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**ASSOCIATES OF CLUSTERS AS UNITS OF FLUID VISCOUS FLOW**

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*The article considers a cluster-associate viscosity model based on the conception of chaotized particles. The authors have developed formulas for calculating the distribution of associates by the number of clusters included in them, by medium-integral number of clusters in the associates, by the portion of associates in the liquid. Conditions to verify the cluster-associate model of fluid viscous flow are recommended. The method of verification is based on the law of conservation and transformation of energy at a sudden stop of fluid flow with registered temperature rise due to back aggregation of clusters into associates, having been destroyed at fluid flow. Taking into account the dual effect of temperature makes it possible to describe the entire temperature range of the existence of the liquid from the melting point to the critical temperature.*

**Keywords:** associate, cluster-associate viscosity model, structure, chaotized particles, crystal-particles, clusters aggregation, thermal barrier, bond order, fluid-particles, vapour-particles.

**Problem statement. The theoretical part**

The authors developed the concept of chaotized particles that ignores specific structure of any masses in a solid, liquid and gas, and differentiates them only by the fact whether they overcome or not thermal barriers at melting and boiling points. Particles that are not able to overcome the melting barrier are named crystal-mobile particles, and their portion according to the Boltzmann distribution is expressed as

$$P_{crm} = 1 - \exp[-\Delta H_m / (RT)]. \quad (1)$$

Particles with energy level above the boiling heat are named vapour-mobile particles with their portion

$$P_{vm} = \exp[-\Delta H_b / (RT)]. \quad (2)$$

Intermediate energy particles between  $\Delta H_m$  and  $\Delta H_b$ , occupy a niche, referred to as fluid-mobile particles:

$$P_{lqm} = 1 - P_{crm} - P_{vm} = \exp[-\Delta H_m / (RT)] - \exp[-\Delta H_b / (RT)]. \quad (3)$$

According to their energy status crystal-mobile particles are responsible for long-range bond order, while fluid-mobile particles – for short-range bond order, and vapour-mobile particles – for zero bond order.

Of greatest interest at this point is the liquid state of a substance, which is known to be like the solid state near to the crystallization point, and in the boiling point zone it resembles the gaseous state. In these conditions, clusters – crystal-like forms are quite evidently detected in the liquid. This confirms the results of our work on the dominant presence in the liquid the crystal-particles that serve as a reservoir for the virtual self-organizing clusters of them.

In this regard, we have suggested that one of the most important characteristics of a liquid, its viscosity is based on the proportion of crystal-particles; this has made it possible to express the

temperature dependence of the viscosity with regard to the temperature dependence of the crystal-particle portion (1) using a single reference point:

$$\eta = \eta_r (T_r/T). \quad (4)$$

The verification of this formula by reference viscosity data showed that a stronger dependence is actually implemented:

$$\eta = \eta_r (T_r/T)^a. \quad (5)$$

on condition that  $a > 1$ .

### Justification (verification) of the cluster-associate liquid model

The fact of stronger interconnection of the viscosity of the liquid with crystal-particle portion indicates that larger masses than clusters, which we call associates of clusters affect the viscosity. The literature refers to the possible formation of associates on the same grounds as the formation of clusters, i.e. by aggregation, but at a higher level.

Since this specifies the overall picture of virtual self-organization of particles in a liquid, following the unified fundamental Boltzmann distribution to overcome some thermal barriers of chaotic motion of particles, this hypothesized suggestion of cluster-associate model of a liquid and its viscous flow has required more rigorous justification.

First of all, attention was drawn to the fact that determined from the Frenkel equation the activation energy of viscous flow in most cases amounts to hundreds, and for slag systems thousands of kilojoules per mole. These values are far superior to the energy of rupture of a covalent bond and therefore can not be attributed to any particular mole of a chemical substance, since it is known that at viscous flow just weak van der Waals forces of attraction of 2-20, with an average of 10-11 kJ/mol are overcome. Consequently, in this case mentioning the mole we should mean a larger mass. Cluster associate is the most likely item for such a mole based on its most loose and bulky configuration.

