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The Concept of Randomized Particles as the Basis of Cluster and Associate Theory Viscosity and Flow

V. P. Malyshev and A. M. Makasheva

Chemical and Metallurgical Institute Named after Zh. Abishev, Karaganda 100009, Kazakhstan

Abstract: Using thermal barriers at the melting point ΔH_m and RT_m, it is shown that the latter directly reflects the chaotic process, since it is equal to the kinetic energy reserve of chaotic (thermal) particle motions, and the first additionally takes into account the energy expenditure for overcoming the potential energy of the interconnection of particles, which is typical for inorganic compounds. Therefore, to determine the share of crystal-mobile particles responsible for the viscosity of the melt, the chaotization barrier of RT_m should be used, since in the virtual clusters the potential binding energy is conserved, thereby compensating for the heat expense of breaking these bonds upon melting. Therefore, to analyze the share of crystal-mobile particles, it is necessary to use the formula of their share in the form: $P_{crm} = 1 - exp\left(-\frac{T_m}{T}\right)$. On the basis of the distribution of clusters previously found by the authors in terms of the number of crystal-mobile particles included in them, it was shown that all non-single crystal-mobile particles are responsible for the viscosity, and for flowability all single particles, including crystal-mobile, liquid-mobile and vapor-mobile. This ensures the superiority of the share of single particles over the share of crystal-mobile particles arranged in non-single clusters at the melting point, and thereby the fluidity of the melt. Based on the share distribution of clusters in terms of the number of particles entering into them, the share of non-single clusters responsible for the viscosity of the melt is expressed as: $P_{cl} = P_{crm}^2 = [1 - exp(-T_m/T)]^2$. The probabilistic meaning of the formation of clusters from non-single crystal-mobile particles is extended to the formation of associates, which made it possible to disclose the meaning of the second level of the exponential dependence of viscosity in the cluster and associate model: $\eta = \eta_1 (T_1/T)^{a_2 (T_2/T)^b}$, where the first level is responsible for the formation of clusters, and the second—for associates. This form corresponds to the physical hierarchy when combining crystal-mobile particles. The previously proposed method for processing viscosity data for the cluster and associate model assumed the use of three reference points from the available experimental array of values of viscosity at different temperatures. This method is supplemented by using the entire set of data on the viscosity with the preservation of two reference points and processing the rest to determine the exponent b, which has the meaning of aggregation degree of associates, from the linearized dependence: $\ln \frac{\ln(\eta/\eta_1) \ln(T_1/T_2)}{\ln(T_1/T) \ln(\eta_2/\eta_1)} = b \ln(T_2/T)$. The new method was tested on reference data and showed its high statistical adequacy.

Key words: Randomized particles, viscosity, fluidity, cluster, associate, liquid lithium, heat of melting, heat of boiling.

1. Introduction

The concept of randomized particles is based on the fact that to each substance in each aggregate state there is inherent not only structural certainty, but also chaotization of the structure due to the disordered thermal motion of the particles. Thus, a solid state is characterized not only by the crystalline form, but also by the plasticity, which can be considered as a predisposition to a liquid state; solubility, that is, a tendency to destroy the crystal; equilibrium vapor pressure, and hence the presence of high-energy particles in the solid state. In the liquid state, dynamically unsustainable (virtual) fragments of the solid phase and equilibrium with the vapor are detected. The gaseous state contains virtual microdroplets and microcrystals of the solid phase. These features are considered in our works [1, 2].

The features noted allow us to state that at least three classes of energetically different particles are present in each aggregate state—those that are

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Corresponding author: Astra Mundukovna Makasheva, doctor of technical sciences, professor, research fields: physical chemistry, metallurgy.

responsible for maintaining the crystalline state; the second—for the realization of the liquid state, and the third—for the most free gaseous state. Since they are all part of the Boltzmann distribution, they can be distinguished with the help of suitable energy barriers. As such, in the first approximation we are recommended to use the heats of melting ΔH_m and boiling ΔH_b.

2. Forms of Expression of the Concept of Randomized Particles

Then, bearing in mind the equality of the sum of the shares of all three classes to unity and the attribution of particles sub-barrier to the heat of melting to those that are responsible for the least energy-intensive solid state and, by virtue of their virtuality, called crystal-mobile, their share will be expressed as

$$P_{crm} = 1 - exp\left(-\frac{\Delta H_m}{RT}\right) \qquad (1)$$

The most high-energy particles, called vapor-mobile, are super-barrier with respect to the heat of boiling, and their share is

$$P_{vm} = exp\left(-\frac{\Delta H_b}{RT}\right) \qquad (2)$$

The share of liquid-mobile particles has an energy interval between the heats of melting and boiling, that is, the share minus the share of crystal-mobile and vapor-mobile particles:

$$P_{lqm} = 1 - P_{crm} - P_{vm} = exp\left(-\frac{\Delta H_m}{RT}\right) - -exp\left(-\frac{\Delta H_b}{RT}\right) \qquad (3)$$

All three energy shares are contained in all three aggregate states, changing with increasing temperature as follows: the share of crystal-mobile particles in the interval from absolute zero to infinity decreases from unity to zero; on the contrary, the relative content of the vapor-mobile particles increases from zero to unity, and consequently the share of the liquid-mobile particles passes through a maximum, first increasing from zero to the maximum value, then decreasing to zero.

