Non-equilibrium process of transfer of momentum in medium with relaxation microstructure

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Abstract. The non-equilibrium process of transfer of the momentum of polymer media with an evolving nonequilibrium relaxation microstructure is considered. For the basic conditions of deformation, the regularities for the structural and dynamic components of the stress tensor with conjugate forces are obtained and analyzed, which are consistent with experiment.

1. Introduction
Concentrated solutions of polymers, copolymers, viscoelastic oils, colloy systems, emulsions, latexes, paints, polymerized mixed fuels, biophysical cultures and various modifications of such media are endowed with a complex internal microstructure and, as a result, have special physicochemical properties. Depending on the conditions of deformation, even near equilibrium, they are able to exhibit nonlinear - viscous and nonlinear - relaxation properties, partially store energy supplied from the outside in the form of the first and second difference of normal stresses (tensor deviator), and relax the stressed state of the medium.

The consequence of these properties represents non-instantaneous and non-local (delayed) responses of the medium to external disturbances, which determine the processes of transfer of momentum to the state of equilibrium.

Despite the great variety of such media and their flows in the processes and apparatuses of chemical technology, they are characterized by one fundamental property: all transport processes by a nonequilibrium relaxation mechanism are irreversibly aimed at neutralizing external disturbances that deflect the system from thermodynamic equilibrium.

At the present time, the phenomenological approach is widespread in the methods of describing the momentum of ordinary structureless media, endowed with the properties of viscosity, thermal conductivity, and diffusion near their equilibrium [1, 2]. The phenomenological theory, based on the principles of linear nonequilibrium thermodynamics, is used to model transport processes in continuous, structureless media endowed with the properties of viscosity, thermal conductivity, and diffusion near their equilibrium. It is assumed that the mechanical reaction of the medium at a given time is determined by the instantaneous values of the strain rate and remains in a deformed state after the removal of disturbances. The linear rheological relation for momentum transfer (Newton model) has the character of an instantaneous (without relaxation time lag in the development of the process) and local response of the medium to external influences, that is, regardless of the state of a representative point of a continuous medium from the relaxation and thermal state of points of its immediate environment. In the study of irreversible (due to the production of entropy) transfer processes in the whole of a nonequilibrium system, it is assumed that the relationships between the
state variables near equilibrium always obey the same relations as for the locally equilibrium state of the subsystem.

For a boundary value problem, the state variables of an open nonequilibrium system, as a result of energy and matter exchange between subsystems, become dependent on spatial coordinates and time.

The media considered in this work have a relaxation nonequilibrium microstructure, which manifests itself in the field of shear, entropy, and diffusion forces [3].

If the time of a non-stationary technological process is less than the relaxation time of the medium to a new equilibrium state, then such a state of the medium is no longer equilibrium. In this case, a non-instantaneous (delayed in time) response of the medium to external disturbances is manifested.

The process of transfer of momentum, together with the equation of motion, determines the thermodynamic characteristics of the motion of the medium and underlies numerous processes of convective transfer of heat, mass, generalized charge, etc. Research in this direction is important not only from an applied, but also from a scientific point of view. Non-instantaneous and non-local phenomena in transport processes in media with a nonequilibrium microstructure lead to the need to formulate and solve a wide range of transport phenomena problems taking into account the coordinated influence of the medium relaxation time and the technological process time.

In this regard, the work has both applied and scientific value; it is aimed at closing the fundamental law of conservation of momentum relative to a nonequilibrium momentum flow with forces coupled to them, which allows the analyze of the influence of microstructural and relaxation (delayed non-instantaneous and non-local) properties on transfer processes.

2. Investigation of the processes of transferring the momentum

In the isothermal approximation, the system of equations for studying the process of transfer of momentum in media with a nonequilibrium microstructure includes [4]: a set of continuity equations

\[ \frac{d}{dt} \rho V_i = 0 \]

momentum conservation equations:

\[ \rho (\partial V_i / \partial t + V_j \partial V_i / \partial x_j) = \partial P_{ij} / \partial x_j \]  

(1)

To clarify the clear influence of non-instantaneous and non-local effects on the dynamic characteristics of the nonequilibrium process of transfer of momentum, we will perform an analytical solution to the problem.

