

Mechanics of multi-component media with exchange of mass and non-classical supplies

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Abstract. An approach for description of internal evolution processes in materials basing on the Euler equations and the mass balance equations containing source terms is proposed. Dynamics of the complex material such as structured liquids in nanochannels, metals with dissolved hydrogen and various impurities are discussed within a two-component continuum model. The effect of stress state on the internal structure of the materials is investigated.

1 Motivation and some examples

The classical equations of continuum include the equations of momentum and mass balance and the equation of state. As a rule, the mass balance equation after linearization is not used for further solution of problems. However, in some cases the mass balance equation plays a very important role. Primarily these are problems examining materials with a complex internal structure – materials with various impurities, structured liquids in nanochannels, metals with dissolved hydrogen. In these cases, we must begin the research with the mass balance equations and the analysis of source terms.

One of possible approaches, which allows us to consider the influence of internal degrees of freedom on structural reconstructions at a material, is the description of unknown particle kinematics of continuous media by phenomenological transport equations of substance (for example Fick' laws). The diffusion equations, that describe the relative motion of particles within a representative volume, should complement the basic equations of motion of a continuous media. This usually leads to the following difficulties.

First, the diffusion transfer of mass (which can change the internal structure of the material) may depend on the stress state of the material. This leads to necessity to choose diffusion coefficients using experimental data and thus makes it is impossible to build a general mathematical model describing materials with complex structures.

Secondly, it is known that the mass diffusion transfer inside material can cause in changes the internal structure of the material. It is not derived directly from the phenomenological equations. Usually to describe this phenomenon, we have to introduce artificial parameters associated with the concentration change in the equation of state of the material.

The aim of those lectures is to propose a different approach which allows us to describe internal evolution processes in the material. The approach is based on usage the Euler equations and the mass balance equations containing source terms. Choosing by some means the source terms that determine the mass transfer between a moving substance and the media, we can derive the equation of state of the substance. Besides the effect of stress state on evolution processes in the material (the diffusion of impurities) taken into account by introduction to the basic equations of dissipative term with a coefficient depending on the spherical part of the strain tensor. Then the classical evolution equations arise as a particular case within our approach.

In this section we show how this approach may be used to some model problems. In 1.2 we give a brief exposition of the law of particles conservation. An example of a chemical adsorption of substances is given in 1.3. Selecting the source terms in the mass balance equation allows us to control the process of adsorption. In 1.4 we discuss the connection of rheological models of materials and continuum models and shows how the choice of the source terms can affect the equation of state of the material. In 1.5 using continuum mechanics we obtain diffusion equation and introduce the resistance force to the diffusion flux being proportional to its velocity. The diffusion coefficient depends on the normal deformation basic media.

1.1 Particle balance and mass balance equation

Let $\eta(\mathbf{r}, t)$ be the number density at a given point \mathbf{r} of an inertial reference system. Specifying by dN the number of particles in the elementary volume dV we can write

$$dN = \eta(\mathbf{r}, t)dV, \quad \eta \geq 0.$$

The mass density $\rho(\mathbf{r}, t)$ and the number density are connected by the relation

$$\rho = m\eta, \tag{1}$$

where m is the mass of one particle. Let V be a volume in the reference frame and the boundary of V be a closed surface $S = \partial V$. It is assuming that the total number of particles in media remains unchanged and we can

formulate the following particle balance equation

$$\frac{d}{dt} \int_V \eta(\mathbf{r}, t) dV = - \int_S \eta \mathbf{n} \cdot \mathbf{v} dS = - \int_V \nabla \cdot (\eta \mathbf{v}) dV, \quad (2)$$

where \mathbf{v} is the velocity of particles. In the local form Eqs.(2) can be written

$$\frac{\partial \eta}{\partial t} + \nabla \cdot (\eta \mathbf{v}) = 0. \quad (3)$$

Using (1) we can get the mass balance equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (4)$$

If the density of particles can be changed, the particle balance equation should be modified as follows

$$\begin{aligned} \frac{d}{dt} \int_V \eta(\mathbf{r}, t) dV &= \int_V \chi(\mathbf{r}, t) dV - \int_S \eta \mathbf{n} \cdot \mathbf{v} dS \\ &= \int_V [\chi(\mathbf{r}, t) - \nabla \cdot (\eta \mathbf{v})] dV. \end{aligned} \quad (5)$$

Here the function χ is the rate of production (destruction) of particles at a point of the reference frame. Then equations (3) and (4) take the form

$$\frac{\partial \eta}{\partial t} + \nabla \cdot (\eta \mathbf{v}) = \chi \quad (6)$$

or

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = J. \quad (7)$$

Here the functions χ and $J = m\chi$ are co-called source terms and characterize the rate of mass production (destruction) of particles.

Now we present some examples where the equation (7) is used for description of various phenomena.

1.2 Adsorption of impurities

The first example is a chemical adsorption of substances (see Whitham (1974)). The situation is that a fluid carrying dissolved substances or particles (impurities) flows through a fixed bed and impurities being carried is partially adsorbed on the fixed solid material in the bed. The fluid flow is idealized to have a constant velocity v . Then if ρ_f is the density of the

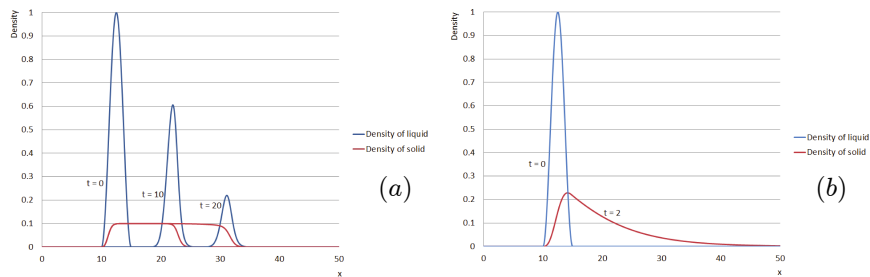


Figure 1. The density of the adsorbed substance: (a) the uniform distribution $v = 1$, $k_1 = 4$, $k_2 = 0$, $A = 0.1$, $B = 1$; (b) the uneven distribution $v = 20$, $k_1 = 4$, $k_2 = 0$, $A = 0.7$, $B = 1$.

material carried in the fluid, and ρ_s is the density deposited on the solid, the conservation equations have the forms

$$\frac{\partial \rho_s}{\partial t} = J, \quad (8)$$

$$\frac{\partial \rho_f}{\partial t} + \frac{\partial}{\partial x}(\rho_f v) = -J, \quad (9)$$

where the source term is as follows:

$$J = k_1(A - \rho_s)\rho_f - k_2\rho_s(B - \rho_f). \quad (10)$$

The first term of (10) represents deposition from the fluid to the solid at a rate proportional to the amount in the fluid, but limited by the amount being already on the solid up to the capacity A . The second term is the reverse transfer from the solid to the fluid. The numerical solution of the system (8)–(10) is carried out. Depending on the system parameters, we have the uniform distribution of the adsorbed substance (Figure 1a) and the non-uniform distribution of the adsorbed substance (Figure 1b).

Let us find the analytical solution under certain simplifications. The system (8)–(10) can be rewritten as

$$\begin{aligned} \frac{\partial}{\partial t}(\rho_f + \rho_s) + v \frac{\partial \rho_f}{\partial x} &= 0, \\ \frac{\partial \rho_s}{\partial t} &= k_1\rho_f(A - \rho_s) - k_2\rho_s(B - \rho_f). \end{aligned}$$

For relatively slow changes in the densities and relatively high reaction rates k_1 , k_2 , the second equation is taken in the approximate quasi-equilibrium

form in which the $\partial\rho_s/\partial t$ is neglected and

$$\rho_s(\rho_f) = \frac{k_1 A}{k_2 B + (k_1 - k_2)\rho_f}.$$

Substituting this expression into the first equation of the system (8)–(10) yields

$$\frac{\partial\rho_f}{\partial t} + c(\rho_f) \frac{\partial\rho_f}{\partial x} = 0, \quad c(\rho_f) = \frac{v}{1 + \partial\rho_s/\partial\rho_f}.$$

Thus, the density changes propagate at the speed of $c(\rho_f)$. If the densities concerned are small, the value of $c(\rho_f)$ is approximately equal to

$$c = \frac{k_2 B}{k_1 A + k_2 B} v.$$

The propagation speed depends on the reaction rates involved, being slower for substances with larger attraction toward the solid.

