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First principles calculation and simulation of correlation functions and functions of metal melts' radial distribution

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Majority of technological processes in metallurgy are based on the extensive use of gases, liquids and granular materials. From this point of view, the viscoelastic theory, which is based on one of the most important melting process's features, that is establishment of proximity of the liquid state to the crystalline state near the melting point, is of interest. Development of the given theory allows establishing and predicting metal melts' properties, based on interparticle interactions.

Keywords: correlation function, interatomic distance, potential energy, melt

INTRODUCTION

Theoretical descriptions of processes occurring in melts are based on the Stokes – Kirchhoff theory, which, within the frame of classical hydrodynamics, revealed phenomenological connections between molten systems' kinetic properties. Nowadays, the viscoelastic theory is widespread, distinguishing feature of which is a unified description of the liquid and solid states, that is, proximity of the liquid state to the crystalline state near the melting point. In other words, such a theory makes it possible to predict the melt properties on the strength of hydrodynamic motion equations [1], based on interatomic interactions. When describing individual molecules within the frame of the density functional, the assumption that the electronic states of individual chemical bonds and electrons that are not involved in the bonds formation are independent of each other, is used as an approximation. Molecules convergence during the semiconductor melt formation leads to a perturbation of the states on the bonds, which can be comparable with interaction of the bonds inside the molecule. Therefore, it is necessary to use separate bonds as an initial approximation when considering liquid semiconductors. Given model is convenient in the case when bonds formation leads to quasilattice structures. In the frame of hydrodynamic method for solving a system of equations, only specifically existing initial conditions are possible, and its asymptotic solution is possible only in the large times limit. Dimensional theory leads to the conclusion that velocity correlation function decreases inversely with time, and with a proportionality factor equal to the system's dimensions. This suggests that the correlation function does not decrease exponentially. As shown in many papers, the decrease is slow and leads to a divergence of diffusion coefficient.

This comparison would give a good agreement if we exclude small times area where classical hydrodynamics is unsuitable. Indeed, the time intervals corresponding to this area are shorter than the time required making several collisions. Therefore, in the given case, it is required to consider the melt at the quantum level.

Density functional's important advantage [2], as is well known, is the possibility of using the first principles of quantum chemistry for estimating density distribution's energy and electronic characteristics, and from this information to draw a picture of the energy bands. Given model can be applied to liquid semiconductors.

RESULTS AND DISCUSSION

Let in the quasilattice of a unitary volume in the energy interval from E to $E+dE$ there are dZ quantum states (taking into account spin). Denote by $N(E)$ states density, i.e. states number in the unitary interval of energy for unitary volume of quasilattice. Then, by the definition of states density, we write:

$$N(E)=\frac{dZ}{dE} \tag{1}$$

If the probability of an electron filling the state with energy E is equal to $f(E,T)$, then the number of electrons dn that are in the states dZ, will compose the quantity:

$$dn=f(E,T)N(E)dE \tag{2}$$

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Correspondingly, the quantity of electrons, for which the possible interval of energy lies within the limits $[E_1, E_2]$, will be equal to:

$$n = \int_{E_1}^{E_2} f(E,T)N(E)dE \qquad (3)$$

Let us find an expression for the quantum states density in the case when the surface of equal energy of the conduction band and the valence band are spheres. Then you can get an expression for the quantum states density at the bottom of the conduction band, which has spherical symmetry:

$$N(E) = 4\pi\left(\frac{2m_n}{h^2}\right)^{\frac{3}{2}}(E - E_c)^{\frac{1}{2}} .$$

Similarly, one can determine the states density near the upper edge of the valence band. But on the other hand, the above expression is related to the Thomas-Fermi-Dirac functional by the following relation:

$$(E - E_c)^{\frac{1}{2}} = \frac{\rho^3(3\pi^2)^3}{\sqrt{2}} . \qquad (4)$$

After simple transformations for the states density can be written:

$$N(E) = 4\pi\left(\frac{2m_n}{h^2}\right)^{\frac{3}{2}}\frac{(3\pi)^3}{\sqrt{2}}\rho^3$$

where $\rho = \{\rho_{1s}, \rho_{2s}, \rho_{1p}, \rho_{2p}, ...\}$.

