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Molecular Dynamics Modelling of Liquid Fe-C Alloys

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Abstract. Properties and structure of liquid Fe-C alloys with carbon concentration up to 20 at% at temperatures up to 2500 K were calculated using molecular dynamics modelling. Interaction between Fe-Fe and Fe-C atoms was described using the embedded atom potential (EAM). The Morse potential was chosen for Fe-C pair interaction, while C-C pair interaction was presented in the form of the repulsive potential. Parameters of potentials were adjusted using experimental data for density, internal energy, bulk modulus and distance between Fe and C atoms in liquid Fe-C alloys near the liquidus temperature. Calculated density and molar volume of Fe-C alloys at 1873 K decreased with increasing carbon concentration; a temperature coefficient of density of liquid alloys was, practically, independent of the carbon concentration. Carbon content of the alloys had a negligible effect on the distance between Fe-Fe and Fe-C atoms and on a sum of coordination numbers Fe-Fe and Fe-C. Distribution of atoms in the first coordination sphere in the Fe-C alloys was close to statistical.

Keywords. Molecular dynamics, embedded atom potential, liquid alloys, Fe-C system.

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1 Introduction

Fe-C is a major system in steelmaking. Properties of Fe-C alloys are of significant interest; they have been intensively studied in both liquid and solid states. The Fe-C phase diagram, properties of solid alloys and thermodynamic properties of liquid Fe-C solutions are well established. Experimental data on physical properties of liquid alloys and their structure obtained by different researchers are scattered and often inconsistent. Even difference in such fundamental property as density of liquid Fe-C alloys, measured by different researchers is significant [1–3]. Discrepancies in experimental data were caused by difficulties of high temperature experiments and high reactivity of liquid Fe-C alloys with respect to refractory materials and gases. Experimental data on properties and structure of liquid Fe-C alloys were reviewed in [4–7].

Vertman and Samarin [4] studied physical properties of Fe-C liquid alloys and concluded that liquid solutions with above 9 at% C contain unstable colloid-type complexes. In alloys, obtained by fast cooling of liquid Fe-C solutions (>9 at% C), authors [8,9] observed cementite and austenite with the carbon concentration less than 9 at%. On the basis of these data, authors [10] suggested that solutions with 9 at% to 22 at% C in the range of 1573 K to 1973 K consisted of two phases, which are cementite clusters and a Fe-C solution with 9 at% C.

Baum et al. [5] analysing experimental data on structure and properties of liquid alloys concluded that their structure changes at certain temperature. This fact was used for the so called temperature-time processing of liquid industrial alloys to improve their properties in the solid state [5].

Structure of the Fe-C liquid alloys was studied using XRD in [11] and neutron diffraction in [12]. No anomaly in structural properties of the Fe-C solutions was reported in these works.

The aim of this paper is to develop a molecular dynamics (MD) model of liquid Fe-C alloys to describe their properties and structure in a broad range of concentrations (up to 20 at% C) and temperatures (up to 2500 K).

The MD modeling depends on potentials which describe interactions between Fe-Fe, Fe-C and C-C atoms in the solution. In this work, the embedded atom model was used for Fe-Fe and Fe-C pairs, while C-C interaction was described using a repulsive potential.

In the embedded atom model (EAM), potential energy U of a system includes potentials of pair interactions $\phi(r_{ij})$ between atoms i and j and energy of individual atoms i, which is expressed through the effective electron density ρ in the point of location of an atom i by function $\Phi(\rho)$.

$$U = \sum_i \Phi(\rho_i) + \sum_{i<j} \phi(r_{ij}). \tag{1}$$

Effective electron density ρ is calculated by equation (2):

$$\rho_i = \sum_j \psi(r_{ij}), \tag{2}$$

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where $\psi(r_{ij})$ is a contribution to the electron density from an atom j. Functions $\Phi(\rho)$, $\phi(r)$ and $\psi(r)$ are adjusted using experimental properties of the system which is modelled. Total force acting on the atom i includes terms generated by cooperative interactions (EAM term) and pair i-j interactions.

The MD model and calculation procedure were presented in [13] in application to the Fe-S system. To construct a model of the Fe-C solution which properties and structure are close to the real system, potential parameters used in the MD modeling were adjusted using some experimental data for the solution. They included density, internal energy of Fe-C alloys, bulk modulus and average distance between Fe-C atoms. Bulk modulus was determined from the speed of sound in liquid iron and two Fe-C alloys near eutectic temperature measured in [14, 15]. Potential parameters were varied in such a way to get the best fit of models' internal energy, bulk modulus and Fe-C distances to experimental data. These parameters were used in modelling of Fe-C alloys in broad range of carbon concentration and temperature to calculate alloys' internal energy, bulk modulus, structure and self-diffusion coefficients of iron and carbon.

