0},\hat{c}_{Bk0},\hat{h}_{k0}\right)$ is carried out, all the processes in question affect the relaxation. This method was used earlier in [2, 4].

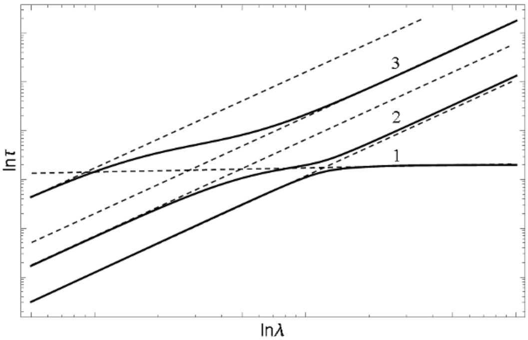
In Fig. 10.1 dependences $\tau=\tau_k(\lambda),\ k=1,2,3$ are shown. The limiting cases $\lambda\longrightarrow 0$ and $\lambda\longrightarrow\infty$ correspond to viscous or diffusive relaxation processes:

- The viscous (horizontal) asymptotic is determined by the constant relaxation time $\tau\equiv\tau_v$. In this limit, the processes are described by an equation of the type

$$\frac{\partial \boldsymbol{u}}{\partial t}=-\frac{\boldsymbol{u}}{\tau_v},$$

with $\boldsymbol{u}=\hat{\boldsymbol{u}}\exp\left(-t/\tau_v\right)\sin\left(2\pi x/\lambda\right)$

Fig. 10.1 Branches of the relaxation times and their asymptotics



- The diffusion (oblique) asymptotics are determined by the interdiffusion coefficient D at $\tau = \lambda^2/4\pi^2 D$. In this limit, the relaxation process is described by an equation of the type
$$\frac{\partial \boldsymbol{u}}{\partial t} = D\frac{\partial^2 \boldsymbol{u}}{\partial x^2}$$
with $\boldsymbol{u} = \hat{\boldsymbol{u}} \exp\left(-4\pi^2 t/\lambda^2\right) \sin\left(2\pi x/\lambda\right)$. The equation written for concentrations is called Fick's second law.

In the limit at $\lambda \to 0$ a cubic equation for D_0 is obtained. The exact solution of it is cumbersome and difficult to analyze, and for this reason an approximate solution is used. According to Vieta's theorem, solutions of the cubic equation $aD_0^3 + bD_0^2 + cD_0 + d = 0$ satisfy the system

$$D_1^0 + D_2^0 + D_3^0 = -\frac{b}{a},\ D_1^0 D_2^0 + D_1^0 D_3^0 + D_2^0 D_3^0 = \frac{c}{a},\ D_1^0 D_2^0 D_3^0 = -\frac{d}{a} \tag{10.36}$$

Suppose that $D_1^0 \gg D_2^0 \gg D_3^0$, then the system (10.36) has the solution

$$D_1^0 \approx -\frac{b}{a},\ D_2^0 \approx -\frac{c}{b},\ D_3^0 \approx -\frac{d}{c} \tag{10.37}$$

Approximate solution (10.37) has an acceptable accuracy (not exceeding 11% for any coefficient) already with the ratio $D_1^0 = 10D_2^0 = 100D_3^0$. For D_k^0, $k = 1,2,3$ the eigenvectors have the form $\hat{\boldsymbol{u}}_k^0 = \left(\hat{c}_{Ak}^0, \hat{c}_{Bk}^0, \hat{h}_k^0\right)$.

