

Calculation of Surface Tension and Viscosity of Liquid Transition Metals

Sevilay UÇAR, Turgay ARMAĞAN, Sehban KARTAL

Abstract— The results of calculations of structure and some surface properties such as, isothermal compressibility, surface tension and viscosity for liquid 3d transition metals, Ti, Ni and V, near melting temperatures are presented. We used the parameters of the Wills-Harrison (WH) approximation in conjunction with the Bretonnet-Silbert (BS) local model pseudopotential, which is suggested separate description of the s- and d—electron states are calculated using Dubinin procedure [1]. Isothermal compressibility and surface tension properties of Ti, Ni and V are calculated using extended Mayer's empirical formula in terms of hard sphere diameter and packing fraction which calculated using Waseda's formula [2]. We have obtained in very good agreement near melting point with available experimental data.

Index Terms— transition metal, scaled particle theory, surface tension, viscosity.

I. INTRODUCTION

It is well known that the high-temperature properties of liquid transition metals are extremely important for thermochemistry. In this work, we calculated to the some surface properties of transition metals using the scaled particle theory, a suitable pseudopotential and hard sphere model.

This paper is organized as follows. In section 2, we summarize the theoretical derivation of the isothermal compressibility, surface tension and viscosity of the some liquid transition 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 transition metals such as Ti, Ni and V, compared with the available experimental and theoretical data are presented in section 3. The final section is devoted to the summary and conclusions.

II. THEORY

A. ISOTHERMAL COMPRESSIBILITY AND SURFACE TENSION

The isothermal compressibility K_T is one of the most important thermodynamic properties of a substance. Its theoretical study is today's task because the value of K_T defines the thermodynamic stability of a system, as a parameter of the critical point and the state equation along isotherms:

Revised Version Manuscript Received on May 23, 2015.

MSc. Sevilay UÇAR, Maltepe University, Faculty of Engineering and Natural Sciences, Maltepe, Istanbul-Turkey.

Prof. Dr. Turgay ARMAĞAN, Istanbul University, Physics Department, 34459 Vezneciler, İstanbul-Turkey.

Prof. Dr. Sehban KARTAL, Istanbul University, Physics Department, 34459 Vezneciler, İstanbul-Turkey.

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{B_T} \quad (1)$$

Here V , P , T and B_T are volume, pressure, temperature and isothermal bulk modulus of a given system respectively [3-6]. Theoretical studies on the derivation of isothermal compressibility for the liquid transition metals as the realized in references [3-6] are related to (1) on the base of a calculation of the free energy of a two-component plasma (TCP), (b) the perturbation theory with respect to the pseudopotential formalism for the interionic interactions and (c) a one-components plasma (OCP) as a reference system. The following relationship for the compressibility K_T and surface tension γ_S of the liquid metals has been proposed from the scaled particle theory (SPT) using extended Mayer's empirical formula [7] as

$$K_T \cdot \gamma_S = \sigma_i \left[\frac{2 - 3\eta + \eta^2}{4(1 + 2\eta^2)} \right] \quad (2)$$

where σ_i is the effective ion hard sphere diameter, η is the packing fraction [8]. The applicability of this relation is then confirmed by the study of Egelstaff et al., [9]. With the help of Eq. (2), it is feasible to calculate surface tension or isothermal compressibility in accordance with the availability of experimental data for K_T or γ_S respectively [10]. In this paper, we used to Waseda's [2] formula for packing fraction. To incorporate temperature dependency, the following relation between temperature and packing fraction is used.

$$\eta = A \exp(-BT) \quad (3)$$

where, the parameters A and B are listed in Waseda's book.

B. PSEUDOPOTENTIAL FORMALISM FOR THE CALCULATION K_t

Bretonnet and Silbert have proposed a model potential for liquid transition metals [11]. This model potential has the following form which is constructed by the superposition of the s-p and d-band contributions

$$U_{ei}(r) = \begin{cases} \sum_{m=1}^2 B_m \exp\left(\frac{r}{ma}\right) & r < r_c \\ -\frac{Z_s e^2}{r} & r > r_c \end{cases} \quad (4)$$

where a , r_c and Z_s are the softness parameter, core radius

Calculation of Surface Tension and Viscosity of Liquid Transition Metals

and s -electron occupancy number respectively. B_1 and B_2 are given in terms of the parameters a, r_c and Z_s through the expressions;

$$B_1 = \frac{Z_s e^2}{r_c} \left(1 - 2 \frac{a}{r_c} \right) e^{\frac{r_c}{a}} \quad (5)$$

$$B_2 = 2 \frac{Z_s e^2}{r_c} \left(\frac{a}{r_c} - 1 \right) e^{\frac{r_c}{2a}}$$