2 Properties of Liquid Fe-C Alloys Used for Calculation of the Model Potentials

Density of pure liquid iron is well established; at 1873 K, it is equal to $7.03 \cdot 10^3$ kg m^{-3} [16]. Data on the density of liquid Fe-C alloys reported in literature have a significant scattering, although in some cases these data were obtained using the same method [3]. Density of Fe-C alloys in [1] was studied by the gamma penetration method, which is highly sensitive to the density change and is more accurate at high temperatures [1]. Fe-C system was modelled using data from [1]. However, experimental data reported in [1] do not cover the whole range of temperatures and compositions studied in this work. To assess the density of different alloys at the same temperature, the temperature coefficient of density of $-0.87 \cdot 10^{-4}$ K^{-1} was used. This temperature coefficient was established for the Fe-B liquid alloy containing 3.3 mass % B, also by the gamma-penetration method [1].

Thermodynamic properties of the liquid Fe-C alloys were analysed in [17–22]. In the MD modelling, internal energy of the system is calculated relative to monatomic motionless gaseous components. Therefore, experimental thermodynamic properties of the Fe-C liquid alloys should be re-calculated for the standard states pure monatomic motionless gaseous iron and carbon. Internal energy of pure iron at 1873 K for this standard state is −315.92 kJ mol^{-1} [22]. Enthalpy of atomisation of graphite (transition to the monatomic gas) at 298 K is 716.68 kJ mol^{-1} [23]. Enthalpy change of graphite in the process of heating from 298 K to 1873 K is 31.83 kJ mol^{-1}, while enthalpy change of monatomic gas in the same temperature interval is 32.84 kJ mol^{-1} (ideal gas, $\Delta H = (5/2)R\Delta T$). Therefore, the enthalpy of graphite atomization at 1873 K with respect to monatomic gas at 1873 K is $\Delta H = 716.68 + 32.84 - 31.83 = 760.69$ kJ mol^{-1}. Then the internal energy change for transfer of graphite to monatomic gas at 1873 K is $\Delta U = \Delta H - RT = 702.12$ kJ mol^{-1}.

Enthalpy of mixing of liquid iron with graphite at 1873 K was found in [19] from the thermodynamic modelling of the Fe-C system and analysis of the Fe-C phase diagram. Thermodynamic data for the Fe-C system reported in [20, 21] were established experimentally; the relative partial enthalpy of carbon in the liquid Fe-C alloys at 1873 K is presented in [20, 21] in the form of the following equation (standard states for iron and carbon in the solution are liquid iron and graphite at 1873 K):

$$\Delta H_\mathrm{C} = 22\,600 + 24\,330 \cdot (1 - X_\mathrm{Fe}^2) \quad (\mathrm{J\,mol^{-1}}). \tag{3}$$

X_Fe in the above equation is a mole fraction of iron in the solution. The relative partial enthalpy of iron can be found using the Gibbs-Duhem equation as follows:

$$\Delta H_\mathrm{Fe} = -24\,330 \cdot X_\mathrm{C}^2 \quad (\mathrm{J\,mol^{-1}}), \tag{4}$$

where X_C is the mole fraction of carbon. Then, the enthalpy of formation of a liquid Fe-C solution from liquid iron and graphite can be calculated by equation (5):

$$\Delta H_\mathrm{m} = X_\mathrm{Fe}\Delta H_\mathrm{Fe} + X_\mathrm{C}\Delta H_\mathrm{C} = X_\mathrm{C}(46\,930 - 24\,330 X_\mathrm{Fe}) \quad (\mathrm{J\,mol^{-1}}). \tag{5}$$

The enthalpy of formation of Fe-C liquid solution presented in [18] is close to values calculated by equation (5).

To calculate the energy of formation of the Fe-C liquid solution from gaseous motionless monatomic iron and carbon at 1873 K, the internal energy of iron (−315.9 kJ mol^{-1}) and graphite (−702.1 kJ mol^{-1}) should be taken into account. The atomisation energy of iron, 315.9 kJ mol^{-1} was calculated with respect to motionless gas, while the atomisation energy of carbon, 702.1 kJ mol^{-1} was calculated with respect to moving gas with energy $(3/2)RT$; the energy of atomisation of graphite to motionless gas at 1873 K is $702.1 - 23.4 = 678.7$ kJ mol^{-1}. Therefore, the energy of formation of the liquid Fe-C solution from motionless gaseous iron and carbon can be calculated using equation (6):

$$U = -315.9 \cdot X_\mathrm{Fe} - 678.7 \cdot X_\mathrm{C} + \Delta H_\mathrm{m} \quad (\mathrm{kJ\,mol^{-1}}). \tag{6}$$

