Self-consistent model of fluid structure in volume and boundary layer

V S Novosadov, R Kh Dadashev, R A Kutuev, D Z Elimkhanov, Z I Dadasheva, and Kh S Talkhigova

1 Moscow State University of Food Production, 11, Volokolamske sh., Moscow, 125080, Russia
2 Academy of Sciences of the Chechen Republic, 13, prospect named after M. Esambayev, Grozny, Russia
3 Chechen State University, 17a, Dudayev Boulevard, Grozny, 364060, Russia

E-mail: novosadov@list.ru, raykom50@mail.ru, kra-07@mail.ru, edzhabrail@mail.ru, zarema-69-69@mail.ru, talhigova@mail.ru

Abstract. The study proposes the self-consistent theory that combines an activation model, a free volume model and a cluster model. The theory makes it possible to explain why the flow of fluid in slip conditions requires extremely minimal tangential stresses and describes the real structure of the fluid in the boundary layer, as well as to explain why the fluid is almost not squeezed out of the capillary gap.

1. Introduction
At present, various fluid models have been developed. In general, these models can be divided into two groups: in one of them monoatom is taken as a structural unit, and in the other – clusters. Each of these models has its own advantages and disadvantages. In certain approximations these models describe some properties and processes that occur at the interfacial boundary. However, despite a relatively good coincidence of the theory with the experiment for simple polyatomic fluids, the existing models are only the first approximation to describe viscosity and diffusion coefficients in solutions.

It seems interesting to develop a self-consistent fluid model that combines an activation model, a free volume model and a cluster model. The paper analyzes the main models of fluid structure: monoatomic, hole theory, activation models, free volume models and a cluster model. The cluster fluid model is proposed, which explains peculiarities of fluid structure in volume and boundary layer.

2. Methods and materials
In order to understand and describe the processes of wetting, spreading and capillary flow of fluid, the impregnation of porous materials, let us consider the structure and diffusion permeability of fluid using the model of microgroups (clusters) [1–5]. In general, the existing fluid models are divided into two groups: in one of them the monoatom is taken as a structural unit, and in the other – microgroups. From the analysis of the fluid structure and methods of its stabilization (homogenization) it is possible to significantly improve the quality and properties of the fluid, in particular metal melts and solders.

Self-consistent fluid theory shall combine an activation model, a free volume model and a cluster model. It should answer the following questions: why for fluid flow under slip conditions the required
threshold minimum shear tangents $\tau$ do not exceed $10^{-6}$ N/m², comparable to measurement error; how the fluid structure changes over the thickness of the boundary layer, and why it is almost impossible to extrude the fluid from the gap. Tangential stresses for the movement of the fluid particle at the free flow rate $U$ decrease from the wall deep into the fluid according to the law of change of the thickness of the boundary layer. This is obviously due to particular structure of the fluid in the boundary layer, which prevents it from being extruded out of the gap. Based on the analysis of the main fluid models [1–14] the following conclusions can be drawn about its structure. The numerical simulation [6] within the monatomic model shows that the mean square displacement $d$ of the diffusing particle makes $\sim 1.5$, i.e. less than 0.5 of the average distance between the fluid atoms. In other models [14] the value $d$ for self-diffusion in fluid metals is $0.4...1.1$, i.e. $10...40\%$ of the interatomic distance. Unfortunately, based on the analysis of radiograms of the radial distribution of the monatomic fluid, no definite conclusions can be drawn regarding the structure (especially for polyatomic fluids). The hole models [7–10] (Frenkel Ya.I., Glesston S.) represent a relatively rough approximation of the real movement of the fluid molecule. Ignoring the features of interaction between molecules, the Stokes-Einstein equation makes it possible to establish a link between diffusion coefficient $D$ and viscosity $\eta$.

The model seems fair for fluid metals in case of ionic radius of monovalent ion used as a particle radius. Regardless of the fluid model, the temperature dependence $D(T)$ and $\eta(T)$ is determined by the exponential dependence with the corresponding values of the activation $Q_D$ and $Q_\eta$, which in reality is confirmed within a limited temperature range. Within the framework of the hole theory of fluid (Frenkel Ya.I., Eyring D. et al.) it is assumed that cavities (“holes”), which have a certain equilibrium concentration, arise and burst in fluid as a result of fluctuation in various places. Frenkel estimates the radius of holes making less than $\sim 10$ nm, which in order of magnitude corresponds to the size of the cluster. These calculations can only be considered as estimates, as it is illegal to use surface tension in the calculation of macroscopic concepts. As already noted, numerical modelling of particle paths indicates that there is no stick-slip phenomenon of particles and thus the basis for introducing the concept of activated state disappears. The activated and primary states become indistinguishable.

