The Young–Hoshino pseudopotential for lithium: calculations of structure and thermodynamics

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Abstract. The recently proposed Young–Hoshino model pseudopotential for lithium has been applied to the calculation of structure and thermodynamics. A slight modification of the model potential is necessary and this produces better core size and long range tail of the interionic effective pair potential than the original model.

Keywords. Lithium; pseudopotential; structure; thermodynamics.

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1. Introduction

In the study of physical properties of metals and alloys it is normally required to choose a pseudopotential either in local or non-local form. Lithium is an important exception where the simple pseudopotentials are less successful and therefore this metal plays a role in the research of metals and alloys particularly in the area of liquid alloys (Alblas *et al* 1984; van der Lugt and Geertsma 1984; Ruppersberg and Reiter 1982). Based on physical ideas stronger than those used for constructing local pseudopotentials, Hoshino and Young (1986) proposed a local pseudopotential for Li which after consistent parametrisation have virtues of non-local pseudopotential and produces some of the basic features of metallic Li. This pseudopotential is, however, not suitable for computing atomic properties. We, therefore slightly modify the pseudopotential, based again on physical grounds, and show that better consistencies are thereby brought in the size of the core and tail of the effective interionic potential. We then compute the structure and the thermodynamics of liquid Li through the standard perturbation techniques.

2. Analysis of the model

2.1 *Young–Hoshino (YH) pseudopotential for Li*

Hoshino and Young (1986) proposed a realistic pseudopotential for Li which makes a full self-consistent field potential valid for all electrons and pseudise for s-scattering by introducing a repulsive δ-function located at the origin. Thus in real space,

$$v(r) = v_{\mathrm{HXC}}(r) + \beta\delta(r), \tag{1}$$

In the q-space the bare ion potential becomes

$$v(q) = -(4\pi Ze^2/q^2)\{3 - 2(2\alpha)^4/[(2\alpha)^2 + q^2]^2$$
$$+ 2\Gamma\gamma q^2/[q^2 + \gamma^2]^2[1 + D\exp(-\lambda q^2)] - \beta q^2/4\pi\}, \tag{2}$$

where α, γ, Γ, D and λ are the constants in the full Hartree field (described accurately using exponential form of Slater 1s orbitals) corrected for exchange and correlation in a local density approximation and are obtained as described by Hoshino and Young. The strength parameter $\beta \sim 24$–26 was chosen to describe most of the properties discussed. The electron-ion form factor is given by

$$u(q) = v(q)/\varepsilon(q), \tag{3}$$

where $\varepsilon(q)$ is the appropriate dielectric function of the electron gas. With Ichimaru–Utsumi (1981) local field correction this gives features near $q = 2k_F$, that can be obtained for Li by elaborate non-local pseudopotential calculations (Meyer and Young 1965; Taylor 1982) (figure 1). It produces good liquid resistivity through Ziman formula using experimental structure factor. It is also somewhat in agreement with highly qualitative band gap measurements.