The following values of energy for the Fe-C liquid alloys were calculated at 1873 K:

C, at%	0	5	10	15	20
U, kJ mol^{-1}	−315.9	−331.2	−348.1	−364.9	−381.6

Another property which was used for the construction of the MD model of the Fe-C liquid alloys is a bulk modulus K_T. The bulk modulus for pure liquid iron at 1820 K was found in [14] to be equal to 69.9 GPa. Reference [15] reported data on the speed of sound (w) in the Fe-C liquid alloy, containing 14.4 at% C at 1600 K: $w = 4000\ \mathrm{m\,s^{-1}}$. Speed of sound is related to the bulk modulus by the following equation:

$$w = \sqrt{\frac{K_T}{d}\frac{C_p}{C_V}}, \tag{7}$$

where C_p and C_V are heat capacities at constant pressure and volume correspondingly; d is the alloy density. The density of the Fe-C alloy with 14.4 at% C at 1820 K was estimated as described above at $6.67 \cdot 10^3\ \mathrm{kg\,m^{-3}}$. Heat capacities C_p and C_V were calculated by the MD method: $C_p = 29.46\ \mathrm{J\,mol^{-1}\,K^{-1}}$ and $C_V = 26.19\ \mathrm{J\,mol^{-1}\,K^{-1}}$, $C_p/C_V = 1.125$. This ratio depends very little on small variations of the potential. Using these data and equation (7) K_T is found equal to 94.8 GPa, and isothermal coefficient of compressibility $\beta_\mathrm{T} = K_\mathrm{T}^{-1} = 1.05 \cdot 10^{-11}\ \mathrm{Pa^{-1}}$. Reference [14] reports $\beta_\mathrm{T} = 1.28 \cdot 10^{-11}\ \mathrm{Pa^{-1}}$; the difference can be attributed to different values of alloy density used in [14] and in this work. The bulk modulus for the Fe-C liquid alloy with 11.8 at% C at 1600 K calculated using the speed of sound from [14] at $d = 6.79 \cdot 10^3\ \mathrm{kg\,m^{-3}}$ gives $K_\mathrm{T} = 112.5$ GPa.

Average Fe-C distances in Fe-C alloys were taken from experimental neutron study of this system in [12].

3 Construction of Potentials for Liquid Fe-C Alloys

As mentioned above, functions $\Phi(\rho)$, $\phi(r)$ and $\psi(r)$ defining the EAM potentials (equation (1)) were adjusted using experimental properties of the Fe-C system. The functions $\Phi(\rho)$, $\phi(r)$ and $\psi(r)$ for pure iron were suggested in [22] and for the Fe-S system in [13]. The $\Phi(\rho)$ and $\psi(r)$ functions for the two-component system can be presented in the following form [13, 22]:

$$\begin{aligned} &\psi_k(r) = p_{k_1}\exp(-p_{k_2}r), \\ &\Phi_k(\rho) = a_{k_1} + a_{k_2}(\rho-\rho_{k_0})^2 + a_{k_3}(\rho-\rho_{k_0})^3 \\ &\qquad\qquad\qquad\qquad\qquad\qquad \text{at } \rho \geq 0.8\rho_{k_0}, \\ &\Phi_k(\rho) = \alpha_k\rho^{1/2} + \beta_k\rho \qquad\qquad \text{at } \rho < 0.8\rho_{k_0}, \end{aligned} \tag{8}$$

where subscript k is assigned to iron or carbon; p_{k_1}, p_{k_2}, ρ_{k_0}, a_{k_1}, a_{k_2} and a_{k_3} are adjusted parameters. Coefficients α and β can be expressed through parameters a_{k_1}, a_{k_2} and a_{k_3} because at $\rho = 0.8\rho_{k_0}$ the function $\Phi(\rho)$ and its first derivative with respect to ρ are continuous. Therefore, the EAM potential of a pure component of the alloy is defined by 8 adjusted parameters.

The pair Fe-Fe potential $\phi_\mathrm{FeFe}(r)$ was calculated using Schommers algorithm as described and tabulated in [22]. Parameters defining the functions $\Phi(\rho)$ and $\psi(r)$ for pure iron were found in [22] using the temperature dependence of density as follows: $p_{\mathrm{Fe}_1} = 4.4176$, $p_{\mathrm{Fe}_2} = 1.5860$ Å^{-1}, $a_{\mathrm{Fe}_1} = -1.7016$ eV, $a_{\mathrm{Fe}_2} = 0.3188$ eV, $a_{\mathrm{Fe}_3} = 0.3064$ eV, $\rho_{\mathrm{Fe}_0} = 1.000$. The same parameters were used for iron in modelling of liquid Fe-S solutions [13]. They will also be used for the modelling of liquid Fe-C alloys, assuming that parameters of the EAM of iron do not change when iron is in the solution.

