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Direct Correlation between Fluid Cluster Structure and Its Viscosity

The research purpose is to prove the probability of a direct quantitative correlation between proportion of these clusters and liquid viscosity. A quasi-polycrystalline clustering model of the liquid (in particular, melts) should be used. The Boltzmann distribution, the concepts of the chaotic particles and the virtual cluster size distribution should be applied to achieve this purpose. This study analyzed the complete reference data on the temperature dependences of the dynamic viscosity for the alkali metals. As a result, a directly proportional correlation between viscosity and cluster content in liquid has been determined. It has provided the probability for the quantitative concept of the quasi-polycrystalline clustering model on the liquid state of matter due to its properties. The concept of the chaotic particles in direct correlation to the Boltzmann distribution has been used as a basis. The Boltzmann energy spectrum has been used for the kinetic energy of the chaotic thermal particle motion in the solid, liquid and gaseous states of matter. As a result, their three energy classes have been distinguished with their presence in all aggregate states and in the sum constantly equal to one. Formulas to calculate the proportion of the virtually ordered clustering and complete chaotic fluid components were deduced. These formulas have been derived with using the particle distributions by the energy class and cluster sizes.

Keywords: Boltzmann distribution, randomized particles, probability, virtuality, cluster, melt, viscosity, alkali metals.

Introduction

The most adequate physical model of a liquid and, in particular, of melts, is the quasi-polycrystalline model [1–4]. The most relevant physical model for liquids (namely, melts) is a quasi-polycrystalline model [1–4]. This model examined the melt as a combination of two structural components such as clusters and the separating clusters. Thus, clusters were microvolumes with an ordered particle arrangement, close as in a crystal. By contrast, the separating clusters had a disordered zone with the chaotic and loose particle arrangement. The disordered zone has formed a continuous three-dimensional cellular network in the melt, which filled the gaps between the clusters. The gaps were disorderly oriented in relation to each other.

The clusters and a disordered zone were thermodynamically unstable. After the energy fluctuations, they continuously regenerated each other. The volume ratio filled with clusters and a disordered zone was established by a temperature of the melt. Thus, the temperature rise led to a decrease in the proportion of clusters due to an increasing of their disordered zone. It was assumed that the cluster zone disappeared at some temperature. It probably corresponded to a “contrary flexure” on the “physical property-temperature” curve and transition of the curvilinear section to a straight-line one.

This idea of the cluster disappearance was questionable. Thus, any contrary flexures, i.e. breaks were not actually observed on such curves. The straight-line proportions were an asymptotic approximation in the decreasing curvature region with the single temperature dependence of the physical property. In any case, there was no prohibition to form clusters based on fundamental laws relating to the liquid nature. In addition, the quasi-polycrystalline model had no analytical expression or the mathematical semi empirical interpretation.

As a result, the physical model was insufficiently developed. Since, some paradoxes of the temperature correlation of viscosity were not explained by the quasi-polycrystalline model [5]. Also works were being studied to determine the shape and structure of clusters with using their formation based on the solid phase nanoparticles during the melting of matter [6]. To date, the analysis of the unstable clustering phase in the liquid demonstrated that the structural approach dominated despite the advantage of such phase in a state without structure [7–10].

Thus, the obvious virtuality of the cluster existence and the disordered zone in the liquid has showed that a probability interpretation of its nature and all aggregate states of matter was relevant. Academician M.A. Leontovich's point was fundamental to use the Boltzmann distribution (an energy spectrum) on the kinetic energy of the chaotic (thermal) particle motion to the gaseous and liquid, solid states of matter [11].

The research purpose is to substantiate the probability of a direct quantitative correlation between proportion of these clusters and liquid viscosity. A quasi-polycrystalline clustering model of the liquid (in particular, melts) should be applied. The Boltzmann distribution, the concepts of the chaotic particles and the virtual cluster size distribution should be used to realize this purpose.

