

CALCULATION OF THE STRUCTURE FACTOR OF LIQUIDS METALS

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Abstract

Applying the solution of the Percus-Yevick equation to a one component system and using a screened pseudopotential, a model is developed for calculating the structure factor of liquid metals at different temperatures and densities. The model was tested using both simple and non-simple liquid metals. The results obtained were in very good agreement with experimental values for all the metals used to test the model. The model can reproduce the peak positions in the structure factor of liquid metals within the limit of experimental errors. Also the study revealed that the peak positions in the structure factor of liquid metals occur when the screened potential is a minimum. Also, increase in temperature increases the magnitude of the structure factor but does not affect the peak positions. The model can be use to calculate the structure factor of liquid metals at different temperatures and densities.

Keywords: One component, structure, factor, screened potential

1. Introduction:

Liquid metals and alloys are classified as simple liquids: liquids that are composed of spherical and nearly spherical "molecules" and are predominantly two-body central bonding forces. The appropriate dynamic units of liquid metals and alloys have sufficient symmetry that for fixed volume, their mutual interactions can be written as functions of their mutual separations only (Ashcroft and Stroud, 1978). Liquid metals are characterized by a mixture of ions and conduction electrons moving nearly freely through an array of ions, and also by strong correlation between them (Takeda et al; 1996). The interactions between atoms in the liquid are sufficiently treated using the one component system with hard sphere interactions. In the one component system, the positive ions move about in a neutralising background of constant density. This is physically realistic only when the atoms are completely ionized at very high densities and low temperature (Ross et al; 1981).

The static structure factor of liquid metals is one of the important properties characterizing the liquid metals. A detailed knowledge of the structure factor is essential for a qualitative understanding of not only the structure of the liquid, but also of other numerous properties of liquid metals and alloys (Greenfield et al;

1971). The static structure factor is a measure of the inter-particle correlation in the reciprocal space. Accurate knowledge of the structure factor is crucial for studying numerous thermodynamic and transport properties of any fluid system. The structure factor is used to calculate thermodynamic, kinetic and other properties of liquid metals (Allahyarov et al; 1995). Knowledge of the static structure factor within a large range of the wave vector provides information on both macroscopic properties, obtained in the limits of very small wave vector and the microscopic structure at higher momenta (Jovic et al; 1977). Experimentally, the structure factor of liquid metals and alloys are determined using X-ray diffraction and neutron diffraction techniques (Burkel, 1999, Komarnytsky et al; 1996, Knoll, 1977, Jovic et al; 1977, Block et al; 1977, Greenfield et al; 1971).

Over the years, theoretical study of the structure factor of liquid metals has attracted much attention. Different researchers have used different approaches to study the structure factor of liquid metals. Common observation is that an approach works for a particular liquid metal or liquid metals that have similar characteristics (Ravi et al; 2001, Sigh and Holz, 1983, Ailawadi and Miller, 1976, Wang et al; 2005, Rosik et al; 2004,

Farzi and Safari, 2005, Bhuiyan et al; 1999). These may be due to (i) the use of an effective potential that depends mainly on the electron density (ii) the use of hard spheres interactions as initial approximation; this cannot be effective in the description of expanded liquids because hard sphere systems do not have critical point (iii) the use of effective potential as a real potential of ion-ion interaction.

In this paper, using the one component system, the solution of the Percus-Yevick equation, a suitable potential and screening factor, a model is developed for calculating the structure factor of liquid metals at any density, temperature, and packing fraction.

2. Theoretical consideration and calculation

Consider a system of N particles of volume V at a temperature T. In this system, there is thermodynamic limit (N, V, and N/V = density). The pair potential between the particles can be written as

$$w(r) = \begin{cases} \infty & r < d \\ v(r/d) = e^2/\epsilon_0 r & r > d \end{cases} \quad (1)$$

where d is the hard core diameter, e is the electronic charge of the particles. ϵ_0 is the static dielectric constant of the system. Since the electron background is uniform, its dielectric constant is unity. The charged particles are present with oppositely charged background, which preserves over-all electrical neutrality. This system is a two-component system with the following properties

$$\rho_1 e_1 + \rho_2 e_2 = 1 \quad (2)$$

$$g_{12} = g_{21} = g_{22} = 1 \quad (3)$$

where g_{ij} is the radial distribution function between species i and j and $\rho_i = N_i/V$. Subscript 1 is for the charged sphere while 2 is for the background particles.

The background particles are not involved in any correlation, it merely sets the zero of energy for the system and it does not have direct effect on the structure of the hard sphere fluid. This assumption reduces our system to a one component system such that $\rho = \rho_1, e = e_1, g = g_{11}$.

