Application of the Corresponding-States Correlations to the Viscosity and Self-Diffusivity of Various Metallic Liquids

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ABSTRACT

The corresponding-states correlations were applied to transport coefficients, i.e., viscosity and diffusivity, for various metallic liquids for which experimental data are presently available in order to test the correlations. The corresponding-states correlations for transport coefficients have spreads of ± 20% to 50% or more. A better correlation is proposed for the melting-point viscosity of metallic liquids.

1. INTRODUCTION

Transport coefficients in metallic liquids, i.e., viscosity and diffusivity, are of critical importance both from a scientific and a technological viewpoint. Therefore, a number of studies have been made on their theoretical and semi-theoretical calculations and measurements. A well-known example for calculating transport coefficients is based on the principle of corresponding-states. Helfand and Rice /1/ first derived the corresponding-states correlations through a dimensional analysis of the statistical equations for transport in liquids. Several workers applied corresponding-states correlations to transport coefficients in liquid metals; Pasternak /2/, Wittenberg and DeWitt /3/ and Waseda and Ohtani /4/ applied the correlations to the viscosity and self-diffusivity of six to sixteen liquid metals available at that time. Their results show that the applicability of the corresponding-states principle is comparatively good. As a result, corresponding-states methods are believed to be useful for estimating transport coefficients. However, investigations for various metallic liquids are needed in order to test and develop the correlations.

In this paper, corresponding-states correlations are applied to the viscosity and self-diffusivity of various metallic liquids for which experimental data are presently available. Furthermore, a better correlation is proposed for the melting-point viscosity of metallic liquids.

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2. EXPRESSIONS FOR VISCOSITY AND DIFFUSIVITY BASED ON THE PRINCIPLE OF CORRESPONDING STATES

Helfand and Rice /1/ derived the following equations for reduced viscosity μ^* and self-diffusivity D^*, respectively, on the basis of the principle of corresponding states:

$$\mu^* = \frac{\mu \sigma^2}{m^{1/2} \varepsilon^{1/2}} \tag{1}$$

$$D^* = \frac{D\, m^{1/2}}{\varepsilon^{1/2}\, \sigma} \tag{2}$$

where μ is the viscosity, D the diffusivity, m the atomic mass, ε the characteristic energy parameter, and σ the distance parameter. In order to avoid determination of explicit values for σ, Pasternak converted Eqs. 1 and 2 into the following dimensionless expressions to be correlated with the reduced temperature T^* (T^* is defined as $T/\varepsilon/k$)

$$\mu^* (V^*)^{2/3} = \frac{N^{1/3}\, V^{2/3}\, \mu}{(MR\varepsilon/k)^{1/2}} \tag{3}$$

$$D^*/(V^*)^{1/3} = \frac{N^{1/3}\, M^{1/2}\, D}{(R\varepsilon/k)^{1/2}\, V^{1/3}} \tag{4}$$

where V^* is the reduced volume; N the Avogadro's number, V the atomic (molar) volume, M atomic weight, R the gas constant, and ε/k the energy parameter (k the Boltzmann's constant). According to Chapman /5/ and Pasternak /2/, the term ε/k is approximately equal to

$$\frac{\varepsilon}{k} = 5.20 T_m = \frac{T}{T^*} \tag{5}$$

On the other hand, Waseda and Ohtani /4/ suggested that ε/k is approximately equal to $1.41 T_m$ based on the analysis of the shape of pair potentials for liquid metals. It should be noted, however, that the corresponding-states principle is essentially valid for use in a linear relationship between ε/k and T_m, regardless of the value of the proportionality constant.

3. RESULTS AND DISCUSSION

A. Viscosity of Metallic Liquids

The reduced quantities $\mu^* (V^*)^{2/3}$ for thirty-four metallic elements were calculated using Eq. 3. Values for viscosity μ and atomic volume V (i.e., density ρ, as $V = M/\rho$) were taken from the handbook /6/ published recently.