1.3 Rheological models of materials. The equations of state and source terms

The concept of a rheological model of a material is given by Reiner (1958); Palmov (1998). Rheological models are often used to describe the materials with complex internal structure, in particular dispersed systems of two or three phases. Rheology considers such materials as homogeneous, the mechanical properties of which coincide with the properties of real materials. A mathematical model of the mechanical properties of the material is given by the constitutive equation (the equation of state). To compose the constitutive equations for materials with complex rheological properties each basic property material is modeled by suitable rheological element. For example the elasticity is simulated by an elastic spring (the Hooke element), the viscosity is simulated by a viscous damper (the Newton element) and the plasticity is simulated by a dry friction damper (the St.Venant element). By combining the fundamental rheological elements either in series or parallel we form the rheological model with the complex material properties.

Our aim is to show the connection of rheological models of materials and continuum models. Consider as an example the Maxwell material. This viscoelastic material whose rheological model consists of a Hooke element and a Newton element in series. The constitutive equations for this material in the simplest one-dimensional case is as follows:

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\mu}, \quad (11)$$

where ε is the strain, σ is the mean normal stress, E is elastic modulus, μ is the viscosity coefficient. It is shown that the rheological equation of state (11) can be obtained from the mass conservation law (7). The rheological material has a complex internal structure and the mass exchange between the material and the media is possible, for example, due to change in a phase state of the material. Suppose that the material is initially at rest with the density ρ_0 and the perturbation quantity $\tilde{\rho} = \rho - \rho_0$ and the velocity v are small. Then, linearizing the equation (7) and expressing the velocity in terms of the displacement u , we obtain

$$\frac{\partial \tilde{\rho}}{\partial t} + \rho_0 \frac{\partial^2 u}{\partial x \partial t} = J.$$

Assuming $\varepsilon = \partial u / \partial x$, it yields

$$\frac{\partial \tilde{\rho}}{\partial t} + \rho_0 \frac{\partial \varepsilon}{\partial t} = J. \quad (12)$$

The mean normal stress is assumed to be a function of relative mass density ρ_0/ρ

$$\sigma = k \left(1 - \frac{\rho}{\rho_0} \right). \quad (13)$$

The coefficient k links the stress to a change of mass density. Substituting (13) into (12), we find

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{k} + \frac{J}{\rho_0}. \quad (14)$$

In order to obtain the equation of state of the material we need to define the source term J . It is done as follows:

$$J = -\alpha \tilde{\rho}, \quad \alpha \geq 0,$$

where the coefficient α determines the rate of exchange processes between the material and the media (in this case dissipation of the material) and, taking into account (13) we arrive at the following expression

$$J = \frac{\alpha \rho_0}{k} \sigma,$$

Then, substituting the last expression in (14), we get

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{k} + \frac{\alpha}{k} \sigma. \quad (15)$$

The constitutive equation (15) describes the Maxwell material by using a mass balance equation. The equation (15) coincides with the rheological

constitutive equation (11), when $E = k$ and $\mu = k/\alpha$. It is noted that if there are no exchange processes between the material and the medium $\alpha = 0$ ($J = 0$), then (15) is the equation of state describing the Hooke material.

It is shown that the rheological constitutive equation for the Kelvin–Voigt material (viscoelastic material with the rheological model that represents a parallel connection of a Hooke element and a Newton element) can be obtained from a continuous two-component model of the media.

1.4 Diffusion equation

Consider a flux of particles moving in a media (the penetration of a substance, such as a liquid, gas, or vapor, through a solid or another liquid; motion special liquids). Assume that we can neglect the exchange of particles between the medium and diffusion flux. The diffusion equation is generally obtained from the law of mass conservation, assuming that the mass diffusion flux is proportional to the density gradient (Fick’s first law)

$$\rho \mathbf{v} = -\kappa_D \nabla \rho,$$

and the corresponding diffusion equation (Fick’s second law) is

$$\frac{\partial \rho}{\partial t} = \kappa_D \nabla^2 \rho.$$

The constant κ_D is the diffusion coefficient. It depends on the properties of the media and the type of the diffusion liquid. We obtain the diffusion equation using the system of equations describing the motion of a homogeneous substance (liquid). For this purpose we consider fluxes in which the entropy of a liquid element is constant. Then, the system of equations of a flux motion is determined by the law of mass conservation, described by equation (4), and the equation of motion (the equation of dynamics)

$$\rho \frac{d\mathbf{v}}{dt} = \rho \mathbf{F} - \nabla p, \quad (16)$$

where p is the pressure at the point of the diffusion flux, \mathbf{F} is the mass external force. Equation (4) and (16) should be supplemented by an equation of state, defining the density as a function of pressure

$$\rho = \rho(p). \quad (17)$$

The specific form of the equation of state is related with the nature of matter flux. It introduces into the equation (16) a dissipative term, i.e., we

assume that the force of interaction between matter flux and the medium is proportional to the velocity of the flux and the equation (16) can be written as

$$\rho \frac{d\mathbf{v}}{dt} = \rho \mathbf{F} - \nabla p - \beta \mathbf{v}. \quad (18)$$

The force $\beta \mathbf{v}$ is obtained by linearization of the known formula used in hydraulics, see Loitsyansky (1987), where the square-law of resistance is given. The coefficient β , which can depend on the stress state of the medium (strain field), is defined below. Supposing that the forces of inertia can be considered as negligibly small (examples of such flows, see Batchelor (1967)), \mathbf{v} is defined by the equation (18) and substituting it into the equation (3), we can be obtained

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \left(\frac{1}{\beta} \nabla p \right) - \rho \nabla \cdot \mathbf{F} - \mathbf{F} \cdot \nabla \rho. \quad (19)$$

Usually the mass external force occurs under the force of gravity $\nabla \cdot \mathbf{F} = 0$ and the last term in equation (19) is negligibly small, then

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \left(\frac{1}{\beta} \nabla p \right). \quad (20)$$

Suppose that the substance is initially at rest with pressure p_0 and density ρ_0 . Assuming the density values of the perturbation $\tilde{\rho} = \rho - \rho_0$ and pressure $\tilde{p} = p - p_0$ are small, we can assume that the equation of state has the form

$$\tilde{p} = c_0^2 \tilde{\rho}, \quad (21)$$

where c_0 is speed of propagation of sound waves in a fluid. Substituting (21) in (20), we obtain

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \left(\frac{c_0^2}{\beta} \nabla \rho \right), \quad \beta = k \frac{\rho_0}{D(\varepsilon)}, \quad (22)$$

where the coefficient k of resistance to the motion of matter is a dimensionless number which depends on physical state of the medium, $D = D(\varepsilon)$ is the size of through passage section (flow section), which can depend on a stress state of the medium. Indeed, for structures under uniaxial compression the size of flow section can change and to determine the dependence $D = D(\varepsilon)$ it is necessary to consider the state of stress the basic media. Thus, the obtained equation (22) is the diffusion equation of the flux of matter, taking into account the influence of the stress state of the medium. In the absence

of deformation of the medium $D = D_0$, equation (22) coincides with the classical diffusion equation (19), where

$$\varkappa_D = k \frac{c_0^2 \rho_0}{D_0}. \quad (23)$$

Introduction of the dissipative terms and the resistance coefficient β are discussed further in detail to describe the motion of fluid flow in nanochannels (Section 3) and flow motion of mobile hydrogen particles (Section 4).

1.5 Conclusion to section 1

The approach which allows us to describe internal evolution processes in the material with the help of the Euler equations and the mass balance equations containing source terms is proposed. Now it is of interest to extend the results to models of two-component continuum. According to the remarks from above the lectures are organized as follows. A mechanical two-component model of the solid of complex structure is presented in section 2. This model is used in sections 3 and 4. In section 3 we propose a mathematical model of a fluid flow in a two-dimensional nanochannel, which is caused by the motion of one of the confining walls parallel to the other immovable wall. The two-component model of the material, in which atomic hydrogen dissolved, is constructed in section 4.

2 Two-component model of media

The rational mechanics of continuous media ignores such an important physical property of any real material as its discrete structure. It is clear that the model of a solid in the framework of the rational mechanics should have a complex structure in order to reflect the properties of discrete structure of the matter. Such a complex structure is determined by the presence of internal degrees of freedom and the influence of dynamics of the material. The presence of these degrees of freedom can result in change of the basic macroparameters which are usually used for description of the material by means of the classical equations of continuum mechanics.

As shown by Sobolev (1991); Sobolev (1997), one of the approaches to description of the continuous media behaviour is to introduce two-component models. These models allow one to explain some physical phenomena which have not been properly understood. In particular, these are the question a fluid flow behaviour in nanochannels, problem of hydrogen diffusion in metals.

