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Evaluation of pressure and volumetric modules in melted systems

In the article there were estimated the pair potential and pressure of bulk modules in molten systems. There are given appropriate formulas for calculating the compressibility of electron melts. The polytherms of compressibility for selenium, tellurium, germanium and silicon are calculated. For the calculation of bulk modules, melts of metals and semiconductors are considered as a two-component liquid consisting of ions and electrons. According to the virial theorem, a part of the pressure associated with the dynamics and interaction of the ion subsystem is estimated. Since the isothermal bulk modulus is a static exponent, we determined it under conditions where the pressure and volume in the system change slowly, and the temperature of the melt changes very slowly or remains constant. The adiabatic bulk modulus, i.e. dynamic, was determined under conditions of heating of the melt caused by compression. Under adiabatic compression a change in temperature and pressure is allowed. This phenomenon occurs in fast processes, i.e. when there is no heat exchange due to the inertia of the thermal properties of the melts. This behavior of adiabatic compressibility is characteristic of metallic melts. We have found that the instantaneous dynamic modulus calculated in the pair approximation model is identical to the dynamic modulus calculated in the full theory in the second order, and also differs markedly from the statistical module. The explanation of this fact consists in neglecting the members of the electron-ion interaction of a higher order than the second, and also the unsatisfactory modification of the pseudopotential by means of an amendment to the Hartree energy. We obtained the relationships that make possible to calculate the compressibility of melts. Theoretical calculated polytherms of compressibility for semiconductors are given in the article.

Keywords: cluster structure, polyterms of compressibility, semiconductor, function of radial distribution, structural factor, adiabatic compressibility, paired potential, of the pressure of volumetric modules.

The molten metals and their alloys are widely used in the national economy. This interest is especially great in heating engineering, nuclear energy technology, electronic engineering and in other industrial sectors, as well as for meeting the needs of the metallurgical production and in the engineering design of new technology in this field. The greatest attention devoted to the molten metals is in the metallurgy, which is conditioned by the necessity of passing the liquid phase before crystallization. The practical significance of the expected results of the work lies in the possibility of using new ideas about the structure of melts, based on computer simulation, which allows modeling the properties of the melt at the atomic level. This is important for the development of optimal technological processes in non-ferrous and ferrous metallurgy, in pyrometallurgy in general, occurring at the phase interface, as well as for similar processes in the technology of inorganic materials (silicon, selenium, tellurium, germanium, etc.), including number for nanocoatings, films and other special technologies.

It is necessary to consider some correlations for the calculation of the solid modules in the molted systems. Metal melts and melts of semiconductors can be considered as double-base liquid consisting of ions and electrons, then according to the virial theorem, a part of pressure which is connected with dynamics and interaction of ionic subsystem can be evaluated, i.e.

$$P_{ion} = \frac{1}{3\Omega}\left\{2K - \sum_{i<j}\left[R_{ij}\frac{\partial V_{eff}(R_{ij})}{\partial R_{ij}} + R_S\frac{\partial V_{eff}(R_{ij})}{\partial R_S}\right]\right\}, \quad (1)$$

where K — is kinetic energy.

For the calculation of the total pressure per size P_{ion} it is necessary to add the pressure, which is created by the fermi-gas that is equal to the sum of the derivative energy $E_0(\Omega)$ and $E_P(\Omega)$ with the opposite sign $P_{eg} = -(\partial E_0/\partial\Omega) - (\partial E_P/\partial\Omega)$.

One may rewrite the pressure P_{ion} in the integral form, containing explicitly dependence on the structure $g(R)$. If we represent the kinetic energy through the temperature, then

$$P_{ion} = \frac{1}{6\Omega}\int_0^{\infty} g(R)\left[R\frac{\partial V_{eff}(R,R_C)}{\partial R} + R_S\frac{\partial_{eff}(R,R_S)}{\partial R_S}\right]dR + \frac{kT}{\Omega}. \quad (2)$$

The derivative $\frac{\partial V_{eff}}{\partial R_S}$ in the expression for pressure is specific for the melts so far as $V_{eff}(R,R_S)$ is not only the distance function but also the function $\Omega = \Omega(R_S)$. It points out that the result is an effect of dielectric dependence of penetration function, which defines indirect interaction of ions from the compactness of shielding electronic subsystem nz, at the same time $n = \frac{N}{\Omega} = \frac{3}{4\pi z R_S^3}$. The calculation done for Na [1] shows that thecomponents P_{ion} and P_S^0 which are parts of pressure P_{eg}, have the values close to zero.

