Models and Equations for Atomic Transport Coefficients of Liquid Metals: Viscosity and Self-Diffusivity

T. Iida,[1,a] N. Tripathi,[1,b] M. Isac,[1] and R.I.L. Guthrie[1,c]

[1]McGill Metals Processing Centre, 3610 University Street, McGill University
Montreal, Quebec, H3A 2B2, Canada

[a] takamichi_iida@hotmail.com, [b] nagendra4@yahoo.com
[c] rod@mmpc.mcgill.ca

Keywords: viscosity, self-diffusivity, transport coefficient, model, accurate prediction

Abstract. The current article presented appropriate models using a new parameter recently introduced by the authors to accurately predict the atomic transport coefficients, i.e. viscosity and self-diffusivity, of liquid metallic elements at their melting points. The models for both the melting-point viscosity and self-diffusivity are expressed in terms of well-known physical quantities; atomic mass, atomic volume, melting point, melting-point surface tension, and the new parameter ξ_T. Moreover, the authors derived expressions for the temperature dependence of the atomic transport coefficients of liquid metallic elements in terms of melting point temperature. These two models give very good agreement with experimental data for various metallic liquids. Using the models, self-diffusivities were predicted for liquid aluminum, calcium, and magnesium.

Introduction

The atomic transport coefficients, i.e., viscosity and self-diffusivity, of liquid metallic elements are of critical importance to the understanding, design, and quantification of any liquid metal processing operations. Since the 1970's, there has been a renewed interest in the atomic transport coefficients of almost all liquid metallic elements, following the advent of mathematical modelling techniques supported by powerful computers. Even so, experimental data for the atomic transport coefficients of liquid metallic elements are relatively scanty, in particular, self-diffusivities. At present, experimental viscosity data are available for about 50 liquid metallic elements, and of these, data are reliable for only 30 or so metallic elements [1]. On the other hand, it would appear that experimental self-diffusivity data are only available for 20 and under. In this connection, experimental data for surface tension are available for 65 and more liquid metallic elements [2]. The measurements of the atomic transport coefficients of metallic liquids are time-consuming and expensive, and require considerable expertise. As such, the development of reliable, universal models for predicting the atomic transport coefficients of liquid metallic elements is needed.

The current article presents the appropriate models using a new parameter recently introduced by the authors to accurately predict the atomic transport coefficients of various liquid metallic elements. Further to this, the authors also predict values for the self-diffusivity of liquid aluminum, calcium, and magnesium that have not been measured experimentally.

Viscosity Model for Liquid Metallic Elements

Melting-Point Viscosity. Recently, the authors presented a model for accurate viscosity predictions of pure liquid metals at their melting points. The model is based on a relationship between viscosity and surface tension of a liquid metal in terms of the new parameter, as follows [1,3]:

$$\mu_m = 0.369 \frac{M^{1/2} \gamma_m}{\left(\xi_T T_m \right)^{1/2}} \tag{1}$$

where μ is the viscosity, M is the atomic mass, γ is the surface tension, ξ_T is the new parameter recently introduced by the authors, T is the temperature in K, and subscript 'm' denotes 'melting point'. Values for ξ_T can be calculated using experimental data for the velocity of sound in liquid metals [1,3]. This new parameter gives an indication of the extent of an atom's hardness or softness, and is useful in discussing anharmonic effects of atomic motions in liquid metals [1,3]. The viscosity model represented by Eq. 1 gives very good agreement with experiment [1,3].