It should be borne in mind that energy barriers ΔH_m and ΔH_b are used in Eqs. (1)-(3), taking into account the sum of the kinetic energy of the thermal motion of particles and the potential energy of their attraction. The purely thermal characteristic of the phase transitions will be characterized by the thermal energy reserves RT_m and RT_b. Using these values as thermal barriers, the randomized component in the share of crystal-mobile, liquid-mobile and vapor-mobile particles will be more clearly identified:

$$P_{crm} = 1 - exp\left(-\frac{T_m}{T}\right) \qquad (4)$$

$$P_{vm} = exp\left(-\frac{T_b}{T}\right) \qquad (5)$$

$$P_{lqm} = exp\left(-\frac{T_m}{T}\right) - exp\left(-\frac{T_b}{T}\right) \qquad (6)$$

In this case, at the points of melting and boiling, the ratio of the proportions of these particles is found, which is close to the proportion of the golden section (0.618:0.382), which can serve as a theoretical system explanation of macrotransitions from one state to another, since the maximum possible equilibrium content of particles is responsible for the stability of the same macro state of the system.

Thus, at the melting points the value of the share of crystal-mobile particles is:

$$P_{crm,m} = 1 - exp(-1) \approx 0.632 \qquad (7)$$

which, with a further increase in temperature, decreases, and the system loses its crystalline connection.

At the boiling points, the share of particles that hold the system in the condensed state is:

$$P_{cond} = 1 - P_{vm} = 1 - exp(-1) \approx 0{,}632 \qquad (8)$$

is also close to the proportion of the golden section, and an increase in temperature leads to a loss of liquid macrostate.

But this very state is far from homogeneous and includes virtually coexisting phases of three classes of particles. A new interpretation of viscosity requires the detailed liquid state in terms of the form of existence of these particle classes. First of all, this refers to the crystal-mobile particles.

3. Combinations of Crystal-Mobile Particles in a Liquid

To the known general theoretical propositions on the formation of solid phase nuclei in a liquid [3-5], we can add a more detailed treatment of the fractional distribution of nuclei of the solid phase, according to what is now called clusters, depending on their size at any temperature, taking into account the nature of the substance. These clusters are formed from crystal-mobile particles as incapable of overcoming the energy barrier of melting, even in the liquid state of matter. Here they themselves form chaos from the virtual embryos of the solid phase, creating a viscous consistency by the presence, as it were, of the non-melted fragments of the crystal lattice. At the same time, knowledge of the general share of crystal-mobile particles, previously not known, on the basis of Eqs. (1) or (4) substantially facilitates the solution of the problem of the distribution of clusters as a function of the number of particles in them, and hence also their sizes. This solution was found by us in two ways [1].

The first method took into account the probability of direct formation of *n*-particle clusters, including single-particle clusters, from the original set of crystal-mobile P_{crm} particles as a result of *n*-particle collisions:

$$P_{crm,n} = P_{crm}^{n} \,. \qquad (9)$$

To ensure the equality of the sum of the probabilities of the formation of all *n*-particle clusters to their total share P_{crm}, it was required to use the well-known formula for expanding the suitable function $(1 - x)^{-1}$ in a series and by transforming it identically to the corresponding expression P_{crm} through $P_{crm,n}$:

$$P_{crm} = (1 - P_{crm}) \times$$
$$\times \left(P_{crm} + P_{crm}^2 + P_{crm}^3 + P_{crm}^4 + \cdots + P_{crm}^n + \cdots\right) \qquad (10)$$

This follows the formula for the distribution of *n*-particle clusters within their general content P_{crm}:

$$P_{crm,n} = \left(1 - P_{crm}\right)P_{crm}^{n} \,. \qquad (11)$$

We arrive at the same result in determining the probability of formation of the *n*-particle cluster $P_{crm,n}$ due to mutual transformations with the $(n - 1)$-particle cluster in the reaction

$$nK_{n-1} = (n-1)K_n \,, \qquad (12)$$

where K_{n-1}—cluster of $(n - 1)$ particles, K_n—cluster of *n* particles.

Under equilibrium conditions, the collision probability *n* clusters of K_{n-1} is equal to the collision probability $(n - 1)$ of clusters K_n

$$P_{K_{n-1}}^{n} = P_{K_n}^{n-1} \,. \qquad (13)$$

As a result of sequential consideration of the formation of clusters, beginning with monomers, first without taking into account their transformation into a subsequent cluster, and then this account leads to the result, identical as Eq. (11)

$$P_{crm,n} = P_{crm}^{n}(1 - P_{crm}). \qquad (14)$$

Making sure that the share of *n*-particle clusters, starting with a single-particle cluster, can be fairly rigorously taken into account, one can proceed to the justification of viscosity and fluidity as caused by the content of bound (actually cluster) and free (single) particles.

4. Viscosity and Fluidity as a Function of the Content of Virtually Bound and Free Particles in a Liquid

The previously noted dominance of crystal-mobile particles at the crystallization point explains the predisposition and the transition to a solid state at this point due to the critical level of their dominance, close to the proportion of the golden section (~ 0.62:0.38). As the temperature rises, the share of these particles, although decreasing, remains above the share of liquid-mobile and vapor-mobile particles, up to equalization with them at the boiling point [1]. It turns out that the liquid in the entire range of the liquid state turns out to be largely crystal-like, despite the apparent expression of fluidity, starting from the melting point. This paradox is resolved due to the content of a certain share of mobile single (free) particles in the crystal-mobile particles, which according to Eqs. (11) and (14) is equal to

$$P_{crm,1} = (1 - P_{crm})P_{crm}. \quad (15)$$

Single crystal-mobile particles differ from other crystal-mobile particles, arranged in clusters in accordance with Eq. (11), with a greater energy intensity and serve as a transitional link to the above-barrier particles of the heat of melting, liquid- and vapor-mobile.

