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Possibility of rarefaction shock wave under short pulse laser ablation of solids

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Attention is drawn to a phenomenon that may give a radically different explanation for the recent observations of the system of dark rings above a solid surface vaporized by a short laser pulse. If a substance is heated to near-critical temperature, the existence of the compression shock wave becomes impossible, whereas the rarefaction wave takes a form of shock. The rarefaction shock can be considered as an interface in the expanding near-critical substance to form Newton rings in time-resolved optical microscopy experiments. The qualitative picture of the laser-ablated material expansion in vacuum with the generation of the rarefaction shock is discussed. [S1063-651X(99)50410-8]

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In recent work [1] using time-resolved optical microscopy, the system of Newton rings was observed above a solid surface vaporized by a short laser pulse in vacuum that implied the formation of a sharp interface in the expanding material. The rings show up at the near-threshold laser fluences lasting about 100 ns and disappear with increasing laser fluence [2]. To explain this unusual phenomenon, a harmonious theory based on the decay of metastable state of matter into a two-phase mixture has been proposed [3]. According to this theory, the outer liquid layer of the irradiated target swells under the pressure of the vaporized inner layers, which represent a vapor-drop mixture. In this paper, attention is drawn to another intriguing phenomenon that can give rise to shock generation in the expanding substance, thus causing interference of the probe laser pulse.

As early as 1946, Zeldovich [4] pointed out that in the vicinity of the critical point ‘‘liquid-vapor’’ 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 at constant volume c_v. As a result, rarefaction shock waves can be generated in a substance heated to the critical temperature, while the compression waves become nonsharp with the width proportional to the distance the wave has traveled. A comprehensive theoretical study of the possibility of the rarefaction (negative) shock waves was performed in [5]. The rarefaction shock wave was first observed in freon-13 near its critical point only in 1980 [6,7].

A typical p,v-diagram is sketched in Fig. 1. Far from the critical point, adiabatic compressibility of the substances, be they gases, liquids, or solids, decreases with increasing pressure [e.g., adiabat(I)], which is to say that $(\partial^2 p/\partial v^2)_S > 0$. According to the Jouguét condition for the entropy change in a low-intensity shock wave given by

$$S_1 - S_0 = \frac{1}{12T_0}\left(\frac{\partial^2 p}{\partial v^2}\right)_S (v_0 - v_1)^3 \tag{1}$$

(subscripts 0 and 1 denote the variables in front of and behind the shock wave, respectively), entropy increases with the compression of the substance [4,8]. For a typical adiabat (I) that is convex down, it can easily be shown [8] that the speed of sound c_0 is smaller than the wave velocity D_0 in the low-pressure region and $c_1 > D_1$ behind the wave; that is, the condition of existence of the compression shock waves and impossibility of the formation of the rarefaction shock waves.

At the critical point, $(\partial^2 p/\partial v^2)_T = 0$. In the critical isotherm II ($T = T_c$, T_c being the thermodynamic critical point), there is a part with $(\partial^2 p/\partial v^2)_T < 0$ (a portion of curve CA). The isotherms close to the critical one with both $T < T_c$ and $T > T_c$ exhibit the same behavior (e.g., curve III). If the value c_v is large enough [$\geqslant 20$ cal/(mol·K) [4]], the adiabat follows close to the isotherm (dotted curve) and thus, a portion of adiabat BD is convex upwards as well (abnormal adiabat); that is, $(\partial^2 p/\partial v^2)_S < 0$. In such cases the right-hand side of Eq. (1) becomes negative and this expression transforms to the condition of existence of rarefaction shock waves and impossibility of compression shock waves. Correspondingly, in the adiabat portion BD, the speed of sound increases with decreasing pressure, which is the case in the vicinity of the critical point [9]. Notice that such a portion of the adiabat can lie off the region of condensed matter. Thus, the substance that expands following this adiabat does not need to be two-phase as is taken in model [3] where expansion along a subcritical adiabat (IV) is assumed. Another radical distinc-

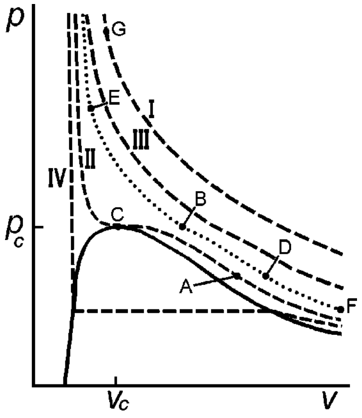

FIG. 1. A typical p,v-diagram. A qualitative picture is shown, which does not correspond to any real substance. To impact the essence of the discussed phenomenon, the details are presented in an exaggerated form.