Temperature Dependence of Viscosity. The temperature dependence of viscosity data on liquid metals can be described by an Arrhenius type equation [1]:

$$\mu = \mu_0 \exp \left(\frac{H_\mu}{R\ T} \right) \tag{2}$$

where μ_0 and H_μ are constants, R is the gas constant. H_μ is sometimes called the apparent activation energy (for viscous flow). It has long been known that a simple empirical relationship exists between H_μ for liquid metals and their melting points T_m. Figure 1 shows a plot of $log\ H_\mu$ vs. $log\ T_m$ for various metallic liquids.
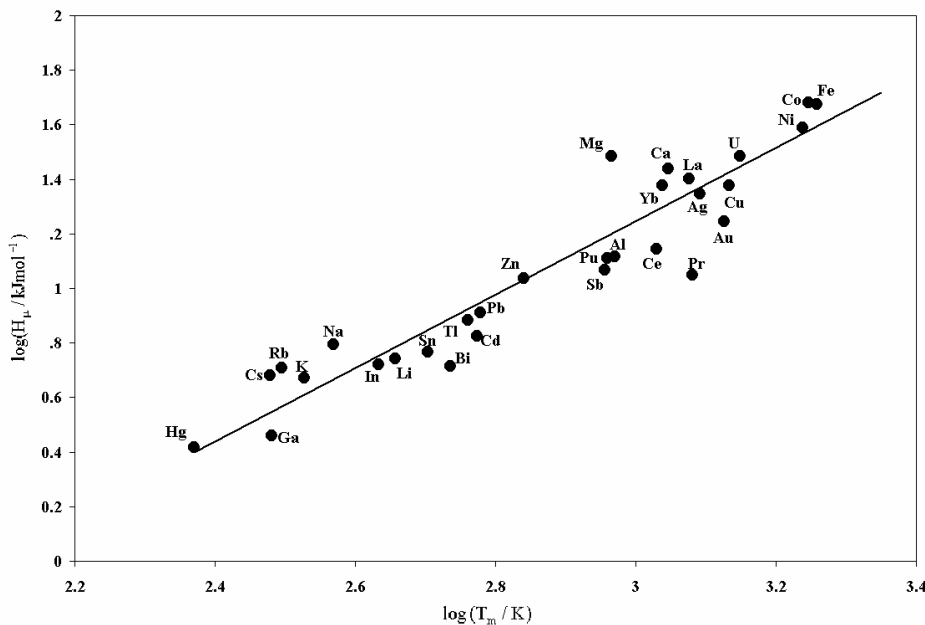

Fig 1: A plot of $log T_m$ vs. $log H_\mu$.

The data for H_μ and T_m were taken from the authors' recent publication [1]. A linear relationship between the two variables shown in Fig. 1 is expressed as:

$$H_\mu = 1.59\ T_m^{1.35}, \quad (\text{in J mol}^{-1}) \tag{3}$$

Table 1 lists H_μ values measured and calculated using Eq. 3, together with corresponding δ_i, Δ and S values needed for statistical assessment [1,3,4] of the model (refer to the note given in Table 1). Equation 3 performs reasonably with the apparent activation energy for a liquid metal's viscous flow giving global delta and relative standard deviation values of 22.0 % and 0.281, respectively (Accurate experimental determination of H_μ for liquid metals is a non-trivial task). Incidentally, the numerical factors appearing in Eq. 3 were determined so as to give the minimum S value for the 30 metallic liquids listed in Table 1. This minimization approach [1,4] is also used in the evaluation of the numerical constants in Eqs. 5, 7, and 9.

Table 1. Comparison of measured and calculated energies of apparent activation for viscous flow of liquid metallic elements, together with values for δ_i, Δ and S.