Functions $\Phi(\rho)$ and $\psi(r)$ for the EAM of carbon were constructed in the form of equations (8) with the following parameters: $p_{\mathrm{C}_1} = 2.600$, $p_{\mathrm{C}_2} = 1.3250$ Å^{-1}, $a_{\mathrm{C}_1} = -3.3000$ eV, $a_{\mathrm{C}_2} = 2.0000$ eV, $a_{\mathrm{C}_3} = 0.0$ eV, $\rho_{\mathrm{C}_0} = 0.8500$. These parameters were found by trials as described in [13]. The pair Fe-C interaction $\phi_\mathrm{FeC}(r)$ was described by the Morse potential presented by equation (9):

$$\phi_\mathrm{FeC}(r) = \varepsilon_\mathrm{FeC}[e^{-2\alpha(\frac{r}{r_\mathrm{FeC}}-1)} - 2e^{-\alpha(\frac{r}{r_\mathrm{FeC}}-1)}]. \tag{9}$$

Parameters ε_FeC, α and r_FeC for this potential were adjusted to reproduce the density of liquid Fe-C alloys, average distance between Fe and C atoms, energy of formation of the Fe-C solution and bulk modulus. The following values of these parameters were obtained: $\alpha = 4.2$, $\varepsilon_\mathrm{FeC} = 0.5450$ eV and $r_\mathrm{FeC} = 2.23$ Å.

Published data for the Fe-C liquid alloys are not sufficient for the construction of a multi-particle potential for pair C-C interactions. This potential was assumed to be repulsive as presented by equation (10). The same form of potential was used for the S-S pair in the MD modelling of the Fe-S system in [13].

$$\phi_\mathrm{CC}(r) = \varepsilon_\mathrm{CC}(r_\mathrm{CC}/r)^6. \tag{10}$$

Parameters of this potential were found as follows: $\varepsilon_\mathrm{CC} = 1.8767$ eV and $r_\mathrm{CC} = 2.236$ Å.

4 Molecular Dynamics Modelling

Molecular dynamics models of the Fe-C liquid solutions were built up with 998 and 2997 atoms in the basic cube using the Verlet algorithm. A radius of the Verlet sphere was 9.01 Å; the potentials were cut off at 8.60 Å for all pairs. MD modeling was carried with the time step Δt equal to $0.01 \cdot t_0$, where $t_0 = 7.608 \cdot 10^{-14}$ s. The duration of one run was 5000 to 10 000 steps. NVE, NVT and NPT ensembles were investigated. Temperature of the model was monitored via the atoms velocity; pressure was maintained close to ambient by adjusting the length of the basic cube edge.

All potentials but $\phi_\mathrm{FeFe}(r)$ were defined analytically; the $\phi_\mathrm{FeFe}(r)$ potential was introduced in the form of a table with a step 0.05 Å and interpolated as a function of distance *r* with a special computer program.

The bulk modulus was calculated using two MD models with a slightly different edge length of a basic cube (by 0.04 Å to 0.06 Å).

The potential parameters were adjusted by calculating the model pressure under condition that its absolute mean value should not exceed 0.05 GPa (the ambient pressure in real experiment was about 0.0001 GPa), and comparing the calculated internal energy, bulk modulus and distance between Fe and C atoms with experimental data. Thermal pressure fluctuated in the range 0.3 GPa to 0.4 GPa.

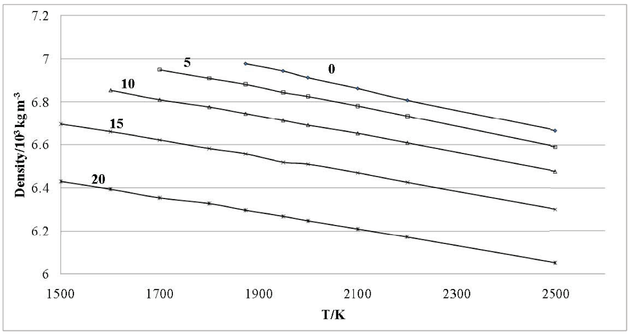

Figure 2. Density of the MD models of liquid Fe-C alloys. Carbon concentration, at% is shown above the curves.

5 Results and Discussion

5.1 Density

Calculated density of MD models of liquid iron in the temperature range from 1820 K to 2500 K is presented in Figure 1 in comparison with experimental data [24–27]. Calculated density is in a good agreement with experimental data at 1820 K to 1950 K. However, at temperatures above 1950 K the calculated density is higher than experimental data. At 2500 K, difference between calculated and experimental values reaches approximately 2.5 %, what is close to the experimental error of density measurement of liquid metals at high temperatures.

