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Molecular dynamics simulation of Li surface erosion and bubble formation

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Abstract

Structure and dynamical properties of liquid Li containing He atoms were studied by the Molecular Dynamics method at various temperatures and densities and the diffusion coefficients were calculated. A new model of liquid Li surface is developed that shows the stratification of surface layers. The liquid Li sputtering yield, due to bombardment by slow He ions, was calculated for the new model and the result is compared with conventional models. Bubble formation in liquid Li is studied by simulation of cavity growth mechanisms in bulk liquid Li system wit 3-D periodic-boundary conditions. Our results show that small cavities are easily dissolved at certain temperatures. A cavity with a diameter of 50 Å grows by consuming neighboring small cavities in accordance with the classical nucleation theory. The mechanism of bubble growth and explosion could significantly contribute to the surface erosion at high ion fluxes and explain some controversial experimental results.
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1. Introduction

Bombardment characteristics of light low-energy ions on a liquid Li surface and their diffusion properties have attracted much attention because of the potential use of liquids as a plasma-facing component (PFC) for future tokamak devices.

Molecular dynamics (MD) method is capable of studying important collision processes and providing a realistic study of the diffusion motion in liquid Li. MD simulation of diffusivity in bulk liquids is a well-studied area [1–4]. The coefficients of self-diffusion in liquid Li have been measured with nuclear magnetic resonance method [5] and by capillary methods [6]. The diffusion constants for H isotopes dissolved in liquid Li were measured in [7,8].

Experiment [9] using surface X-Ray scattering from pure liquid metals (Hg, Ga, In) and from alloys have revealed that the planar ionic density in these systems have periodic oscillations near the surfaces in the direction normal to the surface and this layering (stratification) extends within a few atomic diameters (~5 Å for Hg, Ga). Surface roughness of liquid metals, which is due to the thermal capillary waves, is about 1.5 Å. Surface roughness of non-metal liquids is much bigger (≈7 Å)

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than that of metals and the stratification effect was not observed for such systems [10].

He bubble formation phenomenon is yet another important mechanism that could significantly contribute to surface erosion at high D^+, He^+ fluxes from the plasma when liquid metal becomes saturated with the light atoms [11]. The aim of this paper is to study diffusion in liquid Li and the He bubble formation, by using an atomistic MD simulation method.

2. Computational model

Structure and dynamical properties of liquid Li were studied by MD method at various temperatures and densities. Li self-diffusion coefficients and the diffusion coefficients of He and hydrogen isotopes were calculated as Fourier-transforms of the velocity autocorrelation functions and as mean-square-displacements of particles.

Two different types of effective inter-ionic potential for liquid Li were used for this work. The first potential was developed for five different temperatures: 470, 525, 574, 725, and 843 K and corresponding densities along the melting line in [3] (CGP-potential). The second Li–Li potential, was developed based on a local density approximation and is given in an analytic form [12] (LBP-potential). This potential is available for wide temperature and density ranges.

The sputtering yield of a liquid Li surface by low-energy He ion collisions was calculated by MD simulation. Li–He interactions were modeled by using a potential between Li ions and He atoms given in [13], and He–He interaction was determined via a simple pair-wise potential, with the binding energy and the equilibrium distance from [14].

A smooth liquid Li surface was modeled by adding a Lennard-Jones (LJ) potential to interactions of Li ions near the surface, additionally to many-body LBP-potential (LBP + LJ potential). Surface structure of liquid metal was studied by calculating the average pair-distribution function within the thin layers near the metal surface, for the following three different potential combinations.

At low He fluxes, bubble formation of He was studied by a set of the mass action laws that was solved numerically for the equilibrium concentrations of single He atoms, dimers, and larger clusters in liquid Li. The binding energies of He clusters were estimated through a simple formula: $\varepsilon_k = 4\pi[(r_{k-1}^2 + r_1^2) - r_k^2]\gamma$, where γ is the liquid Li surface tension, and r_k is the radius of a He cluster with k-atoms.

