

MOLECULAR DYNAMICS SIMULATIONS OF BUBBLE FORMATION AND CAVITATION IN LIQUID METALS

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Thermodynamics and kinetics of nano-scale bubble formation in liquid metals such as Li and Pb were studied by molecular dynamics (MD) simulations at pressures typical for magnetic and inertial fusion. Two different approaches to bubble formation were developed. In one method, radial densities, pressures, surface tensions, and work functions of the cavities in supercooled liquid lithium were calculated and compared with the surface tension experimental data. The critical radius of a stable cavity in liquid lithium was found for the first time. In the second method, the cavities were created in the highly stretched region of the liquid phase diagram; and then the stability boundary and the cavitation rates were calculated in liquid lead. The pressure dependences of cavitation frequencies were obtained over the temperature range 700–2700°K in liquid Pb. The results of MD calculations for cavitation rate were compared with estimates of classical nucleation theory (CNT).

I. INTRODUCTION

Bubble formation in liquid Li and enhanced sputtering due to bubble bursts in liquid metal have attracted much attention because of the important feasibility studies of using liquids as a plasma-facing component (PFC) for future tokamak devices [1]. The important parameters defining the enhanced sputtering yield of liquid lithium due to light fusion ion bombardments is as follows: average bubble size, concentration of bubbles, cavitation rate of such bubbles, and the sputtering yield per fusion particle bombarding the metal surface. These tasks are tremendously difficult as there are no theoretical methods that can predict the erosion rate due to bubble burst. Atomistic computer simulation methods such as MD or Monte Carlo (MC) can significantly advance our understanding of the bubble formation and stability, generation of shock waves at the

cavitation, and calculation of the enhanced sputtering yield.

Liquid metals such as lead are an important component of the promising heat-transfer materials in the new type of power reactors with fast deuterium-tritium fuel ignition [2]. The performance of such systems is substantially deteriorated by continuity loss (cavitation) in the heat-transfer material. This is caused by the negative stresses that arise due to microexplosions in the working chamber. Therefore, the cavitation kinetics in the heat transfer material under dynamic tensile stresses is an important task which should be understood, in order to control the system functioning.

MD method is capable of studying the important collision processes, such as sputtering and reflection yields, sticking probability for various ions colliding with PFC surfaces and provides a realistic study of the diffusion motion of impurity atoms in liquid metals. The Li self-diffusion and He diffusion coefficients are important parameters for using liquid Li for He retention and were studied in a previous paper [3]; and the MD method for calculating the cavitation rates in liquid Pb was developed in [4].

MD study of gas bubbles and cavity formation in simple bulk liquids is a well studied area of statistical mechanics [5-19]. CNT of bubble formation has been reviewed in [5]. Density profiles $\rho(r)$, normal and tangential components of the pressure tensor $p_N(r)$ and $p_T(r)$, using both the Irving-Kirkwood and Harashima definitions of pressure were obtained in [6] and applied to a Lennard-Jones fluid. The surface tension of a LJ fluid was determined by MD simulation in [7-9] by using the Tolman's length in the limit of small curvatures. MD study of water at elevated temperatures was conducted in [10]. The authors of [11] concluded that there is no curvature dependence of the surface tension. The probability of finding a void in a LJ liquid was studied in [12]. Surface tensions of bubbles and droplets followed

were calculated in [13,14] for a LJ liquid. The surface tension of bubbles was shown to be much less (15% of the planar surface). This finding strongly deviates from that of a droplet which surface tension was much bigger than that of flat surface.

Spinodal lines (or thermodynamic limit of metastability) for monatomic and diatomic liquid oxygen modeled via one- and two-center LJ interatomic potentials were calculated by MD in [15]. A kinetic limit of metastability which defined as a lowest density, at which the liquid was homogeneous, was also calculated.

A nonequilibrium MD method was employed to study a local liquid heating that was generating bubbles in [17]. Structure of a curved interface and many physical properties of bubbles, droplets and cavities in a LJ-liquid were studied by a MC method in [18-20] and by analytical methods such as Density Functional (DF) method, van der Waals, and a Mean-Field theory in [21-24].

The aim of this paper is to develop a method of studying metastable liquid metals at negative pressures, by calculating stability, density, pressure, surface tension and Gibbs energy of stable nucleus, by using MD simulation method.

II. COMPUTATIONAL MODEL

Two different MD models of bubble formation were developed in this paper. First model defines the critical radius of the bubble by using the CNT and using MD as a means for obtaining the surface tension of the cavities in liquid metal. As an example, this model was applied to cavities in liquid lithium.