Element		H_μ / [kJmol^{-1}]		δ_i %	Element		H_μ / [kJmol^{-1}]		δ_i %
		Mea.	Cal.				Mea.	Cal.	
Aluminium	Al	13.1	16.3	-19.6	Lithium	Li	5.52	6.14	-10.1
Antimony	Sb	11.7	15.6	-25.0	Magnesium	Mg	30.5	16.0	90.6
Bismuth	Bi	5.19	7.85	-33.9	Mercury	Hg	2.61	2.52	3.6
Cadmium	Cd	6.70	8.83	-24.1	Nickel	Ni	38.9	37.3	4.3
Calcium	Ca	27.5	20.7	32.9	Plutonium	Pu	12.9	15.8	-18.4
Cerium	Ce	14.0	19.6	-28.6	Potassium	K	4.69	4.10	14.4
Cesium	Cs	4.79	3.54	35.3	Praseodymium	Pr	11.2	22.9	-51.1
Cobalt	Co	48.1	38.5	24.9	Rubidium	Rb	5.13	3.71	38.3
Copper	Cu	23.9	27.0	-11.5	Silver	Ag	22.2	23.7	-6.3
Gallium	Ga	2.88	3.56	-19.1	Sodium	Na	6.25	4.68	33.5
Gold	Au	17.6	26.4	-33.3	Thallium	Tl	7.64	8.49	-10.0
Indium	In	5.24	5.70	-8.1	Tin	Sn	5.83	7.10	-17.9
Iron	Fe	47.4	39.8	19.1	Uranium	U	30.5	28.3	7.8
Lanthanum	La	25.2	22.6	11.5	Ytterbium	Yb	23.8	20.1	18.4
Lead	Pb	8.14	8.96	-9.2	Zinc	Zn	10.9	10.9	0.0
								$\Delta(30)^*$ %	22.0
								$S(30)^*$	0.281

* Numerical figures in parentheses denote the number of samples.

The performance of the models was evaluated by determining relative differences between the calculated and measured physical quantities, e.g. H_μ, D_m [1,3,4].

$$\delta_i = \frac{(\chi_i)_{mea} - (\chi_i)_{cal}}{(\chi_i)_{cal}} \times 100, \ (\%)$$

where $(\chi_i)_{mea}$ and $(\chi_i)_{cal}$ are the measured and calculated physical quantities, respectively.

$$\Delta = \frac{1}{N} \sum_{i=1}^{N} |\delta_i|, \ (\%), \ \text{where } N \text{ is the number of samples.}$$

$$S = \frac{1}{100}\sqrt{\overline{\delta_i^2}} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{(\chi_i)_{mea} - (\chi_i)_{cal}}{(\chi_i)_{cal}}\right\}^2}$$

The parameter S corresponds to the relative standard deviation.

Using Eqs. 1, 2, and 3, and the conditions $T = T_{\mathrm{m}}$, $\mu = \mu_{\mathrm{m}}$, we obtain the following equation for the viscosity of liquid metallic elements:

$$\mu = \mu_0 \, \exp\left(\frac{1.59 \; T_{\mathrm{m}}^{1.35}}{R \; T}\right) \quad , \quad \mu_0 = \frac{\mu_{\mathrm{m}}}{\exp\left(\dfrac{1.59 \; T_{\mathrm{m}}^{0.35}}{R}\right)} \tag{4}$$

Figures 2 gives a comparison of measured values for the viscosity of liquid titanium [5,6] with values calculated on the basis of Eqs. 1 and 4, and the hard-sphere model [6], respectively. As is clear from Fig. 2, the model represented by Eqs. 1 and 4 is in very good agreement with experimental viscosity values over a wide temperature range, including undercooled region.
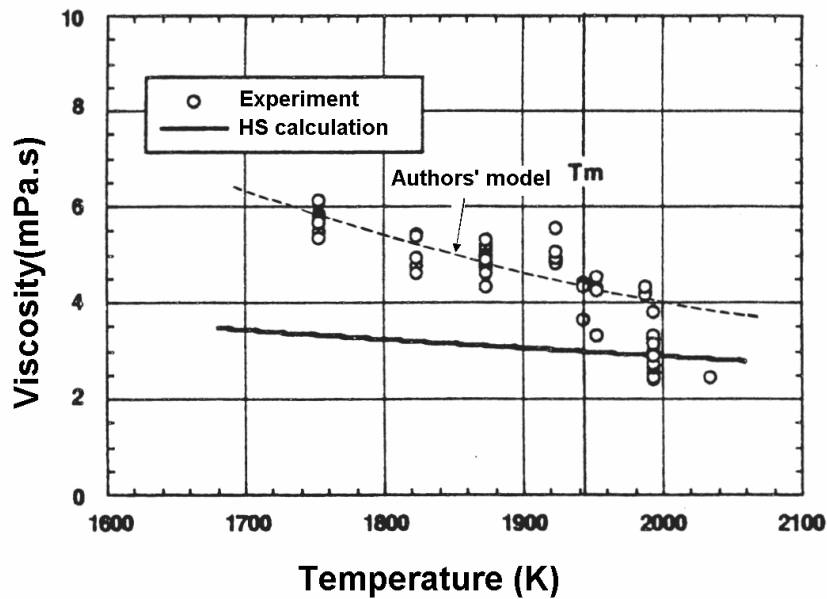