Fig. 1 presents the viscosity correlation obtained from Eq. 3 for the same ten metallic liquids as those investigated by Pasternak /2/. The solid lines and curves represent the correlation for the metallic liquids, and are drawn in the temperature range where the experimental data are available. As can be seen in Fig. 1, with the exception of gallium and zinc, the viscosity

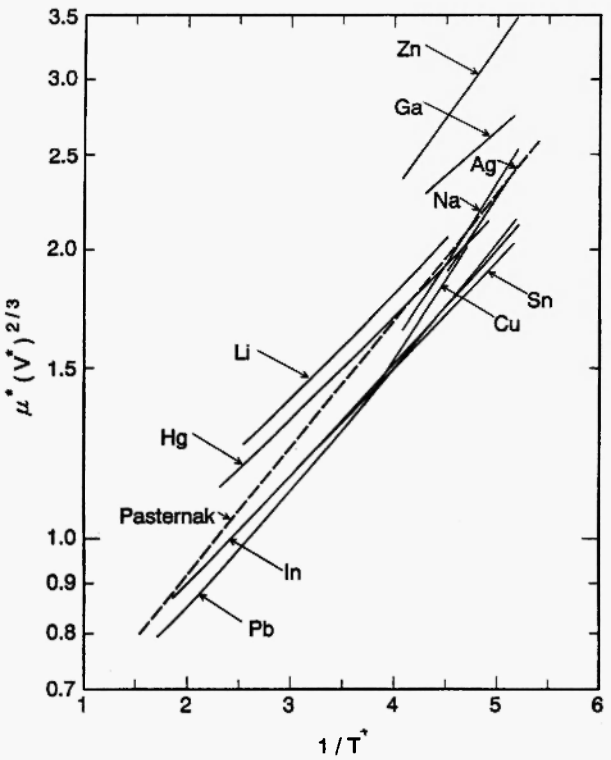

Fig. 1: Relationship between $\mu^* (V^*)^{2/3}$ and $1/T^*$ for the same ten metallic liquids as those investigated by Pasternak /2/. The broken line indicates Pasternak's relationship.

correlation for the metallic liquids can be approximated by Pasternak's linear relationship which has a spread of ± 20%.

Fig. 2 shows the viscosity correlation for another twenty-four metallic liquids. The open circle plots indicate the experimental data available only at a temperature near the melting point. The lines and plots in Fig. 2 lie within the maximum deviation of ± 50% from Pasternak's linear relationship. The results in Figs. 1 and 2 indicate that the corresponding-states principle provides a rough correlation for the viscosity of metallic liquids. The reason for the rough correlation would be mainly due to the assumptions used in the derivation of the corresponding-states principle. In addition, the experimental values for some metallic liquids appear to be unreliable. The large deviation on antimony and bismuth may be caused by the difference in the shapes of the pair potentials from those of other liquid metals, pointed out by Waseda and Ohtani /4/.

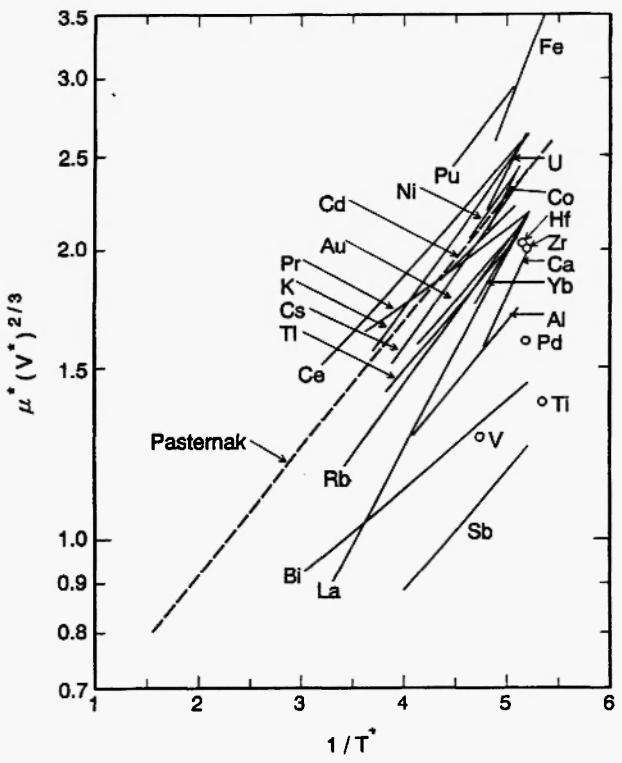

Fig. 2: Relationship between $\mu^* (V^*)^{2/3}$ and $1/T^*$ for another twenty-four metallic liquids and Pasternak's relationship.

B. Diffusivity of Metallic Liquids

Fig. 3 presents the diffusivity correlation obtained from Eq. 4 for the same ten metallic liquids as those investigated by Pasternak /2/. As seen in Fig. 3, the correlation can be represented approximately by Pasternak's linear relationship which has a spread of ± 20%. Fig. 4 shows the diffusivity correlation for another eight metallic liquids. Excepting germanium, bismuth and antimony, the lines also lie within the range of ± 20% deviation of the Pasternak's relation. The lines of germanium, bismuth and antimony show larger deviations: about 4, 2.2 and 2 times, respectively. The results in Figs. 3 and 4 show again that the corresponding-states principle provides a rough correlation for the diffusivity of metallic liquids.

