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Application of liquid metal compressibility theory to the liquid rare earth metals

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A simple analytical expression for the isothermal compressibility of liquid rare earth metals such as Dy, Ho, Er and Lu has been analytically obtained by use of the exact relation for the isothermal compressibility of a two – component plasma, the perturbation theory with respect to the local pseudopotential of the electron – ion interaction, and a one – component plasma as a reference system. Due to the fact that there are no experimental data for the isothermal compressibility of the liquid rare earth metals, the calculated data based on the obtained formula are compared with the values estimated by Waseda and Ueno.

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1. Introduction

The isothermal compressibility, χ_T, is one of the important thermodynamic properties of a material in the liquid state. It defines the thermodynamic stability of a system, as a parameter of the critical point and the state equation along isotherms [1,2];

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{1}$$

Here V is the volume, P is the pressure and T is the temperature of a system.

Most theoretical studies of the isothermal compressibility of liquid metals are based on a calculation of the free energy of a two-component electron-ion plasma under two assumptions [3]: (a) weakness of the electron-ion interaction in the framework of the pseudopotential theory and (b) description of an efficient potential for indirect interactions between ions through electrons, which is short range. In the calculation of the thermodynamic properties of liquid metals for the description of the ion subsystem, the method of simple liquid theory is used [4].

This paper is organized as follows. In section 2, we summarize the theoretical derivation of the isothermal compressibility of the liquid metals from the exact relation for the isothermal compressibility of a two – component plasma (TCP), using perturbation theory with respect to the pseudopotential of the electron-ion interaction and the one – component plasma (OCP) model as a reference system. The results obtained for application to the liquid rare earth metals such as Dy, Ho, Er and Lu, with a comparison of the estimated values of Waseda and Ueno [5] are presented in section 3. The final section is devoted to the summary and conclusions.

2. Liquid metal isothermal compressibility

Ions weakly coupled to an electron gas constitute a primitive model for the liquid metal, called an electron-ion plasma model or two-component plasma model. Such a TCP-model can obviously be constructed in terms of the pseudopotentials for the interparticle interactions. In general, any pseudopotential has a Coulombic and a non-Coulombic part, i.e.,

$$U_{ab}(q) = \frac{4\pi Z_a Z_b e^2}{q^2} + \phi_{ab}(q) \tag{2}$$

where a and b denote the various species $(a, b = i \text{ or } e)$.

The isothermal compressibility of a two-component electron-ion plasma can be expressed in terms of $P_{ab} = \lim_{q\to 0} P_{ab}(q,0)$, the long wavelength limit value of the exact static polarization $P_{ab}(q,0)$ [2], and $\phi_{ab} = \lim_{q\to 0}\phi_{ab}(q)\left(|\phi_{ab}| < \infty\right)$, the long wavelength limit value of the non-Coulombic part, $\phi_{ab}(q)$, by

$$n_e^2\chi_T = \frac{-Z_i\left(P_{ee}P_{ii} - P_{ei}^2\right)}{P_{ee} + Z_i^2 P_{ii} - 2Z_i P_{ei} - \left(\phi_{ii} + Z_i^2\phi_{ee} + 2Z_i\phi_{ei}\right)\left(P_{ee}P_{ii} - P_{ei}^2\right)} \tag{3}$$

(for the derivation of (3) please see ref. [1]). In the study of liquid metal plasmas, one assumes $\phi_{ii} = \phi_{ee} = 0$, hence for the calculation theory with respect to the electron-ion pseudopotential, we can neglect $P_{ei}\left(orP_{ie}\right)$. Thus (3) simplifies to

$$n_e^{\,2}\chi_T = -\frac{Z_i^{\,2}P_{ee}P_{ii}}{P_{ee}+Z_i^{\,2}P_{ii}-2Z_i\phi_{ei}P_{ee}P_{ii}} \tag{4}$$

Working on the pseudisation problem, Thakor et al. [6] proposed that a pseudopotential could be applied beneficially to the liquid rare earth metals such as Dy, Ho, Er and Lu. In this work, we take this potential as the electron-ion pseudopotential in real space

$$U_{ei}(r) = \begin{cases} 0 & r < r_c \\ -\left(\dfrac{Z_i e^2}{r}\right)\left[1-\exp\left(-\dfrac{r}{r_c}\right)\right] & r \geq r_c \end{cases} \tag{5a}$$

or its Fourier Transform in reciprocal space;

$$U_{ei}(q) = \left(-\frac{4\pi Z_i e^2}{\Omega q^2}\right)\left\{\cos qr_c - \left[\frac{qr_c\exp(-1)}{1+q^2r_c^{\,2}}\right]\times\left(\sin qr_c + qr_c\cos qr_c\right)\right\} \tag{5b}$$

