The ionic structure of liquid sodium obtained by numerical simulation from “first principles” and \textit{ab initio} “norm-conserving” pseudopotentials

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\textbf{Abstract.} The physical properties of disordered matter depend on the "atomic structure" i.e. the arrangement of the atoms. This arrangement is described by the structure factor \( S(q) \) in reciprocal space and by the pair correlation function \( g(r) \) in real space. The structure factor is obtained experimentally while the numerical simulation enables us to obtain the pair correlation function. Liquid sodium is one of the elements the most studied and one can wonder about new scientific contribution appropriateness. The majority of theoretical calculations are compared with the experiment of Waseda. However two other posterior measurements have been published and give different results, in particular with regard to the height of the first peak of the structure factor. Three models of pseudopotential are considered to describe the electron-ion interaction. The first is a local pseudopotential with the alternative known as "individual" of the model suggested by Fiolhais \textit{et al.}. The second model considered is that of Bachelet \textit{et al.}. This one, ab-initio and "norm conserving", is non local. The last model is that proposed by Shaw known as "first principles" and "energy dependent". Various static dielectric functions characteristic of the effects of exchange and correlation have been used and developed by Hellal \textit{et al.}. We calculated the form factors (pseudopotential in reciprocal space) and deduce the normalized energy-wave-number characteristic \( F_N(q) \), the interatomic pair potential \( V_{\text{eff}}(r) \), then the pair correlation function \( g(r) \) by molecular dynamics. The structure factor \( S(q) \) is obtained by Fourier transform and is compared with the experiment. Our calculations with the Bachelet and Shaw pseudopotentials are close to the last experiments of Greenfield \textit{et al.} and of Huijben \textit{et al.}. Our results are discussed.

1. \textbf{Introduction}

Without any doubt, sodium is, from a theoretical point of view, one of the most studied metals. It is the prototype metal for which the pseudopotential method applies to wonder. One can quote some examples: calculations by pseudopotentials of OPW Harrison type \cite{1}, by empirical models (Ashcroft), \cite{2} by “first principles” models (Shaw) \cite{3}. These former works, when they relate to ionic structure of the molten metal, are generally compared with only one experiment. Several experiments of the ionic structure factor obtained either by techniques of X-ray scattering or by neutron diffraction, present notable differences as will be shown. In this work, we used the “first principles” model potential of Shaw \cite{3}. This model is energy dependent. The energy is usually determined by using a method due to Animalu and Heine \cite{4}. We used an alternative selfconsistent method to determine the Fermi energy. The same calculations are also carried out with the more recent pseudopotential proposed by Fiolhais \textit{et al.} \cite{5}. Finally, we present, firstly at our knowledge, the ionic structure of liquid sodium calculated with the \textit{ab initio} model pseudopotential of Bachelet, Hamann and Schlüter.
Our work proves that the structure calculated with Shaw model, is in good agreement with the experimental results of Huijben et al. [7]. The calculations with the pseudopotential of Fiolhais et al. lead to a fairly well agreement with Waseda experiment [8]. On the other hand, BHS-based calculations describe worse the height of the first peak of the static structure factor. More satisfactory are the oscillations that are in phase with the experimental structure factor. Later one, unless otherwise stated, we use atomic units through: $\hbar = m = e = 1$.

2. Theoretical Background

2.1. Pseudopotential construction

The model-pseudopotentials that we used in present calculations have respectively the following expressions:

i) The “first principles” optimized model-pseudopotential (OMP) of Shaw [3] is non-local and energy-dependent, it is derived from atomic calculation and has the following expression

$$w_0(r) = -\frac{Z_v}{r} - \sum_{\ell=0}^{l_{\text{max}}} \Theta(R_{\ell} - r) \left( A_\ell - \frac{Z_v}{r} \right) P_\ell$$

where $P_\ell$ is the projecting operator on the sub-space with angular momentum $\ell$, and can be written

$$P_\ell = \sum_{m=-\ell}^{m=\ell} |\ell,m\rangle \langle \ell,m|$$

$Z_v$ is the chemical valence, $R_{\ell}$ and $A_\ell$ are two sets of parameters that verify the optimization condition $A_\ell(E) = \frac{Z_v}{R_{\ell}(E)}$.

