

Nucleation and the spall strength of liquid metals

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Abstract. This article presents calculation of the nucleation rate for liquid metals (Al, Fe, Mo) based on molecular dynamic simulation for embedded atom method (EAM) potentials. The dependence of nucleation rate on pressure and temperature could be approximated accurately in the form of classical nucleation theory taking into account surface tension dependency on pore radius $\sigma = \sigma_0 / (1 + 2\delta/r)$, where σ —surface tension, δ —the Tolman length. Basing on the results of the calculations, we have developed a model allowing calculating the spall strength of liquid metals under tension using such parameters as surface tension, viscosity, which could be measured experimentally. The obtained results for Mo and Al are consistent with experimental data and direct MD calculations at strain rates approx. 10^{10} – 10^{11} s^{−1}.

1. Introduction

The possibility of nanostructuring of surfaces under the influence of sub-picosecond laser pulses is studied intensively. In particular, in experiments on irradiation of aluminium [1, 2] simple nanostructures were obtained which looks like clusters consisting of annular or single crater, linear single- or two-dimensional surface nanogrids with ablative grooves or ridges instead of grooves, respectively. It was observed that this structures were quasi-periodic and an interval between spikes remained constant, which was interpreted as a result of instability in the spinodal decomposition of melt tension. However, the mechanisms of formation of nanostructures are still poorly understood.

Thus, the interest in metals at high negative pressures is associated with the phenomenon of ablation caused by the action of subpicosecond laser pulses to the surface of the metal. The process of laser ablation involves entrainment of matter from the surface of the sample and the formation of the nanocraters. In molecular dynamics [3, 4] and hydrodynamic [4] calculations of the process the following steps are observed: melting of the material, melt stretching, the emergence and growth of cavities in the metastable liquid phase.

Attempts to define the limit tensile strength in the liquid metals at high strain rates on the basis of experiments with subpicosecond laser pulses are presented in [4]. Also in the paper [5] spall strength was defined for Pb and Sn on the basis of experiments with shock-wave loading. The value of tensile strength is evaluated from the velocity profile of the contact boundary between the sample and a barrier made of material with lower dynamic impedance.

Ablation and surface structuring are inseparably related with the processes of nucleation in the metastable states and in many respects determine the ultimate strength. Therefore, in this paper, characteristics of stretched molten metastable states and the processes attendant to the



cavity appearance are analyzed for aluminum, iron and molybdenum basing on the molecular dynamics simulation. As well, a model to determine the tensile strength for the metal melts was build.

This work could be divided into several sections. The first section is devoted to determination the value of the nucleation rate for the molten metal from the molecular dynamics simulation. The obtained results were approximated in form of classical nucleation theory. Also dependencies of surface tension on the cavity radius derived from MD simulations and from approximations of data on nucleation rate are compared. The second section discusses ways of determination the tensile strength of the melt metal.

All potentials involved are of the embedded atom method type (EAM-potential). By now there are performed many works devoted to the description of processes of nucleation in different phases of model systems described by the Lennard-Jones 6-12 [6]. Article [7] shows a comparison of the phase diagrams of the two systems, normalized to the critical parameters, one of which is described by the Lennard-Jones 6-12, and the other—EAM-potential for aluminum. From this comparison, it is evident that not all the phase states of the systems described by EAM-potentials may be obtained using Lennard-Jones potential. This suggests the need for a model to determine the tensile strength for the EAM-potentials directly.

All calculations were performed using the software package for atomistic simulations LAMMPS.

2. The calculation of the nucleation rate

In many works the classical nucleation theory (CNT) is applied for analysis of the lifetimes of stretched liquids. But as will be shown below, the results of the MD simulations could not be accurately described with the formulas in the form presented in the work of Deryagin [8, 9]. In the present research it is shown which correction should be taken into account to reach an agreement of the theory with the results of molecular dynamics simulations on the example of several potentials for aluminum [10, 11], iron [12] and molybdenum [13]. Chosen potentials for metals are selected so that the model systems had different surface tension, since this value substantially affects the nucleation rate and dynamic strength. Thus, the largest value of surface tension (molybdenum [13]) differs from the smallest (aluminum) at about 4-5 times at the same temperature.

