

Corresponding states theory and transport coefficients of liquid metals

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Received 17 February 2004; accepted 6 April 2004

Available online 27 April 2004

Abstract

A study of the applicability of CST towards predicting transport coefficients in liquid metals has been undertaken with particular emphasis on alkali metals. Characteristic parameters were obtained from six different first principles calculations of inter-ionic potentials of *simple* metals reported in the literature. A wide variation was observed in the characteristic parameters as reported by various authors. Among these, the potential parameters of Shyu et al. provided the best correlation of experimental diffusivity and viscosity data for alkali metals over moderate temperature ranges. However, use of the Goldschmidt diameter as the characteristic distance parameter and $k_B T_m$, where T_m is the melting temperature, as the characteristic energy parameter gave as good, if not better, results for alkali metals. This parameter set was not found to be satisfactory when non-alkali metals were also included. Chapman's characteristic parameters, obtained from a fit to the viscosity data, provided a reasonable correlation of the diffusivity data to most, but not all metals studied. Fundamental issues associated with attempting to group all liquid metals under a single corresponding states theory as well with the conventional use of the potential well-depth and the distance at which the potential becomes zero as characteristic parameters for liquid metals have been pointed out. A preliminary statistical analysis has been performed to assess the reliability of our predictions in view of the experimental uncertainties in viscosity and diffusivity data.

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Keywords: Corresponding states; Transport coefficients; Liquid metals

1. Introduction

The central idea of corresponding states theory (CST) is the existence of a universal relation between dimensionless parameters formed using the physical quantities of interest. The existence of such a relation may be established by a dimensional analysis or by use of a mathematical equation, if one exists, connecting the relevant quantities. An example of the latter is the van der Waals equation of state from which an explicit expression between the reduced quantities (pressure, volume and temperature) can be obtained. Often, it might not be possible to get a convenient analytical expression connecting the reduced or dimensionless quantities. In such a case, one may use limited experimental data to

obtain such an expression once the appropriate dimensionless variables have been identified. An example of this approach is the case of transport coefficients where one may formally express diffusivity or viscosity in terms of molecular parameters using statistical mechanics, and compute these coefficients numerically. However, these calculations tend to be computationally intensive and it is convenient to have simpler analytical expressions especially when one is interested in estimating these quantities for a wide range of systems and conditions. CST provides a useful and powerful, but by no means the only, option. It is a particularly attractive approach for liquid metals where the presence of long-range interactions not only adds to the computational complexity but also renders the widely used hard sphere theories less effective than they are for simple liquids. In this work, the applicability of CST to the estimation of diffusivity and viscosity of liquid metals is examined.

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However, it is useful and instructive first to present a terse review of the relevant literature and to outline the motivation for the present work.

2. Literature review and motivation for current work

One of the earliest applications of CST to transport coefficients of liquid metals is the work of Chapman [1]. Chapman used kinetic theory to obtain suitable dimensionless quantities for viscosity, density and temperature in terms of a characteristic energy (ε) and a characteristic distance (σ) parameter. His equations also predicted a quadratic dependence of the reduced viscosity on the reduced density. To obtain a correlation for the temperature dependence of viscosity, he adopted the Lennard-Jones (L-J) parameter, ε_{LJ} , and the Goldschmidt diameter, σ_{GS} , for Na and K as their characteristic energy and distance parameters, respectively. This, in turn, allowed the development of a plot of the viscosity versus temperature in terms of the *reduced* variables using experimental viscosity data. Chapman then deduced the values of the characteristic energy parameter, ε , for a range of other metals by forcing their experimental viscosity data to conform to the plot obtained for Na and K. The Goldschmidt diameter was chosen as the distance parameter for all metals.

Following Chapman, Pasternak and Olander [2] used the parameters provided by Chapman to obtain a correlation for the diffusion coefficient using experimental data for nine liquid metals. Riazi and Daubert [3] used a dimensional analysis to connect the diffusivity, viscosity and thermal conductivity of liquid metals with each other as well as with temperature and density. Also, following the lines of generalized CST for thermal equations of state, they developed a correlation between reduced diffusivity and reduced temperature with the acentric factor as a parameter.

At this juncture, it is worthwhile to point out a few features of the procedure adopted by Chapman [1]. The real merit of the procedure lies in the characteristic parameters it provides which may then be used to predict, for instance, other transport coefficients such as diffusivity. But it is not truly a test of CST as an accurate

model for the viscosity of liquid metals because the characteristic energy parameter, except for two metals, is not determined a priori and/or using independent means but by using the experimental viscosity data. Thus, the ε value for all but two metals serves merely as a fitting parameter. Chapman [1] had recognized this and he tried to develop a fundamental basis to the found parameters by noting that the ε value, which represents the depth of the L-J potential well, increased, as was expected, with the melting temperature of the metal, T_m . But this does not invalidate the comment made above and hence his analysis merely demonstrates the internal consistency of the experimental results. It may be noted that Chapman's characteristic energy parameters [1] are generally larger by several factors than the well-depth of potentials determined by first principles calculations, some of which are listed in Table 1 for alkali metals. In some of the calculations, the well-depth actually decreases with increase in T_m . Furthermore, these calculations reveal that the L-J potential is not suitable for liquid metals. For one, liquid metal potentials have a softer repulsive core and secondly they exhibit long-range oscillations not exhibited by the L-J potential.

