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Abstract. We have studied the static structure and some thermodynamic properties of liquid lithium by using the variational modified hypernetted chain (VMHNC) approximation as the liquid state theory and several effective interatomic pair potentials, derived from different pseudopotentials already proposed in the literature. We also propose a new interatomic pair potential derived from the neutral pseudoatom method (NPA).

1. Introduction

The present paper is devoted to the theoretical study of some structural and thermodynamic properties of liquid lithium. This atom has two s core electrons and one valence electron so, for normal pressures, it represents the simplest metal in nature. However, comprehension of its properties from a fundamental level is still seriously lacking. In many aspects, lithium is a special case among the alkali metals. For instance, it is practically immiscible with all the other alkalis, which are all miscible among themselves [1].

Concerning the experimental determination of its static structure factor, special problems also appear, specifically in normalizing and correcting the raw intensity obtained in a diffraction experiment. It must be noted that in an x-ray scattering experiment the x-rays are diffracted by both core and conduction electrons. In the case of lithium, the conduction electrons amount to 33% of the total number of electrons, compared with 9% in Na, or 1.8% in Cs. This implies that the delocalization effects in the form factor must be very important for lithium [2]. Moreover, the inelastic (Compton) scattering is rather substantial for lithium (as compared with the other alkali metals) and the theoretical calculations of the Compton scattering also suffer from an inadequate knowledge of the implications of the delocalization effects [3]. In neutron diffraction experiments, the Placzek correction is larger than usual because of the small atomic mass of the lithium nucleus, and it is not yet clear whether the usual corrections are adequate [3–5]. In fact, different treatments of these corrections can lead to very different static structure factors [3,6].

From a theoretical point of view, the study of simple metals is closely related to pseudopotentials. The lack of p core electrons in lithium represents a hindrance (rather than a simplification) when one tries to design a reasonable pseudopotential for this system. In principle the pseudopotential can be of local or non-local character. Intuition says that a non-local pseudopotential should be better suited for lithium than a local one. This is easily understood if one considers that the absence of p core electrons implies that *no pseudization is needed* for p valence electrons, while s valence electrons do have to be pseudized. This

would imply not only a strong non-locality, but also a strong p pseudopotential, since it would be the whole ionic potential.

Notwithstanding the preceeding remarks, pseudopotential theory has been used to study both liquid and solid lithium. In fact, local [7–10] as well as non-local [11–15] pseudopotentials have been proposed for lithium. Most of them have been tested only with very approximate liquid state theories, while others have been applied together with computer simulations to obtain the structure but not the thermodynamic properties of the system.

In this paper we calculate both the static structure and some thermodynamic properties of liquid lithium as predicted by some of those pseudopotentials. Moreover, we also propose a new effective interionic potential computed from first principles by using the neutral pseudoatom (NPA) method [16–18]. The NPA is concerned with the way the 'atom'—which in this context involves the ion and electron polarization cloud—is modified by the uniform jellium in which it is embedded, rather than by another ion as in pseudopotential theory. We also show that, at the level of a local description, the NPA yields an interionic pair potential that is free of adjustable parameters, with the atomic number as the only input data.

These potentials are used in conjunction with a recently proposed liquid state theory, the variational modified hypernetted chain (VMHNC) approximation [19]. We have recently reformulated this theory for pure systems and extended it to the case of mixtures [20]. We have also proved its reliability by comparing its predictions with the results of computer simulations both for pure [21] and multicomponent systems [20].

The paper is organized as follows. In section 2 we summarize the main features of the liquid state theory used. In section 3 we briefly describe the NPA method to obtain the displaced valence electronic density, which is the basis of our new local pseudopotential. In section 4 we list the pseudopotentials studied in this work and the results are presented in section 5. Finally, we sum up and discuss our results.

2. Liquid state theory: the VMHNC

In this section we briefly review the main features of the VMHNC. For additional details see [19, 20, 22].

The starting point of almost all integral equation theories of liquids is the Ornstein–Zernike equation which for an isotropic, homogeneous system can be written as

$$h(r) = c(r) + \rho \int dr' \, h(|r - r'|)c(r') \tag{1}$$

which defines the direct correlation function (DCF) $c(r)$, in terms of the total correlation function $h(r) = g(r) - 1$, where $g(r)$ is the pair distribution function (PDF) and ρ is the number density. This relation is supplemented with the exact closure relation [23]

$$c(r) = h(r) - \log[g(r)e^{\beta\phi(r)+B(r)}] \tag{2}$$

where $\phi(r)$ is the interatomic pair potential, $\beta = (kT)^{-1}$ is the inverse of the temperature times the Boltzmann constant and $B(r)$ denotes the bridge function, for which some approximation must be made. The usual approach for choosing the bridge function is based on the 'universality' hypothesis of the bridge functions [23]. This means that, except for small differences of detail, the bridge functions are the same for all the systems, the only difference being a relabelling of the parameters defining them.