Experimental

The Boltzmann distribution and the concept of chaotic particles as a virtual basis

$$P_i = N_i / N = \exp[-\varepsilon_i / kT] / \sum_{i=1}^n \exp[-\varepsilon_i / kT], \quad (1)$$

where P_i and N_i are share and number of particles with average ε_i kinetic energy; N is the total amount of particles in the system; k is the Boltzmann constant; n is the number of energy levels taken into account.

A significant advantage of the shared distribution was able to interpret P_i as the particle content with a certain energy level and probability to form and detect them. Therefore, the laws of the accidental events based on combining of the probability of the elementary events were used for them. The different fundamental property for this distribution was a universal expression of the thermal energy reserve at any temperature in an aggregate state as kT (per mol RT). And it did not depend on the continuous or discrete nature of this distribution [12–15].

The ability was additionally created to determine the proportion of the super-barrier, sub-barrier and inter-barrier particles, i.e. any energy classes. Thus, the total proportion of such particles was equal to one. As a result, a faithful scientific basis was to develop the chaotic particles concepts and to apply their crossing or not crossing the thermal barriers of RT_m melting and RT_b boiling [16, 17].

This concept has demonstrated three particle energy classes at all temperatures and in all aggregate states:

the *crystal-mobile* particles with energy no more than the thermal barrier RT_m and proportions:

$$P_{crm} = 1 - \exp[-RT_m / (RT)] = 1 - \exp(-T_m / T), \quad (2)$$

the *liquid-mobile* particles with energy above RT_m , but no more than RT_b and proportions:

$$P_{lqm} = \exp(-T_m / T) - \exp(-T_b / T), \quad (3)$$

the *vapor-mobile* particles with energy above RT_b and proportions:

$$P_{vm} = \exp(-T_b / T) \quad (4)$$

upon condition

$$P_{crm} + P_{lqm} + P_{vm} = 1. \quad (5)$$

In this instance, this nature has been displayed with the melting and boiling points relevant to energy levels of kT_m and kT_b .

The temperature range showed that the regions of the crystalline, liquid, vapor states and *crm*, *lqm*- and *vm*-particles in each of them should be well defined. The real properties of these states corresponded to it.

The feature of the liquid-mobile particles was compared to the crystal-mobile and vapor-mobile particles. The proportion of the first above in the full temperature range (from zero to infinity) varied from 1 to 0. The proportion of the second above varied from 0 to 1. As a result, the feature was defined by difference between unity and sum of the oppositely varying fractions of *crm*- and *vm*-particles, as per (3). Thus, the fraction of *lqm*-particles varied from zero to zero passing through some maximum. Its position is analytically calculated by (3) and corresponds to a temperature:

$$T_{lqm,max} = (T_b - T_m) / \ln(T_b / T_m). \quad (6)$$

The obvious dominance of the crystalline particles was observed up to the boiling point. This predominance was characteristic for the Boltzmann energy spectrum. As a result, the lower levels were more filled than the upper ones. The crystal-mobile particles were low-energy and realized their dominance. They reduced their proportion in a liquid state from the predominant one at a melting point to others at the boiling point. Thus, it was requested to determine their form in the liquid. If it was abstract from a specific structure of clusters, it can be argued that *crm*-particles should be associated or virtually condensed. If the particles

constantly hit with each other and with all other particles, they should correspond to some virtual distribution by the number of particles included in cluster, i.e. to be one-, two-, three- and n -particle clusters. Herewith, abstraction from a specific cluster structures did not mean its ignoring. By contrast, it should be examined as separation of the chaotic basis to make the certain structures under influence of the potential energy for attraction or repulse of particles. The last mentioned above were explicitly analyzed in some papers, namely, in a review of [18].

In order to determine such distribution, it should be stated that a quantitative expression for the total matter proportion was first received by a quasi-polycrystalline clustering model of the liquid state based on the chaotic particles concept. It was as a reservoir to form the clusters. Thereat, this proportion was compliant with the universal criteria for the structural stability of the complex systems [19–21], specifically, by the proportion of the golden section.