Calculated density of the Fe-C model in a broad range of temperatures (from liquidus to 2500 K) and compositions (up to 20 at% C) is shown in Figure 2. Table 1 presents calculated properties, including density of liquid Fe-C alloys at 1600 K to 1873 K in comparison with experimental data from [1–3].

Density of alloys consistently decreases with increasing carbon concentration and temperature. Plots of density as a function of temperature for alloys with different carbon content are practically parallel, what means that temperature coefficient of density changes insignificantly with carbon concentration.

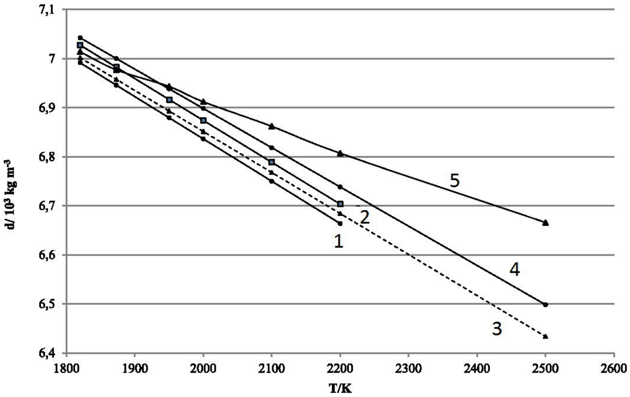

Figure 1. Density of liquid iron; 1–4: experimental data; 1 from [24]; 2 – [25]; 3 – [26]; and 4 – [27]. 5: calculated by the MD modelling.

Calculated pressure was quite low for all liquid alloys; maximum pressure (absolute value) was 0.031 GPa for the alloy containing 11.8 at% C.

5.2 Internal Energy and Bulk Modulus

Calculated internal energy of MD models of liquid Fe-C alloys agrees well with experimental data at 1873 K; the difference between calculated and experimental values of internal energy for the alloy containing 20 at% C is below 1.5%.

The calculated bulk modulus for the Fe-C alloy with 15 at% C at 1600 K is also in agreement with the experimental value (within 2.5%) established in [14, 15]; however, the difference between the calculated and experimental bulk modules for Fe-C alloy containing 11.8 at% C is much higher, near 20% for the alloy. The accuracy of experimental data on bulk modulus determined from measurements of the speed of sound in liquid alloys at high temperature is uncertain; it is not expected to be high; bulk modulus for the alloy with 11.8 at% C apparently is overstated. It can be concluded that the agreement between the experimental and calculated bulk modulus in general was satisfactory.

5.3 Diffusion

Self-diffusion coefficients D of iron and carbon in the Fe-C liquid alloys were calculated from the slope of the mean square of displacement of atom's position plotted versus time during 5000 time steps, one step was $7.608 \cdot 10^{-16}$ s. Apart from a Fe-C alloy with a low carbon concentration (0.2 at%), these plots were linear. Calculated self-diffusion coefficients are given in Table 2.

Their values are typical for an inorganic liquid. For the alloy with 0.2 at% C, in which iron diffusion can be considered as in pure iron, the self-diffusion coefficient can be

C, at%	T, K	Density, 10^3 kg m^{-3}				Pressure, GPa	Internal energy, kJ mol^{-1}		Bulk modulus, GPa	
		Exp [1]	Exp [2]	Exp [3]	MD		MD	Exp	MD	Exp [14, 15]
0	1820	6.99	7.05	7.10	7.014	0.028	−315.88	−315.92	62.0	69.9
0	1873	–	7.03	–	6.977	−0.012	−314.18	−313.70	–	
5	1873	6.91	6.63	–	6.882	0.030	−333.15	−332.87	–	–
10	1873	6.88	6.50	–	6.741	−0.026	−351.02	−349.70	–	–
11.8	1600	–	6.66	7.03	6.784	−0.031	−364.95	–	93.5 ± 1.1	112.5
15	1600	–	6.67	6.95	6.657	0.030	−374.60	–	97.3 ± 1.1	94.8
15	1873	6.82	6.51	–	6.559	0.013	−365.99	−366.4	–	–
20	1873	–	–	–	6.297	0.006	−377.33	−383.0	96.9 ± 1.1	–

Table 1. Properties of MD models of Fe-C liquid alloys.

