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On the question of the applicability of the principle of thermodynamic similarity in liquid alkali metals

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Abstract. In this paper, we have created an interparticle interaction potential for liquid alkali metals using ab-initio simulations and machine learning. The resulting family of potentials was tested by molecular dynamics simulation, in which the liquid metals were heated to the melting point and the resulting system was then averaged. The simulation results show that near the melting point, the radial distribution function and the static structure factor are reproduced. This results indicates that the principle of corresponding states is fulfilled in liquid alkali metals.

1. Introduction

At present, the structural features and properties of alkali metals are of great interest to researchers. Firstly, this class of metals is the first one after the fully studied inertial gases, which makes it possible to test, generalize and adapt new models to existing experimental data. Secondly, liquid alkali metals have many practical applications, for example, coolants in nuclear reactors, purification of alloys from impurities, the creation of photovoltaic cells. The high chemical activity of this metals is explained by the presence of one electron on the outer shell. Therefore, when studying these metals in their pure form, where the alkali metal atom is represented as a "positive ion and ns^1 electronic structure", on which many different theories of simple metals were tested and well studied experimentally [1, 2, 3, 4]. It was shown in the Ref.[5] [5] that the interaction potential for liquid alkali metals has an oscillating form, due to the periodicity in the arrangement of the electronic structure (Friedel oscillations). For lithium, good agreement was achieved between the simulation results and experimental data [6]. It was also shown the possibility of fulfilling the principle of thermodynamic similarity [7] in liquid alkali metals near the melting point. Authors have shown that this approach is correct and the pair oscillating potential makes it possible to describe the structural characteristics in other liquid alkali metals.

2. Obtaining the coefficients of potentials for alkali metals

The interaction potential is assumed to be paired due to the fact that alkali metal melt is consists of positively charged ions and electrons moving between them, creating oscillations in the structure. To determine the interaction potential, we need a functional dependence of the interaction energy on distance and a set of parameters. In our case, the set of parameters will be chosen on the assumption that for alkali metals the potential will have one dependence:

$$U(r) = A \exp(-\eta(r - r_0)) + \frac{B}{r^n} \cos(kr + \phi), \tag{1}$$

where the first term characterizes the short-range repulsion, the second term characterizes periodic oscillations in the electronic structure. The potential parameters for considered systems were obtained by machine learning: the algorithm is a controlled random search with local mutation [8]. The convergence criterion of the machine learning algorithm is the forces acting on the atoms obtained from the earlier ab-initio simulation in the VASP package (100 system configurations) [9, 10]. Initial conditions for ab-initio simulation: 54 particles, bcc lattice type, NVT ensemble, final simulation temperatures are 475 K, 390 K, 343 K, 320 K, 303 K respectively for lithium, sodium, potassium, rubidium, cesium, respectively. The lattice constants are chosen in such a way as to correspond to the quantitative density of the systems in the experiment and are equal to 3.557, 4.282, 5.386, 5.772, 6.215 Åfor lithium, sodium, potassium, rubidium, cesium, respectively. The parameters for the potentials obtained in the course of machine learning are shown in Table 1:

Table 1. Potential parameters for alkali metals.

Element	A	η	r_0	B	n	k	ϕ
Li	3	3.5	1	9.068	4.24	-1.995	3.440
Na	35.73	6.593	1	20.16	4.532	-1.675	3.595
K	2.7527	2.82863	2.47148	2	1.661	-1.358	-0.574
Rb	1.00047	2	2.88956	0.5	2	1.379	4.137
Cs	$1.416*10^-5$	1.019	13.66	14.44	2.778	0.883	13.793