The classical approaches usually introduce additional parameters in the constitutive equations. In this case the required phenomenological relations

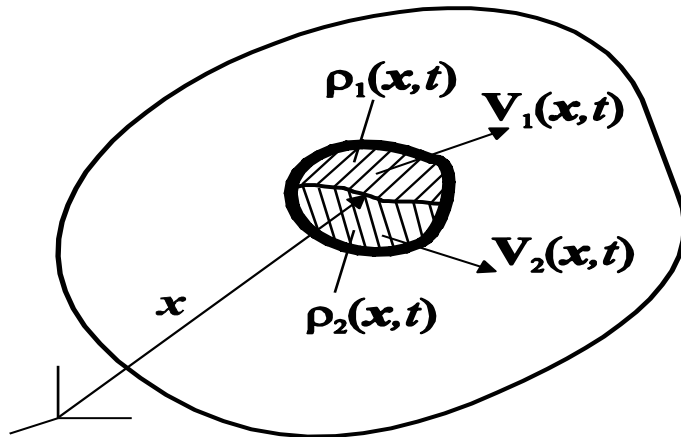


Figure 2. A schematics of the two-component model.

allow determining these new variables. The basic equations for the two-component model introduced in the present paper emphasize the essential role of the internal structure of the material and enable description of the above-mentioned physical phenomena.

2.1 The basic assumptions and equations

We postulate a model of the material with a carrying medium whose components are particles described by the displacement vector $\mathbf{u}_1(x, t)$. An additional set of particles interacting with each other and with the carrying medium is attached to the carrying medium. The absolute displacement of particles of this additional medium is given by vector $\mathbf{u}_2(x, t)$. Both sets are supposed to be mutually penetrating continuous media. In other words, we introduce the concept of the material point that has a complex structure and consists of two components. In the expressions for displacements the argument \mathbf{x} is the position vector of the material point in actual configuration, i.e. Euler's description is taken, see Figure 2.

Physically, the different components of the material occupy different spatial volumes. In this regard there arises a question of the conditions of interaction of parts of the introduced solid on their internal boundaries. An axiomatic construction of the model reduces to assignment of interaction force \mathbf{R} and the mass exchange J between the components. Realization of these representation results in a two-component model.

The law of mass conservation in the local form for each component and

for the overall material is supposed to hold:

$$\frac{\partial \rho_1}{\partial t} + \nabla \cdot (\rho_1 \mathbf{v}_1) = J, \quad (24)$$

$$\frac{\partial \rho_2}{\partial t} + \nabla \cdot (\rho_2 \mathbf{v}_2) = -J, \quad (25)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0.$$

Here ρ_1, ρ_2, ρ are densities of components and the overall material, respectively. The right hand side of equations in (24), (25) have the source terms J which point out the possibility of exchange of particles between the components.

By virtue of the law of momentum conservation we have

$$\rho \mathbf{v}(x, t) = \rho_1 \mathbf{v}_1(x, t) + \rho_2 \mathbf{v}_2(x, t)$$

Here and in what follows we assume the following expression for the density of the overall material: $\rho = \rho_1 + \rho_2$.

Velocities of the components and the center of mass of the material point are expressed as follows:

$$\mathbf{v}_i(x, t) = \frac{d_i \mathbf{u}_i(x, t)}{dt}, \quad i = 1, 2, \quad \mathbf{v}(x, t) = \frac{d\mathbf{u}(x, t)}{dt}.$$

Here

$$\frac{d_i}{dt} = \frac{\partial}{\partial t} + \mathbf{v}_i(x, t) \cdot \nabla, \quad \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}(x, t) \cdot \nabla$$

denote the material derivatives.

The motion of the overall material point is governed by the law of dynamics in the local form

$$\nabla \cdot \boldsymbol{\tau} + \rho \mathbf{F} - J(\mathbf{v}_1 - \mathbf{v}_2) = \rho \frac{d\mathbf{v}}{dt}.$$

The mass external force \mathbf{F} can be given by

$$\rho \mathbf{F} = \rho_1 \mathbf{F}_1 + \rho_2 \mathbf{F}_2.$$

The equation of dynamics is convenient to rewrite in the form of two equations

$$\nabla \cdot \boldsymbol{\tau}_1 + \rho_1 \mathbf{F}_1 + \mathbf{R} - J \mathbf{v}_1 = \rho_1 \frac{d\mathbf{v}_1}{dt}, \quad \nabla \cdot \boldsymbol{\tau}_2 + \rho_2 \mathbf{F}_2 - \mathbf{R} + J \mathbf{v}_2 = \rho_2 \frac{d\mathbf{v}_2}{dt} \quad (26)$$

where \mathbf{R} is the force of interaction of two components of the material of complex structure. The interaction force \mathbf{R} has an expression which is explicitly

determined by the specific structure of the medium under consideration. In addition to this, the overall stress tensor of the material point is supposed to be the sum of the stress tensors of separate components

$$\boldsymbol{\tau} = \boldsymbol{\tau}_1 + \boldsymbol{\tau}_2$$

Let us note that the above equations for the two-component body (the two-component medium) are in agreement with the equations of mechanics of continuous heterogeneous media developed for modeling diverse mixtures (see Nigmatulin (1990)).

The basic equations of moment and mass balance can be complemented by the equations of energy balance and the second law of thermodynamics for the each component. These equations are given in Indeitsev and Naumov (2009), where the problem of propagation of mechanical and temperature pulses in solids are studied. In the present paper we do not consider a heat exchange between the components.

Now we construct two-component model for the fluid flows in nanochannels.

3 Features of fluid behaviour in nanochannels

New equations that describe the behavior of fluids in nanochannels and take into account the molecular structure of the fluid and results of real and numerical experiments are presented. The Poiseuille flows are considered. The obtained results show that it is possible to describe the structural transformations in thin layers by using the continuum mechanics methods. New degrees of freedom of the material are introduced via the second continuum that makes up for the role of the forming new phase of a state. In the models considered here, the properties of the new phase are determined by the influence of rigid boundaries with a different structure.

3.1 Introduction

Fluid flows in micro- and nanochannels are of great interest from both the viewpoint of fundamental science and practical applications (Drummond and Israelachvili (2001)). By virtue of this, modeling of such a flow became one of most quickly developing trends in hydrodynamics. The topicality of this modeling is also supported by the results of numerous experiments that have been conducted during last two decades (see, for example Gourdon and Israelachvili (2003); Thomson and Robbins (1990)) and revealed great differences between the behavior of fluids in volumes with a size of 50 molecular diameters or smaller and the predictions of classical continuum

theories. These experiments showed a substantial increase of the effective viscosity of the fluid in such volumes as compared with its macroscopic value. Classical hydrodynamics, that does not allow for atomic (molecular) structure of fluid, does not present adequate description of fluid flows in nanochannels with a width of 50 molecular diameters or smaller. It is well known that the classical Poiseuille flow is described by the Navier–Stokes equations and the velocity profile in this case has a parabolic shape. Nevertheless, the fact that some fluids flowing in rather narrow gaps begin to feel the boundaries, which leads to restructuring of the profile, have long attracted the attention of researchers. Moreover, in their numerous studies Deryagin et al. found that fluids at the boundary with a solid body form layers with an ordered structure that determines special features of fluids in these layers (Deryagin and Zheleznyi (1974)).

To describe this flow, we suggest new equations that describe the behavior of fluids and take into account the molecular structure of the fluid and results of real and numerical experiments. Numerical experiments were conducted by computer modeling and by the molecular dynamics (MD) method formulated by Allen and Tildesley (1989).

3.2 Proposed model and main equations

To describe the fluid flow in the channel, we use the two-component model (see Abramyan (2010)). We assume that the fluid in the channel is affected by the walls, i.e., has a possibility to be structured. The medium outside the channel is a usual molecular viscous fluid. The motion of the latter in the interior of the channel filled with a certain structured medium is similar to the flow through a ‘sieve’ whose ‘feed through’ cell dimensions significantly depends on the density of the ordered phase. We assume that, in the process of the fluid flow, the main resistance force is the reaction of fluid particle interaction with the structure cells, which is proportional to the difference of velocities of particles of the interacting components. At rest, without any applied external loads, the channel is filled with a medium which is ordered under the action of the channel walls. It is natural to assume that this phenomenon is inhomogeneous over the layer thickness, namely, the medium particles in the central part of the layer experience lesser influence of the walls than the particles on the boundary with the surfaces. We consider some specific cases in which the influence of the walls is such that, as a rule, the structures near the walls are more concentrated than those in the middle. The stressed state of the ordered medium is modeled as the pure shear stress.

