Rarefaction shock wave: Formation under short pulse laser ablation of solids

Nadezhda M. Bulgakova
Institute of Thermophysics, prospect Lavrentyev 1, 630090 Novosibirsk, Russia

Igor M. Bourakov and Natalia A. Bulgakova
Novosibirsk State University, Pirogova Street 2, 630090 Novosibirsk, Russia

(Received 27 November 2000; published 29 March 2001)

We investigate formation, dynamics, and decay of the rarefaction shock wave under the conditions of ultrashort pulse laser ablation of solids. On the basis of the Euler equation and the van der Waals equation, we consider the planar and spherical expansion into vacuum matter heated instantaneously above the thermodynamic critical temperature. When the expansion occurs along an abnormal adiabat, in a part of which $(\partial^2 p/\partial v^2)|_S<0$, a rarefaction shock wave moving toward the target is formed. After its reflection from the nonvaporized material of the target, a thin dense layer of the expanding material is found to be formed. We suggest that this is the explanation for interference patterns observed experimentally above laser ablated surfaces. It has been speculated that the rarefaction shock wave may be formed on nova outbursts.

DOI: 10.1103/PhysRevE.63.046311 PACS number(s): 47.40.−x, 79.20.Ds, 68.35.Rh

Much progress in technological applications of pulsed laser ablation (PLA) (depositing a variety of thin films, the development of new materials, surface modifications) has generated growing attention to the investigation of the fundamental mechanisms of laser vaporization of materials in recent years. It is well known that at different laser powers different mechanisms of PLA are operative [1]. For nanosecond laser pulses of moderate powers, the mechanism of normal vaporization gives way to phase explosion with increasing laser fluence [2]. For high laser powers inherent in nuclear fusion experiments, a substance experiences the direct transition from the solid to the plasma. For femtosecond laser pulses, starting from an ablation threshold, the vaporization may be considered as a direct solid-vapor transition [3] when a substance may be heated only slightly above its critical point ''liquid-vapor,'' thus showing abnormal properties. In particular, in the vicinity of the critical point the value $(\partial^2 p/\partial v^2)|_S$ (p, v, and S are the pressure, the specific volume and the entropy, respectively) becomes negative for a substance with a reasonably high specific heat c_v, resulting in generation of a rarefaction shock wave (RSW) [4,5]. However, almost no attention has been paid to a laser fluence range where a substance is heated close to its liquid-vapor critical point [6]. It is of crucial importance to examine such regimes in order to explain a number of unexplained phenomena observed under PLA and, on the other hand, laser ablation may be a promising technique for studying the fundamental aspects of the critical phenomena, particularly, their manifestation in fast processes. Spectacular hydrodynamics of the rarefaction shock waves suggesting their reflection from the solid surface, interaction between them and with the compression waves under their transformation from the shock to widening structure can initiate a large body of investigations. The credible occurrence of the RSW in stellar matter is also worthy of consideration and may open up the way for the simulation of nova outbursts under lab conditions.

The first observation of a RSW near the liquid-vapor critical point was realized in 1980 in freon-13 [7,8]. Commenting on this fact, Zeldovich [9] pointed out that with the RSW, a substance might be transferred instantaneously from a state above the critical point to a stable or unstable state near it that could be studied with the method of light reflection [10]. One of us proposed [11] that this was possibly realized in experiments [12–14] where, using time-resolved optical microscopy, a system of interference patterns (Newton rings) was observed above a solid surface vaporized by a short laser pulse in vacuum. In this paper we present the results on the simulation of the PLA plume dynamics under the conditions typical for the initial stage of ultrashort laser ablation of solids. The formation and the evolution of the RSW, particularly its reflection from the nonvaporized layer of the target, are followed. Although we use a very simple approach, the qualitative agreement with the measurements [12–14] gives us confidence that the RSW may be the reason for the formation of the Newton rings. Finally, we touch on the possibility of the RSW formation in stellar matter.