At high He fluxes, a MD model for bubble nucleation is developed based on the classical nucleation theory. According to this theory, nucleation of the bubble is a process controlled by the energy barrier which defines the critical bubble radius: bubbles smaller than the critical one tend to shrink in size and collapse; those bubbles that are larger – tend to continuously grow.

The statistical uncertainties of the MD calculations were kept to be less than one percent and the details of the assumptions could be obtained elsewhere [1–3,17].

3. Results and discussion

Fig. 1 shows MD results for calculations of the self-diffusion coefficient in bulk liquid Li for various

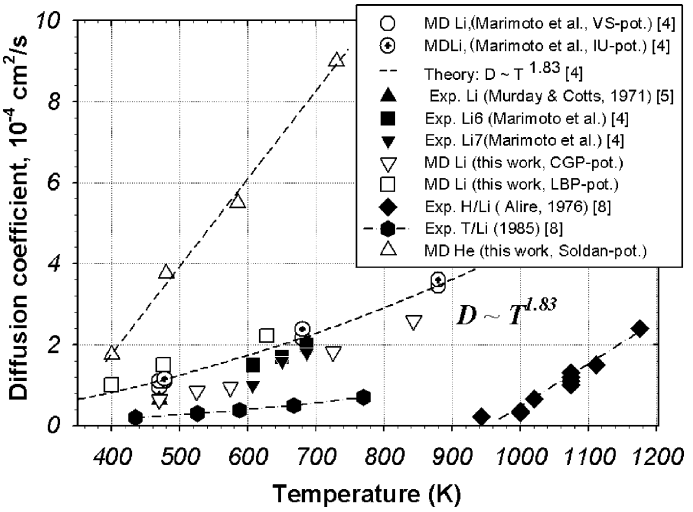

Fig. 1. Comparison of the Li self-diffusion coefficients obtained by MD with available experimental data of Li [4–6]. Additionally, our results of the He diffusion coefficients and experimental data for H/Li [7,8] are also shown.

temperatures and compared to experimental results [5–8]. The comparison with experimental data shows that the CGP-potential [3] obtained for bulk liquid Li gives the calculated results that are very close to the experimental data obtained by two different methods. The LBP-potential obtained for low-dimensional systems like small clusters [12] gives diffusion coefficients slightly higher than the experiments.

Since the surface roughness of the simulated liquid greatly affects the dynamics of a slow ion collision with the surface, a combined potential has been used based on LBP and LJ functional forms to create a smooth liquid surface. This LBP + LJ-potential was applied to the Li ions residing near the surface. The depth and the equilibrium distances of the LJ-potential were adjusted to the experimental surface tension and cohesion energy of liquid Li [15].

Fig. 2 shows simulation results where $z\,df = dN/dz$, is the distribution function of Li ions along z-axis (normal to the surface) and it was calculated as the number of Li ions within thin layers parallel to the surface. The dash line in this figure is the zdf obtained by using CGP-potential, and the dash-dot line is zdf for the surface modeled by pure LBP potential given in Ref. [12], the solid line $-zdf$ for the surface consisting of the bulk system, interacting with LBP, that was covered by the ions interacting via the Lennard-Jones potential (LBP + LJ-potential).

The important result is that the simulation of a smooth surface obtained with the combination of two interatomic potentials, did give the layered structure that agrees with experimental observations [9]. Additionally, such a combination of two potentials clearly shows the relaxation of the surface into the bulk liquid, which was predicted by the liquid metal surface theories. Meanwhile, both the bulk CGP- and cluster LBP-potentials do not show the relaxation of the surface.

