Kinetics of a phase transition during laser evaporation of a metal

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(Submitted February 21, 1984)
Kvantovaya Elektron. (Moscow) **11**, 2432–2437 (December 1984)

A study is made of a change in the degree of nonequilibrium of an evaporation process occurring under different regimes of interaction between laser radiation and the surface of an absorbing medium. A numerical solution of the heat conduction equation for a condensed medium is used together with the equations of gasdynamics for a vapor subject to an allowance for additional relationships on the irradiated surface governing the kinetics of a nonequilibrium phase transition. The results obtained indicate the existence of a nontrivial region of transient evaporation characterized by a constant Mach number $M = 1$ between limits that depend strongly on the laser interaction regime.

In contrast to the supercritical laser evaporation regime, when the state of matter varies continuously,[1] in the subcritical range there may be a sharp interface between the phases where we have to formulate the laws of conservation of mass, momentum, and energy transfer, as well as additional relationships that govern the kinetics of a phase transition. The simplest example of such a relationship is the Hertz–Knudsen formula linking the transfer of mass across an interface to the temperature of the surface of a condensed medium T_s and its saturated vapor pressure $P_{\text{sat}}(T_s)$:

$$j^0 = p_{\text{sat}}/(2\pi R T_s)^{1/2}, \tag{1}$$

where R is the gas constant. Equation (1) applied in the limiting case when we can ignore collisions in the gaseous phase and return of the evaporated particles to the interface. This return flux is governed by the conditions of gasdynamic expansions beyond a Knudsen layer adjoining directly the interface and corresponding to the region of large discontinuities in the gasdynamic parameters. Under certain assumptions about the nature of the nonequilibrium function (of the kind used earlier to discuss the structure of shock waves[2]) expressions have been obtained[3,4] for the gasdynamic parameters when the Mach number at the interface is $M = 1$.

The value $M = 1$ corresponds to the evaporation in vacuum or when the surrounding gaseous medium is at a low pressure. If the ambient pressure is not negligible compared with p_{sat}, we then have $M < 1$. Steady-state evaporation under these conditions has been investigated by a variety of methods (see, for example, Refs. 5–9). It must be stressed that a reduction in M is not necessarily associated with the presence of an ambient gaseous atmosphere. In the case of rapid variation of the temperature of the irradiated surface the process of evaporation may be hindered by the reaction of the evaporated substance. An additional counterpressure that affects the evaporation kinetics appears also when laser radiation is absorbed strongly in an erosion plasma.[9–11] The screening effect of such a plasma has been considered on several occasions,[12,13] but no allowance has been made for a change in the degree of nonequilibrium of the evaporation process.

We shall consider the behavior of M in a plasma-free regime of laser evaporation for different variations of the temperature of the irradiated surface. The topic is important because of the special role that the Mach number M plays in the advanced evaporation process: it governs the degree of nonequilibrium of this process. Under phase equilibrium conditions we have $M = 0$. For $M = 1$ a flux of matter amounting to $j_0 = 0.82j^0$ across the interface is maximal and the recoil pressure $p_s = 0.55p_{\text{sat}}$ on the irradiated surface is minimal.

When the condition $M = 1$ is satisfied the behavior of a condensed medium during the action of a laser pulse can be considered independently of the gasdynamic problem of vapor expansion analyzed on the basis of the single-phase variant of the Stefan problem in which the temperature at the interface depends weakly (logarithmically) on the interface velocity.[14] This approach is used widely in theoretical studies of laser evaporation in the range of moderate radiation intensities when we can ignore the absorption in an erosion plasma.[15–21]

The nature of variation of M is important also in the problem of the stability of a plane evaporation front.[20,21] In the subsonic evaporation regime when $M < 1$, the behavior of the interface depends on the gasdynamic perturbations in the flux of the evaporated matter. This case is in many respects analogous to the problem of stability of a slow combustion front.[22,23] In the problem of slow burning of the liquid subject to an allowance for the surface tension σ and for the constant front velocity v, it is found that the perturbed interface $h \sim \exp(\Omega t + ikx)$ is described by the dispersion equation

$$\Omega^2 + 2\Omega kv - k^2 vu + \sigma k^3/R_0 = 0, \tag{2}$$

where u is the velocity of the gas of density which is regarded (for the sake of simplicity) as negligible compared with the density of the liquid R_0. This means that the deformation of the interface is accompanied by the appearance of a pressure

$$p = h(\sigma k^2 + R_0 v\Omega - R_0 vuk). \tag{3}$$

Such a reaction pressure builds up perturbations of the interface.