We introduce the following dimensionless parameter

$$x = \frac{r}{d}, \quad \eta = \frac{1}{6}\pi\rho d^3, \quad \gamma = \frac{\beta e^2}{d}, \quad k = (24\eta\gamma)^{1/2} \quad (4)$$

where d is the effective hard core diameter, η is the packing fraction, γ is the ion-ion coupling strength and k is the Debye Huckel inverse screening length.

The mean spherical model integral equation consists of the Ornstein-Zernike equation (Palmer and Week, 1973)

$$h(x) = c(x) + \rho d^3 \int h(|x-x'|)c(x')dx' \quad (5)$$

together with the closure relations $h(x) = -1$ or $g(x) = 0$ for $x < 1$ $c(x) = -v(x) = -\gamma/x$ for $x > 1$ β/kT , where k is Boltzmann constant, T is temperature and $h(x) = g(x) - 1$ and $c(x)$ is the direct correlation function. Equation (5) is solved for $c(x)$ in $x < 1$ and for $h(x)$ in $x > 1$. The solution of equation (5) for $c_0(x)$ (Palmer and Week, 1973, Singh and Holz, 1983, Ravi et al; 2001) is

$$c_0(x) = A + Bx + Cx^2 + Dx^3 + Ex^5 \quad \text{for } x < 1 \quad (6)$$

where

$$A = -\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{Q^2}{4(1-\eta)^2} - \frac{(1+\eta)Qk}{12\eta} - \frac{(5+\eta^2)k}{60\eta} \quad (7)$$

$$B = 6\eta M^2, \quad C = \frac{k^2}{6} \quad (8)$$

$$D = \frac{\eta}{2}(A + k^2u), \quad E = \frac{\eta k^2}{60} \quad (9)$$

Here,

$$Q = \frac{1+2\eta}{1-\eta} \left[1 - \left[1 + \frac{2(1-\eta)^3 k}{(1+2\eta)^2} \right]^{1/2} \right] \quad (10)$$

$$M = \frac{Q^2}{24\eta(1-\eta)} - \frac{(1\oplus.5)\eta}{-\eta^2} \quad (11)$$

$$u = -\frac{(1+\eta-0.2\eta^3)}{12\eta} - \frac{(1-\eta)Q}{12\eta k} \quad (12)$$

The static factor is described by the Fourier transform C(q) of the Ornstein-Zernike direct

correlation function as

$$S(q) = [1 - \rho C_0(q)]^{-1} \tag{13}$$

Fourier transforming equation (6) gives (Palmer and Week, 1973)

$$\rho C_0(q) = \frac{24\eta}{q^6} \left\{ \begin{aligned} &Aq^3(\sin q - q \cos q) + Bq^2[2q \sin q - (q^2 - 2)\cos q - 2] + \\ &Cq[(3q^3 - 6)\sin q - (q^2 - 6)q \cos q] + D[(4q^3 - 24)q \sin q \\ &- (q^4 - 12q^2 + 24)\cos q + 24] + E[6(q^4 - 20q^2 + 120)q \sin q \\ &- (q^6 - 30q^4 + 360q^2 - 270)/q - \gamma q^4 \cos q \end{aligned} \right\} \tag{14}$$

In the long wavelength limit, equation (13) reduces to

$$\lim_{q \rightarrow 0} S_0(q) = \frac{q^2 \sigma^2}{24\eta\gamma} \left[1 + \frac{\alpha - 1}{24\eta\gamma} q^2 \sigma^2 \right] \tag{15}$$

where,

$$\alpha = 24\eta \left[\frac{A}{3} + \frac{B}{4} + \frac{C}{5} + \frac{D}{6} + \frac{E}{8} + \frac{\gamma}{2} \right] \tag{16}$$

We assume a weak electron-ion coupling, which is the basis of a pseudopotential approach. Within the linear screening approximation, the static structure factor of liquid metal is given by

$$S(q) = \frac{S_0(q)}{1 + \rho \beta V_{sc}(q) S_0(q)} \tag{17}$$

Where,

$$V_{sc}(q) = \frac{v^2(q)}{\Phi(q)} \left[\frac{1}{\epsilon(q)} - 1 \right] \tag{18}$$

Is the attractive screening correction to the direct ion-ion potential. $\Phi(q)$ is the Fourier transform of bare Coulombic interaction between two electrons. q is the wave vector dependent dielectric function. The dielectric function used in this work is the modified Hartree dielectric function in the low wave vector limit (Harrison, 1967) as the modified dielectric function give good account of ionic correlation in metals. Also, with this dielectric function, at small q , components of the potential are well screened and the dielectric function used is

$$\epsilon(q) = \frac{4\pi m e^2 k_f}{\pi \hbar^2 q^2} \tag{19}$$

where m is the electronic mass, e is charge of an electron, and k_f is the Fermi wave factor.

