

A model for the pressure dependence of diffusion in condensed matter

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Abstract. In the present paper, a model has been used to develop a simple relation to study the pressure dependence of self-diffusion in solids and liquids that has two adjustable parameters. The computation done in each substance is found to be in very good agreement with the experimental data. It is interesting to note that the present relation is also capable of giving the activation volume in solids and liquids. The activation volume computed in the solids is found to be in very good agreement with the data available.

Keywords. Self-diffusion; activation volume; condensed matter.

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1. Introduction

It is a general knowledge that the defects in solids and liquids play an important role and help one to understand the diffusion mechanism whereas the pressure dependence of diffusion may give information regarding the diffusion carriers in the equilibrium. According to the pressure dependence of diffusion, there are certain substances for which the plot between $\ln D$ and P^{-1} is linear whereas there are certain substances for which the plot is non-linear. Therefore, the aim of the present paper is to develop a model which can successfully represent the self-diffusion of solids and liquids with pressure irrespective of whether the plot is linear or not by considering vacancy mechanism.

Recently, Zener model [1] has been successfully employed by Dass and co-workers [4,5] to explain the pressure as well as the temperature dependence of diffusion in solids where the model considers single vacancy mechanism under the isothermal and isobaric conditions. As far as liquids are concerned, no particular model is as successful as Zener model is in solids. Therefore, in the present paper, a new model is used to study the pressure dependence of self-diffusion, which is applicable

Table 1. Parameters of self-diffusion in solids and liquids.

Substance	T (K)	Pressure range (kbar)	$D'(0, T)$ ($\text{cm}^2/\text{s/kbar}$)	Z (kbar^{-1})	RMSD (cm^2/s)	Ref.
<i>Solids</i>						
Na	288.0	0.0–9.281	-14.38×10^{-10}	-0.4572	1.9×10^{-15}	[7]
Au	692.0	0.0–5.525	-0.8438×10^{-15}	-0.1374	2.9×10^{-17}	[8]
Cd	574.15	0.07–8.07	-1.1887×10^{-9}	-0.1307	5.1×10^{-11}	[9]
Zn	623.85	0.133–8.71	-0.2159×10^{-9}	-0.1100	7.8×10^{-12}	[10]
Ag	766.0	0.0–5.588	-1.5015×10^{-10}	-0.1370	4.7×10^{-12}	[8]
<i>Liquids</i>						
2-Ethylhexyl benzoate	333.0	0.0–4.5	-3.883×10^{-6}	-0.9169	38.3×10^{-9}	[11]
Tetramethylsilane	298.0	0.0–4.0	-3.5303×10^{-5}	-0.9744	4.0×10^{-7}	[12]
CH ₃ OD	303.0	0.02–4.905	-7.3941×10^{-6}	-0.3551	4.7×10^{-7}	[13]
NH ₃	273.0	0.1–2.0	-3.3277×10^{-5}	-0.61866	1.3×10^{-7}	[14]
C ₆ F ₆	343.0	0.001–2.0	-3.8139×10^{-5}	-1.1682	2.6×10^{-7}	[18]
1-Pentanol-OH	272.9	0.05–2.0	-7.8777×10^{-7}	-0.82502	2.5×10^{-9}	[15]
1-Pentanol-OD	272.2	0.05–2.0	-8.9406×10^{-7}	-0.87433	4.5×10^{-9}	[15]
2-Pentanol-OH	273.8	0.05–2.0	-9.6877×10^{-7}	-1.1710	6.8×10^{-9}	[15]
2-Pentanol-OD	272.7	0.05–2.0	-8.9588×10^{-7}	-1.0968	2.2×10^{-9}	[15]

Table 2. Activation volume in solids at zero pressure.