Then the total share of virtually free particles in the liquid is expressed as

$$P_{fr} = P_{crm,1} + (P_{lqm} + P_{vm}) =$$
$$= P_{crm}(1 - P_{crm}) + (1 - P_{crm}) = 1 - P_{crm}^2. \quad (16)$$

In this case, the share of bound (not free) crystal-mobile particles turns out to be equal to $1 - P_{fr} = P_{crm}^2$, and it is this, as shown in Ref. [1] with the example of simple substances, correlated with the viscosity of the melts.

Thus, a certain set of free particles is contained in the liquid, which, in view of their non-association, must determine the free fluid's proper behavior—its spreading and the ability to assume the shape of its enclosing vessel.

In the variant of representing the share of randomized particles through the thermal barriers RT_m and RT_b (Eqs. (4)-(6)) for the share of free particles at the melting point, we obtain

$$P_{fr,m} = 1 - P_{crm,m}^2 =$$
$$= 1 - [1 - exp(-T_m/T_m)]^2 \cong 0.600! \quad (17)$$

The proximity to the proportion of the golden section means that even at the point of solidification of the liquid, it must maintain fluidity due to the prevailing share of free particles with all the predisposition of the substance to crystallization, in view of the same proximity to the critical invariant of stability for the total share of crystal-mobile particles (Eq. (7)).

As we showed earlier in Ref. [1], the share of free particles at the melting point identical to Eq. (17) is obtained using Eq. (1) for the share of crystal-mobile particles with the thermal barrier expression as ΔH_m and using the melting entropy equality $\Delta S_m = \Delta H_m/T_m$ its positional component [6], which is close in magnitude to the universal gas constant R:

$$P_{fr,m} = 1 - \left[1 - exp\left(-\frac{\Delta H_m}{RT_m}\right)\right]^2 =$$
$$= 1 - [1 - exp(-R/R)]^2 = 0.600. \quad (18)$$

This invariant was verified from the reference values of ΔH_m and T_m for metals [1] and confirmed the idea that when melting the contribution of the chaotization of the structure is decisive in comparison with the vibrational and electronic components, since there is neither breaking of bonds, not loss electrical conductivity unlike most inorganic compounds, the melting of which requires not only overcoming the chaotization barrier of RT_m, but also the potential energy of attraction or coupling of particles, which are summed up in the value of ΔH_m.

Probably, virtually existing clusters in the liquid state of matter due to excess energy of attraction form supercluster combinations—associates and aggregations of associates. The ratio $\Delta H_m/(RT_m)$ for simple substances and for their compounds is presented in Table 1 for the number of metals of the first group and their halides according to reference data [7].

It can be seen from the table that pure metals are characterized by a ratio $\Delta H_m/(RT_m)$ close to unity and not exceeding it in the range of 0.765-0.901 with an average value of 0.844. This indicates that the heat of melting is consumed only to overcome the chaotization barrier. For all halides of the main subgroup of the first group, this ratio significantly exceeds the value of the chaotic barrier RT_m, which makes it possible to form supercluster associates and aggregates of associates. Thus, for the halides under

Table 1 Melting temperature (T_m, K), heat of fusion (ΔH_m, J/mol), thermal chaotization barrier (RT_m, J/mol) and their ratio $\Delta H_m/(RT_m)$ for simple substances and their compounds by the example of elements the first group of the periodic table and their halides.

Substance	T_m	ΔH_m	RT_m	$\frac{\Delta H_m}{RT_m}$	Substance	T_m	ΔH_m	RT_m	$\frac{\Delta H_m}{RT_m}$
Li	454	2,887	3,775	0.765	RbCl	988	18,400	8,215	2.240
Na	371	2,690	3,085	0.872	CsCl	918	15,900	7,633	2.083
K	337	2,325	2,802	0.830	LiBr	825	17,600	6,859	2.566
Rb	313	2,344	2,602	0.901	NaBr	1,020	26,100	8,481	3.078
Cs	302	2,133	2,511	0.850	KBr	1,007	25,500	8,373	3.046
LiF	1,121.4	27,090	9,324	2.906	RbBr	955	15,500	7,940	1.952
NaF	1,269	33,350	10,551	3.161	CsBr	909	–	7,558	–
KF	1,131	27,020	9,404	2.873	LiI	742	14,600	6,169	2.367
RbF	1,106	17,300	9,196	1.881	NaI	933	23,600	7,757	3.042
CsF	976	21,700	8,115	2.674	KI	954	24,000	7,932	3.026
LiCl	883	19,900	7,342	2.711	RbI	915	12,500	7,608	1.643
NaCl	1,073.8	28,160	8,928	3.154	CsI	894	–	7,433	–
KCl	1,044	26,530	8,680	3.056					

consideration, the excess of the heat of melting above the chaotization barrier is within the limits of their ratio from 1.643 to 3.161 with an average value of 2.637 with the average values for fluorides close to 2.699, chlorides—2.649, bromides—2.660 and iodides—2.520. Probably, this should determine the degree of association of clusters, which is directly related to the viscosity of the fluid in its new representation on the basis of the concept of randomized particles [1].