In summary, the central problem in the use of CST thus lies in the choice of physically realistic characteristic parameters. A true evaluation of the applicability of CST to transport coefficients can be obtained only if the characteristic parameters are determined a priori using independent means, without any reliance on the experimental data of the very quantities we wish to predict. With the availability in the literature now of a large number of first principles calculations of liquid metal potentials, it would be worthwhile to reevaluate the applicability of CST to liquid metals. With this in view, it is necessary first to examine the factors that led to the choice of the characteristic parameters used in this work.

3. Characteristic parameters for CST of transport coefficients

3.1. Motivation for choice made in this work

The present work is based on the choice of the potential well-depth, $|u_{\min}|$, and the inter-atomic distance

Table 1
Characteristic distance (σ) and energy (ε) parameters of alkali metals

Metal	Chapman σ (Å), ε (K)	$\{\sigma_{GS}, k_B T_m\}$ σ (Å), ε (K)	Shyu et al. σ (Å), ε (K)	Hafner and Heine σ (Å), ε (K)	Kumaravadivel and Evans σ (Å), ε (K)	Jank and Hafner σ (Å), ε (K)	Gonzalez et al. σ (Å), ε (K)	Kambayashi and Chihara σ (Å), ε (K)
Li	3.14, 2350	3.14, 453.5	2.73, 567.1	2.92, 950.3	2.76, 957.3	2.59, 759.5	2.54, 949.5	2.59, 1038.2
Na	3.84, 1970	3.84, 369.5	3.33, 445.6	3.41, 1546.9	3.21, 677.4	3.12, 612.6	3.23, 429	3.29, 541.2
K	4.76, 1760	4.76, 336.5	4.12, 421.4	3.81, 1988.4	4.03, 574.7	4.18, 312.6	3.88, 474.5	4.11, 507
Rb	5.04, 1600	5.02, 311.9	4.41, 402.2	3.86, 2070.9	4.33, 519.5	4.58, 279.5	4.16, 483.5	4.52, 409.4
Cs	5.40, 1550	5.40, 301.6	4.76, 385.5	3.95, 2201.6	4.63, 541.6	5.03, 211.6	4.66, 515.5	5.08, 466

at which the potential vanishes, r_0 , as the characteristic energy and distance parameters, respectively. The rationale and the justification of this choice is presented here.

To motivate the discussion, we briefly discuss the work of Helfand and Rice [4] who assumed the inter-atomic potential u to be of the form

$$u(r) = \varepsilon f(r/\sigma), \quad (1)$$

where r is the inter-atomic distance and the parameters ε and σ have the units of energy and length, respectively. Using the statistical-mechanical expressions for the diffusion coefficient (D) and viscosity (μ) in terms of the ensemble average of the corresponding autocorrelation functions, they obtained the following relations:

$$D^* = D^*(T^*, \rho^*) \quad (2)$$

and

$$\mu^* = \mu^*(T^*, \rho^*), \quad (3)$$

where

$$D^* = \frac{D}{\sigma} \sqrt{\frac{m}{\varepsilon}}, \quad \mu^* = \frac{\mu \sigma^2}{\sqrt{m \varepsilon}}, \quad T^* = k_B T / \varepsilon, \quad \rho^* = \rho \sigma^3. \quad (4)$$

In Eq. (4), m is the mass of an atom, T is the absolute temperature, ρ is the number density (number of atoms per unit volume) and k_B the Boltzmann constant. The starred (*) quantities are the dimensionless ones. Clearly, the L-J potential

$$u_{LJ}(r) = 4\varepsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r} \right)^{12} - \left(\frac{\sigma_{LJ}}{r} \right)^6 \right], \quad (5)$$

is of the same form as Eq. (1). Moreover, for the L-J potential, the value of the potential at its minimum is given by $-\varepsilon_{LJ}$ and the inter-atomic distance at which the L-J potential becomes zero is given by σ_{LJ}

$$|u_{\min}^{LJ}| = \varepsilon_{LJ}, \quad r_0^{LJ} = \sigma_{LJ}. \quad (6)$$

Thus, if the inter-atomic potential is of the L-J type then the potential well-depth and the inter-atomic distance at which the potential vanishes may be taken as the characteristic energy and distance parameters, respectively, to form the dimensionless quantities in Eq. (4).

However, as already pointed out above, L-J potentials are not an accurate representation of interactions in liquid metals. One may still use the dimensionless parameters in Eq. (4), if the liquid metal potential can be expressed in the form of Eq. (1) with the ε and σ not necessarily having the same significance, indicated by Eq. (6), as they do for the L-J potential. Alternately, one may start with the liquid metal potential and carry out an analysis similar to that of Helfand and Rice and extract the appropriate dimensionless parameters. Both of these avenues are complicated by the lack of convenient-to-use, accurate, analytical expressions for liquid

metal potentials. In this work, we assume that $|u_{\min}|$ and r_0 are appropriate characteristic parameters for liquid metals too, at least as a first-order approximation. The rationale for this choice is discussed in detail below.

As already remarked in Section 1, in case it is not feasible to extract the dimensionless parameters from a mathematical equation, one may carry out a dimensional analysis of the relevant quantities. For instance, for viscosity we may consider the set

$$\{\mu, \rho, T, m, k_B, \sigma, \varepsilon\}.$$

At this stage ε and σ are simply *any* set of characteristic energy and distance parameters. Of course, the implicit assumption is that they are sufficient to characterize the interaction, an assumption which would be examined later. Using standard techniques of dimensional analysis [3], three independent dimensionless parameters may be formed. It may be noted that this does not imply the set of dimensionless parameters is unique but it can be shown that that the set in Eq. (4)

$$\{\mu^*, \rho^*, T^*\}$$

is a valid set. A similar case can be made for the diffusion coefficient as well. Dimensional analysis, however, does not specify exactly what ε and σ are. They are usually chosen to be $|u_{\min}|$ and r_0 probably because these are the two most easily recognizable and extractable features of the potential. A further motivating factor is that such a choice has a rigorous basis at least for L-J potentials. However, a *fundamental* reason is the finding [5] that the potentials of alkali metals near their melting points collapse into the same curve when they are scaled by $|u_{\min}|$ and r_0 . This means that the potential is of the form given by Eq. (1) with $\varepsilon = |u_{\min}|$ and $\sigma = r_0$. Then, as pointed out earlier, the dimensionless groups given by Eq. (4) follow *rigorously*.