It turned out that dividing the activation energy of viscous flow by  $a$  indicator which values are independently found by reference data at different temperatures according to the formula (5) and varies for different substances from a few to hundreds, in all cases the results are obtained, remaining within 2-20 kJ/mol. This means that the  $a$  indicator has a meaning of the degree of cluster association and is an average number of clusters in the associate. Therefore, as the unit of viscous fluid flow, cluster associates should be considered; on their destruction external energy (potential or mechanical) is spent to initiate movement. [1]

The obtained values of the degree of clusters association for each substance showed a clear decreasing dependence on temperature, and it once again pointed to the reasonability of meaning  $a$  as representing an assembly of supracluster mass, which should be subjected to determinate destruction with increase in temperature. For the entire temperature range, the average value of the degree of cluster association was necessary for processing the data on the activation energy of viscous flow, which is obtained for the entire temperature range as well. But to adequately represent the temperature dependence of the viscosity it was necessary to take into account the effect of temperature on the  $a$  indicator. This was done as follows.

Since the dynamics of changing the content of cluster associates with respect to temperature is substantially similar to the dynamics of changes in the content of the clusters, then the temperature dependence  $a = f(T)$  can be expressed as in (5) in the following way:

$$a = a_2 (T_2/T)^b, \quad (6)$$

where  $a_2$  is the degree of association for the second reference point,  $\eta_2, T_2$ ;  $b$  is a measure of lowering of the degree of the cluster association, it is constant for the given substance.

Denoting the coordinates of the first reference point in (5) as  $\eta_1, T_1$ , we obtain the dependence of viscosity on temperature, the effect of which is taken into account both for clusters and associates

$$\eta = \eta_1 (T_1/T)^{a_2 (T_2/T)^b}. \quad (7)$$

To find the numerical values of  $a_2$  and  $b$  in addition to the second, the third reference point,  $\eta_3, T_3$ , must be used and then we obtain the expressions

$$a_2 = \frac{\ln(\eta_2/\eta_1)}{\ln(T_1/T_2)}, \quad (8)$$

$$b = \frac{\ln(a_3/a_2)}{\ln(T_2/T_3)}, \quad (9)$$

where

$$a_3 = \frac{\ln(\eta_3/\eta_1)}{\ln(T_1/T_3)}. \quad (10)$$

Account of dual effect of temperature allows the most rigorous description of the entire temperature range of the existence of the liquid from its melting point to the critical one. This could not be have done by purely fundamental or entirely empirical dependences of viscosity [3]. The proposed dependence apparently most optimally combines both the fundamental basis of the liquid state, which obeys the Boltzmann distribution, and, as the occasion requires, the supporting empirical points in the studied temperature range, due to particular complexity of the aggregate state under study.

### Discussion of the numerical data

As an example, the results of processing the reference data on viscosity [4] of sodium are provided. For the latter in [39]  $T_m=371\text{K}$ ,  $T_b=1156\text{K}$ ,  $T_{cr}=(2573)\text{K}$  were found. Within the temperature range for the reference values of viscosity from 373 to 2273K, reference points  $T_1=423\text{K}$ ,  $\eta_1=0.542\text{mPa}\cdot\text{s}$ ;  $T_2=1073\text{K}$ ,  $\eta_2=0.170\text{ mPa}\cdot\text{s}$ ;  $T_3=1923\text{K}$ ,  $\eta_3=0.106\text{ mPa}\cdot\text{s}$  were selected and the following dependency was calculated

$$\eta = 0,542(423/T)^{1,245(1073T)^{0,2483}}, \text{ mPa}\cdot\text{s}. \quad (11)$$

The previously known equation [26] now has the form

$$\ln \eta = - 3,6735 - 0,4583 \ln T + 542,781/T, \text{ P}. \quad (12)$$

Comparison of the data is presented in Table 1.

The evident agreement of calculated using the proposed model and reference data implies the soundness of the assumption of the  $b$  indicator constancy, which may be due to the nature of each substance. As to the degree of association of clusters, it consistently decreases. Both features were characteristic of all the above elements [5], as well as greater correlation coefficients in comparison with any other empirical dependencies.

