

Universality in the effective pair interaction of d -shell metals – Compressibility and vacancy formation energy of $3d$ -liquid metals

A K KARMAKAR and R N JOARDER

Department of Physics, Jadavpur University, Calcutta 700 032, India

MS received 23 May 1997; revised 6 October 1997

Abstract. Like liquid alkali metals d -shell liquid metals show scaling behaviour in structure and interaction potentials. A realistic interaction potential model, properly parametrized can reasonably describe the universality in the isothermal compressibility and vacancy formation energy of $3d$ -liquid metals in electron ion plasma model.

Keywords. Universality; effective pair-potential; $3d$ -liquid metals.

PACS No. 61.25

1. Introduction

It is now well established that for liquid alkali metals, the structure factors and pair distribution functions when suitably expressed scaling behaviour follows very well [1]. In transition metals, in spite of the fact that the incomplete d -shell contributes substantially to the properties, the liquid structure factors can be put into the same class of simple liquid metals such as Al [2]. A large number of diffraction data on the liquid structure factors of these metals are now available in the literature [2]. A plot of structure factors, $S(Q)$ versus Q/Q_{\max} where 'max' refers to the value of wave vector at which $S(Q)$ is maximum is shown in figure 1 and it is evident that the structure factors scale reasonably well. It is therefore expected that the basic function i.e., the intermolecular potential energy function should scale similarly and thereby show certain universality in the average behaviour of different properties. But unfortunately, all the experimental structure factor data, accessible from diffraction experiments, are devoid of accurate low Q data – in fact the data below $Q \simeq 1.0 \text{ \AA}^{-1}$ is rarely available. Since the accuracy of the effective pair potential extracted from diffraction data depends strongly on the low Q data [3], it is not easy to use the integral equations to extract the effective pair potential and see how the scaling property in the potential operates in these liquids. We have therefore addressed the problem somewhat indirectly. Earlier works from this laboratory have shown that at least for the liquid $3d$ -transition metals, the simplified Wills–Harrison model potential [4] in slightly modified form [5, 6] works quite well as far as the structure and thermodynamic properties are concerned. We have therefore thought it useful to test this model potential in some detail to see whether the effective pair potentials for various

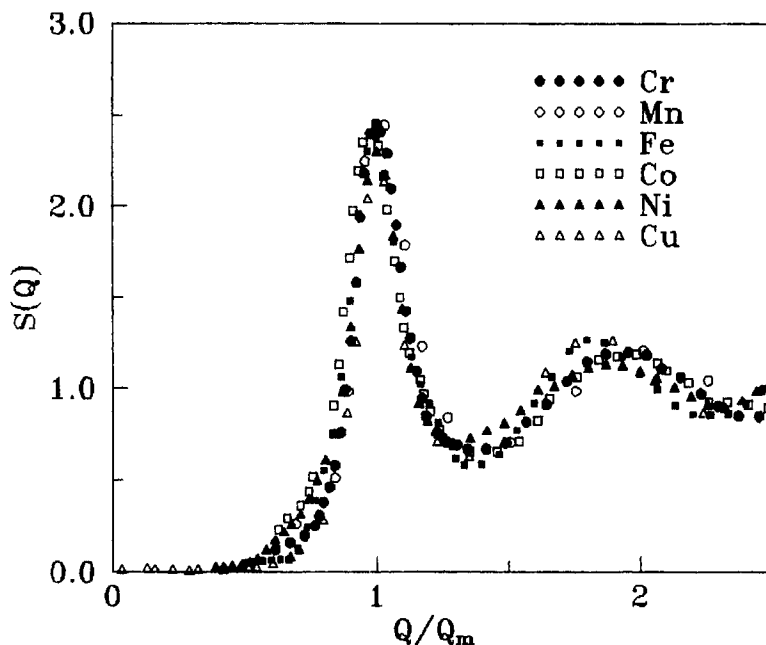


Figure 1. Scaling of experimental structure factors [2] of some 3d-liquid transition metal (all at or near their melting points).

members of 3d-series too scale properly. We have then obtained the structure factors using these potentials following the method described in ref. [6] and then Fourier transformed to obtain pair distribution functions. Both structure factors and pair distribution functions agree well with experimental data. It is also tested how these computed structure factors and pair distribution functions scale. In § 3, the scaling behaviours via the isothermal compressibility, a quantity directly linked to the long wave limit of structure factor are also investigated.

