

Structure, thermodynamic and surface properties of liquid metals investigated by Square well potential

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Abstract: The auto correlation function, $S(k)$ (where $k = \frac{4\pi}{\lambda} \sin\theta$) and its Fourier component $g(r)$ are important quantities characterizing the structure of a liquid. Experimentally these quantities have been determined using neutron or X-ray scattering intensities. Wertheim's solution of the fundamental statistical mechanical equation given by Percus and Yevick for hard spheres mixture is invoked with square well attractive part as a perturbation tail to evaluate the direct correlation function $C(k)$ in momentum space through which structure factor, $S(k)$ of liquid metals were derived. Radial distribution function, $g(r)$ is obtained by Fourier analysis of computed $S(k)$ from which the coordination numbers of ten liquid metals were computed. Surface tension of atomic liquids in terms of diffusion coefficient has been determined under square well interaction. The computed values of structural dependent coordination number, diffusion coefficient and surface tension of these liquid metals are compared with the available experimental results and a good agreement is found between the computed and experimental results

Keywords: Square well potential, structure factor, Diffusion coefficient, coordination Number, surface tension

1. Introduction

The subject of statistical mechanics has been successfully applied in various fields including the prediction of the microscopic function, $S(k)$ of liquid metals [1-3]. A detailed knowledge of the $S(k)$ or $g(r)$ is essential for a quantitative understanding of the structure of liquids and is also sufficient to determine numerous other equilibrium and non equilibrium properties [4]. Wertheim [5] and Thiele [6] (WT) solved Percus-Yevick's (PY) equation for hard sphere fluids to obtain the hard sphere direct correlation function $C_{hs}(r)$. Liquid metals static structure factors behave like hard sphere fluids and calculations for thermo-physical and thermodynamic properties with such reference system have been found to be reasonable in many cases [7]. However, the hard sphere reference system lacks realistic properties because thermodynamics and the relation between thermodynamics with $S(k)$ or $g(r)$ are different for hard sphere and real fluids [8]. Hence, it is important to include attraction between the particles in deriving structure factor of liquids. Further, it is pointed out that the success of any theoretical model depends on its experimental confirmation [9, 10]. Thus in this work the square-well (SW) attractive tail has been perturbed over hard sphere reference system (WT) to evaluate the direct correlation function $C(k)$ in momentum space in order to compute $S(k)$ of real liquids. The analytical solution of this model in the mean spherical model was introduced by Rao *et al.* [11- 13]. The model is applied to set of liquid metals to obtain microscopic structural characteristics with their application in the determination of various properties of the considered systems.

The SW potential includes both repulsive and attractive parts and easy to solve numerically and hence it is most suitable for different theoretical techniques, such as integral equations or perturbation theories. The SW potential has been successfully applied for metallic liquids [3, 11-14],



colloidal particles [15, 16], hetro-chain molecules [17, 18] and complex systems [19, 20]. Here we consider that the multi-particle interactions are due to the sum of pair wise interactions.

The study of surface tension of melts is of fundamental importance and the better understanding of these properties is helpful in material processing technology. Several authors have reported that the surface properties of liquids are very much depending on their bulk micro structural characteristics and their transport properties.

In this work, self-diffusion coefficient, D , of liquids were determined using microscopic structure $S(k)$, $g(r)$ and pair wise interaction SW. Obtained D of considered liquids were employed in the determination of surface tension, γ_{ST} , recently published by many authors with different approaches [21, 22]. Lu *et al.* [23] reported that the γ_{ST} is not well known experimentally even for many simple metals.

2. Theoretical formalism

2.1. Evaluation of static structure factor and coordination number

The SW is an extension of hard sphere potential as it retains hard sphere repulsive properties but allows the particles to attract one another and the interaction energy $U(r)$ between two square well particles separated by a distance r is given by

$$\beta U(r) = \begin{cases} \infty & ; \quad r < \sigma \\ -\varepsilon & ; \quad \sigma < r < \lambda\sigma \\ 0 & ; \quad r > \lambda\sigma \end{cases} \quad (1)$$

where, σ is the hard core diameter, $\sigma(\lambda-1)$ and $\varepsilon(<0)$ are the breadth and depth of the potential well, $\beta = 1/k_B T$.