Within this idea of universality, the actual choice of the bridge functions is somewhat arbitrary, mainly dictated by the availability of simple expressions for them, either analytic or derived from computer simulation. These functions are usually given in terms of one or more parameters, so a criterion is needed in order to determine these parameters as functions of the thermodynamic state. Different choices of the bridge functions, and different criteria to determine the parameters defining them, give rise to different versions of the MHNC.

In the context of the VMHNC, the bridge functions to be used are those obtained within the Percus–Yevick (PY) approximation for the hard sphere system [24], $B_{PY}(x, \eta)$, where $x = r\rho^{1/3}$ and η is the packing fraction of the spheres. These bridge functions have very suitable expressions because they are given almost in closed form and, most important, behave well as functions of x, namely they are continuous and differentiable everywhere. Note that these functions only depend on one parameter, the packing fraction η of the spheres. The VMHNC criterion to determine this parameter as a function of the thermodynamic state is to minimize a free energy functional $f^{VMHNC}(\beta, \rho, \eta)$ with respect to variations in η. The form of this functional is the following [19, 20, 22]

$$f^{VMHNC}(\beta, \rho, \eta) = f^{MHNC}(\beta, \rho, \eta) - \Delta^{(0)}(\eta) \tag{3}$$

where f^{MHNC} is the configurational part of the MHNC free energy functional

$$f^{MHNC} = \frac{1}{2} \int dx\, g(x)[\beta\phi(x/\rho^{1/3}) + B(x)] - \frac{1}{2} \int dx\, [\tfrac{1}{2}h^2(x) + h(x) - g(x)\log g(x)]$$
$$- \frac{1}{2}\frac{1}{(2\pi)^3} \int dk\, \{\log[1 + \tilde{h}(k)] - \tilde{h}(k)\} \tag{4}$$

with $\tilde{h}(k)$ being the Fourier transform (FT) of $h(r)$, and for reasons discussed elsewhere [20, 22] we take $\Delta^{(0)}(\eta)$ as

$$\Delta^{(0)}(\eta) = f_{PY}^{MHNC}(\eta) - f_{PYV}(\eta) - \delta_\phi(\eta). \tag{5}$$

Here $f_{PY}^{MHNC}(\eta)$ is the MHNC free energy functional (equation 4) when PY hard sphere distribution functions with packing fraction η are used, together with PY hard sphere bridge functions with the same η. The term $\delta_\phi(\eta)$ is a fitting function, given by

$$\delta_\phi(\eta) = f_{CS}(\eta) - f_{PYV}(\eta) \tag{6}$$

where f_{PYV} and f_{CS} denote the PY virial and the Carnahan–Starling [25] free energies for hard spheres.

This completes the specification of the VMHNC. Let us only point out the main features that place this theory among the most suitable ones to apply to liquid metals.

First, it is an integral equation theory of liquids. This fact avoids the need of artificially splitting the potential into a 'reference' part and a 'tail', as is compulsory, for instance, in the case of perturbation theories of liquids. Furthermore, its application is much simpler than in the case of perturbation theories of admitted similar accuracy (e.g. the WCA + ORPA procedure [26]). Second, the minimization of the free energy is performed in a specific thermodynamic state, i.e. the VMHNC is a 'local' theory. Other versions of the MHNC [23], and also some other integral equation theories of liquids [27], are 'global', which means that an integration along a thermodynamic path is needed in order to determine the properties of a single state. The locality of the theory is very important when it

applies to liquid metals because the effective pair potentials depend on the thermodynamic state [28], and therefore care must be taken when different states are involved in the calculation. When using a local theory there is no concern about this problem, since only one state is involved. Third, the VMHNC incorporates the consistency between two of the thermodynamic routes, namely the energy and the virial routes. And last, but not least, the thermodynamic inconsistency between these two routes and the compressibility route is diminished, although not eliminated. This is a very attractive feature of the VMHNC because the effective interatomic pair potentials obtained from pseudopotential theory lead to an intrinsic inconsistency, the so-called electronic or Brovman inconsistency [29] which prevents the virial and compressibility routes from being consistent, even in an exact theory of liquids.

3. Displaced valence electronic density: the NPA

The first step in the calculation of the effective interatomic pair potentials proposed in this work is the computation of the valence electronic density displaced by an ion embedded in a homogeneous electron gas. This computation is made within the NPA model, which is briefly described below.

In a zeroth-order approximation, a metal can be described as a homogeneous electron gas of mean density n_0 neutralized by a uniform positive background (the *jellium* model). However this model is exceedingly simple to describe the electronic structure of any real metal because in this case the positive charge is not uniformly distributed (it is concentrated at the ions, instead) and, furthermore, the ions attract the valence electrons which pile up around them, thus screening the ionic potential. A pseudoatom is now formed by the nucleus, the core electrons and the screening cloud. With these considerations in mind we can decompose the total electron density, $\rho_e(r)$, as a sum of localized densities that follow the ions in their movement:

$$\rho_e(r) = \sum_i n(|r - R_i|) = \sum_i n_c(|r - R_i|) + n_v(|r - R_i|) \tag{7}$$

where R_i denote the ionic positions, $n_c(r)$ is the core electronic density and $n_v(r)$ the valence electronic density (the screening cloud). The main aim of the NPA is the computation of $n_v(r)$; it proceeds as follows [17, 18, 22, 30].