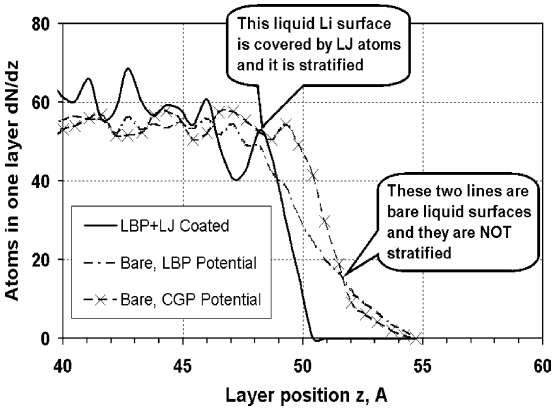

Fig. 2. zdf, the distribution of Li ions over z-axis normal to the surface calculated as the number of Li ions within thin layers parallel to the surface.

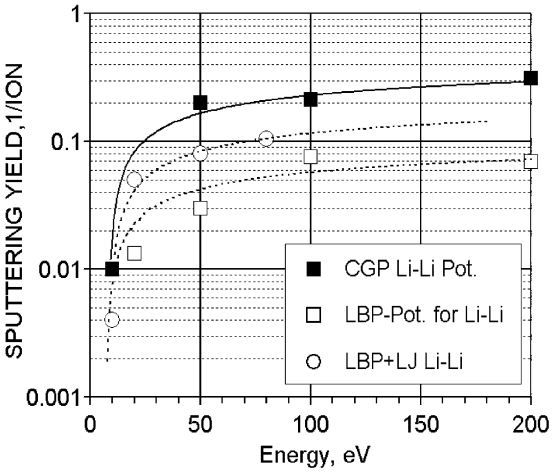

Fig. 3. He^+/Li sputtering yields for three Li–Li Potentials calculated by our MD.

Sputtering coefficients were calculated for slow He^+ ions, with energies of 10–200 eV, colliding at a near normal incident angle with the liquid Li surfaces built by three types of interatomic potentials. Fig. 3 shows the calculated results for the He^+/Li sputtering yields for three Li–Li potentials: solid squares were obtained by using the CGP bulk-potential only [3]; the open squares are the results obtained by using the cluster LBP-potential [12]; the open circles were obtained by LBP + LJ-potential at 470 K, at a near normal incidence. The difference between the results is sizeable (≈7 times at energies greater than 50 eV). The combined potential (LBP + LJ) gives intermediate results. These results were obtained for a near normal incidence angle. Our preliminary results at 45° of incidence show that the difference could even be greater.

He equilibrium bubble concentrations obtained by solving the Saha equations [16] show that at low He fluxes, the concentrations of the He clusters are negligible. At high He fluxes, He bubble nucleation and growth in liquid Li was simulated by MD method and compared with the classical nucleation theory [17]. According to this theory, bubbles smaller than a critical bubble size should eventually be dissolved in liquid. The bubbles that are larger than the critical bubble size should grow. Upon continuous growing, such bubbles move toward the open surface and eventually blow up, thus producing splashing and macroscopic erosion of the liquid surface.

Fig. 4(a)–(f) show the dynamic evolution of three cavities that were placed in liquid Li at 470 K. The liquid Li system has 3-D periodic boundary conditions. The diameters of the cavities were 55, 43, and 36 Å. Fig. 4(a), shows the initial time instant of the liquid containing three cavities; (b) the time instant is 1 ps; the 43 Å cavity