To describe the expansion of a material vaporized from the target surface in vacuum, we used an approach applied in [15] to study the propagation of a weak perturbation in a substance near the liquid-vapor critical point *outside the two-phase region*. We consider a thin layer of a solid target to be heated instantaneously to a temperature above its critical value so that at the initial instant the vaporized substance retains a high density, which is less than that of the solid state but greater than the critical density. The vaporized material is allowed to expand freely into vacuum. Unless specified, we assume the expansion to be planar. For the initial expansion stage, this is a reasonable assumption for many experimental PLA conditions as a typical irradiation spot radius (0.1–1 mm) is much greater than the thickness of the vaporized layer (50–100 nm) [13]. As will be seen from the following discussion, this assumption is valid throughout the expansion time considered. The expansion is governed by the compressible nondissipative conservation equations for mass, momentum and energy (the Euler equations) that are written in the planar case as

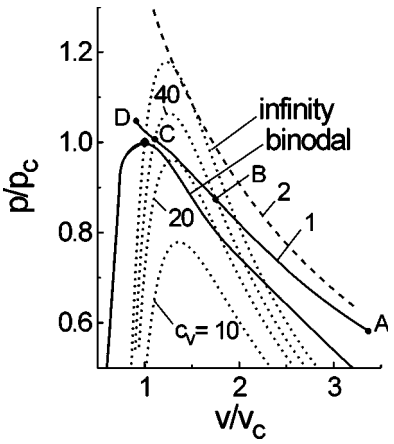

FIG. 1. *p-v* phase diagram used for choosing the initial conditions. The lines with $(\partial^2 p/\partial v^2)|_S=0$ are given for $c_v/R=10$, 20, 40, and infinity. For the regime studied ($c_v/R=40$) all the adiabats follow above the region of condensed matter (binodal). The adiabat 1 is abnormal with a portion where $(\partial^2 p/\partial v^2)|_S<0$. The line 2 is the normal adiabat.

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x}(\rho u)=0,$$

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}=-\frac{1}{\rho}\frac{\partial p}{\partial x},$$

$$\frac{\partial}{\partial t}\left(e+\frac{u^2}{2}\right)+u\frac{\partial}{\partial x}\left(e+\frac{u^2}{2}\right)+\frac{1}{\rho}\frac{\partial}{\partial x}(pu)=0.$$

Here x is the distance across the vapor slab counted from the target layer that does not undergo ablation (subthreshold material), ρ is the mass density, u is the velocity, p is the pressure, and e is the internal energy. These equations are augmented by the van der Waals equation of state

$$\left(p+\frac{a}{v^2}\right)(v-b)=T$$

and the caloric equation

$$e=c_v T+\frac{a}{v},$$

where T is the temperature, v is the specific volume, c_v is the specific heat at constant volume (here we consider c_v to be constant), the coefficients a and b are equal to $9T_c v_c/8$ and $v_c/3$, respectively, with the index c denoting the critical parameters. The system of the equations was written in the dimensionless form with T_c, p_c, v_c, L_0, and $u_0=\sqrt{T_c/M}$ as the characteristic parameters (L_0 is the initial thickness of the expanding layer and M is the mass of the vaporized particles). As we study the material expansion in vacuum that implies rapid widening of the calculation region, the equations are most conveniently solved in the Lagrangian mass coordinates. The calculation region was divided into 100 cells. The velocity was calculated at the cell boundaries

