



## Molecular dynamics simulation of fluid sodium



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### ARTICLE INFO

#### Article history:

Received 14 March 2016  
 Received in revised form  
 6 July 2016  
 Accepted 6 July 2016  
 Available online 9 July 2016

#### Keywords:

Liquid metals  
 Molecular dynamics simulation  
 Potential energy function  
 Sodium

### ABSTRACT

Liquid metals are known to interact via many-body (density-dependent) potential energy functions. While the form of such potentials is complicated, they consist of a large number of adjustable parameters, making their implementation in molecular simulation packages difficult. In this work we developed two methods to predict the microscopic structure and dynamics in liquid sodium. One of the methods involves calculation of the potential of mean force, in an iterative cycle, in such a way to be able to reproduce the experimental radial distribution function of liquid sodium at 378 K (close to the freezing point). This potential of mean force is shown to be able to well reproduce the structure and dynamics in liquid sodium in the vicinity (up to a temperature  $\approx 600$  K) of the initial state point at which it is derived. However at higher temperatures it fails to reproduce the experimental densities and diffusion coefficients accurately. The other method consists of employing a simplified two-parameter potential energy function, namely the Lennard-Jones potential in which the exponents are adjusted, for simulation of fluid sodium along the liquid-vapor coexistence curve. It is shown that this potential energy is able to predict the densities of liquid and vapor sodium over a wide range of temperatures, ranging from 378 K to 2300 K, in close agreement with experiment. In this case, the calculated diffusion coefficients of liquid sodium are: underestimated at low temperatures, in good agreement with experiment at moderate temperatures, and overestimated at very high temperatures.

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### 1. Introduction

Liquid metals are of fundamental applications from both technological and scientific points of view. Technologically they are used in industrially important high-temperature operations [1]. They are also used in the fabrication of recently developing nano-scale materials such as metal-coated carbon nanotube composites [2] and nanowires [3], having extraordinary mechanical and thermal properties. Among metals, alkali metals are good candidates for research. This is due to their interesting characteristics, such as low melting point, low vapor pressure, high critical temperature, and high thermal conductivity, as well as their fundamental importance as “simple metals”, having a single electron in their valance shell. However, despite their simple chemical structure, liquid metals are not easily tractable from either experimental or theoretical points of view. Because of their high reactivity and handling with high temperatures, experimental measurements on liquid alkali metals are difficult. On the other hand, in most

theoretical treatments of the liquid state one is limited to a proper description of the interatomic forces.

During the past decades pairwise additive potentials (pair potentials) have extensively been used in the molecular simulation studies of liquid metals. Such models are shown to result in a good agreement in the predicted structural properties of liquid alkali metals with experiment over a limited temperature/pressure range. At this point it is worth considering that the pair potentials, almost used in all molecular simulation studies, include the multi-body effects (in an average way) at the state points they are parameterized. This is due to the fact that the parameters of such pair potentials are tuned against bulk properties. Therefore, the term pair potential used in this work must be distinguished from pure two-body potentials that are for instance derived from *ab initio* simulations, and only describe the interaction between two particles.

Although fluid alkali metals are simple monatomic systems, it is known that they do not obey pair potentials with a harsh repulsive branch and a short-range attractive branch, such as the Lennard-Jones (12-6) potential [4–7]. In this respect, Monte Carlo and molecular dynamics simulations on liquid alkali metals are done using the so-called embedded atom model (EAM) potentials [8–12]. The EAM potential is a many-body interatomic potential, consisting a

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### Nomenclature

$c_4$ and $c_5$	constants in Eq. (3)
$D$	diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$g$	radial distribution function
$k_B$	Boltzmann constant ( $\text{J K}^{-1}$ )
$P$	pressure (kPa)
$r$	interparticle distance
$T$	temperature (K)
$U$	potential energy ( $\text{kJ mol}^{-1}$ )
$V$	volume ( $\text{m}^3$ )

### Greek symbols

$\rho$	density ( $\text{kg m}^{-3}$ )
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pair function and a many-body embedding interaction function. The embedding potential of an atom depends on the electron density in the region where the center of atom locates. This effective electron density, created at a position of an atom, depends nonlinearly on the contributions from neighboring atoms. Therefore, three adjustable functions (the embedding function, an effective electron density function, and a pair interaction function), consisting a number of fitting parameters must be known to be able to use EAM potentials for molecular simulation purposes. The number of fitting parameters, reported in the literature, ranges between 5 and 20 [8–12].

