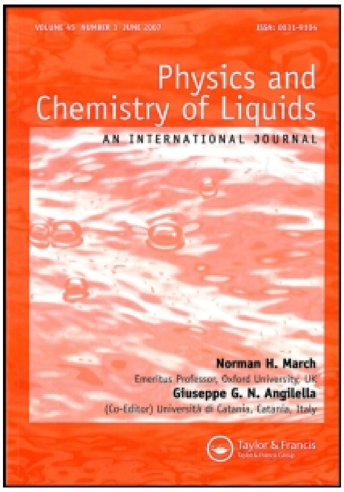

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Interatomic Forces in Solid and Liquid Metals; the Question of Pseudopotential Transferability

S. M. M. Rahman[a]; M. Hasegawa[ab]; K. Hoshino[ac]; W. H. Young[d]
[a] School of Mathematics and Physics, University of East Anglia, Norwich, UK [b] Department of Physics, University of Dhaka, Dhaka-2, Bangladesh [c] Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima, Japan [d] Department of Engineering, Niigata University, Niigata, Japan

To cite this Article Rahman, S. M. M. , Hasegawa, M. , Hoshino, K. and Young, W. H.(1987) 'Interatomic Forces in Solid and Liquid Metals; the Question of Pseudopotential Transferability', Physics and Chemistry of Liquids, 17: 1, 21 — 28
To link to this Article: DOI: 10.1080/00319108708078538
URL: http://dx.doi.org/10.1080/00319108708078538

Phys. Chem. Liq., 1987, Vol. 17, pp. 21–28
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Printed in the United Kingdom

Interatomic Forces in Solid and Liquid Metals; the Question of Pseudopotential Transferability

S. M. M. RAHMAN*, M. HASEGAWA‡, K. HOSHINO§
and W. H. YOUNG

School of Mathematics and Physics, University of East Anglia,
Norwich NR4 7TJ, UK

(Received 27 November 1986)

Ashcroft empty core pseudopotentials and Ichimaru and Utsumi screening are used to calculate interatomic pair potentials which reproduce the measured entropies of some liquid and hot solid metals. It is found that the empty core radii vary rather continuously with volume from phase to phase. This variation can, however, be rather strong in some cases (e.g. Na, Mg) if not in others (e.g. Al). Such a possibility should be considered, therefore, whenever volume changes are significant and, in particular, across solid–liquid phase boundaries.

In Na and Mg, the interatomic force appears to be at least semi-quantitatively given over the small region between the effective collision diameter in the liquid and the nearest neighbour distance in the solid; elsewhere, it is scarcely tested by the fitting exercise. In Al and Ge, the analysis is consistent with a loss (partial or total) of minimum of the pair potentials in the nearest neighbour regions. The importance of these regions for the solid state analyses is thus reduced and their quantitative accuracies cannot therefore be verified by the present study.

Key words: empty core pseudopotentials, interatomic pair potentials, phase boundaries.

1 INTRODUCTION

It is fairly common practice to parametrise a bare electron-ion pseudopotential using measured solid state quantities such as band gaps and

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* Permanent address: Department of Physics, University of Dhaka, Dhaka-2, Bangladesh.

‡ Permanent address: Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima 730, Japan.

§ Permanent address: Department of Engineering, Niigata University, Niigata 950-21, Japan.

phonon spectra and apply it unchanged to the liquid. We have, recently, had occasion to query this procedure in the specific context of the interatomic forces and we present below some illustrative calculations from which a few general conclusions might be drawn.

We consider simple metals only. In such cases, the effective Hamiltonian for the ions is often viewed as the sum of two volume dependent parts, one being position independent and the other a pairwise contribution. We focus on the latter and take care to consider only properties not seriously affected by the former. We avoid, for example, the low wavenumber parts of the liquid state structure factors, where density fluctuations are important and, for the same reason, the compressional long wavelength modes in the solid state phonon spectra. Specifically, for liquids, we focus on the effective hard sphere packing fractions which describe the structure factors at and around the principal peaks, while for the solids we consider the Einstein temperatures and the elastic shear moduli.

It is assumed that the reader is familiar with the general method[1] of calculating interatomic potentials by pseudopotential theory and we remark only that we use the empty core Ashcroft[2] electron-ion interaction and Ichimaru and Utsumi[3] screening for this purpose. This is a procedure recently adopted by Hafner and Heine[4].

2 PARAMETER FITTING FOR Na AND Mg

We begin by considering two particularly simple metals and focus on a single property namely the measured[5] entropy S per atom.