In § 4 the vacancy formation energies of several members of the 3d-metal series are studied via Minchin *et al* [7] formalism. These authors have given the Faber's formula [8] for the vacancy formation energies in a direct space formalism, and have applied to mono-, di- and polyvalent metals. More recently Bhatia and March [9] have used the Minchin *et al* formalism to estimate this quantity for solid argon at the melting temperature. Das *et al* [10] successfully applied the method for liquid alkali and several other metals at or near their m.p.'s. We have reinvestigated this formalism for several liquid metals of 3d-transition series using both one component plasma (OCP) and charged hard sphere (CHS) plasma models for reference. It is evident that vacancy formation energies of several members of 3d-series too scale though in somewhat limited sense.

2. W-H model for effective potential of 3d-liquid metals and liquid structure

According to Wills and Harrison (W-H) [4], the effective pair potential of transition metals consists of an s-electron contribution, $u_s(r)$, a d-band bonding term $u_d(r)$, and the

Effective pair interaction of *d*-shell metals

Table 1. (a) Input parameters for $u(r)$ of transition metals ($Z_s = 1.5$ throughout) in liquid state at or near m.p. (b) Input parameters for CHS/OCP reference at or near the m.p.

Liquid metals with solid state structure	(a)				(b)		
	N_c	Z_d	r_d (au)	r_c (au)	Liquid metals	Packing density η	Charge parameter Γ
Ti (hcp)	12	2.5	2.04	1.88	Ti	0.437	110
Mn (bcc)	8	5.5	1.63	2.00	Mn	0.449	110
Fe (bcc)	8	6.5	1.51	1.61	Fe	0.438	110
Co (hcp)	12	7.5	1.44	1.48	Co	0.444	110
Ni (fcc)	12	8.5	1.34	1.36	Ni	0.442	110
Cu (fcc)	12	9.5	1.266	1.09	Cu	0.450	120

repulsive contribution $u_{dd}(r)$, from the shift of the *d*-band centres

$$u(r) = u_s(r) + u_d(r) + u_{dd}(r). \quad (1)$$

The *s*-electron contribution to the pair potential is given by the Ashcroft empty core form of the bare pseudo-potential and in terms of number of *s*-electrons, and Ashcroft core radius, r_c the detailed expression is available in ref. [6]. In the construction of dielectric screening function same Geldart-Vosko (GV) [11] local field factor as in ref. [6] was used. The *d*-electron contributions are expressed in terms of the number of *d*-electrons, Z_d , and the *d*-state radii r_d ; N_c is the nearest neighbour coordination number and expressions are also given in refs [4] and [6].

For all the 3*d*-transition metals $Z_s = 1.5$ is used in the calculation. Z_d and r_d are obtained as in ref. [4]. Values of r_c derived from the free atom *s*-state ionization potential lie between the two sets of values given by Wills and Harrison as pointed out earlier [6] and same values are used in the present calculations. The input parameters are listed in table 1.

The computed effective pair potentials of several liquid 3*d*-metals are shown in figure 2(a). The depth and position of the potential minimum are affected by the choice of r_c s, and near the minimum the potentials are dominated by the *d*-electron contribution. The potentials in general are stronger than typical liquid alkali metal potentials but the softness of the core potential appears almost alike. The Friedel oscillations [6] are almost absent. For comparison we have also shown the effective pair potential of liquid sodium at the melting point (m.p.) [12]. In figure 2(b) the scaled property of the effective pair potential (in respect of position and depth) for a few members of 3*d*-metal series is shown. The potentials are reasonably scaled.

The structure factor $S(Q)$'s obtained from effective pair potential through low order perturbation theory like random phase approximation (RPA) agree extremely well with experimental data [6]. When Fourier transformed we get pair distribution function, $g(r)$ which too agrees well with experimental data. Both $S(Q)$ and $g(r)$ are seen to scale surprisingly well. The scaling behaviour of $S(Q)$ and $g(r)$ in respect of the first peak height are depicted in figures 3(a) and (b) respectively. These functions scale reasonably even at higher temperatures (figure 3(a)).