The valence electronic density $n_v(r)$ is itself decomposed into two contributions, $n'_v(r)$ and $n''_v(r)$, that is, $n_v(r) = n'_v(r) + n''_v(r)$. The first contribution arises when an ion is introduced into a jellium in which a cavity has been made. That is, $n'_v(r)$ is the valence electronic density displaced by a total external potential

$$V'_{ion}(r) = V_{ion}(r) + [(1/r) * v(r)] \tag{8}$$

where $*$ denotes the convolution operation, $V_{ion}(r)$ stands for the bare ionic potential and $v(r)$ specifies the shape of the cavity. This cavity is included in order to make $V'_{ion}(r)$ as weak as possible, and this can be achieved by imposing that the total charge of the cavity be equal to Z_v, the valence of the ions. This will compensate the behaviour of $V_{ion}(r)$ for distances larger than the ionic size, resulting in a weak $V'_{ion}(r)$ for large r. However, for small distances $V_{ion}(r)$ diverges as $-Z_{at}/r$, where Z_{at} is the atomic number of the ions, and therefore, $V'_{ion}(r)$ will not be weak for small r. Moreover, the contribution of the core electrons to $V'_{ion}(r)$ is influenced by the presence of the valence electrons. This

means that $V'_{ion}(r)$ and $n'_v(r)$ must be evaluated self-consistently, and within a theory able to cope with strong potentials. This theory is the density functional theory (DFT) [31]. Specifically, we use the Kohn–Sham formalism [32] and the local density approximation (LDA) [33] for electronic exchange and correlation effects, which are introduced through the parametrization given by Vosko *et al* [34] to the exchange and correlation energy density.

The second contribution to the valence electronic density, namely $n''_v(r)$, corresponds to the electron density that screens, in linear response theory (LRT), the charge distribution given by the cavity $v(r)$

$$\tilde{n}''_v(q) = -(4\pi/q^2)\chi(q)\tilde{v}(q) \tag{9}$$

where the tilde denotes FT, and $\chi(q)$ is the density response function. To be consistent with the assumptions made in the calculation of $n'_v(r)$, the exchange and correlation effects are included in $\chi(q)$ through the LDA local field.

Details on why linear response is to be used at this stage, as well as criteria to determine which is the optimum shape of the cavity, $v(r)$, are discussed elsewhere [22, 30]. Suffice to say that in these calculations we use a spherical cavity of size given by the Wigner–Seitz radius R_{WS}.
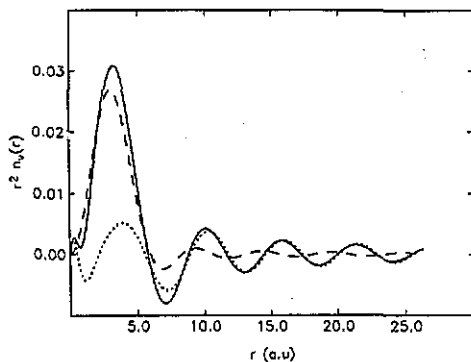

Figure 1. Displaced valence electronic density for lithium at the triple point. The full curve shows the total electronic density, $r^2 n_v(r)$, whereas the other curves show its two components $r^2 n'_v(r)$ (dotted curve) and $r^2 n_v''(r)$ (broken curve).

Figure 1 shows the computed valence electronic density $n_v(r)$ displaced by an lithium ion embedded in an electron gas of mean density n_0 corresponding to liquid lithium at the triple point. In this figure, we have also included the two contributions to $n_v(r)$, that is, $n'_v(r)$ and $n''_v(r)$. Note that $n'_v(r)$ screens a total zero charge whereas $n''_v(r)$ screens a total Z_v charge; this explains the strong difference between them, mainly around the core region. Two aspects of this figure also deserve some comment; first, the natural appearance of the Friedel oscillations for large r, which signal the metallic character of the system, and second, the oscillations for small r, which are due to the orthogonality of the valence electronic wave functions to the core 1s states.

The final goal of these calculations is the construction of a local pseudopotential that, in linear response, reproduces the NPA displaced valence electronic density. However, the very definition of pseudopotential makes impossible the appearance of orthogonality oscillations in the valence electronic density, since no bound states can exist. Therefore,
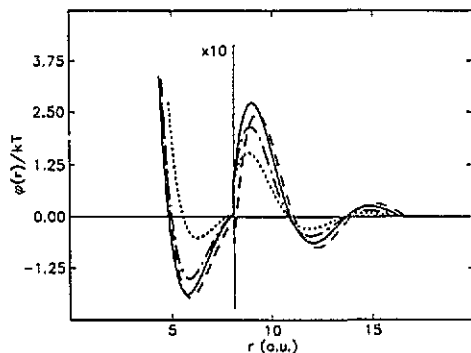
Figure 2. Effective interionic pair potentials obtained for lithium at $T = 470$ K: full curve, NPA + local; broken curve, WT; chain curve, DJ; dotted curve, Ashcroft.

before constructing the local pseudopotential, the NPA valence electronic density has to be pseudized. This is achieved by introducing a pseudized valence electronic density, $n_{ps}(r)$, defined as

$$n_{ps}(r) = \begin{cases} A - Br^2 & r < R_M \\ n_v(r) & r > R_M \end{cases} \tag{10}$$

where A, B and R_M are chosen [35] so that n_{ps} is everywhere continuous and differentiable, and that it integrates to the same charge as $n_v(r)$ (global norm conservation).