If one neglects changes of the pair potential $V_{eff}(R)$ of solidity during the pressure estimation, the result turns out to be overstated. It follows that in the models with stiff fixed compactness which reproduce complex N,Q,T one have to do with the great positive pressures. Such situation is observed while calculating the force coefficients in a crystal. The shown conclusion doesn't indicate the inexactness of mentioned models for a hot metal. The equilibrium should be considered simultaneously for its both subsystems — ionic and electronic, as far as the positive pressure of ionic subsystem defines bulk effects in the electronic subsystem.

As is known, in the theory of condensed systems there is «compressibility sums rule» which describes how much up-build model of the system is self-consistent. The reciprocal value of the volumetric module is equal to the mentioned compressibility. These sizes are important at the consideration of the property of condensed systems. In the crystal the quiescent volumetric module β_{st} equal to the second derivative energy by volume, must be consistent with the dynamic bulkmodulus β_{din}, which is a combination of the elastic constants calculated from the phonon dispersion relation by the «long» wave method [2].

Indicated correlation is defined by the interatomic interaction with the constant volume and doesn't depend on the volume-dependent components of energy. In this self-consistent model correlation between the form of the effective interaction if Q = const and derivatives of the energy in volume, contains mentioned components and defines the «compressibility sums rule».

As is shown in the work [3], the properties are examined well in case of crystalline Na. Subsequently it turned out that the sum rule is not satisfied because of the non-self-consistency of the metal model constructed on the basis of the assumption of perturbation theory in the second order in terms of the pseudopotential.

It gives the reason to assert that the components which emerge in the dynamic matrix in the third and fourth orders in the long-waved limit give the contribution of the second order. This inconsistency results from the inclusion of this contributions while calculating the statistic modules and neglecting them in dynamic modules. But the inclusion of these highest terms at the dynamic arraying, which correspond to the triplet and quadrupole interaction, is possible in essence [2]. Conducted calculations with the crystalline Na [3] have shown that it is necessary to vary Hartree energyfor bringing into concordance of evaluable static module to the experimental β_{st}. But in such variation the dynamic modulus β_{din}, which is well consistent with the experiment, turns out to be too overstated.

The feasible explanation of this is in the fact that the components of the third and the fourth orders become more important in the dynamic matrix, in the field with the little q. In the present case to preserve the consent with the experiment there is necessary the modification of the pseudo-potential itself in this mentioned field. In such case the Hartree energy variation will correspond to this modified pseudo-potential.

The statistic isothermal modulus of flexibility of the liquid phase is the following pressure derivative by volume:

$$\overline{\beta}_{st} = -\Omega\left(\frac{\partial P}{\partial \Omega}\right)_T . \tag{3}$$

The dynamic isothermal modulus is identified by the long-wave by the structural factor range $S(q)$:

$$\overline{\beta}_{din} = \frac{kT}{\Omega S(0)} . \tag{4}$$

Both of these modules must match in the consistency theory. However, application of the perturbation theory in the second order on the pseudo-potential and definition of the dynamic modulus through $S(q)$ in the model with the potential that is independent on the compactness will lead to the diversions like in the case of the crystal. The exact formula for the static modulus is like this:

$$\overline{\beta}_{st} = \overline{\beta}_{ion} + \overline{\beta}^0_{stp} + \overline{\beta}_e + \frac{kT}{\Omega} , \tag{5}$$

where

$$\overline{\beta}_{ion} = \frac{1}{18\Omega}\int D(g(R))D(V_{eff}(R))dR + \frac{1}{18\Omega}\int g(R)D^2V_{eff}(R)dR ,$$

where D is a statement which is input to shorten the writing:

$$D = R\frac{\partial}{R} + R_S\frac{\partial}{\partial R_S} .$$

The physical value of the derivatives remains the same like in the case of the equation (2). Summing up all, one may write:

$$\overline{\beta}^0_{stp} = \frac{1}{18\Omega} R_S \frac{\partial}{\partial R_S} R_S \frac{\partial}{\partial R_S}\left[V\,(R=0)\right] + P^0_{stp} ; \tag{6}$$

$$\overline{\beta}^0_e = \frac{1}{9\Omega} R_S \frac{\partial}{\partial R_S} R_S \frac{\partial E}{\partial R_S} + P'_e . \tag{7}$$