The so-called molecular liquid is fed into the channel, and this liquid

interacts with the structure. This interaction force mainly depends on the density of the ordered structure, and hence on the so-called flow section (the distance between particles of the ordered medium). The larger the particle density, the lesser the flow section through which the incoming particles can pass, and hence the force of the two media interaction is the largest. Thus, this interaction of two media, like the viscous friction force, depends on the difference of their particle velocities: it is the larger the higher the velocity of motion of one component relative to the other. In this case, it is assumed that this dependence is linear.

Obviously, as the incoming particles of the molecular liquid move with an input velocity greater than a certain value, the liquid has the tendency to pass freely through the immovable structured medium with possible separation of particles of the latter. This means that if the input pressure is sufficiently high, then the liquid medium can ‘destroy’ the structure where it exists. Otherwise, if the pressure is insufficient, then the velocities of the applied particles are small, the structure density increases, and the flow rate of the constantly incoming liquid decreases. If the incoming liquid particles are sufficiently slow, then the structuring continues until complete sedimentation of liquid particles, i.e., the channel is ‘choked up’ and the liquid cannot pass through it anymore.

It is important to note that, in the equations of mass balance, there arise source terms determining the rate of transformation of liquid-like particles into solid-like particles and conversely. We assume that the sedimentation rate must be proportional to the particle concentration in the liquid, and the separation rate must be proportional to the structured medium concentration. Obviously, as the number of the liquid particles decreases, the number of solid-like particles increases, and hence the inverse process may occur.

Since an ordered structure is formed for certain pressure and velocities, the flow rate through each cross-section of the channel decreases in time. The main effect considered in this problem is the phenomenon of molecular liquid sedimentation on the structure, which may result in the so-called ‘choking’ effect.

Let us denote the number density of fluid particles per unit volume by n_f , the number density of solid (structured, precipitated) particles per unit volume by n_s , and $n_f + n_s = 1$. Then $\rho_s = mn_s$ and $\rho_f = mn_f$ are the density of the solid and fluid particles, m is the mass of particle. Assuming that the rate of solid particles are close to zero, we write the basic equations

of moment and mass balance in the form

$$\nabla \cdot \left[-\mathbf{I}p + \mu(\nabla \mathbf{v} + (\nabla \mathbf{v})^T) \right] = \rho_f \frac{d\mathbf{v}}{dt} + J\mathbf{v} + \mathbf{R}, \quad (27)$$

$$\frac{\partial \rho_f}{\partial t} + \nabla \cdot (\rho_f \mathbf{v}) = J, \quad \frac{\partial \rho_s}{\partial t} = -J. \quad (28)$$

Here p is the pressure of fluid fraction (liquid phase), \mathbf{I} is the unit tensor, $\mathbf{v} = \mathbf{v}_f$ is the velocity vector of the fluid particles, μ is the equivalent viscosity of fluid fraction, J is the rate of sedimentation (adhesion) and separation of liquid particles at the checkpoint of the reference system, \mathbf{R} is the force of interaction between the fractions. Using $n_s = 1 - n_f$, the equations (28) can be rewritten as

$$\begin{aligned} \frac{\partial n_f}{\partial t} &= J/m, \\ \nabla \cdot (n_f \mathbf{v}) &= 0. \end{aligned}$$

The source terms J has the following form

$$J = \begin{cases} -k_1 n_f, & |\mathbf{v}| < v_*, \\ k_2 (n - n_f), & |\mathbf{v}| > v_*, \end{cases}$$

where k_1 and k_2 are constants obtained experimentally, v_* is a certain critical velocity. The source term is defined by to the above-described scenario of the events. The forces of interaction between the particles have the following form:

$$\mathbf{R} = \frac{kn_f}{D(n_s)} \mathbf{v}, \quad (29)$$

where k is the constant obtained from experimental data, $D(n_s)$ is the cell characteristic open area dimension. Taylor series expansion of $D(n_s)$ about the equilibrium point is given by $D(n_s) = D_0 - D_1 n_s$. Then equation (29) has the form

$$\mathbf{R} = k g(n_f) \mathbf{v}, \quad g(n_f) = \frac{n_f}{D_0 - D_1(1 - n_f)} \quad (30)$$

where D_0 is the characteristic open area dimension of the structured cell.

The conditions at the initial time moment are chosen as follows (see Figure 3):

$$n_s(0, y) = n_{s0}(y), \quad n_f(0, y) = n_{f0}(y)$$

For the problem of the Poiseuille flow we take the following initial and boundary conditions

$$p|_{x=0} = p_0, \quad p|_{x=L} = 0, \quad v|_{x=0} = v|_{x=L} = 0.$$

They correspond to the assumption that the structure is more ordered near the walls and less ordered near the channel center. As follows from expression (30), the quantity $g(n_f)$ depends on the molecular liquid fraction in the entire volume n_f and on the values of the coefficients D_0 and D_1 . As $n_f \rightarrow 1$, the quantity $g \rightarrow 1/D_0$ and the value of the characteristic open area dimension of the structured cell D_0 increases. In this case, the quantity \mathbf{R} contained in the equation (27) tends to zero, and the equation itself tends to the classical form.

The solution of the above-posed problem for different sets of parameters confirms the qualitative applicability of the two-component model for describing the effect under study. The choking effect was investigated for different types of initial ordering of the medium, i.e., for different characters of the wall action and for two types of the source term.

Now we consider the obtained diagrams using the mathematical and computer models. The results given below show that the wall material structure itself significantly affects the liquid flow.

In the first computer experiment, we considered a channel whose walls affected by the incoming liquid so that the medium was structured mainly near the walls and significantly less near the center of the channel. Prescribing a certain initial pressure at which the liquid particles were incoming and the other necessary parameters, we observed a regime in which the velocity profiles and the concentration of each of the media had the form shown in Figure 4a and Figure 4b.

In the second computer experiment, we considered a channel whose walls affected the incoming liquid so that the medium was structured very strongly near the input and the walls and significantly less near the center of the channel. The character of the observed regime is shown in Figure 5a for $H = 100$ nm and $L = 200$ nm. The diagrams for the two above-described experiments clearly illustrate the choking regime and show that the input pressure was insufficient in these experiments, which is testified

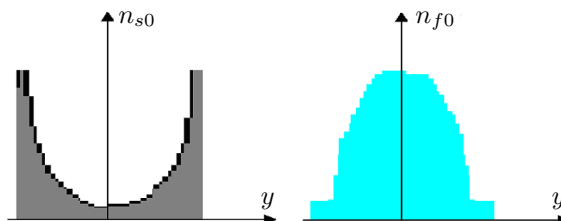


Figure 3. Distribution of particles of the structure and molecular fluid.

by the decrease in the flow rate of the incoming media (see Figure 5b). The computations showed that by increasing the excess pressure in the channel, one can obtain the converse effect, namely, the structured media becomes disordered. We did not calculate how the characteristic open area dimension affects the flow rate.

In the third computer experiment, we considered a channel in which the structured medium distribution was similar to the preceding distribution but the source term in the mass balance equation had the form

$$J = -k_1\rho_f(A - \rho_s)H(v_* - v) + k_2\rho_s(B - \rho_f)H(v - v_*) \quad (31)$$

The first term describes the sedimentation (ordering) at a rate proportional to the quantity of the matter in the liquid and bounded by the quantity of the already ordered medium till the saturation A . The second term describes the converse transition. The simulation results are shown in Figure 6. The results obtained confirm that there is a blocking effect, which is illustrated by an increase in solid-like phase concentration and a decrease in liquid flow rate for a certain pressure regime. We note that, under the assumption of strong effect of the walls strongly on the medium in the channel, this model more clearly illustrates the action of these forces on the process of structurization (see Figure 6a).