For the maximum of three diffusion coefficients, there is the following expression

$$\begin{aligned} D_1^0 &= e_A D_A + e_B D_B + e_H D_H, \\ e_k &= \frac{1}{k_G}\left(1 + k_G - \phi_k^0 - h_0 V_k \frac{f_{kH}}{f_k} + K k_G \frac{V_k^2}{f_k}\right),\ k = A, B, \\ e_H &= \frac{1+k_G}{k_G}\left(1 - \frac{f_{Hv}^2}{f_H\left(f_v + \frac{2(G+G_v^0)}{\gamma_0^2}\left(1 + \frac{G_v^0}{G}\right)\right)}\right), \end{aligned} \tag{10.38}$$

where the coefficients e_k, $k = A, B$, e_H are dimensionless, and $\phi_k^0 = c_k^0 V_k$, $k = A, B$ are the volume fractions of components k at the perturbed state. The coefficient D_1^0 in (10.38) meets a structural scheme with a sequential connection of three diffusion elements and the diffusion rate is limited by the fastest component. For example, assume that $D_A \gg D_B \gg D_H$, then $D_1^0 = e_A D_A$ can be derived. In the absence of stress gradients and microstructure, the Darken interdiffusion coefficient $D_1^0 = D_A + D_B$, explained the Kirkendall experiment, is occured [18, 19]. The value of D_2^0 is defined as

$$
\begin{aligned}
D_2^0 &= \frac{e_{AH} D_A D_H + e_{BH} D_B D_H + e_{AB} D_A D_B}{e_A D_A + e_B D_B + e_H D_H},\\
e_{AB} &= 1 + \frac{\varepsilon_V^{e0}}{k_G} + K\left(\frac{V_A^2}{f_A} + \frac{V_B^2}{f_B}\right) - \frac{h_0}{k_G}\left(\frac{f_{AH} V_A}{f_A} + \frac{f_{BH} V_B}{f_B}\right),\\
e_{kH} &= (c_0 - c_k^0) V_k \frac{f_{AH} f_{BH}}{k_G f_k f_H} + \frac{e_H}{1 + k_G}\left(1 + k_G - \phi_k^0 + K k_G \frac{V_k^2}{f_k}\right)\\
&\quad - \frac{f_{kH}^2}{f_k f_H k_G}(1 + k_G - \phi_k^0), \; k = A, B.
\end{aligned}
\tag{10.39}
$$

Similarly, suppose $D_A \gg D_B \gg D_H$ in (10.39) that gives $D_2^0 = e_{AB} D_B$. Thus, the diffusion rate is determined by the slow flux of component B. In the case of concentration diffusion, there is the Nazarov – Gurov interdiffusion coefficient $D_2^0 = D_A D_B / (D_A + D_B)$ [20]. The third diffusion coefficient has the following structure

$$
\begin{aligned}
D_3^0 &= \frac{e_{AB}^H D_A D_B D_H}{e_{AH} D_A D_H + e_{BH} D_B D_H + e_{AB} D_A D_B},\\
e_{AB}^H &= \frac{k_G e_H}{1 + k_G}\left(1 + \frac{\varepsilon_V^{e0}}{k_G} + K\left(\frac{V_A^2}{f_A} + \frac{V_B^2}{f_B}\right)\right) - \frac{K\,(f_{AH} V_B - f_{BH} V_A)^2}{f_A f_B f_H}\\
&\quad - \frac{k_G + \varepsilon_V^{e0}}{k_G f_H}\left(\frac{f_{AH}^2}{f_A} + \frac{f_{BH}^2}{f_B}\right).
\end{aligned}
\tag{10.40}
$$

The coefficient D_3^0 in (10.40) meets a structural scheme with a parallel connection of diffusion elements and for the case $D_A \gg D_B \gg D_H$ the relation $D_3^0 = e_{AB}^H D_H / e^{AB}$ is fair. Thereby, the relaxation time is determined by the microstructure flux. The coefficients in (10.38) — (10.40) correspond to small relaxation times because of $\lim_{\lambda \to 0} \tau = \lim_{\lambda \to 0} \lambda^2 / 4\pi^2 D = 0$, and they are able to describe the fast interdiffusion processes caused by the microstructural features and (or) the dynamics of microstructure development.