3.2. Discussion of parameter sets

Having made the above choice, it is now worthwhile to briefly examine the available literature on these parameters. In this work, we have considered the following sets of parameters:

(a) The parameters of Chapman [1] obtained from viscosity data.

(b) The set $\{\sigma_{GS}, k_B T_m\}$.

Here, T_m is the melting temperature [6] and σ_{GS} is the Goldschmidt diameter [7]. One distinct advantage of this set is that these are standard parameters and readily available for all metals. Thus, it would be interesting to see if they do as well or better than the other sets of parameters. Moreover, the effectiveness of $k_B T_m$ as a scaling parameter has been observed for liquid alkali metals [5].

In addition, we considered parameters obtained from first principles calculations of the effective inter-ionic potentials by

- (c) Shyu et al. [8] (from which Ranganathan and Pathak [9] and Balucani et al. [5] have extracted the characteristic parameters).
- (d) Hafner and Heine [10].
- (e) Kumaravadivel and Evans [11].
- (f) Jank and Hafner [12].
- (g) Gonzalez et al. [13,14].
- (h) Kambayashi and Chihara [15].

For reasons to be outlined below, we restricted ourselves primarily to *simple* metals as far as first principles calculations are concerned. While in (c)–(f), pseudo-potential theory is employed, in (g) and (h), the framework of density functional theory is used.

The two crucial inputs to a pseudo-potential calculation of the inter-ionic potential are a model for the pseudo-potential and an expression for the exchange-correlation correction to the dielectric constant. In (c) and (d) a simple, local pseudo-potential, called the empty-core potential is used while in (e) and (f), a more rigorous non-local optimized potential is employed. It has been pointed out [11] that the empty core model may be adequate for alkali metals provided a suitable choice of the core radius is made. While Shyu et al. find the radius by fitting to neutron scattering data, Hafner and Heine use the solid-state band structure energies for this purpose.

As regards the exchange-correlation correction factor, the expression of Ichimaru and Utsumi [16], adopted by Hafner and Heine, satisfies the consistency conditions in compressibility sum rule and the short range correlation. In this respect, it is superior to the correction function of Singwi et al. [17] or its refined version due to Vashishta and Singwi [18] used in (c) and (e), respectively. However, Jank and Hafner [12] found very little difference in the inter-ionic potential calculated using the Ichimaru–Utsumi and the Vashishta–Singwi corrections.

In the pseudo-potential framework, which is widely regarded as applicable for sp-metals, the liquid metal is treated essentially as a one-component fluid of ions with the electrons taken into account only in the determination of the effective inter-ionic potential. Moreover, the electron–ion correlation is regarded as weak thereby enabling the use of linear response theory. The importance of non-linear effects have been pointed out even for simple metals [19]. These effects can be taken into account within a density functional theory framework employed by Chihara and co-workers ([15, and references therein]). In this framework, the liquid metal is regarded first as an electron–ion mixture and expressions obtained for the electron–ion and ion–ion correlation functions in terms of effective potentials which are in turn obtained by regarding the liquid metal as a nuclei–electron mixture. Though Gonzalez et al. [13] use a similar framework, they introduce additional approximations to simplify their calculations. Further, their

expressions for the local field corrections are different from those used by Chihara and co-workers.

Table 1 displays the parameters of alkali metals for (a)–(h). *In this table, following convention, we denote $|u_{\min}|$ and r_0 by ε and σ , respectively.* It is clear from the table that the ε and σ values reported by various authors differ widely. This reflects the sensitivity of these parameters in particular and the potential in general to the inputs required for computing the potential. For instance, Kumaravadivel and Evans [11] show the effect of the choice of the pseudo-potential as well as that of the exchange correlation correction factor on the potential. For liquid sodium, they show that a variation of as high as 100% is possible in the well-depth. For polyvalent metals such as Al, the sensitivity to the correction factor is even higher. Apart from quantitative discrepancy, one may find widely differing qualitative trends as well. For instance, in the case of alkali metals, while the calculations of Shyu et al. [8] and Jank and Hafner [12] show a decrease in the well-depth as one moves from Li to Cs, the opposite trend is reflected by the calculations of Hafner and Heine [10]. The calculations of Kumaravadivel and Evans [11] and Kambayashi and Chihara [15] display the former trend from Li to Rb while those of Gonzalez et al. [14] follow the latter trend from Na to Cs.

Another point worth noting is that, for liquid metals, the parameters ε and σ are dependent on the temperature (and hence on the density). Kumaravadivel and Evans have pointed out that large errors (as large as a factor of 5) may result in using parameters evaluated for the solid state especially for metals with high melting points. Sharma and Tankeshwar [20] have reported calculations for liquid Rb in which they report an increase by a factor of two of the well-depth over a 1500 K temperature range. Over this range σ decreases by about 10%. As regards the parameters reported in Table 1, except for those of Hafner and Heine, all others are based on liquid state close to the melting temperature. Due to the lack of sufficient information, it is perhaps reasonable to assume them to hold for all temperatures in the present calculations. Further, the temperature range of the data that considered in this work is by and large within 200–300 K.