In the second model, the rate of a spontaneous phase transition was defined by a mean number of critical nuclei formed in unit volume per unit time, that is, by the cavitation frequency J . In this work, the cavitation frequency was calculated as $J = 1/(\langle \tau \rangle V)$, $\langle \tau \rangle$ is the mean lifetime, V is the simulation box volume.

According to the CNT, nucleation of a microscopic bubble is a process controlled by the energy barrier which is defined by an interplay between the volume and surface free energy contributions into the total energy. Therefore, the MD models developed in this work should be able to predict the energy barrier and the critical bubble size.

Structure and dynamical properties of liquid Li were studied by MD method at various temperatures and densities along the melting line for solid lithium.

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, ρ , g/cm³: 0.513, 0.508, 0.505, 0.484, and 0.480, along the melting line in [25].

The second Li-Li potential was developed based on a local density approximation and is given in an analytic

form [26]. This potential is convenient for modeling liquid Li surfaces by MD method as it is applicable for wide temperature and density ranges.

Interatomic interactions between lead particles were modeled via a glue many-body EAM potential for Pb developed in [27].

Although the liquid metal used as a plasma facing material of the fusion device in reality contain gases such as hydrogen or helium, two our MD bubble models consider cavities containing only metal atoms, i.e. without any light ions or atoms. Such simplification of the model is based on the calculation results that the total energies, pressure tensors, and surface tensions of the cavities do not drastically change if helium atoms were placed inside the cavity, due to a weak interaction of helium with lithium. Therefore, our models are not applicable to hydrogen bubbles as hydrogen can form a chemically stable hydride with metals.

The radial densities, pressure tensors, surface tensions around a bubble in liquid lithium were calculated in analogy with the droplet capillary theory [6,22]. Similar approach was used in [13,14] where bubble and droplet formation and their stability were studied by MD in a LJ-system.

The average radial densities $\rho(r)$ and pressures were calculated as a ratio by dividing the number ΔN of particles confined within a narrow spherical layer dr to the value of dr :

$$\begin{aligned} \langle \rho(r_k) \rangle &= \left\langle \frac{\Delta N}{\Delta r} \right\rangle_k, k=1 \dots n \\ P(r) &= P_N(r) + P_{Tr}(r), \\ P_{Tr}(r) &= P_N(r) + \frac{r}{2} \frac{dP_N(r)}{dr}, \\ P_N(r) &= P_{Kin}(r) + P_U(r), \\ P_{Kin}(r) &= \rho(r) k_B T, \\ P_U(r) &= -\frac{1}{4\pi r} \sum_k \left| \vec{r} \cdot \vec{r}_{ij} \right| \frac{1}{r_{ij}} \frac{dU(r_{ij})}{dr_{ij}}, \\ \gamma_S^3 &= -\frac{1}{8} (P_l - P_g) \int_0^\infty r^3 \frac{dP_N}{dr} dr. \end{aligned} \quad (1)$$

$P_N(r)$ is the normal and $P_{Tr}(r)$ the transverse components of the pressure tensor $P(r)$ of the cavity and r is the distance from the center of the cavity. See the details in ref. [6] where similar formulas were used for an exactly opposite case – droplet formation in gas. $P_{Kin}(r)$ is the kinetic and $P_U(r)$ – the potential terms of the pressure, U is the interaction potential for which an EAM many – body potential was used, P_l and P_g are the liquid and the gas pressures inside the cavity.

$$\begin{aligned} R_S &= \frac{2\gamma_S}{P_l - P_g}, \\ R_e &= \frac{1}{\rho_l - \rho_g} \int_0^\infty r^3 \frac{d\rho}{dr} dr. \end{aligned} \quad (2)$$

R_s is the radius of the surface of tension and R_e – the equimolecular dividing radius [14].

$$\frac{\gamma_s}{\gamma_\infty} = 1 - \frac{2\delta}{R_s}, \delta = R_e - R_s \quad (3)$$

Where γ_s – the bubble surface tension, γ_∞ – the surface tension of a flat plane, δ – a typical thickness of the curved interface, and δ/R_s is a small parameter in the Tolman's formula (3).

The surface tension of the cavity gives the free energy barrier according to the main CNT formula:

$$\Delta\Omega(r) = -\frac{4}{3}\pi r^3 \cdot \Delta\omega + 4\pi r^2 \cdot \gamma_s, \quad (4)$$

$$\Delta\omega = P_g - P_l,$$

Where the first term is a volume gain contribution (negative term) and the second term – is the surface energy loss contribution (positive term).

Systems with up to 50,000 atoms in the simulation box were studied. Three-dimensional periodic boundary conditions were used. The trajectories of atomic motions were calculated by the numerical integration of a system of classical equations of motion using the difference scheme of the second order of accuracy with a 1 fs time step. Constant temperatures were set and maintained using a Langevin thermostat scheme.