An important model system is the MSMA and was first proposed by Lebowitz and Percus [22] which expressed $g(r)$ and the direct correlation function $C(r)$ as

$$\left. \begin{aligned} g(r) &= 0 & ; & \quad r < \sigma \\ C(r) &= -U(r)/k_B T & ; & \quad r > \sigma \end{aligned} \right\} \quad (2)$$

We write the Ornstein-Zernike direct correlation function (DCF) of square well fluid in momentum space under MSMA as

$$C(k) = C_{hs}(k) + C_{sw}(k). \quad (3)$$

With

$$\rho C_{hs}(k) = - [24 \eta / (x)^6] [\alpha (x)^3 \{ \sin(x\sigma x - x \cos(x)) + \beta (x)^2 \{ 2x \sin(x) - (x^2 - 2) \cos x - 2 \} + \gamma \{ (4x^3 - 24x) \sin(x) - (x^4 - 12x^2 + 24) \cos x - 24 \} \}]. \quad (4)$$

$$\rho C_{sw}(k) = [24 \eta \varepsilon / k_B T] (x)^3 [\sin(\lambda x) - \lambda x \cos(\lambda x) + x \cos(x) - \sin(x)]. \quad (5)$$

where, $x = k\sigma$, ρ is the number density, ε and λ represent depth and breadth respectively, of the square well and the other terms that enter in Eq. (4) are given by following expressions [24].

$$\alpha = \frac{(1 + 2\eta)^2}{(1 - \eta)^4} \quad (6)$$

$$\beta = - \frac{6\eta (1 + \eta/2)^2}{(1 - \eta)^4} \quad (7)$$

$$\gamma = \frac{\eta \alpha}{2} \quad (8)$$

Where η is called packing fraction i.e. volume occupied by the atoms divided by total volume and is given by

$$\eta = \frac{\pi \rho \sigma^3}{6}. \quad (9)$$

The $S(k)$ of one component liquid can be given in terms of $C(k)$ as

$$S(k) = [1 - \rho C(k)]^{-1}. \quad (10)$$

The Fourier inversion of $S(k)$ gives the radial distribution function, $g(r)$.

$$g(r) = 1 + \frac{1}{2\pi^2 \rho} \int_0^\infty k^2 [S(k) - 1] \frac{\sin(kr_{nm})}{kr_{nm}} dk. \quad (11)$$

Further we derived self-diffusion coefficients of all the concerned liquid metals using well known Einstein's formula $D = \frac{k_B T}{\zeta_H + \zeta_S + \zeta_{HS}}$. Here ζ_H , ζ_S and ζ_{HS} are the friction coefficients due

to hard, soft and hard-soft part of the potential function respectively and are obtained in line with Ref. [4] under Helfand's linear trajectory principle using a SW tail as a soft perturbation over hard sphere reference system and can be given as follows

$$\zeta_H = \frac{8}{3} \rho \sigma^2 (\pi m k_B T)^{1/2} g^{HS}(\sigma) \quad (12)$$

$$\zeta_S = -\frac{1}{3} \frac{\rho}{4\pi^2} \left(\frac{\pi m}{k_B T} \right)^{1/2} \int_0^\infty \frac{1}{\rho} k^3 U^{SW}(k) [S(k) - 1] dk. \quad (13)$$

$$\zeta_{HS} = -\frac{1}{3} \rho g^{HS}(\sigma) \left(\frac{m}{\pi k_B T} \right)^{1/2} \times \int_0^\infty [k\sigma \cos(k\sigma) - \sin(k\sigma)] U^{SW}(k) dk. \quad (14)$$

Here $U^{SW}(k)$ is the Fourier transform of SW potential

$$U^{SW}(k) = \frac{4\pi\epsilon}{k^3} [Ak\sigma \cos(Ak\sigma) - \sin(Ak\sigma) - k\sigma \cos(k\sigma) + \sin(k\sigma)] \quad (15)$$

2.2. Relation of self-diffusion coefficient in bulk liquid metals to surface properties.

The detail studies of surface properties of condensed matter help in understanding their metallurgical processing. The surface tension of elemental liquids can be given by statistical mechanical approach under zeroth order approximation as [25]

$$\gamma_{ST} = \frac{\pi \rho^2}{8} \int_0^\infty \frac{dU(r)}{dr} g(r) r^4 dr. \quad (16)$$

Born and Green [26] derived the coefficient of viscosity of liquid metals using statistical mechanical approach as

$$\eta_V = \frac{2\pi\rho^2}{15} \left(\frac{m}{K_B T} \right)^{1/2} \int_0^\infty \frac{dU(r)}{dr} g(r) r^4 dr. \quad (17)$$

