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V.T. SHVETS, E.V. CHEREVKO

Odesa National Technological University

(1/3 Dvoryans'ka Str., Odesa 65082, Ukraine; e-mails: valtarmax@ukr.net, cherevko@usa.com)

NONLOCAL PSEUDOPOTENTIAL AND THE THERMODYNAMICS OF METALLIC HELIUM

Thermodynamic properties of liquid metallic helium have been studied in the framework of perturbation theory of the second-order in the electron-ion interaction pseudopotential. The latter was determined from the first principles and was found to be nonlocal and nonlinear. The pseudopotential nonlocality leads to the appearance of the first-order terms in the series expansions of the internal energy, free energy, and pressure of liquid metallic helium in the pseudopotential. The diagonal matrix element of this term is of the same order of magnitude as that in the zero-order term. As a result, the first-order term makes a substantial contribution to the internal and free energies, so that their dependences on the density and the temperature become stronger. Accordingly, the pressure at which the liquid phase of metallic helium can be realized increases. This pressure is an order of magnitude higher than the corresponding pressure in metallic hydrogen and is currently unattainable experimentally. The analysis of the entropy made it possible to determine the region of existence for the liquid metallic helium phase and the conditions for its crystallization. A comparison between the densities, pressures, and temperatures inside such gas giants as Jupiter and Saturn allowed us to conclude that not only hydrogen but also helium are in the metallic state in the central parts of those planets. However, the pressure in their interiors is insufficient for helium to crystallize.

Keywords: pseudopotential of electron-ion interaction, metallic helium, internal energy, free energy, equation of state.

1. Introduction

The modern theory of metals is based on the theory of pseudopotentials [1], where the interaction potential of conduction electrons with the ionic subsystem (this potential is not necessarily weak) is replaced by a weaker pseudopotential. The latter has an essential shortcoming: it is nonlocal and nonlinear. When constructing it from the first principles, the wave functions of bound electrons have to be applied, and this task becomes too difficult for such a pseudopotential to be used while calculating various properties of most metals. Therefore, model pseudopotentials with fitted parameters are applied, as a rule, if there are enough experimental data to determine them.

Metallic hydrogen is the only metal for which the pseudopotential coincides with the Coulomb potential of proton, and no technical complications arise [2]. However, among other metals, there is a metal, namely, metallic helium, for which the wave functions of bound electrons can be described using simple and accurate analytical expressions, and the pseudopotential found from the first principles is quite suitable for practical calculations [3]. The aim of this paper is to apply the proposed pseudopotential to calculate the equation of state for metallic helium. Currently, this is the only possible way for theoretical calculations of its various properties.

The first report on the experimental production of metallic hydrogen by the shock compression appeared in 1996 [4]. The parameter values reached when the

hydrogen metallization occurred were as follows: a pressure of 1.4 Mbar, a density of 0.64 g/cm^3 , and a temperature of 3000 K. An attempt made in 1988 [5] to obtain metallic hydrogen at static compression up to 3.42 Mbar and under low temperatures was not successful. In 2011, there appeared a report about the production of liquid metallic hydrogen under a static compression of 3 Mbar [6]. Such elements as oxygen (in 2007 [7]) and nitrogen (in 2003 [8]) were also managed to be experimentally obtained in the metallic state.

The theoretical and experimental studies of the helium metallization turned out not so successful. A first attempt to theoretically estimate the ground-state energy and the compressibility of metallic helium, as well as derive the corresponding equation of state, in the framework of the modified Bruckner theory was done quite a long time ago [9, 10]. The obtained results were not of high accuracy, but gave a rather pessimistic estimate for the pressure at which helium has to transit into the metallic state: approximately $20 \times 10^6 \text{ atm}$. In 1974, when the cited articles were published, one could only dream about reaching such pressures under terrestrial conditions. On the other hand, there exist much higher pressures in the interiors of giant planets in the solar system.

About 30 years passed until the first rather successful attempt to obtain helium in the metallic state was made [11]. For this purpose, a combined static and the dynamic compression of heated liquid helium were used. The aggregate state of helium was monitored by observing the light reflectance from the studied specimen. It turned out that the characteristic features of the transition of helium into the metallic state were observed already at a helium density of 1.2 g/cm^3 , which was several times lower than the values obtained at earlier theoretical estimations. Although the pressure in the transition region had not been measured accurately, this parameter, according to the experimental data presented by the cited authors, turned out 1-2 orders of magnitude lower than the earlier theoretical estimates.