At $\lambda \longrightarrow \infty$, the quadratic equation $aD^2 + bD + c = 0$ and the linear equation for τ_3^∞ are obtained. The approximate solution of the quadratic equation is constructed similar to (10.37) under the assumption $D_1^\infty \gg D_2^\infty$. On diffusion asymptotes the eigenvectors have the form $\hat{\boldsymbol{u}}_k^\infty = \left(\hat{c}_{Ak}^\infty, \hat{c}_{Bk}^\infty, \hat{h}_k^\infty\right)$, $k = 1, 2$. The first coefficient D_1^∞ is defined as follows

$$\begin{aligned} D_1^\infty &= e_A^\infty D_A + e_B^\infty D_B, \\ e_k^\infty &= (c_0 - c_k^0)\frac{f_{AH} f_{BH}}{k_G f_H e_H f_k} + \frac{1}{1+k_G}\left(1 + k_G - \phi_k^0 + k_G K \frac{V_k^2}{f_k}\right) \\ &- \frac{1+k_G-\phi_k^0}{k_G f_H e_H}\frac{f_{kH}^2}{f_k}, \; k = A, B \end{aligned} \tag{10.41}$$

and it meets a structural scheme with a sequential connection of two diffusion elements. In the absence of stresses, microstructure, and shear deformations, the coefficient D_1^∞ in (10.41) determines the Darken interdiffusion. The second coefficient D_2^∞ corresponds to a structural scheme with a parallel connection of diffusion elements

$$\begin{aligned} D_2^\infty &= \frac{e_{AB}^\infty D_A D_B}{e_A^\infty D_A + e_B^\infty D_B}, \\ e_{AB}^\infty &= \frac{K V_A^2 V_B^2}{f_A f_B f_H e_H}\left(\frac{f_{BH}}{V_B} - \frac{f_{AH}}{V_A}\right)^2 + \frac{k_G + \varepsilon_V^{e0}}{k_G f_H e_H}\sum_{k=A,B}\frac{f_{kH}^2}{f_k} \\ &- \tfrac{1}{1+k_G}\left(k_G + \varepsilon_V^{e0} + k_G K \textstyle\sum_{k=A,B}\tfrac{V_k^2}{f_k}\right) \end{aligned} \tag{10.42}$$

and it is reduced to the Nazarov – Gurov interdiffusion coefficient at concentration diffusion. The coefficients in (10.41) — (10.42) can describe rather slow diffusion processes due to their conformity to large relaxation times $\lim_{\lambda\to\infty}\tau = \lim_{\lambda\to\infty}\lambda^2/4\pi^2 D \to \infty$. The viscous relaxation time for the third branch τ_v^∞ has the form

$$\tau_3^\infty = \frac{1+k_G}{k_G \beta_H f_H e_H}. \tag{10.43}$$

The asymptote meets the eigenvector $\hat{\boldsymbol{u}}_3^\infty = \left(0, 0, \hat{h}_3^\infty\right)$, therefore it characterizes the microstructure relaxation in the absence of its mobility and diffusion of components.

In Fig. 10.2 the influence of thermodynamic f_{AH}, f_{BH}, e_H and kinetic D_H coefficients on the interdiffusion coefficients, determined for the asymptotic cases $\lambda \to 0$ and $\lambda \to \infty$, is shown for a coupled system. For this purpose, the dimensionless functions $\tilde{D}_k^{0,\infty}(e_H) = D_k^{0,\infty}(e_H)/D_k^{0,\infty}(1)$, $\tilde{D}_k^0(D_H) = D_k^0(D_H)/D_k^0(0)$, and $\tilde{D}_k^{0,\infty}(f_{kH}) = D_k^{0,\infty}(f_{kH})/D_k^{0,\infty}(0)$, $k = A, B$ are considered. They are constructed in the coordinates of their argument, when the remaining coefficients being parameters of function are fixed. Depending on the parameter values, the qualitative graphs, shown by solid or dotted line, are different. The accepted parameters and range of arguments provide a small change in the value of the functions, which allows for placing dependences for different diffusion coefficients on the same figure. Using other parameter values and ranges of argument can dramatically increase the values of functions (by several orders of magnitude), which indicates the coefficients f_{AH}, f_{BH}, e_H and D_H significantly affect the interdiffusion coefficients during the course of coupled physical and mechanical processes. It was found that:

