A comparative study on temperature dependent diffusion coefficient of liquid Fe

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ABSTRACT

The self-diffusion coefficients, D, of liquid Fe at different temperatures have been investigated using hard sphere (HS) theory and universal scaling laws (USLs). Inter-ionic interaction is derived from both pseudopotential proposed by Brettonet–Silbert (BS) and many body potential obtained from embedded atom method (EAM). Temperature dependent effective HS diameter, $\sigma(T)$, and excess entropy, S_{ex}, are the premier ingredients of the study. The former ingredient is calculated using both variational modified hypernetted chain, VMHNC, integral equation theory and Linearized Weeks–Chandler–Andersen, LWCA, thermodynamic perturbation theory together with an empirical relation of Protopapas et al. (1973) [2] whereas the later one is calculated using VMHNC theory alone, with BS and EAM potentials. We observe that D increases with increasing temperatures. The obtained results are compared with those predicted by Protopapas et al. The comparison suggests that USL of Dzugutov and HS theory with BS potential are better choices to predict $D(T)$ of liquid Fe.

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1. Introduction

The physics of diffusion in the condensed state attracted scientists for its multiple technological applications; for example, binary solidification and glass formation. Industrially important many reactions are controlled by diffusion of the reactant species. When temperature increases, the metal in the liquid state becomes more sensitive to the external perturbations such as convection effects [1]. In this situation, usually, experimental techniques fail to measure diffusion coefficient, D. Therefore, theoretical understanding on diffusion process for high temperature melts is required.

Despite the experimental limitations in measuring D, the study of diffusion of liquid metals at high melting temperature is not a new issue. Several attempts have been made using different theories [2–5] and computer simulation methods [6–14]. Temperature variation also has the significant influence on diffusion process of liquid metals. However, a few studies [2,4,15–18] have been reported in this regard where liquid Fe received little attention. It should be mentioned here that, Korkmaz et al. [4] used an evanescent pseudopotential proposed by Fiolhais et al. [19] and Ornstein–Zernike integral equation with Rogers–Young

closure up to a few temperature limits (near melting) to study the temperature dependent $D(T)$ for liquid Fe.

From the early 70s to the present decade, various studies have been reported on the diffusion coefficients of liquid transition metal from various point of view. For example, Rice [20] and Vadovic and Colver [21] proposed empirical formulas based on hard sphere (HS) interaction, Rosenfeld [6] and Dzugotov [8] proposed universal scaling laws (USLs) relate reduced diffusion coefficients and excess entropy involving liquid structure. Afterwards, these USLs were revised and thoroughly studied by several authors [11,12,16,4,17,18,22] to determine diffusion coefficients of liquid metals. The outcome of those studies is as follows: some reports [11,12,16] show that the USL does not hold for liquid Si; and also deviates at high temperatures [17,18] or at low density state [22]. Therefore, the present work is a great test for the applicability of the USL for liquid Fe at temperatures far from the melting.

In the 80s both variational modified hypernetted chain, VMHNC and Linearized Weeks–Chandler–Andersen, LWCA, theories were developed and in the 90s those were applied to describe liquid structure factor, especially, for liquid transition metals [23–25] and proved to be successful. Beside those, to describe interionic interactions Bretonnet–Silbert (BS) pseudopotential [26] and many body potential from embedded atom method (EAM) are proved to be suitable for liquid transition metals both in solid [27,28] and liquid phase [29,9,10,30]. To the best of our knowledge, no theoretical study on temperature

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dependent diffusion coefficients of liquid Fe is reported yet which shows the role of potentials from different aspects.

In this study, we therefore take an attempt to calculate diffusion coefficient of liquid Fe using BS and EAM potentials along with both VMHNC and LWCA theories. To calculate diffusion coefficients, HS theory and USLs have been employed. One of the main aims of the study is to examine the role of potentials responsible for the best description of the diffusion of liquid Fe as a representative one of the transition metals. The layout of this paper is as follows: in Section 2 we describe theories relevant to the present calculation. Section 3 is devoted to the results and discussion. We summarize the report with some concluding remarks in Section 4.

2. Theories

2.1. Diffusion coefficients

Diffusion coefficients can be studied using different theoretical methods such as linear trajectory theory, small-step diffusion theory, hard-sphere theory, empirical and semi-empirical formulas [3], and universal scaling laws (USLs) [6,8]. An empirical formula based on Hard-Sphere (HS) interaction reads as [21]

$$D = 0.183\sigma\left(\frac{\pi}{kT}\right)^{1/2}\frac{\eta_m/\eta}{0.9385(T_m\rho/T\rho_m)-1} \tag{1}$$

where $\eta = \frac{1}{6}\pi\sigma^3 n$, the packing fraction, σ the HS diameter, n the number density and T the temperature of investigation. In the same decade, based on these macro-parameters, n and T, Rosenfeld [6] proposed an important connection between dynamic diffusion and structural internal entropy of some liquid systems which shows the following scaling law:

$$D_R^* = 0.6e^{0.8S_{ex}} \tag{2}$$

where D_R^* and S_{ex} are the reduced diffusion coefficients and excess entropy of the systems, respectively. The reduced diffusion coefficients and excess entropy in Eq. (2) are defined as

$$D_R^* = D\frac{n^{1/3}}{(k_BT/m)^{1/2}} \tag{3}$$

$$S_{ex} = -2\pi n\int_0^\infty \{g(r)\ln[g(r)]-[g(r)-1]\}r^2\,dr \tag{4}$$

where $g(r)$ is the pair correlation function approximated from the two-body contribution.