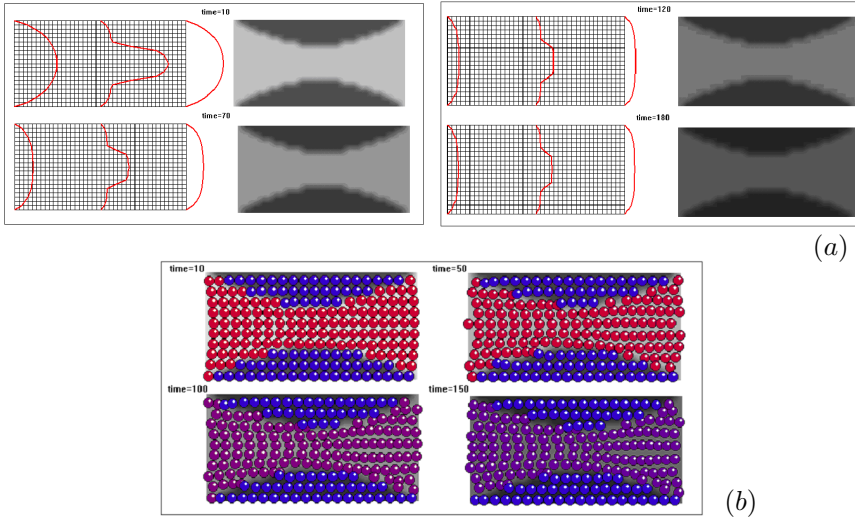


Figure 4. The first experiment. Profiles of velocity and concentration of particles in each component (a), Concentration of particles of each component at different instants of time (b).

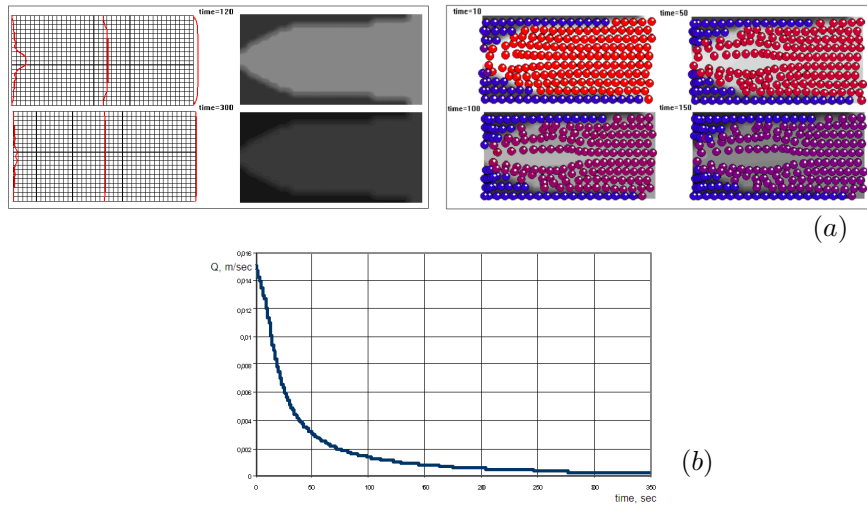


Figure 5. The second experiment. Profiles of velocity and concentration of particles in each component(a), flow rate of molecular fluid in the channel (b).

All the above experiments describe the choking effect in a plane channel. This phenomenon, under the assumption that the medium structuration (sedimentation) must decrease from the walls towards the center of the channel, is most precisely described by using the source term in the form (31). The third experiment clearly shows that the particles begin to settle near the already structured medium. Thus, generalizing all the diagrams obtained by using the mathematical and computer models, we see that the claim of this model to describe the choking effect in the channel with significant influence of its walls taken into account is justified completely.

3.3 Conclusion to section 3

We propose a mathematical model of a fluid flow in a plane nanochannel, that is caused by the motion of one of the confining walls parallel to the other, immovable wall. The values of the resistance forces acting on the walls when the distances between them are less than 50 nm, obtained using the above model, are in good agreement with the experimental results and predictions by the MD modeling. The obtained results show that it is possible to describe the structural transformations in thin layers by using the continuum mechanics methods. We introduce new degrees of freedom of the material by using the second continuum, which plays the role of the

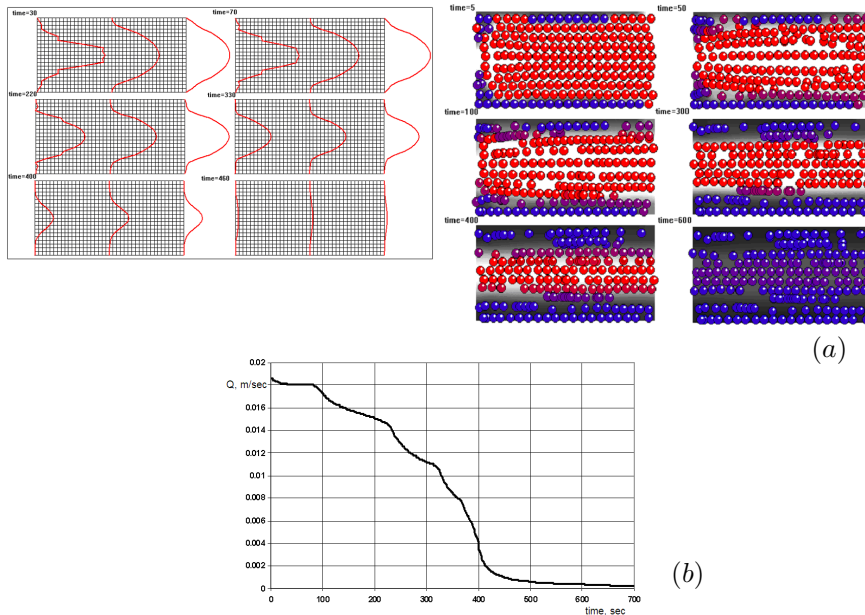


Figure 6. The third experiment. Profiles of velocity and concentration of particles in each component (a), flow rate of molecular fluid in the channel (b).

arising new phase of state. In the models considered above, the properties of the new phase are determined by the influence of rigid boundaries with a different structure. The solutions thus obtained depend on macroparameters, which can be determined using experimental data. This is a significant distinction of this approach from the earlier approaches, where numerous parameters, which are hard to determine, were introduced in the equations of state.

We note that the two-component model can describe quite well such effects as the flow ‘choking’ and the ‘destroyed’ layer reconstruction. This is because the source terms are introduced in the equation of the particle number balance of one or the other component. Depending on the scenario of the events in the material, it is quite possible to control and describe its state by using a suitable source term.

4 Hydrogen diffusion in the crystal structures

Hydrogen embrittlement of materials under load is one of the most important problems of the physics and mechanics of materials. Though the

hydrogen concentration in metals can be very low (about 1 atom of hydrogen in 100,000 atoms of the metal matrix), nevertheless its influence on the mechanical properties of the metals can be of crucial importance. The problem of the effect of low hydrogen concentrations in metals on the strength of material nowadays attracts a lot of attention. As a rule, the hydrogen is accumulated in metals during their exploitation. One of the main sources for hydrogen appearance in metals is water (or steam); however, hydrogen diffusion from gas and oil is feasible as well. The problem of the effect of low hydrogen concentrations in metals on the strength of material nowadays attracts a lot of attention. In metals, the hydrogen is contained in traps with various bonding energies. It has been established (see Polyanskiy (2005) and references therein) that thermo-mechanical loading results in the hydrogen redistribution over the traps. A number of papers were devoted to the influence of hydrogen on the mechanical properties of metals, see e.g. Ahn (2007). The majority of the papers addressing the effect of hydrogen on the strength of materials utilize primarily phenomenological models and do not discuss the problem of redistribution of hydrogen over the traps. The degradation of mechanical properties in these papers is modelled by means of some empirical dependencies. However, there is an open question: how kinetic processes in the material (such as the redistribution of hydrogen) affect its basic strength properties under static and dynamic loads? The aim of our study is to describe the dynamics of the hydrogenated metal and the influence of internal kinetics on metal macroparameters using the fundamental principles of rational mechanics. The hydrogen diluted in structural materials can be conditionally divided into that with low bonding energy and that with high bonding energy. The hydrogen with low bonding energy is diffuse, and its interaction with material is very weak (mobile hydrogen). The high bonded hydrogen interacts with material very intensively. The mechanical material properties degrade owing to this strong interaction. We suggest a one-dimensional model of two-component continuum, which allows us to describe both the hydrogen diffusion and its interaction with the material and, therefore, to find the equation of state for hydrogen-containing media. The first component is represented by the crystal lattice of the initial material including stationary hydrogen atoms embedded (attached) in chemical bonds between atoms (which significantly reduce the strength of the bonds), the second component is represented by free mobile hydrogen atoms dissolved in the material.

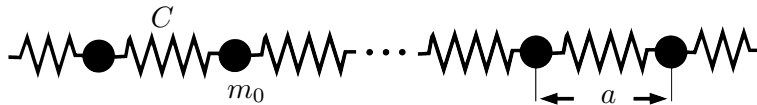


Figure 7. One-dimensional chain of atoms.