C. The Melting-Point Viscosity and Diffusivity Estimated from the Principle of Corresponding-States and Other Theories

The viscosity correlation at the melting point derived from the corresponding-states principle, i.e., Eq. 3, can be represented in the following form:

$$\mu_m = 1.9 \times 10^{-7} \frac{(MT_m)^{1/2}}{V_m^{2/3}} \qquad (6)^4$$

where the subscript m denotes the melting point. Eq. 6 is very similar to Andrade's viscosity formula, the only difference being the replacement of the proportionality constant of 1.8×10^{-7} /7/.

Furthermore, it should be emphasized that at melting temperature the viscosity equations based on the hard sphere model /8,9/ and on the statistical mechanical theory of Born and Green /10/ also become similar to Andrade's formula for melting point

[4] The proportionality constant, 1.9×10^{-7}, is obtained from Eq. 3

$$\mu_m^* (V_m^*)^{2/3} \frac{(5.2R)^{1/2}}{N^{1/3}} = 1.89 \times 10^{-7}$$

The same value is obtained from the Waseda and Ohtani /4/ correlation.

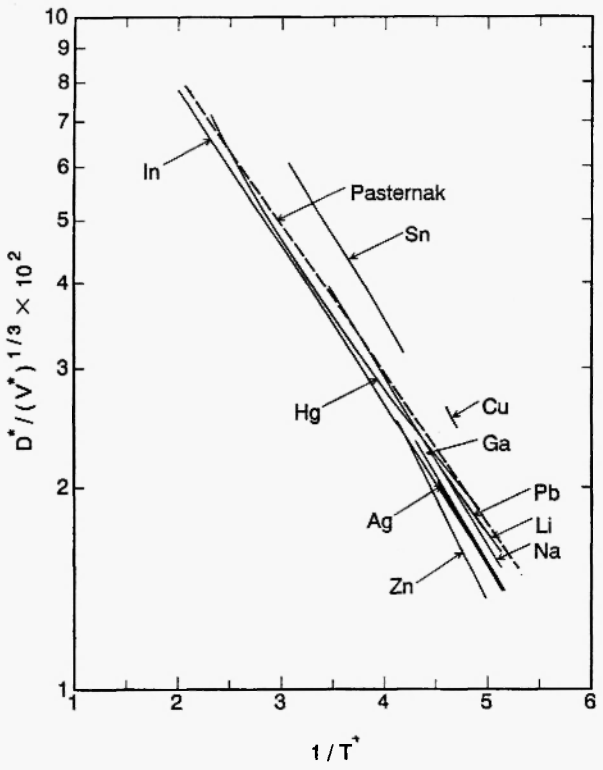

Fig. 3: Relationship between $D^* (V^*)^{-1/3}$ and $1/T^*$ for the same ten metallic liquids as those investigated by Pasternak /2/. The broken line indicates Pasternak's relationship.

viscosity. Andrade's formula has frequently been used for predicting the viscosity values of liquid metals.

Fig. 5 shows the Andrade's relationship for thirty-seven metallic liquids. The data were taken from Lihl *et al.* /11/ for magnesium and from Glazov /12/ for silicon and germanium. As Fig. 5 shows, except for silicon and germanium, the plots lie within the ± 50% error band. Of course, the extent of the deviation is equivalent to that of the corresponding-states principle. A better viscosity correlation is required for both a clear understanding and a reliable prediction of the viscosity of metallic liquids.

The diffusivity correlation for metallic liquids at the melting point derived from the corresponding-states principle, i.e., Eq. 4, can be written as follows:

$$D_m = 1.2 \times 10^{-9} \frac{V_m^{1/3} T_m^{1/2}}{M^{1/2}} \qquad (7)$$

Incidentally, many investigators have proposed relations for melting-point diffusivity similar to Eq. 7 from the empirical and semi-empirical points of view /13/.