Here, Z_i, Ω, q and r_c are the valency, atomic volume, wave vector and core radius, which reflects the ionic size, respectively. The non-Coulombic part of this potential can be written from (2) as

$$\phi_{ei}(q) = \frac{4\pi Z_i e^2}{\Omega q^2}\left[1-\cos qr_c\right] + \frac{4\pi Z_i e^2}{\Omega q^2}\frac{r_c\exp(-1)}{\left(1+q^2r_c^2\right)}\left(\sin qr_c + qr_c\cos qr_c\right) \tag{6}$$

the limit of which as $q \to 0$ is

$$\phi_{ei}^0 = \frac{2\pi Z_i r_c^{\,2} e^2}{\Omega}\left[1+4\exp(-1)\right] \tag{7}$$

In the framework of the OCP model [5]

$$P_{aa} = -n_a^2\chi_a \tag{8}$$

where χ_a is the isothermal compressibility of OCP for a type - a species $(a = i, e)$ [5].

Substituting (7) and (8) into (4) and recalling that $n_e = Z_i n_i$ (the number densities of the ionic species) we get

$$\chi_T = \frac{\chi_e\chi_i}{\chi_e+\chi_i+\dfrac{2\phi_{ei}^0 n_e^2\chi_e\chi_i}{Z_i}} \tag{9}$$

for the isothermal compressibility χ_T of a liquid metal. This is the general form of the isothermal compressibility of a TCP with weak electron-ion interaction and having a non-Coulombic part.

Next, to determine χ_e and χ_i for OCP we use the compressibility sum rules [7]. First, for χ_i :

$$1-\frac{\beta}{n_i\chi_i} = -2n_i\beta f_{ex}^{'}(n_i) - n_i^2\beta f_{ex}^{''}(n_i) \tag{10}$$

Here $\beta = \dfrac{1}{k_B T}$ (k_B is the Boltzmann constant and T is the temperature) and $\beta f_{ex}(n_i)$ is the total excess free energy per ion. We note that $f_{ex}^{'}$ and $f_{ex}^{''}$ are partial derivatives with respect to n_i. For the OCP, a very accurate expression of the free energy is available from Monte Carlo simulations for $\Gamma > 1$ [8]

$$\beta f_{ex} = a\Gamma + 4\left(b\Gamma^{1/4} - c\Gamma^{-1/4}\right) + d\ \ln\Gamma - \left[a+4(b-c)+0.4363\right] \tag{11}$$

where Γ is the plasma parameter defined by $\Gamma = \beta(Z_i e)^2/r_{ws}$, $r_{ws} = \left(3/4\pi n_i\right)^{1/3}$ is the Wigner-Seitz radius for ions, a=-0.897744, b=0.95043, c=0.18956 ve d=-0.81487. Solving χ_i from (10) and substituting these values of $f_{ex}^{'}$ and $f_{ex}^{''}$ by (11), we get

$$\chi_i = \frac{\beta}{n_i g_i(\Gamma)} \tag{12}$$

where

$$g_i(\Gamma) = 1+\frac{4}{9}a\Gamma+\frac{13}{36}b\Gamma^{1/4}+\frac{11}{36}c\Gamma^{-1/4}+\frac{d}{3} \tag{13}$$

Second, for χ_e: The compressibility sum rule of a degenerate electron liquid is given by [9]

$$\chi_e = \frac{\chi_e^0}{g_e(r_s)} = \frac{\chi_e^0}{1-4\lambda r_s\gamma_0(r_s)/\pi} \tag{14}$$

where $r_s = \left[3/(4\pi n_e)\right]^{1/3}/a_0$ is the Wigner-Seitz radius for electrons in a.u. (a_0 is the Bohr radius), $\lambda = (4/9\pi)^{1/3}$, the coefficient $\gamma_0(r_s)$ is

$$\gamma_0(r_s) = \frac{1}{4} - \frac{\pi\lambda}{24}\left[r_s^3\frac{d^2\varepsilon_e(r_s)}{dr_s^2} - 2r_s^2\frac{d\varepsilon_e(r_s)}{dr_s}\right] \tag{15}$$

and $\chi_e^0 = 3/\left(2n_e\varepsilon_F\right)$ is the isothermal compressibility of an ideal electron gas, in which ε_F denotes the Fermi energy. In (15), $\varepsilon_e\left(r_S\right)$ refers to the correlation energy per electron in Rydbergs. Sarkar et al. [10] obtained this correlation energy using the quantum Monte Carlo calculation of Ceperley and Alder [11] over the entire range of r_s values;

