Calculation of an effective three-ionic interactions potential in metallic hydrogen

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Abstract

The pair- and three-proton interaction potentials for metal-phase hydrogen are calculated. Irreducible three-proton interactions are shown to be essential in the development of the metal hydrogen structure. Possible manifestations of the three-ion interactions in the structure of quickly quenched metallic systems are discussed. Existence of amorphous metals is related to manifestations of the three-ion interactions in non-equilibrium conditions when amorphisation front travels through a liquid metal.

I. INTRODUCTION

The inclusion of many-particle interactions into consideration of equilibrium and kinetics properties is the urgent problem in the theory of condensed matter [1], [2]. Calculation of the many-particle interaction potentials is the key to this problem. For simple dielectric and metal liquids and for crystals pair interaction potentials are known at least at a phenomenological level, about the three-particle interaction it cannot be said. This situation is explained by general lack of development of the theory of highly nonuniform electron gas. Thus to calculate the three-particle interactions in various condensed systems one needs to know in an explicit form the three-point nonlinear response functions involving cooperative phenomena in the many-electron system, which is formed from atomic electron shells. Nowadays the problems of calculation of such functions for the majority of systems are not even formulated. It should be stressed that for the most systems even the polarization operator of nonuniform electron gas, which makes up these systems, remains unknown. But there are some exceptions. This refers to the simple metals which can be closely approximated by the uniform gas of free electrons. A discrete nature of the ion subsystem can be taken into account by perturbation theory. The nonlinear response function of uniform gas corresponding to three- and four-pole diagrams have been calculated within the framework of many-particle theory of metals [3].

Calculations of the structural and thermodynamical equilibrium volume properties of metal-phase hydrogen point up the significance of inclusion of many-particle ion interactions, and suggest the possibility of a metastable metallic state at zero external pressure [3]. Comparison of energies corresponding to different crystal structures have led to the conclusion of liquidity tendencies in the structure of metal hydrogen. Energy difference of crystal and liquid phases approaches zero with decreasing pressure [3]. So the liquid state of metal hydrogen is possible to form at zero external pressure.

Calculations of energy and other properties of crystal metals are carried out in the reciprocal space and do not require the explicit form of interaction potentials of ion clusters. In amorphous, liquid and heterogeneous metals the calculations in configurational space are preferable. It provides insight into the nature of local atomic order and gives the assessment of correlations in the positions of atom clusters.

The occurrence of a maximum in the temperature dependence of the third virial coefficient evidences directly the existence of three-particle interactions in simple dielectric liquids [1]. Taking into account the three-atom interaction in the asymptotic form of the Akselrod-Teller three-dipole interaction potential requires the inclusion of a cutoff parameter (the
characteristic length) into the theory and does not explain the wave-vector dependence of the third virial coefficient (on the example of krypton) [3].

In metals the many-ion interactions are directly proven to exist by the anomalies in phonon spectra which could not be reduced to the Kohn’s ones, and conform with the singularities of the many-pole diagrams of uniform electron gas [8].

Interaction potential in liquid Na and K have been calculated previously [8] for three-ion equiangular configurations. The pair-interaction potentials for ions in metal hydrogen have been calculated in [6], where the third-order contributions with respect to electron-ion interaction were shown to be of fundamental importance for development of attractive part of potential. Pair interactions in a liquid metal hydrogen have been calculated within the context of the density-functional method [8]. The potentials were formulated in terms of direct correlation functions of electron-ion system.

Here we present the pair- and three-ion interaction potentials in metal hydrogen at the Wigner-Seitz radius \( r_s = 1.65 \) calculated on a basis of the many-particle theory of metals [3] within the third-order perturbation theory. The computed array of values of three-ion interaction potential makes possible the further calculations of the contributions of these interactions into various properties of metal hydrogen. Possible outcomes of the three-ion interactions affecting local atomic order in amorphous metal systems are discussed.

