MATHEMATICA MONTISNIGRI
Vol XLIII (2018)

ON CRITICAL PARAMETERS MANIFESTATIONS DURING NANOSECOND LASER ABLATION OF METALS

A.A. SAMOKHIN[1], V.I. MAZHUKIN[2,3], M.M. DEMIN[2], A.V. SHAPRANOV[2,3], A.E. ZUBKO[1]

[1] Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia
e-mail: asam40@mail.ru, web page: http://www.gpi.ru/eng/

[2] Keldysh Institute of Applied Mathematics, RAS, Moscow, Russia
e-mail: vim@modhef.ru, web page: http://www.keldysh.ru/

[3] National Research Nuclear University "MEPhI", Moscow, Russia
web page: https://mephi.ru/eng/

Summary. Density fluctuation behavior during nanosecond laser ablation of thin (450 nm) liquid Al film is studied on the basis of previously reported molecular-dynamic simulation of this process induced by constant intensity G laser irradiation. It is shown that at G = 110 MW/cm^2 density fluctuation distribution across the expanding film has a maximum which location approximately coincides with critical density position in expanding plume.

1 INTRODUCTION

Despite several decades of nanosecond laser ablation investigations some important fundamental aspects remain unclarified yet which concern, among others, to the problem of non-equilibrium behavior of irradiated matter in two-phase liquid-vapor region. Such studies are necessary *e.g.* for obtaining information on metal critical parameters most of which can not be determined in quasi-equilibrium experiments. The problem of insufficient information on metal critical parameters is regularly mentioned in current scientific literature as it is seen from citation given below.

[1] “Knowledge of the critical parameters of metals is of fundamental value for estimating their ultimate characteristics in modern technical devices. From the standpoint of general physics, the transition from a gaseous state to liquid metal is also of considerable interest. Experimental investigations of the vapor–liquid (insulator–metal) phase transition and attempts to determine the critical parameters of this transition were initiated as long ago as in the mid-20th century. However, the parameters of critical points were determined only for alkali metals and mercury, while the study of other metals encountered significant difficulties. The transition temperature for most metals turned out to be on the order of one electronvolt or higher, which excluded the possibility of usual stationary measurements. As a result, data on the critical parameters and binodals for most metals are still missing.”

[2] “The onset of the phase explosion can be expected at ~10 % below the critical temperature [69–71] and the calculated values are consistent with experimental value of the critical temperature of Al ranging from 4,700 to 9,500 K [77,78], with an average value of 6,700 K “recommended” in a recent review [78].”

[3] “We make some predictions with respect to the critical parameters of Al, Cu and W (critical parameters of which lie in the phase domain still inaccessible for experiment) on the

2010 Mathematics Subject Classification: 82D15, 82D35, 82D80.
Key words and Phrases: Molecular dynamics, nanosecond laser ablation, explosive boiling, critical point.

basis of the correspondence between the critical point and unit compressibility line (Zeno line) positions in the temperature–density plane using two new similarity relations.”

[4] “As stated above, the coordinates of the critical points have been reliably determined for only two metals, Cs and Hg. For Cs, T_c = 1938 K, ρ_c = 0.39 g/cm^3, and P_c = 94 atm [39]. In an earlier work, [40], also very close values were obtained, viz., Tc = 1924 K, ρ_c = 0.379 g/cm^3, and P_c = 92.5 atm. Since the 1960s, numerous works have been carried out for mercury [41, 42]. Therefore, its critical properties have been measured more accurately and the coordinates of the critical point are T_c =1750 K, ρ_c = 5.8 g/cm^3, and P_c = 1650 atm. Determination of the critical point for other metals is a complex task because this point lies at too high temperatures where the binodal is very difficult to measure so far. … The situation about all other metals, non-alkali and other than mercury, is even more difficult since reliable static experiments with them are carried out at temperatures of ~2000 K at most [43]. … At higher temperature only dynamic measurements can be carried out, which do not allow reliable determination of the phase transition [44, 45] so far. Therefore, as a rule, there are data on the nonalkali metals only in the liquid’s low-temperature domain far from the potential critical point.”

Properties of different dielectric liquids in near-critical region were investigated for many years both theoretically and experimentally. In particular in the last decades space density fluctuation behavior for liquids in equilibrium conditions was considered in many papers with the help of molecular dynamic modeling (MDM) and thermodynamic calculation (see e.g. [5,6] and refs therein). However nonequilibrium fluctuation behavior which is pertinent to laser ablation processes remains far less investigated.

Space density fluctuation growth before an explosive boiling of radiation heated thin (~50nm) liquid film was demonstrated with the help of molecular dynamic modeling in [7].

Рост пространственных флуктуаций плотности перед взрывным вскипанием тонкой жидкой пленки (~50 нм), нагреваемой лазерным излучением с постоянной интенсивностью, был продемонстрирован с помощью молекулярной динамики (МД) в [7].

In our further investigations [8-12] non-equilibrium pressure P, temperature T and density ρ behavior during ablation of thin (450 nm) liquid Al film under the action of nanosecond laser pulses was considered in the framework of MDM for different constant intensities G = 33, 44, 66 and 110 MW/cm^2. It was found that the recoil pressure demonstrates several pulsations due to repeating explosive boiling processes which are clearly visible at G = 33 and 44 MW/cm^2 and vanishes at higher intensities when mean recoil pressure exceeds approximately the value 0.6 compared with critical pressure P_c = 1400 bar in the model used. In the present paper density fluctuations behavior is extracted from MDM results [12] for the intensity 110 MW/cm^2 which provides realization of transcritical ablation regime.