$$\varepsilon_e\left(r_S\right) = \frac{1 + a_0 r_S + a_1 r_S^2 + a_2 r_S^3 + a_3 r_S^4}{b_0 + b_1 r_S + b_2 r_S^2 + b_3 r_S^3 + b_4 r_S^4 + b_5 r_S^5} \text{ mRyd} \quad (16)$$

where

$a_0 = 0.24837857$ $a_1 = 0.00611973$

$a_2 = 0.00069664$ $a_3 = 3.63367823\ 10^{-6}$

$b_0 = 0.00450109$ $b_1 = 0.00540115$

$b_2 = 0.00035051$ $b_3 = 0.00002577$

$b_4 = 9.88887829\ 10^{-7}$ $b_5 = 5.1105284\ 10^{-9}$

Finally, substituting (12) and (14) in (9) we get the isothermal compressibility of a liquid metal as

$$\chi_T\left(dyn^{-1}cm^2\right) = \frac{\beta}{n_i \mathrm{X}\left(\Gamma, r_S\right)} \quad (17)$$

where

$$\mathrm{X}\left(\Gamma, r_S\right) = g_i\left(\Gamma\right) + \left(\frac{\beta}{\chi_e^0 n_i}\right) g_e\left(r_S\right) + 2n_e\beta\phi_{ei}^0 \quad (18)$$

3. Results for the liquid rare earth metals

In this section, we apply (17) to the liquid rare earth metals selected as Nd, Dy, Ho, Er and Lu. During the execution of our computer program for the calculation of χ_T, the following input data have been used: (i) the experimental number densities of the rare earth metals are taken from [5] and [6] and (ii) the core radii r_c from (5a) as the parameter of the potential are determined by

$$r_c = 0.51(Z_i)^{-1/3} R_a$$

where R_a is the atomic radius [12]. In Table 1, we show our numerical results with the comparison with Waseda's [5] estimated data, which has been taken via internet, because so far as we know such studies have not yet been carried out.

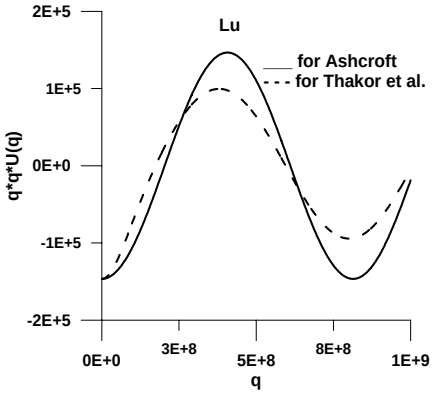

Fig. 1 - $q^2U\left(q\right)$ versus q for liquid Lu.

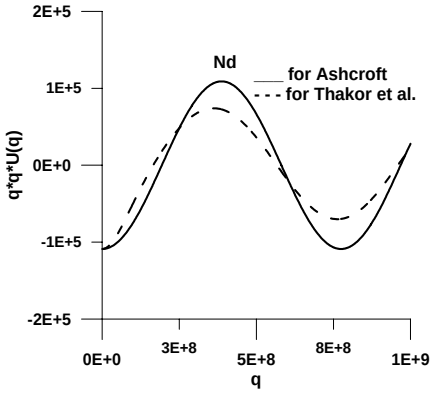

Fig. 2 - $q^2U\left(q\right)$ versus q for liquid Nd.

As seen from Table 1, some discrepancies have been observed between our calculated values and the estimated values. They may be ascribed mainly to the close dependence on the selected pseudopotential models, i.e. the Thakor et al. and Ashcroft empty-core pseudopotentials. To show this clearly, we plot these pseudopotentials in Figures 1, 2 for Lu and Nd, respectively.

Table 1. The isothermal compressibilities of the rare earth metals near their melting point

Metal	T(K)	$q_F(A^{-1})$	r_c(A)	$\chi_T\times10^{-12}$ cm^2 / dyn Thakor et al.	$\chi_T\times10^{-12}$ cm^2 / dyn Ashcroft	Estimated According to WASEDA
Nd	1323	1.0361	0.8113	3.01969	3.12788	3.41
Dy	1703	1.0511	0.7899	2.81045	2.9115	2.97
Ho	1753	1.1255	0.7868	1.88540	1.9533	1.92
Er	1793	1.1028	0.7828	2.12599	2.2018	2.28
Lu	1953	1.1439	0.7725	1.74587	1.81089	1.88

As seen from Figs. 1 and 2, the graphs for the Ashcroft and Thakor et al. pseudopotentials give different curves and the deviation between them becomes more evident. Therefore, the calculated values of the isothermal

compressibility differ from one another. The difference between the values of χ_T of the same metal increases with the amount of the deviation in the first peaks of the pseudopotential curves. Similar results have been obtained for the other rare earth metals, namely Dy, Ho and Er.

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