Transport and Surface Properties of Liquid Metals using their Diffusion Data

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Abstract—The atomic diffusion in liquid Na, K, Cs, Mg, Al, In and Pb have been evaluated from the well-known Einstein’s formula of self-diffusion coefficient, \( D = \frac{k_B T}{\xi} \) under square well (SW) interaction. The friction coefficient, \( \xi \) of liquid metals has been computed on the basis of Helfand-Rice-Nachtrieb approach under Helfand’s linear trajectory (LT) approximation. Shear viscosity of liquid metals were determined using modified Stokes-Einstein equation for SW potential. Dzugutov’s scaling was modified for SW interaction and has been employed to compute excess entropy of the considered liquids. The isothermal compressibility of liquid metals was determined using equation of state of SW potential. Surface entropy of these liquids has been determined through temperature derivative of surface tension. Dzugutov’s scaling law has also been tested in these liquid metals. It is found that the various transport and surface properties of these liquid metals extracted from the diffusion coefficients are in a good agreement with the experimental data.

Keywords: Diffusion Coefficients, Excess Entropy, Surface Entropy, Coefficient of Viscosity

INTRODUCTION

Diffusion is the transport of mass from one region to another region on an atomic scale. It is caused by random molecular motion that leads to complete mixing [1]. Liquid state are much diffusive than the solid state. In metals, there is a high atomic mobility just above their melting temperatures, and this is one of the most characteristic properties of liquids. The study of diffusion in liquid metals is of great interest because of various scientific and technological reasons. The transport properties of liquids together with structural and thermodynamic information can provide experimental basis for theories of the liquid state [2].

Transport properties like viscosity and diffusion coefficient of liquids are correlated by Stokes-Einstein relation. Thus the self-diffusion coefficients can be used for calculating other transport coefficients like shear viscosity [3]. In recent years different scaling laws relating the equilibrium thermodynamic properties, excess entropy with dimension less transport coefficients have been reported by many authors [4–7]. Dzugutov [4] proposed a universal scaling relationship between the excess entropy of a liquid and the diffusion coefficient which is one of the important scaling law, which links the dynamic behavior of liquid parameters with microscopic reducing parameters and then excess entropy. The excess entropy of a system is the total entropy minus the ideal gas contribution. This work represents another test of the mentioned scaling law with square well (SW) model under Random Phase Approximation (RPA).

THEORY

D is evaluated from the well-known Einstein’s formula, \( D = \frac{k_B T}{\xi} \). Here \( \xi \) is the friction coefficient experiences by the atoms of same kind. We feel that the pair wise interaction would have significant role in the determination of D and hence \( \xi \) of liquid metals has been computed on the basis of Helfand-Rice-Nachtrieb approach using square well model. Details calculations have been reported elsewhere [8] so it will not be repeated here. \( \xi \) is the combination of reference, soft and soft-reference part. Here, the reference part is the hard sphere potential.

\[
\xi = \xi^R + \left[ \xi^S + \xi^{SR} \right]
\]

\[
\xi^S = \left( \frac{128 \pi k_B T}{9} \right)^{\frac{3}{2}} \rho \sigma^2 g(\sigma)
\]
The shear viscosity coefficient, $\eta_v$, is obtained under the SW model with the Stokes-Einstein relation

$$\eta_v = \frac{k_BT}{2\pi r_m D}$$

(13)

We also derive the structure factor in long wavelength limit, $S(0)$, through equation of state for SW potential in random phase approximation [13]

$$PV = \frac{1}{(1-\eta)^2} - \frac{4\varepsilon}{k_BT} \lambda^3 - 1$$

(14)

$$\frac{V}{RT} + \frac{P}{RT} \frac{dV}{dP} = \frac{d}{dP} \left( 1 + \frac{\eta}{1-\eta}\right) \frac{1}{1-\eta}$$

(15)