Within the framework of the non-activation models in order to calculate the diffusion coefficient Cohen and Turnbull [11] applied the “free volume model” (the difference between the volume of fluid and the self-volume of molecules), which is continuously redistributed between different areas of the solution. The particle moves when a cavity of more than some critical volume $V_{kr}$ and the redistribution of the free volume does not require work. However, here too, the diffusion motion of particles essentially remains uneven, so that this model is not quite consistent. The best correspondence of theory with experiment in all models is obtained by using ionic radii as diffusion units. To describe the temperature dependence of viscosity, the simple exponential dependence is used in viscosity modeling. Despite a fairly good coincidence of the theory with the experiment for simple polyatomic fluids, the existing models can serve only as the first approximation to describe viscosity and diffusion coefficients in solutions. According to the data given in [1–3], the cluster model quite well describes the self-diffusion and dynamic viscosity coefficients. The models proposed in [1–3] allow determining the dimensions of cluster radii: $r = 0.46$ (Pb)...2.3 (Fe)...6.2 (Li) nm. Inter-cluster breaks at melting temperature occupy a small volume and vary within $1...6\%$. Inter-cluster breaks result in a large number of activated atoms having at least one broken bond on the “surface” of the cluster and serve as a measure of fluid disordering. The concentration $C_0$ – activated atoms for different metals at $T_{pl}$ is within $10...40\%$ indicating that a significant proportion of $is$ are activated. The cluster has a lifetime $t_\omega$ of about $10^{-7}...10^{-8}$ s and can only be conditionally isolated over a period of time greater than its thermal oscillation period $t_\omega$ near some equilibrium position ($t_\omega \sim 10^{-11}...10^{-10}$ s). According to the cluster model [1–3], both individual atomic groups (clusters) and activated atoms in inter-cluster breaks will participate in the elementary act of diffusion in the fluid. Thus, the resulting mass transfer coefficient $D_0$ is composed of members: $D_{cl}$ – cluster diffusion coefficient and $D_a$ – diffusion coefficient by inter-cluster mechanism in the zone of inter-cluster breaks.
However, there is a question of justifying the form of clusters. The authors use a simple cubic shape or sphere inscribed in a cube, with inter-cluster breaks creating a free volume of 1...6%. It should be noted that when the spherical particles are laid, the least dense cubic laying and the denser hexagonal laying are distinguished. Porosity of such medium does not depend on the radius of spheres and makes: at cubic laying 47.64% and at hexagonal – 25.94%, which is almost an order of magnitude more than free volume in fluid 1...6% (on average we accept 3%). The amount of movement of cluster $d$ is greater than 2, which conflicts with the main fluid models. Besides, the theory does not consider the possibility of a vacancy in the cluster, although it is postulated that the size of the cluster is determined by the sphere of stress in the vacancy area. The absence of vacancies in the cluster of fluids excludes the possibility of activation mechanism of diffusion “on the body of the cluster”, and therefore in the volume of fluids.

3. Results

On the role of stress in the interfacial boundary area. The surface of the solid phase, like macrodefect, represents a powerful stimulating factor that changes the structure of the fluid at the interfacial boundary. Wetting in the process of formation of the structured layer of clusters in the area of interfacial boundary [4] creates stresses [5].

\[ \sigma = \sigma_1 + \sigma_2\left(\frac{\Delta a}{a}MCP\right) + \sigma_z^p, \]

where $\sigma_1$ – stress in the surface layer of the solid phase (surface stress) due to surface layer rearrangement; $\sigma_2$ – takes into account the contribution of dilatations due to the crystallographic mismatch between the parameters of crystal lattices of cluster atoms and the solid substrate. This contribution can be as high as about 5\times10^4 MPa [15]. Obviously, this value is overestimated and will be reduced by stress relaxation when the dislocation structure of the surface layer is rearranged. It was experimentally established that the dilation effect does not allow explaining from the state diagram the influence of coatings on the solid substrate at the level of stress in the contact zone. These stresses will also be determined by the difference in metallochemical properties (MCP), which are determined by the features of the electronic structure of the contacting phases. $\sigma_z^p$ – defines the diffusion and concentration stresses arising during mass transfer, which are caused by different mobility of atoms crossing the interfacial boundary of solid and fluid phases (diffusion) and the appearance in the solid phase of atoms of a different variety (concentration). The length of stress field in the area of interfacial boundary in metal systems exceeds tens of microns. The effect of contact strengthening of solder joints depending on the gap proves the correct estimates. If the thickness of the soft layer of solder is less than 50...70 $\mu$m, it is possible to obtain equivalent-strength joints. For organic compounds, the length of this field is reduced by an order of magnitude.