2 STATEMENT OF THE PROBLEM

Physical and mathematical statement of the laser ablation problem for thin liquid metal (Al) film irradiated with nanosecond laser pulses of different constant intensities is described in [12]. MDM results for the film behavior are obtained in 3D volume with infinite dimension in X, Y directions where periodical boundary conditions are used (period L_x = L_y = 37.3 nm) while in Z direcrion the computation domain length is L_z = 2 μm with non-reflecting boundary condition. The value of L_z is chosen to describe properly considered ablation process of the film with initial thickness H_z = 449 nm, temperature T_0 = 6340 K, density ρ_0 = 1.29 g/cm^3 and pressure P_0 = 0 at t = 0. The total number of particles taken into account is $N_{total} = 17.9\times10^6$ atoms.

Density fluctuations $\delta\rho$ in MDM are usually calculated in accordance with the relation [5, 6]

$$\delta\rho^2 = \langle\Delta\rho^2\rangle = \langle(\rho - \langle\rho\rangle)^2\rangle = \langle\rho^2\rangle - \langle\rho\rangle^2 \quad (1)$$

where $\rho(z,t)$ – density distribution which is obtained with the help of initial averaging 3D particle configuration over the volume $V_e = L_x\times L_y\times\Delta Z_e$ with ΔZ_e = 1 nm and time interval Δt = 5 ps. The values of ΔZ_e and Δt are also a step of the MDM results presentation. The time dependence in $\rho(z,t)$ will not be explicitly indicated further. Angle brackets $\langle\ldots\rangle$ denote spatial averaging over volume $V_m = L_x\times L_y\times\Delta Z_m$, where $\Delta Z_m >> \Delta Z_e$.

In the case of a spatially homogeneous system, $\langle\rho\rangle$ does not depend on the z coordinate, which is a necessary condition for the applicability of the last equality in formula (1). Under considered laser ablation conditions $\langle\rho\rangle = \rho_m(z)$ is z-dependent.

$$\delta\rho^2(z) = \langle\Delta\rho^2\rangle = \langle(\rho - \rho_m)^2\rangle \quad (2)$$

$$\rho_m(z) = \frac{1}{\Delta Z_m}\int_{z-\Delta Z_m/2}^{z+\Delta Z_m/2} \rho(z')\,dz' = \langle\rho\rangle \quad (3)$$

The averaging procedure $\langle\ldots\rangle$ in (2) and further is determined by the equation (3) with the averaging size ΔZ_m = 15 nm. Variation of ΔZ_m in the range of 15–20 nm affect but little the calculation results the fluctuations magnitude $\delta\rho$.

Figure 1 shows schematically the total computational domain $V_\Sigma = \{L_x\times L_y\times L_z\}$, the subregion $V_l = \{L_x\times L_y\times H_z\}$ of a liquid film irradiated by laser radiation from the right and some positions of a large $V_m = \{L_x\times L_y\times\Delta Z_m\}$ and elementary $V_e = \{L_x\times L_y\times\Delta Z_e\}$ volumes of averaging.

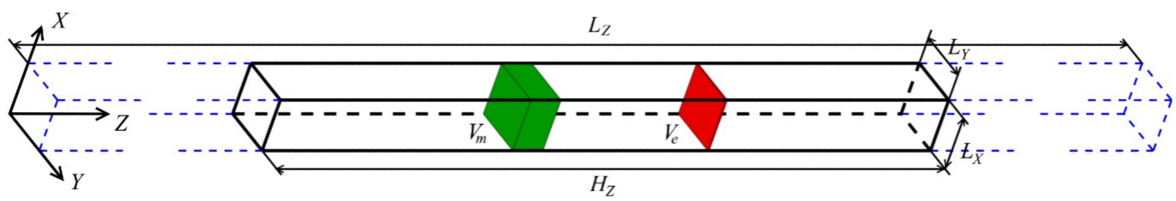

Fig. 1: A diagram of the full computational domain V_Σ used to simulate the ablation processes in a liquid film in the sub-region V_l and some positions of the averaging volumes V_m and V_e.

3 RESULTS AND DISCUSSION

Fig. 2-7 shows calculation results at G = 110 MW/cm^2 for 2D density distribution in X and Y directions together with curves of density $\rho(z)$ and derivative $\langle\partial\rho_m/\partial z\rangle$ (curves 1 and 2), density fluctuations $\langle\delta\rho\rangle$ (increased by factor 35 with respect to the ρ scale) (curves 3), temperature (curves 4), pressure (curves 5) distributions at different times 25, 200, 350, 650, 800, 925 ps, respectively. Additional space averaging $\langle\ldots\rangle$ in density derivative $\langle\partial\rho_m/\partial z\rangle$ and fluctuations $\langle\delta\rho\rangle$ is performed to smooth the curves (curves 2 and 3).