One may write the analogous formula for the dynamic modulus $\overline{\beta}_{din}$, as long as it is also calculated in the model with the potential independent on the compactness. Since the model is self-consistent, the dynamic and static modules calculated in it coincide. The analogous conclusion may be done even in the case of calculation of the crystal compressibility, which is realized in the reciprocal space. Thus, it is expected the following correlation to be accomplished:

$$\overline{\beta}_{din} = \overline{\beta}'_{ion} + kT/\Omega , \tag{8}$$

where

$$\overline{\beta}_{ion} = \frac{1}{18\Omega}\int Dg(R)\frac{R\partial}{\partial R}V_{eff}dR + \frac{1}{18\Omega}\int g(R)\frac{R\partial}{\partial R}V_{eff}dR .$$

The equation (4) gives more simple formula for $\overline{\beta}_{din}$. The equivalence of the equations (4) and (6) is in essence particular case of the matched condition between n and $n+1$ the partial distribution functions. The equation (8) doesn't contain the direction to the calculation of the statistic calculation (5). However, in the calculations on the equation (5) one has to face the following problems: for the calculation such the function of the radial distribution is required $q(R)$ which would coincide with the complete theory, i.e. for that the identity was realized:

$$S(0) = \int\left\{\left[g(R)-1\right]/\Omega\right\}dR , \tag{9}$$

equal $\frac{kT}{\Omega\overline{\beta}_{st}}$. It requires the consideration of the components of the third and the fourth orders in the field of the minor $q-s$. As these components coincide to the calculation of the effective interactions between the tree and four ions, it is an awkward task. It is therefore natural to make the assumption that the function $q(R)$, calculated in a computer experiment with a pair effective potential at Q = const, does not lead to large errors, excluding the long-wave region.

Just this very function $q(R)$ is put in the equation (5) and (8); the equations (5) and (8) require the values of the derivatives of functions $q(R)$ in volume which can be taken by the repetition of the computer experiment with different source compactness.

It is therefore natural to make the assumption that the function $g(R)$, calculated in a computer experiment with a pair effective potential at Ω = const, does not lead to large errors, excluding the long-wave region.

The present situation is the extreme laborious task. So it is more convenient to confine with the approach:

$$g(R,R_ST)=\frac{1}{\Omega}f(R/R_S,T)\,, \tag{10}$$

where $f(R/R_S,T)$ is the function which provides similar change of the structure with the compactness in at the constant temperature.

However, the assumption (10) is correct for the crystal structure, but is not obligatory for a liquid. That is why this approach follows to:

$$Dg(R)=\frac{R\partial g(R/R_S)}{\partial R}+R_S\frac{\partial g(R/R_S)}{\partial R_S}=-3g(R)\,. \tag{11}$$

Taking into account the derived result let’s rewrite the equation (4) as in this way:

$$\overline{\beta}_{ion}=\frac{1}{18\Omega}\int g(R)(D^2-3D)V_{eff}(R)dR\ . \tag{12}$$

The value for $\overline{\beta}_{ion}$ = 0,097 which has been found without variation of Hartree energy conforms with experimental which is equal to 0.0973 as in case of the crystal. The value which is determined by the computer experiment amounts 0.032±0,002 that leads to $\overline{\beta}_{abc}\Omega=0.078\pm0.005$.

Equation (10) indicates that the modulus obtained by Eq. (12) is an «instantaneous» bulk modulus, which, as shown in [4], is the upper limit of the adiabatic bulk modulus and is approximately 10 % larger than the isothermal bulk modulus Na. The results which are given in the work coincide with above-mentioned ones. Besides that, the low differences are indicative of that the approach (10) is acceptable for such differences. Further one may calculate with the help of the equation (12) in the same approach. The variation of Hartree energy gives a result of 0.105 and it also coincides with the experiment, if we take into account the upper limit of the real compressibility. In case of crystalline state the correction of Hartee energy gives the considerable contribution that is necessary to achieve the concordance with the experiment.