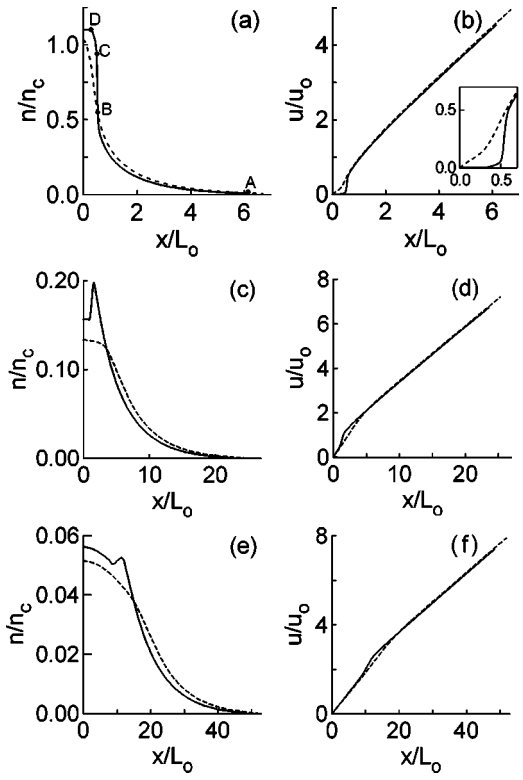

FIG. 2. Evolution of the density (left) and velocity (right) profiles in the expanding vapor slab with $c_v=40$ and $n_0/n_c=1.1$ normally to the vaporized surface at the time moments: $t/\tau=1.5$ [(a),(b)], 4 [(c),(d)], and 7.5 [(e),(f)] ($\tau=L_0/\sqrt{T_c/M}$). $x=0$ corresponds to the position of solid surface (the boundary of subthreshold material). The solid lines correspond to expansion along the abnormal adiabat ($T_0/T_c=1.01$). The dashed lines are for the normal adiabat ($T_0/T_c=1.1$).

while the other parameters were calculated in the center of the numerical cells. This allows us to use the only boundary condition $u=0$ in the solid wall (subthreshold material), whereas at the outer boundary we set $T=0$ and $\rho=0$. It should be pointed out that, in distinction to the compression shock waves [16], there is no necessity to use an artificial viscosity when solving the problem of the RSW formation. The solutions were smooth for all the regimes considered.

The initial conditions were chosen on the basis of the analysis of a typical *p-v* phase diagram (Fig. 1). In the figure the lines with $(\partial^2 p/\partial v^2)|_S=0$ are given by the dotted curves for the different values of c_v so that $(\partial^2 p/\partial v^2)|_S<0$ under these curves. The calculations were performed for $c_v/R=40$ and for different initial conditions: (1) the expansion along the abnormal adiabats with a portion convex up, like the adiabat 1 in Fig. 1; (2) the expansion along the normal adiabats convex down everywhere (e.g., adiabat 2 in Fig. 1). Note that the adiabat 1 crosses the curve with $(\partial^2 p/\partial v^2)|_S=0$ for $c_v=40$. At the initial moment, the particle number density, $n_0=1/v_0$, and the temperature T_0 were uniformly distributed within the layer.

The temporal evolutions of the density and velocity distributions in the expanding layer for the adiabats 1 and 2 are shown in Fig. 2. The initial conditions were the following:

$n_0/n_c=1.1$ (for both adiabats), $T_0/T_c=1.01$ (the adiabat 1), and 1.1 (the adiabat 2). At an early stage the vaporized material experiences sharp rarefaction at the boundary. The subsequent layers of the vapor drawn into the expansion fall in the different regions of the abnormal adiabat [the corresponding parts of the adiabat 1 in Fig. 1 and the solid curve in Fig. 2(a) are indicated with the same letters]. The outer layer AB has already passed the portion of the adiabat with abnormal properties and belongs to the normal portion of the adiabat. The sharp density jump BC (i.e., the RSW) corresponds to the abnormal portion of the adiabat 1 with $(\partial^2 p/\partial v^2)|_S<0$. The density profile is slightly smoothed in the top part, CD, due to the corresponding short normal portion of the adiabat. The expansion along the abnormal adiabat proceeds more steeply as compared to the expansion along the normal adiabat. The difference is better seen in the velocity profiles [Fig. 2(b)]. The velocity under RSW formation experiences steep bending (see inset where the bending part of the velocity profile is given in an enlarged view), which is not inherent for the normal adiabatic expansion. This suggests that the material is drawn into the motion suddenly, following which the linear velocity profile typical for free adiabatic expansion into vacuum is set [17]. On reflection of the RSW from the solid surface, a steep decrease in the vapor density takes place near the wall that results in the formation of a thin layer of dense material moving away from the target [solid line in Fig. 2(c)]. It should be underlined that the RSW causes the formation of such a layer as, for the expansion along the normal adiabat, the density profile is smooth [dashed curve in Fig. 2(c)]. On the other hand, all the expanding material has already passed the abnormal portion BC of the adiabat 1 so that not the RSW but its consequences are shown in Fig. 2(c) by the solid curve. The velocity profile also keeps the features of the RSW [Fig. 2(d)]. On further expansion, both the density and velocity profiles are smoothed off [Figs. 2(e,f)]. At this time the expansion can still be considered as planar because the width of the expanding layer is still less than the typical size of the irradiated spot.

