

A POLYDISPERSE HARD SPHERE MODEL FOR INTERIONIC CORRELATIONS IN METALLIC MELTS

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The main idea of this work consists in a new way of the treatment of interionic correlations in a liquid metallic system. To model the non-hard-sphere behavior of interatomic distances, we represent the ionic subsystem of a melt as a polydisperse fluid of hard spheres characterized by diameters continuously distributed according to some size distribution function. Using this approach, we obtain smooth pair correlation functions of some model melt, where the sizes of particles are distributed by some general normalized nascent delta function. This method can be used for any other function that satisfies the conditions of the distribution function.

Since the ions behave themselves as a classical fluid in metallic melts, the influence of different contributions of the interionic pair potential to the structure and properties of such systems is considered in the next way [1]: it is now generally accepted that the structure of simple fluids, at least at high densities, is largely determined by geometric factors associated with the packing of particles caused by the strong short-range interionic repulsion. In contrast, the long-range attractive interactions can, in the first approximation, be regarded as giving rise to a uniform background potential that provides the cohesive energy of a fluid, but has little effects on its structure formation. So, the ion-ion repulsion in a liquid metal can be regarded as the main factor determining the ionic arrangement and interionic correlations consequently.

In this way, Ashcroft and Lekner [2], proposed to treat this interaction in simple liquid metals in the hard-sphere (HS) approximation. They used the known solution of the Ornstein-Zernike (OZ) equation with HS Percus-Yevick closure (PY) [3]. Such a method gives a simple closed form for the fluid structure factor $S(q)$ (SF) which depends only on the effective packing density of the fluid η . The results obtained by Ashcroft and Lekner are in good correlation with experimental structure factors of single-component metallic melts if packing densities η are in the interval 0.44–0.46. There are almost no deviations of experimental SF and HS SF in a region of first two-three maxima, but these deviations are distinctly observable in a short-wave limit ($q \rightarrow \infty$): the oscillation amplitude of the experimental SF decreases much faster (like the exponent e^{-q}) than

the HS one (approximately q^{-2}). The mismatch of experimental and HS interionic correlations comes vivid if we present the pair correlation function (PCF) $g(r)$ as

$$g(r) = 1 - \frac{1}{2\pi^2\rho} \int_0^\infty [1 - S(q)] \frac{\sin qr}{qr} q^2 dq \quad (1)$$

and consider its behavior at distances semiequal to the hard-sphere diameter of a particle ($r \simeq \sigma$). There is a strong second-order gap from 0 to a pointed maximum in the HS result that looks quite unphysically as compared with the experimental smooth maximum at a nearby position which corresponds to the most probable distance of neighbors. This is an uncorrectable feature of the HS solution of the OZ–PY equation for a single-component system treated like a monodisperse fluid (sizes of particles are constant).

To avoid this effect, someone, whose work needs data on structure correlations in fluids, often uses the direct method that is based on the iterative solution of the corresponding OZ equation in the soft-core approximation (for a real space):

$$h(r) = c(r) + \rho(h \cdot c)(r) \quad (2)$$

and the closure relation

$$h(r) = -1 + e^{-\beta u(r) + h(r) - c(r) + B(r)}, \quad (3)$$

where $u(r)$ – a pair potential that characterizes the ion-ion repulsion and it should not be equal to infinity inside the core diameter of an ion (in contrast to the HS model), $c(r)$ – a direct correlation function, $h(r) = g(r) - 1$ – the total correlation function, ρ – the mean number density of a fluid, and $\beta = (k_B T)^{-1}$ – the Boltzmann temperature coefficient. $B(r)$ is the “bridge” function and is determined by an approximation used for the closure relation construction (like PY, HNC – hypernetted chains, *etc.*). The second term in Eq. (2) is the spatial convolution of the total and direct correlation functions [also called $\gamma(r) = (h \cdot c)(r)$ – an undirect correlation function].

