Comparative evaluation of the properties of liquid metals at high temperatures and pressures by the methods of classical and first-principle molecular dynamics

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Introduction

❖ A priority area of computer simulation pertains to the prediction of properties exhibited by metals under extreme conditions, when it is difficult or impossible to carry out experimental studies, e.g., at high temperatures and pressures and/or under shock compression.

❖ Shock compression data was usually processed using approximate methods. It is only recently that the method of classical molecular dynamics (MD) has become popular for the description of highly compressed states. However, this method is implemented not in its traditional form employing approximation of pair potentials [1], but using the embedded atom model (EAM) [2–5], which allows multi-particle interatomic potentials of metals to be calculated.

❖ *Ab-initio* quantum-mechanical MD constitutes another method potentially feasible for determining properties under shock compression [6]. It allows metals properties to be calculated without using any model representations. The method in question solves the issue associated with the self-consistent of electronic and atomic structures, however, this method requires much power and computer time.

1. Computer simulation technique

1.1. Classical Molecular Dynamics

The EAM-MD simulation, which considers collective interaction, has proven to be more effective and accurate. In the embedded atom model, the potential energy of a metal is expressed as

$$U_{pot} = \sum_i \Phi(\rho_i) + \sum_{i<j} \phi(r_{ij})$$

where $\Phi(\rho_i)$ is the embedding potential of the i-th atom, which depends on the effective electronic density ρ_i at the atomic centre, whereas the second sum over atomic pairs contains the ***usual*** pair potential. Created by the surrounding atoms, the effective electronic density at the atomic position is calculated using the following formula

$$\rho_i = \sum_j \psi(r_{ij})$$

where $\psi(r_{ij})$ is the contribution to the electronic density from the neighbouring j. These terms should not be taken literally. In fact, this is just a computational scheme using functions that do not necessarily fit their names.

1.2. First Principle Molecular Dynamics

❖ There are several software packages that implement the FPMD method. In this work, we studied the properties of several liquid metals through the SIESTA program [7]. The advantages of this program include its free availability, presence of a block for modelling systems at final temperatures, as well as its capability to perform sufficiently accurate calculations and simulate systems with a relatively large number of particles (up to 1000).

❖   Using the SIESTA code, we built FP MD models for 4 liquid metals having the following characteristics: NVT-ensemble; Nose thermostat; DZP basis set; 452 atoms in a supercell; periodic boundary conditions; time step of 1 fs; maximum number of steps set at 1000; pseudopotentials taken from the SIESTA database.

Results and discussion

❖ In order to assess the actual consistency of these two methods, data obtained for the same states of a metal should be compared. As for the MD method, the parameters of an EAM potential for a given metal are selected in such a way so that the pressures of models in the states on the shock adiabatic are close to the actual ones. Therefore, the error involved in calculating the pressure for an EAM potential should be close to that associated with the shock compression experiment.

❖ The error involved in calculating pressure via the **first-principle** method depends on the choice of a calculation algorithm. This work was aimed at evaluating this error in the case of the SIESTA package.

❖   The calculations were performed under typical shock-compression conditions for four different types of metals: alkali metal Na (T = 4000 K), anomalous metal Bi (T = 10000 K), as well as transition metals Fe (T = 6000 K) and Ni (T = 4450 K).