Before carrying out further calculations and collecting statistics, the value of the surface tension was determined on the flat interface for each of the potentials. For this purpose a free surface was created in equilibrium state of the molten metal. Then the normal and tangential components of the stress tensor were calculated [14]. The value was obtained by the formula:

$$\sigma_0 = \frac{1}{2} \int_0^L [p_n(z) - p_t(z)] dz,$$

where L —length of simulation box along the z -axis (here normal to the dividing surface), p_n and p_t —the normal and tangential components respectively. Consequently, temperature dependence of surface tension for Mo was obtained [13] (figure 1).

The next step was necessary to collect statistics on the lifetimes of metastable systems. For this aim hydrostatic stretching of the molten metal was performed at a fixed temperature by rescaling coordinates of the particles and the size of the simulation box. On the basis of this simulation several points were chosen corresponding to a large negative pressure with parameters close to the point of fracture. From 30 to 100 calculations were carried out for each set of parameters. To generate different trajectories, an integration step was varied slightly. Then, it was counted how many systems are not disintegrated before a certain time t . The obtained data were approximated by the formula:

$$N_s = N_{s0} \exp(-t/\tau), \quad (1)$$

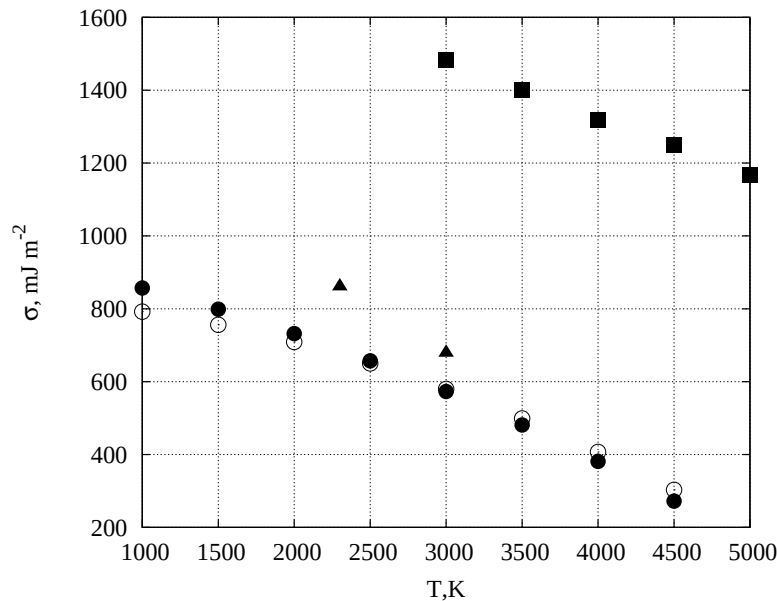


Figure 1. Temperature dependence of surface tension for Mo [13] (squares), Fe [12] (triangles), Al [11] (filled circles), Al [10]—(hollow circles) based on MD calculations.

where N_s —number of systems, τ —characteristic lifetime (figure 2). The nucleation rate was found from simple relation with characteristic lifetime:

$$J = (N\tau)^{-1},$$

where N —number of atoms in simulation box. This method was proposed in [15].

The dependencies of nucleation rate on temperature and pressure are presented in figure 3 for iron and molybdenum and 3 and 4 for aluminum, as described by EAM potentials [12] and [13]. Calculations of the nucleation rate and surface tension were carried out in the framework of a model system. It should be mentioned that some model systems did not comply fully real one, but there was no aim to use the potentials that accurately describe the actual metal melts. In this case, it is important to check the applicability of a given theory. For example, aluminum potentials [10, 11] fairly well reproduce the surface tension (close to the experimental values). But in range up to 2000 K aluminum potential [10] slightly lowers the surface tension, which affected on the nucleation rate dependence on temperature and pressure—the nucleation rate is higher for the potential [10] compared with the potential [11]. For 3000 K, where surface tension for these two potentials are the same, the values of the nucleation rates are equal. The potential [12] for iron lowers the surface tension in comparison with experiment. In this case, one should expect overstatement of the nucleation rate and understatement of tensile strength in comparison with the real system.