After some number of iterations, the solution converges, and we get the smooth PCF of a fluid that looks very similar to the experimental results. The time and the accuracy of such an approach depend on the iterative method and the Fourier transformation method we should use, by getting the convergence of the OZ solution.

Now we propose another way of constructing the correlation functions (SF, PCF) of a liquid metal using the exact HS solutions of the OZ equation, but PCF would keep its natural smoothness at short-range distances. So, in this work, we regard a metallic melt as a fluid, in which the size of particles is characterized by some random HS diameter σ , whose distribution is set by a continuous function $f(\sigma)$. The other properties (like mass, charge, etc.) of particles are constant and associated to the geometric center of such particles.

Such distribution function as $f(\sigma)$ has the interpretation of a size-distribution and means that $f(\sigma')d\sigma$ represents the fraction of particles in the system characterized by a σ value in the range $[\sigma', \sigma' + d\sigma]$. Thus, $f(\sigma)$ should be positive, $f(\sigma) \geq 0$, and it should be integrated over the whole range of possible σ :

$$\int_0^{\infty} f(\sigma)d\sigma = 1. \tag{4}$$

Hence, this function can also be interpreted as a probability density function. The conclusion is that we should study a single-component polydisperse fluid that consists of hard spheres, whose sizes are distributed by $f(\sigma)$, and they are dispersed in whole system's volume. Here, we should notice also that, due to the polydispersity definition, such size-distribution function is a local characteristic of the system (this means that the size-distribution function describes the sizes of different polydisperse particles independently) and stays constant through the whole space occupied by this system.

Recently, the correlation functions and thermodynamic properties of polydisperse fluids [4] and colloids [5] were theoretically studied by generalizing the OZ system of equations from a multicomponent mixture of hard spheres with a finite number of components to the polydisperse case. According to this approach, the correlation functions of a polydisperse fluid satisfy a continuous system of partial OZ equations (for a reciprocal space):

$$h(\sigma', \sigma'', q) = c(\sigma', \sigma'', q) + \rho \int_0^{\infty} f(\sigma)h(\sigma', \sigma, q)c(\sigma, \sigma'', q)d\sigma. \tag{5}$$

The partial direct correlation functions $c(\sigma', \sigma'', q)$ are known exactly due to the Baxter solution [6] of the OZ–PY equation for a multicomponent system of HS. The quantities $h(\sigma', \sigma'', q)$ are the Fourier transforms of the partial total correlation functions that define the dependence of the corresponding probability densities for a pair of particles with diameters σ' and σ'' to exist on the distance between these two particles. Consequently, such functions contain all spatial and size pair correlations needed for the description of the structure of a polydisperse HS fluid.

As was stated before, all physical properties of a metallic melt except the size of a hard sphere are associated to the geometric center of a metallic ion. Hence, the interionic PCF and SF of such metallic melt should be equal to the “number-number” PCF [1] and the “total structure factor” [7, 8] of a polydisperse fluid that were defined as

$$g(r) = 1 + \int_0^{\infty} \int_0^{\infty} f(\sigma')f(\sigma'')h(\sigma', \sigma'', r)d\sigma'd\sigma'', \tag{6}$$

$$S(q) = 1 + \rho \int_0^{\infty} \int_0^{\infty} f(\sigma')f(\sigma'')h(\sigma', \sigma'', q)d\sigma'd\sigma''. \tag{7}$$

These two expressions were obtained by generalizing the result of Blum and Stell [9] for the structure function of a fluid containing a finite number of components to the case where the fraction of components is described by a continuous distribution using the normalization condition for $f(\sigma)$ Eq.(4) and transforming the summation over discrete fractions of components to the integration of a continuous size-distribution over the whole range of possible sizes of particles. Such an expression as $f(\sigma')f(\sigma'')h(\sigma', \sigma'', x)$ can be also interpreted within probability analysis: it is a product of probability densities $f(\sigma')$ and $f(\sigma'')$ for two independent random events (one HS has a diameter σ' , whereas the other one has a diameter σ'') and the size pair cross correlation related to the fact that these events occur in a polydisperse fluid simultaneously, which gives $h(\sigma', \sigma'', x)$ implicitly. Hence, the interionic PCF and SF of a melt in the form of Eqs. (6) and (7), respectively, are nothing more but the average values of the partial PCF and SF of some polydisperse fluid. The unknown $h(\sigma', \sigma'', x)$ in Eq. (6) or Eq. (7) should be found from Eq. (5).