Here m is the atomic mass of the liquid metals. Eqs. (16) and (17) were derived on a strong scientific basis for hard sphere model but it is not easy to get the numerical solution of the integral equations. A striking result can be obtained using Eqs. (16) and (17) with the well-known Stokes-

Einstein relation, $\eta_V = k_B T / (2\pi a D)$, here a , the nearest neighbor distance, can be taken as first peak position of $g(r)$ for real liquids as [27]

$$\gamma_{ST} = \frac{(k_B T)^{3/2}}{m^{1/2}} \frac{15}{32 \pi a D}. \quad (18)$$

Since, D can be evaluated from well-known Einstein's relation using the SW long range interaction and hence the surface tension of liquid metals is obtained through Eq. (18).

3. Results and discussion

The WT solution of PY hard sphere fluid within the MSMA with SW perturbation can be solved numerically with the input data: temperature, T , atomic density, ρ , and the SW parameters. The input parameters of liquid metals are listed in Table 1.

TABLE 1. Input parameters of liquid metals with σ as the diameter, ϵ/k_B as the depth, λ as the breath of the square well potential and ρ as the number density.

Metals	Temperature (K)	σ (nm)	ϵ/k_B (K)	λ	ρ (10^{25} m^{-3})
Sodium	378	0.330	111.60	1.65	2430
Potassium	343	0.411	96.14	1.65	1276
Cesium	303	0.481	109.5	1.70	0813
Magnesium	953	0.275	127.82	1.43	3900
Aluminum	943	0.245	160.00	1.30	6459
Indium	433	0.283	173.76	1.70	3686
Lead	613	0.297	70.00	1.4	3099
Silver	1273	0.260	500.00	1.75	5159
Copper	1423	0.225	300.00	1.68	7408
Gold	1373	0.260	600.00	1.73	5271

The peak positions and peak heights of the computed $S(k)$ and $g(r)$ for all the considered liquid metals are presented in Table 2 with their experimental data, which give the detailed information regarding the principal peak and structural characteristics of the metals. From Table 2, it is seen that the agreement between our computed $S(k)$ and the experimental results [28] around the first peak appears to be very good.

TABLE 2. Theoretical and experimental values of first positions (k) and peak heights $S(k)$; first peak positions (r) and peak heights $g(r)$ of liquid metals.

Metals	First Peak of $S(k)$				First Peak position $g(r)$			
	Theoretical		Experimental		Theoretical		Experimental	
	k (nm^{-1})	$S(k)$	k (nm^{-1})	$S(k)$	r (nm)	$g(r)$	r (nm)	$g(r)$
Na	20.0	2.7	20.0	2.7	0.36	3.24	0.37	2.42
K	16.0	2.6	16.0	2.6	0.45	2.80	0.46	2.35
Cs	14.0	2.5	14.0	2.7	0.50	3.61	0.51	2.58
Mg	25.0	2.5	24.0	2.5	0.29	2.84	0.31	2.46
Al	27.0	2.4	27.0	2.4	0.27	2.47	0.28	2.83
In	23.0	2.4	23.0	2.5	0.30	2.64	0.31	2.66
Pb	23.0	2.5	23.0	2.5	0.32	2.34	0.32	2.98
Ag	26.0	2.3	26.0	2.5	0.28	2.98	0.28	2.58
Cu	30.0	2.4	30.0	2.7	0.25	2.35	0.25	2.75
Au	26.0	2.4	26.0	2.5	0.28	2.68	0.28	2.77

The calculated results for $S(k)$ of these metals at their respective temperatures together with their experimental results entire momentum space are depicted in Figure 1.