D. Prediction of the Viscosity of Metallic Liquids Using the Equation Proposed by Iida and Co-Workers

Iida and co-workers /9,14/ reconsidered Andrade's model theory and proposed an expression for the viscosity of metallic liquids in terms of fundamental physical parameters such as the pair distribution function and the average interatomic frequency:

$$\mu = \frac{8\pi}{9} \nu_\ell \, m n_0^2 \int_0^a g(r) r^4 \, dr \qquad (8)$$

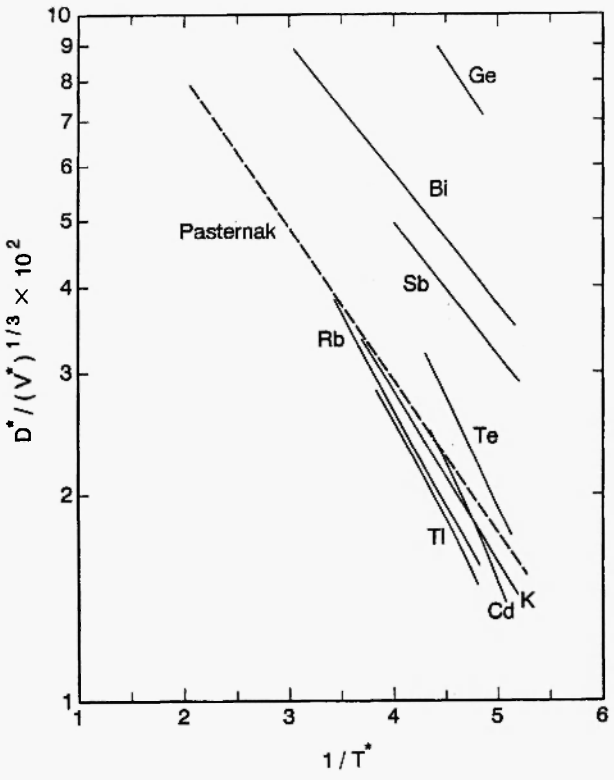

Fig. 4: Relationship between $D^* (V^*)^{-1/3}$ and $1/T^*$ for another eight metallic liquids and Pasternak's relationship.

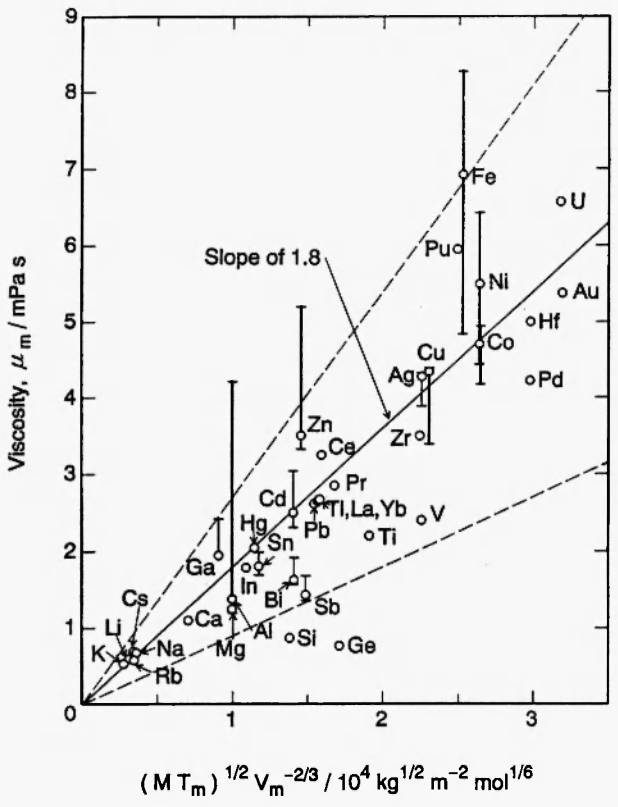

Fig. 5: Andrade relationship for the melting-point viscosity of metallic liquids. The broken lines represent ± 50% error band. The bars indicate the scatter of experimental data.