Table 1 - Reference data [4] and calculated data from (12) and (11) on the dynamic viscosity of the liquid sodium.  $a$  is the degree of association of clusters (for the fragment  $1.2456(1073/T)^{0.2483}$  in (11))

$T$ , K	$\eta[4]$ , мПа·с	$\eta(12)$ , мПа·с	$\eta(11)$ , мПа·с	$a$	$T$ , K	$\eta[4]$ , мПа·с	$\eta(12)$ , мПа·с	$\eta(11)$ , мПа·с	$a$
$T_m = 371$	–	0,729	0,670	1,621	1323	0,141	0,142	0,141	1,182
373	0,687	0,721	0,664	1,619	1373	0,137	0,138	0,136	1,172
423	0,542	0,573	0,542	1,569	1423	0,133	0,133	0,132	1,161
473	0,451	0,475	0,457	1,527	1473	0,129	0,130	0,129	1,151
523	0,387	0,407	0,395	1,489	1523	0,126	0,126	0,126	1,142
573	0,341	0,356	0,348	1,456	1573	0,123	0,123	0,122	1,133
623	0,306	0,318	0,312	1,426	1623	0,120	0,120	0,120	1,124
673	0,278	0,288	0,283	1,399	1673	0,117	0,117	0,117	1,116
723	0,255	0,263	0,260	1,374	1723	0,115	0,114	0,114	1,107
773	0,237	0,243	0,240	1,351	1773	0,113	0,112	0,112	1,100
823	0,221	0,226	0,224	1,330	1823	0,110	0,110	0,110	1,092
873	0,208	0,212	0,210	1,311	1873	0,108	0,107	0,108	1,085
923	0,196	0,200	0,198	1,293	1923	0,106	0,105	0,106	1,078
973	0,186	0,189	0,187	1,276	1973	0,105	0,103	0,104	1,071
1023	0,177	0,180	0,178	1,260	2023	0,103	0,101	0,103	1,064
1073	0,170	0,172	0,170	1,246	2073	0,101	0,100	0,101	1,058
1123	0,163	0,165	0,163	1,232	2123	0,100	0,098	0,099	1,051
$T_b = 1156$	–	0,160	0,159	1,223	2173	0,098	0,096	0,098	1,045
1173	0,156	0,158	0,156	1,218	2223	0,097	0,095	0,097	1,040
1223	0,151	0,152	0,151	1,206	2273	0,096	0,093	0,095	1,034
1273	0,146	0,147	0,145	1,194	$T_{cr} =$ (2573)	–	0,086	0,089	1,002

It should be borne in mind that the degree of cluster association for each temperature is a representative data item representing the actual associates distribution by the number of clusters included in them. This assertion is based on the similarity to the distribution of clusters by the number of involved crystal-particles, as regularities of exchange collisions between the associates in terms of probability representation should be identical to those implemented for clusters.

Thus, in our paper [6] based on the probability of intercluster exchange transformations and mathematical limit expression for the sum of the probabilities of  $n$ -particle collisions the following expression for the  $n$ -particle clusters proportion was obtained

$$P_{\kappa,n} = P_{crm}^n (1 - P_{crm}), \quad (13)$$

that for each temperature taking into account (1) takes the form

$$P_{\kappa,n} = \left[ 1 - \exp\left(-\frac{\Delta H_m}{RT}\right) \right]^n \exp\left(-\frac{\Delta H_m}{RT}\right). \quad (14)$$

In this case the medium-integral value of the number of crystal-particles in the clusters found by the mathematical analysis of the formula (13) is equal to the set of clusters with particle content from  $n_{c,m}$  to  $n_{c \rightarrow \infty}$ :

$$\bar{n}_{\kappa} = n_{\kappa,H} - 1/\ln P_{crm} = n_{\kappa,H} - (\ln \{1 - \exp[-\Delta H_m/(RT)]\})^{-1}, \quad (15)$$

where  $n_{c,m}$  is the smallest number in a set of particles in the cluster, which is usually given for a particular purpose.

In turn, the proportion of crystal-particles contained in clusters, beginning with  $n_{c,m}$ -particles is expressed as

$$P_{K,n_{K,H+\infty}} = P_{crm}^{n_{K,H}} = \{1 - \exp[-\Delta H_m / (RT)]\}^{n_{K,H}}. \quad (16)$$

Supracluster masses – associates – may be formed from clusters of any size and make their own any size, up to tending to infinity as clusters do. Associates are formed with corresponding sharp decline in the probability of their conservation and content in the total mass according to the formula similar to (13). To use similarity is important to determine which part or all of the crystal-particles with their common proportion  $P_{crm}$  may participate in the formation of associates of clusters. This problem can generally be solved as follows.