Thus, the problem reduces to the creation of such a mathematical model of the temperature dependence of viscosity, in which, on the one hand, a fundamental connection with the Boltzmann distribution through the concept of randomized particles would be taken into account and, on the other hand, the shape of the model could be directly expressed in terms of the degree of cluster association, which destruction would correspond to an activation barrier, usually found by the Frenkel equation.

Since it is viscosity, rather than fluidity, that is directly experimental determination, it is expedient to make a direct comparison of the experimental temperature dependence of viscosity and the share of crystal-mobile particles (Eq. (4)), which reflects the influence of the thermal barrier of chaotization of RT_m on the formation of virtual structural forms in liquids—clusters, associates and aggregations.

5. Development of Cluster and Associate Model of Viscosity

Since the temperature dependences of certain structural and chaosensitive characteristics of matter in various aggregate states are in the Boltzmann distribution, it is possible to directly compare these dependences when they are presented in a normalized form and provide single numerical limits of variation over a wide temperature interval. Conceptually, this corresponds to the comparative methods of calculating the physicochemical properties developed in the works of M. Kh. Karapetyants [8, 9]. This allows us to exclude from consideration the very fundamental temperature dependence of a property having a complex and not fully disclosed expression.

Thus, the viscosity of the liquid substance with increasing temperature decreases from a certain value of η_1 near the melting point at $T_1 < T_m$ to a value tending to zero for $T \to \infty$. At the same time, the share of virtually-connected (not free) crystal-mobile particles, determined by the chaotization barrier Eq. (4) and equal to P_{crm}^2, decreases from the value $[1 - exp(-T_m/T_1)]^2$ to zero. This initial position for comparing the viscosity and the share of crystal-mobile particles can be expressed in the form of inequalities as follows:

$$T_1 \le T \le \infty, \tag{19}$$

$$\eta_1 \ge \eta \ge 0, \tag{20}$$

$$[1 - exp(-T_m/T_1)]^2 \ge [1 - exp(-T_m/T)]^2 \ge 0 \tag{21}$$

The dependence Eq. (20), normalized with respect to the initial conditions, looks like

$$1 \ge \eta/\eta_1 \ge 0. \tag{22}$$

To normalize the dependence Eq. (21), it is necessary to carry out some identical transformations.

The extraction of the square root does not change the direction of the inequality

$$[1 - exp(-T_m/T_1)] \ge [1 - exp(-T_m/T)] \ge 0. \tag{23}$$

Subtracting a unit from each part, and then multiplying by (– 1), taking into account the change in the direction of the inequality we obtain:

$$exp(-T_m/T_1) \le exp(-T_m/T) \le 1. \tag{24}$$

After logarithm and multiplication by (– 1), we arrive at expression

$$T_m/T_1 \ge T_m/T \ge 0, \tag{25}$$

in which one can normalize on the left-hand side of the inequality:

$$1 \ge \frac{T_1}{T} \ge 0. \tag{26}$$

Here, agreement is already reached with inequality Eq. (22) both with respect to the numerical limits and the direction of the inequalities. Moreover, the inequality Eq. (26) is not distorted and will assume a more general form if all its parts are raised to an arbitrary real number *a*:

$$1 \ge \left(\frac{T_1}{T}\right)^a \ge 0. \tag{27}$$

In this form, we can equate the internal parts of inequalities Eqs. (22) and (27), noting that they are subject to the fundamental Boltzmann distribution:

$$\frac{\eta}{\eta_1} = \left(\frac{T_1}{T}\right)^a, \tag{28}$$

from which we obtain the temperature dependence of the viscosity

$$\eta = \eta_1 \left(\frac{T_1}{T}\right)^a. \tag{29}$$

As it turned out when processing reference data for simple substances [1], the exponent a is temperature-dependent and has the meaning of the degree of association of clusters, since the assignment of the activation energy of the viscous flow of melts determined by the Frenkel’s equation on the basis of experimental data to this value gives a constant value, commensurate with the binding energy of the van-der-Waals forces of attraction of the particles. On this basis, the authors put forward the hypothesis that the viscous flow occurs due to the destruction of cluster associates with the preservation of the clusters themselves.

At the same time, it was suggested that the very dependence of the degree of association of clusters on temperature obeys the Boltzmann distribution, and therefore it is expressed similarly to Eq. (29) with its reference point a_2 at T_2

$$a = a_2 \left(\frac{T_2}{T}\right)^b, \tag{30}$$

where *b* gets the meaning of the degree of aggregation of associates.

As a result, a hierarchical viscous model was constructed:

$$\eta = \eta_1 (T_1/T)^{a_2 (T_2/T)^b}, \tag{31}$$

which is adequate hierarchical subordination of clusters, associates and aggregations of associates and in general the complex nature of viscous flow.

In this case, the postulated expression Eq. (30) can be obtained from the comparison in the general form of the temperature dependences of the degree of association of clusters and the share of underbarrier particles of the viscous flow the activation energy *U*, since this energy is expended on the destruction of associates within the cluster and associate model of viscosity.