Now, from $n_{ps}(r)$, application of LRT leads to an effective local pseudopotential, $\tilde{v}_{ps}(q)$, given by

$$\tilde{n}_{ps}(q) = \chi(q)\tilde{v}_{ps}(q) \tag{11}$$

and application of standard second-order pseudopotential perturbation theory leads to an effective interatomic pair potential, $\phi(r)$, obtained by

$$\phi(r) = Z_v^2/r + \phi_{ind}(r) \tag{12}$$

where the FT of the indirect part is given by

$$\tilde{\phi}_{ind}(q) = \chi(q)[\tilde{v}_{ps}(q)]^2. \tag{13}$$

We finish here this brief description of the NPA method and for further details, we refer the reader to [17, 18, 22, 30]. We only point out that the choice of a local pseudopotential, as given by equation (11), is an *ansatz* made so as to avoid the introduction of any adjustable parameters and, at the same time, to preserve the full information contained in the computed NPA displaced valence electronic density $n_v(r)$. With this procedure, we obtain a local pseudopotential which in LRT gives the non-linear displaced valence electronic density calculated by the NPA method.

4. Effective interionic pair potentials for lithium

In this section we describe the other pseudopotentials considered in this work. The first one to be considered is Ashcroft's empty core pseudopotential [7]. This is undoubtedly the

most popular local pseudopotential and we shall only mention that it contains one adjustable parameter, the core radius r_c.

Consider the behaviour of the ionic potential in lithium ($V_{ion}(r) \rightarrow -3/r$ for small r, $V_{ion}(r) \rightarrow -1/r$ for large r). Ashcroft's expression is correct outside the core, but as Hoshino and Young (HY) [8] have pointed out, the use of a zero value inside for p as well as s electrons does not seem to be a good approximation. Instead, they proposed a different local pseudopotential. As mentioned above, the ionic potential has to be pseudized only when considering s valence electrons and this can be achieved by using the following pseudopotential

$$v_{ps}^{HY}(r) = V_{ion}(r) + \beta\delta(r) \tag{14}$$

where $\delta(r)$ is the Dirac delta function, and β is an adjustable parameter. The delta term only scatters s valence electrons, since these are the only electrons whose wave function can be non-zero at the origin. The ionic potential was calculated using DFT, and then it was parametrized. However, this pseudopotential has some unphysical features concerning its FT. Note that the FT of a delta function is a constant, so when $q \rightarrow \infty$, HY's pseudopotential goes to a constant (β) instead of decaying to zero as it should.

To correct this unphysical feature, Das and Joarder (DJ) [9] proposed replacing β in the expression of the FT of HY's pseudopotential by

$$\beta/(1 + q^2 r_0^2)^2 \tag{15}$$

where r_0 dictates the decay to zero of the FT of the pseudopotential, and is another adjustable parameter. This procedure amounts to a broadening of the Dirac δ-function, without introducing significant non-s scattering.

From these pseudopotentials, application of equations (12) and (13) leads to the corresponding effective interatomic pair potentials for lithium.

Up to now, all the pseudopotentials considered have been local ones although non-local pseudopotentials have also been proposed for lithium [11–15]. We shall only consider here the Heine–Abarenkov-type pseudopotential of Dagens, Rasolt and Taylor (DRT) [11]

$$v_{ps;l}^{DRT}(r) = \begin{cases} A_l & r < R_l \\ -Z_v/r & r > R_l \end{cases} \tag{16}$$

where $A_{l \geqslant 1} = A_{l=1}$ and $R_{l \geqslant 1} = R_{l=1}$; so it has four adjustable parameters (A_0, A_1, R_0 and R_1). These were varied until the valence electronic density displaced by $v_{ps;l}^{DRT}(r)$, within the LRT, reproduced the result of an NPA-type calculation [11, 17]. We can therefore refer to it as an NPA + non-local pseudopotential. Note that DRT's NPA calculation differs from the present one in two important points. First, they did not consider the electronic correlation, and second, they took $V_{ion}(r)$ from the free ion, instead of computing it self-consistently. With the values of the parameters thus fitted, the effective interatomic pair potential is constructed via LRT. For non-local pseudopotentials, however, the displaced valence electronic density and the indirect part of the effective interatomic pair potential are not computed through equations (11) and (13) respectively, but by means of a rather more complex formalism [36]. The main disadvantage of non-local pseudopotentials is, within this context, that the effective interatomic pair potential is not uniquely determined by the displaced valence electronic density, i.e. different non-local pseudopotentials can give rise to the same displaced electronic density but to different interatomic pair potentials.

