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Hard-Sphere Model for Self-Diffusion in Liquid Metals*

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Self-diffusion coefficients have been calculated by the method of Ascarelli and Paskin, using the new hard-sphere equation of state developed by Carnahan and Starling. The results show a higher temperature dependence and yield, in general, a more accurate description of liquid-metal data.

The Enskog relationship[1] for the self-diffusion coefficient of a dense fluid composed of hard spheres is given by

$$D = \tfrac{1}{2} l \,(\pi k T/m)^{1/2} 1/(z-1), \qquad (1)$$

where l is the hard-sphere radius, m is the atomic mass, and z is the hard-sphere compressibility. Two years ago, Ascarelli and Paskin[2] considered (1) and formulated an expression for the coefficient of self-diffusion in liquid metals. Recognizing that at atmospheric conditions, the repulsive hard-sphere pressure must be balanced approximately by the attractive van der Waals pressure, they evaluated the van der Waals constant at the melting point. Further, they initially considered a correction factor for backscattering given by $0.73(\eta_m/\eta)^{1/2}$ but later, in a note added to the manuscript, they recommend a backscattering correction of $0.73(\eta_m/\eta)$, where η is the packing factor and the subscript refers to the melting point. Thus, their final form for hard-sphere dense fluids is

$$D = \frac{l}{2}\left(\frac{\pi k T}{m}\right)^{1/2} \frac{0.73(\eta_m/\eta)}{(z_m T_m \rho/T\rho_m) - 1}, \qquad (2)$$

where z_m is the melting point compressibility evaluated by using a suitable equation of state.

Ascarelli and Paskin obtained z_m using the Percus-Yevick equation of state

$$z = (1+\eta+\eta^2)/(1-\eta)^3 . \qquad (3)$$

However, more recently a hard-sphere equation has been developed by Carnahan and Starling[3] using an analysis of the reduced virial series. This new equation, which has been shown to be superior to any existing hard-sphere equation of state including that of Percus and Yevick, is

TABLE I. Rigid-sphere compressibility at the melting point.

Equation of state	z_m
Percus and Yevick	9.932[a]
Carnahan and Starling	9.385

[a] Ascarelli and Paskin used a value of 10.

TABLE II. Comparison of experimental and calculated self-diffusion coefficients at the melting point.

	$D(10^{-5}\ \mathrm{cm^2/sec})$			
Substance	Expt [a]	Using (4)	Using (3)	Ascarelli-Paskin [b]
K	3.90	3.97	3.73	3.86
Na	4.27 [c]	4.37	4.10	4.20
In	1.66	1.84	1.73	1.78
Sn	2.05	2.00	1.87	1.92
Zn	2.02	2.57	2.41	2.52
Pb	2.19	1.72	1.62	1.70
Hg	1.17	0.99	0.98	0.98
Li	6.5	7.23	6.78	7.0
Ga	1.66 [d]	1.76	1.65	•••

[a] Unreferenced values given in Ascarelli and Paskin (Ref. 2).

[b] Using (3) and correction factor $0.73(\eta_m/\eta)^{1/2}$.

[c] R. Meyer and N. Natchtrieb, J. Chem. Phys. 23, 1851 (1955).

[d] E. Broome and H. Walls, Trans. AIME 245, 739 (1969).

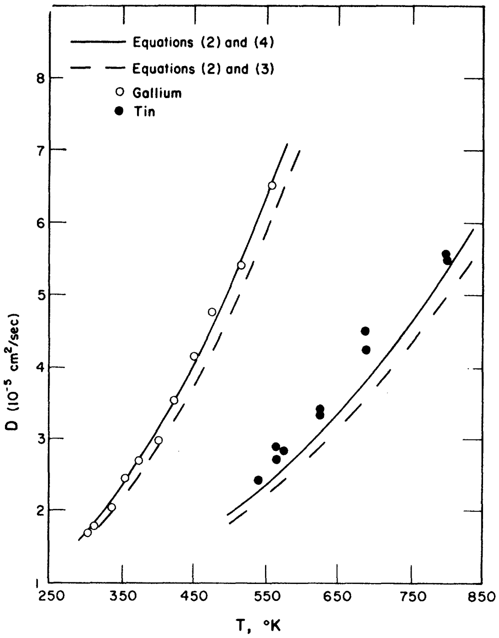

FIG. 1. Temperature dependence of self-diffusion coefficients for gallium and tin.

$$z=(1+\eta+\eta^2-\eta^3)/(1-\eta)^3 \; . \tag{4}$$

Assuming that for all simple fluids at the melting point $\eta_m = 0.45$, the values for z_m are calculated from (3) and (4) (see Table I).

Values of the self-diffusion coefficient for several liquid metals at their melting points were calculated with (2) using values of z_m from Table I. These values are compared with experimentally measured self-diffusion coefficients, along with the original self-diffusion coefficients calculated by Ascarelli and Paskin using the correction factor $0.73(\eta_m/\eta)^{1/2}$ (see Table II).

The agreement of all calculated values with the melting-point data is remarkable, particularly when, as pointed out by Ascarelli and Paskin, the error of the data is generally on the order of 10%.

The temperature dependence of (2) using (3) and (4) for gallium[4] and tin[5] is illustrated in Fig. 1. It is observed that the Carnahan-Starling equation of state coupled with the backscattering correction of $0.73(\eta_m/\eta)$ yields a higher temperature dependence. Consequently, the data are more accurately represented over the full temperature range. Similar results have been obtained on comparing with available data for sodium,[6] mercury,[7] cadmium,[8] lead,[8] silver,[9] and zinc.[10] Data for indium[5] compare better using (3).

In conclusion, the equation of state recently proposed by Carnahan and Starling yields the higher temperature dependence hoped for by Ascarelli and Paskin. Experimental data over the entire temperature range appear to be much better represented for most liquid metals tested.

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Temperature Dependence of the $AuGa_2$ Elastic Moduli

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An anomalously large temperature dependence of the elastic behavior of $AuGa_2$ occurs near 85 °K. A singular exception (c_{44}-type shear) should provide some knowledge of the band responsible for the unusual elastic and magnetic behavior.

Numerous reports have now been published which indicate that the intermetallic compound $AuGa_2$ exhibits anomalies in its physical properties which are not shared by the isostructural compounds $AuAl_2$ and $AuIn_2$. The Ga^{71} Knight shift and spin-lattice relaxation times, and the magnetic susceptibility for $AuGa_2$ show a strong temperature dependence between 20 and 300 °K.[1] The Seebeck coefficient of $AuGa_2$ has an unusual temperature dependence in which the sign of the coefficient reverses at 14 °K and again at 145 °K.[2] These anomalies are not found in $AuAl_2$ and $AuIn_2$. However, the electrical resistivity,[2] the Hall coefficient,[2] the electronic and lattice specific heats,[3] and the de Haas-van Alphen studies of the Fermi surface[4] of these three compounds do not indicate any distinction of the $AuGa_2$ behavior.[5] To explain the anomalies in the magnetic measurements, Jac-