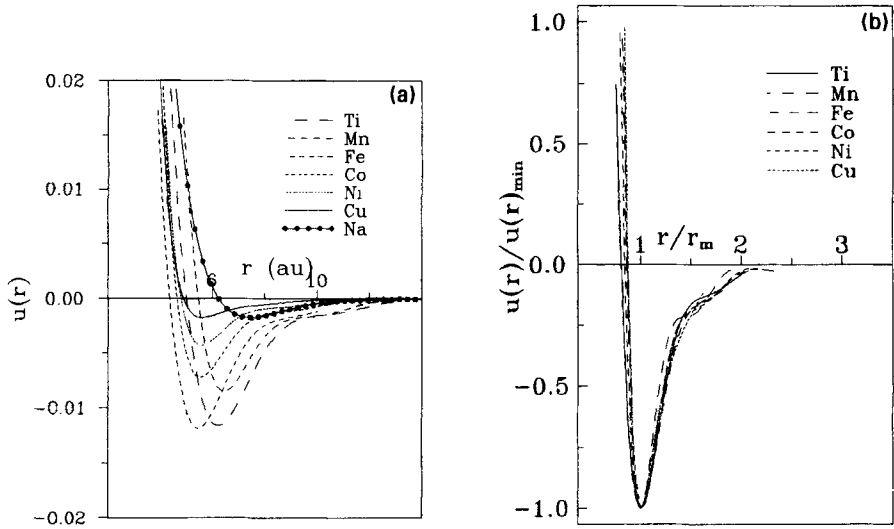


Figure 2. (a) Effective pair-potentials (in au) of six 3d-liquid metals alongwith that of Na ($r_c = 1.69$ au and with GV local field); (b) Scaled effective pair-potential of six 3d-liquid metals.

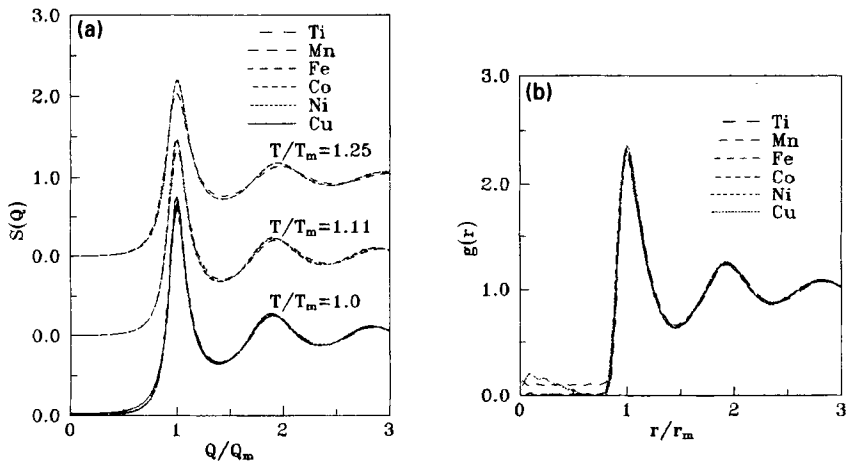


Figure 3. (a) Calculated $S(Q)$ vs. Q/Q_m of six 3d-liquid metals at $T/T_{mp} = 1.0, 1.11, 1.25$. At higher temperatures $S(Q)$ is given for three metals e.g., Fe, Co, Ni. (b) Calculated $g(r)$ vs. r/r_m of six 3d-liquid metals (at or near their melting points).

3. Isothermal compressibility

Isothermal compressibility, χ_T is related with the structure factor as [3]

$$S(0) = \rho k_B T \chi_T, \quad (2)$$

where $S(0)$ is the long wave limit of the structure factor $S(Q)$. Using the compressibility equation of state the scaling behaviour of the compressibility χ_T , of the 3d-transition

Effective pair interaction of d-shell metals

Table 2. Scaled values of $S(0)$ i.e., $-\eta\tilde{h}(0)^{-1}$ of some liquid 3d-transition and alkali metals.

Transition metals	Ti	Mn	Fe	Co	Ni	Cu	Average value
CHS plasma	0.45	0.46	0.46	0.45	0.45	0.46	0.45
Experimental	0.45	0.46	0.45	0.45	0.45	0.46	0.45
Alkali metals [1]	Li	Na	K	Cs	Rb		
CHS plasma	0.443	0.461	0.468	0.463	0.469		0.46
Experimental	0.433	0.460	0.467	0.462	0.468		0.46

liquid metals can be described in the form

$$S(0) = 1 + 4\pi\rho \int_0^\infty [g(r, T) - 1]r^2 dr = 1 + \tilde{h}(0) \quad (3a)$$

or

$$\frac{\tilde{h}(0)}{\eta} = 24\sqrt{2} \int_0^\infty [g(r^*, T) - 1]r^{*2} dr^*, \quad (3b)$$

which is a constant at or near m.p. because it depends only on the pair distribution function $g(r^*, T)$ which is scaled well. In eq. 3(b) $r^* = r/r_m$, r_m being the position of first $g(r)$ maximum and η is the hard core packing density. Further eq. 3(a) can be put into the form

$$S(0) = 1 + 24\sqrt{2}\eta_{mp}(\rho/\rho_{mp}) \int_0^\infty [g(r^*, T) - 1]r^{*2} dr^*. \quad (3c)$$