4.1 Two-component model

Let us consider the simplest one-dimensional model of a metal rod, in which atomic hydrogen is dissolved. Let N be the total number of particles per unit volume, N_0 be the number of the particles connected by undamaged bonds per unit volume, N_H^+ be the number of hydrogen particles attached to a lattice per unit volume, N_H^- be the number of mobil hydrogen particles per unit volume. Furthermore, n_0 , n_H^+ and n_H^- are the corresponding concentrations of the above-mentioned particles, respectively.

The first component is a lattice structure with bonded hydrogen (in the frame of elastic theory). The relation between the strain ε and the stress σ can be represented as $\sigma = E\varepsilon$, where E is the equivalent module of the lattice defined below. We denote the velocity and the density of the first component by v_1 and $\rho_1 = \rho_0 + \rho_H^+$. Here $\rho_0 = m_0 n_0$, $\rho_H^+ = m_H n_H^+$, m_0 , m_H are the mass of lattice atoms and bounded hydrogen atom.

The second component is flow of mobile hydrogen particles of the internal structure of a material (inviscid compressible liquid) and p is the pressure of flow, v_2 , $\rho_2 = \rho_H^-$ is the velocity and the density of the second component, $\rho_H^- = m_H n_H^-$.

Equation of state (rheological model). We consider the lattice as a one-dimensional chain consisting of identical particles with a mass of m_0 (mass of atom in a crystal lattice of a material) which are connected with each other by identical nonlinear springs with the lengths a , Fig. 1. The equation of movement in the long-wave approximation is as follows (Zhilin (2006))

$$m_0 \ddot{u} = -a[f(a(1 + u'))]'. \quad (32)$$

For small strains $\varepsilon = \partial u / \partial x$ we have the following equation

$$\ddot{u} - v_0^2 u'' = 0, \quad v_0^2 = \sqrt{\frac{C}{m_0}} a,$$

because $f[a(1 + \varepsilon)] \approx -Ca\varepsilon$.

It is known that, when hydrogen dissolves in materials, some of the hydrogen atoms are embedded in existing atomic bonds, breaking them and

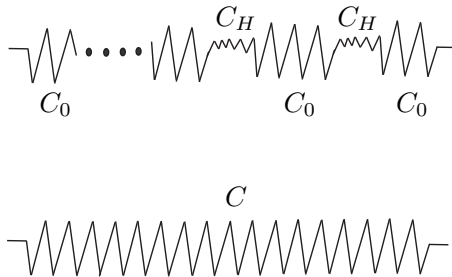


Figure 8. Model of a chain with hydrogen atoms planted on the bonds.

creating new bonds, its stiffness is much smaller than the initial stiffness (see Indeitsev and Semenov (2008)). This effect also takes place for a congestion of lattice defects: dislocations, vacancies, *etc.* By combining the elements with the old and new bonds in series one obtains the model of the lattice with bonded hydrogen (see Figure 7). It is possible at the assumption $m_0 \gg m_H$. Then the equivalent rigidity of the new bond C can be found from the equation

$$\frac{N}{C} = \frac{N_0}{C_0} + \frac{N_H^+}{C_H}, \quad N = N_0 + N_H^+,$$

where C_0 is the rigidity of pure material in the absence of hydrogen, C_H of the material with all bonds occupied by hydrogen. The nonlinear force f in (32) can be accepted for small strains as

$$f = -Ca\varepsilon = -E\varepsilon.$$

Then using $n_0 = N_0/N$ and $n_H^+ = N_H^+/N$ we obtain the constitutive equation for the lattice structure with bonded hydrogen

$$\sigma = E\varepsilon, \quad E = \frac{E_0 E_H}{n_0 E_H + n_H^+ E_0}. \quad (33)$$

The equivalent elastic modulus for the lattice E can decrease essentially, since $E_H \ll E_0$ ($C_H \ll C_0$) and depends strongly on the concentration of the attached (bonded hydrogen) particles n_H^+ . The number of the lattice-settled hydrogen particles depends on the stress state of the lattice at every point and, generally, on time. The unknown functional dependence of E on $n_H^+(\varepsilon, x, t)$ should be determined from the model of the two-component continuum.

Main equations. Substantive provisions of the theory of two-component continuum can be found in the second section (Krivtsov and N.F. Morozov (2001)); therefore, we are presenting only final equations. The equation of dynamics for the lattice structure (the first continuum) is given by

$$\frac{\partial \sigma}{\partial x} = \rho_1 \frac{\partial v_1}{\partial t} + Jv_1 + R. \quad (34)$$

The equation (34) has new force terms in the right part. Capturing of hydrogen mobile particles in the lattice practically does not influence the change of inertial characteristics of the lattice structure, i.e. $\rho_H^+ = m_H n_H^+ \ll \rho_0$, but the velocity of the change of those characteristics J results in the occurrence of jet force Jv_1 , whose neglecting is impossible. The term R determines the force of interaction between the first and second components and depends on internal processes in the material.

The dynamic equation for the second component (mobile hydrogen particles) is as follows:

$$-\frac{\partial p}{\partial x} = \rho_2 \frac{\partial v_2}{\partial t} - Jv_2 - R, \quad \rho_2 = \rho_H^- = m_H n_H^-. \quad (35)$$

Similarly to a case of compressed liquid, the state equation determining a connection between pressure p and density ρ_H^- takes the form

$$p - p_0 \cong c_H^2 \rho_H^-. \quad (36)$$

The equation of mass balance for the first component is

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial(\rho_1 v_1)}{\partial x} = J,$$

or taking into account an invariance of ρ_0 for ρ_H^+ we have

$$\frac{\partial \rho_H^+}{\partial t} + \frac{\partial(\rho_H^+ v_1)}{\partial x} = J.$$

In terms of the concentration of bonded hydrogen the equation for the mass balance has the form

$$\frac{\partial n_H^+}{\partial t} + \frac{\partial(n_H^+ v_1)}{\partial x} = J/m_H. \quad (37)$$

Mobil hydrogen obeys a similar equation of mass balance:

$$\frac{\partial \rho_H^-}{\partial t} + \frac{\partial(\rho_H^- v_2)}{\partial x} = -J \quad \text{or} \quad \frac{\partial n_H^-}{\partial t} + \frac{\partial(n_H^- v_2)}{\partial x} = -J/m_H. \quad (38)$$

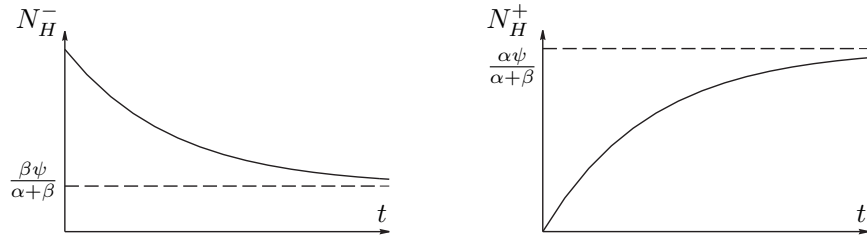


Figure 9. Dependencies of n_H^- and n_H^+ on time.

Interaction between the components. Interaction between the stationary lattice and flow of mobile hydrogen, that has not been attached yet, is described similarly to the flow of compressed liquid, see Loitsyan-sky (1987). Since the velocity of the hydrogen particles is very low and the suggested approach is linear, we assume that the interaction force is proportional to the difference in the continuum particles velocities:

$$R = k \frac{\bar{\rho}_H}{D(\varepsilon)} [v_2 - v_1]. \quad (39)$$

Here k is determined in terms of the material properties, $D(\varepsilon)$ is the effective cross section of the flow of the second component Indeitsev and Osipova (2011) (it is the size of through passage section, which depends on strain ε is introduced in (39).) The larger is the deformation, the smaller is the quantity D , since it is more difficult for mobile hydrogen to move in strained media.

Since the concentrations are low, the source terms J has the following form

$$J = \alpha n_H^- - \beta n_H^+ \quad (40)$$

where α and β are positive parameters determined by interaction between bonded and mobile particles of hydrogen. The physical meanings of the coefficients α and β can be defined as follows. For the small velocities v_1 and v_2 the terms $\partial(n_H^+ v_1)/\partial x$ and $\partial(n_H^- v_2)/\partial x$ in (37), (38) can be neglected. Than the problem for n_H^- and n_H^+ takes form

$$\frac{dn_H^+}{dt} = \alpha n_H^- - \beta n_H^+, \quad \frac{dn_H^-}{dt} = -\alpha n_H^- + \beta n_H^+ \quad (41)$$

with the initial conditions

$$n_H^+|_{t=0} = 0, \quad n_H^-|_{t=0} = \psi.$$

The solution of (41) is

$$n_H^+ = \frac{\alpha\psi}{\alpha + \beta}(1 - e^{-(\alpha+\beta)t}), \quad n_H^- = \psi \left[1 - \frac{\alpha}{\alpha + \beta}(1 - e^{-(\alpha+\beta)t}) \right]. \quad (42)$$

The parameters α and β define the rate of hydrogenation of the lattice (and its rate of hydrogen loss) and they should be prescribed, e.g. by using experimental data. The problem (41) describes interchange of hydrogen particles between the components under the condition that the velocity of diffuse hydrogen is small. In this case almost all mobile hydrogen is built in the lattice; hence $\alpha \gg \beta$ (see Figure 9).

