

Calculation of thermodynamic and transport properties of less simple metals

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Abstract Thermodynamic properties like entropy and specific heat capacity at constant pressure and atomic transport property like shear viscosity coefficient have been investigated for nine less simple liquid metals namely Zn, Cd, Hg, In, Tl, Sn, Pb, Sb and Bi. The interionic pair potentials are derived from Bretonnet-Silbert model for local pseudopotential. The linearised WCA theory for liquid state has been used to estimate the hard sphere diameter, a basic ingredient, for calculating the physical quantities. Agreement of the calculated values for most of the systems with experimental ones is found to be quite good.

Keywords Less simple metals, specific heat capacity, shear viscosity

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Recently, we have investigated the thermodynamic and atomic transport properties of liquid transition and noble metals by using the N-body potentials [1]. Although the N-body potentials have proved to be successful for transition and noble metals, these have their own limitations of applicability to other metallic systems. In this work, we have investigated the thermodynamic and atomic transport properties of less simple metals namely Zn, Cd, Hg, In, Tl, Sn, Pb, Sb and Bi. Elements lying at the bottom of the three transition metal series have completely filled *d* bands. Nonetheless their physical properties are significantly influenced due to the *sd*-hybridization [2, 3]. This is the reason to call those metals as less simple ones. Therefore, a complete description of these systems needs a model that can take into account the effect of *sd*-mixing in the interionic interaction.

Recently, Bretonnet and Silbert (BS) have proposed a model to describe the interionic interaction of liquid transition metals [4]. The model treats *sp* and *d* bands separately within the well defined prescription of the pseudopotential theory. The *sp*-band is described via the empty core model; the *d*-band contribution is derived from the *d*-band scattering phase shift by using the inverse scattering approach. The BS model is simple to handle numerically. Moreover, the local form permits one to extend this model to other systems for which *sd*-hybridization effect is

significant. The BS model has also proved to be successful for liquid transition metal calculations [5].

The knowledge of the static structure factor or its Fourier transform namely the pair correlation function, is the prerequisite for a complete description of static, thermodynamic as well as transport properties of liquid metals. Very recently, Itami and Sugimura [6] reported that hard sphere (HS) results for shear viscosity for liquid Sn agree better with the corresponding space laboratory data [7]. Furthermore, HS analytic expressions for the above physical properties are well documented [8]. Therefore, it is natural to choose the HS reference as a first approximation in the perturbative calculation. The liquid state theory used in the present case is the linearized Weeks-Chandler-Andersen (LWCA) method [9].

The study of viscosity is important for the metallurgical and industrial purposes. For example, the rates of many industrially important reactions are limited by the diffusion of reactant species. Moreover, knowledge of viscosity is required in the theoretical determination of critical cooling rates for glass formation. The aforementioned aspects and prospects of the BS model encouraged us to do this work.

In the Bretonnet-Silbert model, the contribution due to nearly free electron band formed by *s*- and *p*- states is separated from

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the due to d -band. The local pseudopotential may be written as [4]:

$$w_0(r) = \sum_n B_n \exp(-r/na) \quad \text{if } r < R_c, \quad (1)$$

$$= -Z_s e^2 / r \quad \text{if } r > R_c,$$

where R_c stands for empty-core radius, Z_s for effective number of valence electrons per atom and a for softness parameter. The effective interionic potential $\phi(r, \rho)$ with ρ the ionic number density, is obtained by usual procedure [8]. The dielectric function relating the local field correction was taken from Ichimaru and Utsuni [10]. The values of R_c were taken from Harrison [11]. The effect of hybridization between s and d electrons was accounted for by changing the relative occupancy of s and d bands. By integrating the partial s -density of states resulting from the self-consistent band structure calculation, Moruzzi *et al* [12] have found that $Z_s \sim 1.3$ is the most reasonable value for the elemental systems. This is also supported by self-consistent calculations of Moriarty [13]. This value is in conformity with the effective charge transfer situation. It is observed that the potential is not very sensitive to Z_s . Change of Z_s does not change $S(q)$ significantly; only a small change of peak value was noticed. The softness parameter a has been fixed by fitting the theoretical structure factor, $S(q)$, with the experimental $S(q)$ at large q (Potential profiles are available on request from authors). The Weeks-Chandler-Andersen [14,15] (WCA) theory describes the static structure factor for system of particles interacting *via* a repulsive potential $\phi(r)$ through a corresponding system of effective hard spheres. LWCA liquid state theory [9] was used to determine the effective hard sphere diameter.

For hard sphere liquid, the expression for the total entropy S is the sum of ideal gas entropy and excess entropy [16]. The specific heat at constant volume $C_V = T(dS/dT)_V$ and the specific heat at constant pressure is :

$$C_P = C_V + \frac{NT\alpha_V^2}{\rho\chi_T} \quad (2)$$

where α_V is the thermal expansion coefficient.