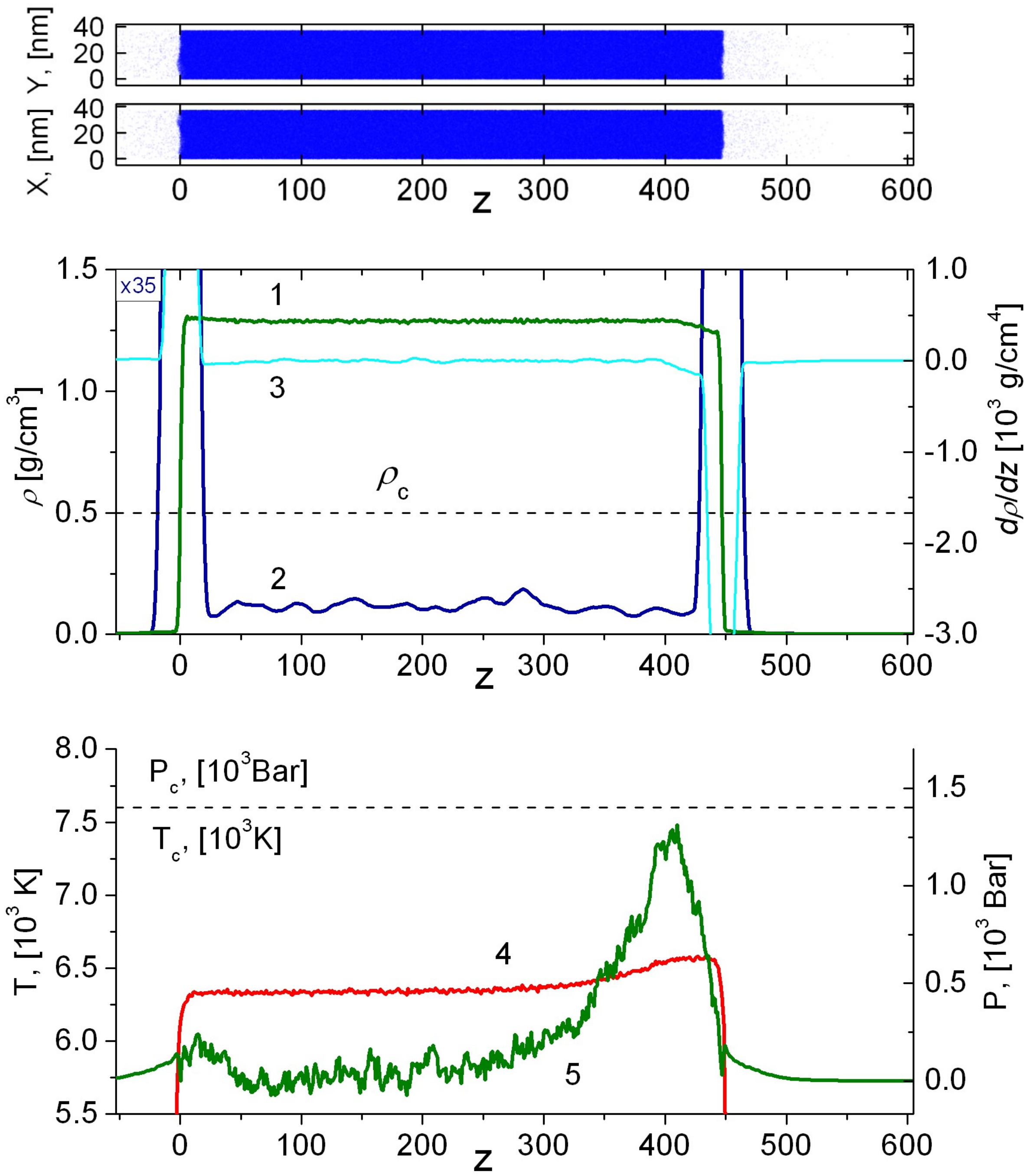

Figure 2: 2D density distribution in planes *Z-X* and *Z-Y* together with curves of density ρ and its derivative $\langle\partial\rho_m/\partial z\rangle$ (curves 1 and 2), density fluctuations $\langle\delta\rho\rangle$ (increased by factor 35 with respect to the ρ scale) (curves 3), temperature T (curves 4), pressure P (curves 5) distributions at t = 25 ps. Dashed lines is the model critical parameters values T_c = 7600 K, P_c = 1400 bar, ρ_c = 0.5 g/cm^3.