The complete set of equations. In this section we summarize the equations derived in previous sections to represent the motion of the metal rod containing dissolved hydrogen. We have

$$\frac{\partial \sigma}{\partial x} = (\rho_0 + m_H n_H^+) \frac{\partial v_1}{\partial t} + Jv_1 + R, \quad \sigma = \frac{\varkappa E_0}{n_H^+ + \varkappa n_0} \varepsilon, \quad (43)$$

$$-\frac{\partial p}{\partial x} = m_H n_H^- \frac{\partial v_2}{\partial t} - Jv_2 - R, \quad p - p_0 = m_H c_H^2 n_H^-, \quad (44)$$

$$\frac{\partial \rho_0}{\partial t} + \frac{\partial(\rho_0 v_1)}{\partial x} = 0, \quad (45)$$

$$\frac{\partial n_H^+}{\partial t} + \frac{\partial(n_H^+ v_1)}{\partial x} = J/m_H, \quad \frac{\partial n_H^-}{\partial t} + \frac{\partial(n_H^- v_2)}{\partial x} = J/m_H, \quad (46)$$

$$R = k \frac{m_H n_H^-}{D(\varepsilon)} [v_2 - v_1], \quad J/m_H = \alpha n_H^- - \beta n_H^+. \quad (47)$$

Here $\varkappa = E_H/E_0$. The set of governing equations (43)–(47) is much too complicated for a direct mathematical analysis and we will restrict our attention by the simplest case – static stress state of the hydrogenated metal rod under the uniaxial tension/compression.

4.2 Static stress state

We suppose that the first material component (lattice with bonded hydrogen) is initially at the static stress state, so that the strain ε_0 and the stress σ_0 are related by $\sigma_0 = E\varepsilon_0$. The initial static stage is then disturbed slightly, and we suppose that the perturbation quantities $\tilde{\sigma}$, $\tilde{\varepsilon}$, \tilde{v}_1 , \tilde{n}_H^+ , \tilde{n}_H^- and \tilde{v}_2 are small in magnitude. Then we find the solution of the problem in the following form

$$\varepsilon = \varepsilon_0 + \tilde{\varepsilon}(x, t), \quad \sigma = \sigma_0 + \tilde{\sigma}(x, t), \quad v_1 = 0 + \tilde{v}_1, \quad v_2 = v_{20} + \tilde{v}_2 \quad (48)$$

$$n_H^+ = n_{H0}^+ + \tilde{n}_H^+(x, t), \quad n_H^- = n_{H0}^- + \tilde{n}_H^-(x, t) \quad (49)$$

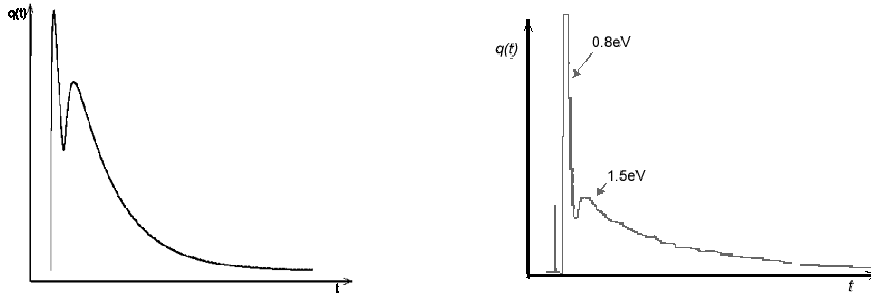


Figure 10. Extraction curve: (a) the theoretical one by Eq.(54), (b) experimental curve for titanium alloy PT-7M indicating the binding energies that correspond to separate peaks of the curve.

Substituting (48), (49) into (43)–(47) we obtain the linear approximation for the first component

$$\frac{\partial \sigma_0}{\partial x} = 0, \quad \sigma_0 = E_0 \varepsilon_0 \left[1 - \frac{n_{H0}^+}{n_{H0}^+ + \varkappa n_0} \right], \quad (50)$$

$$\frac{\partial n_{H0}^+}{\partial t} = \alpha n_{H0}^- - \beta n_{H0}^+, \quad (51)$$

for the second component

$$c_H^2 \frac{\partial n_{H0}^-}{\partial x} = -k \frac{n_{H0}^-}{D(\varepsilon_0)} v_{20}, \quad (52)$$

$$\frac{\partial n_{H0}^-}{\partial t} + \frac{\partial (n_{H0}^- v_{20})}{\partial x} = -\alpha n_{H0}^- + \beta n_{H0}^+ \quad (53)$$

Bounded hydrogen. Equations (51)–(53) can be reduced to the equation for concentration of bonded hydrogen n_{H0}^+ that takes form

$$\frac{\partial^2 n_{H0}^+}{\partial t^2} + (\alpha + \beta) \frac{\partial n_{H0}^+}{\partial t} - \frac{c_H^2 D(\varepsilon_0)}{k} \left[\beta \frac{\partial^2 n_{H0}^+}{\partial x^2} + \frac{\partial^3 n_{H0}^+}{\partial x^2 \partial t} \right] = 0. \quad (54)$$

Equation (54) is the equation of the mixed type, it contains terms inherent in the hyperbolic equation and terms of a parabolic kind. It means that at the assignment of the finite initial perturbation one should expect a characteristic front of movement of increase (or decrease) in a bonded hydrogen number density, i.e. an exposed strong dispersion.

Numerically solving the equation (54), we shall receive the charge of hydrogen from the free end of a core. Experimental dependencies of the

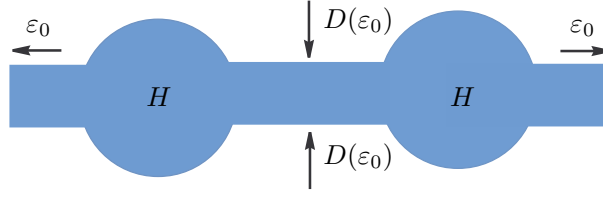


Figure 11. Model of closing of channels and places of a congestion of hydrogen.

charge of the hydrogen (Figure 10b), obtained on the precision hydrogen analyzer AV-1 (see Polyanskiy (2005)) qualitatively coincide with theoretical curves (Figure 10a). Here $q(t)$ is the change rate of the concentration of bonded hydrogen in the cross section.

Example: approximate analytical solution. Suppose that the lattice structure does not initially contain bonded hydrogen and mobil hydrogen is distributed in the material as follows

$$n_{H0^-}|_{t=0} = \frac{\Psi}{2} \left(1 + \cos \frac{2\pi x}{\lambda} \right),$$

where λ is the characteristic size of internal structure (such as the distance between the lattice atoms). Then we can analyze (54) following the initial conditions

$$n_{H0^+}|_{t=0} = 0, \quad \frac{\partial n_{H0^+}}{\partial t}|_{t=0} = \frac{\alpha\Psi}{2} \left(1 + \cos \frac{2\pi x}{\lambda} \right). \quad (55)$$

Here Ψ is the limit value of the bonded hydrogen density. We seek a solution in the form

$$n_{H0^+} = \frac{\Psi}{2} \left(1 + \cos \frac{2\pi x}{\lambda} \right) q(t), \quad (56)$$

and $q(t)$ satisfies the equation:

$$\ddot{q} + [\alpha + \beta + \gamma D(\varepsilon_0)]\dot{q} + \beta\gamma D(\varepsilon_0)q = 0, \quad q|_{t=0} = 0, \quad \dot{q}|_{t=0} = \alpha \quad (57)$$

where $\gamma = (2\pi c_H)^2/3k\lambda^2$. Solving equation (57) by assuming that $\beta \ll \alpha$ and $\alpha \ll \gamma D(\varepsilon_0)$, we obtain

$$n_{H0^+}(x, t) = \frac{\alpha\Psi}{2(\alpha + \gamma D(\varepsilon_0))} \left(1 + \cos \frac{2\pi x}{\lambda} \right) \left[1 - \exp \{ -(\alpha + \gamma D(\varepsilon_0))t \} \right]. \quad (58)$$

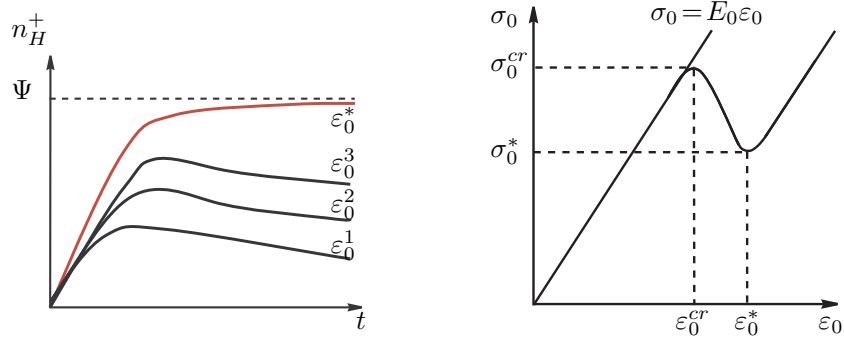


Figure 12. Behavior of concentration of the bonded hydrogen at a tension of a sample depending on the enclosed strain (a), the diagram of strain-stress in view of influence of the bounded hydrogen (b).