To solve the OZ equations, Eq. (5), for the total correlation functions $h(\sigma', \sigma'', q)$, we should calculate the integrals over σ . This can be done, for instance, by introducing orthogonal polynomials $p_i(\sigma)$ associated to the

size-distribution function of the system $f(\sigma)$ [4]:

$$\int_0^\infty f(\sigma)p_i(\sigma)p_j(\sigma)d\sigma = \delta_{ij}, \quad (8)$$

where δ_{ij} – the Kronecker delta. In general cases, the polynomials $p_i(\sigma)$ must be constructed numerically starting from $p_0(\sigma) = 1$, using either the Gram–Schmidt algorithm,

$$p_i(\sigma) = \sigma^i + \sum_{j=0}^{i-1} \frac{\langle \sigma^i, p_j \rangle}{\langle p_j, p_j \rangle} p_j(\sigma), \quad (9)$$

or the three-term recurrence rule

$$a_i = \frac{\langle \sigma p_i, p_i \rangle}{\langle p_i, p_i \rangle}, b_i = \frac{\langle p_i, p_i \rangle}{\langle p_{i-1}, p_{i-1} \rangle},$$

$$p_{i+1}(\sigma) = (\sigma - a_i)p_i(\sigma) - b_i p_{i-1}(\sigma), \quad (10)$$

but adding one more starting condition for the polynomials $p_1(\sigma) = \sigma - a_0$. In Eqs. (9) and (10), we used the notation

$$\langle p, q \rangle = \int_0^\infty f(\sigma)p(\sigma)q(\sigma)d\sigma$$

for an inner product of two real functions $p(\sigma)$ and $q(\sigma)$ with a weight-function $f(\sigma)$ (here, it should be a size-distribution).

Now all size-dependent functions can be expanded in such a way that [4]

$$y(\sigma', \sigma'', x) = \sum_{i=0}^\infty \sum_{j=0}^\infty y_{ij}(x)p_i(\sigma')p_j(\sigma''), \quad (11)$$

where the coefficients are given by

$$y_{ij}(x) = \int_0^\infty \int_0^\infty f(\sigma')f(\sigma'')y(\sigma', \sigma'', x) \times p_i(\sigma')p_j(\sigma'')d\sigma'd\sigma''. \quad (12)$$

These two relations are valid in both real and reciprocal spaces (by setting x to either r or q , respectively) and for both direct and total correlation functions (by setting y to either c or h , respectively). If we use the OZ equations (5) together with decompositions of the direct and total

correlation functions (11) in the reciprocal space and the orthogonality relation (8), we obtain

$$h_{ij}(q) = c_{ij}(q) + \rho \sum_{k=0}^\infty h_{ik}(q)c_{kj}(q). \quad (13)$$

Then, by collecting the identical terms of these equations to the matrices $\hat{H}(q) = \{h_{ij}(q)\}$ and $\hat{C}(q) = \{c_{ij}(q)\}$, it is easy to find the solution of the system of equations (13) as

$$\hat{H}(q) = \hat{C}(q)[\hat{I} - \rho\hat{C}(q)]^{-1}, \quad (14)$$

where \hat{I} is the identity matrix.