Solids	T (K)	Activation volume (cm^3/mol)		Ref.
		Present	Others	
Na	288.0	10.77	11.43	[17]
			11.1 ± 0.2	[16]
Au	692.0	7.59	7.43	[8]
Cd	574.15	6.82	7.83	[17]
			7.65 ± 0.1	[9]
Zn	623.85	4.04	3.99	[17]
			3.97 ± 0.05	[10]
Ag	766.0	7.78	7.312	[8]

in both solids and liquids. The results so obtained are found to be in very good agreement with the experimental data in each case as shown in table 1. Further, the present relation is also capable of giving the activation volume which is reported in tables 2 and 3.

Table 3. Activation volume in liquids at zero pressure.

Liquids	T (K)	Activation volume (cm^3/mol)
2-Ethylhexyl benzoate	333.0	25.7
Tetramethylsilane	298.0	22.5
CH_3OD	303.0	6.9
NH_3	273.0	8.2
C_6F_6	343.0	29.8
1-Pentanol-OH	272.9	17.2
1-Pentanol-OD	272.2	18.0
2-Pentanol-OH	273.8	24.3
2-Pentanol-OD	272.7	23.9

2. Theory

The aim of the present paper is to study the pressure dependence of self-diffusion in those solids and liquids in which the self-diffusion coefficient decreases with the increase in pressure. To achieve the desired aim, we propose that the ratio of second to first pressure derivative of self-diffusion in a substance is a pressure-independent parameter, i.e.,

$$\frac{\left[\frac{\partial^2 D(P,T)}{\partial P^2}\right]_T}{\left[\frac{\partial D(P,T)}{\partial P}\right]_T} = Z. \quad (1)$$

The successive integration of eq. (1) gives the relations as

$$\left[\frac{\partial D(P,T)}{\partial P}\right]_T = D'(0,T)e^{ZP} \quad (2)$$

and

$$D(P,T) = D(0,T) + \frac{D'(0,T)}{Z}[e^{ZP} - 1]. \quad (3)$$

However, the diffusion coefficient can also be expressed as [2]

$$D(P,T) = D_0 e^{-g^{\text{act}}(P,T)/RT}, \quad (4)$$

where D_0 is the pre-exponential factor and is considered to be pressure independent [4]. $g^{\text{act}}(P,T)$ represents the Gibb's activation energy and is defined as the sum of Gibb's formation energy (energy required to create the vacancy) and Gibb's migration energy (energy required to surmount the potential barrier).

Differential of eq. (4) with respect to pressure gives the activation volume (to be interpreted as the isothermal change in the real volume of the substance associated with an actual diffusion jump) which is expressed as

$$V^{\text{act}}(P, T) = \frac{\partial}{\partial P}(g^{\text{act}}(P, T)) = -RT \frac{D'(P, T)}{D(P, T)}. \quad (5)$$

Self-diffusion coefficient in the case of solids and liquids is found to decrease with the increase in pressure leading to positive activation volume. Further, the magnitude of $D'(P, T)$ will decrease with the increase in pressure and hence gives rise to the fact that the second derivative of diffusion is positive. Hence, it is clear from eq. (1) that Z too has to be negative; otherwise the second derivative will not be positive. These results are found consistent with the experimental data as shown in table 1.

We have not reported the results for the substances in which the self-diffusion coefficient is found to increase with the increase in pressure due to insufficient experimental data and eventually will give negative activation volume. However, we feel confident that present theory will be applicable to these substances also.

The relation represented by eq. (1) can also give higher-pressure derivative of self-diffusion coefficient, i.e.

$$\left[\frac{\partial^N D(P, T)}{\partial P^N} \right]_T = Z^{N-1} \left[\frac{\partial D(P, T)}{\partial P} \right]_T, \quad (6)$$

where $N \geq 2$.

It is interesting to mention that the idea used here is not new. Kumari and Dass [2,3] had used this idea for the first time to obtain an equation of state (EOS) by proposing that the ratio of second to first pressure derivative of bulk modulus is a pressure-independent parameter. Furthermore, the idea was extended to study the pressure dependence of sound velocity in liquid metals [6] wherein it was assumed that the ratio of second to first pressure derivative of sound velocity is a pressure-independent parameter. This time, the idea has been successfully applied to study the self-diffusion in both solids and liquids.