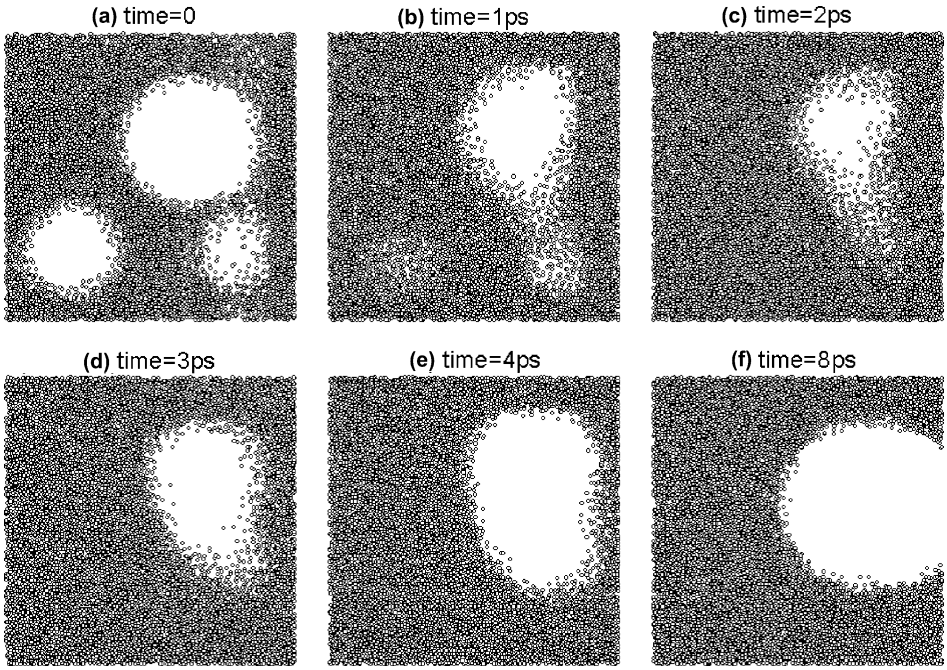

Fig. 4. (a)–(f) Dynamics of cavity growth in liquid Li is shown by snapshots of Li ion positions within a thin layer around the cavities, with the thickness of 20 Å.

has almost disappeared but the smallest 36 Å cavity still exists due to the proximity to the largest 55 Å cavity and it starts to join the large cavity; (c) the time instant is 2 ps and there exists only one cavity which changes the shape because it is not stable; $4(d-e)t = 3$ and 4 ps, the shape of the cavity is slowly becomes round; (4f) final geometry of liquid has one large cavity with almost ideal spherical shape. The critical radius estimated by this MD simulation is about 55 Å, for the liquid Li at 470 K. The effect, which is shown in Fig. 4 is called 'bubble coalescence' and it occurs due to the decrease of the total system energy during the growth.

Our new findings may help to understand the non-linear and large enhancement of the sputtering yield observed at very high incident He and H incident fluxes when the saturation of a liquid metal target becomes noticeable. Experiment [11] predicts a non-linear enhancement of the sputtering yield for irradiation of liquid Ga–In–Sn alloys with D_1^+, D_2^+, and D_3^+ ions. After a super-critical bubble is formed, it would start consume small under-critical bubbles, small cavities, vacancies, and He atoms and grow continuously and eventually will blow up at the surface thus generating shock wave and surface sputtering by rare-faction waves. Our preliminary MD simulations of the bubble blast near the liquid surface show that the initial velocities of the ejected debris are of the order of the sound speed, which complies well with the shock-wave mechanism of the yield enhancement.

4. Conclusions

Diffusion coefficients and the structure of bulk liquid Li were studied by the molecular dynamics (MD) method at various temperatures and densities along the melting line for solid lithium. The obtained Li self-diffusion coefficients and the diffusion coefficients of He were in good agreement with available experimental data.

The structure of the liquid Li surface was studied and a simulation model was proposed that shows the stratification of the surface layers in liquid Li, which is in accordance with experimental studies.

Bubble formation in liquid Li was also studied by simulating the nucleation and growth of cavities of various sizes in a bulk liquid Li system by the MD method. Our results show that the small cavities will be easily dissolved in a liquid at 470 K. However, if the cavity size becomes larger than a critical one, the cavity grows. This is the first MD simulation of the existence of a critical cavity in liquid Li; and it complies well with the predictions of the classical nucleation theory. We conclude that bubble formation mechanism in liquid Li has a high probability in saturated states. It could significantly contribute to surface erosion thus explain recent controversial experimental results.

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