



# Transport coefficients and validity of the Stokes–Einstein relation in metallic melts: From excess entropy scaling laws



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## ABSTRACT

Using the pair correlation function obtained via square well (SW) model [Mishra et al., 2015 Chem. Phys. 457 13], we calculate the pair excess entropy of liquid metals and determined the diffusion coefficients via Dzугutov's excess entropy–diffusivity scaling relation. Further, the applicability of the Stokes–Einstein relation for SW potential is validated by comparing the computed shear viscosity coefficients ( $\eta_v$ ) of liquid metals with the available experimental data. Reduced  $\eta_v$  of considered systems has been derived and scaled with the excess entropy. We compute isothermal compressibility, surface tension and surface entropy of the investigated liquids by using diffusion coefficient data obtained from excess entropy scaling law. It is found that the computed values are in good agreement with the corresponding experimental data. Thus, we demonstrate that the Dzугutov scheme can be applied successfully to SW liquid metals to correlate their microscopic structural functions with their surface and thermodynamic properties.

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## 1. Introduction

In recent past, the considerable efforts have been shown to study the structural dependent transport properties like diffusivity and viscosity of several liquid metals and alloys [1–10]. To establish a relationship between transport coefficients with microscopic structural functions is scientifically important but one of the challenging tasks in condensed matter physics. Diffusivity and viscosity of liquid metals, as two important characteristics, are controlling parameters, which influence the various metallurgical processes like microscopic structural evolution, crystal growth, glass transition etc. [9,11–14]. In recent times, various scaling laws relating the excess entropy of a liquid and its transport coefficients have been reported and also reconfirmed within the frameworks of different interatomic potential functions [15–30]. We believe with others that the limited experimental studies on viscosity and diffusivity of liquid metals and alloys have been reported [9,14,18,32], however, numerous molecular dynamic simulations for transport phenomena in metallic liquids based on the embedded atom method and first-principles calculations are of merit [4,9,11,32,33] but could not satisfy the experimental data in total. Studies on transport properties of liquid metals are of great interest because of various scientific and technological reasons. A uni-

versal relation between dimensions less parameters using desired physical quantities can also be obtained via corresponding state theory [34]. The transport properties of liquids together with structural and thermodynamic information provide basis of liquid state theory.

Moreover, viscosity coefficient can be related with diffusion coefficient via Einstein's relation and thus the shear viscosity can be determined in terms of the computed self-diffusion coefficient of liquid metals using Stokes–Einstein or Sutherland–Einstein relation [4,11].

Recently, Dzугutov [15] proposed a universal scaling law for dense liquids on the basis of his simulation results, which correlates the dimensionless diffusion coefficient  $D^*$  with the excess entropy  $S_E$  in  $K_B$  (Boltzmann's constant) unit per particles relating to an ideal gas,  $D^* = a \exp(S_E)$ , where 'a' is numerical constant, which can be obtained by plotting  $D^*$  against  $S_E$ . This is one of the most important scaling relationships for metallic melts, which links the dynamic behavior of liquids with the microscopic structural and reducing parameters. The excess entropy,  $S_E$ , is defined as the total entropy of the liquid minus the ideal gas contribution at the same temperature and pressure [31].

We do not find much work in literature on the excess entropy scaling laws for viscosity and diffusivity with square well (SW) potential, which force us to measure the pair excess entropy and atomic diffusion coefficient of diverse liquid metals (Na, K, Cs, Mg, Al, In, Pb, Ag, Cu and Au) using scaling law proposed by Dzu-

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gutov [15] with SW interatomic potential under Random Phase Approximation (RPA). Dzугutov [15] scaling law for reduced diffusion coefficient and Liu et al. [28] scaling law for reduced viscosity coefficient were modified for SW liquids because such liquids possess all characteristics of real fluids [7].

The validity of the Stokes-Einstein (SE) relation has been established for number of metallic melts [31] and is accepted by many authors [29,31]. The shear viscosity in liquid metals was computed by incorporating their diffusion coefficients values and interatomic separation (first peak position of radial distribution function) as a microscopic structural parameter in the widely used SE relation. Further, isothermal compressibility and surface entropy, of the considered melts have been computed by using recently reported methods [29].

The SW model is an excellent model in the theory of simple liquids, in which the potential energy of an equilibrium homogeneous system is considered as the sum of central, spherically, symmetrical pair wise interactions between the particles with a constant depth and breadth [7,9,35]. Three parameters SW pair potential is given by

$$\phi_{\text{SW}}(r) = \begin{cases} \infty & ; \quad r < \sigma \\ -\frac{\varepsilon}{k_B T} & ; \quad \sigma < r < \lambda\sigma \\ 0 & ; \quad r > \lambda\sigma \end{cases} \quad (1)$$

where  $\sigma$  is the hard core diameter,  $\sigma(\lambda - 1)$  and  $\varepsilon$  ( $< 0$ ) are the breadth and depth of the potential well respectively. It is found that the various transport and surface properties of the considered liquid metals, obtained from their microscopic structural parameters using the SW model, are in good agreement with their corresponding experimental results.