C, at%	T, K	Density, 10^3 kg m^{-3}	$D \cdot 10^{-9}$, m^2 s^{-1}	
			Fe	C
0	1820	7.01	3.68 [22]	–
0.2	1700	7.05	2.87	–
0.2	1800	7.01	3.50	–
0.2	1873	6.98	3.95	–
0.2	1950	6.94	4.34	–
0.2	2000	6.92	4.37	–
0.2	2100	6.86	5.45	–
0.2	2200	6.83	6.31	–
0.2	2500	6.66	7.64	–
5	1873	6.88	3.68	4.76
10	1873	6.74	3.58	4.33
15	1600	6.66	2.42	2.11
15	1873	6.56	4.21	4.19
20	1873	6.30	4.07	3.96

Table 2. Self-diffusion coefficients of iron and carbon in the MD models of Fe-C liquid solutions.

presented by the following equation:

$$D_{\mathrm{Fe}} = 1.296 \cdot 10^{-17} T^{2.5895} \quad (\mathrm{m}^2\,\mathrm{s}^{-1}). \tag{11}$$

The iron diffusion coefficient as a function of temperature can also by written in the Arrhenius form:

$$D_{\mathrm{Fe}} = 5.32 \cdot 10^{-9} \exp(-4909/T) \quad (\mathrm{m}^2\,\mathrm{s}^{-1}), \tag{12}$$

where the effective activation energy E_{A} is 40,810 J mol^{-1}. Experiments in the temperature interval between 1613 K and 1873 K give the E_{A} values from 58 to 67 kJ mol^{-1} [28]. Measurement of diffusion coefficients in liquid metals at high temperatures is often affected by convective mass transfer [29], which makes apparent diffusion coefficients higher than their true values. However the agreement between model and experimental data on iron self-diffusion coefficient is reasonable (see Table 2).

Carbon self-diffusion coefficient at 1873 K decreases with increasing carbon concentration. It can be noticed that at 1873 K, $D_{\mathrm{Fe}} < D_{\mathrm{C}}$ in alloys containing 5 at% to 10 at% C, and $\mathrm{D_{Fe}}$ is slightly higher than D_{C} in alloys with 15 at% to 20 at% C. Carbon concentration in the alloy with 0.2 at% C was too low for calculation of the self-diffusion coefficient.

Experimental data on carbon self-diffusion coefficient are rather scattered. In accordance with [30, 31], D_{C} increased from $4.3 \cdot 10^{-9}$ m^2 s^{-1} to $7.0 \cdot 10^{-9}$ m^2 s^{-1} when temperature increased from 1620 K to 1860 K. However, the carbon self-diffusion coefficient at 1600 K reported in [28] was much higher, $6 \cdot 10^{-9}$ m^2 s^{-1}. The approximately 50 % difference in D_{C} values obtained in [28] and [30] can be explained by uncontrolled convection. Carbon self-diffusion coefficients ccalculated by molecular dynamics modelling were lower than experimental values with a factor 1.5–2.

5.4 Structure

Calculated pair correlation functions for the Fe-C liquid alloy with 10 at% C at 1873 K are shown in Figure 3. Table 3 presents structural parameters of the Fe-C alloys. A position $\langle r_1 \rangle$ of the first peak of the calculated total correlation function (2.50 Å to 2.52 Å) is slightly below the experimental $\langle r_1 \rangle$ value determined in [11] by the X-ray diffraction. The $\langle r_1 \rangle$ measured in [11] is in the range from 2.54 Å for 0 at% C to 2.62 Å at 20 at% C. The average Fe-C distance in the MD model (2.22 Å to 2.24 Å) is in a good agreement with neutron diffraction data obtained in [12].

Coordination numbers were calculated within the sphere with radius 3.40 Å for the pair Fe-Fe, 3.20 Å for Fe-C and 3.40 Å for C-C. No carbon segregation was observed in the MD models of the Fe-C liquid alloys. A total number of iron atoms was close to 13 in the first coordination sphere of

Parameter	Carbon concentration, at%				
	0.2	5	10	15	20
r_1 (Fe-Fe), Å	2.52	2.52	2.52	2.52	2.53
r_1 (Fe-C), Å	2.22	2.22	2.23	2.23	2.24
r_1 (C-C), Å	–	4.46	4.39	4.23	4.16
$\langle r_1 \rangle$, Å	2.50	2.51	2.51	2.49	2.52
Z(Fe-Fe)	12.6 ± 1.11	12.2 ± 1.14	11.7 ± 1.60	11.2 ± 1.14	10.5 ± 1.13
Z(Fe-C)	0.02 ± 0.14	0.55 ± 0.59	1.19 ± 0.79	1.82 ± 0.74	2.52 ± 0.75
Z(C-Fe)	≈ 10	10.4	10.7	10.3	10.1
Z(C-C)	0	0	0.06 ± 0.24	0.16 ± 0.38	0.55 ± 0.66
ρ_t	1.036	1.048	1.052	1.081	1.065

Table 3. Structural data for the MD model of the Fe-C liquid alloys at 1873 K.