Fig. 2: A comparison of measured values for viscosity of liquid titanium with those predicted using the hard-sphere model [6] and the authors' model.

The uncertainties in viscosity calculations using Eqs. [1] and [4] are nearly equal, or equal, to the experimental uncertainties in the viscosity measurements which are estimated to be 1-20 % [7,8].

Self-Diffusivity Model for Liquid Metallic Elements

Melting-Point Self-Diffusivity. It has been known for a long time that an equation for self-diffusivity of liquid metals at their melting points is expressed in terms of $(T_{\mathrm{m}}/M)^{1/2} V_{\mathrm{m}}^{1/3}$.

$$D_{\mathrm{m}} = 1.32 \times 10^{-9} \left(\frac{T_{\mathrm{m}}}{M}\right)^{1/2} V_{\mathrm{m}}^{1/3} \tag{5}$$

where D is the self-diffusivity, and V is the atomic volume. This type of equation in terms of $(T_{\mathrm{m}}/M)^{1/2} V_{\mathrm{m}}^{1/3}$ was derived through a combination of the modified Stokes-Einstein relation and the Andrade formula for melting-point viscosity [8], as well as the hard-sphere model [8-12] and the corresponding-states principle [8]. By combining the modified Stokes-Einstein formula with Eq. 1, we can now derive a model for self-diffusivity in liquid metallic elements. At the melting point, the modified Stokes-Einstein formula is given by [8]:

$$D_m = \frac{kT_m}{\zeta\left(V_m/N_A\right)^{1/3}\mu_m} \tag{6}$$

where k is the Boltzmann constant, ζ is a constant, and N_A is Avogadros' number.

Substituting Eq. 1 into Eq. 6, we have an equation for the melting-point self-diffusivity in liquid metallic elements in terms of the new parameter ξ_T.

$$D_m = 6.69 \times 10^{-16}\left(\frac{\xi_T T_m}{M}\right)^{1/2}\frac{T_m}{V_m^{1/3}\gamma_m} \tag{7}$$

Table 2 compares measured values for the melting-point self-diffusivity of various liquid metallic elements with those calculated using Eqs. 5, and 7, and a listing of δ_i, Δ, and S values for the assessment of the models. The data [1,2,13] used for calculating self-diffusivities and experimental self-diffusivity data [14-18] are given in the references. It is extremely difficult to assign experimental uncertainties for self-diffusivity measurements, but 5-25 % would seem to be a fair estimate [16], except for bismuth. Roughly speaking, the melting-point self-diffusivity values calculated from Eqs. 5, and 7 are nearly equal, or equal, to those obtained experimentally. However, Eq. 7 gives better Δ and S values of 14.3 % and 0.183, and made improvements to the results calculated from Eq. 5, especially for antimony.

