

Evaluation of activation energies and other properties from structural studies of liquid metals and their extension to liquid Ag–In alloy

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Abstract

Using a hard sphere reference system with square well attractive tail the structure factors are computed for pure metals and then extended to Ag–In binary alloy. The agreement between the theoretical and experimental values is good. Further new equations have been derived for the temperature variation of diffusion coefficients and they are applied successfully to pure metals and extended to the binary Ag–In alloy. The applicability of these equations is verified by evaluating the activation energies and comparing them with literature values for these systems. The chemical short-range order parameter has been computed as a function of composition for Ag–In system through structural studies in the long wave limit, which gives valuable information regarding the nature of the liquid alloy at various compositions.

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1. Introduction

The subject on structural studies of liquid metals and alloys with their applications in recent days [1–4] is being investigated to understand the complexities of liquids. There are liquids of various types of clusters and structures for example liquid selenium has various types of structures like ring structure, chain structure and helix type. Thus a single radius for liquid selenium is not appropriate. Hence one should possibly consider more than one radius to get the correct structure factor. Thus it should be treated as multi component system.

Liquid metal structure factors resemble closely to hard sphere reference systems, and calculations to evaluate static and dynamic properties have been found to be quite reasonable in many cases [5]. It must be mentioned that short range forces primarily determine the structure of a liquid and the relatively long-range attractive part of the potential provides a uniform attractive background. Hence even if one gets the results correctly, with just hard sphere part we cannot conclude that the model can be judged according to the success with which we account for determining the properties of liquids, as the hard sphere potential lacks realistic properties. Thus in evaluating the properties we take into consideration an attractive part with hard sphere reference system. The square well fluid is the simplest one possessing the basic characteristics of a real fluid. Recently application of square-well potential to liquids is being worked to evaluate various properties [6–8]. It is an excellent model [9]

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for liquids in which internal degrees of freedom of individual particles are not important. Here we consider, that pair wise potential plays a significant role and multiparticle interactions do not play a major role. We apply the square well model to a sample of liquid metals to compute the activation energy of the metals. Further we also extend these concepts to binary alloy taking Ag–In system as an example. We also formulate expressions for the temperature gradient of diffusion coefficients from the structural aspects of liquid metals and alloys.

It may be mentioned that several authors have reported X-ray and neutron diffraction results of different liquid alloys but the resulting picture is not entirely satisfactory. This is due to the fact that a unique set of partial structure factors cannot be determined from two diffraction measurements [10]. A model calculation provides a way to compute the three partial structure factors. We then compute total structure factors, which are incorporated to evaluate activation energy.

2. Theory

We use square well as an attractive tail over hard sphere reference system to evaluate the structure factors of liquid metals [11,12]. Thus we write the Direct Correlation Function (DCF) of square well fluid as

$$C(r) = C_{\text{hs}}(r) + C_{\text{sw}}(r). \quad (1)$$

We use Wertheim's [13] solution of Percus–Yevick's equation for hard spheres along with a square well [14] attractive minimum as a perturbation over hard sphere reference system to evaluate the structure factors. The self-diffusion coefficient of the metals can be written as

$$D = \frac{k_{\text{B}}T}{\xi}. \quad (2)$$

Here ξ is the friction coefficient, which is a sum of the friction coefficients arising from the forces of hard-core and soft part given as follows:

$$\xi = \xi^{\text{H}} + [\xi^{\text{S}} + \xi^{\text{SH}}]. \quad (3)$$

The contribution from the partial friction coefficients i.e. hard core (ξ^{H}), the soft part (ξ^{S}) and the hard soft part (ξ^{SH}), which incorporate the radial and structural aspects, are given as follows:

$$\xi^{\text{H}} = \frac{8}{3} \rho g(\sigma) \sigma^2 (\pi m k_{\text{B}} T)^{1/2}, \quad (4)$$

$$\xi^{\text{S}} = -\frac{1}{3} \frac{\rho}{4\pi^2} \left(\frac{\pi m}{k_{\text{B}} T} \right)^{1/2} \int_0^\infty k^3 u^{\text{S}}(k) G(k) dk \quad (5)$$