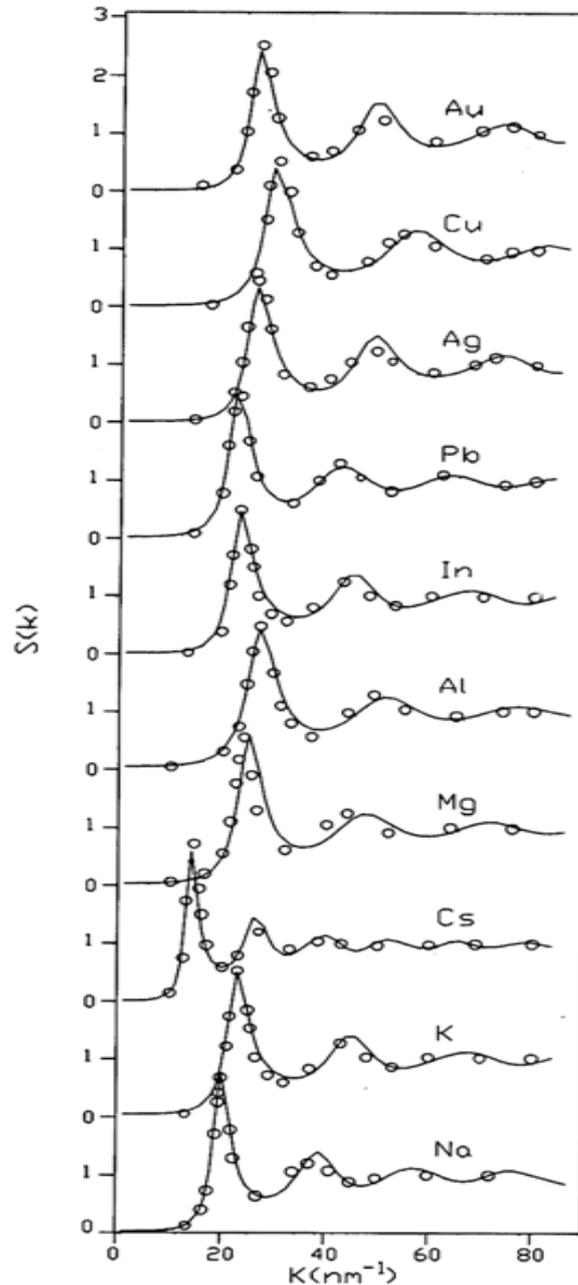


Figure 1. $S(k)$ against k for liquid metals; (—) theoretical values, (ooo) experimental values.

We find from Figure 1 that structure factors of all the considered metals become constant around one in high k region. It shows the presence of short range order in liquid materials.

The peak positions and peak heights of the $g(r)$, computed from Eq. (11), for all the considered metals with their experimental values are listed in Table 2 and also presented in Figure 2(a) and Figure 2(b). The ratio of the positions of the first and second peaks of the calculated and the experimental $g(r)$ for all the liquids taken under investigation is about 0.51 and 0.53 respectively. This

suggests that our model calculation of $g(r)$ gives the structural properties of real liquids fairly well. The deviation of $g(r)$ from unity is a measure of the local order around the reference atoms.

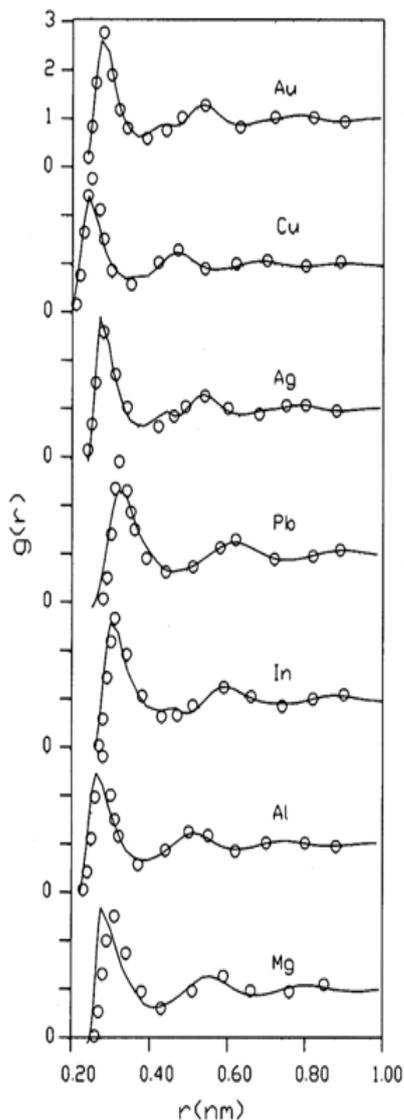


Figure 2(a). $g(r)$ against r for liquid metals; (—) theoretical values, (ooo) experimental values.