In spite of the above limitations, it would be worthwhile to investigate the effectiveness of the above parameters as we are more interested at this stage in qualitative trends. Further, as shown below, even though two sets of parameters might be different from one another, it is possible that there might be some kind of internal consistency within each set that leads to satisfactory results as far as the applicability of CST is concerned.

As mentioned above, we have restricted ourselves to *simple* or sp-bonded metals as they are the most widely studied. A notable exclusion is that of transition metals

for which calculations are not as widely reported as for the simple metals. Further, the presence of the d-band electrons in the transition metals requires a different approach to the calculation of their pair potentials. Thus, though values of ε and σ are available [21] for some common transition metals such as Fe, Co, Ni, etc. we did not include them in our consideration as the authors, for the reason cited above, did not report calculations for the simple metals. Thus, the simple and transition metals could not be treated within the same framework. In fact, this qualitative difference in approach for different classes of metals, and here we may also mention noble metals and rare-earth metals [22,23], suggests that it may not be physically realistic to expect all the liquid metals to obey a single CST. Nevertheless for parameter sets (a) and (b) above, the applicability of CST has been tested here for a wider range of metals.

4. Results and discussion

4.1. Outline of calculations

Evidently, given the functional form of Eqs. (2) and (3), three-dimensional plots are needed to check the applicability of CST for viscosity and diffusivity. However, by assuming a dependence on say, ρ^* , we may resolve this problem. For this purpose, the result of Chapman [1] is used here who found, theoretically, a quadratic dependence of μ^* on ρ^* . However, Chapman's definition of μ^* is different from ours although his definitions of ρ^* and T^* are the same as that given by Eq. (4). In fact, the two definitions of reduced viscosity are related by

$$\mu^* = \mu_{\text{ch}}^* \sqrt{T^*}. \quad (7)$$

Thus, Chapman's hypothesis of density dependence implies

$$\mu_{\text{ch}}^* = \rho^{*2} f_{\text{ch}}(T^*). \quad (8)$$

From Eqs. (7) and (8), we obtain

$$\mu^* = \mu^*(T^*, \rho^*) = \rho^{*2} \sqrt{T^*} f_{\text{ch}}(T^*) = \rho^{*2} f(T^*),$$

where

$$f(T^*) = f_{\text{ch}}(T^*) \sqrt{T^*}. \quad (9)$$

Thus, a plot of $\mu^* \rho^{*-2}$ versus T^* should yield the universal function f if CST were valid. What we have shown here is that if $\mu_{\text{ch}}^* \rho^{*-2}$ is a universal function of T^* , then so is $\mu^* \rho^{*-2}$ as defined in this work. Further, Eq. (9) gives the precise relation between the two universal functions. For the diffusivity, we assume an inverse square dependence of D^* on ρ^* . This is based on the Stokes–Einstein relation [3] which points to an inverse relation between diffusivity and viscosity. No doubt, these are crude approximations; but we found that by

varying the dependence on the reduced density for both D^* and μ^* , there was no significant change in the results, though in some cases, especially for diffusivity, a weaker density dependence was found to give better results. While it would be profitable to undertake a more detailed study of the nature of the density dependence for both viscosity and diffusivity, we do not pursue it here.

We now briefly describe our calculations. Experimental data on temperature dependence of the diffusivity for about 16 liquid metals have been culled from the literature. On the other hand, viscosity data is more widely available and therefore we have used data for 23 metals. Detailed references for the data can be found in [24]. For metals not listed there, the data were taken from [25]. Then using the potential parameters that we have considered for this investigation, the dimensionless quantities were calculated using Eq. (4). The density at a given temperature of each metal studied herein is calculated using the following expression due to Crawley [6]:

$$\rho = a + b(T - T_m).$$

Crawley has tabulated the a and b values for a large number of metals. It may be noted that potential parameters in most cases were available only for alkali metals, the calculations of Kumaravadivel and Evans [11] being an exception. Although potentials for non-alkali simple metals were provided by Hafner and Heine [10], we could not use them either due to lack of viscosity and/or diffusivity data or due to the difficulty involved in obtaining the characteristic parameters from the plots provided. However, Chapman's parameters are available for a wider range of metals while the set $\{\sigma_{\text{GS}}, k_{\text{B}} T_m\}$ is known for nearly all metals.

4.2. Alkali metals

The main results of this work are summarized in Figs. 1–4. Since the values of the required parameters for alkali metals are available in all the sets (a)–(h), these are considered separately in Fig. 1(a)–(e) for diffusivity and in Fig. 2(a)–(c) for viscosity. Of course, they have a special significance in belonging to the same group in the periodic table.