Further development of the chaotic particles concept proved the virtuality of their existence in the form of cluster distribution by the number of the included particles. The equality conditions of probabilities for the mutual conversion of clusters were applied, thus, it led to the maximum uncertainty of their system [17].

$$P_{cm,n} = (1 - P_{cm}) P_{cm}^n, \quad (7)$$

where P_{cm}^n is the proportion of n -partial clusters.

As applied to the quasi-polycrystalline model of a liquid [1–4], it has been required to use the found particle distributions by the energy classes and cluster sizes to distinguish the virtually ordered cluster and fully chaotic components of the liquid. The last above mentioned was represented by single particles. It included all liquid-mobile, vapor-mobile and single crystal-mobile particles. They were the most energy-intensive in their class and as a transition to liquid-mobile ones. The total proportion of such particles calling as free, as described in (2)–(5) and (7) should be [17]

$$P_{fr} = P_{cm,1} + (P_{lqm} + P_{vm}) = P_{cm} (1 - P_{cm}) + (1 - P_{cm}) = 1 - P_{cm}^2. \quad (8)$$

Thereafter, the cluster zone should take a proportion of

$$P_{cl} = 1 - P_{fr} = P_{cm}^2. \quad (9)$$

Integrally, the chaotic component of matter was studied. It was a primary basis to examine the ordered component through the characteristics of dependence. Besides, the probabilistic distribution of clusters according to the number of the included particles created a reservoir to form the supracluster compounds — associates. The associates were detected in the liquid crystallization area [22]. The recording this loss of simplicity required the special study in relation to the liquid properties as described in our paper [20] with regard to viscosity. In all cases, the Boltzmann distribution was an inexhaustible source to develop the theory of a matter [23–25].

It should be previously to assure oneself of the most direct quantitative correlation of any physicochemical liquid property with the found cluster proportions. This could be exemplified by a dynamic viscosity for the most typical liquid metals of the basic subgroup of the first group of the periodic element system.

Results and Discussion

The correlation of the dynamic viscosity of the liquid alkali metals to their cluster content should be present below.

The chaotic particles concept and the quasi-polycrystalline clustering model of a liquid demonstrated that its viscosity should not be defined by all proportion of the crystal-mobile P_{cm} particles. It should be determined by its part belonging to non-single virtual formations. Thus, it should be equal to P_{cm}^2 . It might be illustrated with the most complete reference data on the temperature dependences of the dynamic viscosity of alkali metals [26, 27].

Data correlation of η , mPa·c, with $P_{cm} = 1 - \exp(-T_m/T)$ and $P_{cm}^2 = [1 - \exp(-T_m/T)]^2$ in the range from T_m to T_b are resulted in Tables 1–5 and Figures 1–5.

Table 1

The dependence of the dynamic lithium viscosity on the temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters

T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2	T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2
$T_m = 453.7$	–	0.632	0.400	1073	0.238	0.345	0.119
473	0.566	0.617	0.380	1173	0.219	0.321	0.103
573	0.453	0.547	0.299	1273	0.204	0.300	0.089
673	0.379	0.490	0.240	1373	0.191	0.281	0.079
773	0.328	0.444	0.197	1473	0.180	0.265	0.070
873	0.290	0.405	0.164	1573	0.170	0.251	0.063
973	0.261	0.373	0.139	$T_b = 1615$	–	0.245	0.060

Table 2

The dependence of the dynamic sodium viscosity on the temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters

T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2	T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2
$T_m = 371$	–	0.632	0.400	773	0.237	0.381	0.145
373	0.687	0.630	0.397	873	0.208	0.346	0.120
473	0.451	0.544	0.296	973	0.186	0.317	0.100
573	0.341	0.477	0.227	1073	0.170	0.282	0.085
673	0.278	0.424	0.180	$T_b = 1156$	–	0.274	0.075

Table 3

The dependence of the dynamic potassium viscosity on the temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters

T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2	T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2
$T_m = 337$	–	0.632	0.400	773	0.166	0.353	0.125
373	0.441	0.585	0.354	873	0.146	0.320	0.103
473	0.303	0.510	0.260	973	0.132	0.293	0.086
573	0.234	0.444	0.198	$T_b = 1032$	–	0.279	0.078
673	0.193	0.394	0.155				