The present work proposes to use a local pseudopotential that, within the LRT, reproduces the NPA electronic pseudodensity, i.e. an NPA + local pseudopotential. Note that by means of equations (11) and (13), the effective interatomic pair potential is uniquely derived from the displaced valence electronic density. Moreover, the pseudopotential thus constructed has no adjustable parameters.

Finally, to complete the specification of the interatomic pair potentials we note that, within the LRT, the electronic exchange and correlation effects are introduced through a local field correction in the response function $\chi(q)$. A wide variety of expressions are available for the local field term, although for the NPA + local and NPA + non-local approaches, the proper choice is the LDA local field term, so as to be consistent with the approximations made in the computation of the displaced electronic density. For the other pseudopotentials, the Ichimaru–Utsumi (IU) local field term [37] represents the best available expression since it satisfies all the self-consistency requirements.

Recently, Walker and Taylor (WT) [15] have adjusted the indirect part of the DRT potential by using Padé approximants, which yield analytic expressions for the interatomic pair potential in terms of the coefficients and the poles of the approximants. These were computed for 19 different densities and adjusted to a quadratic form in the density. A similar adjustment was also performed for the volume term of the total internal energy. In our study we have used these WT parametrized expressions.

Summing up, the different pseudopotentials studied in this work are the following: Ashcroft's pseudopotential, with one adjustable parameter (r_c); HY, with one adjustable parameter (β); DJ, with two parameters (β, r_0); WT (DRT), with four parameters fitted to an NPA-type calculation; and NPA + local pseudopotential, which is free of parameters.

In the case of pseudopotentials with one parameter, we have fitted it by adjusting the height of the first peak of the static structure factor $S(q)$ whereas when two parameters are available, we have imposed the additional condition that $S(0)$ is also reproduced. The results of the fitting are shown in table 1. In the case of HY's pseudopotential, no value of the parameter could be found so as to obtain an overall agreement with experiment, probably due to the unphysical behaviour of the pseudopotential, and also because of the large depth shown by the first minimum of the corresponding interatomic pair potential.

Table 1. Fitted values in atomic units of the parameters for the different pseudopotentials considered in this work.

Pseudopot.	Ashcroft	HY	DJ
Parameters	$r_c = 1.44$	—	$\beta = 19.0, r_0 = 0.3$

5. Results

5.1. Structure

The present study has been carried out for liquid lithium at three different thermodynamic states specified by the temperatures and number densities given in table 2.

In figure 2 we show, for lithium at $T = 470$ K, the corresponding interatomic pair potentials obtained from these pseudopotentials. It is observed that DJ, WT and the present NPA + local pseudopotentials are rather similar, particularly for the depth and position of the first minimum. In fact, this resemblance is also shared with the recent pair potentials

proposed for lithium by Jank and Hafner [14] and by Chihara [10]. Jank and Hafner use a non-local pseudopotential based on an orthogonalized plane wave expansion of the conduction band states whereas Chihara starts from an effective local pseudopotential obtained using the DFT in the quantal hypernetted chain approximation. In comparison, the simple Ashcroft's pseudopotential leads to a much shallower pair potential.

Table 2. Thermodynamic states studied in this work.

T(K)	470	595	725
ρ (Å^{-3})	0.044 512	0.043	0.042

Now, from those interatomic pair potentials, application of the VMHNC approximation allows one to obtain the corresponding liquid correlation functions. We consider here the static structure factor $S(q)$ of liquid lithium at the above-mentioned thermodynamic states and figures 3–5 show the calculated $S(q)$ corresponding to the different pseudopotentials considered. For $T = 595$ and 725 K, only the results of the Ashcroft and the NPA + local pseudopotentials are shown, because the WT results are practically indistinguishable from the NPA + local ones and the same happens concerning the DJ and Ashcroft pseudopotentials.
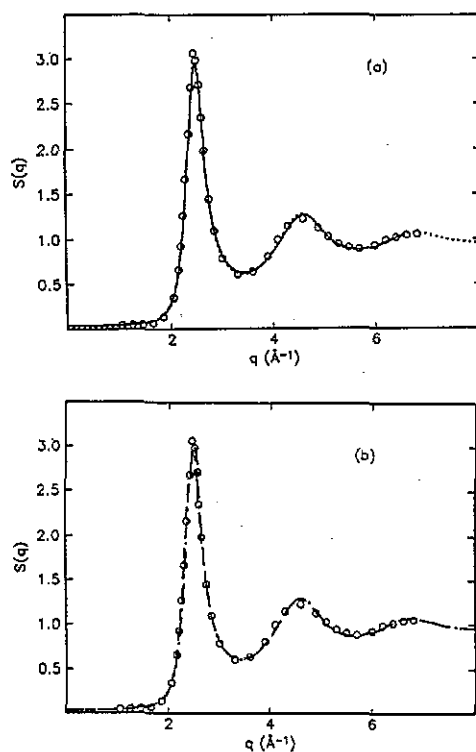