For the (hot) solid, any value of the latter allows us to extract an Einstein temperature $\theta(T)$ using the equation

$$S/k_B = 3\left\{\frac{\theta/T}{e^{\theta/T}-1} - \ln(1 - e^{-\theta/T})\right\} \tag{1}$$

and $\theta(T)$, in its turn, is related to the interatomic potential $\varphi(r)$ by[6]

$$\frac{3M}{\hbar^2}(k_B\theta)^2 = \sum_{R\neq 0}(\nabla^2\varphi)_{\mathbf{R}} \tag{2}$$

Here, M is the atomic mass and the R are the lattice sites relative to an atom at the origin. Using the observed volumes $\Omega(T)$ per atom, we can therefore fit the empty core radii r_c to experiment at each volume considered and we show such dependences in Figure 1.

In the liquid, it has been long recognised[7] that hard sphere packing provides an appropriate lowest order description of structure factors

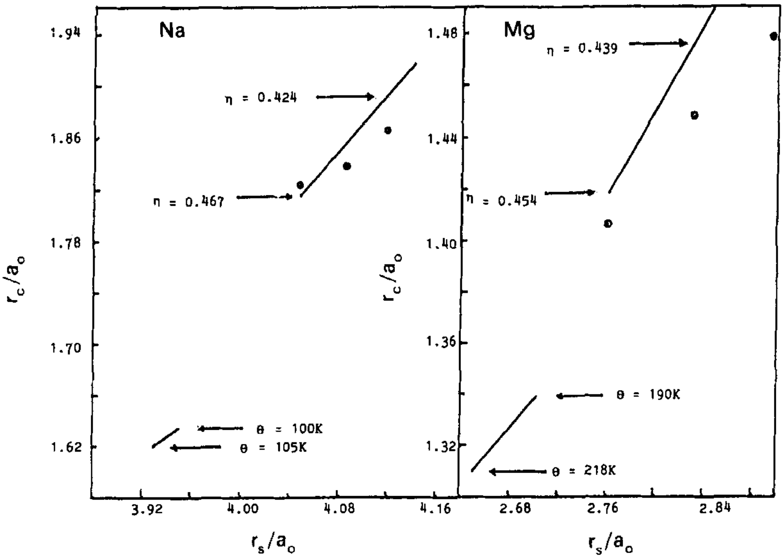

Figure 1 Empty core radius r_c versus *electron* separation parameter $r_s = (3\Omega/4\pi z)^{1/3}$. Here z is the valency (1 for Na, 2 for Mg). Selected Einstein temperatures θ and packing fractions η, describing the entropies in the two phases, are quoted. The points are obtained by matching Percus-Yevick hard sphere peak heights to those of some structure factors measured by Waseda[9].

(provided the low argument region is avoided). Likewise, the entropy per atom in this case can be described[8] in the hard sphere form

$$S/k_B = \tfrac{5}{2} + \ln[\Omega(Mk_BT/2\pi\hbar^2)^{3/2}] - \eta(4 - 3\eta)/(1 - \eta)^2 \qquad (3)$$

Here, η is the packing fraction, given by $\eta = \pi\sigma^3/6\Omega$, where σ is the effective hard sphere diameter. In general, the Gibbs-Bogoliubov method[1] can be used to determine $\sigma(T)$ for a given interatomic potential $\varphi(r)$ but, in simple cases (such as the descriptions of Na and Mg to be given in this paper) where a principal minimum value $\varphi_{\min}$ exists around the nearest neighbour position, the easily applied formula[1,7]

$$\varphi(\sigma) - \varphi_{\min} \approx \tfrac{3}{2}k_BT \qquad (4)$$

suffices instead. Our procedure for the liquids, then, is to extract σ's from (3) at the observed $\Omega(T)$'s and obtain, by pseudopotential theory, the r_c's which lead to these values. Such results are shown in Figure 1 alongside their solid state counterparts.

One might also expect r_c to depend on the property fitted. To illustrate this point, we show, in Figure 1, some results obtained by fitting the principal peaks of the structure factors, observed by

Waseda[9], to those of the Percus-Yevick hard sphere solution[10]. In addition, we must also remember that experimental error will affect the result and, in this context, we mention that the Waseda work is only one of a number we could have selected.

A perusal of Figure 1 shows that r_c has volume dependence and that, notwithstanding the difficulties mentioned above, there is a discernible trend in its variation from one phase to the other.