Table 4

The dependence of the dynamic rubidium viscosity on the temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters

T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2	T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2
$T_m = 312.5$	–	0.632	0.400	673	0.212	0.371	0.138
373	0.435	0.567	0.322	773	0.185	0.332	0.111
473	0.316	0.484	0.234	873	0.165	0.301	0.090
573	0.252	0.420	0.177	$T_b = 961$	–	0.278	0.077

Table 5

The dependence of the dynamic cesium viscosity on the temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters

T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2	T, K	$\eta, mPa \cdot c$	P_{crm}	P_{crm}^2
$T_m = 301.7$	–	0.632	0.400	673	0.221	0.365	0.130
373	0.469	0.555	0.308	773	0.192	0.323	0.104
473	0.334	0.472	0.222	873	0.171	0.292	0.085
573	0.264	0.409	0.168	$T_b = 944$	–	0.274	0.075

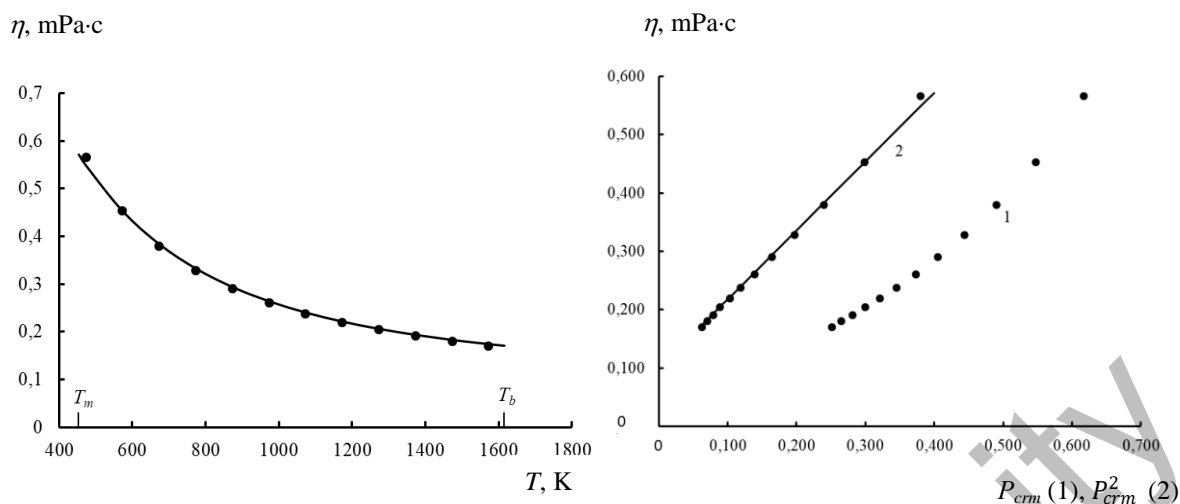


Figure 1. The dependence of the dynamic lithium viscosity on temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters (lines by (10))