The accuracy which is taken from the calculation as a whole is note worse than for the crystal [5] and can be explained approximately in the same way like before. One of the possible explanations applies to the substantial modification of the pseudo-potential at low $q-s$, what about it was told above. It is corroborated by the calculation with the components of the third and fourth order, i.e. including the triplet and quadrupole effective interactions. It is corroborated by the calculated polyterms of adiabatic compressibility for the liquid lead (Fig. 1). Adiabatic compressibility in this process increases monotonously. Such the behavior of the compressibility basically is typical for the metal melts. Thus, one may conclude that the instantaneous dynamic modulus, which is calculated in the modulus of pair approach, is identical with the dynamic modulus, that is calculated in the complete theory on the second order, and also is distinctly differs from the static modulus, on the one hand, and from that one which is calculated in the theory of the second order, on the other hand. The first of them matches to the isometric experimental modulus, while the second one refers the correction to the Hartree energy. Thereby, the situation doesn’t differ from that which was used at the analogical calculations for the crystalline condition of a substance [6].

The possible explanation is in the neglect of the components of electron-ion interaction of the higher order than the second one, also in the inadequacy of pseudo-potential modification by means of the correction to the Hartree energy that leads to the correct result only in the long-wave limit. The above relations enable us to calculate the compressibility of melts. The theoretical calculated polyterms of the compressibility to selenium, tellurium, germanium and silicon are shown on the Figures 1–5.

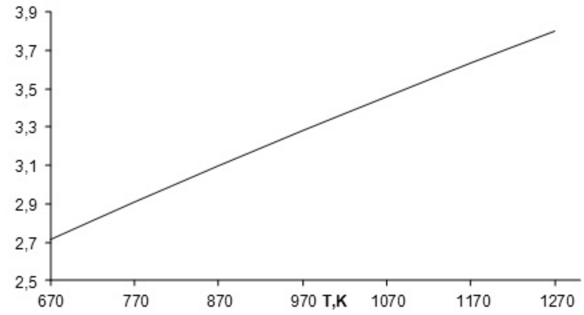

Figure 1. The compressibility polyterms of the lead melt

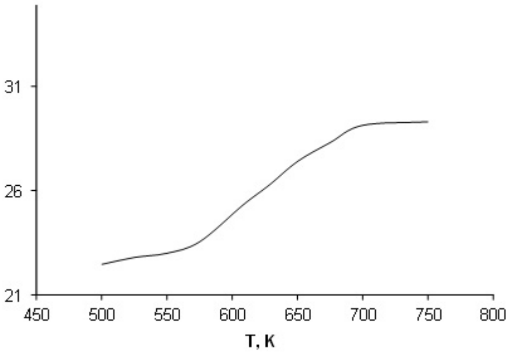

Figure 2. The compressibility polyterms of the selenium melt

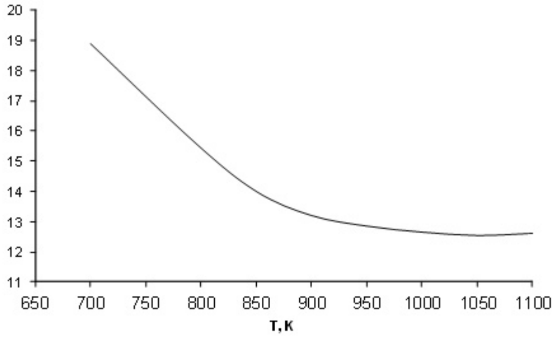

Figure 3. The compressibility polyterms of the tellurium melt

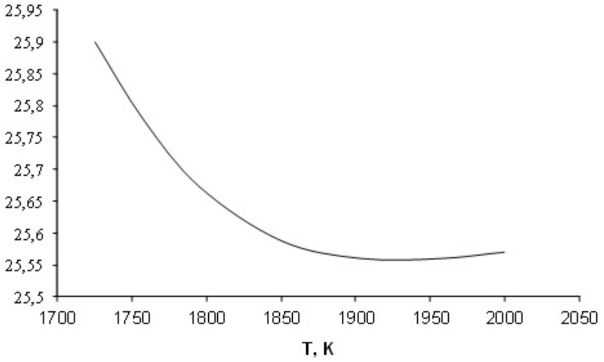

Figure 4. The compressibility polyterms of the silicon melt

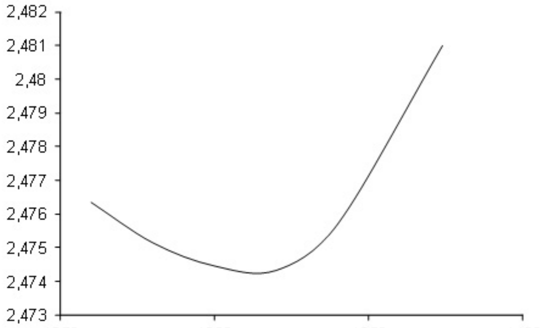

Figure 5. The compressibility polyterms of the germanium melt

The model of the micro-heterogeneous melt with the clusters of the similar size at fixed temperature is, certainly, idealized. In fact, in the real melt there can be the clusters of various sizes. The existence of the clusters not only close to the crystallization temperature, but also at the higher temperatures, in the melts of semimetals and semiconductors is conditioned on the presence in them the two types of the chemical bond — covalent and metallic [1].