The unscreened form factor, e.g. the Fourier transform of Eq. (4) can be written as

$$U_{ei}(q) = 4\pi\rho_i a \left\{ \left[\frac{B_1 J_1}{(1+a^2 q^2)^2} + \frac{8B_2 J_2}{(1+4a^2 q^2)^2} \right] - 4\pi\rho_i Z_s e^2 \frac{\cos qr_c}{q^2} \right\} \quad (6)$$

with

$$J_m = 2 - \exp\left(\frac{r_c}{ma}\right) \left\{ \left[\left(\frac{r_c}{ma} \right) (1+m^2 a^2 q^2) \right] \frac{\sin qr_c}{maq} + \left[2 + \left(\frac{r_c}{ma} \right) (1+m^2 a^2 q^2) \right] \cos qr_c \right\} \quad (76)$$

Here, ρ_i is the ionic number density. The limit as $q \rightarrow 0$ of the non-coulombic part of Eq. (6) can be calculated as

$$\varphi_{nc} = 4\pi\rho_i a \sum_{m=1}^2 m^3 B_m \left\{ \exp\left(\frac{r_c}{ma}\right) \left[\frac{r_c}{ma} \left(2 + \frac{r_c}{ma} \right) + 2 \right] \right\} + 4\pi\rho_i Z_s e^2 \left(\frac{r_c}{2} \right) \quad (8)$$

An electron-ion plasma or TCP model is defined a primitive model of a liquid metal, where ions weakly coupled to an electron gas. In this case, a general form of the isothermal compressibility of a TCP with weak electron-ion interaction and having a non-Coulombic part, Eq. (8) is given as follows;

$$K_T = \frac{K_e K_i}{K_e + K_i + 2\rho_e \rho_i \varphi_{nc} K_e K_i} \quad (9)$$

where K_α is the isothermal compressibility of OCP that for type- α species ($\alpha = e$ or i).

Next, to determine of K_α for OCP we use the compressibility sum rules [12]. First for K_i ;

$$1 - \frac{\beta}{\rho_i K_i} = -2\rho_i \beta f'_{ex}(\rho_i) - \rho_i^2 \beta f''_{ex}(\rho_i) \quad (10)$$

Here, $\beta = (k_B T)^{-1}$ is temperature coefficient and $\beta f_{ex}(\rho_i)$ is the total excess free energy per ion. We note that

$f'_{ex}(\rho_i) = \partial f_{ex}(\rho_i) / \partial \rho_i$ and $f''_{ex}(\rho_i) = \partial^2 f_{ex}(\rho_i) / \partial \rho_i^2$ are the partial derivatives. For the OCP, a very accurate expression of the free energy is available from Monte Carlo simulations for $\Gamma > 1$ [13]

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

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

$$K_i = \frac{\beta}{\rho_i g_i(\Gamma)} \quad (12)$$

where

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

Secondly for K_e ; The compressibility sum rule of a degenerate electron liquid is given by [12]

$$K_e = \frac{K_e^0}{g_e(r_s)} \quad (14)$$

in which

$$g_e(r_s) = 1 - 4\lambda r_s \gamma_0(r_s) / \pi \quad (15)$$

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

$$\gamma_0(r_s) = \frac{1}{4} - \frac{\pi\lambda}{24} \left[r_s^3 \frac{d^2 \varepsilon_e(r_s)}{dr_s^2} - 2r_s^2 \frac{d\varepsilon_e(r_s)}{dr_s} \right] \quad (16)$$

and $K_e^0 = 3/(2\rho_e E_F)$ is the isothermal compressibility of an ideal electron gas.

$$E_F = \frac{\hbar^2}{2m_e} \left(3\pi^2 \rho_e \right)^{2/3} \quad (17)$$

denotes the Fermi energy, $\hbar = h/2\pi$, Planck coefficient and m_e is the electron mass. In Eq.(16), $\varepsilon_e(r_s)$ refers to the correlation energy per electron in Rydbergs and we use by Sarkar's energy form [13], which is

$$\epsilon_e^S(r_s) = \frac{1 + a_0 r_s + a_1 r_s^2 + a_2 r_s^3 + a_3 r_s^4}{b_0 + b_1 r_s + b_2 r_s^2 + b_3 r_s^3 + b_4 r_s^4 + b_5 r_s^5} mRyd \quad (18)$$

where

$$\begin{aligned} a_0 &= 0.24837857 & a_1 &= 0.00611973 \\ a_2 &= 0.00069664 & a_3 &= 3.63367823 \cdot 10^{-6} \\ b_0 &= 0.00450109 & b_1 &= 0.00540115 \\ b_2 &= 0.00035051 & b_3 &= 0.00002577 \\ b_4 &= 9.88887829 \cdot 10^{-7} & b_5 &= 5.1105284 \cdot 10^{-9} \end{aligned}$$