It is, however, to be noted that the form factor takes the form of Harrison's point
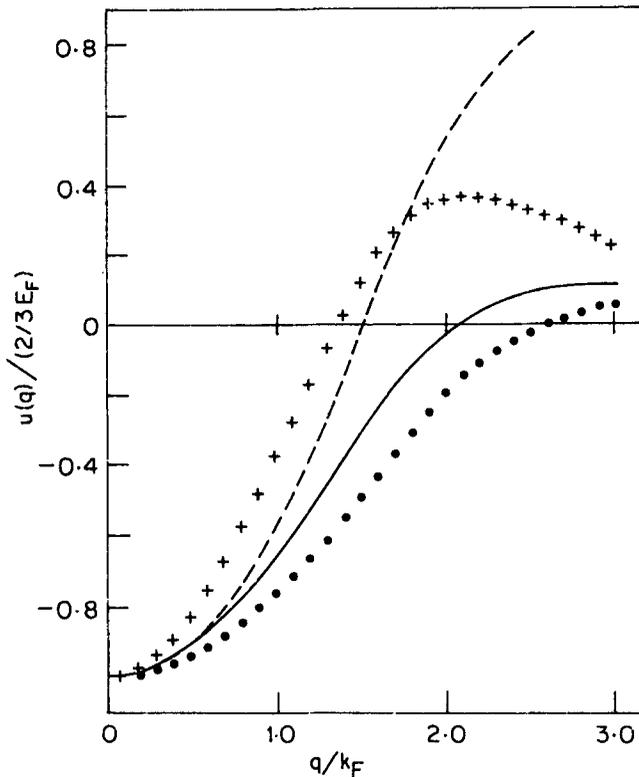
Figure 1. Electron-ion form factor for Li. ($-\cdot-\cdot$) YH model with $\beta = 26$. ($----$) Modified YH model with $\beta = 26\cdot3$ and $r_b = 0\cdot44$ au. ($\cdots$) Ashcroft model with ionic core radius $r_c = 1\cdot06$ au ($+++$) Ashcroft model with ionic core radius $r_c = 2\cdot00$ au.

ion model (Harrison 1966) at large q and does not drop to zero at large q as a true form factor is expected to do. This makes the potential unsuitable for computing the atomic properties. The high q values of the form factor decide the core part of the intermolecular interaction and this primarily decides the structure. So, for the calculation of atomic properties, we slightly modify YH pseudopotential at large q based on physical arguments. This brings out, as we shall see later, better consistencies in the size of the core and the tail of the effective pair potential than the original model.

To obtain reasonable values of the form factor at high q we note that the repulsion arising from the conduction electrons are excluded from the core essentially because of the Pauli's principle. This effect has a range r_b ($\sim$ Bohr radius) and may be assumed to fall off exponentially. More specifically, we consider the general Austin–Heine–Sham form (1962) for the unscreened pseudopotential given by

$$\langle \mathbf{k}+\mathbf{q}|v|\mathbf{k}\rangle = \langle \mathbf{k}+\mathbf{q}|v_{\mathrm{HXC}}|\mathbf{k}\rangle + \sum_t \mathbf{f}(\mathbf{k},t)\langle \mathbf{k}+\mathbf{q}|t\rangle\langle t+\mathbf{k}\rangle. \tag{4}$$

The decay of repulsive term at large q comes from the corresponding decay of $\langle \mathbf{k}+\mathbf{q}|t\rangle$. The leading term in a series for $\langle \mathbf{k}+\mathbf{q}|t\rangle$ in $1/q$ will come from the term in the s-state core functions proportional to $\exp(-r/r_b)$, where r_b is a constant. The leading term of $\langle \mathbf{k}+\mathbf{q}|t\rangle$ will take the form

$$\langle \mathbf{k}+\mathbf{q}|t\rangle \propto \int (\sin qr/qr)\exp(-r/r_b)4\pi r^2\,\mathrm{d}r$$

$$\propto 1/[1+(qr_b)^2]^2.$$

This suggests that the last term in the bracket of (2) is modified by $(q^2/4\pi)/(1+q^2r_b^2)^2$. We shall use this simply modified form of YH pseudopotential to study structure and thermodynamic properties of lithium. Clearly, $r_b = 0$ recovers the original model. We use $\beta \sim 26\cdot3$ in close agreement with the original model and r_b has been chosen so as to produce a good structure factor peak. This choice of r_b is also in accord with the effective interionic potential. However, some adjustments of r_b is necessary for calculations like electron transports and thermodynamics which is not unexpected for a local model potential (Ashcroft and Langreth 1967).