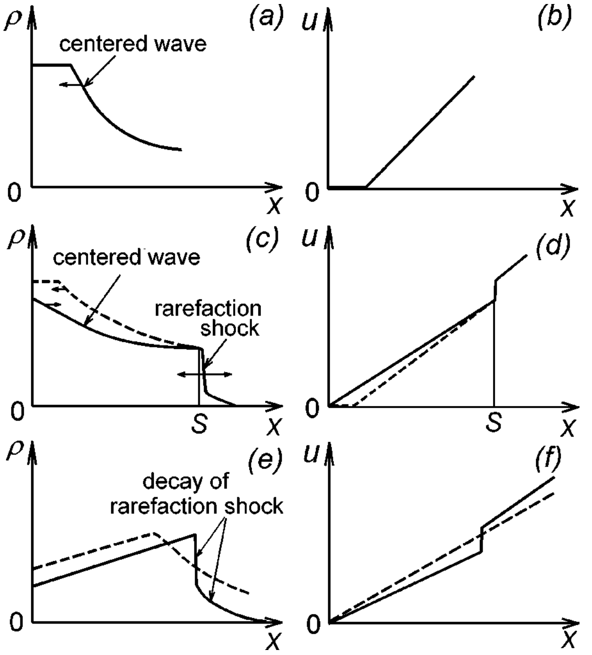

FIG. 2. Evolution of the density (left) and velocity (right) profiles in the expanding ablation plume along the normal to the target. $x=0$ corresponds to the boundary of subthreshold material.

tion of the described phenomenon from that proposed in [3] is the increasing speed of sound behind the rarefaction shock wave, whereas it decreases dramatically during decay of a metastable liquid into a two-phase mixture.

As has been analyzed in [10], for fs-laser pulses the ablation may be considered as direct solid-vapor transition. Near the ablation threshold for short pulse laser ablation, the temperature of the ablated materials reaches 5000–10 000 K (as estimated in [1]) that is near or even above the critical temperature of the studied materials ($T_c \simeq 7890$, 6520, and 5410 K for Ti, Au, and Al, respectively [11]). Let us assume that a thin layer of a solid target has been heated quickly by a laser pulse to a supercritical state ($T > T_c$) in an abnormal adiabat (point E in Fig. 1). The possible scenario of its expansion in vacuum is shown in Fig. 2, where the profiles of the density and the velocity along the normal to the target are shown qualitatively. At the early stage the vaporized material expands freely following the normal portion of the adiabat (EB in Fig. 1), thus taking a smooth sloping profile of the density toward vacuum [Fig. 2(a)] [12] with a linear increase of velocity [Fig. 2(b)]. When the condition $P \leqslant P_c$ (point B in Fig. 1) is reached in the outer region of the plume, the centered rarefaction wave splits into the centered and shock parts [Fig. 2(c)] [7]. The velocity profile exhibits a sharp increase behind the rarefaction shock [Fig. 2(d)]. To the moment of splitting, the centered part of the rarefaction wave can reach the subthreshold material and all the ablated substance is taken into expansion [solid lines in Figs. 2(c) and 2(d)]; otherwise the profiles take the forms shown by the dashed curves. The further scenario depends on what local flow velocity (subsonic or supersonic) is gained by the substance in front of the rarefaction shock (point S). For supersonic velocity, the density jump moves away from the target and with time the expansion picture becomes frozen with possible density and velocity profiles as in Figs. 2(e) and 2(f) (the frozen profiles for expansion along the normal adiabat are shown with the dashed curves); otherwise the rarefaction shock reflects from the nonablated boundary after a time. Thus, a density jump is formed that may be responsible for the interference of a probe signal (Newton rings) observed in [1,2]. Notice that the decay of the rarefaction shock wave is shown in Fig. 2(e). This may occur when the pressure behind the rarefaction wave decreases to a value corresponding to the point D (Fig. 1); that is, the further expansion follows the normal portion of the adiabat DF [7,13]. The picture of the reflection of the rarefaction shock from a solid surface is open to speculation; a general idea can be had from calculations on the basis of a hydrodynamic approach as in [13]. One might expect the initiation of the backflow toward the target as a result of drastic pressure fall near the reflecting wall.