3 INTERATOMIC POTENTIAL TESTS FOR Na AND Mg

A given r_c, at a specified volume, generates a complete pair potential. For example, the curves of Figure 2 correspond to the entropy fits of Figure 1 for the room temperature solids and the liquids at melting (the lowest point on each curve segment). The question now to be considered is the degree to which each such potential, fitted as indicated, has been uniquely defined, in the above way, over all space.

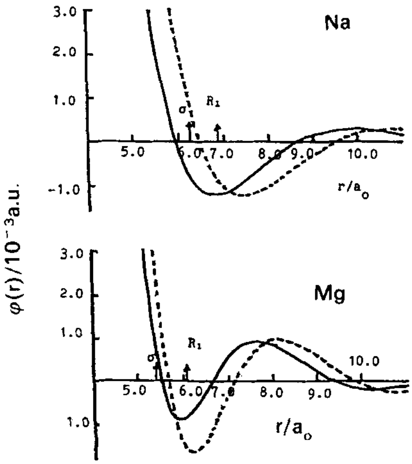

Figure 2 Pair potentials for Na and Mg. In each case the curves are shown for the solid at room temperature (solid line) and the liquid at melting (broken line). The nearest neighbour distances R_1 in the solids and the effective diameters σ in the liquids are indicated.

In the liquid cases, Eq. (4) applies. It is clear from this that only a small portion of the core is probed and even then it is only done in a crude way. Much of each $\varphi(r)$ curve is irrelevant, that part beyond the principal minimum being entirely so (to the extent that Eq. (4) can replace the full Gibbs-Bogoliubov procedure).

Table 1 Calculated nearest neighbour data for Na and Mg (atomic units throughout)

System	N_1	R_1	10^3R	10^3T
Na (bcc)	8	6.91	1.60	0.04
Mg (hcp)	12	6.04	5.4	0.1

N_1 is the number of nearest neighbours, R_1 is the nearest neighbour distance, $R = \varphi''(R_1)$ and $T = R_1^{-1}\varphi'(R_1)$.

In the solid cases, we calculate that only nearest neighbours§§ contribute in effect to Eq. (2), which then becomes

$$(3M/\hbar^2)(k_B\theta)^2 = N_1(R + 2T) \tag{5}$$

Here, $R = \varphi''(R_1)$ and $T = R_1^{-1}\varphi'(R_1)$, where N_1 and R_1 are the nearest neighbour coordination numbers and distances (Table 1). Evidently, therefore, only the curvature around R_1, itself near the potential minimum, is being fitted. The numerical data of the analysis are summarised in Table 1.

One can, in fact, test the data of Table 1 somewhat further. In nearest neighbour approximation, the elastic shear constants can be written down as linear combinations of R and T and the coefficients for some simple cases are shown in Table 2. In this way, using Table 1, we calculate the results of Table 3. These are probably about as good as we are entitled to expect using such simple pseudopotential theory and vindicate the nearest neighbour description, particularly for Na. In the case of Mg, analysis of the observed data shows that they cannot be described in complete quantitative detail for any choices of R and T; nevertheless, the table suggests that the nearest neighbour approximation is tenable at least semi-quantitatively.

Table 2 Coefficients of R and T in shear constant formulae

	Bcc		Fcc		Dia		Hcp (ideal)	
	R	T	R	T	R	T	R	T
$\Omega^{1/3}c_{44}$	$\frac{1}{3} \times 2^{2/3}$	$\frac{1}{3} \times 2^{5/3}$	$2^{-2/3}$	$3 \times 2^{-2/3}$	$\frac{1}{6}$	$\frac{4}{9}$	$\frac{1}{3} \times 2^{1/3}$	$\frac{5}{3} \times 2^{1/3}$
$\Omega^{1/3}\frac{1}{2}(c_{11} - c_{12})$	0	$2^{2/3}$	$2^{-5/3}$	$7 \times 2^{-5/3}$	0	$\frac{1}{2}$	$\frac{5}{3} \times 2^{-5/3}$	$\frac{19}{3} \times 2^{-5/3}$
$\Omega^{1/3}\frac{1}{6}(c_{11} + c_{12} + 2c_{33} - 4c_{13})$ (not applicable to cubic cases)							$2^{-2/3}$	$3 \times 2^{-2/3}$

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§§ We suppose the hcp Mg to have an ideal c/a ratio, 1.63, instead of the actual 1.62, and in this case take $N_1 = 12$.