Here,

$$1 = \frac{\pi\sigma^3}{6} \rho \beta_i - \frac{\eta}{1-\eta} \frac{dV}{dP} - \frac{1}{V} \frac{dV}{dP}$$

(16)

$$S(0) = \beta T \left( \frac{4\eta^2 + 4\eta + 1}{\eta(1-\eta)} - \frac{8\varepsilon}{k_BT} \lambda^3 - 1 \right)$$

(17)

$S(0)$ is an important parameter to evaluate various properties of liquid state [14].

$$S(0) = 1 \left[ \frac{(2\eta + 1)}{(1-\eta)} - \frac{8\varepsilon}{k_BT} \lambda^3 - 1 \right]$$

(18)

where $\eta$ is called packing fraction i.e. volume occupied by the atoms divided by total volume and is given by $\eta = \frac{\pi\sigma^3}{6}$.

$S(0)$ is related to isothermal compressibility, $\beta_i$, as [14,15]

$$S(0) = \rho \kappa_T \beta_i$$

(19)

### RESULTS AND DISCUSSION

The WT solution of PY hard sphere fluid with SW perturbation was solved under RPA for considered liquids with input parameters like temperature, $T$, atomic density, $\rho_n$. The SW parameters of liquid metals along with their working temperature and number density are listed in Table 1, which are taken from Ref. 8.
Table 1: The SW Parameters of Liquid Metals (σ, ε/k_B and λ are Hard Sphere Diameter, Depth and Breadth Respectively) along with their Working Temperature and Pn is the Number Density.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Temperature (K)</th>
<th>σ (nm)</th>
<th>ε/k_B</th>
<th>λ (nm)</th>
<th>Pn (10^{22}m^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>378</td>
<td>0.330</td>
<td>111.60</td>
<td>1.65</td>
<td>2430</td>
</tr>
<tr>
<td>Potassium</td>
<td>343</td>
<td>0.411</td>
<td>96.14</td>
<td>1.65</td>
<td>1276</td>
</tr>
<tr>
<td>Caesium</td>
<td>303</td>
<td>0.481</td>
<td>109.50</td>
<td>1.70</td>
<td>0.0813</td>
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<td>953</td>
<td>0.265</td>
<td>127.82</td>
<td>1.43</td>
<td>4300</td>
</tr>
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<td>Aluminium</td>
<td>943</td>
<td>0.245</td>
<td>160.00</td>
<td>1.30</td>
<td>5235</td>
</tr>
<tr>
<td>Indium</td>
<td>433</td>
<td>0.283</td>
<td>173.76</td>
<td>1.70</td>
<td>3686</td>
</tr>
<tr>
<td>Lead</td>
<td>613</td>
<td>0.297</td>
<td>70.00</td>
<td>1.40</td>
<td>3099</td>
</tr>
</tbody>
</table>

Previously reported diffusion data [8] of the considered liquids were employed to determine scaled diffusion, D* and excess entropy using Eqs. (5) to (8). F of liquid metals are calculated by using our recently reported [8] pair correlation function values in line with Rao and Murthy [16]. These values are presented in Table 2. We modified the Dzugutov scaling law for real liquids in line with Yokoyama approach [9,10] through which excess entropy, S_v were determined. We find from Table 2 that the theoretically obtained values for S_v are in consistent with experimental results [9,10]. The calculated values of η_v is also listed in Table 2 with their corresponding experimental values [10] for comparison and hence Stokes-Einstein relation modified by the first peak position of g(r) instead of hydrodynamic radius works well for SW liquids.