II. CALCULATION RESULTS

In the context of many-particle theory of non-transition metals the energy of a metal is calculated by the use of the adiabatic approximation for electron-ion system. The electron gas energy \( E_e \), provided that ions positions are fixed, can be calculated with the theory of perturbations in the potentials of electron-ion and electron-electron interactions [3]. The energy \( E_e \) fulfills the role of an electron term upon the treatment of the properties of ion subsystem in metal. Together with kinetic energy of ions and energy of their direct interaction, the energy \( E_e \) comprises the effective Hamiltonian of the ion subsystem of metal. \( E_e \) can be considered as a sum of contributions independent of ion positions, dependent on the locations of separate ions, ion pairs, triplets, etc. [3]:

\[
E_e = \varphi_0 + \sum_n \varphi_1(R_n) + \frac{1}{2!} \sum_{m \neq n} \varphi_2(R_n, R_m) + \frac{1}{3!} \sum_{m \neq n \neq l} \varphi_3(R_n, R_m, R_l) + \cdots
\]  \hspace{1cm} (1)

Each term of the series (1) describes interactions of ion groups through the surrounding electron gas and can be represented as a power series in the potential of electron-ion interaction [3]:

\[
\varphi_2(R_1, R_2) = \sum_{i=2}^{\infty} \Phi_2^{(i)}(R_1, R_2),
\]

\[
\varphi_3(R_1, R_2, R_3) = \sum_{i=3}^{\infty} \Phi_3^{(i)}(R_1, R_2, R_3),
\]  \hspace{1cm} (2)

etc., where \( \Phi_n^{(k)}(R_1, \ldots, R_n) \) represents the indirect interaction of the \( n \) ions through electron gas in the \( k \)-order perturbation theory in electron-ion interaction.
The indirect interaction of two ions described by the potential $\Phi^{(2)}_2(|R_1 - R_2|)$ is well studied. The potential $\Phi^{(3)}_2(|R_1 - R_2|)$, corresponding to the energy of indirect two-ion interaction in the third-order in potential of electron-ion interaction, has been calculated previously in [6] for liquid sodium and potassium, and also for metal hydrogen [7]. It is not difficult to obtain an expression for the $\Phi^{(3)}_2(|R_1 - R_2|)$:

$$\Phi^{(3)}_2(R) = \frac{3}{4\pi^4} \int_0^\infty dq_1 q_1^2 \int_0^\infty dq_2 q_2^2 \int_{-1}^1 dx V(q_1)V(q_2)V(q_3) \times$$

$$\times \Gamma^{(3)}(q_1, q_2, q_3) \frac{\sin(q_1 R)}{q_1 R},$$

where $V(q)$ is the form-factor of the electron-ion interaction potential; $\Gamma^{(3)}(q_1, q_2, q_3)$ is the sum of three-pole diagrams.

In the third-order perturbation theory in $V(q)$ the indirect three-ion interaction (the irreducible three-ion interaction) is defined by the expression [8]:

$$\Phi^{(3)}_3(R_1, R_2, R_3) = \frac{3}{2\pi^4} \int_0^\infty dq_1 q_1^2 \int_0^\infty dq_2 q_2^2 \times$$

$$\times \int_{-1}^1 dz V(q_1)V(q_2)V(q_3) \Gamma^{(3)}(q_1, q_2, q_3) \int_0^1 dx \times$$

$$\times \cos \left( x \left( q_1 R_1 \frac{R_2^2 + R_3^2 - R_3^2}{2R_1 R_2} + q_2 R_2 z \right) \right) \times$$

$$\times J_0 \left( q_1 R_1 \left( 1 - x^2 \right)^{1/2} \left( 1 - \frac{R_1^2 + R_2^2 - R_3^2}{4R_1^2 R_2^2} \right)^{1/2} \right) \times$$

$$\times J_0 \left( q_2 R_2 \left( 1 - x^2 \right)^{1/2} \left( 1 - z^2 \right)^{1/2} \right),$$

where $J_0(x)$ is the Bessel function of zero order; $z \equiv \cos(q_1, q_2)$; $q_3 = (q_1^2 + q_2^2 + 2q_1 q_2 x)^{1/2}$; $R_1$, $R_2$, $R_3$ - the distances between the vertices of a triangle formed by the protons.

The pair- and three-proton interaction potentials were calculated at the Wigner-Seitz radius $r_S = 1.65$ which corresponds to zero pressure in the zeroth model of a metal. A permittivity function in the Heldart-Vosko form was employed.

