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Self-diffusion and activation volume in solids from a melting temperature approach

Piyush Kuchhal and Narsingh Dass

Physics Department, University of Roorkee, Roorkee 247667, India

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Abstract. It is shown that the melting temperature approach is quite successful in representing the pressure dependence of the self-diffusion coefficient in solids at different temperatures. Moreover, the approach is also capable of giving the activation volume and compressibility as functions of both the pressure and the temperature. The calculations are performed in the cases of Na, Pb, Cd and Zn.

Recently, it has been shown [1] that the vacancy model of Zener [2] is quite successful in explaining the pressure dependence of self-diffusion in solids. However, the present paper discusses the melting temperature approach in computing the pressure dependence of self-diffusion and activation volume in solids at different temperatures.

In most of the solids, the melting temperature, T_m , is found to increase with increasing pressure [3,4]. On the other hand, the self-diffusion coefficient, $D(P, T)$, is found to decrease with rising pressure, indicating that Gibbs' activation energy, $g^{act}(P, T)$, must increase with increasing pressure. Therefore, there is a possibility that the quantities g^{act} and T_m are related. We suggest a relation between them as

$$g^{act}(P, T) = A(T)RT_m - E(T) \quad (1)$$

where T_m is the melting temperature at pressure P , T is the ambient temperature at which $D(P, T)$ data are available as a function of pressure. $A(T)$ and $E(T)$ are pressure-independent but temperature-dependent parameters and R is the universal gas constant.

Equation (1) can be used to define the diffusion coefficient as

$$D(P, T) = D_0 \exp[-g^{act}(P, T)/RT] \quad (2)$$

where D_0 is the frequency or pre-exponential factor and is given as

$$D_0 = \nu f g a^2. \quad (3)$$

In equation (3), g is a geometrical factor f is correlation factor, a is a lattice parameter and ν is the jump frequency.

Actually, D_0 is a pressure-dependent parameter and can be evaluated [1, 5, 6], but the effect of pressure on D_0 is quite small and hence can be neglected. Therefore, in the present paper, D_0 is taken as a pressure-independent parameter without introducing much error in the results.

Substituting equation (1) into (2), we obtain

$$\ln D(P, T) - \ln D_0 = -[A(T)T_m/T] + [E(T)/RT]. \quad (4)$$

Differentiation of equation (4) with respect to T_m/T keeping T constant gives

$$[\partial \ln D(P, T) / \partial (T_m/T)]_T = -A(T). \quad (5)$$

Therefore, the physical significance of $A(T)$ is that it represents the slope of the straight line obtained by plotting $\ln D(P, T)$ versus T_m/T for a solid at a given temperature T .

Further, at pressure $P = 0$ and temperature T , equation (2) can also be written as

$$\ln D(0, T) - \ln D_0 = -[A(T)T_0/T] + [E(T)/RT]. \quad (6)$$

Equations (4) and (6) can be combined to give

$$D(P, T) = D(0, T) \exp[-A(T)(T_m - T_0/T)]. \quad (7)$$

The melting temperature as a function of pressure can be obtained from Simon's relation [7, 8] given as

$$T_m = T_0[1 + \beta P]^C \quad (8)$$

where T_m and T_0 are the melting temperatures at pressure P and $P = 0$, respectively. Kumari and Dass [4] had identified the Simon constants β and C as

$$\beta = B'_T(0, T_0)/B_T(0, T_0) \quad C = 2[\gamma(0, T_0) - \frac{1}{3}]/B'_T(0, T_0).$$

Here, $B_T(0, T_0)$ and $B'_T(0, T_0)$ are the isothermal bulk modulus and its first pressure derivative, respectively, at zero pressure and temperature T_0 . $\gamma(0, T_0)$ is the Grüneisen parameter. The values of β and C for Na are taken from the article by Dass [9] whereas those for Cd, Zn and Pb are taken from the article by Babb [8]. The values of these parameters are reported in table 1.