One can mention, that the authors refer to [9] using the formulae of classical nucleation theory, where the pre-exponential factor for the low-pressure region contains a factor p_{cr} —pressure of the critical size cavity. But for large negative pressures, the pressure within the nucleus is zero, since there are no particles inside. Using of pre-exponential factor in form [9] leads to incorrect results. This problem has been corrected in work [8]: the distribution function of the bubbles takes into account the pressure distribution.

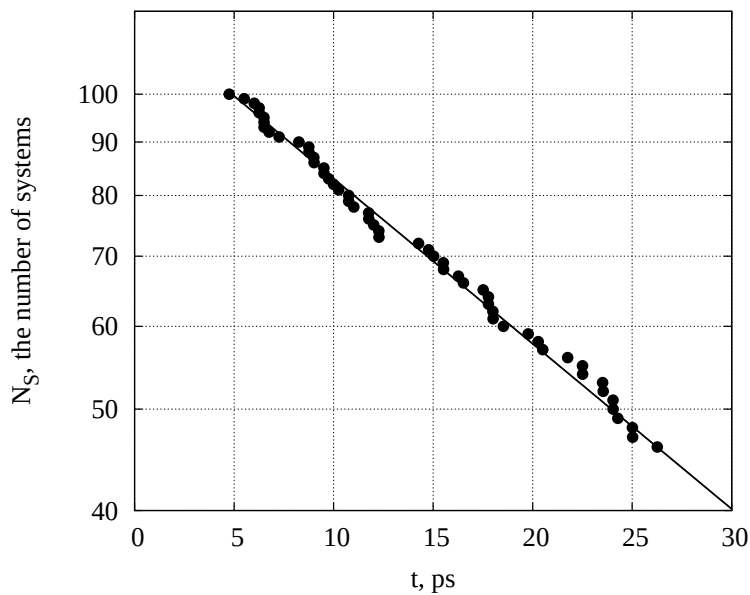


Figure 2. Distribution of MD trajectories over lifetime for molybdenum: approximation in the form (1) is shown by line; $T = 3000$ K, $P = -8.6$ GPa.

For data approximation the following formulae given in [8] were used:

$$J = 4 \frac{\sigma}{\eta} \sqrt{\frac{\sigma}{k_b T}} \exp \left\{ \frac{-W}{k_b T} \right\}, \quad W = \frac{16\pi\sigma^3}{3p^2}, \quad (2)$$

where p —pressure in metastable liquid phase, σ —surface tension, η —viscosity, W —energy of bubble formation. As one can see from comparison of the original MD data the approximations presented on figures 3–5, this method isn't suitable for describing the results of MD simulation. It means, that some correction should be added for better correspondence. The correction for surface tension dependence on cavity radius was chosen to improve the agreement:

$$\sigma = \sigma_0 / \left(1 + \frac{2\delta}{r} \right), \quad (3)$$

where σ_0 —surface tension on flat interface, δ —The Tolman length, r —radius of cavity. This correction affects essentially energy of the cavity formation, that leads to changing the value of the nucleation rate. By varying the Tolman length, one can achieve an agreement of the results of MD simulations with CNT (figures 3–5). The slope of the approximating curve is determined by the dependence of the energy of critical size cavity formation on the pressure and temperature:

$$W^* = 4\pi r^{*2} \sigma^* - 4/3\pi r^{*3} |p^*|,$$

where W^* —energy of critical size bubble formation, r^* —critical radius, p^* —pressure of parent phase, corresponding to critical size of bubble r^* . The difference of the slopes $\log(J) (1/p^2)$ is determined by the difference of energy formation function derivative with respect to pressure, namely by the ratio $C = 3p\delta/(2\sigma_0)$. The smaller the value of C in comparison with one is, the smaller the slope varies. For example, for Mo slopes differ by 1.16 times and $C = 0.16$ ($T = 3000$ K); for Al [13] ($T = 1000$ K) and for Fe ($T = 2300$ K) slopes differ by 1.3 times at