Averaging with respect to x , we find the simplified expression of N_{H0}^+

$$n_{H0}^+ \approx \frac{\alpha \Psi}{\alpha + \gamma D(\varepsilon_0)}. \quad (59)$$

For the small deformations we can assume that the value of the flow cross section D is linearly dependent on ε_0 and

$$D(\varepsilon_0) = D_0 - D_1 \varepsilon_0, \quad D_1 > 0. \quad (60)$$

Then the larger is the deformation, the smaller is the value of D . When $\varepsilon_0^* = D_1/D_0$ we have $D = 0$ and any diffusion of mobile hydrogen becomes impossible, so it goes into a bonded state. The behavior of concentration of the bonded hydrogen at a tension of a sample depending on the enclosed strain ε_0 ($\varepsilon_0^1 < \varepsilon_0^2 < \dots < \varepsilon_0^*$) is shown in Figure 12a.

Stress-strain diagram. Suppose that we have a limiting concentration of the bounded hydrogen $\Psi \gg \varkappa$, where $\varkappa = E_H/E_0$ (in particular, for steel $\Psi \approx 10^{-6}$, $\varkappa \approx 10^{-7} \div 10^{-8}$). Substituting (59) and (60) into (50) yields

$$\sigma_0 \approx \frac{\varkappa E_0 \varepsilon_0}{\varkappa + \alpha \Psi / [\alpha + \gamma (D_0 - D_1 \varepsilon_0)]}. \quad (61)$$

Defining the extrema of the function $\sigma_0(\varepsilon_0)$ we get the critical points of the stress-strain diagram

$$\varepsilon_0^{cr} \approx \varepsilon_0^* \left[1 - \sqrt{\frac{\alpha \Psi}{\varkappa \gamma D_0}} \right], \quad \varepsilon_0^* = D_0/D_1.$$

It should be noted that we obtain the equation of state (61) assuming that the induced strains connected to reorganization of internal structure can be neglected compared with the homogeneous static field of the strains ε_0 .

Figure 12b shows the qualitative representation of the stress–strain diagram, calculated by (61), corresponding to steel and titanium. The part of $\sigma_0(\varepsilon_0)$ dependence with $d\sigma_0/d\varepsilon_0 < 0$ can not be realized. The growth of $\varepsilon_0 > \varepsilon_0^{cr}$ results in hydrogen embrittlement and destruction. However the hydrogen saturation leads to decreasing of the breaking point σ_0^r . Similar $\sigma(\varepsilon)$ curves were observed in the experiments with titanium alloys having large hydrogen concentration and in high-strength steels under various immersion times in NH_4SCN solution (see Takai and Watanuki (2003)).

It should be mention that the dependence (61) is looplike and thereby predicts the first-order phase transition into hydride phase under the load. The stress–strain equation of state (61) agrees well with the corresponding results of the model developed on the basis of statistical mechanics Indeitsev and Osipova (2011).

4.3 Conclusion to section 4

The two-component model of the material, in which atomic hydrogen dissolved, has been constructed. It has been shown that the stress-strain equation of state of the hydrogenated metal is shaped like the Van der Waals loop; therefore, brittle hydride regions are nucleated in metal by the mechanism of the first-order phase transition. This allows us to describe the kinetics of hydrogen in metals, to estimate hydrogen transition from the mobile into the bonded state depending on the stress state.

5 Conclusion

Dynamics of the material with complex internal structure has been investigated within a two-component continuum model. The approach which allows us to describe internal evolution processes in materials basing on the Euler equations and the mass balance equations containing source terms has been proposed. The influence of exchange mass between the components on the internal structure of the materials has been investigated. The source terms determining the mass transfer between material components have been defined. Examples – structured liquids in nanochannels, metals with dissolved hydrogen – have been considered.

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Bibliography

- G. B. Whitham, *Linear and Nonlinear Waves*, Wiley, New York, 1974.
- M. Reiner, *Rheology*, Springer-Verlag, Gottingen Heidelberg, 1958.
- V.A.Palmov, *Vibrations of elastoplastic bodies*, Heidelberg: Springer, 1998.
- L.G. Loitsyansky, *Mechanika zidkosti i gaza (Fluid and gas mechanics)*, Moskva, Nauka, 1987.
- G. K. Batchelor *Introduce to fluid dynamics*, Cambridge University Press. 1967
- S.L. Sobolev, *Transport processes and traveling waves in systems with local nonequilibrium*, In Sov. Phys. Usp., pages 217–229, 1991.
- S.L. Sobolev, *Local non-equilibrium transport models*, Phys. Usp., pages 1043–1053, 1997.
- R.I. Nigmatulin, *Dynamics of Multiphase Media*, Hemisphere, N.Y., 1990.
- D.A. Indeitsev, V.N. Naumov, B.N. Semenov and A.K. Belyaev, Indeitsev D.A. *Thermoelastic waves in a continuum with complex structure*, InZAMM Zeitschrift fur Angewandte Mathematik und Mechanik, page 279–287, 2009.
- C. Drummond and J. Israelachvili, *Dynamic Phase Transitions in Confined Lubricant Fluids under Shear*, Phys. Rev., 041506, 2001.
- D. Gourdon and J. Israelachvili, *Transitions between Smooth and Complex Stick Slip Sliding of Surfaces*, Phys. Rev., 021602 2003.
- P. Thomson and M. O. Robbins, *Shear Flow near Solids: Epitaxial Order and Flow Boundary Conditions*, Phys. Rev., 6830–6837 1990.
- B.V. Deryagin, B. V. Zheleznyi, Z.M. Zorin, et al., *Properties of Fluids in Thin Quartz Capillaries*, Surface Forces in Thin Films and Colloid Stability (Nauka, Moscow), pages 90–94, 1974 (in Russian).
- M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids*, Clarendon Press, Oxford, 1989.
- A.K. Abramyan, N.M. Bessonov, D.A. Indeitsev, L.V. Mirantsev *Influence of the confining wall structure on the fluid flow in nanochannels*, Mechanics of Solids, pages 379–389, 2010.
- A.M. Polyanskiy, V.A. Polyanskiy and D.B. Popov-Diumin *Diagnostics of mechanical condition of structural material by method of high-temperature hydrogen vacuum-extraction*, In Proceedings of the Sixth International Congress on Thermal Stresses, Vienna, Austria, pages 589–592, 2005.
- D.C. Ahn, P. Sofronis, R.Jr. Dodds *Modeling of hydrogen-assisted ductile crack propagation in metals and alloys*, Int. J. Fract., pages 135–157, 2007.
- P.A. Zhilin, *Advanced problems in machanics*, Petersburg: Edition of the Institute For Problems in Mechanical Engineering of Russian Academy of Siences, 2006.

- D.A. Indeitsev, B.N. Semenov *About a model of structural-phase transformations under hydrogen influence*, Acta Mech., pages 295–304, 2008.
- A.M. Krivtsov and N.F. Morozov, *Anomalies in mechanical characteristics of nanometer-size objects*, Doklady Physics, pages 825–827, 2001.
- D.A. Indeitsev and E.V. Osipova, *A statistical model of hydride phase formation in hydrogenated metals under loading*, Doclady Physics, pages 523–526, 2011.
- K. Takai, R. Watanuki *Hydrogen in trapping ttates innocuous to environmental degradation of high-strength steels*, ISIJ International, pages 520–526, 2003.