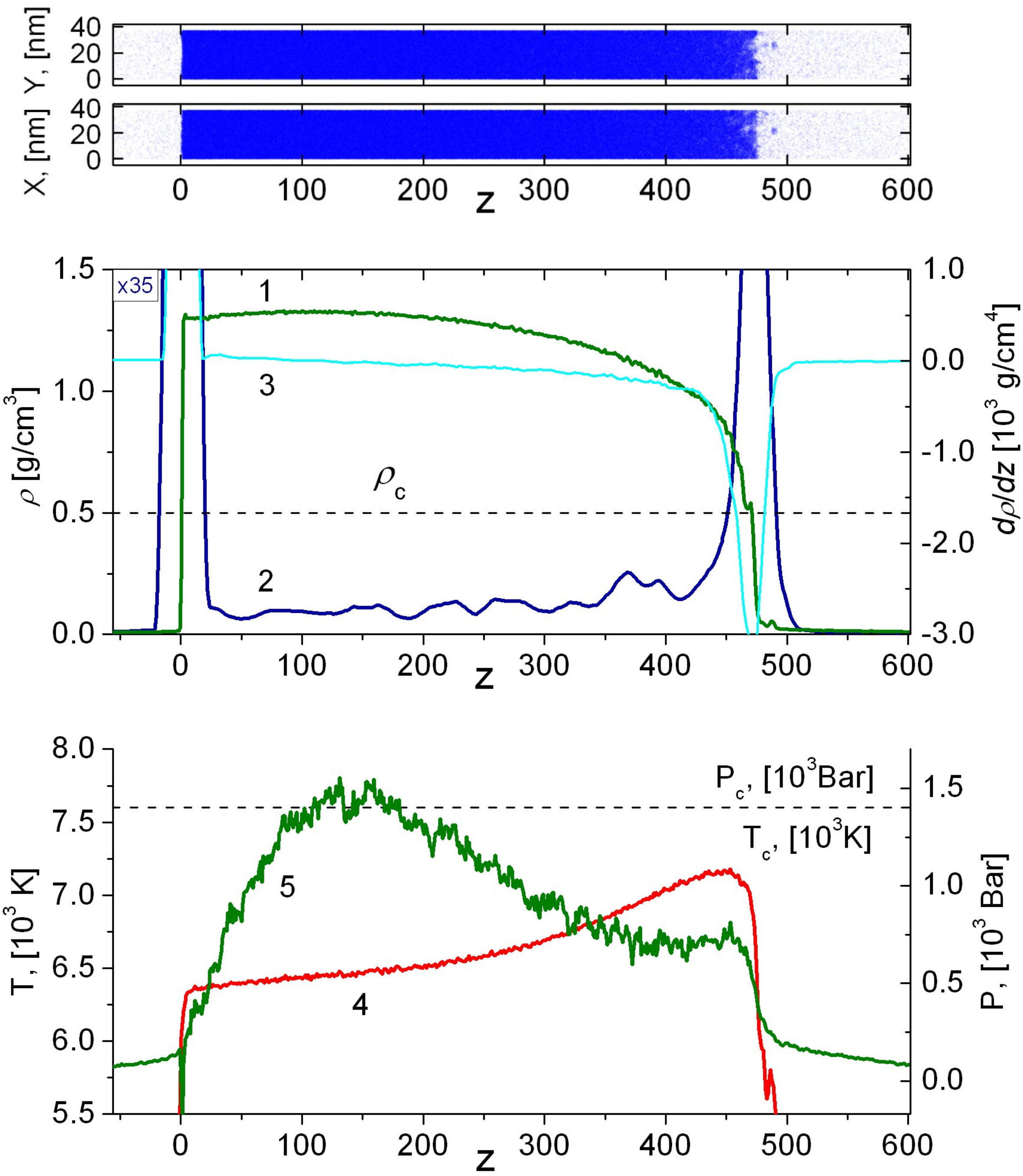

Figure 3: 2D density distribution in planes *Z-X* and *Z-Y* together with curves of density ρ and its derivative $\langle\partial\rho_m/\partial z\rangle$ (curves 1 and 2), density fluctuations $\langle\delta\rho\rangle$ (increased by factor 35 with respect to the ρ scale) (curves 3), temperature *T* (curves 4), pressure *P* (curves 5) distributions at t = 200 ps. Dashed lines is the model critical parameters values T_c = 7600 K, P_c = 1400 bar, ρ_c = 0.5 g/cm^3.