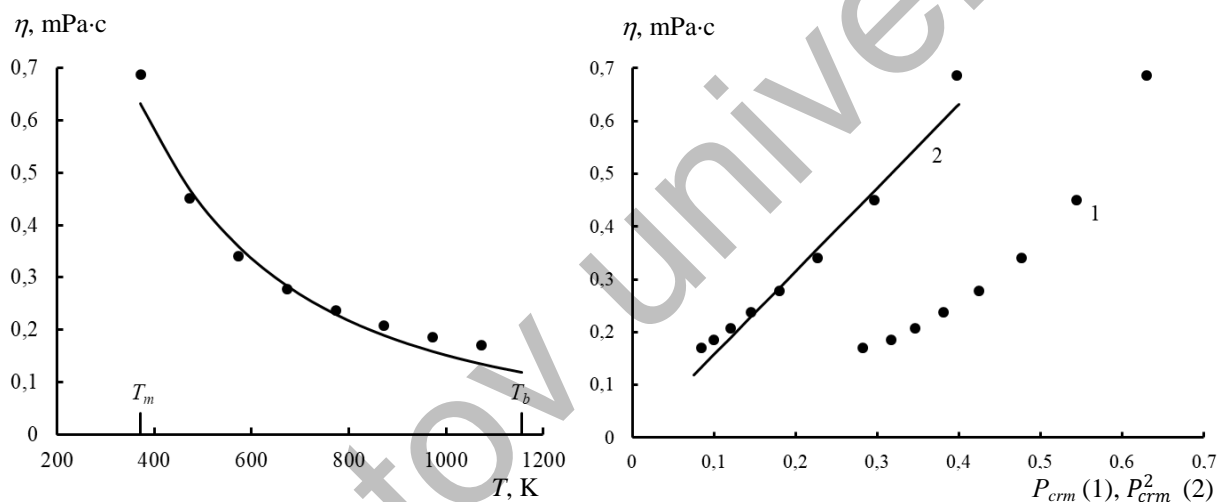


Figure 2. The dependence of the dynamic sodium viscosity on temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters (lines by (10))

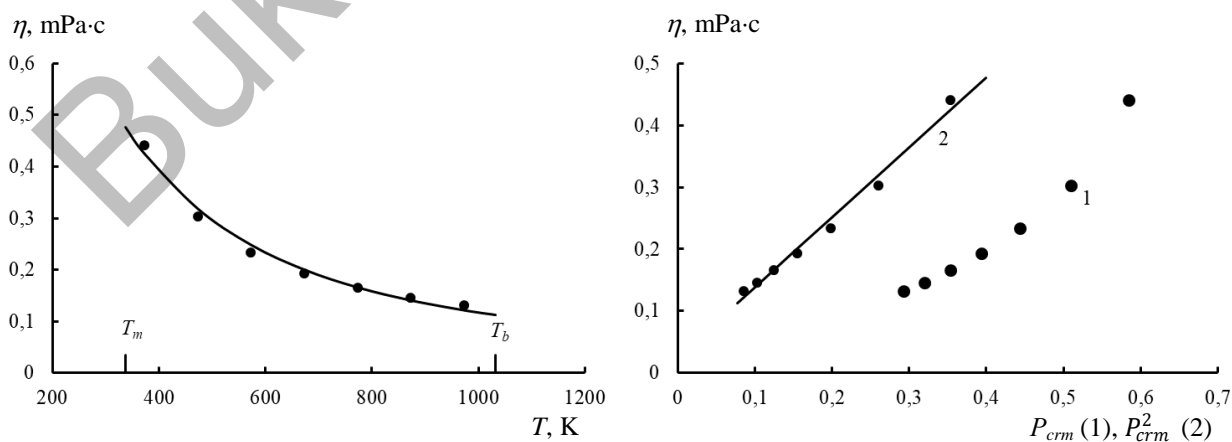


Figure 3. The dependence of the dynamic potassium viscosity on temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters (lines by (10))