## 2. Theory

The excess entropy,  $S$ , per particle in unit of  $K_B$  can be approximated by the two body contribution in terms of the pair correlation function,  $g(r)$  as [1,31,36–38].

$$S = -2\pi\rho_n \int_0^\infty \{g(r) \ln [g(r)] - [g(r) - 1]\} r^2 dr \quad (2)$$

here,  $\rho_n$  is the number density of liquid metals, which are taken from Ref. [9]. It was shown that  $S$  contributes  $\sim 90\%$  total excess entropy  $S_E$  for the Lennard-Jones systems over a wide range of densities [2,38,39]. In the application of Dzугutov's scaling law to real liquids we calculate  $g(r)$  via Fourier transformation of square well model of structure factor,  $S(k)$  as

$$g(r) = 1 + \frac{1}{2\pi^2\rho_n} \int_0^\infty k^2 [S(k) - 1] \frac{\sin(kr_{nm})}{kr_{nm}} dk. \quad (3)$$

$S(k)$  of liquid metals is obtained by perturbing SW potential over the Thiele [40] solution for the hard spheres reference system under the mean spherical model approximation, the procedures are fully explained in Ref. [9] and hence cannot be repeated here.

The SW model of liquids possess all characteristics of real liquids in which the pair wise potential plays a significant role and the multi particle interactions can be given by the sum of pair wise potential [7]. The hard sphere diameter  $\sigma$  in the original equations of the reduced diffusion coefficient  $D^*$  by Dzугutov scaling law [15] and reduced shear viscosity  $\eta_V^*$  by Liu et al. [28] is replaced by the position of the first maximum of  $g(r)$  in the application to real liquids as suggested by many authors [1,18,31]. Thus, under SW interactions these relations can be given as

$$D^* = \frac{D}{\Gamma r_{\text{max}}^2} \quad (4)$$

$$\eta_V^* = \eta_V \frac{r_{\text{max}}}{\Gamma m} \quad (5)$$

here,  $m$  is the atomic mass;  $\Gamma$  is the collision frequency, which is a microscopic reducing parameter as given by Enskog [41] theory depends on first maximum  $r_{\text{max}}$ , in pair correlation function  $g(r)$  in the theory of real liquids [1]. However, microscopic reduction parameters,  $\Gamma$ , can be calculated for the real liquids by following Ref. [1] using temperature  $T$ , number density  $\rho_n$ , and the first peak position  $r_{\text{max}}$  and peak intensity  $g(r_{\text{max}})$  of SW model of  $g(r)$ .

$$\Gamma = 4 r_{\text{max}}^2 g(r_{\text{max}}) \rho_n \left( \frac{\pi k_B T}{m} \right)^{1/2} \quad (6)$$

where other symbols have their usual connotation. The SW method for the calculation of  $g(r)$  for liquid metals has been reported in Ref. [9] and will not be repeated here,  $m$  is the mass of diffusing species in atomic unit. The SE relation is successfully applied for a number of metallic melts and some of molecular systems as well [30]. Jakes and Pasturel [31] found that the ratio  $D\eta_V/K_B T$  as almost constant for pure liquid metals and the effective radius in SE equation is in close agreement with inter-atomic separation in the first coordinated cell obtained via experimental or simulation techniques. The shear viscosity,  $\eta_V$  of liquid metals can be calculated via SE relation [4,11,29] within the framework SW potential as:

$$\eta_V = \frac{K_B T}{2\pi r_{\text{max}} D} \quad (7)$$

here,  $D$  is the self-diffusivity in liquid metals. In the original work of Dzугutov [15] and Yokoyama [4] were used to approximate the pair excess entropy to the total excess entropy i.e.  $S \cong S_E$ , which is calculated by Eq. (2) for liquid metals using  $g(r)$  and thus reduced diffusion coefficient,  $D^*$  from Dzугutov scaling law [15].

$$D^* = 0.049 e^{S_E} \quad (8)$$

Diffusion coefficients,  $D$  of liquid metals can be obtained from Eqs. (2), (4), (6) and (8) as:

$$D = 0.049 \Gamma r_{\text{max}}^2 \exp(S_E) \quad (9)$$

Within this approach the normalized viscosity coefficient,  $\eta_V^*$  is given as  $\eta_V^* = \alpha \exp(\beta S_E)$ , which can be obtained from Eqs. (5), (7) and (9). The coefficients  $\alpha$  and  $\beta$  can be determined by best fit data in plot of  $\ln \eta_V^*$  versus  $S_E$ .

Further, we calculate the surface entropy,  $S_V$  of considered liquids through temperature derivative of surface tension  $\gamma$  defined in terms of diffusion coefficient in Ref. [9]. Temperature derivative of  $\gamma$  is obtained by analytical temperature coefficient of diffusion coefficient, which has been derived by following the procedures given in Ref. [7]

$$\gamma = \frac{15}{32\pi} \left( \frac{k_B}{m} \right)^{1/2} T^{1/2} \times \frac{\xi}{\sigma}. \quad (10)$$

$$\frac{d\gamma}{dT} = \gamma \left[ \frac{1}{2T} - \frac{1}{\sigma} \frac{d\sigma}{dT} + \frac{1}{\xi} \frac{d\xi}{dT} \right]. \quad (11)$$

where the temperature derivative of friction coefficient  $\xi$ , is obtained by thermal evaluation of well known Einstein's diffusion equation within the frameworks of SW model, the method is already reported by Venkatesh and Mishra [7]. The surface entropy of pure liquid at constant volume is defined as [42].

$$S_V = -\frac{d\gamma}{dT} \quad (12)$$

The surface energy of liquid metals can be determined by using the Gibbs-Helmholtz relation [43].

$$E_S = \gamma + TS_V \quad (13)$$

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