## 3. Structure and collective dynamics of liquid alkali metals

Simulation was performed in the LAMMPS package [11] with the following initial conditions: a bcc lattice of $N = 9826$ atoms with periodic boundary conditions. The lattice constants are same as in the ab-initio simulation case with initially zero velocities and accelerations. A canonical NVT ensemble with an integration time step of $\tau = 10$ fs was used, where the systems were heated to the temperature 800 K over 100 000 time steps and held for 70,000 time steps, after which the liquid system were cooled to the following target temperatures: for lithium is 475 K, sodium is 390 K, potassium is 343 K, rubidium is 320 K, cesium is 303 K. This state is located near the melting curve, and there is a fairly extensive experimental material for it. One of the most common ways to check the correctness of the interaction potential is to calculate the radial distribution function of atoms [12]:

$$g(r) = \frac{V}{4\pi r^2 N} \left\langle \sum_{i=1}^{N-1} \frac{\Delta n_i(r)}{\Delta r} \right\rangle \tag{2}$$

and the static structure factor [12]:

$$S(k) = 1 + \frac{N}{V} \int [g(r) - 1] \exp(i\mathbf{kr}) \, d\mathbf{r}, \tag{3}$$

where V is the volume of the system, N is the number of atoms in the system, $\Delta n_i(r)$ is the number of atoms in a spherical layer of thickness Δr, k is the wave vector, and $\mathbf{r}$ is the radius vector of the particle, angular brackets mean averaging over the entire system and over the time sample. The results of calculations of the radial distribution function and the static structure factor are presented below.
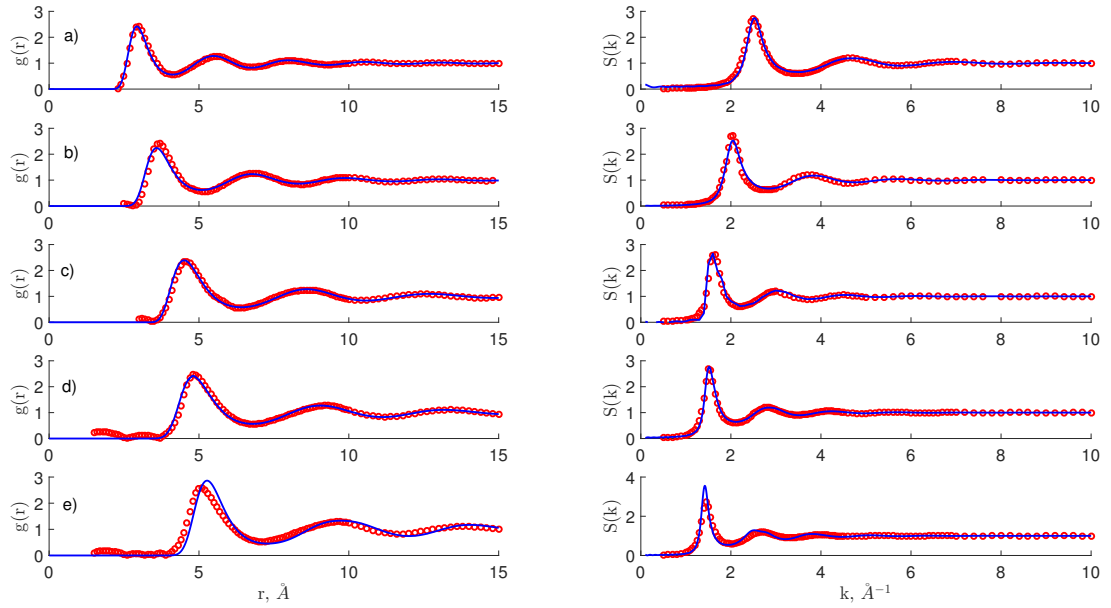
Figure 1. Radial distribution function (left panel) and static structure factor (right panel) for: a) lithium, b) sodium, c) potassium, d) rubidium, e) cesium. Blue line is the simulation results, red circles are the experimental results [13].