Both Chapman's parameters (Figs. 1(a) and 2(a)) as well as the set $\{\sigma_{\text{GS}}, k_{\text{B}} T_m\}$ (Figs. 1(b) and 2(b)) give a reasonably good fit of diffusivity as well as viscosity data for *all* alkali metals. This cannot be said of the parameters of Hafner and Heine (Fig. 1(d)) and of Kumaravadivel and Evans (Fig. 1(e)) where Li clearly does not fit in. Similar behavior was obtained for these parameters for viscosity as well. It is to be noted that though the well-depth of the potentials shows opposite trends in these two cases, the behavior of diffusivity and viscosity from a CST viewpoint is similar. The results concerning

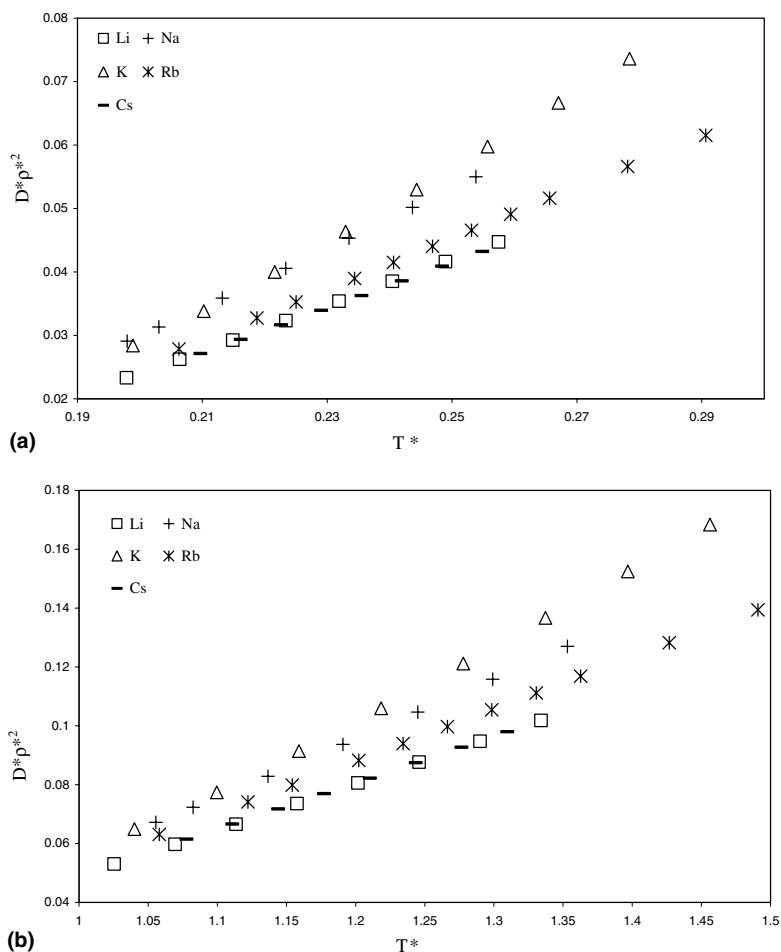


Fig. 1. Plots of $D^*\rho^{*2}$ versus T^* for the various parameter sets. Figures (a)–(e) correspond, respectively, to the parameter sets (a)–(e) for alkali metals.

viscosity using Chapman's parameters are not surprising since the parameters themselves were obtained from viscosity data. However, as pointed out before, Chapman's expression for the reduced viscosity, obtained from kinetic theory, is slightly different from the one used here.

Regarding Li, differing perceptions exist. Balucani et al. [5] exclude Li from consideration due to its "quantum character". Anomalous behavior of Li has also been pointed out by Day et al. [26] and Gonzalez et al. [13]. Also, Li differs from other alkali metals in having no p-electrons in its core. But Ranganathan and Pathak [9], using the parameters of Shyu et al. [8], calculated D^* at the melting point for Na, K, Rb and Cs and found them to be close to 0.03. They then assumed this value to hold for Li at its melting point and found the resulting value of the diffusivity of Li agreed very well with the corresponding experimental value. The present results show that the parameters of Shyu et al. [8] give a good fit for all alkali metals (Figs. 1(c) and 2(c)). This despite the fact that both the pseudo-potential as well as the exchange-correlation model used by them are not as refined as those used in some of the

other parameter sets considered here. While they point to the uncertainties in potential well-depth that can occur when the empty core radius is determined from neutron scattering data, it is shown here that their parameters yield a corresponding states model for transport coefficients of liquid alkali metals. This result also correlates with the corresponding states behavior observed for the potentials of Shyu et al. when ϵ and σ are used as scaling parameters [5]. Furthermore, using these potentials, Balucani et al. [27] have observed scaling behavior for diffusivity and viscosity from simulations near the melting point of the alkali metals.

For the parameters of Jank and Hafner [12], three distinct clusters of points ($\{\text{Li, Na}\}$, $\{\text{K, Rb}\}$, Cs) are found for both diffusivity and viscosity. Thus, no corresponding states behavior can be found even among alkali metals. Similar behavior was found for the parameters of Gonzalez et al. [13,14] for diffusivity but here the distinct clusters were those of $\{\text{Li, Cs}\}$, $\{\text{K, Rb}\}$ and $\{\text{Na}\}$. For viscosity, the scatter was even more. It may be noted here that Jank and Hafner [12] as well as Gonzalez et al. [14] report that the potentials of K, Rb and Cs follow approximately the law of corresponding