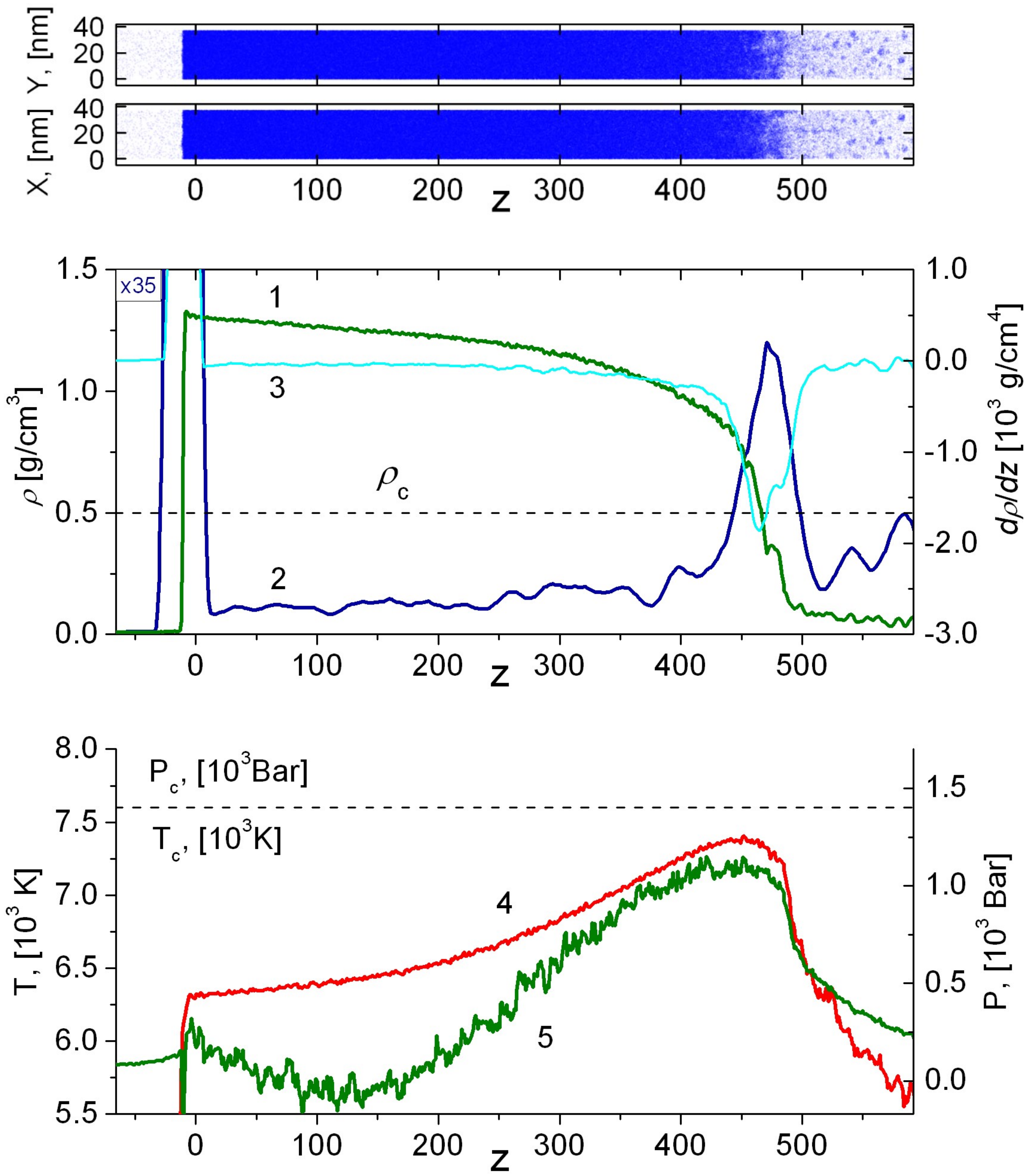

Figure 4: 2D density distribution in planes *Z*-*X* and *Z*-*Y* together with curves of density ρ and its derivative $\langle\partial\rho_m/\partial z\rangle$ (curves 1 and 2), density fluctuations $\langle\delta\rho\rangle$ (increased by factor 35 with respect to the ρ scale) (curves 3), temperature *T* (curves 4), pressure *P* (curves 5) distributions at t = 350 ps. Dashed lines is the model critical parameters values T_c = 7600 K, P_c = 1400 bar, ρ_c = 0.5 g/cm^3.