$$\xi^{\text{SH}} = -\frac{1}{3} \rho g(\sigma) \left(\frac{m}{\pi k_{\text{B}} T} \right)^{1/2} \times \int_0^\infty [k\sigma \cos(k\sigma) - \sin(k\sigma)] u^{\text{S}}(k) dk, \quad (6)$$

$$u^{\text{S}}(k) = \frac{4\pi\epsilon}{k^3} [Ak\sigma \cos(Ak\sigma) - \sin(Ak\sigma) - k\sigma \cos(k\sigma) + \sin(k\sigma)], \quad (7)$$

$$G(k) = \frac{1}{\rho} [S(k) - 1]. \quad (8)$$

The logarithmic variation of the diffusion coefficient with temperature is evaluated from Einstein's equation and it is given by

$$\frac{d \ln D}{dT} = \frac{1}{T} - \frac{d \ln \xi}{dT}. \quad (9)$$

Hence to evaluate $\frac{d \ln D}{dT}$ we have to evaluate $\frac{d \ln \xi}{dT}$. Thus the gradient of the hard sphere part with respect to temperature is given by

$$\begin{aligned} \frac{d \xi^{\text{H}}}{dT} &= \frac{\xi^{\text{H}}}{2T} - \kappa \xi^{\text{H}} + \frac{8}{3} \rho \sigma^2 (\pi m k_{\text{B}} T)^{1/2} \\ &\times \left\{ \frac{2\kappa}{3} [g(\sigma) - 1] + \frac{\kappa}{6\pi^2 \rho} \int_0^\infty k^2 [S(k) - 1] \cos(k\sigma) dk \right. \\ &\left. + \frac{1}{2\pi^2 \rho \sigma} \int_0^\infty k \sin(k\sigma) Z(k) dk \right\}. \quad (10) \end{aligned}$$

The temperature derivative of the soft part and hard soft part of the friction coefficients are given by the following equations:

$$\frac{d \xi^{\text{S}}}{dT} = -\frac{\xi^{\text{S}}}{2T} - \frac{1}{12\pi^2} \left(\frac{\pi m}{k_{\text{B}} T} \right)^{1/2} \int_0^\infty k^3 u^{\text{S}}(k) Z(k) dk, \quad (11)$$

$$\begin{aligned} \frac{d \xi^{\text{SH}}}{dT} &= -\frac{\xi^{\text{SH}}}{2T} - \kappa \xi^{\text{SH}} - \frac{1}{3} \rho \left(\frac{m}{\pi k_{\text{B}} T} \right)^{1/2} \\ &\times \int_0^\infty [k\sigma \cos(k\sigma) - \sin(k\sigma)] u^{\text{S}}(k) dk \\ &\times \left\{ \frac{2\kappa}{3} [g(\sigma) - 1] + \frac{\kappa}{6\pi^2 \rho} \int_0^\infty k^2 [S(k) - 1] \cos(k\sigma) dk \right. \\ &\left. + \frac{1}{2\pi^2 \rho \sigma} \int_0^\infty k \sin(k\sigma) Z(k) dk \right\}. \quad (12) \end{aligned}$$

Here

$$\begin{aligned} Z(k) &= \frac{dS(k)}{dT} \\ &= \kappa [S(k)] \left\{ [1 - S(k)] + \frac{24\eta S(k)}{(k\sigma)^6} \left[\frac{4P\alpha\eta(2+\eta)}{(1+2\eta)(1-\eta)} \right. \right. \\ &\left. \left. + \frac{Q\beta(\eta^2+9\eta+2)}{(2+\eta)(1-\eta)} + \frac{R\gamma(2\eta^2+9\eta+1)}{(1+2\eta)(1-\eta)} - \frac{\epsilon S}{\kappa k_{\text{B}} T^2} \right] \right\}, \quad (13) \end{aligned}$$

and the other coefficients that enter in Eq. (13) are given by the following equations:

$$\alpha = \frac{(1+2\eta)^2}{(1-\eta)^4}, \quad (14)$$

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