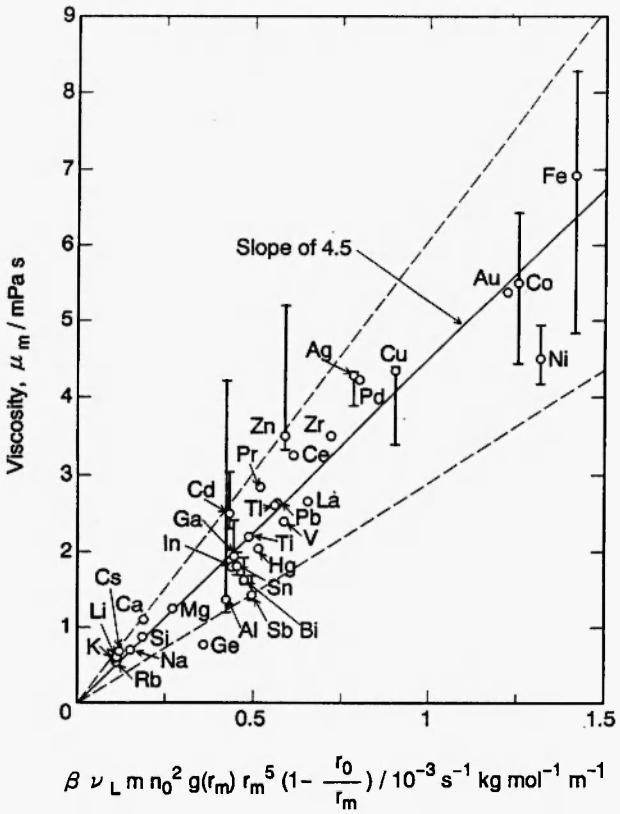

Fig. 6: Iida and co-worker's relationship for the melting-point viscosity of metallic liquids. The broken lines represent ± 35% error band. The bars indicate the scatter of experimental data. The plots for Hf, Yb, U and Pu are impossible due to the lack of the data on surface tension or g(r) curve.

where ν_f is the effective atomic frequency of a liquid metal, n_0 the average number density, g(r) the pair distribution function, a the distance over which the transfer of momentum takes place and r the interatomic distance. Using the empirical relation for the integration of $g(r)r^4$, Eq. 8 can be simplified to:

$$\mu = 4.5\ \nu_L\ m\ n_0^2 g\ (r_m)\gamma r_m^5\ (1-\frac{r_0}{r_m}) \qquad (9)$$

where r_m and r_0 are the positions of the first peak and its left-hand edge in the g(r) curve, respectively. At the melting temperature, Eq. 9 becomes

$$\mu_m = 4.5\ \beta \nu_L\ m\ n_0^2 g\ (r_m)\gamma r_m^5\ (1-\frac{r_0}{r_m}) \qquad (10)$$

where β is the correction factor for Lindemann's melting formula (i.e., the effective atomic frequency of metallic liquids can be represented by the product of Lindemann's frequency, ν_L, and a correction factor, β, which incorporates the surface tension of a metal.).

In Fig. 6, the correlation for the melting point viscosities is plotted as indicated by Eq. 10. As seen, except for germanium, the plots lie within the ± 35% error band. Eq. 10 provides a better correlation than Andrade's formula.

4. CONCLUSIONS

The applicability of the principle of corresponding-states was investigated for the viscosity and diffusivity of various metallic liquids for which experimental values were reported. The results are summarized as follows:

1. The corresponding-states correlation has a spread of ± 50% for the viscosity of thirty-four metallic liquids.
2. The corresponding-states correlation has a spread of ± 20% for the diffusivity of eighteen metallic liquids, except for liquid germanium, bismuth and antimony.
3. The viscosity equation proposed by Iida and co-workers provides a better correlation than Andrade's formula for the melting-point viscosity.

REFERENCES

1. E. Helfand and S.A. Rice, *J. Chem. Phys.*, **32**, 1642 (1960).
2. A.D. Pasternak, *Phys. Chem. Liquids*, **3**, 41 (1972).
3. L.J. Wittenberg and R. DeWitt, *The Properties of Liquid Metals* (S. Takeuchi, ed., Proc. 2nd Int. Conf. Liq. Met.), Taylor and Francis, London, 1973, 555.
4. Y. Waseda and M. Ohtani, *Tetsu to Hagane*, **61**, 46 (1975).
5. T.W. Chapman, *A.I.Ch.E. Journal*, **12**, 395 (1966).
6. Y. Kawai and Y. Shiraishi, eds., *Handbook of Physico-Chemical Properties at High Temperatures*, The Iron Steel Inst. Jpn. (Special Issue No. 41), 1988.
7. E.N.C. Andrade, *Phil. Mag.*, **17**, 497 (1934).
8. H.C. Longuet-Higgins and J.A. Pople, *J. Chem. Phys.*, **25**, 884 (1956).
9. T. Iida and R.I.L. Guthrie, *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford, 1993.
10. M. Born and H.S. Green, *Proc. Roy. Soc., A*, **190**, 455 (1947).
11. F. Lihl, E. Nachtigall and A. Schwaiger, *Z. Metallkde.*, **59**, 213 (1968).
12. V.M. Glazov, *Liquid Semiconductors*, Plenum, New York, 1969.
13. S.J. Larsson, C. Roxgergh and A. Lodding, *Phys. Chem. Liquids*, **3**, 137 (1972).
14. T. Iida, R.I.L. Guthrie and Z. Morita, *Can. Met. Quart.*, **27**, 1 (1988).