The situation with metallic helium in the interiors of the giant planets of the solar system turned out not simple as well [12]. Here, the main difficulty consisted in the poorly researched problem dealing with helium solubility in metallic hydrogen and the influence of the latter on the metallization parameters of the former.

The method of molecular dynamics seems to be rather promising in studying the helium metallization [13, 14]. Here, the interval of examined densities equals $1\text{-}22 \text{ g/cm}^3$, and the temperature interval is 10000-50000 K. An unexpected result of those studies was the gradual character of the helium metallization process, with no drastic phase transition of the first kind. The fraction of the metallized phase was found to equal 10% for the specimen with the lowest analyzed density, and 99% for the specimen with the highest density.

The method of molecular dynamics has its own restrictions. Its results must be compared with those obtained while using other methods of theoretical calculations; in particular, with the results of direct quantum-mechanical calculations from the first principles.

Helium in the metallic state can be easily studied theoretically, only if the atoms are doubly ionized [15]. In this case, the potential of electron-ion interaction is Coulombic, i.e., it is known exactly. The only characteristic of metallic helium that was calculated for singly ionized helium atoms is the effective ion-ion pair interaction [3]. In this work, we use the proposed pseudopotential to calculate various thermodynamic characteristics of liquid metallic helium. We suppose that the concentration of conduction electrons in metallic helium is the same as in metallic hydrogen [4]. In this case, the substance density at the transition point into the metallic state equals 0.64 g/cm^3 for hydrogen and 2.56 g/cm^3 for helium.

This paper was aimed at clarifying the thermodynamic conditions under which the liquid metallic helium phase exists and the possibility of its pressure-induced crystallization. In the framework of our approach, the pressure of helium metallization was found to be an order of magnitude higher than the pressure of hydrogen metallization.

2. Energy of Conduction Electrons

To calculate the zeroth-order pseudopotential contribution to the internal energy of conduction electrons, i.e., the energy of their direct Coulombic and exchange interactions, as well as correlations, let us use the classical expression proposed by Gell-Mann and Bruckner [16] in the form of a power series in the parameter r_s , which is the radius of a sphere whose

volume coincides with the volume per electron,

$$E_0 = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln(r_s) - 0.096. \quad (1)$$

When calculating the pseudopotential of a singly ionized helium atom, we used the wave function of an isolated helium ion in the ground state and the energy of this state. The potential created by a helium ion consists of the Coulombic potential of the helium nucleus and the Coulombic potential of the bound electron whose charge is distributed spherically symmetrically in the space around the nucleus. This potential is local, and the potential energy of interaction between a conduction electron and such an ion looks like

$$V(q) = -\frac{4\pi e^2}{q} \left[z - \frac{16z^4}{(q^2 + 4z^2)^2} \right], \quad (2)$$

where $z = 2$ is the nucleus charge. When adopting the potential in this form, we do not consider that the wave functions of conduction electrons must be orthogonal to the wave functions of bound electrons. In other words, it looks, as if a conduction electron is pushed out of the region occupied by the ion core. Such an orthogonality can be taken into account by substituting the potential in the Hamiltonian of the electron subsystem with the pseudopotential. As a result, there appears the following nonlocal correction to the local potential (2):

$$\langle \mathbf{k} | w_{nl} | \mathbf{k}' \rangle = -\frac{64\pi z^5 (E_{\mathbf{k}} - \varepsilon_0)}{(z^2 + k^2)^2 (z^2 + k'^2)^2}. \quad (3)$$

Here, ε_0 is the energy of the electron ground state in the helium ion, and $E_{\mathbf{k}}$ is the energy of the conduction electron. It is the dependence of the pseudopotential form factor on the energy of conduction electrons that makes the pseudopotential nonlinear.