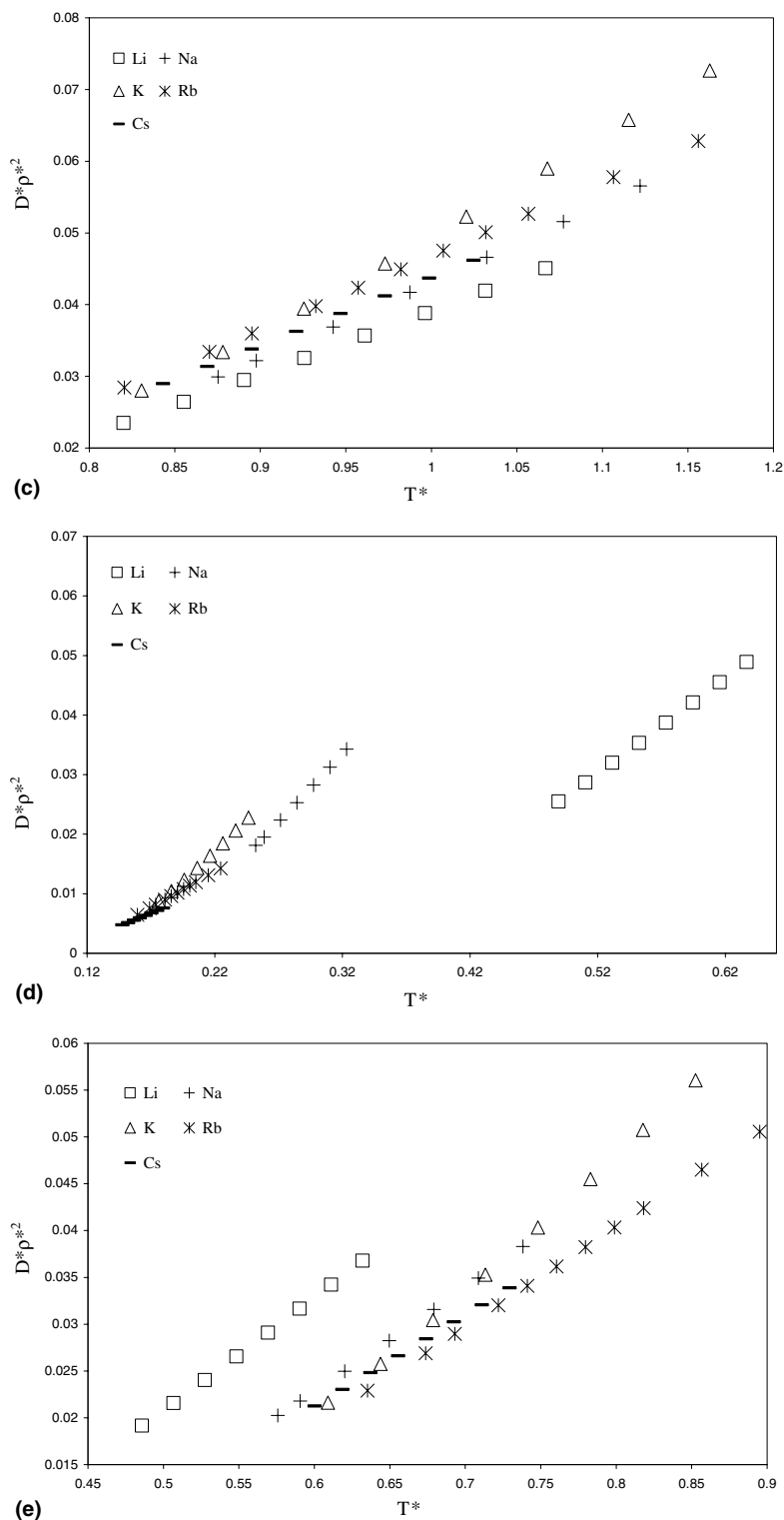


Fig. 1. (continued)

states with the latter specifically reporting a deviation for Na. To some extent, it was reflected in our results as the points for K and Rb cluster together in both cases and those for Na stand out.

The parameter set of Kambayashi and Chihara [15] showed results very similar to those of Gonzalez et al., only the points for Na, K and Rb cluster together more closely. This behavior was found to be more