In our case, we will consider also dynamical structure factor [14, 15, 16, 17, 18, 19]. This quantity is determined from the experiments of inelastic scattering neutrons and X-rays [12]:

$$S(k,\omega) = \frac{1}{2\pi N} \int_{-\infty}^{+\infty} \exp(-i\omega t) \sum_{i,j} \langle \exp\left[-i\mathbf{k}\mathbf{r}_i(0)\right] \exp\left[-i\mathbf{k}\mathbf{r}_j(t)\right] \rangle \, dt. \tag{4}$$

The angular brackets mean averaging over the entire system and over the time sample. To compare the simulation results with the experimental data, the X-ray scattering intensity spectra $I(k,\omega)$ were determined for different values of the wave number k, which is related to the dynamic structure factor $S(k,\omega)$ by the relations [18]

$$I(k,\omega) = E(k) \int R(k, \omega - \omega') S_q(k, \omega') d\omega', \tag{5}$$

$$S_q(k,\omega) = \frac{\hbar\omega/k_B T}{1 - \exp(\hbar\omega/k_B T)} S(k,\omega). \tag{6}$$

4. Conclusions

In the present work, the oscillating potential model (1) is constructed and tested as applied to liquid alkali metals near the melting point. It is shown that such a pair potential accurately reproduces the "structural" features of alkali metal melts and describes experimental data on neutron and X-ray diffraction. It has been established that the resulting model can be used to describe the static structure in a wide range of wave numbers. But in the dynamical structure factor, there is some mismatch between the simulation results, especially in sodium.
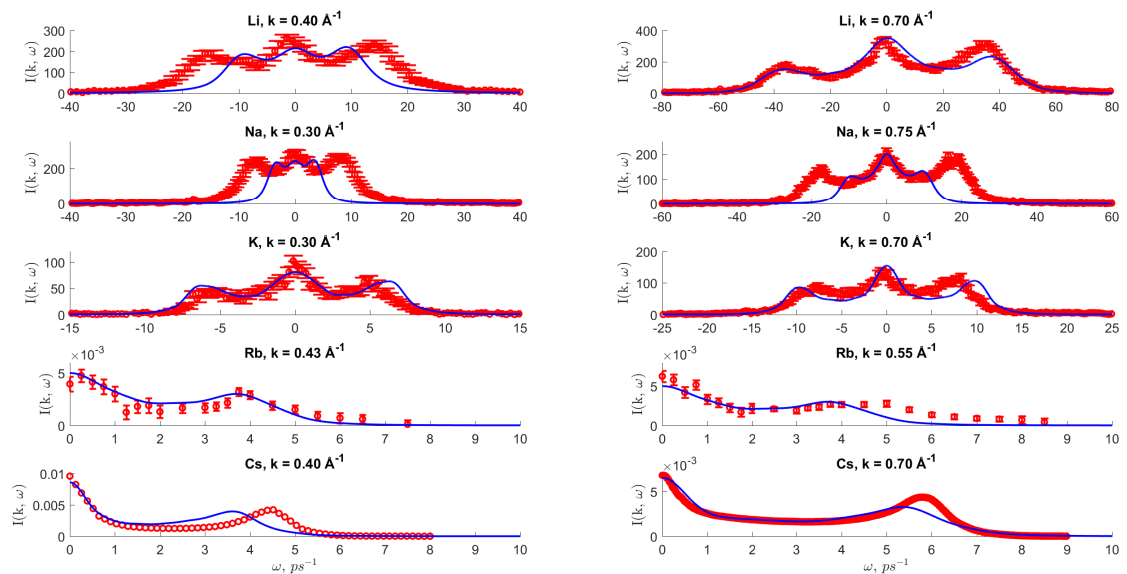
Figure 2. Spectra of inelastic scattering of X-rays and neutrons (red circles) for liquid lithium at a temperature of $T = 475$ K [20], sodium $T = 390$ K [21], potassium $T = 343$ K [22], rubidium $T = 320$ K [23], cesium $T = 303$ K [24]. The experimental errors of the intensity are shown for all liquid metals, except cesium. The results of simulation with model potential are marked as blue line.

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