Initial inequalities:

$$T_2 \le T \le \infty, \tag{32}$$

$$a_2 \geq a \geq 0, \tag{33}$$

$$\left[1 - exp\left(-\frac{U}{RT_2}\right)\right] \geq \left[1 - exp\left(-\frac{U}{RT}\right)\right] \geq 0. \tag{34}$$

In the form normalized with respect to the initial conditions, Eq. (33) takes the form:

$$1 \geq \frac{a}{a_2} \geq 0. \tag{35}$$

To ensure comparability with this equation, inequality Eq. (34) must be brought to agreement on the numerical expressions for the limits and on the direction of the inequalities, for which it is necessary to carry out the identical transformations Eq. (34), similar to the above for comparing the temperature dependences of viscosity and the share of bound crystal-mobile particles.

Subtracting the unit from Eq. (34) and then multiplying by (– 1), we obtain

$$exp\left(-\frac{U}{RT_2}\right) \leq exp\left(-\frac{U}{RT}\right) \leq 1. \tag{36}$$

Logarithm and multiplying by (– 1), we find

$$\frac{U}{RT_2} \geq \frac{U}{RT} \geq 0. \tag{37}$$

By normalization on the left-hand side of the inequality we arrive at the inequality

$$1 \geq \frac{T_2}{T} \geq 0, \tag{38}$$

which in form already corresponds to Eq. (35), but preserves this correspondence in a more general form when raising to power b related to any real number:

$$1 \geq \left(\frac{T_2}{T}\right)^b \geq 0. \tag{39}$$

Equating the internal parts of the comparable inequalities Eqs. (35) and (39), we find their interrelation in the form

$$\frac{a}{a_2} = \left(\frac{T_2}{T}\right)^b, \tag{40}$$

which after the disclosure

$$a = a_2(T_2/T)^b \tag{41}$$

turns out to be identical to the one contained in the hierarchical model Eq. (31), which was required to prove and show.

In order to adapt the cluster and associate model to experimental data in order to adequately describe them and extrapolate to unexplored temperature regions, as a rule, high and super high, approaching not only the boiling point but also the critical temperature, it is required to develop certain data processing techniques to identify unknown parameters models a_2 and b.

6. Methods for Determining the Parameters of the Cluster and Associate Model of Viscosity

As follows from the structure of the hierarchical model Eq. (31), its first level in the form Eq. (29) for the disclosure of the second level Eq. (30) requires the determination of the degree of association a_2 at some second reference point η_2 at T_2. Substituting this point into Eq. (29),

$$\eta_2 = \eta_1(T_1/T_2)^{a_2}, \tag{42}$$

we find the value a_2:

$$a_2 = \frac{\ln(\eta_2/\eta_1)}{\ln(T_1/T_2)}. \tag{43}$$

To identify the exponent b in the hierarchical model Eq. (31), it is necessary to have a third reference point η_3 at T_3, first defining a_3 over the first level Eq. (31):

$$\eta_3 = \eta_1(T_1/T_3)^{a_3}, \tag{44}$$

$$a_3 = \frac{\ln(\eta_3/\eta_1)}{\ln(T_1/T_3)}, \tag{45}$$

and then finding b using Eq. (41):

$$a_3 = a_2(T_2/T_3)^b, \tag{46}$$

$$b = \frac{\ln(a_3/a_2)}{\ln(T_2/T_3)}, \tag{47}$$

or in the expanded form

$$b = \frac{\ln\frac{\ln(\eta_3/\eta_1)\ln(T_1/T_2)}{\ln(T_1/T_3)\ln(\eta_2/\eta_1)}}{\ln(T_2/T_3)}. \tag{48}$$

It is recommended to select the reference points (η_1, T_1), (η_2, T_2) and (η_3, T_3) at the beginning, middle and end of the temperature array of the experimental data, thus, if possible, covering the entire range of the set to be approximated. However, it is possible to process the entire experimental array, thereby eliminating the lack of data processing at the selected three points, describing the remaining identified cluster and associate model and checking the adequacy using the correlation coefficient. To realize the complete approximation of the experimental data by the developed model, we proposed that instead of choosing the third point for determining the exponent *b*, linearize the exponential-power hierarchical model of viscosity with finding the value of the sought-for index by the method of least squares [10].

In principle, it is also possible to search through a variety of combinations of three arbitrary reference points with the exhaustion of all data, for example, using the combination formula for *n* points:

$$C_n^3 = \frac{n!}{3!(n-3)!}. \tag{49}$$

As can be seen from the formula, with increasing volume of the set, the number of combinations of the three reference points (and the corresponding calculations of the parameters and the objective function Eq. (31) itself) increases sharply. So for n = 10 we get

$$C_{10}^3 = 120. \tag{50}$$

There is a possibility of a compromise solution of the problem, when only two reference points η_1, T_1 and η_2, T_2, are chosen arbitrarily (taking into account recommendations in place in the array), and all others are used to determine the exponent *b* by linearizing the cluster and associate model Eq. (31) and finding this index as a proportionality coefficient by the method of least squares.