This equation indicates that variation of $S(0)$ as a function of ρ/ρ_{mp} at higher temperatures should be similar for different members of the series.

Now the long wave limit structure factor $S(0)$ using the RPA expression [13] for transition metals requires the inclusion of d -electron contribution [6]. Thus,

$$S^{-1}(0) = S_0^{-1}(0) + S_s^{-1}(0) + S_d^{-1}(0), \quad (4)$$

where $S_0^{-1}(0)$ is the contribution for the reference system and in the present case it is charged hard sphere (CHS) plasma which depends on parameters η and Γ [14]. η and Γ are taken from ref. [6]. $S_s^{-1}(0)$, $S_d^{-1}(0)$ are the contributions for s - and d -electrons respectively in the long wave limit [6].

The calculated scaled values of $S(0)$ are depicted in table 2. The experimental values based on Waseda's work [2] are also shown. We also give the values for the liquid alkali metals in charged hard sphere plasma model [1]. It is to be noted that all the transition metals are scaled very well in long wave limit. The average value for 3d-transition series are slightly smaller in magnitude in comparison with the liquid alkali metals. The experimental results also show similar difference between liquid transition and alkali metals. In figure 4 we have shown variation of $S(0)/S(0)_{mp}$ as a function of ρ/ρ_{mp} , where ρ refers to number density at elevated temperature and m.p., the melting point. Γ 's at

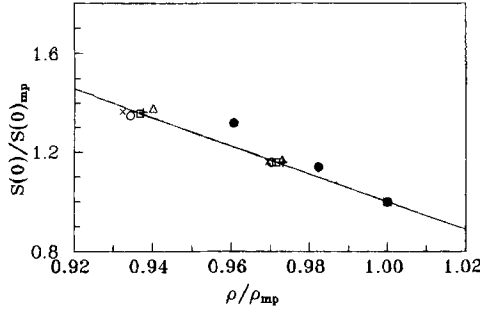


Figure 4. Plot of $S(0)/S(0)_{mp}$ vs. ρ/ρ_{mp} ; Ti (o o), Mn (□ □), Fe (△ △), Co (+ +), Ni (× ×), Cu (● ●).

higher temperatures are obtained by assuming constant Z_s and η 's from an expression given by Waseda [2]. For the temperature range considered ($T/T_{mp} = 1.25$ maximum), the variation of $S(0)$ is linear and almost similar for different members of 3d-series except liquid copper. On various aspects copper appears to behave somewhat differently in comparison with other members [4]. The magnitude of the potential minimum is lowest for copper and it is lower than average thermal energy, $k_B T$ at m.p.

4. Vacancy formation energy

A method for the vacancy formation energy of liquid metals involving pseudopotential and total pressure was evolved from this laboratory [10]. The expression could be conveniently used to compute vacancy formation energy of several simple liquid metals. The method here is extended to liquid 3d-metals. Using the direct space formulation of Minchin *et al* [7] (which neglects atomic relaxation around a vacant lattice site) and total pressure of the liquid metals, the expression of vacancy formation energy, E_v is conveniently written as

$$E_v = -k_B T - \rho(du(\rho)/d\rho) - (\rho/2) \int u(r, \rho)g(r)dr - (\rho^2/2) \int (\partial(u(r, \rho)g(r))/\partial\rho)dr + (\rho^2/2) \int (\partial g(r)/\partial\rho)u(r, \rho)dr, \quad (5)$$

where the terms have their usual meaning as in ref. [10]. Following Bhatia and March [9] we use the Ornstein-Zernike (OZ) relation for the direct correlation function (DCF) and after some manipulation we get the basic equation

$$\frac{E_v}{k_B T} = -1 - (\rho/k_B T)(du(\rho)/d\rho) - (\rho/2)[(\partial S^{-1}(0)/\partial\rho) + (\partial c(r=0)/\partial\rho)] + (\rho^2/2k_B T) \int (\partial g(r)/\partial\rho)u(r, \rho)dr, \quad (6)$$

where $c(r=0)$ is the direct correlation function evaluated at $r=0$. $c(r=0)$ can easily be evaluated knowing $c_0(r)$, the reference part and $c_{RPA}(r=0)$ from the knowledge of

Table 3. Vacancy formation energies of 3*d*-liquid transition metals.