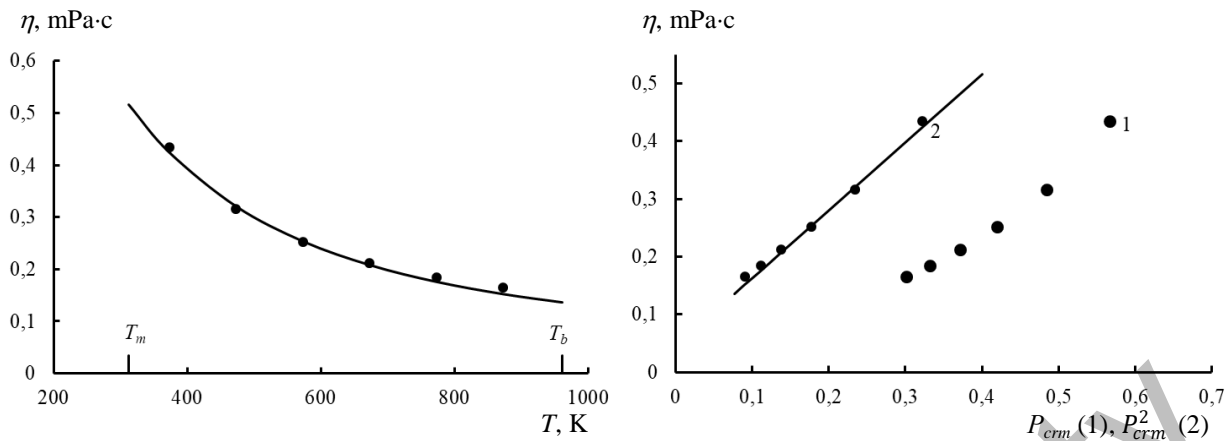


Figure 4. The dependence of the dynamic rubidium viscosity on temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters (lines by (10))

All figures illustrated a uniform variation in the forms of the dynamic viscosity correlations: from obvious nonlinear by temperature to smoothed proportion of the crystal-mobile particles and clear enough straight-line by cluster proportions. Thus, the directly proportional correlation of the viscosity directly with the cluster content in the liquid was proved.

The probability was discovered for the quantitative concept of the quasi-polycrystalline clustering model of the liquid matter state through its properties. Therefore, the chaotic particles concept and the Boltzmann distribution were applied.

In a first approximation, such dependence might be represented as a straight line equation. After calculation of the P_{crm}^2 variable, the viscosity was showed as

$$\eta = a + bP_{crm}^2 = a + b[1 - \exp(-T_m / T)]^2, \tag{10}$$

where a and b are free term and proportionality coefficient, respectively. They could be found by the least squares method. Then they should be used to determine the physical meaning.

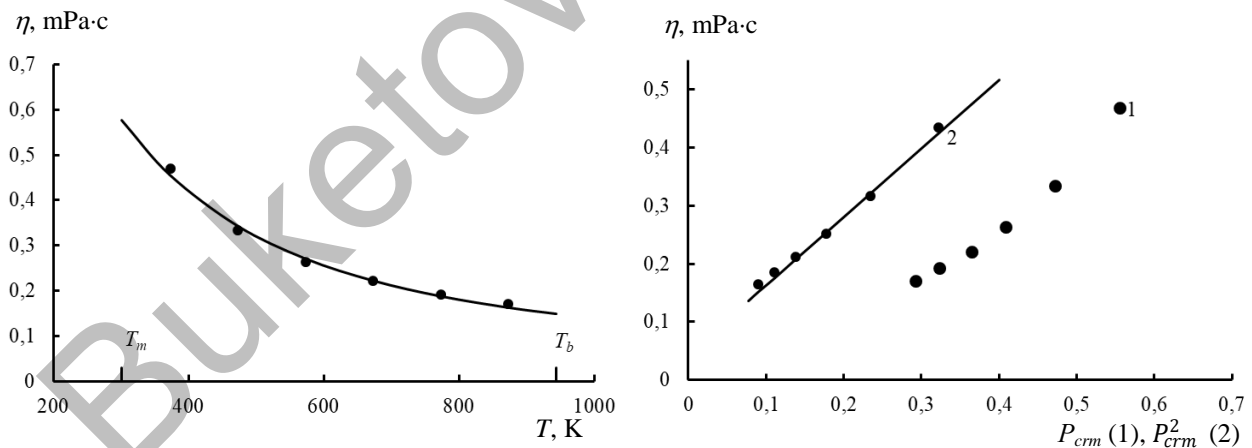


Figure 5. The dependence of the dynamic cesium viscosity on temperature [26, 27] and proportion of the crystal-mobile P_{crm} particles and P_{crm}^2 clusters (lines by (10))

For instance, at a melting point, the equation (10) had a single formula for all substances

$$\eta = a + 0.400b. \tag{11}$$

The different substances were compared by this viscosity value. Since it referred to the liquid phase at a melting point, where the liquid and solid states were in equilibrium. Thus, the direct experimental definition of viscosity was difficult due to the simultaneous presence and uncertain ratio of the solid and liquid phases.