Table 1. Values of melting constants $A(T)$ and $V^{act}(0, T)$, in different solids as functions of temperature. V^{act} in the case of Cd and Zn is along the C -axis

Solids	Melting constant			T (K)	V^{act} (cm ³ mol ⁻¹)		α^{act}	$\frac{K_T^{act}}{K_T}$	References for V^{act}	
	T_0 (K)	β (Kbar ⁻¹)	C		$A(T)$	Present				Theory
Na	370.950	0.1086	0.236	288.00	14.71	11.43	11.1 ± 0.2	7.0	5.1	[14]
				364.45	15.92	12.36	13.0 ± 0.2			
				592.15	16.67	7.62	7.49 ± 0.15			
Cd	594.1	0.022	0.417	574.15	17.11	7.83	7.65 ± 0.10	6.08	5.65	[12]
				549.15	15.90	7.27	7.14 ± 0.14			
				524.15	15.46	7.26	6.90 ± 0.13			
Pb	600.2	0.031	0.416	574.2	22.36	14.36	13.0 ± 0.8	—	8.1	[11]
				526.0	26.61	17.09	15.4 ± 1.7			
				673.95	10.67	4.27	4.28 ± 0.08			
Zn	692.7	0.017	0.417	623.85	9.99	3.99	3.97 ± 0.05	9.0	6.2	[13]
				574.05	9.78	3.91	3.72 ± 0.03			

Differentiation of equation (1) with respect to pressure gives the activation volume, $V^{act}(P, T)$, as

$$[\partial g^{act}(P, T) / \partial P]_T = V^{act}(P, T) = A(T)R \frac{dT_m}{dP}. \quad (9)$$

Equation (9) can alternatively be written as

$$V^{act}(P, T) = A(T)RT_0C\beta(1 + \beta P)^{C-1} \quad (10)$$

with the help of equation (8).

Moreover, the differentiation of $V^{act}(P, T)$ with respect to pressure at constant temperature gives the activation isothermal compressibility, $K^{act}(P, T)$, as

$$\begin{aligned} K^{act}(P, T) &= -[V^{act}(P, T)]^{-1}[\partial V^{act}(P, T)/\partial P]_T \\ &= (1 - C)\beta(1 + \beta P)^{-1}. \end{aligned} \quad (11)$$

According to the present theory, V^{act} involves the diffusion parameter $A(T)$ and, therefore, it varies with pressure as well as with temperature, but, on the other hand, K^{act} does not involve $A(T)$ and, therefore, it is independent of temperature and needs further verification.

The present theory is applied in the case of Na [10], Pb [11], Cd [12] and Zn [13]. The reference number with each solid represents the source of $D(P, T)$ data as a function of pressure at different temperatures. Once the data of $D(P, T)$ and T_m become available for a solid, the plot is drawn of $\ln D(P, T)$ against T_m/T at various temperatures, giving a straight line at each temperature. The straight line between $\ln D(P, T)$ and T_m/T is evident in figures 1 and 2 in the cases of Na, Pb, Cd and Zn. Hence, the slope of the straight line represents $A(T)$. The values of $A(T)$ so obtained are reported in table 1 for each solid at various temperatures, giving a straight line at each temperatures.

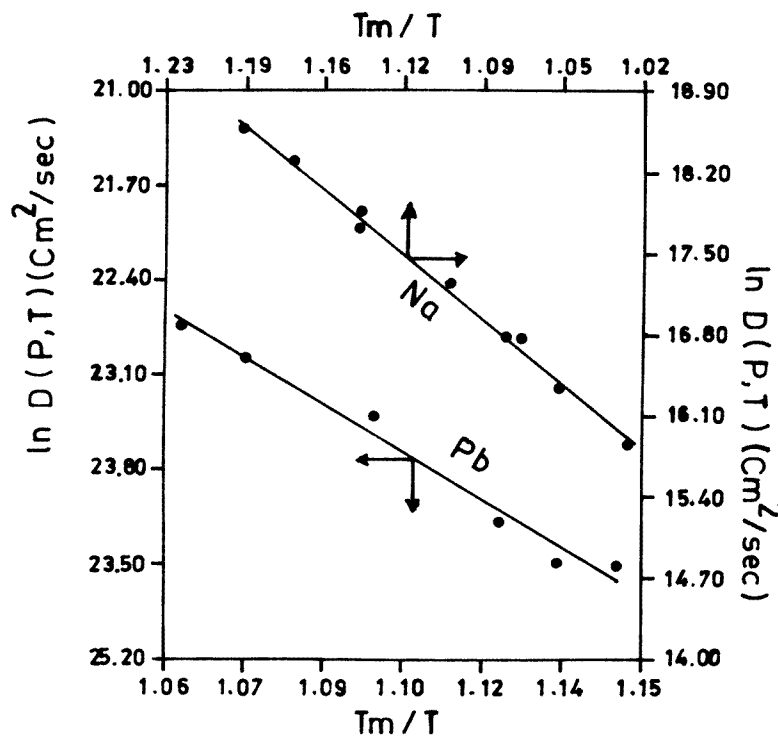


Figure 1. $\ln D(P, T)$ against T_m/T in the case of Na at 364.45 K and Pb at 574.2 K. The solid circles are the experimental points and the solid line is the best-fit curve.