These data give opportunity to the molecular bonds quantum interpretation formed in semiconductors melts, as well as other high-temperature liquids elastic properties. It should be noted that the greatest successes were achieved in this direction in the works of M. Born, G. Green, J. Kirkwood, N. N. Bogolyubov and others. Moreover, the main task of such a statistical theory of liquids is the establishment of a connection between the molecules' properties and the interatomic potential, as well as between the molten systems' thermodynamic and kinetic properties. When studying the melt properties, it is necessary to take into account the set of particles that averages physical quantities. As is known [2], in the case of a crystal, one can obtain, for example, information relating to a single dislocation, but one cannot trace the single impurity atom motion. And in melts, due to the high mobility of its particles and due to the absence of a long-range order (as in the crystal lattice), closest environments of various atoms or molecules can differ quite strongly, both in the number of neighbors and in their spatial arrangement. Since it is not possible to monitor the behavior of an individual atom or group of atoms, the so-called clusters, any melt property measurements results turn out to be averaged over a large number of atoms. When a property, that does not depend on the angular orientation (in space) of the given atom's nearest neighbors, is studied, then during averaging over different atoms, such orientation cannot be reflected in a measurement result, so that only the total number of atoms located at a certain distance from a given atom, is left essential.

In order to describe a given position, we choose a spherical segment with an inner radius r and an outer one R with a center in a simple melt's arbitrary particle core (containing for simplicity only atoms of one element). In this case, the average number of atoms in the given spherical segment will be proportional to the segment's volume. $4\pi r^2 dr$ is determined by the following relation:

$$dn(r) = 4\pi r^2 dr R(r), \qquad (5)$$

where $R(r)$ is the so-called radial distribution's pair function.

Function $R(r)$ by its physical meaning is the particles' number' density, not average, but local with respect to some arbitrary atom selected as the coordinates' origin. In case, when the distance r is sufficiently large compared with the interatomic distance r_a, then there is a probability that the separate atoms will not experience the action of the central particle and, therefore, will be located independently of it. In this case, we have to substitute (5) instead of $R(r)$ normal average density $R(r \to \infty) = R_0$. In the case when the distance from the given atom's center is too small (less than the so-called diameter of the atom), not a single particle core will fall into the spherical segment. Function $R(r)$ has oscillating character at short distances *r*. It is this behavior that corresponds to the melt's structure, since it must exhibit certain features peculiar to the crystal from which this melt was formed. Thus, there must be a preferred distance between the nearest neighbors, analogous to the interatomic distance in a crystal, average number of the nearest neighbors, similar to the coordination number in the lattice, and so on. Existence of ordering elements in the melt, which is ultimately determined by the intrinsic volume of the molecules and interatomic potential features, is determined by the term "short-range order".

Previously, we determined the radial distribution's pair function *R(r)* [2], describing melt particles' average placement around an arbitrary

atom. Now it is necessary to generalize to the case when we are interested in the relative position of the number of atoms. In order to do this, select volume in the melt dV. Let the particles' average number in this atom be equal to $dn = R_0 dV$, where R_0 is particle' number' density (number of particles per unit volume). If we count dV as sufficiently small, then dn will be much less than unit. Therefore, the product $R_0 dV$ can be considered as probability of detecting a melt particle in the volume dV: $dW_1 = R_0 dV_1$. Distinguish the following volume elements in the melt dV_1 and dV_2 near points with radius vectors r_1, r_2. Determine the probability that in volumes dV_1 and dV_2 will be two particles at the same time:

$$dW_{12} = R_2(r_1, r_2) dV_1 dV_2, \quad (6)$$

where the function $R_2(r_1, r_2)$ is a so-called binary correlation function.

Assuming the volumes dV_1 and dV_2

$$dW_{12} = dW_1 dW_2 = R_0^2 dV_1 dV_2.$$

From relations (6) it is seen that at large values $|r_1 - r_2|$ follows $R_2(r_1, r_2) = R_0^2$. Similarly, analogically to the above, we can introduce the probability $dW_{1,2,...,n}$ that in volumes $dV_1, dV_2, ..., dV_n$ will be one particle in each. Define $dW_{1,2,...,n}$ as follows:

$$dW_{1,2,...,n} = R_n(r_1, r_2, ..., r_n) dV_1 dV_2 ... dV_n. \quad (7)$$

Besides that, it is possible to establish a connection between the binary correlation function and the radial distribution's pair function $R(r)$. Probability of two particles being in volumes dV_1 and dV_2 can be represented as a product of two probabilities: firstly, that in the volume dV_1 will be one particle dW_1 and secondly, that on the distance $|r_1 - r_2|$ from the first particle will be the second dW_2. Thus, dW_2 is the probability of the second event, provided that the first one has already come:

$$dW_2 = R(|r_2 - r_1|) dV_2.$$

Probabilities dW can be normalized as follows:

$$\int dW_1 = \int_V R_0 dV_1 = R_0 V = N,$$

where N is the total number of melt particles.

$$\int dW_2 = \int R_2(r_1, r_2) dV_1 dV_2 = N(N-1),$$

and correspondingly:

$$dW_n = \frac{N!}{(N-n)!}.$$

In practice, for calculations convenience, it is advisable to reformulate the correlation functions and probabilities so that the first ones become dimensionless and normalization integrals are equal to unity. In order to do this, we introduce new probabilities of a given configuration of melt n - particles:

$$dW_n = \frac{1}{V^n} F_n(r_1, r_2, ..., r_n) dV_1 dV_2 ... dV_n, \quad (8)$$

where $dV_i = dx_i dy_i dz_i$, x_i, y_i, z_i are the coordinates of the ith particle.