Table 2. Comparison of measured values for the self-diffusivities in liquid metallic elements with values calculated using Eqs. 5 and 7, together with δ_i, Δ, and S values.

| Element | | Self-diffusivity D_m / [$10^{-9}\mathrm{m^2s^{-1}}$] | | | δ_i % | |
| | | | Cal. | | | |
		Mea.	Eq. 5	Eq. 7	Eq. 5	Eq. 7
Antimony	Sb	5.18	3.02	4.48	71.5	15.6
Cadmium	Cd	1.78	2.31	2.18	-22.9	-18.3
Cesium	Cs	2.69	2.62	2.66	2.7	1.1
Copper	Cu	4.00	3.85	4.64	3.9	-13.8
Gallium	Ga	1.63†	1.96	1.42	-16.8	14.8
Indium	In	1.67†	2.05	1.83	-18.5	-8.7
Lead	Pb	1.98†	1.91	2.30	3.7	-13.9
Lithium	Li	6.41†	8.02	5.58	-20.1	14.9
Mercury	Hg	1.03†	1.10	0.75	-6.4	37.3
Potassium	K	3.68†	4.43	4.09	-16.9	-10.0
Rubidium	Rb	2.68†	3.08	2.91	-13.0	-7.9
Silver	Ag	2.57†	3.20	4.20	-19.7	-38.8
Sodium	Na	4.04†	4.89	4.20	-17.4	-3.8
Tellurium	Te	2.72	2.78	2.47	-2.2	10.1
Thallium	Tl	2.01	1.84	2.04	9.2	-1.5
Tin	Sn	2.19†	2.21	2.18	-0.9	0.5
Zinc	Zn	2.05†	2.92	3.01	-29.8	-31.9
				$\Delta(17)$ %	16.2	14.3
				$S(17)$	0.228	0.183

† The mean values determined from two, three or five different values of measured self-diffusivity data for a single metal, which were used for calculating δ_i, Δ, and S values.

Temperature Dependence of Self-Diffusivity. The temperature dependence of self-diffusivity in liquid metals can be expressed by the Arrhenius equation [8,9,15,18] as follows:

$$D = D_0 \exp\left(-\frac{H_D}{RT}\right) \tag{8}$$

where D_0 and H_D are the Arrhenius parameters. H_D is sometimes called the apparent activation energy. The apparent activation energies H_D of self-diffusivity are also related to melting temperatures. Figure 3 shows $\log H_D$ vs. $\log T_m$ plots. A linear relationship between the two variables shown in Fig. 3 is expressed as:

$$H_D = 12.6 T_m^{1.11} \tag{9}$$

Table 3 gives measured and calculated values of H_D together with δ_i, Δ, and S values. Eq. 9 works extremely well with Δ and S values of 12.1 % and 0.148, respectively.

Similarly to viscosity, on combining Eqs. 7, 8, and 9, and the condition $T = T_m$, $D = D_m$, we have the following equation for self-diffusivities of liquid metallic elements.