Now, the values of $D(P, T)$ are computed as a function of pressure with the help of equation (7) as the value of $A(T)$ is known from table 1. The results so obtained are

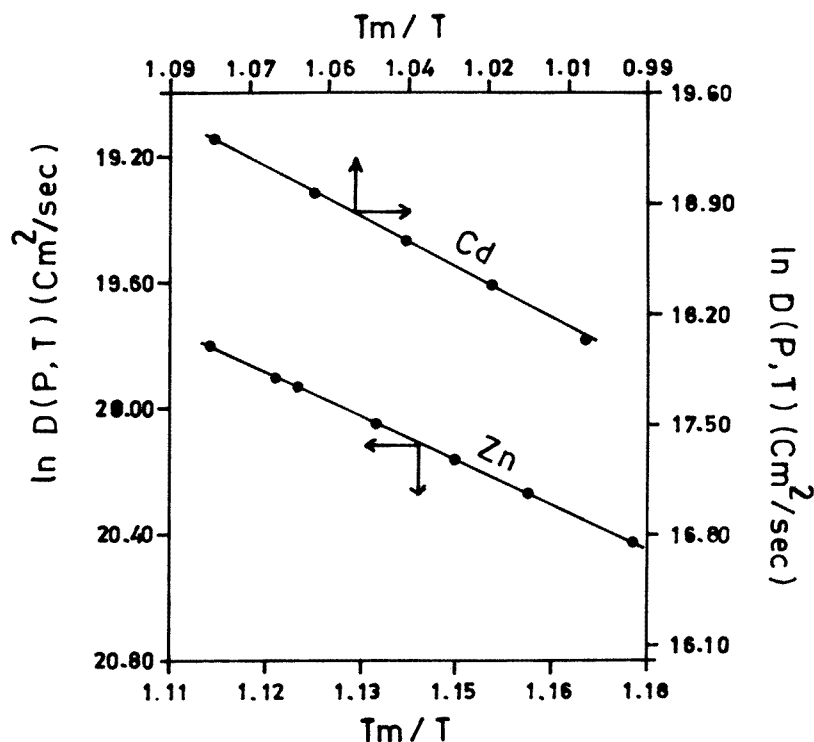


Figure 2. $\ln D(P, T)$ against T_m/T in the case of Cd at 592.15 K and Zn at 623.85 K along the c -axis. The solid circles are the experimental points and the solid line is the best-fit line.

reported for Na in table 2. In table 3, the results are compared for Pb, Cd and Zn at one temperature. The agreement between the calculated and the experimental data of $D(P, T)$ in each solid is very good keeping in mind the uncertainties involved in the measurement of diffusion data.

The values of activation volume at $P = 0$ but at various temperatures are calculated with equation (10). The calculated values of $V^{act}(0, T)$ are compared in table 1 with the available data in the literature. Here again, the agreement is very good. Moreover, the values of $V^{act}(P, T)$ as a function of pressure in the case of Na are also reported in table 2; these are in good agreement with the earlier results [1].

Further, the ratio of $K_T^{act}(0, T)/K_T(0, T)$ and $\alpha^{act}/\alpha(0, T)$ computed from the present theory is reported in table 1. Here $K_T(0, T)$ and $\alpha(0, T)$ represent the isothermal compressibility and the coefficient of thermal expansion, respectively, at pressure $P = 0$ and temperature T , for bulk solids whereas $\alpha^{act} = [V^{act}]^{-1}[\partial V^{act}/\partial T]_P$. These calculations are performed just to give an idea of the magnitude. Thus, it is clear from table 1 that the activation compressibility and activation thermal expansion are always greater than the corresponding properties of the bulk solid.

In conclusion, it may be said that the present theory of the melting temperature approach is quite successful in representing the self-diffusion coefficient, $D(P, T)$, and the activation volume, $V^{act}(P, T)$, as functions of pressure at different temperatures.