For a hard sphere liquid, the theory for shear viscosity was developed by Rice and Allnatt [17]. It may be written as the sum of four different fractions :

$$\mu_V = \mu_V^{(1)}(\sigma) + \mu_V^{(2)}(\sigma) + \mu_V^{(3)}(r > \sigma) + \mu_V^{(4)}(\sigma), \quad (3)$$

where the first and second term on the right are the contributions due to hard part and the third is due to the soft part of the pair potential. The fourth term is the kinetic energy contribution to the viscosity. To get the expressions for the above terms, one is referred to [18].

The effective hard sphere diameter σ evaluated by using the LWCA theory, are presented in Table 1. The value of σ is found to be the smallest in Zn ($=2.32 \text{ \AA}$) and the largest in Bi ($=2.98 \text{ \AA}$). It has been observed that these values are consistent with the detailed profile of the interionic potentials. For example, the position of the first minimum of the potential for Zn lies at the shortest distance ($r = 2.7 \text{ \AA}$) and that of Bi at the largest distance ($r = 3.3 \text{ \AA}$). For the rest of the systems, the position of the minimum of the potential lies in between these two limits

Table 1. Input parameters for calculating pair potential ρ , number density; R_c emptycore radius, a , softness parameter and σ , hard sphere diameter

Elements	T(K)	ρ (\AA^{-3})	R_c (au)	a (au)	σ (\AA)
Zn	833	0.0628	1.270	0.300	2.32
Cd	623	0.0428	1.229	0.255	2.66
Hg	423	0.0397	0.915	0.167	2.68
In	773	0.0355	1.320	0.270	2.82
Tl	773	0.0324	1.134	0.215	2.84
Sn	973	0.0337	1.300	0.266	2.76
Pb	823	0.0301	1.470	0.305	2.96
Sb	933	0.0320	1.059	0.190	2.97
Bi	823	0.0282	1.490	0.310	2.98

Results of calculations for thermodynamic properties namely, the entropy, specific heat at constant pressure, for liquid Zn, Cd, Hg, In, Tl, Sn, Pb, Sb and Bi are presented in Table 2. The smallest value of entropy has been found to be 10.53 times k_B per atom in Zn and the largest value 13.29 in Bi. The discrepancy between theory and experiment is found to be the largest for Hg ($\Delta S = 3.44$) and the smallest for Sb ($\Delta S = 0.4$). The calculated values for all systems are larger than the experimental one because the present calculations are performed at temperature higher than the melting points. Since the change in entropy

Table 2. Calculated values of total entropy S_{tot}/Nk_B and specific heat at constant pressure C_P/Nk_B , in unit of k_B and shear viscosity μ_V (in cP) and their experimental values.

Elements	S_{tot}/Nk_B		C_P/Nk_B		μ_V	
	Theo	Expt	Theo	Expt	Theo	Expt
Zn	10.53	9.0	3.58	3.875	1.303	2.58
Cd	11.00	9.7	3.70	3.815	1.354	2.461
Hg	11.74	8.3	3.54	—	1.391	1.136
In	11.71	9.1	3.63	3.517	1.340	0.845
Tl	13.05	10.9	3.47	3.63	1.516	1.523
Sn	12.81	9.7	3.36	3.33	1.125	1.85
Pb	12.91	11.1	3.60	3.48	1.635	1.632
Sb	12.10	11.7	3.66	3.78	1.452	1.382
Bi	13.29	11.2	3.48	3.565	1.424	1.14

with temperature is proportional to T , i.e. $\Delta S \propto T$ [19], obviously the theoretical values would be higher.

Results of calculations of specific heat C_p at constant pressure, are also presented in Table 2. In this case, the agreement with the experimental data is found to be remarkably good because at high temperature, C_p is nearly independent of temperature. It may be mentioned that C_v diverges when the packing density $\eta (= \pi\rho\sigma^3/6)$ approaches unity. But for metallic densities, η lies between 0.40 to 0.55. This range is much less than one.

Finally, we turn to the results of shear viscosity that are calculated by using the analytic formulas derived for hard sphere liquid by Rice and Allnatt [17]. The calculated values are listed in Table 2 where these are also compared with the available experimental data [22]. The minimum value of viscosity μ_v is found to be 1.125 cP in Sn and the maximum value is 1.635 cP in Pb. For the rest of the systems, the value of μ_v lie in between these limits. However, as far as the agreement with the experiment is concerned, calculated values except for Zn and Cd, are very good. For liquid Zn and Cd, the agreement is just fair. However, Rahman and Bhuiyan [20] investigated the temperature dependence of the shear viscosity for four systems including Cd, In and Bi. Their results at the temperature of present work were found to be 2.7, 1.7 and 1.7 cP respectively. Joarder and Rao [21] in a calculation, found the value of μ_v to be 1.4 cP for Pb. So the calculated values of the present work (except for the Cd) are better in agreement than other theoretical results available.

Therefore, we can conclude that (i) liquid Zn, Cd, Hg, In, Tl, Sn, Pb, Sb and Bi can be represented as a first approximation, by non-interacting hard spheres, although the effects of sd -hybridization exists in these systems; (ii) a proper account of sd -mixing into the interionic interaction gives better description of both thermodynamic and atomic transport properties of liquids

of less simple metals. Thus, the BS model could be a good beginning of the microscopic description for the aforementioned macroscopic properties of the liquids of less simple metals.

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