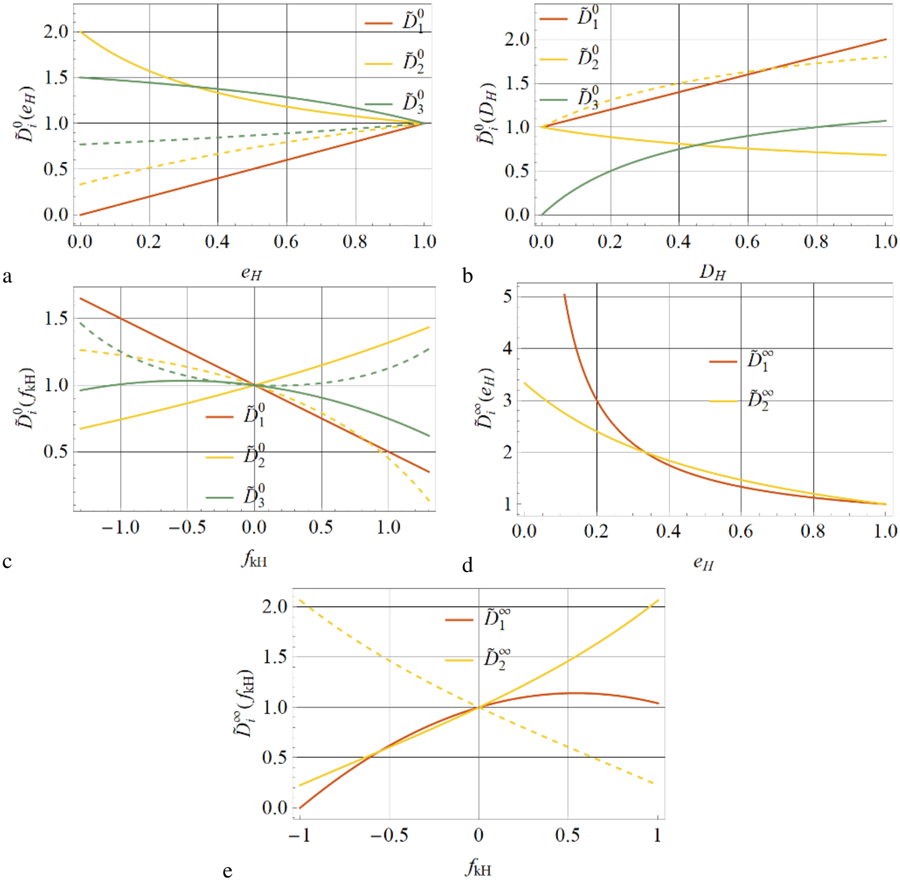


Fig. 10.2: Qualitative dependences of the dimensionless diffusion coefficients.

- The migration of grain boundaries can significantly accelerate the interdiffusion at $\lambda \ll 1$, which may correspond to a fine-grained structure. According to Fig. 10.2b with increasing the microstructure mobility coefficient D_H, the interdiffusion coefficients at small perturbation wavelengths D_1^0, D_3^0 increase, and D_2^0 can both increase and decrease. At large perturbation wavelengths, the diffusion coefficients D_1^∞ and D_2^∞ do not depend on D_H, which is obvious from (10.41) and (10.42).
- For any perturbation wavelengths, the rate of interdiffusion can both significantly increase and decrease depending on the connectivity of the diffusion fluxes and microstructure flux, expressed in coefficients f_{AH}, f_{BH}. In Fig. 10.2c,e the qualitative dependence of the interdiffusion coefficients on the coefficients f_{AH}, f_{BH} is shown.
- The coupling of viscous deformations and microstructure accelerates interdiffusion at large scales $\lambda \gg 1$ and it can both decelerate and accelerate diffusion at small scales $\lambda \ll 1$. According to equation $(10.38)_3$, the greater the value of

thermodynamic coefficient f_{Hv} and shear strain γ_0, the smaller the value of e_H is. Thereby from Fig. 10.2a,d it follows that increasing f_{Hv} or γ_0 leads to raising the interdiffusion coefficients D_1^∞, D_2^∞, reducing the maximum diffusion coefficient D_1^0, and to raising or reducing the diffusion coefficients D_2^0 and D_3^0.