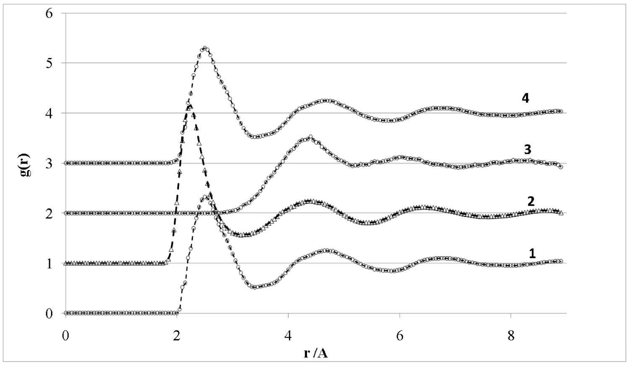

Figure 3. Partial and total correlation functions for the Fe-C alloy containing 10 at% C at 1873 K. All curves but for the Fe-Fe pair are shifted up. 1–3: partial correlation functions 1, Fe-Fe; 2, Fe-C; 3, C-C, 4: total correlation function for X-ray diffraction.

iron and that to 10 in the first coordination sphere of carbon for all Fe-C alloys, while a fraction of carbon atoms in the first coordination spheres of iron was almost exactly equal to the carbon atomic fraction. This means that distribution of atoms in the first coordination shell of Fe atoms in liquid Fe-C alloys is close to statistical. However, coordination number for C-C pairs was lower than that for statistical distribution. For example, the C-C coordination number in the alloy containing 20 at% C at 1873 K is 0.55 ± 0.66 while if atoms were distributed statistically, this number would be approximately 2.0. The lower than statistically-average coordination number for C-C pairs can be explained by the repulsive potential which was used in the MD model for the C-C interaction.

The average distance between the nearest Fe-C neighbours in solutions with 5 at% C to 17 at % C at temperatures 50 K above the liquidus curve found using neutron diffraction equal to 2.24 Å [12], what was close to calculated data (Table 3).

Structural data for the MD model do not support a hypothesis about the formation of clusters in the Fe-C liquid alloys suggested in [4,8,9,10]. No structural changes was observed with temperature either. The analysis of Voronoi polyhedrons (VP) gives the following values of VP volumes for carbon atoms:

C, at%	5	10	15	20
VP volume, Å^3	10.58 ± 0.76	10.55 ± 0.74	10.72 ± 0.80	11.00 ± 0.82

The VP volume of carbon atoms in Fe-C liquid alloys does not change with carbon concentration up to 10 at% C and increases slightly with further growth of carbon content in the solution. MD modeling clearly shows the absence of bimodality in the VP volumes distribution and different carbon structures in the solution, which could be caused by formation of colloid-type components. Therefore, molecular dynamics models constructed in this work were true solutions.

A topological parameter $\rho_t = \langle r_1 \rangle (N/V)^{1/3}$ ($\langle r_1 \rangle$ is the average distance between atoms measured by the position of the first peak of the total correlation function, N/V is the average number of atoms per unit volume of the model) was slightly less than the average value for dense non-crystalline structures 1.08 ± 0.02 [32].

6 Conclusions

Molecular dynamics models of Fe-C alloys constructed with embedded atom model for Fe-Fe, Fe-C potentials and repulsive C-C potential were used to describe properties and structure of Fe-C liquid solutions in a broad range of solution compositions and temperatures.

The alloys density monotonously decreased with increasing carbon concentration. Molar volume also decreased because of a smaller radius of carbon atom in comparison with iron. At 2500 K the calculated molar volume was equal $8.36 \cdot 10^{-6}$ m^3 mol^{-1} for pure iron and

$7.77 \cdot 10^{-6}$ m^3 mol^{-1} for a melt with 20 at% C. Calculated model's density at 1850 K to 1950 K laid between data obtained in [1, 3] and [2].

The MD model's bulk modulus was in a reasonable agreement with experimental data determined from the speed of sound in liquid Fe-C alloys.

Carbon self-diffusion coefficient in MD models of Fe-C alloys at 1873 K decreased with increasing carbon concentration. Calculated self-diffusion coefficient for iron in the Fe-C alloy with 0.2 at% C agreed with experimental value for pure iron. Calculated self-diffusion coefficients for carbon were lower than experimental data with a factor 1.5 to 2, what can be attributed to convection in the measurement of diffusion.

A distance between Fe-Fe and Fe-C atoms and the sum of coordination numbers for pairs Fe-Fe and Fe-C change insignificantly with carbon concentration. The repulsive interaction between C-C atoms resulted in low C-C coordination number. Properties and structure of the MD models of Fe-C liquid alloys were typical for true solutions with no indication on clustering.

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References

[1] G. V. Tyagunov, P. S. Popel and N. S. Kosilov, *Izvestiya Academii Nauk SSSR. Metaly*, **5** (1981), 55–58 (in Russian).