$$D = D_0 \exp\left(-\frac{12.6\ T_m^{1.11}}{RT}\right) \quad,\quad D_0 = D_m \exp\left(\frac{12.6\ T_m^{0.11}}{R}\right) \tag{10}$$
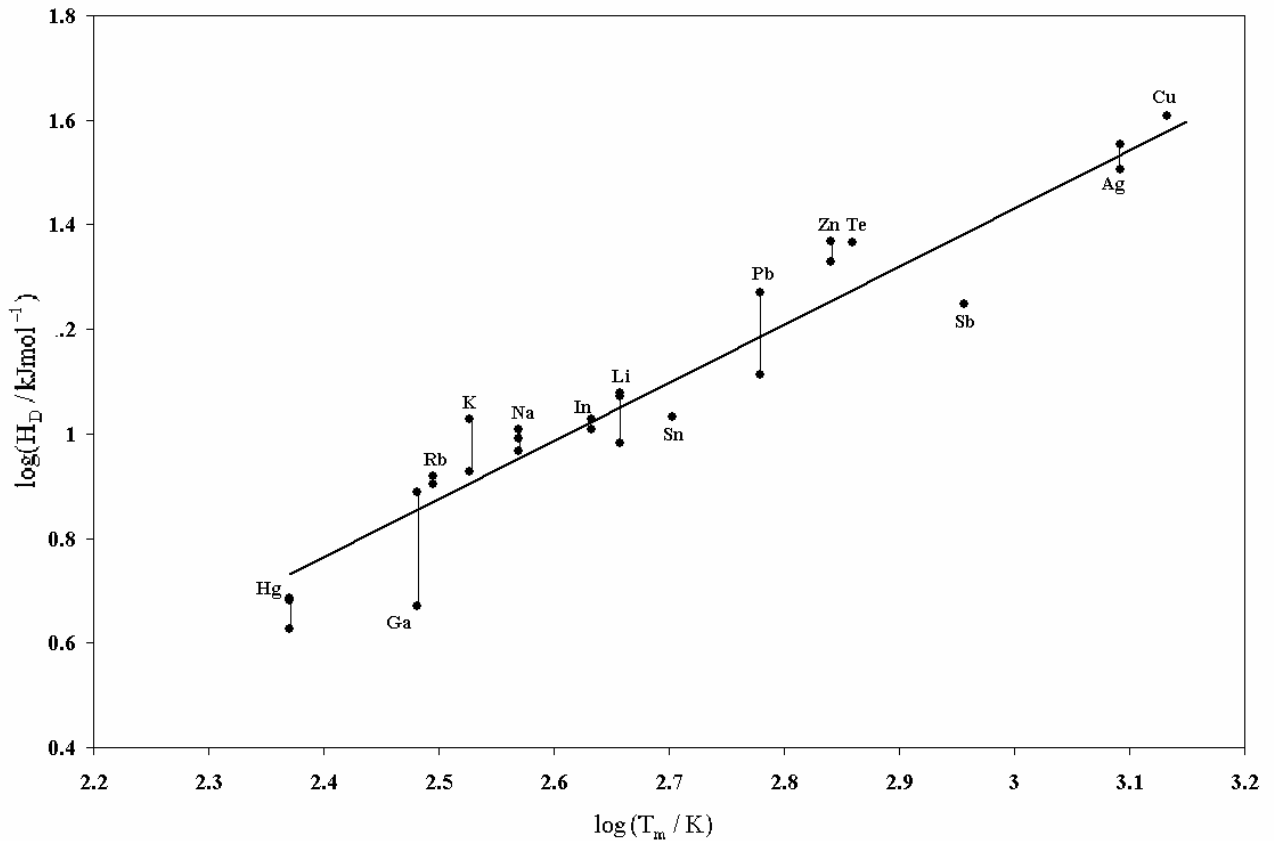

Fig. 3: A plot of $\log T_m$ vs. $\log H_D$.

Table 3. Comparison of the measured and calculated energies of apparent activation for self-diffusivity in liquid metallic elements, together with values for δ_i, Δ and S.

Element		H_D / [kJmol^{-1}]		δ_i %
		Mea.	Cal.	
Antimony	Sb	17.7	24.1	-26.6
Copper	Cu	40.6	37.8	7.4
Gallium	Ga	6.22[†]	7.16	-13.1
Indium	In	10.5[†]	10.5	0
Lead	Pb	15.8[†]	15.3	3.3
Lithium	Li	11.1[†]	11.2	-0.9
Mercury	Hg	4.63[†]	5.38	-13.9
Potassium	K	9.58[†]	8.04	19.2
Rubidium	Rb	8.14[†]	7.41	9.9
Silver	Ag	33.1[†]	34.0	-2.6
Sodium	Na	9.76[†]	8.96	8.9
Tellurium	Te	23.2	18.8	23.4
Tin	Sn	10.8	12.6	-14.3
Zinc	Zn	22.4[†]	17.9	25.1
			$\Delta(14)$ %	12.1
			$S(14)$	0.148