Table 2: The Collision Frequency (Γ), the Scaled Diffusion (D*), Excess Entropy (S_v/K_B) and Shear Viscosity (η_v) of Liquid Metals.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Temperature (K)</th>
<th>Γ (10^{12} s^{-1})</th>
<th>D* 10^{-3}</th>
<th>S_v/K_B</th>
<th>η_v (mPas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>378</td>
<td>26.74</td>
<td>1.36</td>
<td>3.58</td>
<td>3.46</td>
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<tr>
<td>Potassium</td>
<td>343</td>
<td>18.06</td>
<td>1.14</td>
<td>3.77</td>
<td>3.47</td>
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<td>Caesium</td>
<td>303</td>
<td>7.16</td>
<td>1.17</td>
<td>3.73</td>
<td>3.57</td>
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<tr>
<td>Magnesium</td>
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<td>37.69</td>
<td>1.45</td>
<td>3.52</td>
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<tr>
<td>Aluminium</td>
<td>943</td>
<td>44.43</td>
<td>1.42</td>
<td>3.54</td>
<td>3.55</td>
</tr>
<tr>
<td>Indium</td>
<td>433</td>
<td>10.99</td>
<td>1.98</td>
<td>3.21</td>
<td>-</td>
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<tr>
<td>Lead</td>
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<td>9.66</td>
<td>2.48</td>
<td>2.98</td>
<td>3.94</td>
</tr>
</tbody>
</table>

Surface tension, γ and its temperature derivatives, S_v of condensed matter are important and informative parameters for understanding the material processing technology [17–19]. The surface tension, γ is related with various transport coefficients of liquids. Computed values of γ with their experimental values [18] are also presented in Table 3 and we find a satisfactory agreement between them. We have also derived the surface entropy of liquids through analytical expression for the temperature derivative of the SW model of D under linear trajectory principle [8–11]. These results are presented in Table 3 along with their experimental values [18]. It is worth to mention here that the S_v for many metallic liquids is not determined even experimentally [18]. We find from Table 3 that in most of the liquid metals values of surface entropy decreases with increasing their atomic size and vice versa. The structure factor in long wavelength limit, S(0), is related to isothermal compressibility of liquid metals. Table 3 shows our computed results for βT using equation of state of SW potential. There is a fair agreement between the computed value and the experimental values [20–22].

Table 3: Theoretical and Experimental Values of Surface Tension (γ), Surface Entropy (S_v = −dγ/dT) and Isothermal Compressibility (βT) of Liquid Metals.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Temperature (K)</th>
<th>γ(N/m)</th>
<th>S_v = −dγ/dT (mN/m/K)</th>
<th>βT(10^{-9} m^3/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>378</td>
<td>0.176</td>
<td>0.197</td>
<td>0.083</td>
</tr>
<tr>
<td>Potassium</td>
<td>343</td>
<td>0.096</td>
<td>0.110</td>
<td>0.057</td>
</tr>
<tr>
<td>Caesium</td>
<td>303</td>
<td>0.082</td>
<td>0.070</td>
<td>0.044</td>
</tr>
<tr>
<td>Magnesium</td>
<td>953</td>
<td>0.416</td>
<td>0.557</td>
<td>0.096</td>
</tr>
<tr>
<td>Aluminium</td>
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<td>0.801</td>
<td>0.867</td>
<td>0.119</td>
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<tr>
<td>Indium</td>
<td>433</td>
<td>0.251</td>
<td>0.561</td>
<td>0.075</td>
</tr>
<tr>
<td>Lead</td>
<td>613</td>
<td>0.211</td>
<td>0.457</td>
<td>0.275</td>
</tr>
</tbody>
</table>

CONCLUSIONS

We have reported the various surface and transport properties of liquid metals Na, K, Cs, Mg, Al, In and Pb above their respective melting temperatures. Conclusions drawn from the present work are as follows:

1. We have calculated S_v for liquid metals using D data of the SW model. We have estimated η_vγ and S_v of the considered liquids. The present computed values were compared with their corresponding experimental results and we find the agreement is satisfactory.

2. Structure factor in the long wavelength limit S(0) is derived through equation of state for SW potential. S(0) data were employed to compute isothermal compressibility of liquid metals. We find a good agreement between the computed and experimental values of Isothermal compressibility.

3. The diffusion data obtained from perturbation of SW potential over hard sphere reference system gives a good result for the calculation of various Transport and surface properties of liquid metals.
Acknowledgement

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