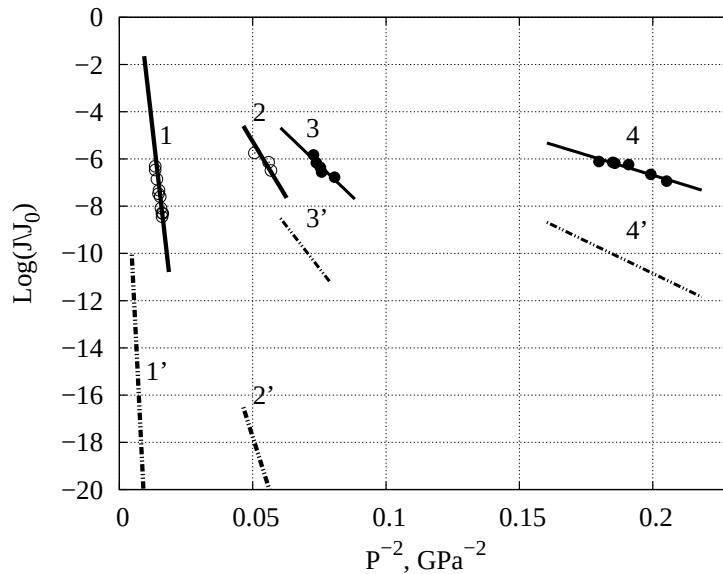


Figure 3. Dependence of nucleation rate on pressure and temperature: dots correspond to the MD simulation of molybdenum (hollow circles) and iron (filled circles); 1, 1'— $T = 3000$ K (Mo); 2, 2'— $T = 5000$ K (Mo); 3, 3'— $T = 2300$ K (Fe); 4, 4'— $T = 3000$ K (Fe); dashed lines (1', 2', 3', 4')—the approximation in form of CNT; solid lines (1, 2, 3, 4)—the approximation in form of CNT taking into account the Tolman correction.

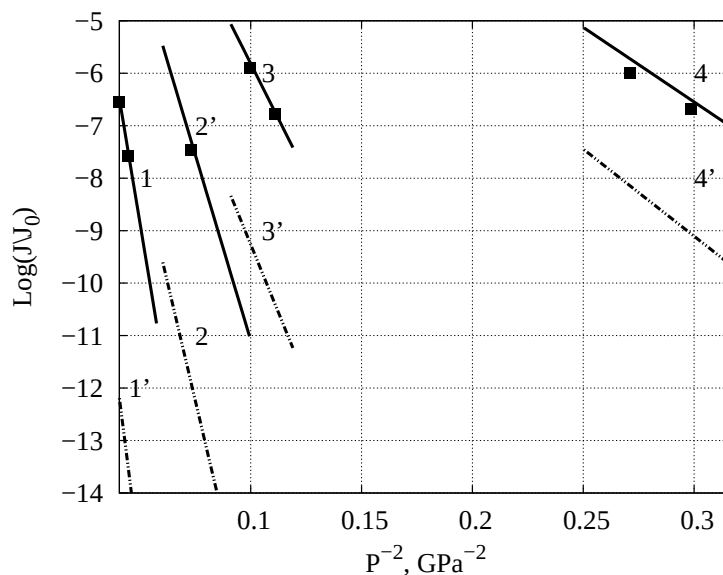


Figure 4. Dependence of nucleation rate on pressure and temperature: dots correspond to the MD simulation of aluminum [10]; 1, 1'— $T = 1000$ K; 2, 2'— $T = 1500$ K; 3, 3'— $T = 2000$ K; 4, 4'— $T = 3000$ K; dashed lines (1', 2', 3', 4')—the approximation in form of CNT; solid lines (1, 2, 3, 4)—the approximation in form of CNT taking into account the Tolman correction.