The covalent bond type that is present and predominant in the crystal, while its passing to the liquid condition can disappear neither just after melting, nor at the further heating. These bonds are laid on the atomic nature itself, which constitute semimetals and semiconductors in the outer electron shell of the atoms and cannot disappear completely at any aggregate substance condition. The question only is in their manifestation degree. If these bonds exist together with the bounds that greatly differ in their energy, then they manifest essentially. The example is the molecular liquids. If these bonds are dipped into the matrix of the other bond types, which is not much differ from them energetically, then their individuality levels on the equalized background of those allied by their energy, but differ in the bond nature, for example, metallic.

Thus, the double-structured melt cluster model (the model of the mixture of cluster and atomic component), reflecting the opportunity of equilibrium existence of the two types of chemical bound (covalent and metallic bonds), different by their nature, but close by their solidity (thermodynamic aspect) and the two mechanisms of the cluster decay (kinetic aspect) allow to explain quite right the main types of the experimental and theoretical polyterm compressibility in the melts of the semimetals and semiconductors.

The Variety of the forms of polyterms compressibility in the electronic melts requires typification, or their analysis allows clearing the mechanism of the aggregation processes and dissolution of extensive objects in the melts.

References

1 Регель А.Р. Периодический закон и физические свойства электронных расплавов: монография / А.Р. Регель, В.М. Глазов. — М.: Наука, 1982. — 296 с.

2 Onuki A. Viscosity enhancement by domians in phase-separating fluids near the critical point. Proposal of critical rheology / A. Onuki // Phys. Rev. A. Gen. Phys. — 1987. — Vol. 35, No. 12. — P. 5149–5155.

3 Torquato S. Computer simulation of nearest — neighbor distribution functions and related quantities for hard-sphere systems / S. Torquato, S.B. Lee // Physica A. — 1990. — Vol. 167, No. 2. — P. 361–383.

4 Medvedev N.N. Aggregation of tetrahedral and quartoctahedral Delaunay simplices in liquid and amorphous rubidium / N.N. Medvedev // J. Phys: Condens. Matter. — 1990. — Vol. 2, No. 46. — P. 9145–9154.

5 Sun T.F. An efficient algorithm for the solution of the correlation function for soft spherical repulsions / T.F. Sun, J.A. Schouten // Mol. Phys. — 1990. — Vol. 69, No. 4. — P. 604–614.

6 Takamiya M. Density functional approach to two-dimensional classical fluids / M. Takamiya, K. Nakanishi // Mol. Phys. — 1990. — Vol. 70, No. 5. — P. 767–781.

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Балқытылған жүйелердегі қысымды және көлемдік модульдарды бағалау

Мақалада балқытылған жүйелердегі көлемдік модульдер қысымы мен жұптық әлеуеті бағаланған. Электрондық балқымалардың сығылғыштығын есептеу үшін сәйкес формулалар келтірілген. Селен, теллур, германий және кремний үшін сығылғыштық политермалары есептелген. Көлемдік модульдердің есебі үшін металдар мен жартылайөткізгіштер балқымалары иондар мен электрондардан тұратын екі компонентті сұйықтық ретінде қарастырылған. Вириал теоремасы бойынша, иондық кішірек жүйенің динамикасы мен өзара әрекеттесуімен байланысты қысым бөлігі бағаланған. Көлемдік серпімділіктің изотермиялық модулі статикалық модуль болып табылғандықтан, оны біз жүйедегі қысым мен көлем баяу өзгерген жағдайда, ал балқыма температурасы өте баяу өзгергенде немесе тұрақты болып қалған жағдайда тауып алдық. Көлемдік серпімділіктің адиабаттық модулі, яғни динамикалық, сығумен туындаған балқыманы қыздыру жағдайында анықталды. Адиабаттық сығу кезінде температура мен қысымның өзгерісі орын алады. Бұл құбылыс тез жүретін үрдістер кезінде, яғни балқымалардың жылулық қасиеттерінің инерциондығы салдарынан жылу алмасу болмаған кезде орын алады. Адиабаттық сығылғыштықтың мұндай сипаты металл балқымаларға тән. Авторлар жұптық жуықтау моделінде есептелген лездік динамикалық модуль екінші тәртіппен толық теорияда есептелген динамикалық модульмен бірдей екендігін анықтады, сонымен қатар статикалық модульден елеулі өзгешелігі бар. Бұл факт неғұрлым жоғары тәртіптегі электрондық-иондық өзара әрекеттесу мүшелерін елемеу, сонымен қатар Хартри энергиясына түзету арқылы псевдопотенциал модификациясының қанағаттанбауымен түсіндіріледі. Авторлар шығарып алған қатынас балқымалардың сығылғыштығын есептеп алуға мүмкіндік береді. Жартылайөткізгіштер үшін сығылғыштықтың теориялық есептелген политермалары жұмыста келтірілген.