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For the potential, $V(q)$, the Ashcroft empty core pseudopotential is used. It is given as

$$V(q) = -\frac{4\pi z e^2}{q^2} \cos q r_c \tag{20}$$

where r_c is Ashcroft core radius obtained from the stabilization condition (Perdew et al; 1990)

$$r_c = \left[\frac{2}{15} \left(\frac{9\pi}{4} \right)^{2/3} r_s^3 + \frac{1}{6\pi} \left(\frac{9\pi}{4} \right)^{1/3} r_s^2 + \frac{1}{5} z^{2/3} r_s^2 + \frac{2}{9} r_s^4 \frac{dE_c}{dr_s} \right] \tag{21}$$

where r_s is the electron gas parameter while E_c is the electron-electron correlation energy of Carpely and Alder (1980) as parameterized by Perdew and Zunger (1981). The Fourier transform of the bare Coulombic interaction between two electrons is

$$\phi(q) = \frac{4\pi e^2}{q^2} \tag{22}$$

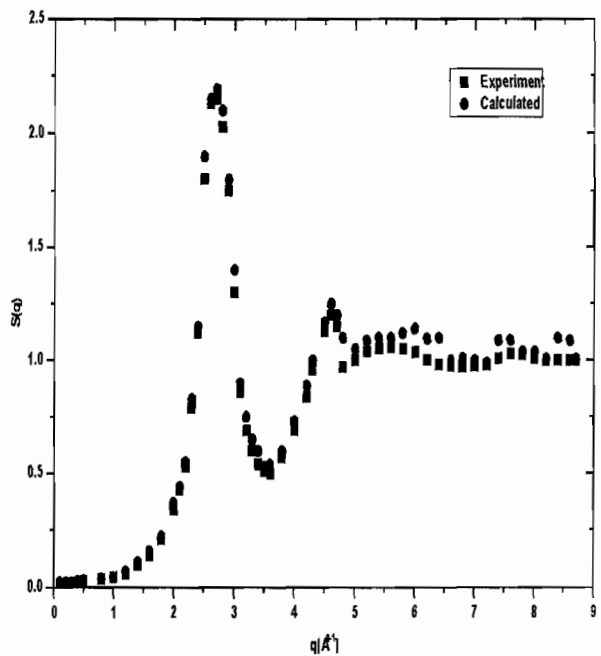


Fig. 1: Experimental and calculated structure factor of aluminium at 666°C. The experimental values were obtained from Jovic et al (1977).

3. Results and Discussion

A computer programme was developed to

calculate the static structure factor of liquid metals at different values of the wave vector, temperature, and density of the liquid metal using equations (17) to (22). Figures 1 and 2 show the calculated and experimental static structure factor of aluminium at the temperatures of 666°C and 707°C . As revealed from the figure, there is a one to one agreement between the experimental static structure factor of liquid aluminium and that calculated in this work. As can be seen from the figure, the first peak is quite high compared to the other humps and the first peak is the most important characteristic feature of the static structure factor of liquid metals. The peak positions occur when the screened potential

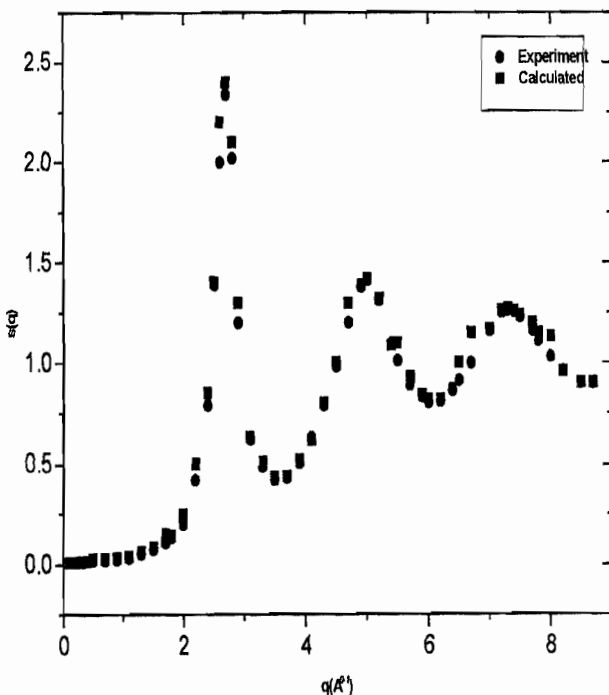


Fig. 2. Experimental and calculated structure factor of aluminum at 800°C . The experimental values were obtained from Jovic et al, (1977).