Features of cluster structure of fluid in volume and boundary layer [5]. Let us consider the velocity field in laminar fluid movement along a capillary of size $d=h<1.5$ mm in which convective flows can be neglected. The distribution of speeds (current lines) along the section near the entrance is almost uniform (Fig. 1). Then, under the influence of viscosity forces, the speeds are redistributed along the section. The layers of fluid at the wall are slowed and a boundary layer is formed, and the central part of the flow (core), where a uniform distribution of speeds is still maintained, moves faster, which is due to the need for a certain flow rate of fluid to pass through the capillary section. Outside the defined initial section ($l_{нач}$), the two boundary layers are closed and then a uniform flow is established at some distance greater than the $l_{экв}$. Thus, the uniform flow in the flat capillary consists of 2 “uniform” boundary layers.

Viscosity is the property of a fluid (opposite to fluidity) to resist shear (sliding of its layers), and tangential stresses occur in the fluid. Fluid braking at the wall is caused by viscosity and changes directly in proportion to the velocity gradient $U$:

\[ \tau = \eta \frac{du}{dy}. \]
Figure 1. Formation of velocity profile at the initial section in capillary

Speed profile diagram (Fig. 1) resembles a deck of cards during slanting. It is reasonable to assume that the current lines consist of a layer of clusters (the map itself), and the gap between the layers represents inter-cluster breaks, most of which are parallel to the flow. When calculating the viscosity of simple monatomic fluids Andrade [12] uses the concept of average distance between layers, but does not determine its absolute value. According to [16], a gap of 0.15 nm (1.5 Å) remains between the liophobic walls of the quartz capillaries at the flow between mercury and the walls, which provides a slip effect. As already noted, numerical modeling clearly indicates that the displacement of particles in the fluid occurs at distances less than 0.5 times the interatomic distance, about 1.5 Å. Obviously, in the case of inter-cluster interaction, this distance should be smaller and commensurate with the amount of inter-cluster discontinuities. In cluster models [1...3] this distance is not defined.

The change of volume observed in experiments when melting (ΔV) can be presented as the sum of three factors: ΔV=ΔVr – ΔVc +ΔVg, where ΔVr – increase in volume due to increase of distance between clusters; ΔVc – reduction of volume due to their regrouping. The value ΔVc = (n'/2n)Kv, where Kc – consolidation coefficient, which changes depending on the type of a crystal lattice in a firm state: n' – number of atoms on a surface of a cluster, n – total number of atoms in a cluster. Therefore, Kv at the capillary wall will be substantially higher than in volume. The third factor ΔVg – increase in volume due to emergence and closure of voids as a result of fluctuation. According to Ya.I. Frenkel’s calculations, the dimensions of these voids are less than 10 nm, which is commensurate with the dimensions of clusters. Repackaging of clusters becomes possible in the process of completion of inter-cluster breaks after melting. Obviously, under the influence of the stress field, this factor should lead to a dense hexagonal packing of clusters regardless of the type of packing of atoms within the clusters. The effect of rearrangement is zero for dense-packed metals and becomes more prominent with the structure of the metal becoming more “loose” in a solid state, thus decreasing the melt volume. The equation for assessment of ΔVr and ΔVc for metals with various type of packing is given in work [3].

For closely packed metals Kv=0 and ΔVc=0 the calculation models are in a relatively good compliance with the experiment. Thus, the most energetically advantageous form of clusters in the area adjacent to the surface should be the hexagonal form. While moving away from the surface and approaching the “normal” fluid at the edge of the boundary layer, the shape of the clusters may change. A simple cubic shape is preferable, which corresponds to the model [3] for fluid in volume. The number of holes and their dimensions will also increase when removed from the surface.