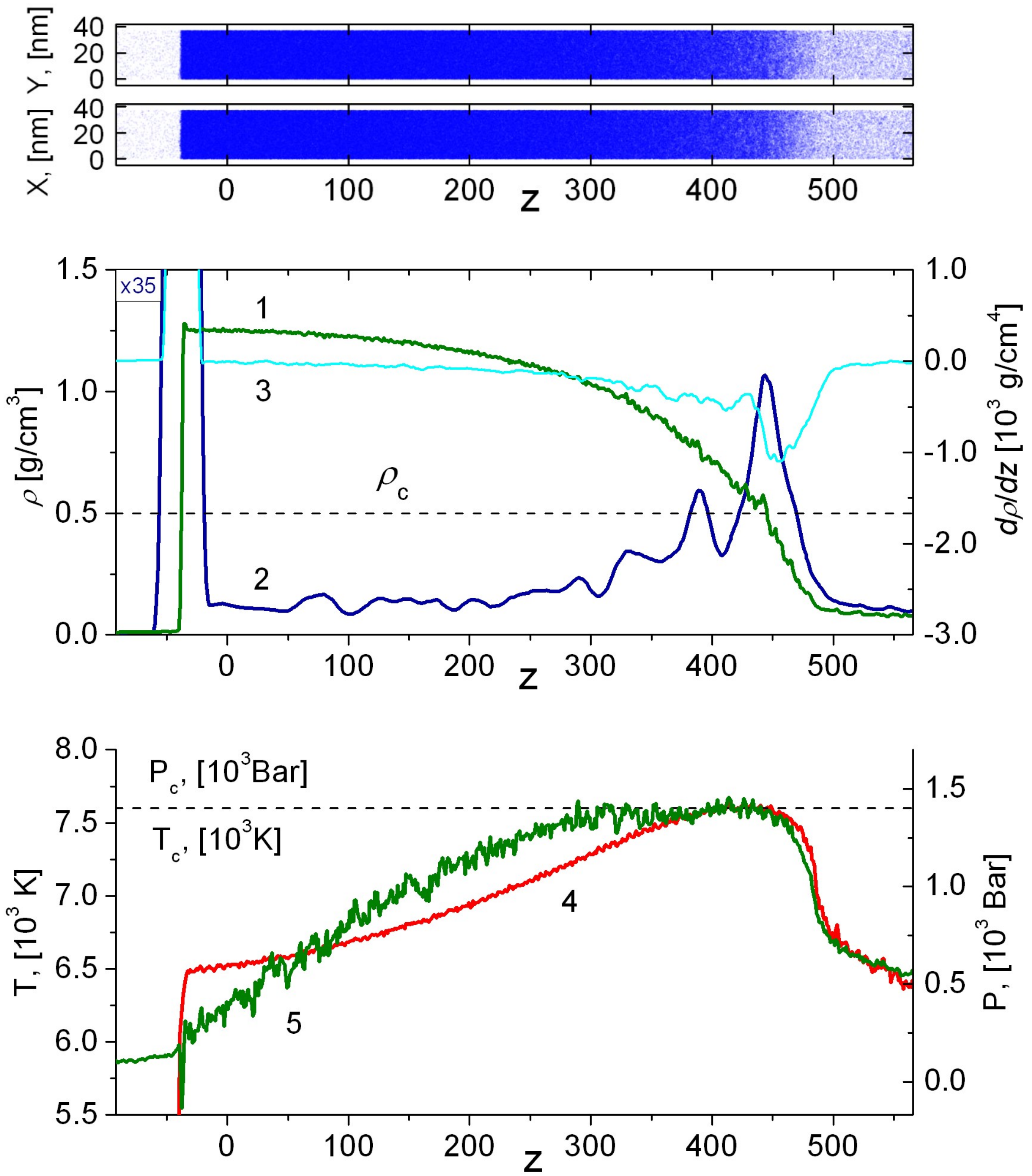

Figure 5: 2D density distribution in planes *Z-X* and *Z-Y* together with curves of density ρ and its derivative $\langle \partial\rho_m/\partial z\rangle$ (curves 1 and 2), density fluctuations $\langle\delta\rho\rangle$ (increased by factor 35 with respect to the ρ scale) (curves 3), temperature *T* (curves 4), pressure *P* (curves 5) distributions at t = 650 ps. Dashed lines is the model critical parameters values T_c = 7600 K, P_c = 1400 bar, ρ_c = 0.5 g/cm^3.

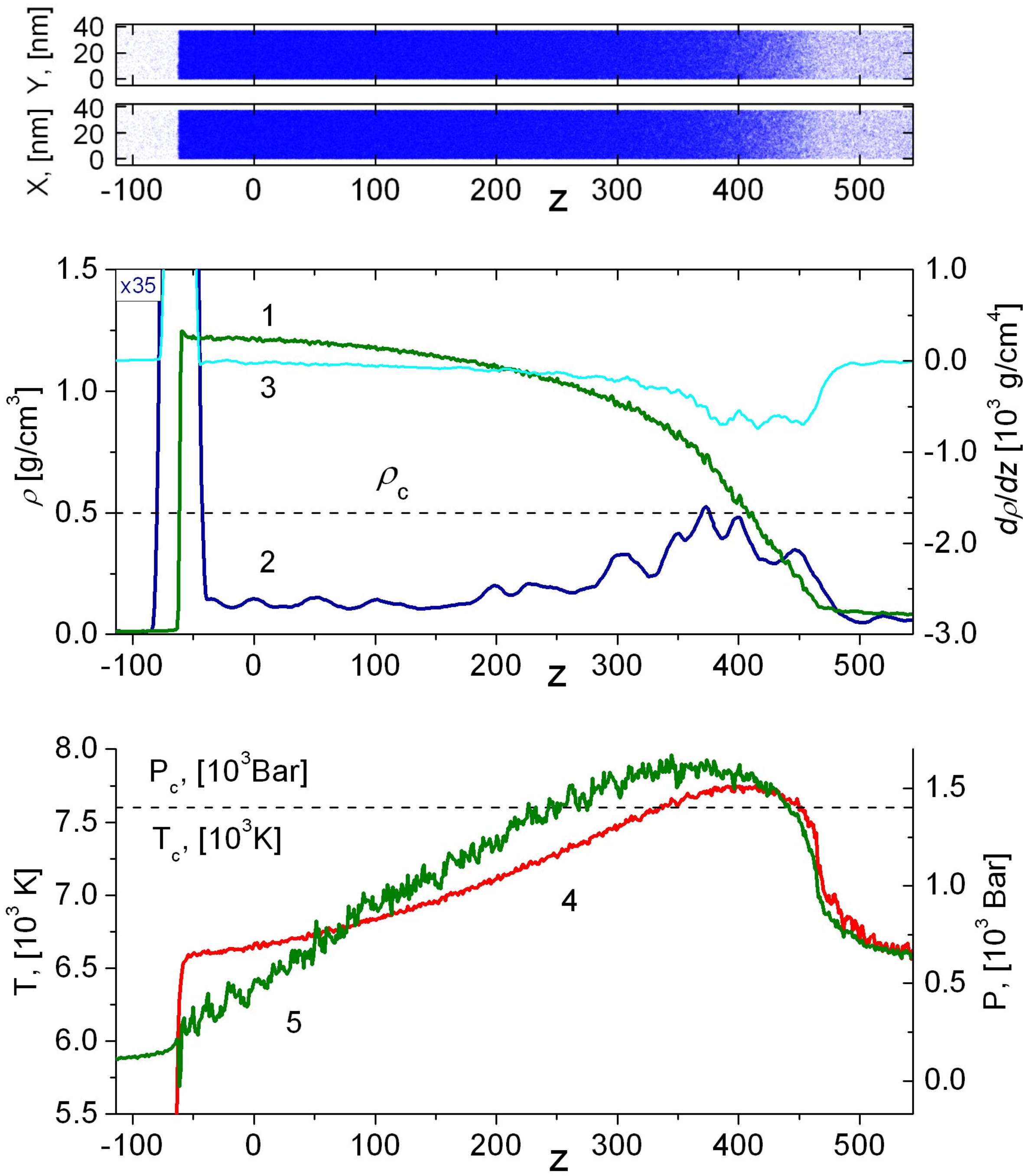

Figure 6: 2D density distribution in planes *Z-X* and *Z-Y* together with curves of density ρ and its derivative $\langle \partial\rho_m/\partial z \rangle$ (curves 1 and 2), density fluctuations $\langle \delta\rho \rangle$ (increased by factor 35 with respect to the ρ scale) (curves 3), temperature *T* (curves 4), pressure *P* (curves 5) distributions at t = 800 ps. Dashed lines is the model critical parameters values T_c = 7600 K, P_c = 1400 bar, ρ_c = 0.5 g/cm^3.