III. RESULTS AND DISCUSSION

3.A. Energy barrier for cavity formation in liquid Li

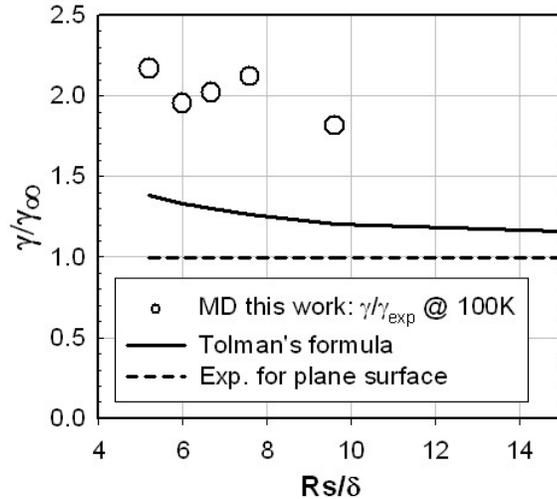


Fig. 1. Fitting the results for surface tension obtained by these MD calculations to the Tolman's formula (see Eq. 3).

Six cavities were studied in this work with the following radii: 3, 4, 5, 6, 7, and $8a_0$, where a_0 is the Li bcc lattice parameter obtained from the density as: $a_0 = (2m_0/\rho)^{1/3} \times 10^8 \text{ \AA}$; $m_0 = 1.15257 \times 10^{-23} \text{ g}$, is the Li atomic mass; density of the liquid lithium $\rho = 0.480 \text{ g/cm}^3$. The temperatures of the system were scaled down a stable

cavity was obtained and were below the binodal line. Each cavity was equilibrated until the temperature was stabilized within $\sim 10 \text{ ps}$, and after that the physical properties such as the radial density, pressure tensors, surface tensions were calculated. If the temperature showed growth by more than 5% of the initial one, the initial temperature was decreased and the simulation started again, until a stable cavity was obtained.

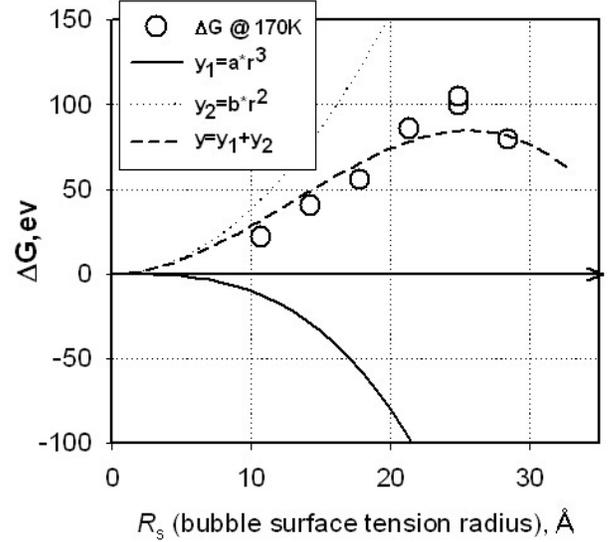


Fig. 2. Free energy barrier calculated by formula 6 in this work for six cavities. One cavity with the radius $7a_0$ was calculated twice with the different system sizes of $20a_0$ and $30a_0$.

By using formulas (1-4), the surface tensions were calculated for all cavity sizes and all temperatures. Fitting of the calculated results for the surface tension to the Tolman's formula is shown in Fig. 1. This comparison shows a big difference between the calculated surface tension and that of the plane surface; and our results are a few times higher than the Tolman's data. Fig. 2 shows our preliminary result obtained for the free energy barrier obtained. The results also show that there exists an energetic barrier for a bubble formation in liquid lithium, in compliance with the CNT.

3.2. Cavitation rate in liquid Pb

The lifetime of a uniform metastable liquid phase along one MD trajectory depends on the initial configuration and distribution of particle velocities and, the initial conditions being equal, integration step. Statistical averaging for the given thermodynamic state is performed over an ensemble of M independent initial configurations, each characterized by the corresponding lifetime τ_i ($i=1-M$). Homogeneous nucleation can be described as a random Poisson process. This model fairly well describes the cavitation process under consideration.

Finding the distributions with a well-defined exponential form requires the accumulation of a large statistic ($M > 100-200$). Generating of a big number of trajectories for statistical analysis is a very efficient task for the parallel calculations on a computer clusters.