When developing a perturbation theory in the pseudopotential parameter, the pseudopotential itself must also be determined in the framework of the perturbation theory. The both expansions must be mutually consistent. Here, we use the pseudopotential form factors that were found in the zeroth-order pseudopotential approximation. This means that the energy of conduction electrons is considered to include only their kinetic energy. This approximation is sufficient when calculating the internal metal energy in the framework of the perturbation theory whose order

in the pseudopotential does not exceed two. Hence, the pseudopotential of electron-ion interaction for a singly ionized helium atom is as follows [3]:

$$\langle \mathbf{k} | w | \mathbf{k}' \rangle = V(\mathbf{k} - \mathbf{k}') + \langle \mathbf{k} | w_{nl} | \mathbf{k}' \rangle. \quad (4)$$

Our only approximation consists in the application of the eigenvalues and eigenfunctions of an isolated helium ion. The matrix elements between plane waves are calculated everywhere.

Owing to the metal electroneutrality, the energy of the first order in the pseudopotential does not include the local part of the pseudopotential and looks like

$$E_1 = \frac{1}{\pi^2} \int_0^{k_F} \langle k | w_{nl} | k \rangle k^2 dk, \quad (5)$$

where

$$\langle k | w_{nl} | k \rangle = -\frac{64\pi z^5}{(z^2 + k^2)^4} \left(-\frac{z^2}{2} + \frac{k^2}{2} \right). \quad (6)$$

It is easy to calculate integral (5) analytically, but the result is rather cumbersome. Although formally this term is of the first order in the pseudopotential, actually it is of the same order of magnitude as the zeroth-order summand. This is a consequence of the contribution averaging over the ionic degrees of freedom and the translational invariance of the system in the liquid state.

The term of the second order in the pseudopotential has the form

$$E_2 = \Delta_1 + \Delta_2 + \Delta_3. \quad (7)$$

The contribution associated with the local part of pseudopotential is as follows:

$$\Delta_1 = -\frac{1}{2\pi^2} \int_0^\infty \frac{\pi_0(q) w^2(q)}{\varepsilon(q)} S_i(q) q^2 dq. \quad (8)$$

Here,

$$\pi_0(q) = \frac{k_F}{2\pi^2} \left[1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left(\left| \frac{2k_F + q}{2k_F - q} \right| \right) \right] \quad (9)$$

is the polarization operator of the non-interacting electron gas,

$$\varepsilon(q) = 1 + [v(q) + \widetilde{v(q)}] \pi_0(q) \quad (10)$$

the effective dielectric permittivity of the interacting electron gas in the Geldart–Vosko approximation [17],

$$v(q) = \frac{4\pi e^2}{q^2} \quad (11)$$

the Coulombic potential of electron-electron interaction,

$$\tilde{v}(q) = -\frac{2\pi e^2}{q^2 + \lambda k_F^2} \quad (12)$$

the local potential of exchange interaction and correlations, $\lambda \approx 2$, and $S_i(q)$ is the pair structure factor of the ion subsystem in the hard-sphere model [18]. For the contribution from the nonlocal part of pseudopotential, we obtain

$$\begin{aligned} \Delta_3 &= \frac{1}{2\pi^4} \frac{m}{\hbar^2} \int_0^{k_F} dk \int_0^\infty dk' k' \langle \mathbf{k} | w_{nl} | \mathbf{k}' \rangle^2 \times \\ &\times \left(\frac{1}{k+k'} + \frac{1}{k-k'} \right) \int_{k-k'}^{k+k'} \frac{S_i(q)}{\varepsilon(q)} q dq. \end{aligned} \quad (13)$$

Finally, the cross term looks like

$$\begin{aligned} \Delta_2 &= \frac{1}{\pi^4} \frac{m}{\hbar^2} \int_0^{k_F} dk \int_0^\infty dk' k' \langle \mathbf{k} | w_{nl} | \mathbf{k}' \rangle \times \\ &\times \left(\frac{1}{k+k'} + \frac{1}{k-k'} \right) \int_{k-k'}^{k+k'} \frac{V(q)}{\varepsilon(q)} S_i(q) q dq. \end{aligned} \quad (14)$$

3. Internal Energy, Entropy, and Free Energy

For the metal entropy, we used the following expression [19]:

$$S = S_e + S_{\text{gas}} + S_{\text{conf}}. \quad (15)$$

Here,

$$S_e = \frac{\pi^2 k_B^2 T}{k_F^2} \quad (16)$$

is the contribution of the ideal degenerate electron gas to the entropy,

$$S_{\text{gas}} = \frac{5}{2} k_B + \frac{3}{2} k_B \ln \left(\frac{M k_B T}{2\pi n_i^{2/3}} \right) \quad (17)$$

the contribution of the classical ionic subsystem to the entropy in the gas approximation,

$$S_{\text{conf}} = k_B \frac{4\eta - 3\eta^2}{(1-\eta)^2} \quad (18)$$

the contribution arising due to the difference between the real ionic subsystem and the classical ideal gas (the configurational contribution), and η is the ion packing density in the hard-sphere model.