Figure 3. Static structure factor for liquid lithium at $T = 470$ K. (*a*) shows the results from the NPA + local (full curve) and Ashcroft (dotted curve) potentials whereas (*b*) shows the results from the WT (broken curve) and DJ (chain curve) potentials. The open circles are the neutron diffraction data of Olbrich *et al* [3].
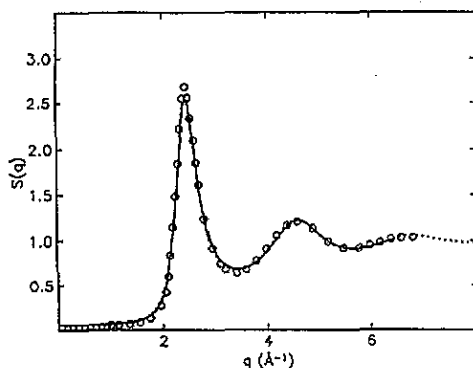
Figure 4. Static structure factor for lithium at $T = 595$ K, as obtained from the NPA + local (full curve) and Ashcroft (dotted curve) potentials. WT results are indistinguishable from the NPA + local ones and the same happens with the DJ results compared with Ashcroft ones (see text).
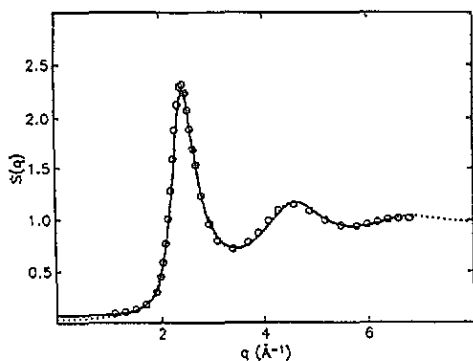

Figure 5. Same as figure 4, but for $T = 725$ K.

It has already been emphasized that the experimental determination of the static structure factor of liquid lithium poses some specific problems. In x-ray diffraction experiments, the analysis of the data is rather problematic because the effects of delocalization of the conduction electrons are rather large, whereas for neutron diffraction experiments the Placzek correction is larger than usual and it is not yet clear whether the commonly used expression for this correction is adequate [38]. Keeping this in mind, we are aware of three different sets of experimental values for the static structure factor of liquid lithium: the neutron measurements of Ruppersberg and coworkers [4], the x-ray results of Waseda [6] and the more recent neutron and x-ray results of Olbrich *et al* [3]. Some important discrepancies can be observed among them: for example, comparison between the neutron results of Olbrich *et al* and the x-ray results of Waseda shows that the main peak in the neutron $S(q)$ is higher by about 10% and at higher values of q a systematic shift in the oscillations appears, with appreciable differences in the range 1.25 Å$^{-1} < q < 2$ Å^{-1} [38].

In figures 3–5 we have also included, for comparison, the experimental neutron diffraction results of Olbrich *et al*. Although we have not included the other experimental data to avoid the figures becoming cramped, the comments below take these data into account.

It is observed that the four different pseudopotentials considered in this work lead to

theoretical values $S(q)$ in rather good agreement with the experimental results. Both NPA-based potentials give a principal peak for $S(q)$ which is slightly lower than that obtained from the neutron data by about 5%, but they are somewhat higher than those obtained from the x-ray data.

The largest difference between the results predicted by the different potentials appears at low q values. In figure 6 we show both the theoretical and experimental small q behaviour of $S(q)$. The experimental value of $S(0)$ is almost exactly reproduced by the WT and DJ potentials. The result for the latter is not surprising for, as stated above, this value was used to fit one of the DJ parameters. We also note that whereas Ashcroft's pseudopotential underestimates $S(0)$, the NPA + local one overestimates it.

There are also large differences between the experimental data. Both the neutron diffraction data and Waseda's x-ray data [6] indicate, at low q, a linear behaviour, whereas the x-ray data of Olbrich *et al* [3] point to a quadratic behaviour. The theoretical $S(q)$ yield, as expected for all cases, a quadratic behaviour at low q. According to Copley and Rowe [39] (see also Matthai and March [40]), a linear behaviour for the experimental $S(q)$ at low q would indicate a deviation from the linear behaviour of the phonon dispersion curve in the liquid. However recent measurements of the dynamic structure of liquid lithium [41, 42] suggest a standard $\omega = cq$ dispersion relation for small values of q.

There seems to be a problem with the analysis of the experimental data, particularly at low q, which needs to be looked into. In the meantime the experimental results for $S(q)$ at low q should be taken with some caution.

5.2. Thermodynamics

We now turn to the thermodynamic properties of liquid lithium at the thermodynamic states given in table 2. The calculations have been carried out for the different pseudopotentials considered in this work.