❖ We calculated the total energy, pressure, self-diffusion coefficients and pair correlation functions (RDF) using both MD methods. In addition, the density of electronic states was determined using the FP MD method.
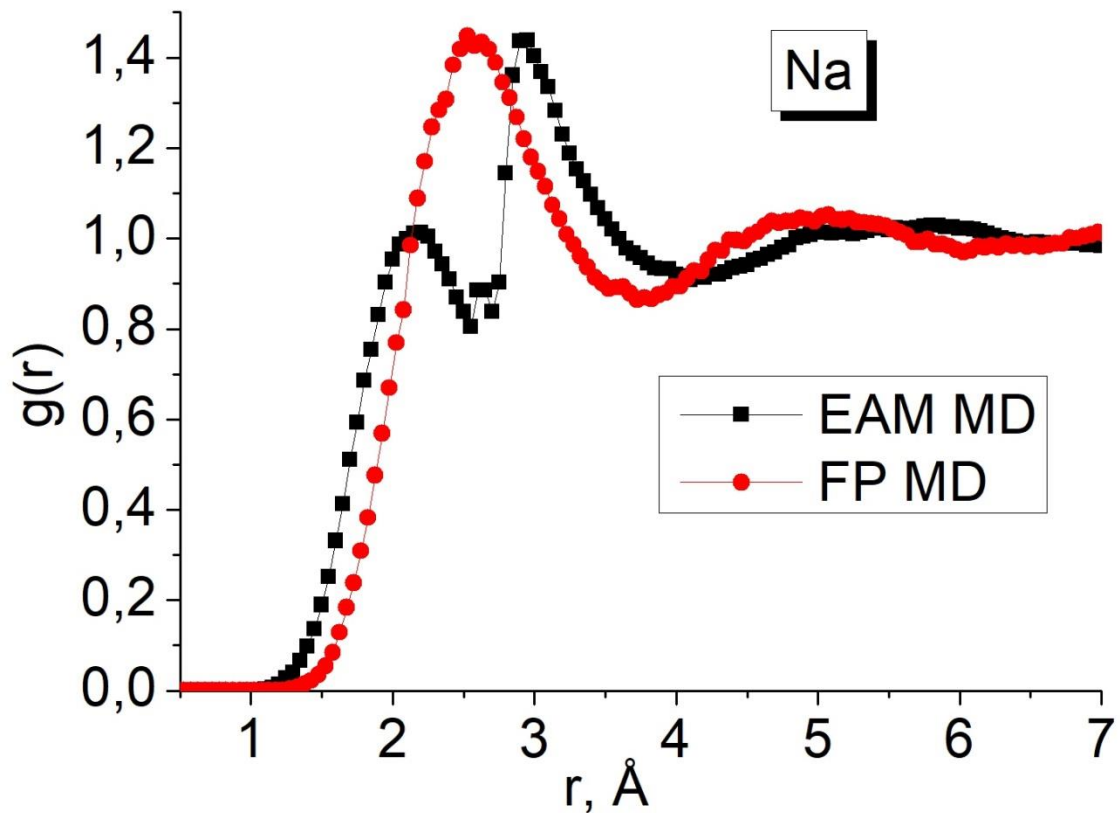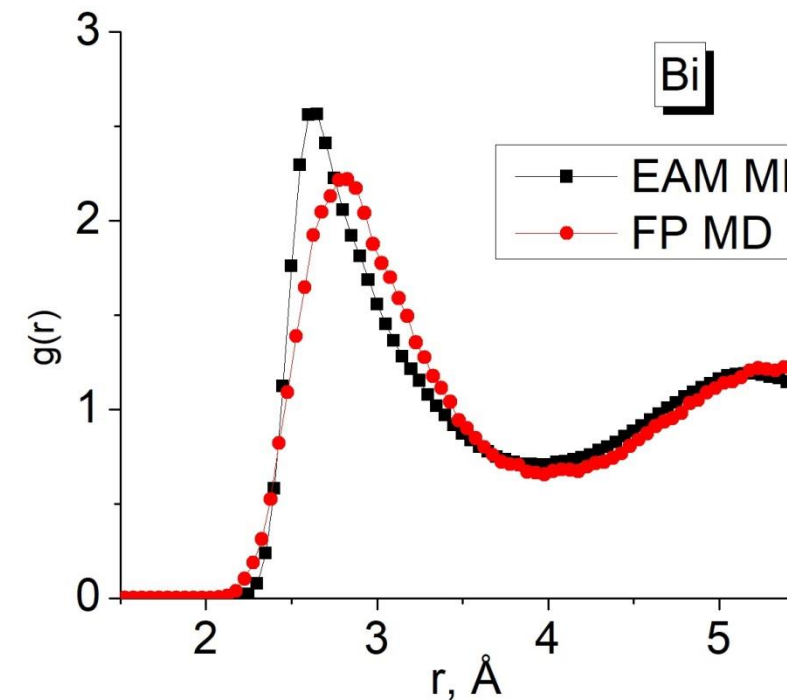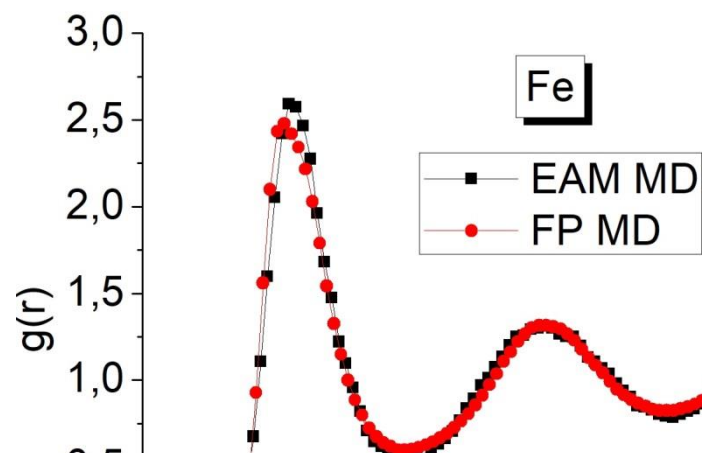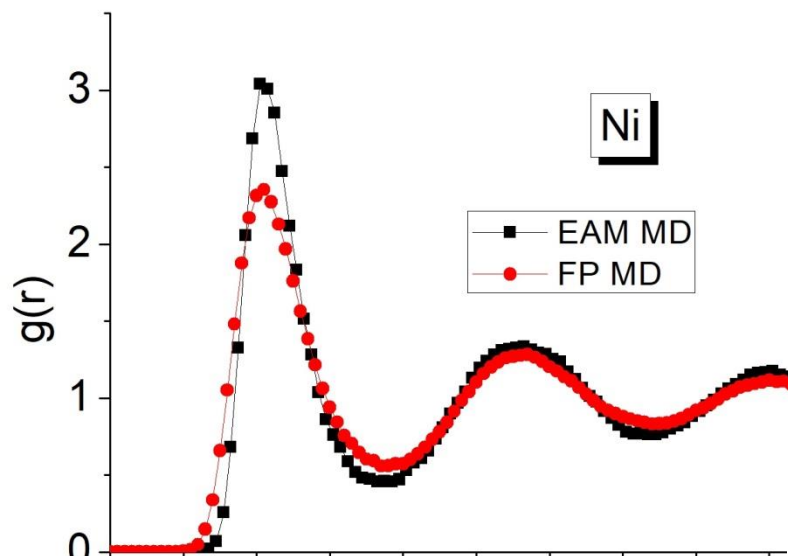
Parameters for computer simulation:
d - density; Z - compression ratio; T - temperature