It was required to ascertain that the straight-line dependence of the discussed data for alkali metals was adequate. With this view, they were processed by the least squares method to obtain the numerical values of parameters of a and b , the R correlation coefficient and its significance for the 95 % confidence level ($t_R > 2$), the determination degree of the received dependencies ($D = R^2$) [28] and the η_m melting viscosity. Results are presented in Table 6 and Figures of 1–5.

Table 6

Parameters of equation (12) for alkali metals

Element	T_m , K	a	b	R	t_R	D	η_m , mPa·c
Lithium	453.7	0.100	1.18	0.9986	813 > 2	0.9971	0.572
Sodium	371	0.000	1.58	0.9815	60 > 2	0.9634	0.632
Potassium	337	0.025	1.13	0.9907	118 > 2	0.9815	0.478
Rubidium	312.5	0.045	1.18	0.9948	189 > 2	0.9896	0.517
Cesium	301.7	0.050	1.32	0.9960	249 > 2	0.9920	0.578

The Table 6 demonstrated that a high adequacy of the straight-line correlation of viscosity with the cluster proportions and directly with temperature was established for all alkali metals. Since, they were displayed by a single equation (10). A high degree to determine these dependencies indicated their proximity to the fundamental pattern based on the physical nature of the liquid state.

Somewhat worse correlation of the data for sodium had a physical explanation. Thus, the experimental values of viscosity were markedly higher than the calculated values at 373 K by two degrees above a melting point. It might be due to the probability of a partial presence of the solid phase within the accuracy of melt temperature maintenance.

For all other alkali metals, the first experimental point was established at a temperature no less than twenty degrees above a melting point.

Herewith, the η_m melting viscosity for sodium was abnormally high. A comparative analysis of the data on this value became difficult because it was a characteristic for the contribution of the chaotic virtual component of the melting viscosity.

The graphical data for sodium showed some residual curvature of the correlation on the cluster proportion. It was less visible on similar dependences for other metals. It indicated a more complex nature of the cluster influence on the melt viscosity. It might be caused by formation of more complex super-cluster virtual structures of less strong cluster associates. This aspect was examined in the monograph [17]. It ended with construction of a more accurate semi-empirical cluster-associated viscosity model. Thus, the cluster association degree was applied, and the correlation with activation energy of fluidity was discovered by the Frenkel-Andrade viscosity model [29–31].

It was important to state that determination of the activation energy was possible due to linearization of this model. It was widespread procedure to analyze and process data for the complex physicochemical patterns in order to define their adequacy and apply them to the real processes.

Conclusions

The probabilistic nature of formation and the virtual existence of the solid phase clusters in liquid were applied to develop the existing quasi-polycrystalline clustering model of the liquid state of matter.

It was studied by Boltzmann distribution of an energy spectrum and the chaotic particles concept with using an additional cluster distribution per the number of the crystal-mobile particles included in them.

The form of this distribution was defined by the equal probability of the mutual cluster conversions and expressed by the virtuality essence of the liquid state.

The proportional correlation of viscosity directly with the cluster content in the liquid was established by the analysis of the most complete reference data on temperature dependences of dynamic viscosity for alkali metals. Probability was provided to quantitative concept of the quasi-polycrystalline clustering model of the liquid state of matter based on its properties with using the chaotic particles concept and the Boltzmann distribution.

It was clear that each straight-line correlation was not functional. In this case, the argument (the cluster proportions of P_{cm}^2) and function (viscosity) were related as cause and effect. The cluster proportions were determined by the fundamental Boltzmann distribution. It was found the proportion of low-energy (the crys-

tal-mobile) particles in it. It was as a reservoir to form (virtual crystallization) clusters. They created more chaotic particles and a thicker consistency of the liquid state. This consistency might be equated with the liquid viscosity. It was quite possible that a similar straight-line correlation of cluster proportions could be discovered with other properties of the liquid, e.g., by density and electrical conductivity.