[2] A. A. Kuprijanov and S. I. Filippov, *Izvestiya Vuzov. Chernaya Metallurgiya*, **9** (1968), 10–15 (in Russian).

[3] I. Jimbo and A. W. Cramb, *Metall. Mater. Trans. B*, **24B** (1993), 5–10.

[4] A. A. Vertman and A. M. Samarin, *Properties of Ferrous Metals Melts*, Science, Moscow, 1969 (in Russian).

[5] B. A. Baum, G. A. Khasin, G. V. Tyagunov and E. A. Klimenkov, *Liquid Steel*, Metallurgiya, Moscow, 1984 (in Russian).

[6] T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals*, Oxford Science Publications, I988.

[7] O. I. Ostrovski, V. A. Grigoryan and A. F. Vishkarev, *Properties of Liquid Metals*, Metallurgiya, Moscow, 1988 (in Russian).

[8] I. V. Salli, *Physical Basics of the Formation of Alloys Structure*, Metallurgiya, Moscow, 1963 (in Russian).

[9] V. M. Zalkin and V. S. Kraposhin, *Fizicheskaya Metallurgiya i Termicheskaya Obrabotka*, **1** (2010), 15–18 (in Russian).

[10] A. S. Aronin, V. S. Kraposhin and K. V. Shakhlevich, *Fizika Metalov*, **12** (1990), 96–101 (in Russian).

[11] E. A. Pastukhov, N. A. Vatolin and V. L. Lisin, *Diffraction Study of Structure of High-Temperature Melts*, Institute of Metallurgy Ural Branch RAS, Yekaterinburg, 2003 (in Russian).

[12] M. Weber and S. Steeb, *Z. Naturforsch*, **33a** (1978), 799–807.

[13] D. K. Belashchenko, O. L. Kuskov and O. I. Ostrovski, *Inorganic Materials*, **43** (2007), 998–1009.

[14] S. I. Filippov, N. V. Kazakov and L. A. Pronin, *Izvestiya Vuzov. Chernaya Metallurgiya*, **3** (1966), 8–14 (in Russian).

[15] L. A. Pronin, N. V. Kazakov and S. I. Filippov, *Izvestiya Vuzov. Chernaya Metallurgiya,* **5** (1964), 12–16 (in Russian).

[16] P. P. Arsent'ev and L. A. Koledov, *Metallic Melts and Their Properties*, Metallurgiya: Moscow, 1976 (in Russian).

[17] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys*, ASM Metals Park, Ohio, 1973.

[18] J. Chipman, *Met. Transactions*, **1** (1970), 2163–2168.

[19] P. A. Gustafson, *Scand. J. Metallurgy*, **14**, pp. 259–267 (1985).

[20] J. F. Elliott, M. Gleiser and V. Ramakrishna, *Thermochemistry for Steelmaking. Thermodynamic and Transport Properties*, Addison-Wesley Publ., NY, 1969.

[21] V. A. Grigoryan, L. N. Belyanchikov and A.Ya. Stomakhin, *Theoretical Basis of the Electrical Steel Melting Processes*, Metallurgiya, Moscow, 1987

[22] D. K. Belashchenko, *Russ. J. Phys. Chem.*, **80** (2006), 758–768.

[23] www.webelements.com

[24] F.N. Tavadze, I. A. Bairamashvili and D. V. Khantadze, *Surface Phenomena in Melts and Forming Solid Phases*, Kabardino-Balkarsk Kniga, Nalchik, 1965, 376–382.

[25] T. Saito, J. Shiraishi and Y. Sakuma: *Trans. Iron and Steel Inst. Japan*, **9** (1969), 118–126.

[26] T. Saito and Y. Sakuma, *J. Japan Inst. Metals*, **31** (1967), 1140–1148.

[27] E. V. Krinochkin, K. T. Kurochkin and P. V. Umrikhin, *Izvestiya Academii Nauk SSSR. Metaly*, **5** (1971), 67–71 (in Russian).

[28] J. B. Edwards, E. E. Hucke and J. J. Martin, *Metals and Mater*. V.2 *Metallurg. Reviews*, **120** (1968), 1–13.

[29] D. K. Belashchenko, *Transport Phenomena in liquid Metals and Semiconductors*, Atomizdat, Moscow, 1970 (in Russian).

[30] D. W. Morgan and J. A. Kitchener, *Trans. Faraday Soc.*, **50** (1954), 51–60.

[31] M. Hillert and N. Lange, *J. Iron and Steel Inst.*, 1965, **203** (1965), 273–274.

[32] D. K. Belashchenko, *Computer Modeling of Liquid and Amorphous Metals*; Moscow Institute of Steel and Alloys, Moscow, 2005 (in Russian).