Liquid metals	T (K)	$\rho \times 10^3$ (au)	$E_v/k_B T$			
			Present CHS	Present OCP	Ref. [18] (at mp)	Expt. (at mp)
Ti	1973	7.66	6.77	4.07	5.50	9.29
Mn	1533	9.70	8.48	5.60	—	—
Fe	1823	11.20	8.79	6.07	—	10.12
Co	1823	11.65	12.83	10.30	12.20	8.16
Ni	1773	11.73	9.30	6.52	11.25	9.41
Cu	1423	10.98	14.42	9.53	8.00	11.26
Average values:			10.09	7.02	9.24	9.64

indirect *s*- and *d*-electron mediated part in RPA. We use $c_0(r)$ for two closely related electron-ion plasma models for liquid metals, namely, the one component plasma (OCP) model of Baus and Hansen [15] as modified by Evans and Sluckin [13] and the charged hard sphere (CHS) plasma model [14].

The expressions for $c_0(r=0)$ in the two electron-ion plasma models are given in [10]. The $c_{\text{RPA}}(r=0)$ term is given by

$$c_{\text{RPA}}(r=0) = -\beta/(2\pi^2) \int v(Q)Q^2 d\mathbf{Q}, \quad (7)$$

where $v(Q)$ has now been arising from the contributions of *s*- and *d*-electron interactions (§ 2). The expressions for $S_0(0)$ for the two models given in ref. [10] plus the *d*-electron terms of § 3 constitute $S(0)$. The volume dependent but structure independent energy has the same functional form as in ref. [10] but the expression for electron gas free energy, F_{eg} is now given as

$$F_{\text{eg}} = \frac{Z_s}{2} \left[0.982/r_s^2 - 0.712/r_s + 0.031 \ln r_s - 0.115 - 2 \left(\frac{\pi k_B}{Q_f} \right)^2 \right] - \frac{\pi^2}{3} k_B^2 n(E_f), \quad (8)$$

where the terms have their usual meaning as in ref. [6].

Now in (6) the last term is structure dependent and can be called structural term while the rest of the terms are in fact thermodynamic terms [16]. So we can put

$$E_v/k_B T = E_v^{\text{therm}}/k_B T + E_v^{\text{struct}}/k_B T. \quad (9)$$

It is in general found that the structural term has minor contribution ($E_v^{\text{struct}}/k_B T < 1$) to the vacancy formation energy and the major part is contributed by the thermodynamical terms [16]. Assuming Egelstaff's uniform fluid model [17] as in ref. [10] this can be shown to be approximately the case. We have therefore computed here the thermodynamic part only and make the comparison with experimental results. The computed results alongwith the experimental values are shown in table 3. The input parameters are all taken as in §§ 2 and 3. The results for CHS plasma model are in general a little bigger than the values for OCP model. The model results agree fairly well with

experimental results. The average calculated $E_v/k_B T$ values for the two plasma models come out to be about 10.1 and 7.0 respectively. The results are better than those of Alonso and March [18] for liquid transition metals at their m.p.'s. The average experimental value (for 5 metals for which vacancy formation energies are available) is about 9.64. Our earlier calculation showed for alkalis (bcc) except for Li an average, $E_v/k_B T$ as 15.6 and 12.2 for CHS and OCP models respectively. The average experimental value is 12.2. For close packed lattice (both non-transition and transition metals) observed $E_v/k_B T \sim 8-9$. Rashid and March [16] have sought to connect this term i.e., $E_v/k_B T$ at m.p. to the corresponding crystal lattice structure. Thus, the present calculation shows some agreement with the proposition of Rashid and March. The graph E_v vs T is approximately linear (not shown) indicating a moderate scaling behaviour for vacancy formation energy for 3d-liquid metals.