Further, it will be possible to require that new probability be normalized to unity $\int dW_n = 1$,

$$\frac{1}{V^n} \int F_n(r_1, r_2, ..., r_n) dV_1 dV_2 ... dV_n = 1. \quad (9)$$

From equations (8) and (9) is seen that:

$$d\omega_n = \frac{N!}{(N-n)!} dW_n.$$

Taking into account the given relations (7) and (9), we can find connection between correlation functions R_n and F_n:

$$R_n(r_1, r_2, ..., r_n) = \frac{N!}{(N-n)!} \frac{1}{V^n} F_n(r_1, r_2, ..., r_n). \quad (10)$$

Note that the correlation functions of two subsequent orders are interconnected by relation (10) which follows from the probability definitions [3-6]. We now introduce the total potential energy of the system:

$$dW_n = A \exp\left[-\frac{U(r_1, r_2, ..., r_n)}{kT}\right] dV_1 dV_2 ... dV_n.$$

Then one can build recurrence relations for F_N, which allows us to find the correlation functions of lower orders:

$$F_N(r_1, r_2, ..., r_n) = V^N A \exp\left[-\frac{U(r_1, r_2, ..., r_n)}{kT}\right].$$

At present, calculation of these integrals can be easily carried out only for gases whose particle density is low. A direct melt correlation functions' definition using statistical mechanics is quite difficult to perform. In such cases, one resorts to numerical methods, such as the Monte Carlo method, using computer technology capabilities. Suppose that we are interested in the average value of some melt extensive physical properties

$M_n(r_1, r_2, ..., r_n)$, defined by the relative position of the n - particles group. In various melt areas $n-$ configurations will be different from each other, so property values of M_n will fluctuate around a given average value. Since the probability of particles' location in dW_n configuration is described by the correlation function $F_n(r_1, r_2, ..., r_n)$, , then averaging of value M_n is performed by integrating with weight F_n :

$$\overline{M}_n = \int M_n(r_1, r_2, ..., r_n) dW_n = \frac{1}{V^n} \int M_n(r_1, r_2, ..., r_n) F_n(r_1, r_2, ..., r_n) dV_1 dV_2 ... dV_n = 1.$$

In the melt containing N particles, the number of various groups of n - particles is equal to $\frac{N!}{(N-n)!n!}$. Therefore, the property value M_n for the total melt volume is:

$$M_n(N) = \frac{1}{V^n} \frac{N!}{(N-n)!n!} \int M_n(r_1, r_2, ..., r_n) F_n(r_1, r_2, ..., r_n) dV_1 dV_2 ... dV_n.$$

The most frequently considered properties depend either on the single particle's coordinates, or on particle pairs' mutual distances, that is, the properties determined by pair interactions. In the first case:

$$\overline{M}_1(N) = \frac{N}{V} \int M_1(r_1) F_1(r_1) dV_1.$$

From equation (10) follows that $F_1(r_1) = \frac{V}{N}$, $R_1 = \frac{V}{N}$, $R_0 = 1$, therefore:

$$\overline{M}_1(N) = \frac{N}{V} \int M_1(r) \, dV .$$

We can write for a property determined by pair interactions:

$$\overline{M}_2(N) = \frac{N(N-1)}{2V^2} \int M_2(r_1, r_2) F_2(r_1, r_2) dV_1 dV_2.$$

After a few transformations we have:

$$\overline{M}_2(N) = \frac{R_0}{2} \int M_2(r_1, r_2) R(|r_2 - r_1|) dV_1 dV_2.$$

Denoting $|r_2 - r_1|$ through r, we write:

$$\overline{M}_2(N) = 2\pi N \int_0^\infty M_2(r) R(r) r^2 dr. \qquad (11)$$

An important example of the equation application (11) is melt total energy calculation in the approximation, when the system's potential energy can be represented as the sum of particles pair interaction energies.

If the pair potential is denoted by $U(r)$ and taking into account that the average kinetic energy of a monatomic particle is 3/4kT, then for mechanical energy the following relation is valid:

$$U = \frac{3}{2} NkT + 2\pi N \int_0^\infty U(r) R(r) r^2 dr.$$

CONCLUSION

Results described above show that the knowledge of correlation functions $F_1, F_2, ..., F_n$ is necessary for the calculation of a whole row of metal melt thermodynamic properties. Methods of quantum statistical physics allow us to express coefficients of shear and bulk viscosities using correlation functions. This makes it possible to discover matter construction's physical nature through secondary quantization operators; thereby a powerful apparatus of quantum physics can be connected for research.

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