The linearization of Eq. (31) can be carried out by double logarithm. The first leads to expression

$$\ln(\eta/\eta_1) = a_2(T_2/T)^b \ln(T_1/T).$$

By grouping it in the form

$$\frac{\ln(\eta/\eta_1)}{\ln(T_1/T)} = a_2(T_2/T)^b,$$

it goes to the second logarithm:

$$\ln\frac{\ln(\eta/\eta_1)}{\ln(T_1/T)} = \ln a_2 + b\ln(T_2/T). \tag{51}$$

Taking into account the expression for a_2 in Eq. (43) and the transfer of lna_2 to the left-hand side of Eq. (51), we obtain the equation

$$\ln\frac{\ln(\eta/\eta_1)}{\ln(T_1/T)} - \ln\frac{\ln(\eta_2/\eta_1)}{\ln(T_1/T_2)} = b\ln(T_2/T),$$

or in the final form

$$\ln\frac{\ln(\eta/\eta_1)\ln(T_1/T_2)}{\ln(T_1/T)\ln(\eta_2/\eta_1)} = b\ln(T_2/T), \tag{52}$$

which can be identified with the equation of a straight line emerging from the origin, $y = bx$, (without a free term) if we denote the left-hand side as y, and in the right-hand side the equality $x = \ln(T_2/T)$.

For such an equation, the direct least-squares method is reduced to form

$$b = \frac{\sum_{i=1}^{n} y_i}{\sum_{i=1}^{n} x_i}, \tag{53}$$

where x_i, y_i—the coordinates of the experimental points calculated by Eq. (52).

It should be taken into account that when processing the experimental data, the two reference points η_1, T_1 and η_2, T_2, should be excluded not only as already used to identify the model Eq. (31), but also as leading to uncertainty when substituted in Eq. (52). This is all the more necessary if the coefficient *b* (it is also an indicator of the degree of aggregation of associates) is calculated for each experimental point and then the mean value

$$\bar{b} = \frac{1}{n}\sum_{n=1}^{n} \frac{y_i}{x_i}. \tag{54}$$

In the case of the most adequate subordination of the experimental data of the tested model Eq. (31), both values in Eqs. (53) and (54) should practically coincide, since by the method Eq. (54) the presence of a free term in the equation of the line is allowed, which would affect the difference between *b* and $\bar{b}$. Only a coincidence will indicate the natural character of this model. In addition, using equality Eq. (54), one can verify that the resulting set b_i is homogeneous on the basis of known statistical criteria and estimate the accuracy of the averaged value.

To illustrate the effectiveness of the proposed method of processing and describe the experimental data on the temperature dependence (31), the values of η obtained over a wide range of temperatures, for example, relating to liquid lithium [7], should be used as a standard.

Earlier [1] they were processed at three reference points T_1 = 523 K, η_1 = 0.503 mPa·s; T_2 = 1,073 K, η_2 = 0.208 mPa·s; T_3 = 1,923 K, η_3 = 0.145 mPa·s and are represented by the cluster and associate model Eq. (31):

$$\eta = 0.503(523/T)^{1.0413(1073/T)^{0.1478}}. \qquad (55)$$

which was characterized by an ideal adequacy, with the nonlinear multiple correlation coefficient $R \to 1$ within eight significant digits. In the same place, the approximating equation from the monograph [11] is:

$$\ln \eta = 1.7563 - 0.659 \ln T + 304.248T, \qquad (56)$$

where the viscosity is given in g/(cm·s)—Poise (1 Pa·s = 10 P). Here the correlation coefficient turned out to be high (R = 0.99811), but worse than the model Eq. (55), and the calculated data were systematically underestimated against reference experimental data. These data, as compared to all the others, are given in Table 2.

To identify the cluster and associate model using the proposed method, only the first two experimental points mentioned above were used as references, and therefore the linearized Eq. (52) assumed the calculated form

$$\ln\left[0.9603\frac{\ln(\eta/0.503)}{\ln(532/T)}\right] = b\ln(1{,}073/T), \quad (57)$$

with $y = \ln\left[0.9603\frac{\ln\left(\frac{\eta}{0.503}\right)}{\ln\left(\frac{532}{T}\right)}\right]$ and $x = \ln\frac{1073}{T}$.

The results of calculations of y and x from the reference data for the viscosity of liquid lithium [7] are given in Table 2. According to this data, by Eq. (53), the calculated value b = 0.1451 is obtained, and then Eq. (55) takes a somewhat modified form

$$\eta = 0.503(523/T)^{1{,}0413(1073/T)^{0{,}1451}}. \qquad (58)$$

The indices b in Eqs. (55) and (58) are practically the same, differing by 1.9%, which led to an equally adequate description of the experimental data set (Table 2), as well as Eq. (55), with the coefficient of nonlinear multiple correlation R = 0.99988, close to unity, with the high significance of this coefficient, t_R = 24648 >> 2, respectively, with R = 0.999996 and t_R = 73959 >> 2 for Eq. (55).

It should be noted that in order to calculate the coefficient of nonlinear multiple correlation and its significance, the formulas given in the monographs [12, 13] were used to estimate the adequacy of complex dependencies:

$$R = \sqrt{1 - \frac{(n-1)\sum_{i=1}^{n}\left(y_{ei} - y_{p,i}\right)^2}{(n-k-1)\sum_{i=1}^{n}(y_{ei} - \overline{y_e})^2}}, \qquad (59)$$

where $y_{e,i}$, $y_{p,i}$, $\overline{y}_e$ —respectively, experimental (reference), calculated and average experimental values of the functions being compared, k—the number of operating factors (in this case k = 1, since the dependence is only on temperature); n—the number of points to be checked;

$$t_R = \frac{R\sqrt{n-k-1}}{1-R^2} > 2, \qquad (60)$$

where t_R—Student's test for a 95% confidence level (for higher confidence levels, the critical value of t_R increases).

It is also necessary to take into account that the value $D = R^2$ determines the degree of determination (functionality) of the tested dependence [14]. According to this index, Eqs. (55) and (58) with their values $R^2 \to 1$ and R^2 = 0.99976 can be assigned to functional ones.