5. Conclusion

The W-H model for liquid transition metals is easily applicable effective pair potential model for the study of various structural and thermodynamic properties of liquid 3d-transition metals. The effective pair potentials of this series are scaled well. The structure factors $S(Q)$ calculated in RPA and pair distribution functions $g(r)$ also scale surprisingly well. The long wave limit of structure factor $S(0)$ and its equivalent expression $\eta h(0)^{-1}$ is found to be constant which indicates again a good scaling behaviour and difference with liquid alkali metals is evident.

The experimental liquid structure factor data for several members of 3d-series depicted in figure 1 however show limited scaling. It is clear that there exist some limitations in spite of the fact that all the data shown here are due to Waseda's single-set measurements and accuracies in $S(Q)$ and $g(r)$ were claimed about 4%. The coordination numbers evaluated from these data varied between 10.6 and 11.6 for different members of the series indicating good similarity of nearest neighbour structures in the liquid state. The solid state structures, however are different either fcc/hcp or bcc for different members of 3d-series. Similar is the case with evaluated hard core packing densities which varied between 0.44 and 0.45 except for Ti and V indicating once again the similarity with limited variations. As pointed out by Waseda and Tamaki [2] the measurements in this kind of work, particularly in the data collection, were affected by the experimental difficulties arising from the high temperatures due to active chemical reactivity of the liquid samples compared to measurements at lower temperature (below 1373 K). In this connection we would also like to mention that the experimental liquid structure factor data of alkali metals too show the scaling property with limitations among various members of the series [1]. So the scaling depicted in figure 1 for liquid 3d-series is not unreasonable.

We have also applied W-H model potential to obtain vacancy formation energies of several liquid 3d-metals in Minchin *et al* formalism. We have evaluated the thermodynamic part only and the average value agrees fairly well with the known average values for the 3d-series. Here also scaling is evident and difference from liquid alkali metals is clear probably implying the structural distinctions of the two series.

Acknowledgements

The authors are grateful to CSIR, New Delhi and IUC-DAEF, Indore for financial support.

References

- [1] M J Huijben and W van der Lugt, *Acta Crystallogr.* **A35**, 431 (1979)
N Matsuda, H Mori, K Hoshino and M Watabe, *J. Phys. Condens. Matter* **3**, 827 (1991)
A Bari, P Pal and R N Joarder, *Pramana – J. Phys.* **42**, 395 (1994)
- [2] Y Waseda and S Ueno, *Sci. Rep. Res. Inst. Tohoku Univ.* **A34**, 15 (1987)
Y Waseda, *The structure of non-crystalline materials* (Mc-Graw Hill, New York, 1980)
Y Waseda and S Tamaki, *Philos. Mag.* **32**, 273 (1975)
- [3] N H March, *Liquid metals* (Pergamon Press, London, 1968)
- [4] J M Wills and W A Harrison, *Phys. Rev.* **B28**, 4363 (1983)
- [5] C Hausleitner and J Hafner, *J. Phys.* **F18**, 1025 (1988)
- [6] A Bari, T Das and R N Joarder, *J. Non-Cryst. Solids* **136**, 173 (1991)
A Bari and R N Joarder, *Indian J. Pure Appl. Phys.* **30**, 256 (1992)
- [7] P Minchin, A Meyer and W H Young, *J. Phys.* **F4**, 2117 (1974)
- [8] T E Faber, *An introduction to the theory of liquid metals* (Cambridge University Press, London and New York, 1972)
- [9] A B Bhatia and N H March, *J. Chem. Phys.* **80**, 2076 (1984)
- [10] T Das, T Nammalvar, L B Bhuiyan and R N Joarder, *Phys. Status Solidi* **B157**, 93 (1990)
- [11] D J W Geldart and S H Vosko, *Can. J. Phys.* **44**, 2137 (1966)
- [12] N W Ashcroft, *Phys. Lett.* **23**, 48 (1966)
- [13] R Evans and T J Slukin, *J. Phys.* **C14**, 3137 (1981)
- [14] T Das, A Bari and R N Joarder, *Indian J. Pure Appl. Phys.* **27**, 37 (1989)
- [15] M Baus and J P Hansen, *Phys. Rep.* **59**, 1 (1980)
- [16] R I M A Rashid and N H March, *Phys. Chem. Liquids* **19**, 41 (1989)
- [17] P A Egelstaff, D I Page and C R T Heard, *J. Phys.* **C4**, 1453 (1971)
- [18] J A Alonso and N H March, *Phys. Chem. Liquids* **20**, 235 (1989)