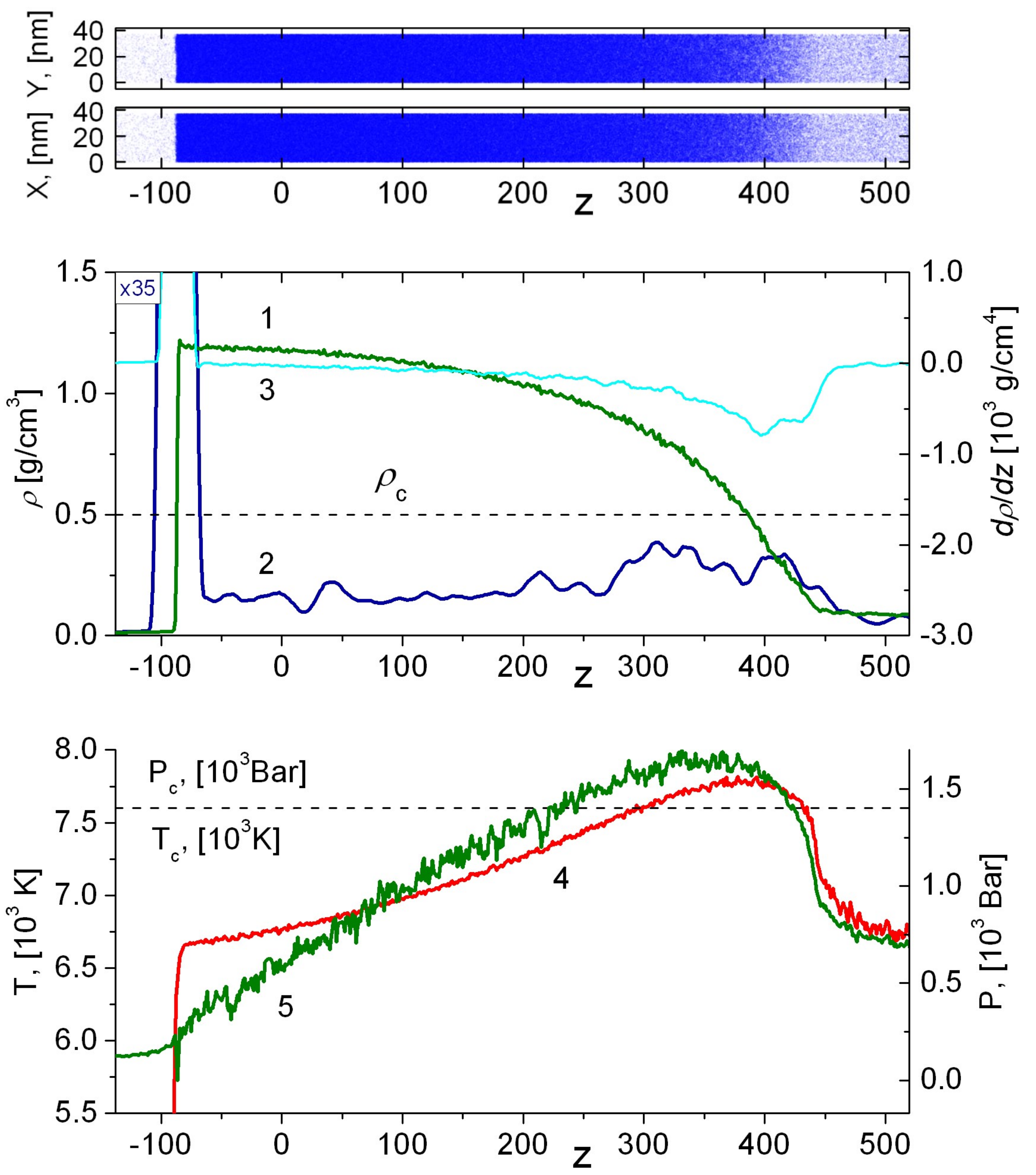

Figure 7: 2D density distribution in planes *Z-X* and *Z-Y* together with curves of density ρ and its derivative $\langle \partial\rho_m/\partial z\rangle$ (curves 1 and 2), density fluctuations $\langle \delta\rho\rangle$ (increased by factor 35 with respect to the ρ scale) (curves 3), temperature *T* (curves 4), pressure *P* (curves 5) distributions at t = 925 ps. Dashed lines is the model critical parameters values T_c = 7600 K, P_c = 1400 bar, ρ_c = 0.5 g/cm^3.

Dashed lines are the model critical parameters values T_c = 7600 K, P_c = 1400 bar, ρ_c = 0.5 g/cm^3. Very large initial fluctuations values at both film sides are due to sharp density jump at liquid-vapor boundary. At irradiated film side the density jump disappears quickly due to the ablation process which begins with surface evaporation and then transforms to supercritical fluid expansion.

During such fast heating explosive boiling and spinodal decomposition processes have no sufficient time to develop in contrast to cases of smaller intensities where the effect of explosive boiling process is clearly visible in recoil pressure behavior [12]. Instead of such manifestations at smaller intensities at G = 110 MW/cm^2 only some nanodroplets appearance in ablation plume occurs during time interval ~200-550 ps which ends just before maxima pressure and temperature attain its critical value at 650 ps (fig. 5).