Table 3 Elastic shear moduli (all in 10^{-3} a.u.)

	c_{44}	$\frac{1}{2}(c_{11} - c_{12})$	$\frac{1}{6}(c_{11} + c_{12} + 2c_{33} - 4c_{13})$
Na	0.140 (0.143)	0.009 (0.019)	—
Mg	0.461 (0.558)	0.563 (0.571)	0.666 (0.697)

Calculated values are followed by observed data in parentheses.

4 OTHER SYSTEMS: Al AND Ge

We have considered two further systems, Al and Ge, the interatomic potentials for which are shown in Figure 3. In these cases, the principal minimum has been largely lost and this raises questions, in particular, about the validity of the nearest neighbour force constant description for the solids.

In the case of solid Al, the Einstein temperature varies considerably (from 267 K at room temperature to 229 K at melting) yet r_c, obtained via Eq. (2), remains remarkably constant (Table 4) at about $1.14a_0$. On the liquid side of the transition we assume Eq. (4) can be applied in relation to the shallow minimum and find a packing fraction of $\eta = 0.46$ (0.45) corresponds to $r_c/a_0 = 1.12$ (1.09). It would thus seem that r_c remains rather constant despite a 9% volume increase on melting.

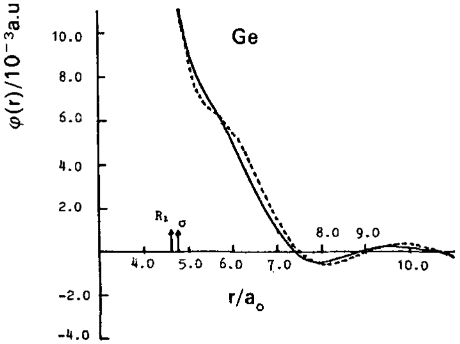

Figure 3 Pair potentials for Al and Ge. Description as in Figure 2 caption.

Table 4 r_c versus r_s for Al and Ge

	Phase	T/K	r_s/a_0	r_c/a_0
Al	Fcc	298	2.07(3)	1.139
	Fcc	933	2.10(6)	1.145
	Liquid	943	2.16(5)	1.12*
Ge	Dia	300	2.09	0.98
	Liquid	1250	2.096	1.03**

* Fitted to $\eta = 0.46$.
** Kahl and Hafner[11] fit.

In contrast with the Na and Mg cases, however, the nearest neighbour approximation (Eq. (5)) does not appear to be accurate. This is signalled by the fact that three sets of neighbours are needed in Eq. (2), the nearest neighbour result for θ falling thereby from 306 K to 267 K. Analysis of the elastic shear constants, using Table 2 (fcc case), leads to the same conclusion; the observed c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ yield R and T not reconcilable with θ. We must conclude that we are not subjecting the curve at the nearest neighbour position to detailed scrutiny.

Finally, we considered Ge because Kahl and Hafner[11] have quite successfully described the liquid state structure factor in this case. Solid Ge, at room temperature, has just about the same density as liquid Ge at melting. (This is so because the normal solid state expansion on heating is nullified by a *contraction* on melting). It will be seen from Table 4 that the corresponding r_c fits are also much the same. Once again, however, Eq. (5) is inadequate for describing θ, the nearest neighbour result falling from 254 K to 235 K on including the third shell in Eq. (2). Table 2, in fact, shows very directly that the Ge potential of Figure 3 is incompatible with a nearest neighbour description; according to Figure 3, T is negative and this implies instability to [110] shear. Once again, it would seem that the analysis tells us little quantitatively about the potential at the nearest neighbour position.

5 CONCLUSIONS

As a result of the above analysis, there is some reason to believe that the shapes of the interatomic potentials for Na and Mg are semi-quantitatively known over a limited range (from slightly below σ to just beyond R_1 in Figure 1). The absolute values are, however, untested in this region (and we find it difficult to see how to do so convincingly). Outside these segments, the remainder of the curves remain untested.

In the cases of Al and Ge, the solid state evidence points to the qualitative feature of loss (partial or total) of minimum in the nearest neighbour region. Mutatis mutandis, the shape in this region cannot be quantitatively tested by the above techniques. Furthermore, the absolute values within this region and all features outside remain untested.

Finally, we return to the original impetus for this project. The results indicate that pseudopotential parameters can sometimes carry significant volume dependence. In particular, therefore, it is not safe practice to assume that parametrisations obtained in the solid state can be applied unchanged in the liquid, and vice versa. If, however, the volume dependence can be ascertained in one phase, there appears to be some evidence in favour of its extrapolation for usage in the other.

Acknowledgement

We are grateful to the SERC and to the Royal Society and the Nuffield Foundation for their support.

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