However, the parameters of the model in the metal must be evaluated at energy $E - \Delta$. We have two methods to calculate the core shift $\Delta$. The first one is due to Animalu and Heine [4] and has been precised by Ballentine and Gupta [9]. This method requires the knowledge of experimental values of ionisation and of cohesion energies [10]. We will notice that the core shift can also be self-consistently determined following Hallers et al. [11] prescriptions. Hereafter, to distinguish these two types of procedures, the model-pseudopotential with the first procedure is denoted OMP-I and the second one with the core shift self-consistently calculated, is quoted OMP-II.

ii) The ab initio pseudopotential of Bachelet, Hamann and Schlüter [6] is norm-conserving and has the property, in principle, to be “transferable” from the atomic reference to others physical or chemical environments. This energy-independent model-pseudopotential is also generated from atomic calculations but, unlike OMP model, without spectral energies. Its well-known expression, for lighter elements as sodium for which one can neglects the spin-orbit effect is given by:

$$\hat{V}_{\ell}^{\text{ion}}(r) = \sum_{\ell} \hat{V}_{\ell}^{\text{ion}}(r) P_\ell$$

The component $\hat{V}_{\ell}^{\text{ion}}(r)$ of the pseudopotential is decomposed into a long-range Coulomb part (or $\ell$-independent core part) $\hat{V}_{\text{core}}(r)$ and a short-range ($\ell$-dependant) pseudopotential part $\Delta \hat{V}_{\ell}^{\text{ion}}(r)$. So that,

$$\hat{V}_{\ell}^{\text{ion}}(r) = \hat{V}_{\text{core}}(r) + \Delta \hat{V}_{\ell}^{\text{ion}}(r)$$

iii) The local and energy-independent model-pseudopotential proposed by Fiolhais et al. [5] is built from DFT calculations for the solid state. It reads:
\[ w_0(r) = \frac{Z}{R_M} \left\{ \frac{1}{x} \left[ 1 - \left(1 + \beta x \right) e^{-\alpha x} \right] - A e^{-x} \right\} \]

where \( x = r/R_M \) and \( R_M \) being the core decay length. The parameters \( \beta \) and \( A \) are given in terms of \( \alpha \) namely,
\[
\beta = \frac{\alpha^3 - 2\alpha}{4(\alpha^2 - 1)} \quad \text{and} \quad A = \frac{\alpha^2}{2} - \alpha \beta
\]
The values of \( \alpha \) and \( R_M \) are fitted by Fiolhais et al. [5] in order to reproduce the dominant electronic density features in the solid state.

2.2 The effective interatomic potential
The effective interatomic pair potential in simple metals has the well-known following expression:
\[
V_{\text{eff}}(r) = \frac{Z^2}{r} \left[ \frac{1}{\pi} \int_0^\infty F_N(q) \frac{\sin(qr)}{q} \right] dq
\]
The normalized energy-wave number characteristic \( F_N(q) \) that has more complicated expression for non-local model-pseudopotential, takes the following form, in the local one:
\[
F_N(q) = \left( \frac{\Omega_o q^2}{4\pi Z_v} \right) \left[ \frac{w_0^*(q)}{1 - G_{xc}(q)} \right] \frac{\varepsilon(q) - 1}{\varepsilon(q)}
\]
where \( w_0(q) \) is the form factor of the bare model-pseudopotential. The local-field correction function \( G_{xc}(q) \) is related to the “electron-test-charge dielectric function” \( \varepsilon(q) \) through the relationship:
\[
\varepsilon(q) = 1 + \left[ 1 - G_{xc}(q) \right] \left[ \varepsilon - \varepsilon_H(q) \right]
\]
On the other hand, the Hartree’s dielectric function \( \varepsilon_H(q) \) has a well-known expression that one can find elsewhere in the literature. In the present work, we only consider forms of the local-field correction that have a theoretical background as those given by Vashista and Singwi [12] (VS), by Ichimaru and Utsumi [13] (IU), and by Singwi et al. [14] (SSTL). We used also two expressions that are recently published [15] and are denoted here LFC-I and LFC-II. These last are also physically founded.