According to the scenario considered, Newton rings can be observed with a delay with respect to the laser pulse and they have to disappear within the time that the plume takes to enter a free-molecular regime of expansion and all sharp irregularities are flattened due to the velocity distribution of the ablated particles. With increasing laser fluence the substance is thrown to a higher adiabat. At some laser fluence it is heated to a normal adiabat I (point G in Fig. 1) when the rarefaction wave is not generated and Newton rings must vanish. This is in general agreement with the experimental results [1,2].

Whether or not the picture described is real can be understood in the context of a rigorous theory, which must take into account the behavior of the material properties and their relaxation in the vicinity of the critical point. As such the problem seems to be currently intractable. First of all, doubts are cast upon the value c_v which has to be large enough for the rarefaction shock formation, and upon the relaxation of the system to a definite state under rapid heating. Nevertheless, the following arguments in favor of the described picture can be advanced:

(i) As mentioned above, the formation of the rarefaction shock near the critical point requires c_v to be higher than $\sim 20\ \mathrm{cal/(mol \cdot K)}$. It is well-known that c_v for most liquid metals is reasonably described by the Dulong-Petit law and is nearly temperature-independent. Near the melting point it is about $6\ \mathrm{cal/(mol \cdot K)}$. For freon-13 under normal conditions $c_v \simeq 16\ \mathrm{cal/(mol \cdot K)}$, which is less than required by the mentioned criterion. The fact of the rarefaction shock discovery in freon-13 argues for much wider variety of the materials that may exhibit this effect [13]. Notice that the criterion was obtained in [4] on the assumption that the c_v value was constant; that is, on the basis of the van der Waals theory of the critical phenomena. As for now, it is common knowledge that, as a liquid approaches its critical temperature, c_v increases sharply, tending to infinity by a near-logarithmic law [9]. This is true for both $T < T_c$ and $T > T_c$. Thus, c_v may reach high values in a range of temperature to satisfy the condition of the rarefaction wave formation.

It should be mentioned that such specific heat behavior is exhibited during slow heating, as commonly used in studies of critical matter. The question is raised as to whether the specific heat manages to relax to the discussed behavior during extremely fast process of fs-laser ablation.

(ii) In a substance heated very quickly to a near-critical temperature (e.g., by a short laser pulse), the fluctuations have not initially been excited but the equilibrium between the nearest neighbors (the correlation at several intermolecular distances) is established rapidly [14]. For nanoscale processes, such as fs-laser ablation plume (the ablation depth is typically 10–100 nm near the ablation threshold), nanoscale fluctuations, which are generated first, are of importance. The time of generation of the fluctuations is proportional to their size. It seems likely that only small-scale fluctuations have a chance to develop on rapid heating and further expansion of a laser plume; that is, the correlation radius (a length scale characterizing the interaction between the fluctuations) is small for such objects. The width of the rarefaction shock that is determined by the correlation radius [7] has to be small as well. What the properties are of small portions of matter heated rapidly to near-critical temperature is unclear. In the ordinary sense, the term ''critical'' may not be applied to such a substance. Conceivably its properties might differ essentially from those of large parcels of the critical matter. Possibly an analogy with atomic clusters may be applied, whose properties differ dramatically from the properties of the bulk. With cluster growth their properties tend to the bulk ones (often nonmonotonically).

Much more research must be done to either validate or disprove the hypothesis proposed. Time-of-flight measurements are unlikely to favor one or the other hypotheses. If it is assumed that the rarefaction shock is responsible for the Newton rings, the velocity of the plume boundary must essentially exceed the value obtained from interference evolution. On the other hand, the inflated liquid layer [3] eventually has to burst and the released two-phase mixture can reach a high velocity during further free expansion. To settle the question, it might be well to analyze the deposit. In a substance that has experienced decay to a two-phase mixture, the droplets are to be observed. The presence of droplets in the deposit will support the model [3], while the lack of droplets in the expanding material will argue for the scenario described (the condensation in the plume expanding in vacuum results in only small clusters up to several atoms per cluster).

If the described phenomenon actually takes place during laser ablation, it will have much potential for yielding information about the behavior of hard-melting substances near the critical point in fast processes. It is worth noting that Zeldovich [14] described the possibility of detecting the rarefaction wave in rapid processes using a technique operating on the basis of interference of probe light beam; see [15].

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