Finding the numerical solution of Eq. (14), expansions Eq. (11) should be truncated at some suitably chosen finite value $L \ll \infty$. Hence, the matrices in Eq. (14) are transformed from the continuous form into a finite-dimensional form (the matrix size is $L \times L$) and the elements of such matrices $c_{ij}(q)$ and $h_{ij}(q)$, with regard for the coefficients of expansions (12), are most conveniently calculated in practical applications via a Gaussian quadrature rule, using the set of L roots $\sigma_{pL}^{(n)}$ ($n = 1, \dots, L$) of the polynomial $p_L(\sigma)$ and the root associated weights $w_{pL}^{(n)}$. This means that Eq. 12 is transformed to

$$y_{ij}(x) \simeq \sum_{n=1}^L \sum_{m=1}^L w_{pL}^{(n)} w_{pL}^{(m)} \times y(\sigma_{pL}^{(n)}, \sigma_{pL}^{(m)}, x) p_i(\sigma_{pL}^{(n)}) p_j(\sigma_{pL}^{(m)}). \quad (15)$$

The roots $\sigma_{pL}^{(n)}$ are the eigenvalues of the three-diagonal matrix

$$\begin{pmatrix} a_0 & b_1^{1/2} & 0 & \dots & 0 \\ b_1^{1/2} & a_1 & b_2^{1/2} & \dots & 0 \\ 0 & b_2^{1/2} & a_2 & \ddots & \vdots \\ \vdots & \vdots & \ddots & \ddots & b_{L-1}^{1/2} \\ 0 & 0 & \dots & b_{L-1}^{1/2} & a_{L-1} \end{pmatrix}, \quad (16)$$

where a_i and b_i are previously defined in Eq. (10), while the polynomial $p_L(\sigma)$ was constructing by the three-term recurrence rule. This eigenvalue problem can be solved fast, by using the QR-decomposition procedure [10]. The associated weights can be found either by using

$$w_{pL}^{(n)} = \left[\sum_{i=0}^{L-1} p_i^2(\sigma_{pL}^{(n)}) \right]^{-1} \quad (17)$$

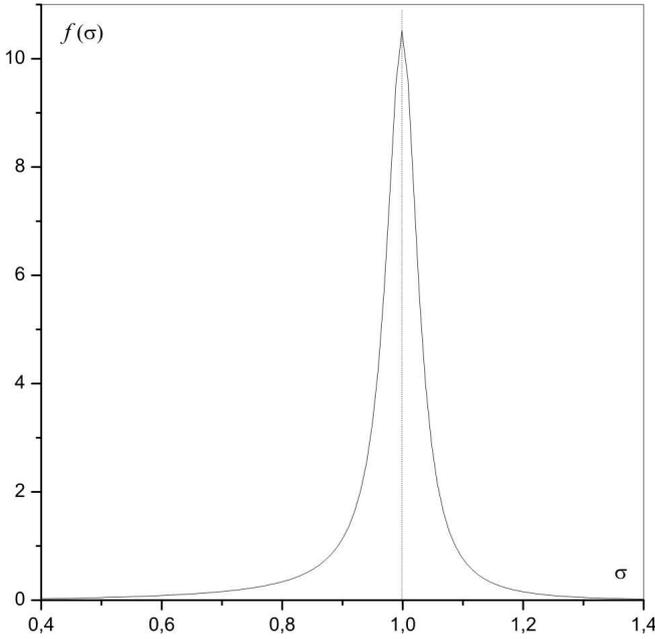


Fig. 1. Size-distribution function for $\bar{\sigma} = 1$ and $\Gamma^2 = 10^{-3}$

or directly from the QR-decomposition.

The numerical studies [11] have shown that $n = 5$ is a sufficiently large value to truncate the expansions and simultaneously to maintain a high accuracy of the results.

Further, we present our computation results, where we apply the polydisperse model of liquid metallic melt. We represent the size-distribution function as a nascent delta function of the form (Fig. 1)

$$f(\sigma) = \|f(\sigma)\|^{-1} \frac{e^{-(\sigma/\bar{\sigma})^2/\ln 2} \left[1 - e^{-(\sigma/\bar{\sigma})^2/\ln 2} \right]}{[\sigma - \bar{\sigma}]^2 + \Gamma^2}. \quad (18)$$

The parameter $\bar{\sigma}$ defines the position of a peak that corresponds to the most probable diameter of HS (in general, $\bar{\sigma}$ represents the length scale of a system), and Γ defines the distribution width and, hence, the polydispersity index of the system.