Standard second-order pseudopotential perturbation theory shows [28] that the total energy of the metal can be written as the sum of a structure dependent term and a volume term (independent of the structure). This latter term includes the the kinetic energy of the ions, the electron gas contribution and the self-interaction energy, that is

$$u = u_{\text{id}} + u_{\text{eg}} + u_{\text{self}} + u_{\text{str}} \tag{17}$$

and a similar partitioning can be performed for the free energy f and the pressure Z, although the density dependence of the potential leads to an explicit contribution to Z_{str} [43]. In the case of non-local pseudopotentials an additional term, due to non-locality, has to be included [15]. This term, which has been computed in this work, is shown in tables 3 and 4 as u_{nl} or Z_{nl}, its contribution to the internal energy and equation of state respectively. Moreover, its contribution to the Helmholtz free energy, say f_{nl}, is such that $f_{nl} = u_{nl}$.

As the self-interaction energy does only depend on the density, then $f_{\text{self}} = u_{\text{self}}$. Therefore the total entropy will be given by

$$s = s_{\text{id}} + s_{\text{eg}} + s_{\text{str}} \tag{18}$$

Although much has been written on the calculation of s_{eg}, the conclusion seems to be [44] that we can do rather well by taking the free electron result $s_{\text{eg}} = (mkT/\hbar^2)(\pi^2 Z_v/9\rho^2)^{1/3}$, where m is the electron mass and $\hbar$ is Planck's constant. In the above relations u denotes the energy per particle in units of kT (U/NkT), f is the Helmholtz free energy per particle in units of kT (F/NkT), s stands for the entropy per particle in units of k (S/Nk), and Z
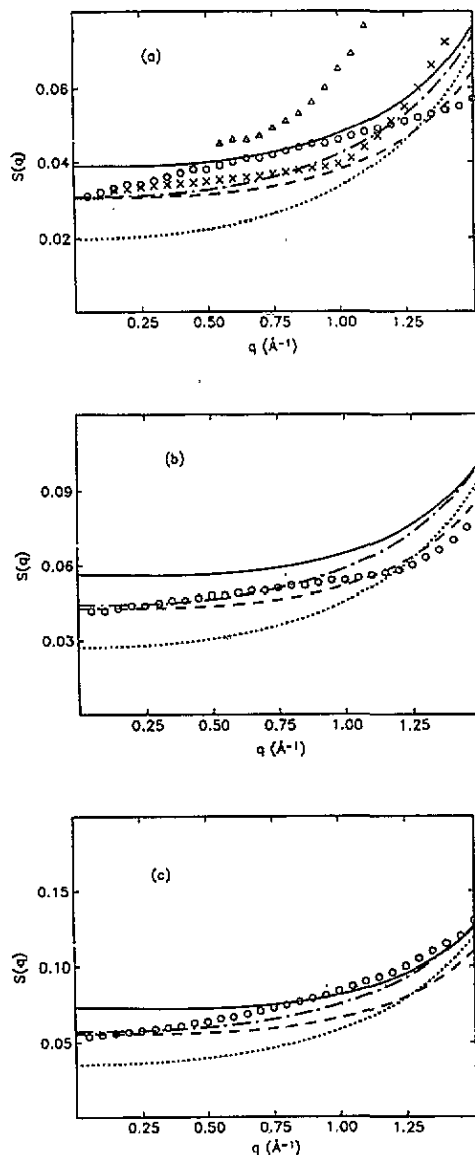
Figure 6. Small angle behaviour of the static structure factors for: (a) $T = 470$ K, (b) $T = 595$ K, (c) $T = 725$ K. The open circles are neutron diffraction data [3],the triangles are x-ray data [3] and the crosses are x-ray data [6]. The meaning of the other curves is the same as in figure 2.

is the compressibility factor $(P/\rho kT)$. In tables 3–5 we show the contributions to the total internal energy and pressure, as obtained from the different pseudopotentials, along with the experimental values [1].

As expected, the most important contribution to the total internal energy comes from the volume term, with the self-interaction term contributing about 66% of the total value, whereas the structural term represents less than 4%. Nevertheless, this latter term reflects rather well the differences among the corresponding interatomic pair potentials, for which the main difference is related to the depth of the first minimum. Ashcroft's pseudopotential

Table 3. Contributions to the internal energy and pressure of liquid lithium at $T = 470$ K, according to the different pseudopotentials discussed in this work.

Pseudopot.	u_{id}	u_{eg}	u_{self}	u_{nl}	u_{str}	u
Ashcroft	1.5	−63.78	−113.76	—	0.35	−175.69
DJ	1.5	−63.78	−129.48	—	−5.57	−197.33
WT	1.5	−63.78	−128.26	9.11	−7.85	−189.27
NPA	1.5	−63.78	−114.92	—	−7.15	−184.35
Experiment [1, 47]	—	—	—	—	—	−176.91

Pseudopot.	Z_{id}	Z_{eg}	Z_{self}	Z_{nl}	Z_{str}	Z
Ashcroft	1.0	−7.89	−6.01	—	14.96	2.07
DJ	1.0	−7.89	−20.55	—	5.78	−21.65
WT	1.0	−7.89	−22.34	13.73	1.78	−13.72
NPA	1.0	−7.89	−7.02	—	16.70	2.80
Experiment [1]	—	—	—	—	—	0.0

Table 4. Same as table 3, but for $T = 595$ K.