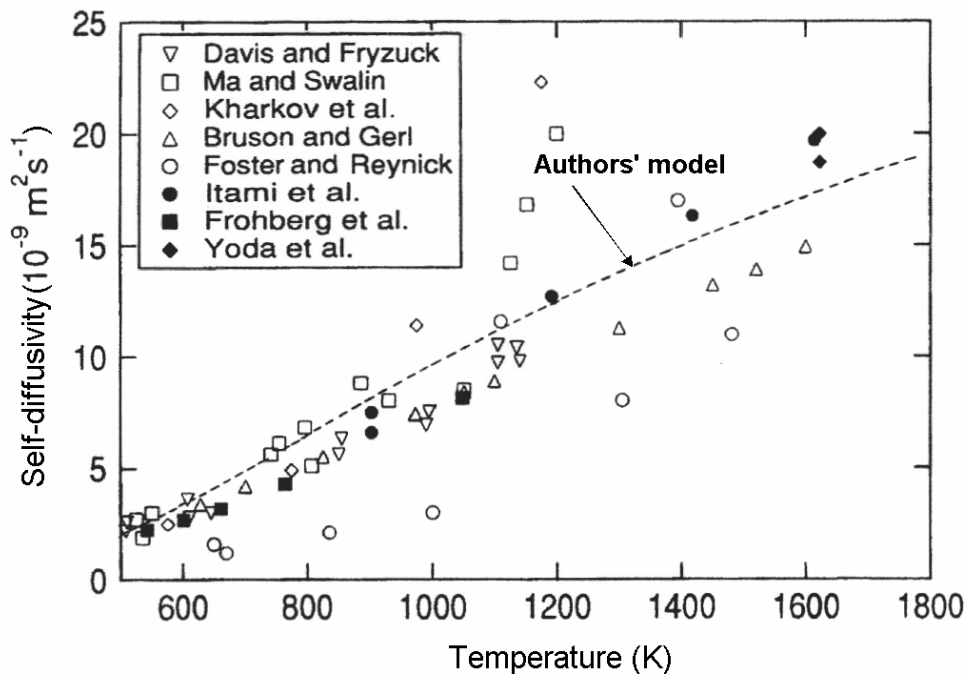† The mean value of two or three different experimental data for a single metal.

Fig. 4: A comparison of experimental self-diffusivity values for liquid tin by several workers with those calculated from Eqs. 7, and 10. Open symbols:experiments on the ground, closed symbols: experiments under microgravity [19].

Figure 4 provides a comparison of measured values for the self-diffusivity of liquid tin [19], as determined by several workers, with values calculated using Eqs. 7, and 10. As is clear from Fig. 4, the equations give very good results.

Equations 1, 4, 7, and 10 allow one to predict transport coefficients, i.e., viscosities and self-diffusivities, of any liquid metals at their typical processing temperature.

Predictions for the Self-Diffusivity in Liquid Aluminum, Calcium, and Magnesium

Using Eq. 1 in a previous publication [1], the authors predicted the viscosities of several transition metals, plus barium and strontium.

Using the model represented by Eqs. 7, and 9, the authors now predict self-diffusivities in liquid aluminum, calcium, and magnesium, for which experimental data are lacking. Table 4 lists predicted values for D_m and H_D for these liquid metals, together with the data [1,2,13] used for calculating their D_m and H_D values. The uncertainties in self-diffusivity predictions using the models proposed by authors are expected to fall within the range of uncertainties in careful future experimental measurements.

Table 4. Self-diffusivities in liquid aluminum, calcium, and magnesium predicted using Eqs. 7, and 9, together with values of the parameters used for predicting their self-diffusivities.