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

$$K_T \left(dyn^{-1} cm^2 \right) = \frac{\beta}{\rho_i X(\Gamma, r_s)} \quad (19)$$

where

$$X(\Gamma, r_s) = g_i(\Gamma) + \left(\frac{\beta}{\rho_i K_e^0} \right) g_e(r_s) + 2\rho_e \beta \phi_{nc} \quad (20)$$

The input parameters used to investigate the structural properties of some liquid transition metals are tabulated in Table 1.

Table 1: Input values for Ti, Ni and V

| | T (K) | ρ (g/cm ³) | m (g) | r _i (Å) | r _a (Å) |
|-----------|-------|-----------------------------|--------|--------------------|--------------------|
| Ti | 1973 | 4.13 | 47.9 | 0.68 | 1.450 |
| Ni | 1773 | 7.90 | 58.71 | 0.72 | 1.250 |
| V | 2173 | 5.36 | 50.941 | 0.59 | 1.310 |

C. VISCOSITY

Viscosity, ν , of liquid metals and alloys is one of the technologically important for transport properties. Although there are a lot of methods to determine the viscosity, those suitable for liquid metals are limited by their chemical reactivity and high melting points. Therefore, a number of expressions have been proposed to link surface tension and viscosity to other, more easily accessible, thermophysical properties. There is a correlation between the viscosity and surface tension. One of this correlation has been examined by Egly and coworkers using the SPT [14];

$$\frac{\gamma_s}{\nu} = \frac{15}{16} \sqrt{\frac{k_B T}{m_e}} \quad (21)$$

where m_e electron mass, k_B is the Boltzman constant and T is the temperature.

III. RESULTS

In the present investigation we have examined the structural and some thermodynamics properties of the 3d transition metals. We have employed a second-order pseudopotential theory that treats the s- and d- electrons separately but in the same footing. The effective pair potentials for liquid

transition metals are obtained from the BS parameterization using Dubinin procedure for a softness parameter. The potential has three essential parameters, the core radius, the softness parameter and the effective s-electron occupancy number. In this work, we calculated to the a softness parameter using the Dubinin formula's with ϵ_d , heavy center of the d-bands of hard-sphere reference system [1]. The values of packing fraction are calculated according to the Waseda's formula. Our calculated packing fraction values are given in Table 2.

Table 2: Comparison the calculated η_{HS} Packing fractions (in a.u.) with the experimental data.

| | η_{HS} (calc.) | η_{HS} [15] |
|-----------|---------------------|------------------|
| Ti | 0.4364 | 0.437 |
| Ni | 0.441 | 0.440 |
| V | 0.4349 | 0.436 |

Using equation (2), (19) and (20), we take an attempt to calculate the isothermal compressibility, surface tension and viscosity for Ti, Ni and V with obtained hard sphere diameters and packing fractions. The obtained results are presented in Table 3-5 and compared with the available experimental and theoretical data for isothermal compressibility, surface tension and viscosity. From the Table 3-5, it is seen that the agreement with the corresponding experimental values rather than theoretical values is reasonably good for titanium, nickel and vanadium.

Calculated values for surface tension using isothermal compressibility and BS potentials are presented in Table 4. The values are closer to the available experimental data than theoretical data.

Table. 3: Comparison the calculated K_T ($10^{-12} cm^2/dyn$) with the Experimental and theoretical values are from Ref. [16-17]

| | T(K) | K_T (cal.) | K_T Rep.[16] | K_T expt.[17] |
|-----------|------|--------------|----------------|-----------------|
| Ti | 1973 | 1.34 | 1.56 | 1.48 |
| Ni | 1773 | 1.43 | 1.26 | 0.98 |
| V | 2173 | 1.56 | 1.23 | 1.10 |