Figure 1 shows computed potentials of the two-proton interactions $e^2/R + \Phi^{(2)}_2(R)$, $\Phi^{(3)}_2(R)$, and $\varphi^*(R) = e^2/R + \Phi^{(2)}_2(R) + \Phi^{(3)}_2(R)$. It is obvious that the interaction $\Phi^{(3)}_2(R)$ significantly renormalizes potential $e^2/R + \Phi^{(2)}_2(R)$. Noteworthy is a minimum in the repulsive part of the potential $\varphi^*(R)$, which arises as a result of the contribution $\Phi^{(3)}_2(R)$. At
\( r_s = 1.72 \) this minimum becomes deeper and as a result the potential \( \varphi^*(R) \) takes the form typical for simple metals. At \( r_s < 1.65 \) the minimum in the repulsive part of \( \varphi^*(R) \) turns shallow and its position shifts towards smaller \( R \).

The potentials of irreducible three-proton interaction \( \Phi_3^{(3)}(R_1, R_2, R_3) \) calculated at different lengths of sides of a three-proton triangle are listed in Table. It should be noted that the number of various \((R_1, R_2, R_3)\) sets is restricted by the triangle axiom to which the distances \( R_1, R_2 \) and \( R_3 \) are subject.

The calculation results can be presented more conspicuously and informatively as plots of versus geometry parameters for selected configurations of protons. Thus, Figure 2 demonstrates the potential curve \( \Phi_3^{(3)}(R, R, R) \), that is, one for proton equiangular triplets. The potential \( \Phi_3^{(3)}(R, R, R) \) corresponds to strong attraction of the triplet at short distances and oscillates at the long ones.

Figure 3 shows plots of the potential \( \Phi_3^{(3)} \) for isosceles ion triplets. It is clear that attractability of proton triplet is actually short-range. An equilibrium local atomic order results from the balance of direct proton interactions, the indirect two-proton ones, and of the irreducible three-proton interactions.

Figure 4 presents a proton energy plotted against the distance to the two others (the isosceles proton triplet). Two protons are placed in abscissa axis at the points \((1,0,0)\) and \((-1,0,0)\) (distances in atomic units). The third proton is sited in ordinate axis. In Fig. 4 is shown that inclusion of the irreducible potential \( \Phi_3^{(3)} \) is of fundamental importance for determination of the equilibrium local order in proton spacing. Attractive nature of the \( \Phi_3^{(3)} \) potential have to reduce the average interionic distances in equilibrium state of metal.

**III. DISCUSSION AND CONCLUSION**

A comprehensive analysis of the atomic properties of simple metals leads to the conclusion that of basic importance is the consideration of three-ion interactions as in polyvalent metals [4], and also in metal hydrogen where the electron-ion interaction is free from a non-coulomb part [3]. Calculations of the two-ion interaction potentials for various simple metals display the similarity of their behavior in all such metals [10]. Our calculations \( \Phi_3^{(3)} \) for equilateral proton triplets, along with the results of [6], demonstrate the similarity of the \( \Phi_3^{(3)} \) behavior in simple metals.

Results of our calculations suggest certain inferences about the possible manifestations of three-particle interactions through the structure of metal systems. The potential \( \Phi_3^{(3)}(R_1, R_2, R_3) \) is symmetric about interchange of ions and therefore in equilibrium conditions the most probable three-ion configurations in liquid metals would be the equilateral triplets.

Experiments on the quick quenching of metals and alloys show that amorphous phase is readily obtainable in the polyvalent metals and their alloys [11] where consideration of many-ion interactions are essential. Under the quick quenching conditions aluminum alloys form quasicrystalline structures with specific 5-fold axes of symmetry forbidden for crystals [12]. The possible reason of quasicrystal formation is manifestation of the three-ion interactions as the amorphisation front moves through a liquid metal.