Element		D_m $10^{-9}\text{m}^2\text{s}^{-1}$	H_D kJmol^{-1}	T_m K	V_m $10^{-6}\text{m}^3\text{mol}^{-1}$	γ_m Nm^{-1}	$\xi_T^{1/2}$
Aluminum	Al	5.71	25.0	933.5	11.31	0.871	0.961
Calcium	Ca	7.71	30.4	1115	29.36	0.360	0.688
Magnesium	Mg	6.76	24.6	923	15.29	0.577	0.804

Summary

The authors have presented two models for accurate predictions of the atomic transport coefficients of liquid metallic elements. The models are expressed in terms of well-known physical quantities; atomic mass, atomic volume, melting point, melting-point surface tension, and the new parameter ξ_T. The models represented by Eqs. 1, 4, 7, and 10 give very good agreement with experiment. Using the model given by Eqs. 7, and 9, the self-diffusivity data were predicted for liquid aluminum, calcium, and magnesium.

References

[1] T. Iida, R.I.L. Guthrie, M. Isac, and N. Tripathi: Metall. Mater. Trans. Vol. 37B (2006), p. 403.

[2] B.J. Keene: Int. Mater. Rev. Vol. 38(4) (1993), p. 157.

[3] T. Iida, R.I.L. Guthrie, and M. Isac: ICS Proc., 3rd Int. Congr. on Science and Technology of Steelmaking, Association for Iron & Steel Technology, Charlotte, NC, (2005), p. 57.

[4] T. Iida, R.I.L. Guthrie, and M. Isac: ICS Proc., 3rd Int. Congr. on Science and Technology of Steelmaking, Association for Iron & Steel Technology, Charlotte, NC, (2005), p. 3.

[5] P.-F. Paradis, T. Ishikawa, and S. Yoda: Int. J. Thermophys. Vol. 23(3) (2002), p. 825.

[6] T. Ishikawa, P.-F. Paradis, T. Itami, and S. Yoda: J. Chem. Phys. Vol. 118(17) (2003), p. 7912.

[7] R.P. Chhabra and D.K. Sheth: Z. Metallkde. Vol. 81(4) (1990), p. 264.

[8] T. Iida and R.I.L. Guthrie: *The Physical Properties of Liquid Metals* (Oxford University Press, Oxford, United Kingdom 1993).

[9] T.E. Faber: *Introduction to the Theory of Liquid Metals* (Cambridge University Press. Cambridge, United Kingdom 1972).

[10] E.T. Turkdogan: *Physical Chemistry of High Temperature Technology* (Academic Press, New York 1980).

[11] R.J. Speedy, F.X. Prielmeier, T. Vardag, E.W. Lang, and H.D. Lüdemann: Molec. Phys., Vol. 66(3) (1989), p. 577.

[12] E.T. Turkdogan: Can. Metall. Q. Vol. 41(2) (2002), p. 151.

[13] W.F. Gale and T.C. Tolemeier: *Simithells Metals Reference Book* (Elsevier Butherworth-Heineman, Oxford, United Kingdom 2004).

[14] *Metals Data Book* (The Japan Institute of Metals edited: Maruzen Company LTD, Tokyo 2004).

[15] K. Nagata, Y. Ono, T. Ejima, and T. Yamamura: *Handbook of Physico-Chemical Properties at High Temperatures* (The Iron and Steel Institute of Japan, Tokyo 1988).

[16] A.S. Chauhan, R. Ravi, and R.P. Chahabra: *Chem. Phys.* Vol.252 (2000), p. 227.

[17] T. Iida and R.I.L. Guthrie: *ibid. 9* (Oxford University Press, Oxford, United Kingdom 1993).

[18] N.H. Nachtrieb: Adv. Phys. Vol. 16 (1967), p. 323.

[19] T. Masaki, T. Fukazawa, S. Matsumoto, T. Itami, and S. Yoda: Meas. Sci. Technol. Vol. 16(2) (2005), p. 327.

Models and Equations for Atomic Transport Coefficients of Liquid Metals: Viscosity and Self-Diffusivity