2.2 *Effective ion–ion potential*

The effective ion–ion potential is given by

$$\Phi(r) = Z^2/r + 1/(2\pi)^3 \int F(q)(\sin qr/qr)4\pi q^2\,\mathrm{d}q, \tag{5}$$
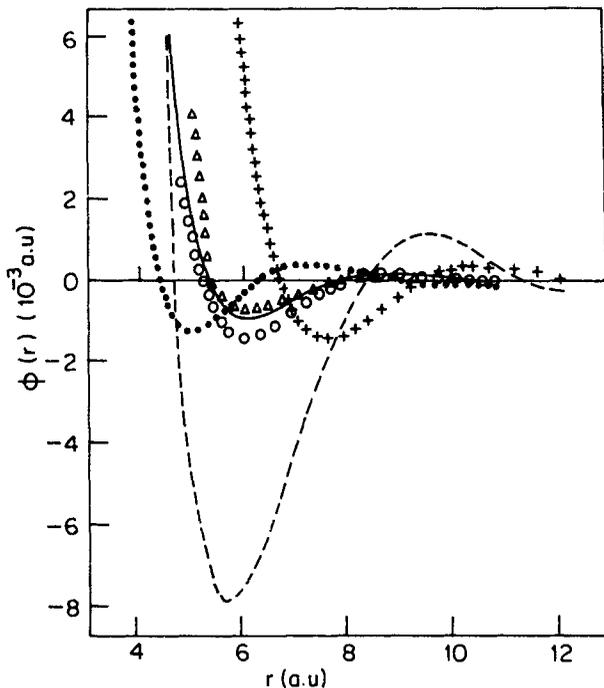
where, Z is the valence (1 for Li) and the energy wave number characteristic, $F(q)$ is given by

$$F(q) = q^2/4\pi(1/\varepsilon(q)-1)v^2(q),$$

where, $\varepsilon(q)$ is the dielectric function given by

$$\varepsilon(q) = 1 + (4\pi/q^2)\chi(q)/[1-(4\pi/q^2)G(q)\chi(q)], \tag{6}$$

with $\chi(q) = (k_F/\pi^2)(1/2+(1-x)/4x\ln|(1+x)/1-x|)$, $x = q/2k_F$ and $G(q)$ is the local field correction of Ichimaru and Utsumi (1981).

Figure 2. Effective interionic potential for Li. (- ---) as in figure 1. (——) as in figure 1. (○○○) Fully non-local pseudopotential of Day *et al* (1979) (△ △ △) $-c(r)k_B T$ from calc. $S(q)$, (···) and (+ + +) as in figure 1.

In figure 2 we show the effective interionic potential for Li with $r_b = 0.44$ au. The effective potential corresponding to the original YH potential is also shown. Although the position of the first minimum is more or less unaffected, the depth of the potential is considerably reduced. For comparison we give the effective pair potential calculated from a fully first principle non-local pseudopotential of Day *et al* (1979). Clearly this slightly modified YH form agrees better with this than the original YH model. We have also obtained $\Phi(r)$ for large r from the calculated structure factor $S(q)$ through the mean spherical approximation (MSA) relation $\Phi(r) = -k_B T c(r)$, where $c(r)$ is the direct correlation function (DCF) obtained from $S(q)$. This relation is known to be very accurate for large r (Barker and Gaskell 1975). The potential so generated from the calculated $S(q)$ compares well with the $\Phi(r)$ obtained from the model pseudo-potential. This is surely a consistency check and choice of r_b is therefore justified. We have not given the corresponding MSA potential from experimental $S(q)$ data because of uncertainties in the low q data of $S(q)$ and $c(r)$ known to be very sensitive to these data. It is however to be noted that the MSA $\Phi(r)$ from experimental $S(q)$ is much better in agreement with the present $\Phi(r)$ than with the original model $\Phi(r)$. $\Phi(r)$ from Ashcroft model with the same screening function but different ionic core radii (fitted to resistivity through Ziman formula, $r_c = 1.06$ au and 2.00 au) are also shown, but none agree with the Day *et al* potential.