Making an estimation of the characteristic RSW times for a laser-vaporized Ti target as an example (the thickness of the vaporized layer of 50–100 nm [13], $\rho_{\text{solid}}=4.5$ g/cm^3, $\rho_c=1.31$ g/cm^3, $T_c=11\,790$ K [18]), we find that the RSW is formed within ~ 100 ps and decays within 1–2 ns after the expansion starts. This is reasonably consistent with the experimental observations [12–14]. Thus, the calculations show that, under expansion of a substance vaporized from a solid surface in vacuum, the conditions can be provided for the formation *in the gas phase* of a dense thin layer moving away from the surface. The layer is formed with a time delay from the expansion start, persists over a period of time, and is a plausible reason for the interference patterns observed in [12–14]. Such a layer can only be formed in a narrow range of laser fluences near the ablation threshold, consistent with the experimental observations. The requirements for the formation of such a layer are the following: (1) The substance has to be heated rapidly to the supercritical temperature; (2) the substance has to have a reasonably high specific heat at constant volume or to reach a high value of c_v during relaxation to the near-critical state [11]. As a result, the substance can be thrown into an abnormal adiabat that lies slightly above the critical point. It follows that the laser power must not be too high; otherwise the substance is brought into the normal adiabat where the considered phenomenon does not occur. The condition (1) is normally realized under femtosecond laser ablation [3]. Consider a regime whereby interference has been observed above an aluminum target: laser fluence of 1.2 J/cm^2 [12] and the thickness of the vaporized layer of 50 nm [13]. This results in a vapor energy of approximately 2 eV per atom, assuming the latent heat of fusion as 396 J/g, the latent heat of vaporization as 10 500 J/g and the reflection coefficient as 0.79 [19]. With such an energy, aluminum vapor expands along an adiabat passing above the critical point. Condition (2) can be obeyed for polymer ablation (e.g. polyethylene [20], polyimide [21], triazano polymer [22]). Conceivably a high value of the specific heat might be reached for the metal substances as well. The thermalization of the electron-lattice system when the lattice decomposes takes place during 1–100 ps after the laser pulse termination. Evidently, the entropy increases in such a process. Passing the critical temperature, the matter may experience short-scale fluctuations of the parameters with corresponding increase in the specific heat. However, this is a subject of further study.

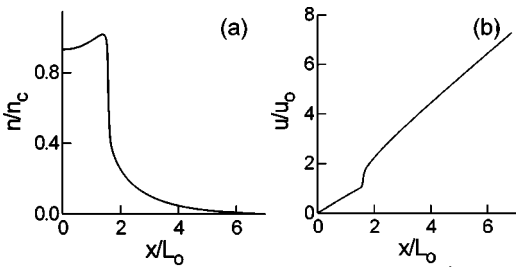

FIG. 3. The profiles of the density (a) and velocity (b) at the early time moment $t/\tau=1$ for the expansion along the abnormal adiabat. The initial parameters are: $c_v/R=40$, $n_0/n_c=2$, $T_0/T_c=1.05$. The expansion proceeds extremely fast: the density near solid surface has been halved to this time.

We assume that, over a period of electron-lattice thermalization, the density in the vaporized layer may undergo a considerable change as compared to that of the solid state. A time of 1–100 ps is small for the development of the gas dynamic motion but is enough for a density decrease of several times as a result of heating. Normally, the critical density of a metal is 3–3.5 times less than that of the solid state [18]. The results shown in Fig. 2 were obtained for an initial density close to the critical one (a short portion CD for the abnormal adiabat 1 in Fig. 1). For a higher value of the initial density, the behavior of the expanding material differs from that shown in Fig. 2. In Fig. 3, the density and velocity distributions are given for the following initial parameters: $c_v/R=40, n_0/n_c=2, T_0/T_c=1.05$. The corresponding abnormal adiabat lies close to the adiabat 1 (see Fig. 1). Before entering the region with $(\partial^2 p/\partial v^2)|_S<0$, the material passes a longer portion of the adiabat as compared with the part CD in adiabat 1. Figure 3 illustrates the initial stage of the expansion dynamics. The calculated results are in good agree-