In reference to correlation between the cluster proportions and viscosity, it might be physically compared with the state of a mechanical mixture of water and sand. The sand played the role as a cluster phase, and created the emulsion viscosity. It was important to state that the rectilinearity of correlation between the cluster proportions and viscosity did not apply to all crystal-mobile particles (P_{cm}). It was applied for two or more partial formations (P_{cm}^2). It was clearly illustrated by the graphical data for alkali metals. In this case, it was of no concern a structure of the formed clusters. Since, the chaotic component of the substance was used. Thus, its contribution to the liquid state was examined. The influence of the potential energy of attraction and repulse of particles might add the general picture of such state as certain cluster structure formation. However, the chaotic component of matter by the kinetic energy of the thermal particle motion was basic to display the formation and properties of matter as a whole.

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Сұйықтықтың кластерлік құрылымының тікелей байланысы және оның тұтқырлығы туралы

Жұмыстың мақсаты — Больцман үлестірімін, ретсіз бөлшектер тұжырымдамасын және кластерлердің виртуалды үлестірілуін қолдана отырып, олардың өлшемдері бойынша сұйықтықтың (атап айтқанда, балқымалар) квазиполикристалды кластерлік моделі аясында осы кластерлердің үлесін сұйықтықтың тұтқырлығымен тікелей сандық байланыс мүмкіндігін негіздеу. Мақалада сілтілік металдардың динамикалық тұтқырлығының температуралық тәуелділігі бойынша ең толық анықтамалық мәліметтерді талдау мысалында тұтқырлықтың сұйықтықтағы кластерлердің құрамымен тікелей пропорционалды байланысы анықталған. Бұл Больцманның таралуына тікелей байланысты хаотикалық бөлшектер тұжырымдамасына негізделген заттың сұйық күйінің квазиполикристалды (кластерлік) моделін оның қасиеттері арқылы сандық түрде білдіру мүмкіндігін қамтамасыз етеді. Заттың қатты, сұйық және газ тәрізді күйлеріндегі бөлшектердің ретсіз жылулық қозғалысының кинетикалық энергиясына қолданылатын Больцмонның энергетикалық спектрі олардың барлық агрегаттық күйлерінде болуымен олардың үш энергетикалық класын ажыратуға мүмкіндік берді, ал қосынды әрқашан біреуге тең. Кластерлердің энергетикалық кластары мен өлшемдері бойынша бөлшектердің таралуы арқылы табылған виртуалды реттелген кластерлік және толығымен хаотикалық сұйықтық компоненттерінің үлесін есептеу бойынша формулалары келтірілген.

Кілт сөздер: Больцманның таралуы, ретсіз бөлшектер, ықтималдылық, виртуалдылық, кластер, балқыма, тұтқырлық, сілтілік металдар.

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О прямой связи кластерного строения жидкости и ее вязкости

Цель работы — в рамках квазиполикристаллической кластерной модели жидкости (в частности, расплавов) с помощью распределения Больцмана, концепции хаотизированных частиц и виртуального распределения кластеров по их размерам обосновать возможность прямой количественной связи доли этих кластеров с вязкостью жидкости. В статье на примере анализа наиболее полных справочных дан-

ных по температурным зависимостям динамической вязкости щелочных металлов установлена прямо пропорциональная связь вязкости непосредственно с содержанием кластеров в жидкости. Этим обеспечивается возможность количественного выражения квазиполикристаллической (кластерной) модели жидкого состояния вещества через ее свойства на основе концепции хаотизированных частиц в прямой связи с распределением Больцмана. Энергетический спектр Больцмана применительно к кинетической энергии хаотического теплового движения частиц в твердом, жидком и газообразном состояниях вещества позволил выделить три энергетических класса с присутствием их во всех агрегатных состояниях и в сумме, всегда равной единице. Приведены формулы по расчету доли виртуально упорядоченной кластерной и полностью хаотизированной составляющих жидкости, найденных с помощью распределений частиц по энергетическим классам и размерам кластеров.

Ключевые слова: распределение Больцмана, хаотизированные частицы, вероятность, виртуальность, кластер, расплав, вязкость, щелочные металлы.

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