It is to be noted that the form factor for $r_b = 0.44$ au has somewhat different form from $q = k_F$ onwards (figure 1). It corresponds to a band gap considerably less than that from positron-annihilation measurement but these experimental data are highly qualitative (Donaghy and Stewart 1967). The precise quantitative status of the Ziman

formula for resistivity is also not known. The calculated resistivity and thermoelectric power are 11 μohm cm and 8·6 μ V/° respectively against the experimental values of 24 μ ohm cm and 22 μ V/°. Somewhat smaller value of r_b ($\sim$0·3 au) will improve these values and also the band gap almost in agreement with experiment. In the original model the thermoelectric power, however, comes out to be negative. There have been a variety of form factors for Li and some, for example, Soma (1979), Popovic *et al* (1971), have the forms similar to this modified form and produce very good bulk modulus, cohesive energy, etc. for Li. The form factor which gives elaborate non-local character is in no way better in these calculations.

2.3 *Core size and tail of the potential*

From the effective interionic potential we estimate the effective hardcore diameter, σ for liquid-state ionic collisions using the Ashcroft–Langreth prescription (1967)

$$\Phi(\sigma) - \Phi_{\min} = 3/2 k_B T, \tag{7}$$

where, $\Phi_{\min}$ is the minimum of the potential $\Phi(r)$. The relation (7) is known to be quite accurate near the melting point (Hafner 1977; Das *et al* unpublished work). The values of σ, packing fraction $\eta = \pi n \sigma^3/6$, n being the mean ion density, hard sphere structure factor at long wave limit, $S_{hs}(0)$ (through PY equation (Waseda 1980)), excess entropy, S^{ex}/k_B (through Carnahan and Starling equation (Waseda 1980)) are displayed in table 1. The observed structure factors lead us to expect a packing fraction of about 0·43 at $T = 573$ K which is in good agreement with the one obtained from (7) (at m.p. 453 K, it is $\sim$0·46, (Waseda 1980)). Obviously, both $S_{hs}(0)$ and S^{ex}/k_B are reasonable. The original YH potential produces at $T = 453$ K with $\beta = 26$ (best β from core and tail analysis (Hoshino and Young 1986), core size $\sigma = 5·15$ and $\eta = 0·47$ which

Table 1. Atomic properties of liquid Li at 573 K.

Through core analysis based on AL prescription					Through ORPA caln. of S(q) in long wave limit						
			$\beta = 26·3$				$r_b = 0·44$ au				
			$-S^{ex}/k_B$					S(0)		$\chi_I \times 10^{-11}$ m² N	
η	σ(au)	$S_{hs}(0)$	Calc.	Obs.	η	σ(au)	I	Calc.	Obs.	Calc.	Obs.
0·42	5·0	0·033	3·42	3·61	0·43	5·1	110	0·03	0·031	8·67	8·69

Through the thermodynamic variational calculation
$\beta = 26·3$ $r_b = 0·65$ au

|		Excess entropy $-S^{ex}/k_B$		*Sp. ht. at const. vol. C_v k_B		Internal energy $-E$(au)	
η	Γ	Calc.	Obs.	Calc.	Obs	Calc.	Obs.
0·43	90	3·40	3·61	3·40	3·40	0·29	0·26

*In the calculation of charge part, the term containing $(\partial\eta/\partial T)_V$ is neglected since $(\partial\eta/\partial T)_V \ll (\partial\Gamma/\partial T)_V$.

appears not very unreasonable (through $S_{hs}(0) = 0.014$ considerably smaller and $S^{ex}/k_B = -4.33$ considerably bigger compared to experimental values). $\beta = 24$ which was the best estimate from band gap considerations, however, does not give good core size and tail of the potential. Ashcroft potentials for $r_c = 1.06$ au and 2.00 au, however fail this core analysis (Hoshino and Young 1986).

