Pseudopotential theory of effective pair interaction in Al

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Abstract   The second-order pseudopotential calculations of interionic pair interaction for Al show a ledge structure in the repulsive region around the nearest neighbour distance and only vestiges of an attractive minimum at second neighbour distance indicating deficiency of a hard-sphere description Inclusion of third-order calculation on the basis of localised *ab initio* pseudopotential, alters the pair potential drastically and a hard-sphere description, in conformity with the empirical ionic pair correlation data, emerges The influence of different commonly used screening functions on the shape of pair potential is also investigated.

1. Introduction

According to second-order pseudopotential energy, the total energy of a metal may be expressed in terms of a density dependent pairwise interionic interaction in addition to the pure density (volume) dependent energy. Higher order energy terms actually contain, addition to some residual volume energy and two-body interactions, interactions between three and more ions. Most simple metals and simple metal based binary systems appear to be well described at the pair potential level and these potentials are being used in atomistic simulations also.

Second-order pseudopotential studies predict oscillatory two-body interaction with deep negative (attractive) minimum favouring a hard-sphere description for most simple metals. This is also supported by earlier first principle calculations by Rasolt and Taylor [1] and by McMahan and Moriarty [2]. For Al, however, there is something of a ledge structure in the repulsive region around the nearest neighbour distance and only vestiges of an attractive minimum at the second neighbour distance indicating deficiency of a hard-sphere description. It is regarded

that some higher order contributions get included in the scheme of self-consistent nonlinear charge density calculations of pair interaction by Rasolt and Taylor. However, their result for Al is very similar to our second order calculation [3]. On the other hand, adopting almost similar procedure of Rasolt *et al*, Manninen *et al* [4] have obtained pair potentials for Al (embedded in a jellium vacancy) which prefers a hard-sphere description. Very recently Mishin *et al* [5] have developed interatomic potential for Al, using embedded atom method (EAM) potential functional based on a large set of experimental and *ab initio* data, which shows pronounced hard-sphere description.

The pair correlation functions $g(r)$, determined with second order pair potential in the high temperature limit ($T \gg T_m$) for all the metals excepting Al, compare well with the existing Monte-carlo calculation [6].

Additional pair potential due to third-order perturbation term in electron-ion interaction is comparatively large and attractive at short distances and shifts the first zero of the potential to smaller distances by several percent [7,8]. For Al, the third-

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order contribution alters the pair potential rather drastically and its inclusion improves the theoretical estimate of $g(r)$ for Al to a reasonable agreement with the experimental results.

2. Basic theory

The total pair potential $\phi(r)$ upto third-order in electron-ion interaction (pseudopotential) may be written formally as the sum of second- and third- order contributions :

$$\phi(r) = \phi^2(r) + \phi^3(r). \tag{1}$$

The second-order effective interionic pair potential $\phi^2(r)$ for simple metals is given by

$$\phi^2(r) = \frac{(Ze)^2}{r} \quad \frac{\Omega}{\pi^2} \int_0^\infty F_N(q;\Omega) \frac{\sin(qr)}{qr} q^2 \, dq, \tag{2}$$

where Z is the valence, Ω is the ionic volume and F_N is the Harrison's [9] energy-wave number characteristic function that embodies electronic band-structure effect including the self consistent electron screening. Pseudopotential form factors involved in F_N are plane wave matrix elements of ion-electron pseudopotential.

The expression for the third-order contribution $\phi^3(r)$ may be written as

$$\phi^3(r) = \frac{1}{2\pi^4} \iiint \varepsilon_3(q_1, q_2, \theta) q_1^2 q_2^2 \frac{\sin(q_1 r)}{q_1 r} d\cos\theta dq_1 \, dq_2$$

$$+ \frac{1}{4\pi^4} \iiint \varepsilon_3(q_1, q_2, \theta) q_1^2 q_2^2 \frac{\sin(\alpha^2 + \beta^2)^{1/2}}{(\alpha^2 + \beta^2)^{1/2}} d\cos\theta dq_1 \, dq_2, \tag{3}$$

where

$$\varepsilon_3(q_1, q_2, \theta) = \Omega^3 \omega_{q_1} \omega_{q_2} \omega_{q_3} g(q_1, q_2, q_3),$$

where ω_q is the screened pseudopotential form factor and $g(q_1, q_2, q_3)$ is a symmetric function of the three modulii q_1, q_2 and q_3 defined by Lloyd and Sholl [10], with

$$q_1 = |q_1|; q_3 = -q_1 - q_2 \; ; \; \theta = \angle q_1, q_2 \; ;$$

$$\alpha = q_2 r (1 - \cos^2 \theta)^{1/2} \text{ and } \beta = (q_1 + q_2 \cos \theta) r$$

The first term of eq. (3) is the contribution of two symmetric terms derived earlier by Hasegawa [7]. The second term was, however, missed out by Hasegawa and developed only recently [11]. It is found to have comparable magnitude as the first term.

In the high temperature limit ($T \gg T_m$), the ionic pair correlation function may be approximated [12] as

$$g(r) = e^{-\phi(r)/kT}. \tag{4}$$

In the present work, we use the localised *ab initio* pseudopotential form factor derived in Ref. [13].