Dzugutov [8] proposed another universal scaling law (USL) based on the microscopic reduction parameters, collision frequency, Γ, and inter-particle distance, σ, which is as follows:

$$D_Z^* = 0.049e^{S_{ex}} \tag{5}$$

where excess entropy is defined as Eq. (4) and D_Z^* is defined as

$$D_Z^* = D\frac{1}{\Gamma\sigma^2} \tag{6}$$

where collision frequency Γ according to Enskog [31] is

$$\Gamma = 4\sigma^2 g(\sigma)n(\pi k_BT/m)^{1/2}. \tag{7}$$

In Eq. (7), $g(\sigma)$ is the radial distribution function evaluated at hard sphere diameter, σ. Eqs. (1), (3), and (6) in this study are used to determine diffusion coefficients of liquid Fe.

2.2. The effective pair potential

2.2.1. Bretonnet and Silbert (BS) potential

Bretonnet and Silbert (BS) have proposed a model potential for liquid transition metals [26]. This model potential includes the contribution of s–p and d-bands and has the following form:

$$w(r) = \begin{cases} \sum\limits_{m=1}^{2} B_m \exp\left(-\frac{r}{ma}\right) & \text{for } r < R_c \\ -\frac{Z_s e^2}{r} & \text{for } r > R_c \end{cases} \tag{8}$$

where a the softness parameter and R_c the core radius are used to control the form of potential. Z_s the s-electron occupancy number. The unscreened form factor can be written as

$$w_0(q) = 4\pi na^3\left[\frac{B_1J_1}{(1+a^2q^2)^2}+\frac{8B_2J_2}{(1+4a^2q^2)^2}\right]-\frac{4\pi nZ_s e^2}{q^2}\cos(qR_c) \tag{9}$$

where the expressions for B_m and J_m are given in Ref. [26]. The effective inter-ionic interaction is

$$v(r) = \frac{Z_s^2}{r}\left(1-\frac{2}{\pi}\int F_N(q)\sin(qr)\,dq\right) \tag{10}$$

where $F_N(q)$ is the normalized energy wave number characteristic

$$F_N(q) = \left(\frac{q^2}{4\pi nZ_s e^2}\right)^2 w_0^2(q)\left[1-\frac{1}{\epsilon(q)}\right][1-G(q)]^{-1}. \tag{11}$$

The dielectric screening function $\epsilon(q)$ is given by

$$\epsilon(q) = 1-\left(\frac{4\pi e^2}{q^2}\right)\chi(q)[1-G(q)]. \tag{12}$$

Here $\chi(q)$ is the Lindhard function and $G(q)$ is the local-field correction as developed by Ichimaru and Utsumi [32].

2.2.2. Embedded atom method

This model potential is developed based on the concept of Stott–Zaremba [33]. In the model, an atom is considered to be embedded in the host consisting of all other atoms. The energy required to embed an atom into the local electron density together with a short ranged core–core repulsion term gives [34]

$$E = \sum_i F_i(\rho_h(r_i)) + \frac{1}{2}\sum_{i\neq j}\phi(r_{ij}) \tag{13}$$

where F_i is the embedding energy for placing the ith atom into the host electron density of ρ_h at position r_i; ϕ is a short ranged doubly screened pair interaction between ith and jth atoms separated by a distance r_{ij}. The host electron density $\rho_h(i)$ is approximated by linear superposition of atomic electron densities

$$\rho_h(i) = \sum_j\rho_j^a(r_{ij}) \tag{14}$$

where ρ_j^a is the atomic density of the jth atom at distance r_{ij} from the nucleus.

The first term on the right of Eq. (13) can be approximated by taking first two terms of Taylor series expansion about the average host electron density, $\overline{\rho}$ [30]. The obtained approximated EAM energy is as follows [34]:

$$E = NE(\overline{\rho}) + \frac{1}{2}\sum_{(i\neq j)}v(r_{ij}) \tag{15}$$

where

$$E(\overline{\rho}) = F(\overline{\rho})-\overline{\rho}F'(\overline{\rho}) \tag{16}$$

and

$$v(r) = \phi(r) + 2F'(\overline{\rho})\rho^a(r) + F''(\overline{\rho})[\rho^a(r)]^2 \tag{17}$$

where $v(r)$ represents the effective pair potential; $F'(\overline{\rho})$ and $F''(\overline{\rho})$ are the first and second derivatives of embedding function evaluated at $\overline{\rho}$, respectively. The parameters, required for EAM potential, are chosen from the work of Bhuiyan et al. (the details are given in Ref. [34]).