The most optimal packing parameter η for simple metallic melts is in the interval 0.44 – 0.46 [2]. So we used $\eta = 0.45$ and the concentration of particles defined by

$$\rho = \frac{\pi\mu_3}{6\eta} = 0.88, \quad (19)$$

where $\mu_i = \int_0^\infty \sigma^i f(\sigma) d\sigma$ is the i -th moment of the size-distribution. The polydispersity index of the studied

system is

$$\text{PDI} = \frac{\mu_2}{\mu_1^2} = 1.01166 \quad (20)$$

and is close to the monodisperse value (PDI = 1).

The number of orthogonal polynomials used in computations is $L = 10$ and exceeds twice the minimal value used in [5] for the gamma-distribution. Needed weights and roots of the distribution are presented below (Table).

Using these data, we made three model calculations of the total correlation function (the PCF and SF can be obtained using the simple rules $g(r) = 1 + h(r)$ and $S(q) = 1 + h(q)$, respectively): the first (mono) – monodisperse model, where effective diameter of HS was defined by

$$\sigma_{\text{mono}} = \left[\frac{6}{\pi} \eta \rho \right]^{1/3}; \quad (21)$$

the second (Q+Q) – polydisperse model, where expansion coefficients were calculated using the “full” quadrature method (15); the third (Q+I) – polydisperse model, where expansion coefficients were calculated using the “half” quadrature method:

$$y_{ij}(x) = \sum_{n=1}^L w_{pL}^{(n)} p_i(\sigma_{pL}^{(n)}) \times \int_0^\infty y(\sigma_{pL}^{(n)}, \sigma, x) f(\sigma) p_j(\sigma) d\sigma. \quad (22)$$

There is no difference between the Q+Q and Q+I approaches, but the method of integration [compare Eq. (15) and Eq. (22)]. The reason why we use both these methods is the smoothness of the resulting curve (Q+I) and the time of calculations (Q+Q is much faster).

Weights and roots of the size-distribution $f(\sigma)$

n	$\sigma_{pL}^{(n)}$	$w_{pL}^{(n)}$
1	0.12937	2.93765×10^{-4}
2	0.33063	3.79458×10^{-3}
3	0.59365	0.0241748
4	0.88995	0.2597
5	1.02381	0.692351
6	1.30168	0.0189444
7	1.71320	7.19768×10^{-4}
8	2.18460	2.12864×10^{-5}
9	2.72607	2.52749×10^{-7}
10	3.38575	5.12095×10^{-10}

