Dynamic Structure of Oxygen in Liquid Potassium Studied by MD Method and Statistical Geometry

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Results of the molecular-dynamics simulation of K-O system in three-component approximation: $(1-\frac{2+q}{q}x)\mathrm{K}+\frac{2x}{q}\mathrm{K}^{q+}+x\,\mathrm{O}^{2-}$ where $0.25 < q \le 1$ are presented. For calculating the MD model, a charge, q, is chosen equal to 1 on the basis of statement that dissolved oxygen in potassium melt forms clusters, $(\mathrm{K_2O})_n$ [1-3]. The MD simulation was conducted for the temperature of 550K as NVT ensemble of 2000 particles (N_K = 1490, $N_{K^+} = 340$, $N_{O^{2-}} = 170$) in a cubic cell with periodic boundary conditions. The cube edge length, L= 54.004 Å, has been selected according to the oxide mass density, ρ_{K_2O} = 2320 kg·m^{-3}, at the given oxygen atomic concentration of 8.5% for unsaturated solution at 550 K [4] and the mass density of liquid potassium, $\rho_K = 777$ kg·m^{-3}.

Born-Mayer's potential without dispersion terms [5] is used for describing (K^+,K^+), (K^+,O^{2-}), (O^{2-},O^{2-}) and (K,O^{2-}) interaction with parameters $Z_{O^{2-}} = -2$, $Z_{K+} = 1$, Pauling's coefficients: $C_{K^+K^+} = 1.25$, $C_{K^+O^{2-}} = 1.0$, and $C_{O^{2-}O^{2-}} = 0.75$, the ionic sizes: σ_{K^+} = 1.39Å and $\sigma_{O^{2-}}$ = 1.33Å, the repulsive parameter: B = 0.21098 eV, the softness parameter: A = 3.45Å^{-1}, and the number of electrons in the outer shell, $n_{K^+} = n_{O^{2-}} = 8$. For (K,O^{2-}) interaction $Z_K = 0$ and $n_K = 1$.

The potential for describing interaction between the neutral potassium atoms (K,K) and ions (K,K^+) is common for two runs. In the first case, it is Lennard-Jones' (*n-m*) potential [6] with parameters: ε = 0.0614 eV, n = 6.5, m = 4.5, r_0 = 4.8359 Å. In the second one, the potential evaluated for treating the electron-ion coupling in the frame of the pseudo-potential concept (*ps*) and linear screening theory [7] with k_f = 0.7076Å^{-1}, R_c = 1.1854Å, and $\nu = 1.8253$.

The potassium/oxygen ternary system was simulated in the condition of charge exchange between each potassium ion and a nearest potassium atom over the 50 time steps. As realizing the charge exchange, the system relaxed to equilibrium. Then, such characteristics as the partial radial distribution function, $g_{\alpha\beta}(r)$, structure factor, $S_{\alpha\beta}(k)$, velocity auto-correlation function, $\Psi_{\alpha\beta}(t)$, frequency spectrum, $f^n_{\alpha\beta}(\omega)$, and self-diffusion coefficients, $D_{\alpha\beta}$, were calculated in given time moments $t \le 1.05\cdot10^{-10}$ s. An addition investigation of cluster configurations has been conducted by statistical geometry method [8].

The influence of both (*n-m*) and (*ps*) potentials is small and not change the main conclusion about the system behaviour. The function, $g_{KK}(r)$, has the same form as, $g_{KK^+}(r)$, the function, $g_{KO^{2-}}(r)$, has a weekly oscillating form, and $g_{K^+O^{2-}}(r)$ has a narrow peak. The function for ions characterised by widened first peak of $g_{K^+K^+}(r)$ and small splitting the first one for $g_{O^{2-}O^{2-}}(r)$. The $\Psi_{K^+K^+}(t)$, $\Psi_{K^+O^{2-}}(t)$, and $\Psi_{O^{2-}O^{2-}}(t)$ are strong oscillatory. The diffusion coefficients of D_{KK}, D_{KK^+}, and $D_{KO^{2-}}$ are in the range of 0.8 to 1.2 10^{-1} [Å^2/ps], $D_{K^+K^+}$, $D_{K^+O^{2-}}$, $D_{O^{2-}O^{2-}}$, in the range of 0.3 to 0.05 10^{-1} [Å^2/ps]. The spectra including potassium partial have dominating frequency of atom vibration at $\varepsilon_{\max}$

in the range of 3.5 to 11.0 meV (Fig. 1a), where ε denotes $\hbar\omega$. Otherwise the oxygen spectrum, $f^{n}_{O^{2-}O^{2-}}(\varepsilon)$, has the main peak of $\varepsilon_{\max} \approx 50$ meV (see Fig. 1b).