It is interesting to note that the present model is valid in solids as well as in liquids and hence no separate model is required for liquids.

3. Results and discussion

Equation (3) has been applied in the case of some solids and liquids as listed in table 1 along with the values of the adjustable parameters $D'(0, T)$ and Z . The computed results are compared with the experimental data in the case of each substance and are found in very good agreement with the experimental data as is indicated by the root mean square deviation (RMSD) that represents the goodness of fit. The results are in good agreement is also indicated in figure 1 for solids and in figure 2 for liquids. This work can be further extended in other solids and liquids.

The computation has also been done for the activation volume. It is interesting to note that the present results for the activation volume in the case of solids as reported in table 2 are found in very good agreement with the available results in literature. The activation volume in the liquids is reported for nine liquids. In literature, we find the theoretical result for the activation volume in the case of ammonia at 273 K as 6.1 cm³/mol [14] whereas the present result is 8.2 cm³/mol and can be said that the present result is in reasonable agreement with the available result. However, we are not in a position to verify the results of activation volume

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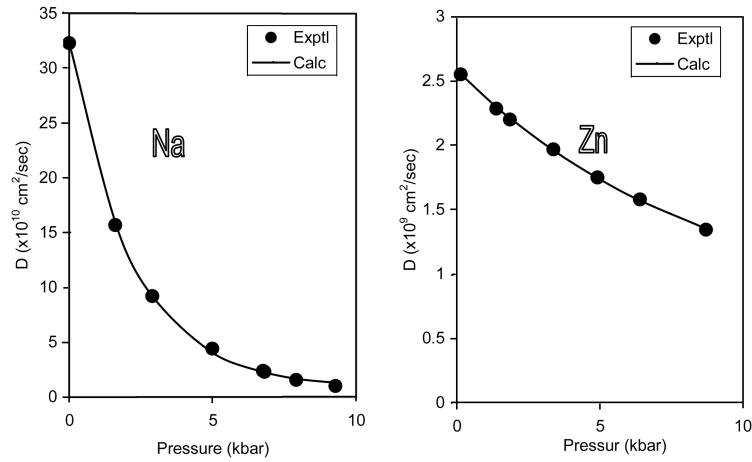


Figure 1. Pressure dependence of self-diffusion in solids.

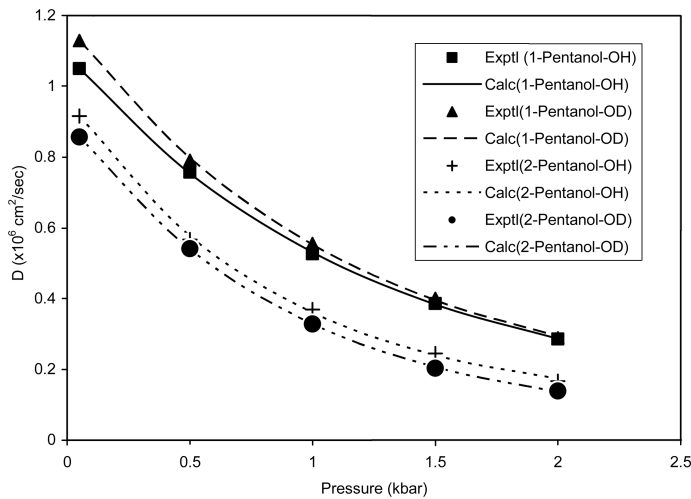


Figure 2. Pressure dependence of self-diffusion in liquids.

in the case of other liquids in the absence of available results in literature. Finally, it can be said that the present model is quite successful in representing the self-diffusion coefficient and the activation volume as a function of pressure in both the solids and the liquids.

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