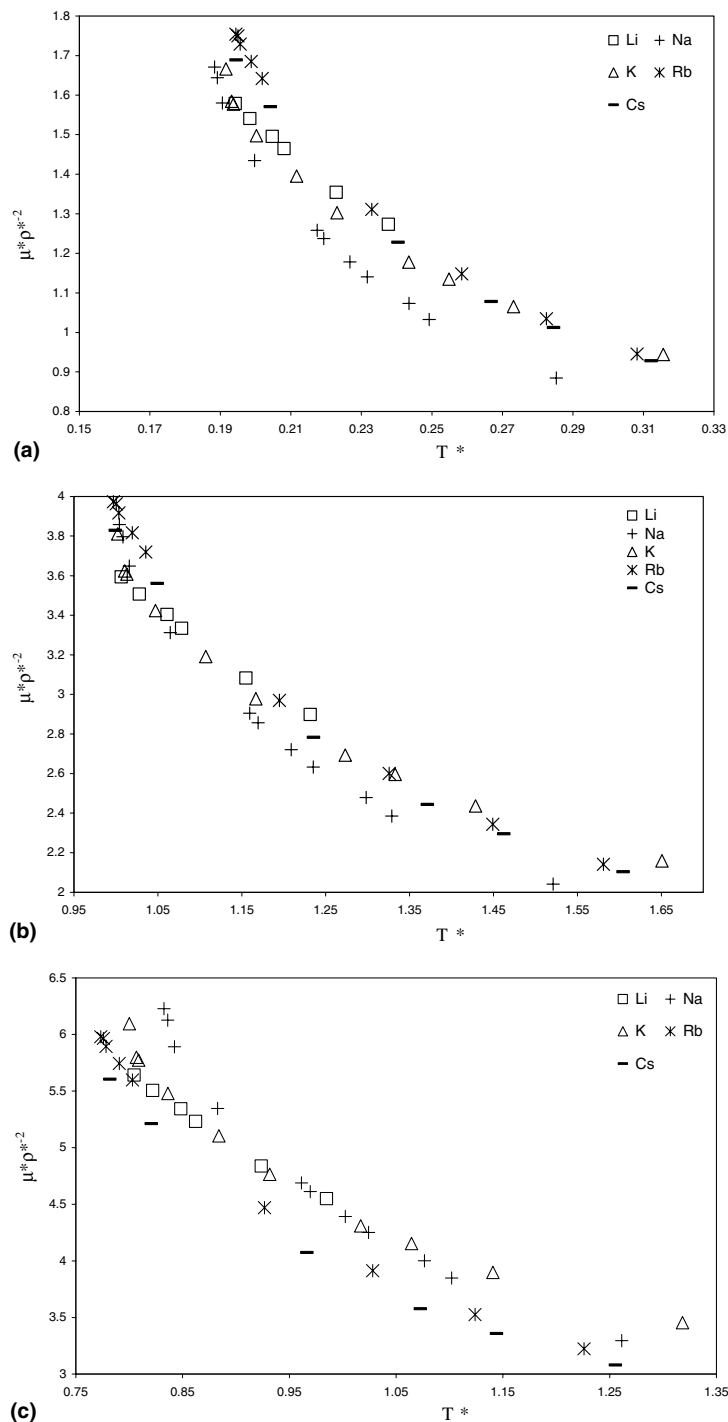


Fig. 2. Plots of $\mu^* \rho^* \sigma^{-2}$ versus T^* for the various parameter sets. Figures (a)–(c) correspond, respectively, to the parameter sets (a)–(c) for alkali metals.

pronounced for viscosity. Interestingly, Kambayashi and Chihara [15] do not observe a corresponding states behavior for their potentials.

Thus, it is clear from the above results that whether a “universal” relation exists between the reduced transport coefficients and the reduced density and temperature depends on the particular parameter set used. Thus, we may classify those sets that suggest a universal rela-

tion, as “desirable” from a CST viewpoint. This does not mean that the other parameter sets have to be rejected altogether but only that they are not suitable within the context of CST. As we have pointed out above, some of the parameter sets that are the result of apparently more rigorous calculations of inter-ionic potentials do not have the scalable property with respect to σ and ϵ .

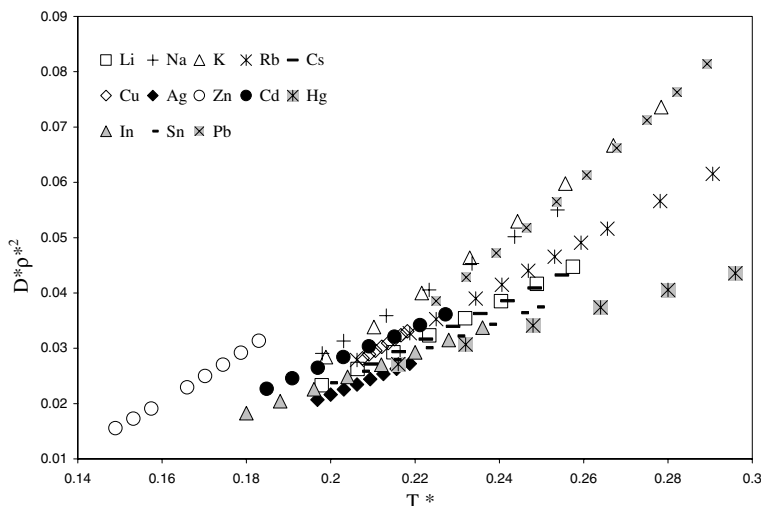


Fig. 3. Plots of $D^* \rho^{*2}$ versus T^* for parameter set (a) for alkali as well as non-alkali metals.

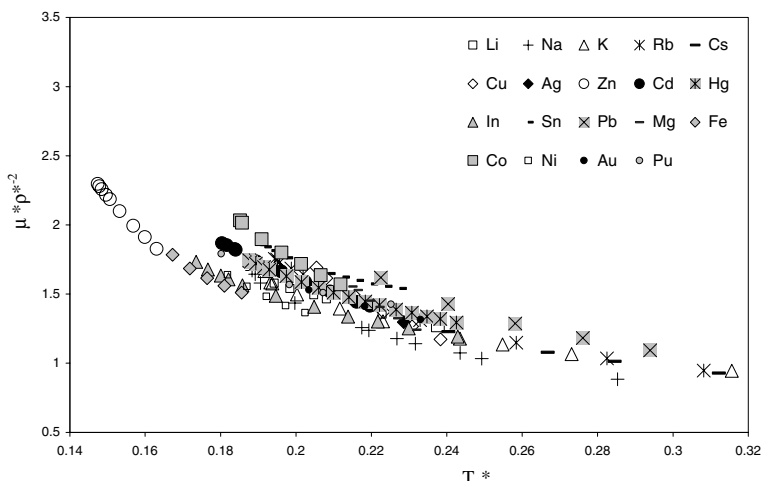


Fig. 4. Plots of $\mu^* \rho^{*2}$ versus T^* for parameter set (a) for alkali as well as non-alkali metals.

4.3. Non-alkali metals

In the case of non-alkali metals, it may be seen that Chapman's parameters (Fig. 3) give a reasonably good behavior of diffusivity for most metals considered, Zn and Hg being exceptions. Noting that the potential parameters were obtained from viscosity data in this case, we may point to a similar result [24] where hard sphere diameters obtained from viscosity data for liquid metals yielded as good a description of their diffusivity as any other hard sphere diameter prescription. As for viscosity, the good correlation displayed by Chapman's parameters (Fig. 4) is not surprising as in fact, the parameters [1] were obtained from a fit to the viscosity data.