In the advanced evaporation regime when $M = 1$ the reaction pressure at the interface depends on the temperature of the surface. If this temperature remains constant, as is assumed in the derivation of Eq. (2), the rate of evaporation

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and the recoil pressure also remain practically constant. Then, instead of Eqs. (2) and (3), we obtain

$$p=\sigma k^2 h; \tag{4}$$

$$\Omega^2+\Omega kv+\sigma k^3/R_0=0. \tag{5}$$

In this case the flux of matter across the interface does not build up perturbations, as in Eq. (2), but results in an additional damping of surface waves. The formal difference between these two regimes is that in the advanced evaporation case a perturbation of the pressure in the vapor flux is described by a superposition of solutions corresponding to two roots of a characteristic equation, whereas in the slow combustion case there is only one solution.

The equation for small pressure perturbations in a vapor stream moving at a velocity u along the Z axis is

$$\left(\frac{\partial}{\partial t}-u\frac{\partial}{\partial z}\right)^2\delta p=u_s^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)\delta p, \tag{6}$$

where u_s is the velocity of sound. In the case of two-dimensional perturbations of the pressure described by $\delta p \propto \exp(\Omega t + ikx - \lambda z)$, we find from Eq. (6) the following characteristic equation

$$\lambda^2(u^2-u_s^2)-2\lambda\Omega u+u_s^2k^2=0, \tag{7}$$

$$\lambda=\left[\Omega u\pm u_s(\Omega^2+u_s^2k^2-u^2k^2)^{1/2}\right](u-u_s)^{-1}. \tag{8}$$

In the relationships (6)–(8) the wave number k is real and we shall regard it as positive, whereas the parameters Ω and λ should be found from a solution of the linearized gasdynamic problem, which in effect yields the dispersion relationship for small perturbations in the flux of the evaporated matter.

In the subsonic evaporation regime when all the characteristic velocities are small compared with the velocity of sound, it follows from Eq. (8) that $\lambda_{1,2}=\pm k$. In this case a solution is obtained using only one root, $\lambda_1=k$, which corresponds to damping of perturbations in the vapor flux at large distances from the interface.[22]

The situation is different at high flux velocities, when $u\geqslant u_s$. If $u_s>u-u_s>0$, it follows from Eq. (8) that

$$\lambda_{1,2}=\Omega/(u\pm u_s)\pm u_sk^2/2\Omega. \tag{9}$$

Clearly, the solution of the problem should be sought in the form that allows for the difference between the two physically admissible roots of the characteristic equation.

In Eq. (24) in an analysis of the stability of the surface of an evaporating liquid the second solution for the pressure is ignored, which is justified only in the subsonic evaporation regime and is unacceptable in the advanced evaporation case when the vapor stream is accelerated to the velocity of sound already in the Knudsen layer.

When the two eigensolutions given in Eq. (9) are used, the gasdynamic problem of the stability of the interface becomes indeterminate because its solution now requires an additional boundary condition, the derivation of which is outside the scope of a linear analysis. If we assume that $M=1$ for small perturbations of the temperature and shape of the interface, we find that the problem of behavior of a condensed medium is closed and its solution gives the boundary conditions for the description of gasdynamic perturbations in a flux of the evaporated matter. A similar hypothesis is used in Refs. 20 and 21.

However, the range of realization of such a regime remains indeterminate. The problem is related directly to the fact that in a nonlinear system of gasdynamic equations the line dividing the regions with $M\geqslant 1$ and $M<1$ depends on the required solution and cannot be determined in advance.

A complete study of the problem of the behavior of M goes beyond the framework of mechanics and continuous media. This applied particularly to the upper limit to M. On the other hand, a solution of the combined problem of condensed and gaseous media subject to an allowance for the phase transition kinetics makes it possible to determine the behavior of M when $M\leqslant 1$.

The problem of evaporation is solved in Ref. 25 for the surface of aluminum subjected to rectangular radiation pulses of microsecond duration and the conclusion that M decreases on reduction in the radiation intensity is formulated without any restrictions. Such a conclusion is unjustified if only because the results obtained in this regime cannot be applied to other cases of variation of the intensity. The dependence of the behavior of M on the laser interaction regime has not been investigated.

Our numerical modeling of laser evaporation shows that in the more general case the behavior of M differs qualitatively from that described in Ref. 25. In an analysis of this process we shall follow Eq. (5) and solve the equation of heat conduction for a condensed medium together with the equations of gasdynamics allowing for the kinetics of the phase transition at the interface between the condensed and gaseous media. In the coordinate system linked to a plane evaporation front $z=0$ the problem under discussion can be formulated as follows:

$$-l<z<0:\ cR_0\left(\frac{\partial I}{\partial t}-v\frac{\partial T}{\partial z}\right)=\frac{\partial}{\partial z}\left(\varkappa\frac{\partial T}{\partial z}\right), \tag{10a}$$