For the electrostatic energy, we used the classical result [19]

$$E_{es} = \frac{z^2}{\pi} \int_0^\infty [S_i(q) - 1] dq. \quad (19)$$

The expression for the internal energy in the second order of the perturbation theory in the pseudopotential looks like

$$E = E_{es} + E_0 + E_1 + E_2. \quad (20)$$

Accordingly, for the free energy, let us use its definition

$$F = E - TS. \quad (21)$$

By differentiating the free energy with respect to the system volume provided the constant temperature, we can obtain the pressure required to hold helium in the condensed metallic state.

4. Results and Their Discussion

A separate study of the system entropy is reasonable, because it allows one to determine the region of existence for metallic helium in the liquid phase. Although the starting point of the plot describing the dependence of the entropy on the density is completely hypothetical (it is based on the assumption that the metallization of helium and hydrogen occurs at the same electron gas concentrations), the end point of the plot has a very definite character, testifying to the transition of metallic helium from the liquid state into the solid one as a result of the helium compression. The point of transition into the solid state can be determined from the vanishing condition $S = 0$ for the metal entropy S as a function of the density and temperature.

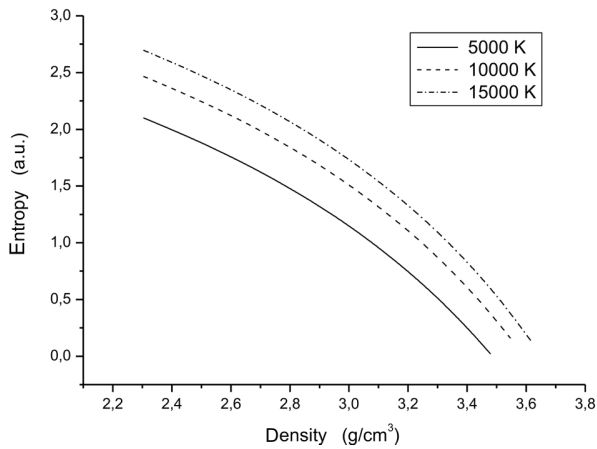


Fig. 1. Dependences of the entropy on the density at various temperatures

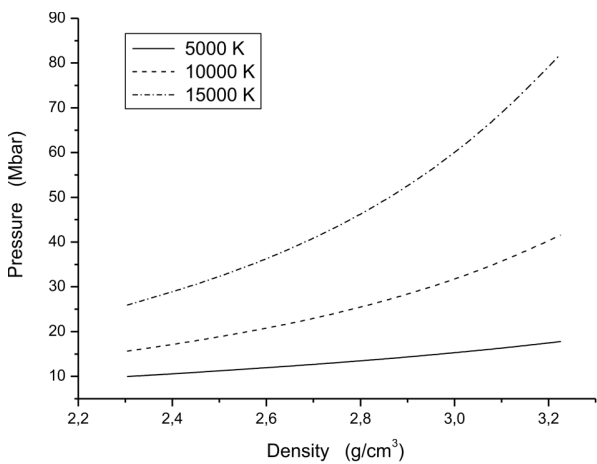


Fig. 2. Dependences of the pressure in liquid metallic helium on the density at various temperatures

In Fig. 1, the dependences of the entropy of liquid metallic helium on its density at various temperatures are shown. At a temperature of 5000 K, starting from the liquid phase of metallic helium with an initial density of 2.56 g/cm^3 , the entropy decreases monotonically, as the density grows, and reaches zero at a density of 3.5 g/cm^3 . At this density value, the pressure-induced crystallization of liquid metallic helium begins. At a temperature of 10000 K, the crystallization occurs at a somewhat higher density of 3.6 g/cm^3 . At a temperature of 15000 K, the crystallization takes place at an even higher density of 3.65 g/cm^3 . Hence, the temperature dependence of the density at which the crystallization occurs is not very strong.