Fluctuation level at times t < 50 ps after irradiation is switched on remains almost constant and equal to its initial value $\delta\rho(t{=}0) = 3\times10^{-3}$ g/cm^3 (fig. 2, 3) except for its values near the film boundaries. At later times t > 200 ps the initial right boundary effect becomes smaller and probably does not affect the fluctuation level due to volume density fluctuation. This conclusion is supported by comparison of curves 2 and 3 behavior in fig. 4 and 5 respectively: maximum of derivative (curves 2) diminishes faster than maximum fluctuation density $\langle\delta\rho\rangle_{max}$ (curves 3) which begins to diminish considerably only in supercritical expansion stages (fig. 5-7). During interval t = 500-650 ps value of $\langle\delta\rho\rangle_{max}$ exceeds approximately by factor 7-10 initial $\langle\delta\rho\rangle$ value and quickly diminishes at later times.

From fig. 2-7 it is also follows that localization of the maximum density fluctuation approximately coincides with critical density localization during transcritical regime of ablated material expansion. At present time it is not clear whether this coincidence is accidental or pertinent to transcritical ablation processes.

4 CONCLUSIONS

In the present paper density fluctuation behavior is analyzed for transcritical regime of laser thin Al film ablation under the constant radiation intensity I = 110 MW/cm^2. It is shown that in this regime the density fluctuation distributions in ablated plume demonstrates a maximum which disapears in supercritical regime. Localization of the maximm approximately coincides with density critical point position. To answer the question whether this coincidence occurs only for I = 110 MW/cm^2 or pertinent to some intensity intervals it is necessary to analyze transcritical ablation regimes at several different irradiation intensities.

Acknowledgements: The authors would like to thank Prof. Klaus Sokolowski-Tinten for helpful discussions.

The work was funded by Russian Foundation for Basic Research, grant No. 16-07-00263 and was supported by the MEPhI Academic Excellence Project (agreement with the Ministry of Education and Science of the Russian Federation of August 27, 2013, project No. 02.a03.21.0005).

REFERENCES

[1] A.L. Khomkin and A.S. Shumikhin, “Critical Points of Metal Vapors”, *Journal of Experimental and Theoretical Physics* **121**(3), 521–528 (2015).

[2] D.S. Ivanov and L.V. Zhigilei, “Combined atomistic-continuum modeling of short-pulse laser melting and disintegration of metal films”, *Physical Review B* **68**, 064114 (2003).

[3] E.M. Apfelbaum, V.S. Vorob’ev, “The predictions of the critical point parameters for Al, Cu and W found from the correspondence between the critical point and unit compressibility line (Zeno line) positions”, *Chemical Physics Letters* **467**, 318–322 (2009).

[4] V.S. Vorob'ev and E.M. Apfelbaum, "The Generalized Scaling Laws Based on Some Deductions from the van der Waals Equation", *High Temperature* **54**(2), 175–185 (2016).
[5] Keiko Nishikawa, Asako Ayusawa Arai, Takeshi Morita, "Density fluctuation of supercritical fluids obtained from small-angle X-ray scattering experiment and thermodynamic calculation", *J. of Supercritical Fluids* **30**, 249–257 (2004).
[6] Shin-Ichi Tsuda, Masato Tomi, Nobuyuki Tsuboi, Shohei Ikawa, Takashi Tokumasu, "Extraction of the Density Fluctuations in Diatomic Fluids Around the Critical Points Using Molecular Dynamics Simulation", *J. Nanosci. Nanotechnol.* **15**(4), 3117-3120 (2015).
[7] V.I. Mazhukin, A.A. Samokhin, A.V. Shapranov, M.M. Demin, "Modeling of thin film explosive boiling—surface evaporation and electron thermal conductivity effect", *Mater. Res. Express* **2**, 016402 (2015).
[8] V.I. Mazhukin, A.A. Samokhin, M.M. Demin, A.V. Shapranov. "Explosive boiling of metals upon irradiation by a nanosecond laser pulse", *Quantum Electronics* **44**(4), 283-285 (2014).
[9] V.I. Mazhukin, A.A. Samokhin, M.M. Demin, A.V. Shapranov, "Modeling of nanosecond laser vaporization and explosive boiling of metals", *Mathematica Montisnigri* **29**, 68-90 (2014).
[10] V.I. Mazhukin, A.V. Shapranov, M.M. Demin, A.A. Samokhin, A.E. Zubko, "Molecular dynamics modeling of nanosecond laser ablation: Subcritical regime", *Mathematica Montisnigri* **37**, 24-42 (2016).
[11] V.I. Mazhukin, A.V. Shapranov, M.M. Demin, A.A. Samokhin, A.E. Zubko, "Molecular dynamics modeling of nanosecond laser ablation: Transcritical regime", *Mathematica Montisnigri* **38**, 78-88 (2017).
[12] A.A. Samokhin, V.I. Mazhukin, M.M. Demin, A.V. Shapranov, A.E. Zubko, "Molecular dynamics simulation of al explosive boiling and transcritical regimes in nanosecond laser ablation", *Mathematica Montisnigri* **41**, 55-72, (2018).

The results were presented at the 17-th International seminar "Mathematical models and modeling in laser-plasma processes and advanced science technologies" (May 26 – June 2, 2018, Budva, Montenegro).

Received May 12, 2018