ment with the picture predicted in [11]. The density jump (i.e., the RSW) moves away from the target starting from its formation [Fig. 3(a)] and the velocity profile exhibits a sharp increase behind the RSW [Fig. 3(b)]. Two sharp interfaces, one of which is the RSW and another is the boundary of the nonablating material, are also formed that may cause the interference (notice that the expansion proceeds extremely quickly). However, the calculations show that this picture is not frozen with time. The RSW comes to a halt, rests for a period, and then starts to move back to the vaporized surface decaying with time as all the expanding material has passed the abnormal portion of the adiabat. Nevertheless, the density jump is still quite sharp at the reflection moment so that the further expansion in its main features resembles that shown in Figs. 1(c)–(f) but with a less distinct density peak.

As was discussed above, the expansion may be assumed to be planar under the typical PLA conditions within the period of the formation and decay of the RSW. However, the planar picture is impaired in the flow near the edges of the irradiated spot. Nonuniform distribution of laser fluence over the irradiation spot, as often takes place in experiments, causes the violation of the planar picture of the flow as well. These factors result in the formation of a sort of ''lens'' necessary for the Newton rings appearance. To study qualitatively the effect of breaking the planar flow on the RSW behavior, we have considered the expansion of a spherical cloud into vacuum with the initial conditions as in Fig. 2. The calculated density profile is shown in Fig. 4. The results show that the density peak is greater in amplitude and exists longer as compared to the planar case. The picture obtained in the calculation for the spherical case turns out to be very similar to that reproduced for nova outburst from the data on the emission lines (inset in Fig. 4) [23]. Since on nova outburst the ejected matter has rather low temperature (6000–8000 K) and consists of a large fraction of heavy elements, the possibility of the RSW formation in stellar matter is open to speculations.

It must be emphasized that our model supposes that the target substance is heated to a supercritical state from where it expands to the gas phase along an adiabat passing *above the region of condensed matter* [11]. Following our approach, the matter does not experience decay to the two-phase state. However, if a metal holds a low specific heat on rapid heating under the conditions considered, then another scenario of its expansion is to be realized [24,25] when the outer liquid layer of the irradiated target swells under the pressure of the vaporized inner layers, representing a vapor-drop mixture. It is worth mentioning that the phenomenon of the RSW formation was also predicted for a two-phase mixture under a pressure close to the critical one [26]. Under such conditions, a complicated picture of the double rarefaction shock structure is to be observed [27] similar to that found in solid iron undergoing a phase transition [28].

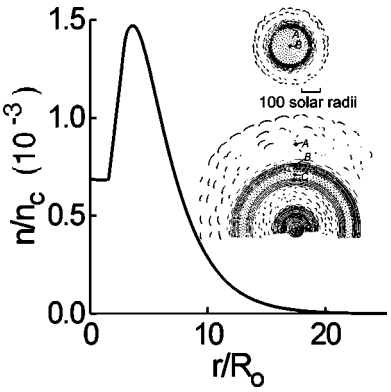

FIG. 4. The radial density distribution for the spherically symmetric expansion along the abnormal adiabat with the initial conditions as in Fig. 2 for time moment $t/\tau=4$. The inset represents the model of nova outburst developed on the basis of data on the emission lines (adopted from Aller [23]). Two stages of outburst are shown. The upper picture is for an early stage and may be referred to a time moment when the RSW has been just formed and moves toward the center [the density profile is analogous to that shown in Fig. 2(a)]. The lower picture corresponds to the density profile given in this figure. The black point in the center shows the main mass of the star. The densest layers of ejected matter with high opacity are shown by the dotted area. Concentric circles are the thinner photospheric layers passing into the transparent cloudy structures. An observer watches the star from above. The dashed curve outlines the region contributing to the formation of the absorption spectrum. Points *A*, *B*, and *C* correspond to the layers ejected sequentially.

The authors would like to thank A. V. Bulgakov, G. A. Khabakhpashev, and E. E. B. Campbell for helpful discussions. The work was supported by the Russian Foundation for Basic Research (Grant No. 99-03-32331a).

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