As for the parameters of Kumaravadivel and Evans, no universality was observed when more metals were included (as compared with alkali metals alone). The

same can be said for the parameter set $(\sigma_{GS}, k_B T_m)$, where a wide range of metals were included. This set which was found to work well for alkali metals alone is unsatisfactory for the wider range of metals considered.

4.4. Reliability of model predictions

Since we have used experimental data to arrive at our conclusions, it is pertinent to examine the effect of taking into account experimental uncertainties in viscosity and diffusivity. Generally, an uncertainty of up to 10% is expected for viscosity while for diffusivity experimental errors can be as high as 25%. A thorough examination of this problem is no doubt of utmost importance and in fact deserving of a separate study. This would require a critical examination of the various sources from which we have obtained the data, the methods employed to experimentally determine the transport coefficients in

each and an estimation of the resultant error. However, an estimate of the reliability of our predictions may be made by a statistical analysis [28]. The results of such an analysis are presented below.

For viscosity, we took the case of parameter set (b) $\{\sigma_{GS}, k_B T_m\}$ where we seem to get the best results for viscosity correlation (Fig. 2(b)). We developed a correlation of the form

$$\mu^* \rho^{*-2} = A \exp(BT^*).$$

The fit was reasonably good ($R^2 = 0.935$) considering the number of data points (42) used [28]. A linear least squares fit between $\ln(\mu^* \rho^{*-2})$ and T^* gave the following values for the parameters:

$$\ln A = 2.3296 \pm 0.052, \quad B = -1.0294 \pm 0.043.$$

Further, the standard deviation turns out to be 0.053. This corresponds to a fit involving $\ln(\mu^* \rho^{*-2})$ thus indicating a 5.3% uncertainty in the viscosity.

For diffusivity, we chose the parameter set of Shyu et al. (Fig. 1(c)) and based on the results obtained sought a linear relation of the form

$$D^* \rho^{*2} = A' + B'T^*.$$

A least squares fit ($R^2 = 0.91$) gave the following values:

$$A = -0.0704 \pm 0.006, \quad B = 0.1158 \pm 0.006.$$

The standard deviation here is 0.0036 but this corresponds to a fit of $D^* \rho^{*2}$ unlike in the case of viscosity where $\ln(\mu^* \rho^{*-2})$ was involved. Since the range of $D^* \rho^{*2}$ is from 0.03 to 0.07, this points to an uncertainty of about 5–12% in D .

Thus, we see that the uncertainty range for the parameters of our model fits are quite small, less than 5% for viscosity and about 10% for diffusivity. That these values are lower than the corresponding experimental uncertainties should increase our confidence in the parameter sets for which CST was perceived as likely to hold based on Figs. 1 and 2. Finally, it may be pointed out that the form of the above correlations for the reduced viscosity and diffusivity were adopted solely for the purpose of the statistical analysis and do not necessarily have any theoretical basis.

5. Summary and conclusions

A study of the applicability of CST to the calculation of diffusivity and viscosity of liquid metals has been undertaken with particular emphasis on alkali metals. This study differs from previous attempts where the characteristic parameters were essentially treated as fitting parameters and obtained from transport coefficient data itself. Eight different sets of parameters have been considered here in order to form the appropriate dimensionless variables, and six of them are obtained from

first principles calculations reported in the literature. An important point is the wide variation in the characteristic parameters obtained from the various calculations as shown clearly in Table 1. Thus, it is clear that despite great advances in this direction, consensus is still elusive. Nevertheless, some of the parameter sets did result in a reasonable correlation between the dimensionless quantities at least for alkali metals. Wherever possible, the results obtained here are correlated with the features of these calculations. We have also attempted to provide a rough estimate of the reliability of our predictions given the experimental uncertainties in the viscosity and diffusivity values used in this work.

For alkali metals, the use of the Goldschmidt diameter as the characteristic distance parameter and $k_B T_m$ as the characteristic energy parameter works as well as any other set of parameters considered. However, no universality behavior is found for this parameter set when non-alkali metals are included. This is also true of the few other parameter sets involving quantum mechanical calculations where parameters were available for non-alkali metals.

However, Chapman's characteristic parameters obtained from viscosity data provides a reasonable correlation of diffusivity data for most but not all metals studied. Inclusion of a wider range of metals and over a larger temperature range is needed to test the efficiency of this method. But from a more fundamental viewpoint, it is not clearly established whether it is physically realistic to expect all metals to obey a single CST, given the qualitatively different features governing the ionic and electronic structure of various classes such as simple metals, transition metals, noble metals, etc. In fact, as pointed out above, even among simple or sp-bonded metals, we have found a reasonable degree of universality only for alkali metals. More extensive studies are required to find out if a limited universality holds among a particular class of metals.

Another aspect that requires further investigation is the suitability of the potential well-depth and the inter-ionic distance where the potential becomes zero as the characteristic parameters. First, both of these quantities are temperature dependent. It would be interesting to see the effect of incorporating this temperature dependence. Further, they are very sensitive to the inputs used for the potential calculations. Despite these limitations, reasonably satisfactory results were obtained for alkali metals. Nevertheless, it would be worthwhile to find out a more reliable set of characteristic parameters and also to establish if two parameters alone are sufficient for liquid metals. It is possible that a different set of characteristic parameters might bring a wider range of metals into a single CST. Finally, a more thorough analysis of the density dependence of the transport coefficients would be fruitful to shed some light on some of the underlying issues in these complex systems.

Acknowledgements

The clarifications provided by Professor J. Chihara of JAERI, Japan are gratefully acknowledged.

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