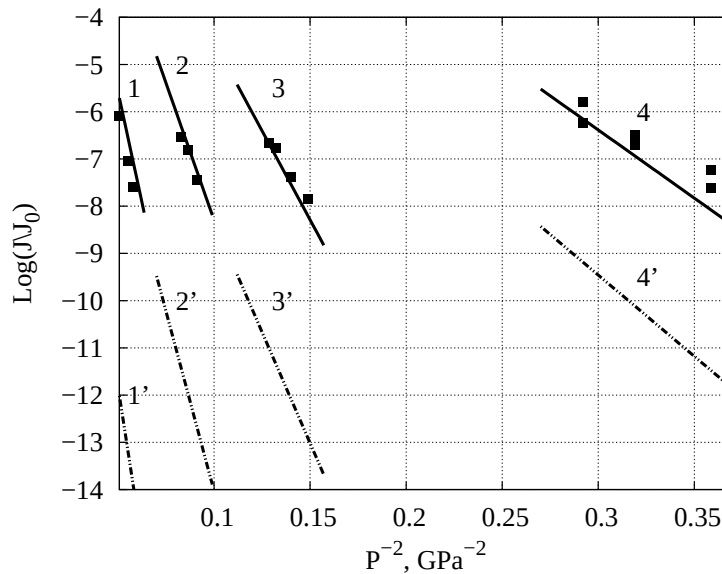


Figure 5. Dependence of nucleation rate on pressure and temperature: dots correspond to the MD simulation of aluminum [12]; 1, 1'— $T = 1000$ K; 2, 2'— $T = 1500$ K; 3, 3'— $T = 2000$ K; 4, 4'— $T = 3000$ K; dashed lines (1', 2', 3', 4')—the approximation in form of CNT; solid lines (1, 2, 3, 4)—the approximation in form of CNT taking into account the Tolman correction.

$C = 0.27$. Therefore, the slope of approximation lines in different forms (with correction and without) changes slightly.

In this paper, the Tolman length was obtained from approximations of MD results: Al [16]— 0.127 Å, Al [11]— 0.32 Å, Al [10]— 0.36 Å, Fe— 0.42 Å, Mo— 0.2 Å (at $T = 3000$ K), 0.4 Å (at $T = 5000$ K)

It was interesting to reproduce the dependence of the surface tension on the bubble radius similar to (3). The following algorithm was used for this simulation. In the metastable system several atoms were removed in a sphere within a radius of few angstroms. Immediately after this operation, the number of atoms was calculated on the free surface of the created pore. Atom was considered to belong to free surface if it is located near the investigated pore and the volume of respective Voronoi cell was more than a certain threshold value (figure 6).

The number of atoms in the surface was controlled by changing the size of the simulation box in order to maintain it on the initial value. Thus the pore radius remained constant for several thousand timesteps. The calculation of this dependence is complicated by the fact that the system is in an unstable equilibrium, and this balance is easily disrupted. From the assumption that the pores stated in mechanical equilibrium with the environment, where the value of surface tension is evaluated from the radius and pressure p^* in the liquid phase:

$$\sigma = p^* r^* / 2.$$

The results of approximation and simulation were compared. It is seen that the dependences are consistent within the uncertainty of the calculations (figure 7).

3. The model for determination of the spall strength

Let us turn to a discussion of a model, which allows determining the tensile strength of the melt metal. This model is described by the following equations. The change of the whole volume (here