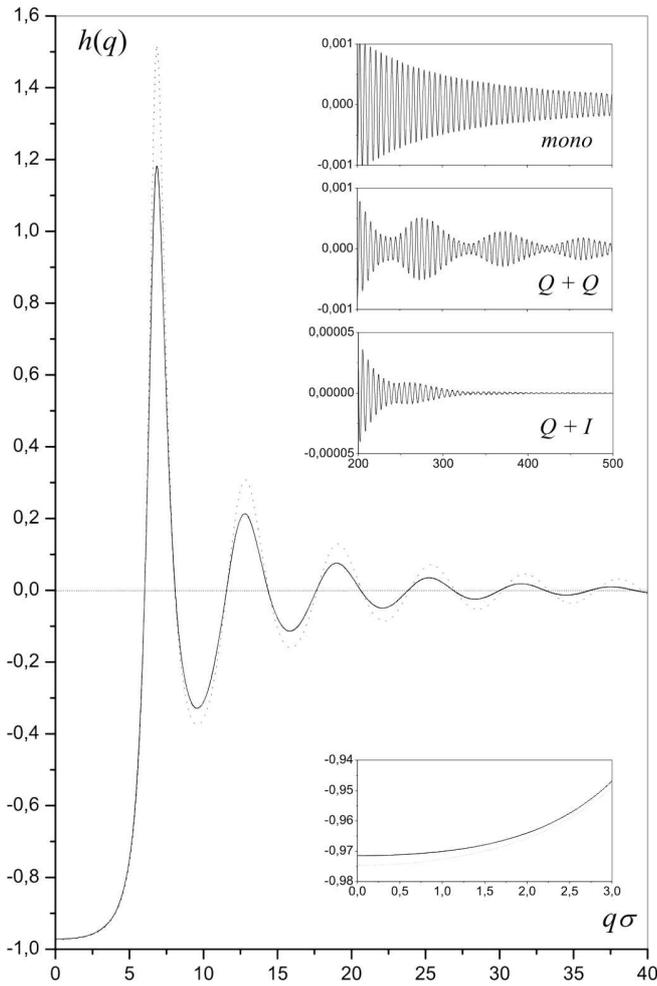


Fig. 2. Reciprocal space presentation of the total correlation functions of a single-component fluid $h(q)$. The monodisperse HS-PY result is the dotted line, Q+Q polydisperse model – dashed line, and Q+I polydisperse model – the solid line. Three pictures on the figure top describe the behavior of large q tails of $h(q)$ for different models and present the rate of convergence. The picture given in the figure bottom describes the behavior of $h(q)$ at the zero range of q (long-wave range)

The calculations of the total correlation function in the reciprocal space $h(q)$ illustrated in Fig. 2 show us that, in region of small q , there is no divergence of the Q+Q and Q+I results. The total correlation functions of both polydisperse models are softer, and the magnitude of the first maximum and the $q \rightarrow 0$ limit are smaller, than the monodisperse HS-PY result. This fact is evident because the effective pair potentials are no longer “hard-spherical”. The difference of the Q+Q and Q+I results is in the convergence to a constant (to 0) in the region of large q . As shown, the total correlation function obtained within the Q+Q approach has a “pulsing”