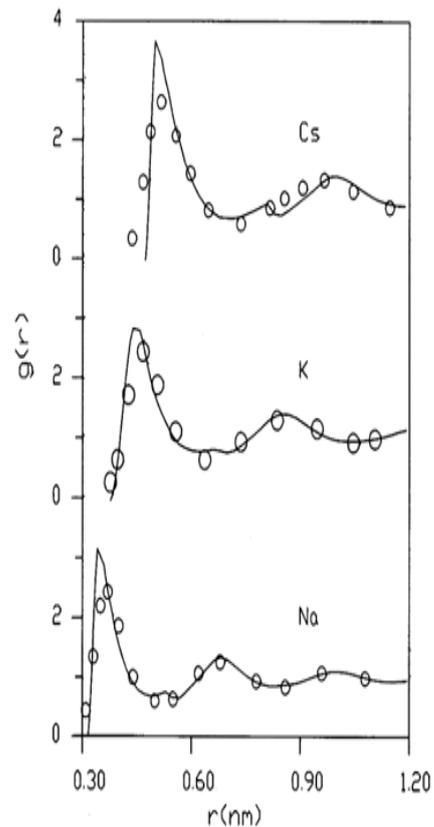


Figure 2(b). $g(r)$ against r for liquid metals; (—) theoretical values, (ooo) experimental values.

Computed values of friction coefficients ζ_H , ζ_S and ζ_{HS} of the considered liquid metals are presented in Table 3. ζ_H is dominating in all cases as per our expectation because hard sphere repulsive forces dominating in the calculation of microscopic structural functions. However, ζ_S and ζ_{HS} also contribute significantly in the case of all liquid metals. These friction coefficients depend on soft part of the potential function.

TABLE 3. Friction coefficients of liquid metals due to hard sphere ζ_H , square well ζ_S and hard sphere- square well interaction ζ_{HS} .

Metals	$\zeta_H \times 10^{-13} (\text{Kg/s})$	$\zeta_S \times 10^{-13} (\text{Kg/s})$	$\zeta_{HS} \times 10^{-13} (\text{Kg/s})$
Na	7.41	1.56	1.94
K	7.55	1.12	1.58
Cs	7.56	1.50	1.89
Mg	11.78	1.36	1.19
Al	11.98	1.76	1.07
In	18.14	4.39	5.38
Pb	25.59	2.04	1.75
Ag	42.28	8.25	12.56
Cu	31.96	2.78	4.53
Au	62.19	11.05	18.65

The diffusivity in liquid metals has been evaluated under LT principle as mentioned in Ref. [4] using well known Einstein equation for coefficient of diffusion [29]. Computed results are compared with available experimental results [27] and presented in Table 4.

The surface tension is related with self-diffusion coefficients of liquids. Since self-diffusion coefficients of liquids are determined using microscopic structural functions along with SW potential and hence computed γ_{ST} is also related microscopic structure of liquids. Computed values of γ_{ST} with their experimental values taken from Ref. [23] are also presented in Table 4 and we find satisfactory agreement between them.

TABLE 4. Theoretical and experimental values of Diffusion coefficient, $D(10^{-9} \text{ m}^2/\text{sec})$ and Surface tension, $\gamma_{ST}(\text{Nm}^{-1})$ of liquid metals.

Metals	D_{Computed}	$D_{\text{Experimental}}$	$\gamma_{ST\text{Computed}}$	$\gamma_{ST\text{Experimental}}$
Na	4.70	4.23	0.176	0.200, 0.197
K	4.28	3.76	0.096	0.110, 0.112
Cs	2.18	2.31	0.082	0.069, 0.070
Mg	5.23	5.63	0.418	0.557, 0.583
Al	4.93	4.87	0.801	0.867, 1.070
In	2.10	2.60	0.251	0.561
Pb	2.87	2.19	0.211	0.457, 0.462
Ag	2.61	2.55	1.026	0.925, 0.910
Cu	4.85	3.97	1.030	1.310, 1.320
Au	2.10	-	1.200	1.145, 1.138

Conclusions

In the present study, we present results of microscopic structural functions of ten liquid metals. The SW potential is analytically solved in repulsive and attractive regions and successfully applied for computing static structure factor and thermodynamic properties of the considered liquids, which are important information for metallurgical industry. Our results indicate that the SW model leads to a good agreement between computed and experimental results of structure factors and derived associated properties and hence such kind of theoretical works increase our confidence in present model. This model calculation provides an option to use the SW potential in the framework of MSMA

to derive the various thermo-physical and thermodynamic properties of liquid metals without using any adjustable parameter.

Perturbation theory with hard sphere reference system is a good first approximation for the study of static and dynamic properties of liquid metals. The resulting correlation between D and γ_{ST} finds successful application for the estimation of γ_{ST} .

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