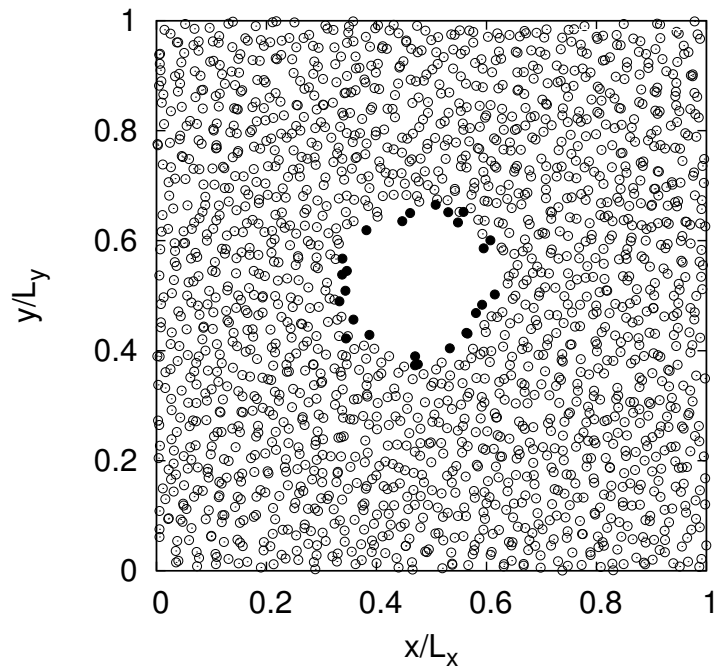


Figure 6. The cut of liquid Mo perpendicular to the z axis: $T = 5000$ K, thickness of the layer is $0.1L_z$; filled dots—atoms of the free surface; empty dots—atoms in volume.

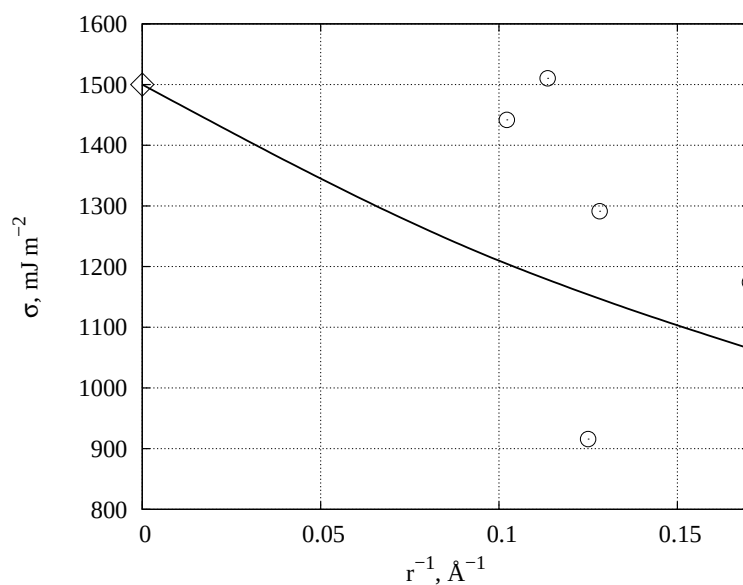


Figure 7. The dependence of surface tension on pore radius for liquid molybdenum: dots show the results of MD calculations (circles—for appropriate critical radii; diamonds—for the flat interface); curve corresponds to surface tension dependence on radius in form (3), where the Tolman length was taken from the data fitting.

we presume that it changes with a fixed strain rate) combines the increments of the condensed phase volume and the cavity volume:

$$\frac{dV_c}{dt} = \frac{dV}{dt} - \frac{dV_{\text{cav}}}{dt}, \quad \frac{dV}{dt} = V\dot{\varepsilon},$$

$\dot{\varepsilon}$ —strain rate, V_c —the condensed phase volume, V —the whole volume, V_{cav} —the net volume of the cavities.

The increase of the void volume is defined by the growth of each cavity separately. Thus the following relation takes place:

$$\frac{dV_{\text{cav}}}{dt} = \int_0^t 4\pi R^2(t_0, t) \dot{R}(t_0, t) \dot{n}(t_0) dt_0 + \frac{4}{3}\pi R^3(t, t) \dot{n}(t),$$

$$V_{\text{cav}}(t) = \int_0^t \frac{4}{3}\pi R^3(t_0, t) \dot{n}(t_0) dt_0.$$

Here $R(t_0, t)$ is the radius of cavity appeared at t_0 ; t is the current time. The rate of bubble appearance could be found from:

$$\dot{n}(t) = J(t)N_V,$$

J —the nucleation rate per a particle per time unit, N_V —the number of particles within the volume V . The growth of pores is taken into account in the form of the Rayleigh–Plesset model:

$$\frac{4\eta\dot{R}(t_0, t)}{\rho(t)R(t_0, t)} + \frac{2\sigma(t)}{\rho(t)R(t_0, t)} + \frac{p(t)}{\rho(t)} + R(t_0, t)\ddot{R}(t_0, t) + \frac{3}{2}\dot{R}^2(t_0, t) = 0,$$

where η —viscosity, ρ —density, σ —surface tension, p —pressure. The first three terms determine growth caused by viscosity, surface tension and tensile stress respectively.

