The Kubo–Greenwood calculation of conductivity of the simple and non-simple liquid metals in a wide temperature range

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Abstract. We calculated the temperature dependences of electroconductivity for the different metals, such as alkalis (caesium), transition metals (iron), and mercury by Kubo–Greenwood formula. Atomic models of 1000–4000 atoms were obtained by Shommers method using the data of diffractional experiments for the wide temperature range. The electronic structure and interaction parameters for supercells of 30–50 atoms were got by LMTO method. The recursion method was used for the calculation of DOS and diffusivity quotients. The lowering of the DOS at the Fermi level was carefully examined.

The results obtained are in good agreement with other authors’ in views on the nature of the metal-nonmetal transition in different liquid metals. The calculated DOS and conductivity for all metals match the experimental data well.

1. Introduction
The nature of the temperature dependence of conductivity of liquid metals and peculiarities of the metal–non-metal transition in melts have been subject of many experimental [1, 2] and theoretical [3] works. One of the most studied elements are alkali metals and mercury. At temperatures near melting point the conductivity of these elements is definitely metallic. As temperature approaches the critical point, the conductivity falls down by several orders, and its value approximates to that of semiconductors.

Despite this resemblance in the behaviour of conductivity of these elements, there is a great difference in the cause of this behaviour. First, the density of alkali metals decreases rapidly with temperature, therefore liquid metals at high temperatures have loose structure in contrast to mercury, that conserves its dense structure up to critical point [3, 2]. Second, mercury atoms have completely filled s-shell, and this might lead to gradual band separation with the formation of pseudogap at Fermi level at liquid–gas transition point [3]. Alkali metals have one electron on s-shell, therefore Fermi level is found at the center of the s-band, and the number of conduction electrons remains high [4].

Resistivity of iron, a 3d transition metal, differs little from that of alkalis and mercury. But, while the solid phase of the metal is thoroughly studied, the determination of its properties in liquid phase represents a difficult, labourious task. Experimentally, high temperatures comprise a problem, from theoretical point of view the problem lies in the structural disorder.

Despite all knowledge accumulated till nowadays concerning the simulation of transport properties of liquid metals, all works in the field were devoted to indirect discussions of these
properties’ behaviour. In this work the method proposed in [5] was used to calculate the conductivity of various metals in the wide temperature range. The paper is written in the following way: in chapter 2 the computational method is discussed, and chapter 3 is devoted to discussing the results.

2. Method
For systems of several thousands of atoms full selfconsistency of electronic structure demands much machine resources. Due to the fact, a researcher faces the problem of getting approximate selfconsistency basing on the results of selfconsistent calculations of small systems. One of the ways to accomplish this is using the linear “muffin-tin” orbitals (LMTO) method [6] and the ability of LMTO TB Hamiltonian to be divided into 2 parts: first, lattice dependent structure constants, and second, atom type dependent potential parameters. To calculate electronic properties we used LMTO–recursion combination, proposed in [7] and developed further in [8]. Ab initio LMTO method was used for small supercell with different MT sphere radii. The dependence of selfconsistent potential parameters on the structure is very little, so they can be described fairly well by the formula with the only parameter, MT sphere radius. At the same time, the structural part of LMTO hamiltonian can be found exactly for systems of any complexity. This allows us to use parametrization to construct TB hamiltonian for the big model.

Hence, the simulation consisted of several stages. To achieve our goal we had to solve the following problems: first, getting the atomic structure model; then, finding selfconsistent LMTO hamiltonian for a small system; third, parametrizing the selfconsistent hamiltonian; and the last, getting electronic structure and properties for the big model.

For disordered systems getting an atomic model is a difficult task itself. We used atomic models of about 4000 atoms obtained earlier [9] by Schommers method using data from works of Tamura [2], Winter et al [10], and Waseda. For every temperature a different model was used, 9 for cesium (in the range of 323–1923K), 5 for mercury (in the range of 293–1723K), and 4 for iron (in the range of 1833–2023K).

Selfconsistent potential parameters were obtained using LMTO method for supercell of 40 atoms and 30–50 empty spheres. TB hamiltonian for atomic models was constructed using exact structure constants and parametrized potential parameters. This approximation is much better than any other way of getting the electronic structure of liquid basing on the spherical symmetry of interaction, due to exact accounting of each atoms’ local environment and real form of atomic potential.

Electronic structure calculation on the big model was carried out by the recursion method [11], and conductivity was evaluated using Kubo–Greenwood formula.

3. Results and discussion
To calculate DOS and transport properties we used atomic models of about 4000 atoms. The obtained density of states was averaged over 10 randomly chosen atomic configurations (further increase of averaging base lead to inessential changes in DOS). From DOS it is clear, that as temperature increases peaks on the density of states widen and fall down. However, while DOS at Fermi energy for cesium remains roughly the same, mercury has its s- and p-zones separate from each other, forming a kind of gap at Fermi energy, which corresponds with the results from work [15].

The conductivity of different metals and its temperature dependence compared with experimental data is shown in Fig. 1. We can see, that our data except for mercury lie within the scope of the experiment. Moreover, the result for the first temperature in iron is the same than that of Bose [5]. The discrepancy of results in mercury may come from two sources: first, from underestimating the localization of electronic states at high temperatures; and second,
Figure 1. Temperature dependence of conductivity for different metals. Filled figures — experimental data ([12] for cesium, [1] for mercury, 1 — [13], 2 — [14] for iron), empty figures — calculation results (for iron 4 — [5]).

from the uncertainty of pseudogap in DOS obtained by recursion method. To estimate the degree of electron localization on atoms we calculated the modified inverse participation ratio (IPR). For alkali metal at temperatures close to melting point IPR appeared to equal zero. Then, with increase of temperature IPR begins to increase. This shows, that in cesium the M–NM transition has to be somehow interconnected with loss of electron mobility. For transition metals IPR is virtually constant on the whole range, and for iron, moreover, close to 0. This fact shows permanency and high degree of delocalization of electronic states in the melt on the whole temperature range, and confirms the hypothesis from [5] about the main role of d-d-transitions in the M–NM transition in iron.

4. Conclusions
Consequently, using the proposed earlier generalization of the LMTO method for the case of disordered systems of different density in the whole range of liquid phase existence, we got numerical results for electroconductivity of different metals at several temperatures. Our calculation was free from fitting parameters and based on the \textit{ab initio} hamiltonian. The results have acceptable accuracy (the error comes to approx. 15%), and reproduce the trend in the change of conductivity with temperature correctly.

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