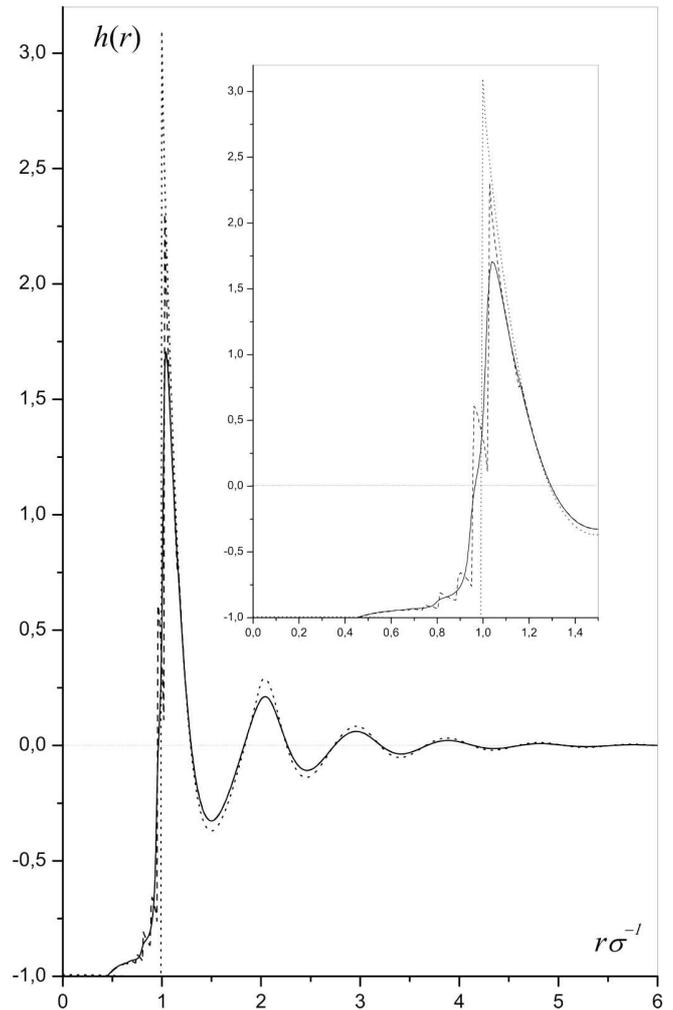


Fig. 3. Real space presentation of the total correlation functions of a single-component fluid $h(r)$. The monodisperse HS-PY result is the dotted line, Q+Q polydisperse model – dashed line, and Q+I polydisperse model – the solid line. The nested picture describes the behavior of $h(r)$ at the range of distances close to the most probable neighbor

character and converges to 0 in the same way as the monodisperse model does. At the same time, Q+I converges even and much faster. Such a difference in the behavior of these two approaches is caused by application of a quadrature rule, in case of the Q+Q approach, to a generalized HS-PY direct correlation function $c(\sigma, \sigma', r)$ that has a breakdown at $r = (\sigma + \sigma')/2$, and hence it cannot be integrated via the quadrature rule accurately. Simultaneously, one direct integration over all sizes in the Q+I approach [see (22)] removes this breakdown, and the quadrature rule can be efficiently used further.

Tails of $h(q)$ define the behavior of $h(r)$ at small distances. So the difference of the Q+Q and Q+I approaches to the calculation of total correlation functions should be more observable in the real space. Using Eq. (1), we can calculate the total correlation function in the real space presentation, and Fig. 3 illustrates our results obtained for $h(r)$ with the use of all three models.

The monodisperse model gives us a standard HS-PY result that is characterized by a strong and pointed first maximum at $r = \sigma_{\text{mono}} = 0.992$ defined by Eq. (21). The Q+Q approach to calculations within the polydisperse model gives us a curve with a set of pointed local maxima located at $r = (\sigma_{p_{10}}^{(n)} + \sigma_{p_{10}}^{(m)})/2$ (only 6 pointed maxima can be distinguished because only 3 roots $\sigma_{p_{10}}^{(n)}$ have enough weight) and looks like a direct sum of the corresponding HS results with the partial concentrations $w_{p_{10}}^{(n)}w_{p_{10}}^{(m)}$. Obviously, this result does not satisfy the condition of smoothness of PCF. The last Q+I result is smooth as was expected. By comparing its form and the form of size-distribution function, we can find a lot of similarities of their behaviors. Simultaneously, all results have the same behavior in the long range.

So, the conclusion is that, by using the Q+I approach and the polydisperse model of melts, we can model its structure and get naturally smooth PCF and SF that converge faster than those of the HS-PY approach. The shape of the first maximum of PCF can be changed by a choice of the distribution function that should satisfy the next conditions: it should be integrated to 1 over a range of all possible sizes, it should be positive, and it should have finite moments. The last condition can be satisfied during the construction of a size distribution in two ways. The first consists in the use of a function limited at some σ_{max} , and the second is the use of a $e^{-\alpha\sigma^p}$ -like function.

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МОДЕЛЬ ПОЛІДИСПЕРСНИХ ТВЕРДИХ СФЕР
ДЛЯ МІЖІОННИХ КОРЕЛЯЦІЙ
В МЕТАЛІЧНИХ РОЗПЛАВАХ

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Резюме

В основу даної роботи покладено новий спосіб розгляду між-іонних кореляцій у рідкій металічній системі. Для моделювання нетвердосферичної поведінки міжатомних відстаней ми представили іонну підсистему розплаву як полідисперсну рідину, що складається з твердих сфер, діаметри яких розподілено згідно з деякою функцією розподілу. Використовуючи такий підхід, ми отримали гладкі парні кореляційні функції модельного розплаву, розміри частинок якого розподілено згідно з нормованою дельта-породжуючою функцією. Цей метод також можна використовувати і у випадку інших функцій, що задовольняють умови функції розподілу.