The overall tail in the present case is quite reasonable. This contention is supported by our calculation of isothermal compressibility (χ_T) in the longwave (LW) limit of structure factor $S(0)$. The tail of the original YH potential was clearly exaggerated because it produces $S(0)$ and hence χ_T in the RPA with $\beta = 26$ considerably larger in magnitude than the observed value. A slightly bigger value of β could give good $S(0)$ and χ_T but corresponding σ and η would be unrealistic. Obviously no Ashcroft potential will suffice in this test (with a choice of arbitrary r_c) as pointed out by Hoshino and Young (1986).

2.4 *Structure factor*

The calculation of structure factor based on this simply modified form of YH potential is surely an interesting exercise. Information about the core is obtainable from the large q behaviour while the small q-behaviour (and at $q = 0$) gives information about the tail of the potential. So the generation of good structure factors in the entire momentum space shows the correctness of the effective interionic potential. Now, various perturbative schemes e.g. WCA, RPA, ORPA with appropriate reference system are available for doing so. Recent investigations show that OCP or a realistic OCP i.e. a CHS system (Chaturbedi *et al* 1981; Pastore and Tosi 1984; Singh and Holz 1984; Das and Joarder 1988) serves as a successful reference system for alkalis. The ORPA calculation of Das and Joarder (1988) for alkalis with Ashcroft potential is very successful in general and we have adopted the same procedure to check the structure factor of Li with this potential. The result is shown in figure 3 and it is clearly very good. One of the best possible calculated structure factors based on the
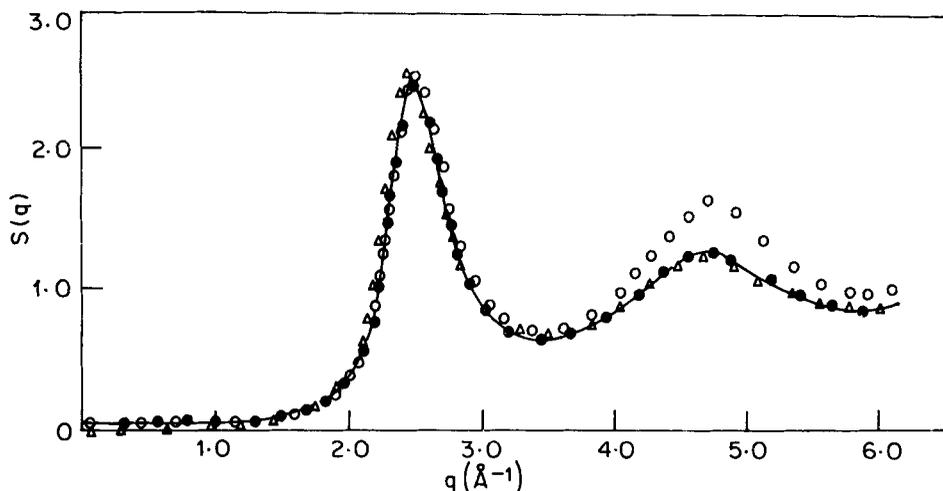
Figure 3. Structure factor, $S(q)$ of liquid Li. (———) Calculated (···) Experimental (Ruppersberg and Egger 1975) (○ ○ ○) Best possible calculated based on the original model with $\beta = 17.0$ (△ △ △) Reference system.

original model with $\beta = 17$ and uniform electron gas dielectric function is shown for comparison. Clearly the original model does not work except near the peak. It is much worse than the reference system structure factor which is also shown.