Pseudopot.	u_{id}	u_{eg}	u_{self}	u_{nl}	u_{str}	u
Ashcroft	1.5	−50.16	−89.70	—	0.46	−137.91
DJ	1.5	−50.16	−101.73	—	−4.04	−154.44
WT	1.5	−50.16	−100.67	6.79	−5.80	−148.35
NPA	1.5	−50.16	−90.45	—	−5.48	−144.60
Experiment [1, 47]	—	—	—	—	—	−138.75

Pseudopot.	Z_{id}	Z_{eg}	Z_{self}	Z_{nl}	Z_{str}	Z
Ashcroft	1.0	−6.36	−4.50	—	11.32	1.46
DJ	1.0	−6.36	−15.53	—	4.36	−16.52
WT	1.0	−6.36	−16.89	10.28	1.38	−10.59
NPA	1.0	−6.36	−5.43	—	12.09	1.30
Experiment [1]	—	—	—	—	—	0.0

Table 5. Same as table 3, but for $T = 725$ K.

Pseudopot.	u_{id}	u_{eg}	u_{self}	u_{nl}	u_{str}	u
Ashcroft	1.5	−41.05	−73.53	—	0.51	−112.57
DJ	1.5	−41.05	−83.19	—	−3.05	−127.29
WT	1.5	−41.05	−82.35	5.43	−4.44	−120.91
NPA	1.5	−41.05	−74.05	—	−4.38	−117.97
Experiment [1, 47]	—	—	—	—	—	−113.87

Pseudopot.	Z_{id}	Z_{eg}	Z_{self}	Z_{nl}	Z_{str}	Z
Ashcroft	1.0	−5.29	−3.58	—	9.18	1.32
DJ	1.0	−5.29	−12.40	—	3.55	−13.14
WT	1.0	−5.29	−13.54	8.23	1.25	−8.35
NPA	1.0	−5.29	−4.23	—	6.27	−2.25
Experiment [1]	—	—	—	—	—	0.0

leads to the shallower attractive part and then to a positive value of the structural term. On the other hand, WT's potential shows the deepest first minimum and the largest (negative) contribution to the structural term. For the total internal energy, it is found that Ashcroft's pseudopotential gives the most accurate values. The present NPA + local pseudopotential also leads to rather good results, the discrepancies being around 4%.

Finnis [45] has argued that, although the volume term is the most important one for the energy, *its derivative with respect to density need not be so when it comes to computing the pressure*. In fact, this is the case for the Ashcroft and NPA + local pseudopotentials, where the structural and volume terms are comparable but with opposite signs, leading to values of the compressibility factor around zero. Moreover, both contributions of the volume term to the compressibility factor are very similar. However, this does not hold for the DJ and WT pseudopotentials, for which the self-interation term is much greater (in absolute value) than the electron gas and structural parts, leading to rather large and negative values of Z.

Finally, table 6 shows the theoretical values obtained for the excess entropy of liquid lithium at several temperatures. All the pseudopotentials considered here show a very good agreement with experiment, with the NPA + local pseudopotential giving the most accurate results. This is a very interesting feature of this pseudopotential because as already pointed out by some authors [18], the excess entropy is a very important magnitude for testing the overall quality of a given interatomic interaction.

Table 6. Excess entropy of liquid lithium in units of Nk for the states considered in this work, according to the different pseudopotentials.

	$T = 470$ K	$T = 595$ K	$T = 725$ K
Ashcroft	−3.53	−3.01	−2.62
DJ	−3.51	−2.97	−2.57
WT	−3.53	−3.03	−2.63
NPA	−3.37	−2.88	−2.50
Experiment [1]	−3.37	−2.90	−2.52

6. Conclusions

We have tested, using a highly reliable liquid state theory, a set of different pseudopotentials for liquid lithium. From this study we have found that HY's pseudopotential has to be discarded as a candidate to describe the properties of liquid lithium since it does not give good results even for the static structure. Its modification, proposed by DJ, leads to very good results for the structure, but shows some problems when it comes to the thermodynamic properties. Ashcroft's pseudopotential, despite having little appeal from a physical point of view, gives rather good results both for the static structure and thermodynamic properties considered in this work.

Concerning the NPA-derived pseudopotentials, it has been found that if the WT non-local pseudopotential is used, the results for the static structure are in excellent agreement with experiment, but problems arise when considering the pressure. On the other hand, if the NPA + local potential is used, rather good results are obtained both for the structure and thermodynamics, while resorting, moreover, to no adjustable parameters.

We therefore conclude that the *ab initio* NPA + local potential proposed in this work is a very promising starting point for the study of liquid lithium. This conclusion is supported by the present theoretical results as well as by recent molecular dynamics results for some dynamic properties, carried out using this potential [46].

Nevertheless, the thermodynamic properties, and even more, the static structure are not too stringent a test for a given interionic pair potential. We note that whereas Ashcroft's potential and the NPA + local one are very different, they yield similar results for the static

structure and thermodynamic properties. It is possible that these differences will show up in the calculations of the dynamic structure and ionic transport properties. We intend to carry out these calculations in the near future and shall report the results on completion.

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