Table. 4: Comparison the calculated γ_S , in (N.m⁻¹), with experimental and theoretical values are from Ref. [8,18]

| | T(K) | γ_S (calc.) | γ_S Rep. [8] | γ_S expt.[18] |
|-----------|------|--------------------|---------------------|----------------------|
| Ti | 1973 | 1.5868 | 1.55 | 1.65 |
| Ni | 1773 | 1.94 | 1.96 | 1.78 |
| V | 2173 | 1.9644 | 1.78 | 1.95 |

Calculation of Surface Tension and Viscosity of Liquid Transition Metals

Table 5: Calculated values for viscosity, in (Pa.s), with experimental and theoretical values are from Ref. [18,19]

| | T (K) | ν (cal.) | ν Rep. [19] | ν expt [18] |
|----|----------|--------------|--------------------|--------------------|
| Ti | 1973 | 4.66 | 3.57 | 2.2-5.2 |
| Ni | 1773 | 4.72 | 4.43 | 4.5-6.2 |
| V | 2173 | 2.59 | 3.51 | 2.4 |

REFERENCES

- [1] N.E. Dubinin, "Interatomic Pair Interaction In Liquid Transition Metals", Act. Phys.Pol.A, 2009, 115,783.
- [2] Y. Waseda, The Structure Of Non-Crystalline Materials, *Mcgraw-Hill Publ. Co.*, New York, 1980.
- [3] V. B. Bobrov, Yu. P. Vlasov and S. A. Trigger, Theory of isothermal compressibility of two-component liquid metal plasmas, TVT, **1992**, 30, 641.
- [4] S. A. Trigger, V. B. Bobrov, Yu. P. Vlasov, Liquid metal compressibility theory using the OCP model as a reference system Physica B, 1994, 193, 291.
- [5] T. Armağan, The isothermal compressibility theory; Application to the liquid metals Pb and Sn, Balkan Physics Letters, 2000, 8, 59.
- [6] S. Uçar and T. Armağan, Application of liquid metal compressibility theory to the liquid rare earth metals, J. of Optoelectronics and Advanced Materials, 2007, 9, 148.
- [7] S. W. Mayer, A molecular parameter relationship between surface tension and liquid compressibility, J. Phys. Chem., 1967 63, 216.
- [8] M. R. Amin, R. C. Gosh, G. M. Bhuiyan, Surface tension of liquid transition and noble metals, J. of Non-Crystalline Solids, 2013, 380, 42.
- [9] P. A. Egelstaff and B. Widom, Liquid Surface Tension near the Triple Point, J. Chem. Phys., 1970, **53**, 2667.
- [10] R. Tahery and H. Modarress, Relationship between Surface Tension, Compressibility and Molecular Parameter, 9. Iranian Chemical Engineering Congress, 23-25 Nov. 2005, Page 515.
- [11] J.L. Bretonnet, M. Silbert, Interionic Interactions in Transition Metals. Application to Vanadium, Phys. Chem. Liq., 1992, 24, 169.
- [12] M Hasegawa, Freezing of the classical one-component plasma: analyses of the non-perturbative density-functional theories, J. Phys.: Condens. Matter, 1992, 4, 5493.
- [13] A. Sarkar, D. Sen, S. Haldar, D. Roy, Static local field factor for dielectric screening function of electron gas at metallic and lower densities, Mod. Phys. Lett., 1998, 12, 639.
- [14] Egry, G. Lohoefer, And S. Sauerland, Surface Tension And Viscosity Of Liquid Metals, Journal Of Non-Crystalline Solids, 156-158, 1993, 830-832.
- [15] Bretonnet, J.L. and Derouche, A., Variational Thermodynamic Calculations For Liquid Transition Metals, *Phys. Rev. B*, 1991, 43, 8924.
- [16] W.A. Harrison, Elementary electronic structure, World Scientific, Singapore, 1999.
- [17] R. N. Joarder and T. Das, Thermodynamics of liquid metals based on charged hard sphere (CHS) model, Phys. Scripta, 1988, 37, 762.
- [18] T. Iida, and R. I. L., Gutrie, The Physical Properties Of Liquid Metals, *Clarendon Press*, Oxford (Gb), 1988.
- [19] G. Kaptay, A unified equation for the viscosity of pure liquid metals, Z. Metallkd., 2005, 96, 1.

MSc. Sevilay UÇAR, Maltepe University, Faculty of Engineering and Natural Sciences, Maltepe, Istanbul-Turkey.

Prof. Dr. Turgay ARMAĞAN, Istanbul University, Physics Department, 34459 Vezneciler, İstanbul-Turkey.

Prof. Dr. Sehban KARTAL, Istanbul University, Physics Department, 34459 Vezneciler, İstanbul-Turkey.