2.3 Molecular Dynamics
To examine the ionic structure of liquid sodium at the temperature \( T = 378 \) K, we used the standard Verlet algorithm [16] to carry out a molecular dynamics (MD) simulation on a (NVT)-ensemble with 8788 atoms initially arranged in a centered-cubic structure with periodic boundary conditions. The size of the cubic super cell \( (L = 71.62 \, \text{Å}) \) corresponds to the experimental number density \( (n = 0.02391 \, \text{atoms} / \text{Å}^3) \) at the temperature \( T = 378 \) K. The cut-off radius of the pair potential is close to \( L/2 \). In order to avoid any memory effect, one carried out an annealing simulation at the temperatures \( T = 5273 \, \text{K}, 2273 \, \text{K}, 1273 \, \text{K}, 673 \, \text{K}, 473 \, \text{K}, 378 \, \text{K} \). To obtain an accurate respectively MD calculation, the equations of motion are integrated with a MD time step equal to \( \delta t \approx 0.7, 0.6, 1.1 \, \text{fs} \) for Shaw,
Bachelet and Fiolhais pseudopotentials respectively. The number of iterations is 36000 corresponding to a MD relaxation time closed to \( \tau = N_{\text{step}} \times \delta t \approx 25, 25, 40 \) ps for Shaw, Bachelet and Fiolhais pseudopotentials. We thus obtain a reliable pair correlation function \( g(r) \) on a range up to \( R_{\text{max}} = 35.8 \) Å and thanks to like Fourier transform, we obtained the structure factor \( S(q) \).

3. Results and Discussion

Our calculations are carried out by using two versions of the “first principles” energy-dependent model-pseudopotentials of Shaw (OMP-I and OMP-II) and by using the \textit{ab initio} “norm-conserving” model-pseudopotential of Bachelet et al. (BHS) and by using the model-pseudopotential of Fiolhais et al., to build accurate interatomic pair-potentials that we used in our molecular dynamics simulations. These interatomic potentials are drawn in figure 1 when we compare calculations obtained by respectively the four models potentials screened with VS dielectric function. In figure 2, we compare the effective potential obtained by using OMP-II model screened with the five dielectric functions quoted above. One can notice that the calculations with non-local pseudopotentials lead to interatomic potential with deeper minimum comparatively with those obtained with the local model potential of Fiolahis et al. For all models, the magnitude of the Friedel oscillations is quickly damped.

In figure 1, the most important core diameter is obtained from the Fiolhais pseudopotential. The depth of this effective potential is two times less important than those of the other effective potentials. Curiously, the depths of the effective potentials obtained by the BHS and OMP-II pseudopotentials are very close. In figure 2, the choice of the exchange correlation function influences weakly the shape of the effective potential calculated with OMP II.

In figure 3, we displayed the pair correlation functions calculated by DM for liquid sodium. These pair correlations functions are calculated from the different effective potentials presented in figure 1. The main peak, obtained from the BHS potential, is \( \approx 6\% \) higher than the others. Furthermore, the oscillations amplitudes are less damped. All others calculated pair correlation functions present nearly the same oscillations. In figure 4 are shown the structure factors corresponding to the calculated pair correlation functions (figure 3) together with the Huijben et al. experimental structure factor. One time again, the structure factor calculated from BHS pseudopotential is different from the others. Precisely, the main peak is \( \approx 12\% \) higher than the experimental one. The other calculated structure factors are in
agreement with the experimental one (Huijben et al. [7]), as well for the height as for the oscillations behaviour.

**Figure 3.** Pair-correlation functions for liquid sodium at 378 K calculated by MD from different model-pseudopotentials with Vashista-Singwi.

**Figure 4.** Static structure factors for liquid sodium at 378 K computed by MD and different model-pseudopotentials: OMP-I (continuous line), OMP-II (dashed line), BHS (dashed-dotted line) and Fiolhais (short-dashed line). The experimental values of Huijben et al. are also shown for the comparison.

In figures 5 and 6, we respectively show the pair correlations functions $g(r)$ and the corresponding structures factors $S(q)$ calculated with the pseudopotential OMP-II and various dielectric functions presented in the text. It is checked here that the influence of the screening on the ionic structure is tiny in the case of the chemical elements with small valence like liquid sodium.

In the figure 7 one compares some experimental structure factors measured for liquid sodium. One can note the disparity of the results concerning the height of the first peak of the structure factor as for theoretical calculations.
4. Conclusions
In this work, we performed, by means of molecular dynamics simulation, the calculation of the ionic structure of liquid sodium at $T=378$ K with pseudopotential-derived pair potential to describe interactions between ions. We have compared three models screened by a dielectric function among five studied. The first point to note is that the choice of the dielectric function has only little effect on the structure factor of liquid sodium contrarily to other elements having higher valence. The second
remark is that the BHS model pseudopotential gives rather good results for the ionic structure of sodium. However, these results are clearly better when we used the Shaw energy-dependent model-pseudopotentials. For the latter, the precise knowledge of the "core shift" is crucial. Its determination in a self-coherent way is not without interest. Indeed, this method can be applied for alloys for which Ballentine-Gupta the method does not.

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