Table 2. Self-diffusion and thermodynamic properties of sodium as functions of pressure and temperature.

$T = 288 \text{ K}$						$T = 364.45 \text{ K}$					
P (kbar)	T_m (K)	$D \times 10^{10}$ ($\text{cm}^2 \text{ s}^{-1}$)		V^{act} ($\text{cm}^3 \text{ mol}^{-1}$)	$K^{act} \times 10^2$ (kbar^{-1})	P (kbar)	T_m (K)	$D \times 10^8$ ($\text{cm}^2 \text{ s}^{-1}$)		V^{act} ($\text{cm}^3 \text{ mol}^{-1}$)	$K^{act} \times 10^2$ (kbar^{-1})
		Expt	Calc					Expt	Calc		
0	370.95	32.3	32.3	11.43	8.14	0	370.95	13.4	13.4	12.36	8.14
1.6060	385.07	15.7	15.7	10.13	6.95	1.266	382.22	8.04	8.19	11.23	7.18
2.894	395.29	9.21	9.31	9.30	6.22	2.416	390.60	5.26	5.68	10.38	6.47
4.991	410.30	4.41	4.33	8.25	5.31	2.452	391.88	5.24	5.37	10.35	6.45
6.760	421.71	2.39	2.42	7.55	4.73	3.759	401.70	3.31	3.49	9.56	5.81
6.809	422.02	2.29	2.38	7.53	4.72	5.647	414.65	2.04	1.99	8.63	5.08
7.908	428.61	1.57	1.69	7.16	4.42	5.658	414.72	1.81	1.98	8.62	5.07
9.281	436.43	1.01	1.14	6.76	4.09	7.560	426.56	1.15	1.18	7.87	4.51
						8.729	433.39	0.862	0.876	7.48	4.22

Table 3. The variation of $D(P, T)$ as a function of pressure (kbar) in Pb, Cd and Zn at one temperature (K).

Zn $T = 623.85$			Cd $T = 549.15$			Pb $T = 526.0$		
P (kbar)	$D (\times 10^{-9} \text{ cm}^2 \text{ s}^{-1})$		P (kbar)	$D (\times 10^{-8} \text{ cm}^2 \text{ s}^{-1})$		P (kbar)	$D (\times 10^{-11} \text{ cm}^2 \text{ s}^{-1})$	
	Calc	Expt		Calc	Expt		Calc	Expt
0.00	2.548	2.548	0.00	3.82	3.82	0.00	2.41	2.41
0.133	2.520	2.550	0.14	3.74	—	0.987	1.63	1.30
1.380	2.293	2.286	1.71	2.918	3.002	1.974	1.106	0.981
1.860	2.211	2.200	4.19	1.906	2.103	3.949	0.523	0.540
3.380	1.973	1.968	6.22	1.472	1.464			
4.920	1.756	1.750	8.18	1.106	1.117			
6.400	1.579	1.580						
8.710	1.338	1.345						

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References

- [1] Kumari M and Dass N 1994 *Phys. Rev. B* **49** 844
- [2] Zener C 1951 *J. Appl. Phys.* **22** 372
- [3] Kraut E A and Kennedy G C 1966 *Phys. Rev.* **151** 668
- [4] Kumari M and Dass N 1988 *Phys. Status Solidi b* **146** 105
- [5] Werner M and Mehrer H 1985 *Phys. Rev. B* **32** 3930
- [6] *Landolt-Börnstein New Series* 1990 Group III vol 26 ed H Mehrer (Berlin: Springer)
- [7] Simon F E and Glatzel G 1929 *Z. Anorg. (Allg.) Chem.* **178** 309
- [8] Babb E S Jr 1963 *Rev. Mod. Phys.* **35** 400

- [9] Dass N 1995 *Phys. Rev. B* **52** 3023
- [10] Mundy J N 1971 *Phys. Rev. B* **3** 2431
- [11] Nachtrieb N H, Henry A R and Stuart A R 1959 *J. Chem. Phys.* **31** 135
- [12] Buescher B J, Gilder H M and Shea N 1973 *Phys. Rev. B* **7** 2261
- [13] Chhabildas L and Gilder H M 1972 *Phys. Rev. B* **5** 2135
- [14] Gilder H M and Lazarus D 1975 *Phys. Rev. B* **11** 4916