This set of integral-differential equations was solved numerically. At the beginning of each timestep the volume of condensed phase is calculated $V_{\text{cav}}(t + \Delta t)$. It was necessary to know $V_{\text{cav}}(t)$, $R(t_0, t)$, $R(t_0, t - \Delta t)$ for all $t_0 \leq t$. After that $R(t_0, t + \Delta t)$ was calculated for all $t_0 \leq t$. For this aim V_{cav} , $p(t)$, $\rho(t)$, $R(t_0, t)$ and $R(t_0, t - \Delta t)$ should be defined. On the next iteration $p(t + \Delta t)$, $\rho(t + \Delta t)$, $R^*(t + \Delta t)$, $J(t + \Delta t)$, $\dot{n}(t + \Delta t)$ are calculated, expressed explicitly in terms of $V_{\text{cav}}(t + \Delta t)$, where $R^*(t + \Delta t)$ —the critical radius at the moment $t + \Delta t$.

Stretching is approximately considered under isothermal conditions, the isotherm is calculated from the molecular dynamics. To determine the nucleation rate formula (2) was used where the surface tension depends on the radius of the pores (3). The value of viscosity is not calculated from the MD, and was taken so that hydrostatic tension diagrams obtained from MD coincide with the corresponding diagrams obtained from this model under the same parameters (temperature, strain rate) (see figure 8). Thus, analytical diagrams were obtained at different strain rates for molybdenum at 3000 K (figure 9). The model agrees well with the results of the MD simulation. This method allows to determine the strength of the metal melt knowing only the surface tension, viscosity, and the equation of state for the substance.

Also the obtained results given by represented model, were compared with work [4] for Al at $T = 2500$ K, $\dot{\varepsilon} = 10^9 \text{s}^{-1}$: 3 GPa (model) and 2.5 ± 0.5 GPa (experiment) respectively.

If the value of strength without amendment is given, the cavity radius dependence of the surface tension could be taken into account using this formula:

$$p = \frac{p_0}{1 + \delta p_0 / \sigma_0}, \quad (4)$$

where σ_0 —surface tension of the flat interface, p_0 —pressure without consideration a radius dependence of surface tension, δ —the Tolman length. This estimation was found in case of slight difference between p and p_0 and rupture of the substance occurred at definite value of the nucleation rate $J(p) = J(p_0)$. The value of dynamic strength given by the formula (4) and the model described in this section do not differ by more than 20%.