The results of calculating the exponent b by the method Eq. (54) are presented in the same table. They differ in some scatter characteristic for the calculation of y_i/x_i from the experimental data, although the average value b = 0.14772 again turns out to be very close to that obtained by the method of three reference points in Eq. (55). Nevertheless, it is expedient to verify the statistical homogeneity of the obtained set b, for example, according to Nalimov's criterion [15, 16]:

Table 2 Ref. [7] and calculated data on the dynamic viscosity of lithium.

T, K	η [7], mPa·s	y_i	x_i	η (58), mPa·s	b_i	η (65), mPa·s	η (55), mPa·s	η (56), mPa·s	a (58)	a (65)	a (55)
$T_m = 453.7$	–	–	–	0.595	-	0.595	0.595	0.599	1.180	1.182	1.183
473	0.566	0.120	0.819	0.566	0.1468	0.566	0.566	0.567	1.173	1.175	1.175
523	0.503	–	-	0.503	-	0.503	0.503	0.499	1.156	1.157	1.160
573	0.453	9.36×10^{-2}	0.627	0.453	0.1537	0.453	0.453	0.447	1.141	1.142	1.143
623	0.412	9.11×10^{-2}	0.544	0.413	0.1675	0.413	0.413	0.405	1.127	1.128	1.128
673	0.379	7.5×10^{-2}	0.466	0.380	0.1610	0.380	0.380	0.371	1.114	1.115	1.116
723	0.352	5.69×10^{-2}	0.395	0.352	0.1442	0.352	0.352	0.343	1.103	1.104	1.110
773	0.328	4.97×10^{-2}	0.328	0.328	0.1516	0.328	0.328	0.320	1.092	1.093	1.093
823	0.308	3.82×10^{-2}	0.265	0.308	0.1440	0.308	0.308	0.300	1.082	1.083	1.083
873	0.290	3.17×10^{-2}	0.206	0.290	0.1537	0.290	0.290	0.282	1.073	1.073	1.074
923	0.275	2.06×10^{-2}	0.151	0.275	0.1367	0.275	0.275	0.267	1.064	1.065	1.065
973	0.261	1.47×10^{-2}	9.78×10^{-2}	0.261	0.1510	0.261	0.261	0.253	1.056	1.056	1.057
1,023	0.249	6.40×10^{-3}	4.77×10^{-2}	0.249	0.1348	0.249	0.249	0.242	1.049	1.049	1.049
1,073	0.238	-	-	0.238	-	0.238	0.238	0.231	1.041	1.041	1.041
1,123	0.228	-5.70×10^{-3}	-4.55×10^{-2}	0.228	0.1246	0.228	0.228	0.221	1.035	1.034	1.034
1,173	0.219	-1.15×10^{-2}	-8.91×10^{-2}	0.219	0.1287	0.219	0.219	0.212	1.028	1.028	1.028
1,223	0.211	-1.8×10^{-2}	-0.131	0.211	0.1381	0.211	0.211	0.205	1.022	1.021	1.021
1,273	0.204	-2.61×10^{-2}	-0.171	0.204	0.1525	0.204	0.204	0.197	1.016	1.015	1.015
1,323	0.197	-3.05×10^{-2}	-0.209	0.197	0.1456	0.197	0.197	0.191	1.010	1.010	1.010
1,373	0.191	-3.73×10^{-2}	-0.247	0.191	0.1510	0.191	0.191	0.184	1.005	1.004	1.004
1,423	0.185	-4.12×10^{-2}	-0.282	0.185	0.1459	0.185	0.185	0.179	0.100	0.999	0.999
1,473	0.180	-4.8×10^{-2}	-0.317	0.180	0.1518	0.180	0.180	0.173	0.995	0.994	0.994
1,523	0.175	-5.28×10^{-2}	-0.350	0.175	0.1507	0.175	0.175	0.169	0.990	0.989	0.989
1,573	0.170	-5.55×10^{-2}	-0.383	0.170	0.1450	0.170	0.170	0.164	0.985	0.984	0.984
$T_b = 1,615$	–	-	-	0.166	-	0.167	0.167	0.160	0.981	0.980	0.980
1,623	0.166	-6.18×10^{-2}	-0.414	0.166	0.1493	0.166	0.166	0.156	0.981	0.980	0.980
1,673	0.162	-6.64×10^{-2}	-0.444	0.162	0.1496	0.162	0.162	0.152	0.976	0.975	0.975
1,723	0.158	-6.97×10^{-2}	-0.474	0.158	0.1470	0.158	0.158	0.148	0.972	0.971	0.971
1,773	0.155	-7.70×10^{-2}	-0.502	0.154	0.1532	0.155	0.155	0.145	0.968	0.967	0.967
1,823	0.151	-7.75×10^{-2}	-0.530	0.151	0.1462	0.151	0.151	0.142	0.964	0.963	0.963
1,873	0.148	-8.24×10^{-2}	-0.557	0.148	0.1479	0.148	0.148	0.139	0.961	0.959	0.959
1,923	0.145	-8.62×10^{-2}	-0.583	0.145	0.1478	0.145	0.145	0.136	0.957	0.956	0.955
1,973	0.142	-8.9×10^{-2}	-0.609	0.142	0.1462	0.142	0.142	0.133	0.953	0.952	0.952
2,023	0.139	-9.10×10^{-2}	-0.634	0.139	0.1435	0.139	0.140	0.130	0.950	0.949	0.948
2,073	0.137	-9.77×10^{-2}	-0.659	0.137	0.1483	0.137	0.137	0.128	0.947	0.945	0.945
2,123	0.135	-0.104	-0.682	0.134	0.1518	0.134	0.135	0.126	0.943	0.942	0.941
2,173	0.132	-0.103	-0.706	0.132	0.1461	0.132	0.132	0.123	0.940	0.939	0.938
2,223	0.130	-0.108	-0.728	0.130	0.1478	0.130	0.130	0.121	0.937	0.935	0.935
2,273	0.128	-0.112	-0.751	0.128	0.1485	0.128	0.128	0.121	0.934	0.932	0.932
$T_{cr} = (3,223)$	–	-	-	(0.100)	-	(0.101)	(0.101)	-	0.888	0.886	(0.885)
Σ	-	-0.9508	-6.5505	-	5.153	-	-	-	-	-	