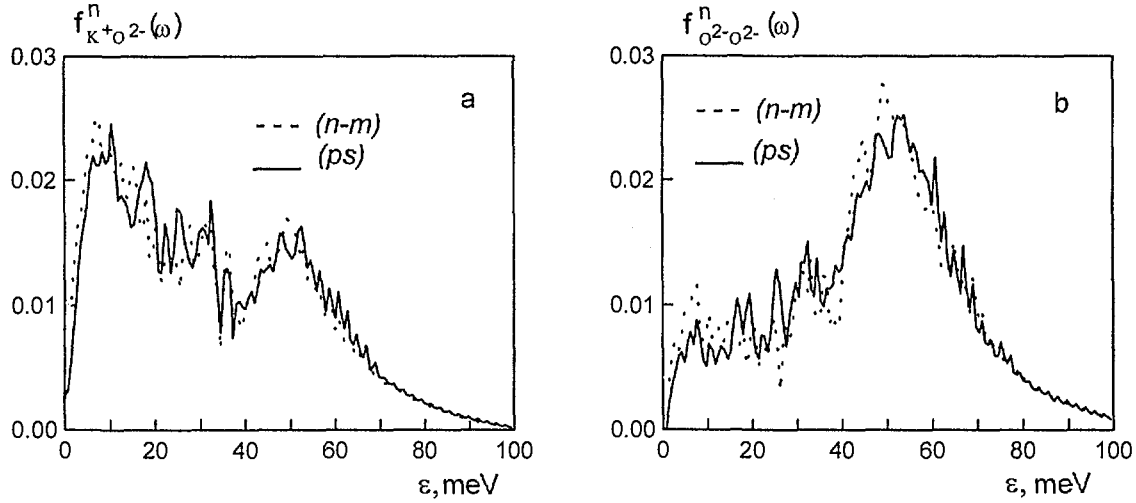
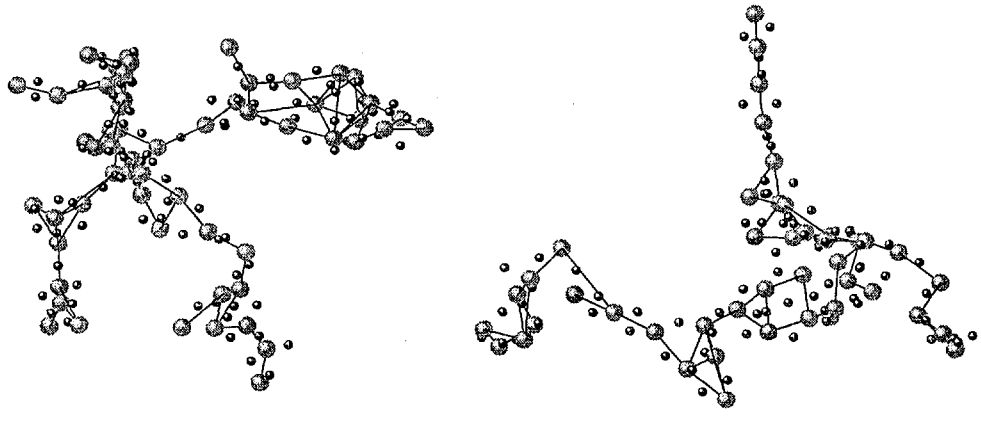


Fig. 1. The partial frequency spectrum for $K^{+}O^{-}$ (a) and $O^{2-}O^{2-}$ (b) at t=1.05·10^{-10} s.

The low values of partial diffusion coefficient for ionic pairs, $D_{K^+K^+}$, $D_{K^+O^{2-}}$, $D_{O^{2-}O^{2-}}$, and strong oscillatory modes of oxygen frequency spectrum reflect the formation of clusters in the unsaturated solution of oxygen in potassium melt [9]. The dominant values of high frequencies in oxygen spectrum, $f^{n}_{O^{2-}O^{2-}}$, and the low ones in partial potassium spectra indicate to oxygen clusterization in potassium melt where such the clusters exchange lightly potassium ions with the melt. This is consistent with the experimental data [10] that oxygen forms in liquid potassium microinclusions of $(K_2O)_n$ type which has the molten cation sublattice. The analysis of atomic configurations in the MD cell by means of the statistical geometry confirms the formation of such the clusters (see Fig. 2), in where big circles are oxygen anions and small circles are potassium cations.

So, the proposed simulation model allows the process of impurity behavior to study as an atomic clusterization in liquid alkaline metals.



a) b)

Fig. 2. The greatest oxygen clusters in the MD run of 1.05·10^{-10} s for (*n-m*) potential (a) and for (*ps*) potential (b).

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