Let us consider a quasi-stationary disturbance in the system is instantly set in motion \( \partial P_{ij} / \partial x_j = 0 \) and is maintained by a constant velocity gradient \( v_{21} = G \). For this case, from the method of variation of arbitrary constants, we find the corresponding moments \( (x_i x_j) \). In this case, the initial condition \( t=0 \) is used: \( \langle x_i^2 \rangle = \langle x_2^2 \rangle = \langle x_3^2 \rangle = 1; \langle x_3 x_1 \rangle = \langle x_4 x_2 \rangle = \langle x_2 x_3 \rangle = 0 \). A consistent solution leads to the following expressions for non-zero moments:

\[ \langle x_2^2 \rangle = \langle x_2^2 \rangle = 1; \langle x_1 x_2 \rangle = \frac{G \alpha}{2} \left(1 - \exp(-2 \alpha - t)\right) \]  

(2)

\[ \langle x_1^2 \rangle = 1 + \frac{G^2 \alpha^2}{4} \left(1 - \exp(-2 \alpha - t)\right) - 2 \alpha \exp(-2 \alpha - t). \]

Equations (2) reflect the structural changes in the polymer system during deformation. The velocity gradient deforms the diagonal component \( \langle x_i x_j \rangle \) of the moment tensor and elastically stretches the component with respect to the initial values \( \langle x_i^2 \rangle = 1 \).

It is seen that the values for the moments in the transient conditions of deformation are characterized by the Deborah number \( De = \alpha / t \) and the Weissenberg number \( We = G \alpha \).

In accordance with equation (2), at \( t \to \infty \), we have:

\[ \langle \bar{x} \rangle = \langle x_1^{\frac{1}{2}} \rangle = \frac{G \alpha}{2} \]  

(3)

Here \( \langle \bar{x} \rangle \) is the tensor macroparameter characterizing the change in the components of the structure of the deformed system as a result of relaxation phenomena, figure 1. In the region of \( 0 < De < 1 \), a nonlinear correlation of the transition from one conformational state to another occurs, as well as changes in the microcomposition of the system that affect the transfer processes. With an increasing \( De \) number, changes in the microcomposition of the system stabilize. In the range of \( We \), the correlation is linear.
Figure 1. Influence of the effects of non-instantaneousness (De) and nonlocality (We) on the magnitude and nature of changes in the components of the structural tensor of macrostates during the transfer of momentum in media with a nonequilibrium microstructure.

Figure 2. Influence of De and We on the magnitude and nature of the change in the shear component of the stress tensor in the nonequilibrium process of transfer of momentum.
Figure 3. Influence of De and We on the magnitude and nature of the change in the first difference of the normal components of the stress tensor in the nonequilibrium process of the transfer of momentum.

3. Conclusion
The process of transfer of momentum in media with a nonequilibrium microstructure occurs according to non-instantaneous and non-local relaxation mechanisms, accompanied by dissipative and configurational phenomena in the microstructure of the medium. The immediacy of the transfer process is characterized by the Deborah number (De); nonlocality is characterized by the Weissenberg number (We). To intensify and control the parameters of transfer processes in media with a nonequilibrium microstructure, it is necessary to match the characteristic time of the technological process and the scale of the deformation rate with the characteristic relaxation time of the medium. Nonlocal in space and non-instantaneous in time processes of transfer of momentum in the media under consideration cannot be described by classical parabolic (instantaneous and local) equations of linear nonequilibrium thermodynamics. In this regard, the transfer of the momentum of the media of a nonequilibrium relaxation microstructure is determined not only by the classical gradients of the corresponding transfer potential but is also a joint solution of the evolutionary equation for the internal macroparameter of the medium. The thermodynamic substantiation of the research results is determined by the relations, which are based on the fundamental principle of fluctuation-dissipation theorems.

4. References
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