When two of the three ions are fixed on a surface or located within amorphous phase and
the third ion remains in the liquid, energetically advantageous would be an isosceles triplet rather than equilateral one. Owing to the attractive nature of $\Phi_3^{(3)}$ the third ion shifts so that one of the angles in the triplet will be more than $60^\circ$. Such isosceles triplets can serve as a basis for generation of amorphons in an amorphous phase. Existence of the 5-fold axes of symmetry in quasicrystals corresponds to the presence of the isosceles triplets with an angle of $72^\circ$. Thus one of the manifestation of three-ion interactions can be the creation of amorphons while propagating the amorphization front in liquid metal.

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Table

| \( R_1 \) | \( R_2 \) | \( R_3 \) | \( \Phi_3^{(3)}(R_1, R_2, R_3) \) |
|---|---|---|---|
| 0 | 0 | 0 | -0.95758 |
| 1 | 1 | 1 | -0.23684 |
| 1 | 1 | 2 | -0.07582 |
| 1 | 2 | 2 | -0.01523 |
| 1 | 2 | 3 | -0.00326 |
| 1 | 3 | 3 | -0.00353 |
| 1 | 3 | 4 | -0.00411 |
| 1 | 4 | 4 | -0.00167 |
| 1 | 4 | 5 | 0.00130 |
| 1 | 5 | 5 | 0.00116 |
| 1 | 5 | 6 | 0.00005 |
| 1 | 6 | 6 | -0.00055 |
| 2 | 2 | 2 | 0.00117 |
| 2 | 2 | 3 | -0.00032 |
| 2 | 2 | 4 | -0.00283 |
| 2 | 3 | 3 | -0.00184 |
| 2 | 3 | 4 | -0.00161 |
| 2 | 3 | 5 | 0.00029 |
| 2 | 4 | 4 | -0.00028 |
| 2 | 4 | 5 | 0.00065 |
| 2 | 4 | 6 | 0.00010 |
| 2 | 5 | 5 | 0.00038 |
| 2 | 5 | 6 | -0.00024 |

| \( R_1 \) | \( R_2 \) | \( R_3 \) | \( \Phi_3^{(3)}(R_1, R_2, R_3) \) |
|---|---|---|---|
| 2 | 6 | 6 | -0.00033 |
| 3 | 3 | 3 | -0.00134 |
| 3 | 3 | 4 | -0.00030 |
| 3 | 3 | 5 | 0.00048 |
| 3 | 3 | 6 | 0.00006 |
| 3 | 4 | 4 | 0.00027 |
| 3 | 4 | 5 | 0.00025 |
| 3 | 4 | 6 | -0.00019 |
| 3 | 5 | 5 | -0.00007 |
| 3 | 5 | 6 | -0.00021 |
| 3 | 6 | 6 | -0.00007 |
| 4 | 4 | 4 | 0.00018 |
| 4 | 4 | 5 | -0.00006 |
| 4 | 4 | 6 | -0.00019 |
| 4 | 5 | 5 | -0.00015 |
| 4 | 5 | 6 | -0.00005 |
| 4 | 6 | 6 | 0.00006 |
| 5 | 5 | 5 | -0.00004 |
| 5 | 5 | 6 | 0.00007 |
| 5 | 6 | 6 | 0.00006 |
| 6 | 6 | 6 | 0.00003 |
(distances in the Table in atomic units, energy in Ry)

Figure Captions

Fig. 1. Potential of the two-proton interactions: 1 - $e^2/R + \Phi_2^{(2)}(R)$; 2 - $\Phi_2^{(3)}(R)$; 3 - $\varphi^*(R) = e^2/R + \Phi_2^{(2)}(R) + \Phi_2^{(3)}(R)$

Fig. 2. Potential $\Phi_3^{(3)}(R, R, R)$

Fig. 3. Potential $\Phi_3^{(3)}$: 1 - $\Phi_3^{(3)}(1 \text{ a.u.}, R, R)$; 2 - $\Phi_3^{(3)}(2 \text{ a.u.}, R, R)$; 3 - $\Phi_3^{(3)}(3 \text{ a.u.}, R, R)$

Fig. 4. Potential $\varphi(R) = 2\varphi^*(R) + \Phi_3^{(3)}(2 \text{ a.u.}, R, R)$: 1 - $2\varphi^*(R)$; 2 - $\Phi_3^{(3)}(2 \text{ a.u.}, R, R)$; 3 - $\varphi(R)$ (see explanations in the text)