$$x_{\substack{max\\min}} = \frac{\left|\bar{x} - x_{\substack{max\\min}}\right|}{S(x)\sqrt{\frac{n-1}{n}}} \le r_{cr}, \qquad (61)$$

$$S(x) = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}\ , \qquad (62)$$

where $x_{\substack{max\\min}}$ —minimax set; $\bar{x}$ —average value; $S(x)$—standard error; n—volume of the set.

The normative tabular values of the Nalimov's criterion for the 5% significance level are given in Ref. [15], which were approximated in Ref. [17] within 5% of the equation.

$$r_{cr} = 1{,}483 f^{0{,}187}, \qquad (63)$$

where $f = n$-2—number of degrees of freedom of the Nalimov's criterion in Eq. (63).

According to the data in Table 2, the value $S(x) = 7.836\times10^{-3}$ was found for b. The largest deviation from the average value of b yields the value $b_{\min} = 0.1252$ at T = 1, 123 K. By Eq. (63) for n = 35 r_{cr} = 2.852. Hence the equality-inequality Eq. (61) is expressed as

$$r_{\substack{max\\min}} = \frac{|0{,}1472 - 0{,}1252|}{7{,}836\cdot10^{-3}\sqrt{34/35}} = 2{,}849 < r_{cr} = 2{,}852, \quad (64)$$

that is, the homogeneity condition is satisfied and the average value of the exponent b = 0.14772 is representative for the whole set b_i. This allows us to introduce it into the computational form of the cluster and associate model Eq. (31):

$$\eta = 0{,}503(523/\mathrm{T})^{1{,}0413(\frac{1073}{\mathrm{T}})^{0{,}1472}} \qquad (65)$$

The results of the calculation are shown in Table 2. Here, an ideal agreement is again observed with the reference data on the correlation coefficient R = 0.999996 for $t_R = 73959 \gg 2$ and $D = R^2 = 0.999992$.

As noted above, the indicator b has the meaning of the degree of aggregation of the associates, or the average number of associates in aggregation. For $b < 1$, some of the associates are not aggregated, and this part is larger, the smaller b. Thus, for $b \to 0$, the degree of association of clusters loses its dependence on temperature and tends to the value a = 1.0413 in this case, close to unity, that is, to the absence of associate formation, more precisely, to the identification of associates and clusters, since the association contains only one cluster. This is typical for metallic liquids due to the non-localized nature of the electronic connection. Probably, for complex inorganic substances, while maintaining the same form of the cluster and associate model, the indicators a and b will have higher numerical values.

Thus, on the latest reference data on the dynamic viscosity of liquid lithium, it is established that the cluster and associate model of the temperature dependence of this characteristic is fully adequate according to the three methods of adaptation of this model: three reference points and two reference points with additional consideration of all other points in the linearization versions of the model with a free member and without it. This indicates the functional nature of the cluster and associate model that reveals the virtual nature of the formation of clusters from crystal-mobile particles, associates from clusters and aggregations from associates equally subordinate to the Boltzmann energy spectrum. It means a decreasing degree of association from temperature, practically indistinguishable in all variants of adaptation of this model. And the closeness of the degree of association of clusters to unity for a typical lithium metal in the entire temperature range means practical identification of associates with clusters and follows directly from the metallic nonlocalized nature of the bond of atoms, unlike the one localized for elements with a covalent bond nature, as established in our book [1]. Therefore, the proposed methods for processing experimental data for temperature dependences of viscosity can be applied to complex substances.

In addition to the applicability of the basic data processing methods to the model Eq. (31), additional ones should be used, taking into account the mathematical extreme nature of the given model and revealed analytically by the conditions of its extrapolation to the critical temperature region for the liquid state of matter [1]. According to reference data for inorganic and organic substances, a correlation was found between the boiling point and the critical temperature [18], close to the proportion of the golden section:

$$T_{cr} = 1{,}603T_b. \tag{66}$$

In this case, the minimum point of the model Eq. (31), is manifested under condition that

$$T_{\eta,min} = T_1 e^{1/b}, \tag{67}$$

if it turns out that $T_{\eta,min} \geq T_{cr}$, it should be attributed to the value of the exponent b, equal to

$$b = 1/\ln(T_{cr}/T_1), \tag{68}$$

than provide decreasing character pattern Eq. (31) up to the critical point (after the viscosity will have to treat gaseous state indistinguishable from liquid).

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