Metal	T_m, K	d_m, g/sm^3	T, K	d, g/sm^3	Z=V/V$_m$
Na	371	0.93	4000	2.69	**0.34**
Bi	544	10.05	10000	17.88	0.56
Fe	1808	7.05	6000	12.96	0.54
Ni	1726	7.79	4450	13.65	0.57

Comparison of the results obtained by the methods of classical (EAM MD) and first-principle (FP MD) molecular dynamics
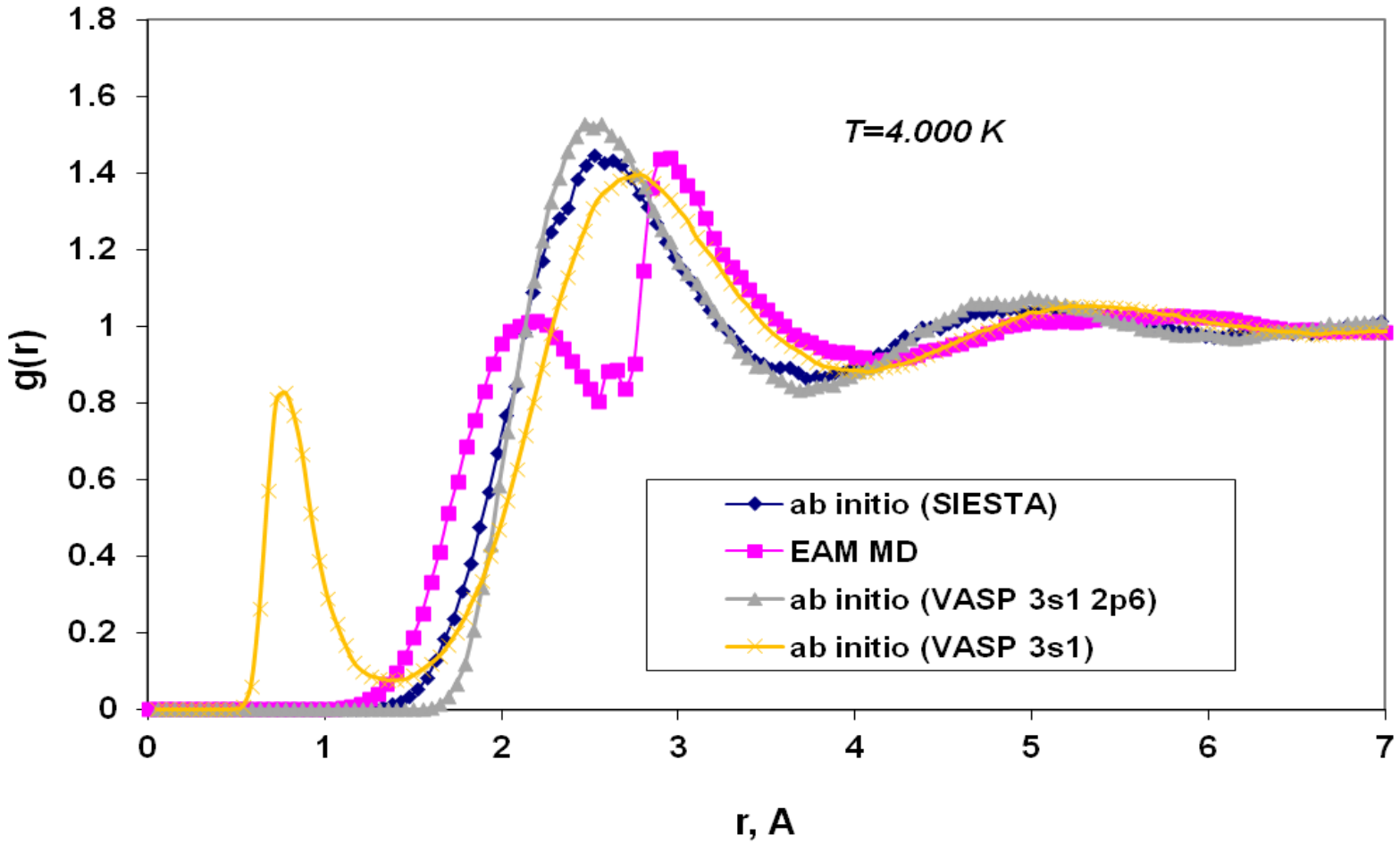
Metal	N		Steps		P, GPa		$D \cdot 10^5$, sm²/sec	
	EAM MD	FP MD	EAM MD	FP MD	EAM MD	FP MD	EAM MD	FP MD
Na	2000	432	5000	1600	70.0	44	81.5	62.4
Bi	2000	432	5000	324	100.7	146	12.8	13.5
Fe	2000	432	5000	249	300.0	340	6.3	6.2
Ni	2048	473	5000	213	281.0	333	6.0	4.3

Radial Distribution Functions

Radial distribution function of liquid Na

$T = 4.000\ K$

ab initio (SIESTA)
EAM MD
ab initio (VASP 3s1 2p6)
ab initio (VASP 3s1)

Conclusion

Comparison of computer simulation methods of EAM MD and FP MD showed mixed results for different types of metals.

❖ The calculations of the properties of transition metals (Fe, Ni) of pressure, diffusion, and short-range atomic structure (RDF) turned out to be very close, differences of 5-7% for diffusion and RDF, slightly larger for pressure.

❖ Significant differences in the results of the two methods for Bi and Na. For Bi, an inverse tendency is observed for diffusion, while for Na, the opposite tendency for pressure and pressure are almost 2 times different.

❖ The most significant differences are observed for short-range order structure (RDF). Bi has an asymmetry of the first peak. According to EAM MD, the right branch is more gentle. For Na, this method gives qualitatively different results - bifurcation of the first peak.

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