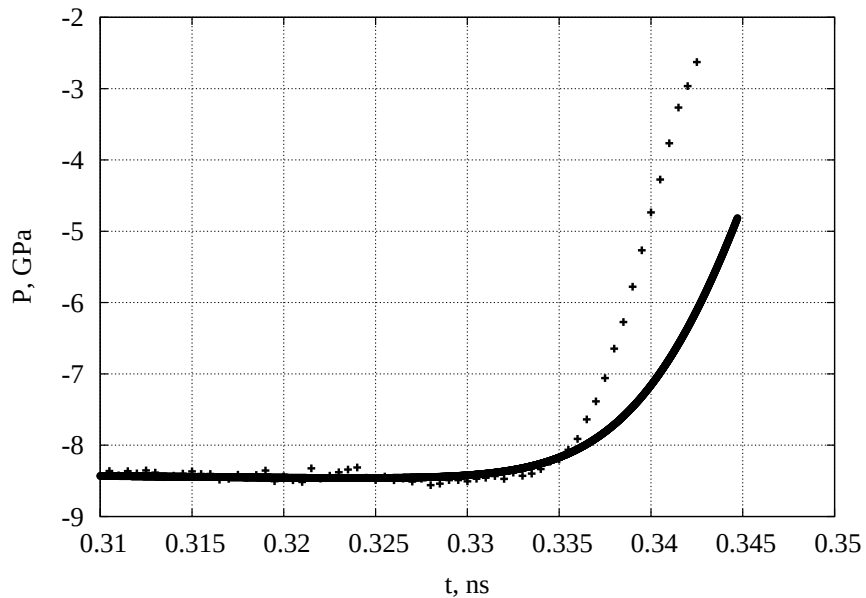


Figure 8. The hydrostatic tension diagrams for molybdenum ($T = 3000\text{ K}$, $\dot{\epsilon} = 3.11 \times 10^7\text{ s}^{-1}$): solid line—the results of calculation based on model for determination of dynamic spall strength for liquid metals; dots—MD simulation of hydrostatic tension at a constant temperature.

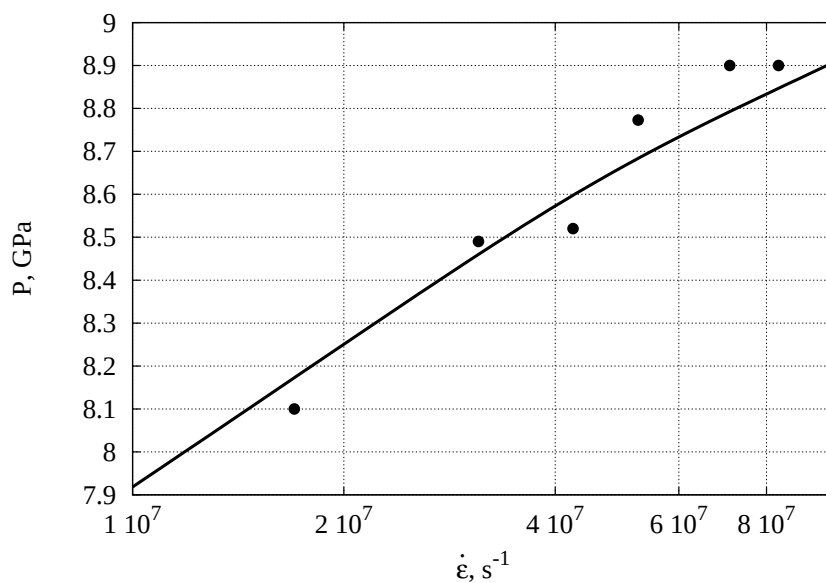


Figure 9. The dependence of the spall strength upon the strain rate for liquid molybdenum at $T = 3000\text{ K}$: curve shows analytical dependence; dots—the results of MD.

4. Conclusion

In frame of this work a molecular dynamic simulation of cavity growth processes was conducted for metastable liquid Al, Fe and Mo at high negative pressure. From the statistics on systems lifetime the nucleation rate was evaluated as a function of pressure at several definite

temperatures. This data was approximated in a form of classical nucleation theory with the correction for dependence of surface tension on cavity radius. In this way it was clarified that the data of MD simulation could be described to a high precision by the CNT with the Tolman correction. The value of the Tolman length was obtained from the approximation for each of the five interatomic potentials. The Tolman length correspond to independent estimation basing on MD calculations and fall in the range of 0.172–0.4 Å. The dependence of Tolman length on the interatomic distance is not observed.

The model for determination of spall strength was developed. Basing on obtained dependences of the nucleation rate on temperature and pressure and equation of state, the dependence of spall strength on strain rate was calculated for Al, Mo.

Also the represented model and the results of MD simulation were compared and found to be in good agreement. Moreover, it was shown, that formula (4) gives right correction to the value of the spall strength without consideration the cavity radius dependence of surface tension, which is also consistent with the developed model.

Thereby, the Classical nucleation theory with Tolman correction allows to describe the nucleation rate and the spall strength for liquid metals with a high precision lean on experimental data such as surface tension and viscosity and data on the equation of state for certain substance.

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