The RPA expression for structure factor is given by

$$S(q) = S_0(q)/[1 + n\beta\tilde{v}(q)S_0(q)], \tag{8}$$

where, $S_0(q)$ is the structure factor of the reference system, $\tilde{v}(q)$ is the electron mediated attraction and other terms have their usual meaning. In ORPA, the attraction is modified in the excluded volume region as followed by Weeks *et al* (1971). The potential $\tilde{v}(r)$ is replaced by an effective potential $\tilde{v}(r)$ such that $\tilde{v}(r) = \tilde{v}(r)$ for $r > \sigma$. The optimal choice of $\tilde{v}(r)$ for $r < \sigma$ in the RPA form of the free energy is based on the requirement that the functional derivative of the free energy with respect to $\tilde{v}(r)$ should vanish for $r < \sigma$. For details please see Pastore and Tosi (1984) and Das and Joarder (1988). In the calculation, η was taken to be that for hard sphere system (Singh and Holz 1984; Das and Joarder 1988) and plasma parameter Γ was adjusted to have best reference structure factor. The good $S(0)$ and isothermal compressibility surely support our earlier contention about the present interionic potential. In this connection it is to be mentioned that the difference between $S(0)$'s in RPA and ORPA is quite small $(< 5\%)$ and this means that the optimization procedure has little effect on $S(0)$ (Das and Joarder 1988).

2.5 *Thermodynamics*

The thermodynamic variational calculation for Li with the simply modified form of YH pseudopotential is performed following the methods discussed by Lai (1985), Ono and Yokoyama (1984), Joarder and Das (1988) and the details are not given here. The basic principle is the Gibbs–Bogoliubov (GB) inequality which gives the free energy of the system given by

$$F \leqslant F_0 + \langle H - H_0 \rangle_0, \tag{9}$$

where, F_0 is the free energy of the CHS reference system and $\langle H - H_0 \rangle_0$ is the ensemble average over all the configurations of the chosen reference system and evaluated with the modified YH potential. F_0 is given by

$$F_0 = 3/2k_BT + V_0 - TS_0, \tag{10}$$

where, V_0 and S_0 are the CHS potential energy and entropy respectively as in Joarder and Das (1988).

Following the same procedure as in Joarder and Das (1988) we minimise the free energy using Γ as a variational parameter. Once the free energy is obtained by the minimization procedure other thermodynamic functions follow directly. Some of the properties calculated are shown in table 1. The r_b value had to be adjusted to have a general consistency in the Γ value with $S(q)$ calculation. In spite of this adjustment the Γ value in the thermodynamic calculation is somewhat less. This difference is not unexpected if we recall the thermodynamic inconsistency (MacGowan 1983) that prevails in such a theory. The calculated properties surely shows the relevance of this simply modified YH pseudopotential in the thermodynamic perturbation study of liquid lithium. It is to be mentioned that the YH pseudopotential in the original

form cannot be applied with any success for this calculation. With $\beta = 17$, Γ comes out to be absurdly small and free energy has very large negative value.

3. Discussion

We have shown in this communciation how YH pseudopotential for Li with a slight modification can be applicable to the calculation of structure and thermodynamics of liquid Li. This form produces an effective pair potential which agrees better with that from the first principle fully non-local pseudopotential of Day et al (1979) than the original form. It has the correct core size and reasonably good oscillatory tail. A good agreement in $S(q)$ throughout and the generation of thermodynamic properties through GB principle support this contention. The effective pair potential obtained from Ashcroft model as pointed out by Hoshino and Young cannot produce the correct core size and isothermal compressibility (in RPA) simultaneously with any value of ionic core radius r_c. It is also known that the Ashcroft model is not very suitable for Li in the structure factor calculations (Pastore and Tosi 1984; Das and Joarder 1988). This impasse exists in the original YH pair potential also and probably arises not because of the weak tail of the Ashcroft pair potential as pointed out by Hoshino and Young but because of the details of the potential. Possibly, a modified theory i.e. a theory containing terms other than only RPA is required to describe $S(0)$ or isothermal compressibility in a better way. This is clearly demonstrated here by the use of ORPA with the modified form of YH pair potential though the latter possesses a relatively weak tail-like Ashcroft potential.

In conclusion, we reiterate that YH potential with the slight modification enjoys the desired simplicity and at the same time generates reasonably the properties of this less simple member of alkali series.

Acknowledgements

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