$$z=-l:\quad \varkappa\frac{\partial T}{\partial z}=0; \tag{10b}$$

$$z=0:\quad R_{0s}v_s=\rho_0u_0,\quad P_s+R_{0s}v_s^2=p_0+\rho_0u_0^2,$$

$$\varkappa\frac{\partial T}{\partial z}=L_vR_{0s}v_s-G, \tag{11}$$

$$T_0=T_s\left|\left(1+r^2\left(\frac{\gamma-1}{\gamma+1}\right)^2M^2\right)^{1/2}-r\left(\frac{\gamma-1}{\gamma+1}\right)M\right|^2,\quad r=(\pi\gamma/8)^{1/2}, \tag{12}$$

$$\rho_0=\frac{1}{2}\rho_{sat}\left\{\left(\frac{T_s}{T_0}\right)^{1/2}\left[(\gamma M^2+1)\exp(b^2M^2)\operatorname{erfc}(bM)-\frac{4r}{\pi}M\right]+\frac{T_s}{T_0}\left[1-2rM\exp(b^2M^2)\operatorname{erfc}(bM)\right]\right\},\quad b=(\gamma/2)^{1/2}, \tag{13}$$

$$0<z<L:\ \frac{\partial\rho}{\partial t}+\frac{\partial(\rho u)}{\partial z}=0,\quad \frac{\partial(u-v)}{\partial t}+u\frac{\partial u}{\partial z}=-\frac{1}{\rho}\frac{\partial p}{\partial z}, \tag{14a}$$

$$\frac{\partial S}{\partial t}+u\frac{\partial S}{\partial z}=0, \tag{14b}$$

$$p=\rho RT,\quad p_{sat}=\rho_{sat}RT_s=p_b\exp[L_v/RT_b(1-T_b/T_s)], \tag{15}$$

where S is the entropy of an ideal gas. The flow of the evaporated matter at $z>0$ is regarded as isentropic with the adiaba-

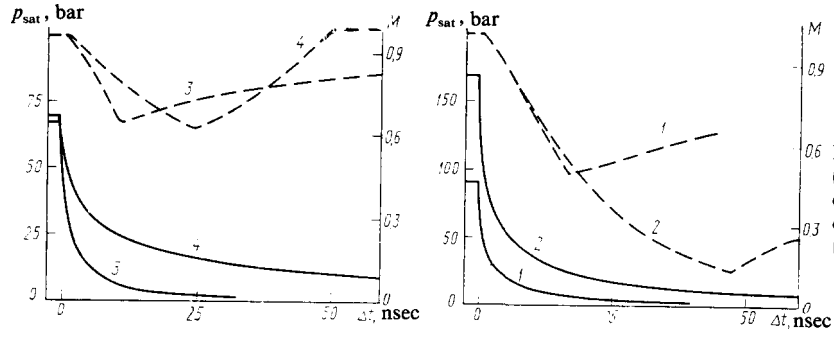

FIG. 1. Behavior of p_{sat} (continuous curves) and of M (dashed curves) calculated for $\Delta t = t - t_0 > 0$ after the end of action of absorbed radiation of intensity $G_0 = 10$ MW/cm^2 (1–3) and 5 MW/cm^2 (4); radiation is stopped at t_0 (μsec): 1) 0.3; 2) 1; 3) 0.25; 4) 2.

tic exponent $\gamma = 5/3$. The phase transition kinetics is described by Eqs. (12) and (13) which, for a given M, describe the temperature T_0 and the density ρ_0 of a gas on the outer boundary of the evaporation discontinuity in terms of the parameters of the saturated vapor.[6,25] The thermophysical parameters c, R_0, $\varkappa$, and L_v and the boiling point T_b at normal pressure p_b used in our calculations were the values typical of aluminum. The intensity of radiation absorbed on the surface of a sample differs from the incident radiation intensity by the absorptivity $A(T_s) < 1$. In the calculations reported below the value of G is specified for the sake of simplicity.

The system (10)–(15) is solved numerically by iteration procedures in the same way as in Ref. 26. A description of the method used in numerical solution of this system will be reported elsewhere. It is clear from Fig. 1 that at the end of interaction with radiation of intensity $G = G_0$ at the moment $t = t_0$, the values of p_{sat} and M fall rapidly. The Mach number M does not decrease to zero and after passing through a minimum begins to rise again, in contrast to the results reported in Ref. 25, where M falls to zero at $t_0 = 1$ μsec for $G_0 = 10$ MW/cm^2 and then remains zero. One of the possible reasons for this difference between the two sets of results is that when the time interval used in numerical integration of the system (10)–(15) is too large, the minimum value of M decreases. The actual form of the evolution $M(t)$ is governed by the relative velocity of the change in the temperature of the irradiated surface and in the reaction pressure exerted in the flux of the evaporated matter.[27]