It is worth mentioning that pair potentials have also been employed to describe fluid alkali metals, but their applicability is restricted to a limited temperature range. In fact liquid alkali metals are better described as arrangements of positively charged ions embedded into a negatively charged electronic background. Therefore, the interatomic potential is represented by a Coulombic term, screened by the negative charge distribution of the conduction electrons. This indicates that the term ‘simple liquid’ is an oversimplification of the interatomic potential in liquid alkali metals. Moreover, to take into account the effect of electron gas on the ionic core, the interatomic potential should be density dependent. In the framework of the so-called pseudo-potential approach, such as the Price potential, an empty core interaction, for the bare ions, screened by the surrounding electron density is introduced in the interatomic potential [13]. Such a potential, consisting a density-dependent variable, is however, applicable over a limited density (temperature) range. At high temperatures, the screening of the ionic Coulomb potentials breaks down and the electrons start to localize. This means that such a potential cannot be employed to describe the properties of liquid alkali metals over a wide temperature range, varying from melting point to the critical point.

However, it has been shown recently that a simple Lennard-Jones (LJ) potential, with a soft repulsive branch (compared to the LJ (12-6)) and with temperature-dependent parameters is able to reproduce the structural properties of liquid potassium from the triple point to the critical point [14]. Owing to the complexity of the EAM potentials, in this work we have examined the possibility of proposing simplified potential models for liquid sodium, as a typical example, and examine the range of temperatures/pressures, over which such potentials can be employed to predict structure and dynamics in fluid sodium.

## 2. Theory

As stated in the preceding section, molecular simulations have

been performed on liquid alkali metals using the EAM potentials. Although the EAM potentials are implemented in a number of molecular simulation codes such as LAMMPS [15], due to the complexity of their functional form, implementation of such potentials is not so easy. In this work two methods were employed to calculate the structural and dynamical properties of fluid sodium via molecular dynamics simulation.

The first method involves construction of the potential energy, using the experimental structure factors (or radial distribution functions). Here a simple Boltzmann inversion of the experimental radial distribution function provides one with an initial guess for the potential energy function [14,16], i.e.,

$$U(r) = -k_B T \ln(g_{\text{exp}}(r)) \quad (1)$$

where  $r$  is the interparticle distance,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $U$  is the potential energy, and  $g_{\text{exp}}(r)$  is the experimental radial distribution function. A molecular dynamics simulation is done using this initial guess to the potential energy and the radial distribution function,  $g(r)$ , is extracted from the results of this simulation. This radial distribution function is compared with the experimental radial distribution function, to generate the next approximation to the potential energy, in an iterative cycle (the so-called iterative Boltzmann inversion method) as [16,17]:

$$U_{i+1}(r) = U_i(r) - k_B T \ln\left(\frac{g(r)}{g_{\text{exp}}(r)}\right) \quad (2)$$

where  $U_i$  and  $U_{i+1}$  are the potential energies at  $i^{\text{th}}$  and  $(i+1)^{\text{th}}$  iterations. A molecular dynamics simulation is done using the generated potential energy in the  $i^{\text{th}}$  cycle and the radial distribution function is calculated from the results. Equation (2) is then used to generate the next guess to the potential energy. This iterative cycle continues until a close match in the calculated and experimental radial distribution functions is achieved. The potential energy calculated in this way is called the ‘‘potential of mean force’’ and is state dependent, i.e., it includes the many-body effects in the system [16,17]. Therefore the potential of mean force is accurate at the temperature and pressure at which it is derived.

In the second method, we assume that a simple LJ-type pair potential is able to predict the structural properties of liquid sodium. Previous reports in the literature show that liquid alkali metals interact through a potential energy function with a much softer potential than the LJ (12-6) potential [13,14]. Based on a comparison of the calculated densities of liquid sodium with experimental values, we observed that a LJ potential of the following form, well predicts the structural properties of liquid sodium:

$$U = \frac{c_5}{r^5} - \frac{c_4}{r^4} \quad (3)$$

where  $c_5$  and  $c_4$  are two coefficients. We emphasize that the LJ potentials with varieties of exponents (such as LJ (12-6)) may also be applicable to predict the pressure-volume-temperature surface of fluid sodium, but their applicability is limited to a very narrow window of temperatures. Reducing the harness of repulsions and increasing the range of attractions, increases the applicability of potential to a much wider range of temperatures. One may also obtain a better tuning of the pair potential  $U$  by introducing the temperature in  $U$  via its coefficients. This is done in Ref. [14] for fluid potassium. However, in this work we decided not to propose a complicated pair potential, rather to check the applicability of a simplified  $U$ .

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