3. Results and discussion

The effective pair potentials are computed with localised *ab initio* pseudopotential in second-order theory for Al. The calculation is made with four different screening functions of Geldart and Vosko (GV) [14], Taylor (T) [15], Ichimaru and Utsumi (IU) [16] and the recently proposed one by Sarkar, Sen, Haldar and Roy (SSHR) [17]. Very similar values are found with IU and T screening functions whereas SSHR and GV forms produce closer results. The calculated phonon spectra from the computed pair potentials (with GV screening function) are found to agree with earlier second-order pseudopotential calculation [13].

In Figure 1 we compare our second order calculation with the result of Refs. 1 and 2. The results are very similar and negate a hard sphere description for the pair potential of Al. But from the high temperature $g(r)$ data for Al [18], the inverted $\phi(r)$ from the simple expression [eq. (4)] differs widely from $\phi^2(r)$. The inclusion of $\phi^3(r)$, however, shows marked improvement and for ($T \gg T_m$) a hard-sphere description in conformity with the empirical ionic pair correlation data emerges.
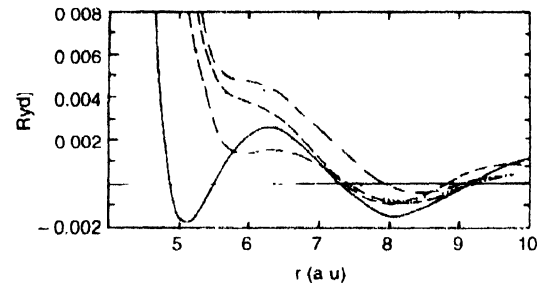
Figure 1. Comparison of the 2nd-order pair potentials of Al with other *ab initio* 2nd-order calculations. Dashed curves represent present calculation, dotted curves due to Dagens *et al* [1] and dash double dot dash curves from ref 18. Pair potentials obtained from calculations upto 2nd and 3rd-order for Al at $T = 1323 \ K$. Solid curves represent 3rd-order calculations and dash dot dash curves represent 2nd-order calculations respectively. The present calculation uses the SSHR local field factor

Figure 2 depicts the phonon dispersion curves obtained from the pair potential and compared with the full third-order
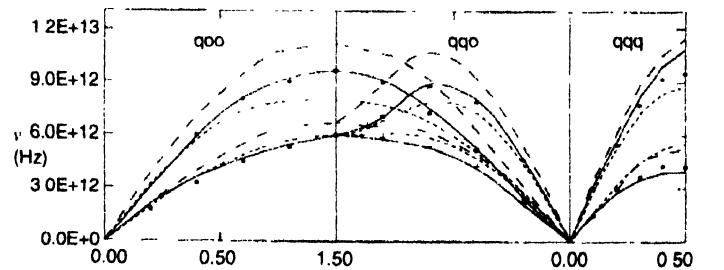
Figure 2. Phonon dispersion curves obtained from pair potentials calculated upto 2nd- and 3rd-order and from full 3rd-order pseudopotential calculations for Al. Solid curves represent pseudopotential calculation, small dashed and long dashed curves represent calculations from 3rd- and 2nd-order pair potentials respectively. Experimental points are indicated by stars, solid squares and plus symbols for longitudinal and two transverse branches respectively

pseudopotential (*ab inito*) calculation. They provide an estimate of the three-body contribution to lattice vibration in Al.

Full third-order calculation which include upto three-body interaction shows reasonable agreement with the experimental results for Al. Our calculation upto second order, overestimates phonon frequencies in all the symmetry directions whereas inclusion of the third order two-body (small dashed curves in Figure 3) lowers the frequencies below the experimental values. Contributions of the three-body interaction turn out to be significant excepting for $[q00]$ and lower $[qq0]$ transverse branches. Near the zone boundary, the three-body contributions to the $[q00]$ longitudinal and the upper $[qq0]$ transverse branches are as high as 15 to 20%. For the $[qq0]$ longitudinal branch, the maximum three-body contribution of about 15% is observed near.6.6 0 point.
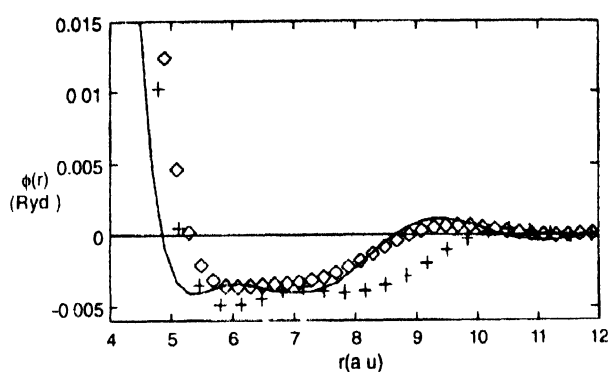

Figure 3. Comparison of pair potentials obtained from calculations upto 2nd (diamond symbols) and 3rd-order (solid curves) for Al using recently proposed LFF Plus symbols are from Ref 5

Very recently, we have proposed a local field factor (LFF) for the most general case of interacting unpolarised electron gas [19]. Calculation of $\phi(r)$ for Al using this LFF gives agreement with the result of Mishin *et al* [5] (Figure 3).

In conclusion, we note that realistic pair potential for simple polyvalent Al is well described within the framework of perturbation theory using *ab-initio* pseudopotential in

conjunction with linear response theory. The present study also highlights the importance of the 3rd order (perturbation) contribution as well as that of the choice of proper local field factor in dielectric screening.

Acknowledgment

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