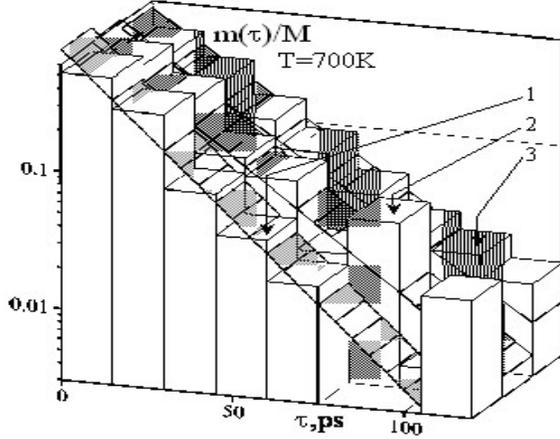


Fig. 3. Number of MD trajectories $m(t)$ from the ensemble of M independent trajectories. For each of the $m(t)$ trajectories, the instant of the beginning of cavitation (lifetime τ_i) lies in the interval $(\tau, \tau + \Delta\tau)$. Calculation results for various pressure P values at $T = 700$ K are shown ($\Delta\tau = 15$ ps): (1) $p = -3.95$ GPa, $M = 46$; (2) $p = -3.91$ GPa, $M = 232$; and (3) $P = -3.89$ GPa, $M = 142$. For comparison, the dependences obtained for the model according to which cavitation is a random Poisson process (2) are shown by straight lines (planes).

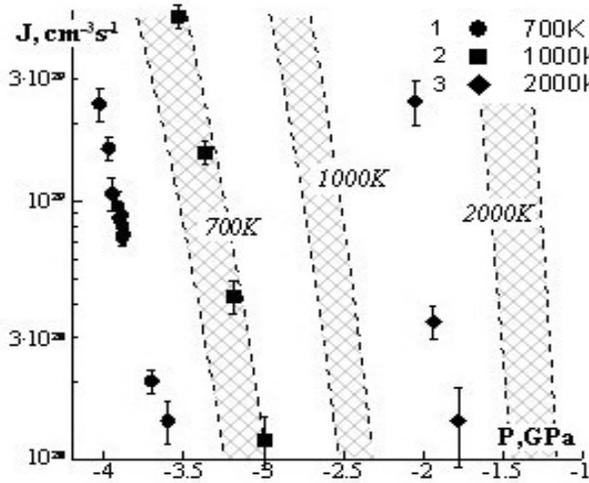


Figure 4. Pressure P dependences of cavitation frequency J along three isotherms: (1) 700, (2) 1000, and (3) 2000 K. Calculation results (solid circles) are given with errors corresponding to the error in mean lifetime determination. The dashed lines are the boundaries of the J - P plane regions corresponding to calculations according to [5] for the temperatures specified above taking into account errors in surface tension values σ for liquid lead.

The rate of a spontaneous phase transition is usually characterized by the mean number of critical nuclei formed in unit volume per unit time, that is, by the cavitation frequency J . In this work, the cavitation frequency was calculated as $J = 1/(\langle\tau\rangle V)$, $\langle\tau\rangle$ is the mean lifetime, V is the simulation box volume. The calculation results are shown in Fig. 4. The calculation results are interesting to compare with classic nucleation theory predictions. In a simple approximation [5], the calculation results qualitatively reproduce correctly the classic nucleation theory estimates, but quantitative agreement worsens as the temperature increases. This difference can be interpreted as systematic lowering of the work ΔG of critical nucleus formation in the approach [5]. The discrepancy between theory and calculation results can be decreased by including the dependence of surface tension on surface curvature.

IV. CONCLUSIONS

Bubble formation in liquid metals (Li, Pb) was studied by MD simulation method by employing many-body EAM-potentials. Six cavity sizes with the radii of $r_{cav} = 10-30\text{\AA}$ were modeled at the density of 0.480 g/cm^3 and at various temperatures below the binodal curve on the phase diagram of the liquid metal. The radial densities, normal and tangential pressure tensors, surface tensions and free energy barrier of small cavities in liquid lithium were calculated at various temperatures. Our simulations have confirmed the existence of the critical radius of the cavity in liquid metal for the first time. The cavity formation in liquid Li complies well with the predictions of the CNT. However, the surface tensions obtained by MD simulations are higher than those predicted by CNT for a flat surface. 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.

The MD method with the realistic interatomic potential for Pb was deployed to calculate the homogeneous cavitation rate pressure dependence in liquid lead under negative pressure near the liquid spinodal. The results of MD simulations are not in agreement with the simple classic nucleation theory approach. At the moment it is not clear if this discrepancy can be attributed to the shortcomings of the potential or the kinetic model deployed. However the method presented gives the possibility of the direct calculation of the cavitation rate. Currently similar calculations are being carried out for liquid Li and Pb-Li alloy under negative pressures.

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