We can hardly talk in the near future about the production of crystalline metallic helium under terrestrial conditions. However, in the bowels of Jupiter, closer to its hard core, the required temperature and density conditions supposedly take place. The polytropic model of Jupiter predicts a density of about 7 g/cm^3 at the center of the planet, with the temperature not exceeding 20000 K. A mismatch between the density of the helium crystallization and the density of the substance in the central part of Jupiter should not be surprising, because helium comprises only a small fraction of the planet mass. Closer to the planet surface, helium is uniformly mixed with hydrogen, which limits the possibility of its density increase, whereas closer to the center, it condenses in the form of liquid droplets [20] embedded in the medium of liquid metallic hydrogen as a quite isolated substance, which has little effect on the total density of the substance. The planet predominately consists of hydrogen, which mainly exists in the liquid metallic state.

Our calculations demonstrate that the pressure of liquid metallic helium within the hypothetical limits of its existence is rather high and exceeds modern experimental capabilities. Figure 2 illustrates the dependences of the pressure in liquid metallic helium on the density for various temperatures. As one can see, the temperature dependence of the pressure is rather strong. In particular, the maximum pressure in the liquid phase is about 40 Mbar at a temperature of 10000 K and about 90 Mbar at a temperature of 15000 K. Note that the polytropic model of Jupiter predicts a pressure of about 60 Mbar at the center of this planet.

Since the temperature at the center of Jupiter approximately equals 20000 K, whereas the pressure required for the crystallization of liquid metallic helium at this temperature reaches a value of 90 Mbar, the crystallization is hardly possible. The pressure in the interiors of Jupiter is enough to metallize helium, but not enough to crystallize it. A similar situation with respect to the helium metallization also takes place in the interiors of Saturn.

5. Conclusions

1. From the theoretical viewpoint, the fundamental difference between liquid metallic hydrogen and liquid metallic helium consists in that the electron-ion interaction in them is described by the local Coulombic po-

tential in metallic hydrogen, and by a nonlocal pseudopotential in metallic helium. This difference brings about substantial physical differences. A hypothetical pressure at which the helium metallization should take place turns out an order of magnitude higher than the corresponding pressure for hydrogen.

2. Conditions in the interiors of the giant planets – Jupiter and Saturn – completely correspond to the conditions of helium metallization. But the experimental values of thermodynamic parameters attained nowadays under terrestrial conditions are insufficient for this purpose.

3. Pressure-induced crystallization of metallic helium is impossible even in the interiors of the giant planets of the solar system.

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В.Т. Швец, Є.В. Черевко

НЕЛОКАЛЬНИЙ ПСЕВДОПОТЕНЦІАЛ І ТЕРМОДИНАМІКА МЕТАЛІЧНОГО ГЕЛІЮ

Досліджені термодинамічні властивості рідкого металічного гелію в другому порядку теорії збурень за псевдопотенціалом електрон-іонної взаємодії. При цьому використано псевдопотенціал, знайдений з перших принципів. Цей псевдопотенціал є нелокальним і нелінійним. Нелокальність псевдопотенціалу приводить до того, що у розвиненні внутрішньої енергії, вільної енергії і тиску рідкого металічного гелію в ряд за псевдопотенціалом присутній член першого порядку. Його діагональний матричний елемент виявляється того ж порядку величини, що і член нульового порядку. В результаті цей член дає важливий внесок у внутрішню і вільну енергію, а залежність їх від густини і температури стає суттєвішою. Відповідно зростає і тиск, при якому може реалізуватись рідка металічна фаза гелію. Цей тиск на порядок перевищує відповідний тиск у металічному водні і на сьогодні є недосяжним на експерименті. Аналіз ентропії дозволив з'ясувати область існування рідкої металічної фази і з'ясувати умови її кристалізації. Порівняння з густинами, тисками і температурами всередині газових гігантів Юпітера і Сатурна дозволило зробити висновок про те, що в центральних частинах цих планет не лише водень, а і гелій перебувають у металічному стані. Проте тиск в надрах планет є недостатнім для кристалізації гелію.

Ключові слова: металізація гелію, псевдопотенціал електрон-іонної взаємодії, внутрішня енергія металічного гелію, вільна енергія металічного гелію, рівняння стану металічного гелію.