structure factor of liquid magnesium metal is in good agreement with experimental results, although the calculated structure factor of liquid magnesium is a little above the experimental values.

given in equation (18) is a minimum. This proves that the static structure factor of liquid metals is sensitive to the potential but not to the details of the potential (Ravi et al; 2001). Comparing figures 1 and 2, it can be observed that increase in temperature causes an increase in the height of the peak of the structure factor but does not cause a change in the position of the peak. This may be due to increase in the distance between the ions with the consequential reduction in the correlation between the ions and a smaller value of the potential between them.

Figure 3 is the variation of the calculated and experimental static structure factor of liquid magnesium metal with wave vector. As can be seen from the figure, the calculated

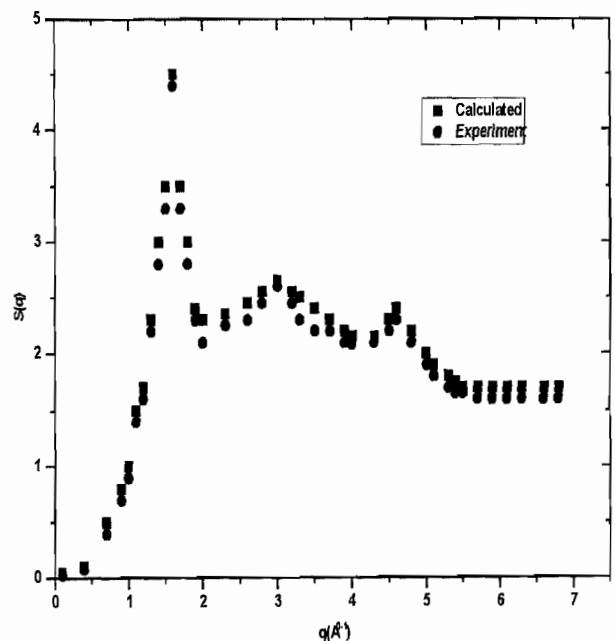


Fig. Calculated and experimental structure factor of potassium at 135°C . The experimental data were obtained from Greenfield et al (1971)

Table 1 shows the calculated and experimental peak position of some liquid metals and the parameters used to calculate them. As can be seen from the table, the model can reproduce exactly the peak position of the following liquid metals: Na, K, Al, Mg, Hg, and could fairly predict the peak position of the other

liquid metals within the range of $q = 0.50 \text{ \AA}$. From figures 1, 2, 3 and table 1, it can be inferred that the liquids whose static structure factor was calculated in this work behave like hard sphere fluids. The success of the model can be attributed to the use of a dielectric function, which effectively screens the potential.

4. Conclusion

The static structure factor of liquid metals

was calculated based on a simple model. From the study, it can be seen that the structure factor of liquid metals depends inversely on the screened potential of the liquid metal. The peak position of the structure factor of liquid metals is an intrinsic property of the liquid metal. Increase in temperature causes an increase in the peak height as a result of reduction in the ion-ion interaction.

Table 1: Experimental and calculated peak positions in the structure factor of liquid metals and the parameters used to calculate them. The experimental values we obtained from Waseda, (1977).

Temperature °C	Density	Parking fraction	Peak position	
			Experiment	Calculated
180	0.504	0.46	2.49	2.20
105	0.928	2.03	2.00	0.46
70	0.826	0.46	1.61	1.60
40	1.47	0.43	1.53	1.70
30	1.84	0.43	1.47	1.70
680	1.545	0.46	2.42	2.50
850	1.37	0.46	1.95	2.20
780	2.38	0.46	1.78	2.10
730	3.32	0.46	1.73	2.10
450	6.91	0.46	2.93	2.60
350	7.954	0.45	2.60	2.50
20	13.55	0.45	2.32	2.40
670	2.37	0.45	2.80	2.80
50	6.082	0.43	2.52	2.70
160	7.03	0.45	2.30	2.60
315	11.27	0.45	2.26	2.70
1150	7.97	0.46	3.00	2.80
1000	9.27	0.45	2.61	2.30
1150	17.2	0.46	2.66	2.30
1900	5.36	0.44	2.71	3.10
1260	5.97	0.45	2.83	2.90
1900	6.27	0.45	3.01	2.60
1550	7.01	0.44	2.78	2.70
1550	7.70	0.45	3.02	2.80
1500	7.72	0.45	3.10	2.80
1580	10.5	0.47	2.81	269

etal

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