First of all, under the terms of uniform obedience to probability laws of interconversion of consolidated particles of any size can be likened to the distribution of associates by the number of contained clusters found by the distribution of crystal-particle in the clusters (13), (14). In this particular case, the proportion of clusters involved in the formation of associates, will be determined by some initial values of  $n_{c,m}$ , and expressed by the formula (16). Hence the distribution of associates in the full range from single-particle to the infinitely large as in (13) and (14) will be expressed as

$$P_{A,n} = P_{K,n_{K,H+\infty}}^n \left(1 - P_{K,n_{K,H+\infty}}\right) = \left(P_{crm}^{n_{K,H}}\right)^n \left(1 - P_{crm}^{n_{K,H}}\right) = P_{crm}^{n_{K,H}n} \left(1 - P_{crm}^{n_{K,H}}\right). \quad (17)$$

Now assume that associates are only formed from clusters starting with  $n_{c,m}$ -particle or further. The proportion of these clusters is expressed by the formula (16), and when  $n_{c,m}=1$  (single-particle clusters), this proportion is equal to the total of the crystal-particle  $P_{crm}$ . Then the proportion of associates, beginning with  $a_n$ -cluster will be expressed as in (16) as

$$P_{A,a_{H+\infty}} = \left(P_{K,n_{K,H+\infty}}\right)^{a_n} = \left(P_{crm}^{n_{K,H}}\right)^{a_n} = P_{crm}^{n_{K,H}a_n}. \quad (18)$$

It is natural that account of single-particle clusters and single-cluster associates will result in value  $P_{A,a_{H+\infty}} = P_{crm}$ , i.e. to the involvement of all the crystal-particles in the content of clusters and associates. In fact this may not be so, and formation of associates can be most probably implemented under some, for example, steric conditions, starting with some  $n_{c,m}$ -particle clusters and is accompanied by the formation of  $a_n$ -cluster and greater associates, and that is recorded by (17).

The verification of these assumptions is possible in concept, since the cluster-associate model of viscous flow implies that it is initiated by associates destruction, i.e. by expenditure of energy. On the contrary, when the flow stops there should occur the reverse associates formation with energy release, and therefore with increase in the liquid temperature. It is necessary to isolate the thermal energy, evolved in this process that has been transformed by relaxation of the kinetic energy of the flow. In this case the actual temperature rise, if it can be measured, can be compared with the expected at different variants of  $n_{c,m}$  and  $a_n$  using the formula (18) by multiplying it by the activation energy of viscous flow in terms of the associate and then comparing it with the change of the heat content in the liquid. This would require a particular experiment with sufficiently sensitive recording equipment.

In addition, it is possible to establish beforehand the consistency of the average degree of cluster association defined by the formula similar to (15) for the average particles number in the cluster,

$$\bar{a} = a_H - 1 / \ln P_{crm}^{n_{c,m}} = a_H - \left( \ln \{1 - \exp[-\Delta H_m / (RT)]\} \right)^{n_{c,m}}^{-1}, \quad (19)$$

which takes into account the proportion of clusters with the number of particles  $n_{c,m}$  and greater, with the degree of association of clusters found from viscosity data on the basis of the model (7) and the formula (18) at the same temperature.

In this case, by varying  $a_n$  it is possible to find its consistent value and use it for the formula (17) evaluation. This opens up a real opportunity for direct verification of cluster-associate model based on the law of energy conservation. Especially since there are no other sources of energy except converting the kinetic energy into heat energy and the energy of association of clusters at the flow stopping.

## Conclusions

1. Based on the developed by the authors conception of chaotized particles, a cluster-associate viscosity model is considered in detail.

2. The formulas for calculating the distribution of associates by the number of clusters included in them, as well as on the medium-integral number of clusters in the associates, and the proportion of associates in a liquid are proposed.

3. The authors developed conditions to verify the cluster-associate model of fluid viscous flow based on the law of conservation and transformation of energy at a sudden stop of a fluid flow with a registered temperature rise due to back aggregation of clusters into associates, having been destroyed at liquid motion.

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