Кілт сөздер: кластерлік құрылым, сығылғыштық политермалары, жартылайөткізгіштер, радиалды үлестірім функциясы, құрылымдық фактор, адиабаталық сығылғыштық, жұптық потенциал, көлемдік модульдардың қысымы.

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Оценка давления и объемных модулей в расплавленных системах

В статье оценены парный потенциал и давление объемных модулей в расплавленных системах. Приведены соответствующие формулы для расчета сжимаемости электронных расплавов. Вычислены политермы сжимаемости для селена, теллура, германия и кремния. Для расчёта объёмных модулей расплавы металлов и полупроводников рассмотрены как двухкомпонентная жидкость, состоящая из ионов и электронов. По теореме вириала оценена часть давления, связанная с динамикой и взаимодействием ионной подсистемы. Так как изотермический модуль объемной упругости является статическим показателем, он определен нами в условиях, когда давление и объем в системе изменяются медленно, а температура расплава очень медленно изменяется или остается постоянной. Адиабатический модуль объемной упругости, т.е. динамический, определен нами в условиях нагревания расплава, вызванного сжатием. При адиабатическом сжатии допускается изменение температуры и давления. Данное явление имеет место при быстропротекающих процессах, т.е. когда отсутствует теплообмен из-за инерционности тепловых свойств расплавов. Такое поведение адиабатической сжимаемости характерно для металлических расплавов. Авторы установили, что мгновенный динамический модуль, рассчитанный в модели парного приближения, идентичен динамическому модулю, вычисленному в полной теории во втором порядке, а также заметно отличается от статистического модуля. Объяснение данного факта состоит в пренебрежении членами электронно-ионного взаимодействия более высокого порядка, чем второй, а также неудовлетворительностью модификации псевдопотенциала посредством поправки к энергии Хартри. Полученные авторами соотношения позволяют вычислить сжимаемость расплавов. Теоретические вычисленные политермы сжимаемости для полупроводников приведены в работе.

Ключевые слова: кластерная структура, политермы сжимаемости, полупроводники, функция радиального распределения, структурный фактор, адиабатическая сжимаемость, парный потенциал, давление объемных модулей.

References

1 Regel, A.R., & Glazov, V.M. (1982). *Periodicheskii zakon i fizicheskie svoistva elektronnykh rasplavov [Periodic Law and Physical Properties of Electronic Melts]*. Moscow: Nauka [in Russian].

2 Onuki, A. (1987). Viscosity enhancement by domians in phase-separating fluids near the critical point. Proposal of critical rheology. *Phys. Rev. A. Gen. Phys., 35(12)*, 5149–5155.

3 Torquato, S., & Lee, S.B. (1990). Computer simulation of nearest — neighbor distribution functions and related quantities for hard-sphere systems. *Physica A, 167(2)*, 361–383.

4 Medvedev, N.N. (1990). Aggregation of tetrahedral and quartoctahedral Delaunay simplices in liquid and amorphous rubidium. *J. Phys: Condens. Matter, 2(46)*, 9145–9154.

5 Sun, T.F., & Schouten, J.A. (1990). An efficient algorithm for the solution of the correlation function for soft spherical repulsions. *Mol. Phys., 69(4)*, 604–614.

6 Takamiya, M., & Nakanishi, K. (1990). Density functional approach to two-dimensional classical fluids. *Mol.Phys, 70(5)*, 767–781.