- The mean stresses at the perturbed state σ_m^0 can affect the values of the interdiffusion coefficients only through thermodynamic coefficients. In expressions (10.39), (10.40), (10.42) the volumetric strains are represented in the explicit form. They are proportional to the mean stresses $\sigma_m^0 = -4G_0\varepsilon_V^{e0}/3$, but due to $\varepsilon_V^{e0} \ll k_G$ their effect is negligible.

Thus, the presence of microstructure can explain substantial increasing in the rate of interdiffusion in metal alloy during viscous deformation. The diffusion rate is positively influenced by both the microstructural variable h, associated with the concentration of grain boundary area, and the intensity of deviatoric inelastic strains I_2^v, being identified with the density of dislocations. Note that the expression for the Helmholtz free energy incorporates the quadratic degree of the last parameter, which meets the fourth power of $\boldsymbol{e}^v$. The thermodynamic coefficient f_{Hv}, shear strain γ_0, and kinetic coefficient D_H significantly contribute to the effective diffusion coefficient (10.38). It also emphasizes the connectivity (generally speaking, not obvious) of diffusion properties and microstructure.

10.9 Conclusion

The effective diffusion and viscous linear coefficients has been studied for the coupled set of equations with incorporating the processes of interdiffusion in a binary alloy, viscoelastic deformations, and microstructure changes. The technique developed in works [2, 3, 4] was used, but to study abnormally fast processes of chemical composition changing in metal alloys under intensive plastic deformations, the presence of microstructure was consistently regarded in the model. The microstructure is described by a scalar internal variable being the concentration of grain boundaries, and by the intensity of deviatoric inelastic strains associated with dislocations of the crystal lattice. Both variables are added to the Helmholtz free energy and the latter is to the second power, which turned out to be necessary. The model problem in question [2, 4], for which effective diffusion and viscous linear coefficients are determined, is also generalized to come close to the loading scheme in Bridgman anvils [1]. To be more precise, the scheme corresponds to the free axial deformation of the rod, constrained on the sides, with torsion. Although it would be more correct to consider a torsion compression scheme, however, to compare with the already existing results of simpler diffusion models in a deformable body, that scheme was adopted. In the future, a torsion compression scheme should be considered. Finally, the model, preferred by specialists in atomic diffusion and based on the experimental method for determining the Kirkendall – Darken interdiffusion coefficients, was adopted as the equations of interdiffusion in a medium experiencing elastic and viscous deformations (see review [5]).

The considered set of coupled equations, linearized in the vicinity of homogeneous stationary solution, was reduced to an eigenvalue problem. For the limiting cases of the perturbation wavelengths, the solution is characterized by a spectrum of effective diffusion coefficients and viscosity. Each of the effective diffusion coefficients depends on the thermodynamic and kinetic coefficients and they can drastically differ from the concentration diffusion coefficients of alloy components. The effective interdiffusion coefficients in the simplest cases meet structural schemes with sequential or parallel connection of diffusion elements.

It was defined that the values of diffusion fluxes are very sensitive to the coefficients associated with microstructural contributions to free energy and the migration of microstructure. Within linear analysis and without estimating the limits of variation of these coefficients, it is difficult to estimate how much the rate of effective diffusion of alloy components may differ from the concentration diffusion coefficients. Qualitative results suggest that regarding effective (and not concentration) diffusion coefficients in a coupled system is necessery to assess the speed of processes and explain their abnormally fast speed.

The analysis of solutions of the eigenvalue problem allows (in limiting cases) for studying not just the behavior of eigenvalues (effective kinetic coefficients) from the parameters (primarily microstructural) of the model. To drastically contribute to the diffusion fluxes, the structure of the eigenvectors corresponding to the "fast" diffusion coefficients obliges the concentration gradients of microstructure and elastic stresses have large values.

Some non-obvious results connecting the diffusion rate with the microstructure in an inelastic deformable crystalline body can be used as some point of view along with the physics of metals.

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