Non-vacancy diffusion mechanism in fluid. Similar to the non-vacancy diffusion mechanism in substitutional solid solutions [15] let us consider possible mechanisms for moving clusters in the fluid volume. We consider two versions of the theory of activated diffusion of clusters: 1) the presence of empty space (“holes”) is not assumed and 2) its presence is justified (Fig. 2). The cluster may be displaced either because of the simple exchange of places with neighbors (Fig. 2-1) or due to collective rotation of the group of atoms (Fig. 2-2) in the neighborhood. If there is a void, it is possible to move the cluster in the same way as to move it to the vacancy (Fig. 2-3), etc. According to the crowdion mechanism (crowdion – one-dimensional compression of atoms on certain sections of a row), cluster movement is a consequence of a sequence of small movements of crowdion in the direction of its orientation. This mechanism provides a significant speed of movement with little activation energy. In accordance with the model shown in Figure 3, it is reasonable to present a boundary layer of variable thickness and viscosity clusters in order to provide a shape for changing the
velocity profile. The thickness of these layers and the concentration of voids will naturally increase when approaching the boundary layer. In the solid body, the pores may have a different shape [17]: spherical, cubic or polyhedral, which is limited to eight planes of type (111) and six of type (100), etc. It is highly likely that the equilibrium shape of the hole will also change as the cluster shape changes. Let us consider the mechanism of pulse transmission in the fluid outside the boundary layer. The dashed line in Figure 3 shows current lines. Let us arbitrarily select any layer and consider the interaction of clusters located in the central layer with nearby layers.

Combining the models of Andrade [12] and G.M Panchinkov [13], it is possible to present the following scenario of pulse transmission from one cluster layer to another. Pulse transmission is accomplished by those clusters whose energy reaches some optimal value and when the cluster is at a distance greater than the equilibrium distance. Pulse transmission will be connected with temporal association of two clusters from adjacent layers. The ultimate energy $\varepsilon$ constitutes a certain fraction of fluid evaporation heat ($E_{\text{eva}}$), namely $\varepsilon = 2E_{\text{eva}}/z$, where $z$ – coordination number. Let us assume that the middle layer cluster has transmitted a pulse of more energy to the layer above. Depending on the pulse energy, the associated cluster will move in the direction of the total pulse. In the next step, its dissociation will occur by creating an inter-cluster rupture to achieve equilibrium size and shape. Further migration of dissociated clusters will be consistent with the non-vacancy mechanisms presented in Figure 3, which is typical of all layers.

In order to explain the ultra-small tangential stresses at the flow of fluid in free volume, it is reasonable to assume that the probability of directing most of the inter-cluster breaks between the layers will be planar oriented, i.e. parallel to the action of applied forces. Such arrangement is energetically more advantageous and allows easy sliding of layers. In the boundary layer, the stress field in the interfacial boundary region will orient the inter-cluster breaks orthotropically, i.e. in the direction normal to the surface. While moving from the surface and decreasing the stress field, the orientation of the inter-cluster breaks will gradually approach (at the periphery of the boundary layer) their location in the fluid volume, allowing easy sliding of the layers. Abnormally high viscosity at the solid surface is caused by the association of clusters in the fluid into agglomerations. Figure 3 shows a diagram of the multilayer distribution of associated clusters in the direction of decreasing the intensity of the association process. This model makes it possible to explain the nature of the change in velocity field at the wall. Figure 3 also shows a diagram of the increase in voids and their dimensions towards the boundary layer.

When the fluid interlayer is deformed to a value of ~ $10 \mu m$ [5], the surfaces approach with increasing density and, accordingly, viscosity of the fluid. In this case, a quasi-solid body structure with high yield strength values is formed in the gap. Inter-cluster fractures normal to the surface make it very difficult for clusters of this layer to slide in the direction of tangential stresses. The yield
strength of this layer approaches these values for the solid phase at high temperatures. This is confirmed by the proximity of the pressure values required to extrude fluids and to provide welded joints during pressure diffusion welding. The yield strength of this layer approaches these values for the solid phase at high temperatures.

4. Conclusion

1. The main models of fluid structure were analyzed: monoatomic, hole theory, activation models, free volume models and cluster model. The cluster model of fluid is proposed, which explains peculiarities of fluid structure in volume and boundary layer.

2. On the basis of the model, the reasons are determined, which ensure easy sliding of fluid in the volume, and make its movement in the boundary layer difficult.

3. It is shown that the difficulty of extrusion of fluid interlayer from gap under pressure is caused by special associative structure of clusters and arrangement of inter-cluster breaks along normal to surface, i.e. formation of quasi-solid body structure in a gap with yield stress close to solid phase at high temperatures.

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