Examples of the behavior of p_{sat} and M in various cases of step-like and continuous reduction of the intensity of the absorbed radiation are plotted in Fig. 2. The difference between M and unity decreases rapidly on increase in the relative change in the intensity. When the intensity at the moment $t_0 = 1$ μsec is reduced to $q = 0.95$ of the initial value $G_0 = 10$ MW/cm^2, the Mach number M remains constant to within 10^{-4}. However, if $G_0 = 5$ MW/cm^2 then at $t_0 = 1$ and 2 μsec when $p_{sat} = 40.5$ and 70.6 bar, we find that with the same accuracy $M = 1$ is constant already for $q = 0.8$. In the case of a gradual reduction of the intensity, the maximum difference between M and unity (Fig. 2) is less than in the case when the radiation is switched off instantaneously (Fig. 1). It is also clear from Fig. 2 that the fall of M begins after a delay relative to the fall of $G(t)$ and p_{sat}.

Graphs showing the changes in p_{sat} and M on modulation of the absorbed intensity in accordance with the law $G(t) = G_0[1 - a\sin(2\pi\Delta t/\tau)]$ ($\tau = 20$ nsec), which is switched on after $t_0 = 2$ μsec from the beginning of the action of radiation of constant intensity $G_0 = 5$ MW/cm^2, are plotted in Fig. 3a. The behavior of M depends strongly on the depth of modulation a and the solution of the problem lies in the range $M < 1$ only after a significant fall of the intensity and remains in this range throughout the period of rise of $G(t)$. If $a = 0.5$, the change in the Mach number $\delta M = 1 - M$ is of the same order of magnitude as the relative change in the temperature of the surface $\delta T_s/T_s$, but δM decreases more rapidly on reduction in a. For $a = 0.2$, the value of δM does not exceed 10^{-1}. This is in agreement with the hypothesis that in this interaction regime the solution of the nonlinear problem does not depart from the region where the Mach number has the constant value $M = 1$.

The behavior of M when a surface is heated by a Gaussian pulse $G(t) = G_0\exp(-t^2/\tau^2)$ ($\tau = 30$ nsec) is also very sensitive to G_0, as demonstrated in Fig. 3b. When the peak value of the intensity G_0 is reduced to 22 MW/cm^2 and $p_{sat}^{max} = 22$ bar, it is found that $M = 1$ to within 10^{-4}.

The results of our numerical modeling thus show that there is a nontrivial region of transient evaporation with a constant value of $M = 1$ and this region depends strongly on

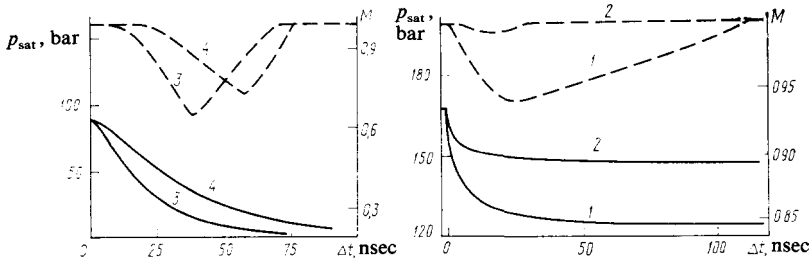

FIG. 2. Behavior of p_{sat} (continuous curves) and of M (dashed curves) at $\Delta t = t - t_0 > 0$ in the case of an abrupt change of the intensity $G = qG_0$ and for smooth switching of $G(t) = G_0\exp(-\Delta t/\tau)$, calculated for $G_0 = 10$ MW/cm^2, $t_0 = 1$ μsec (1,2) and 0.3 μsec (3, 4); $q = 0.8$ (1) and 0.9 (2); $\tau = 25$ nsec (3), 50 nsec (4).

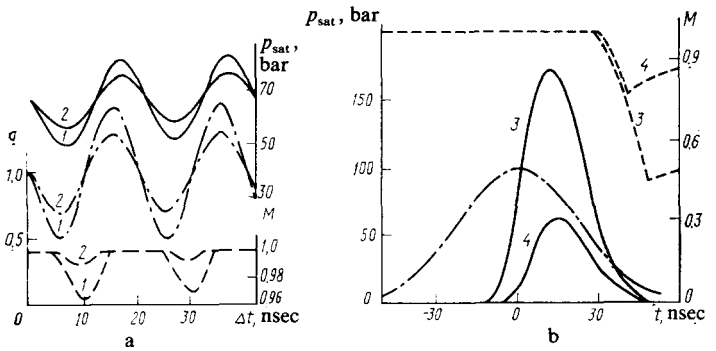

FIG. 3. a) Behavior of p_{sat} (continuous curves) and of M (dashed curves) when the depth of harmonic modulation of the intensity of the absorbed radiation is $a = 0.5$ (1) and 0.3 (2) calculated for $G_0 = 5$ MW/cm^2 (the intensity of the absorbed radiation is represented by the chain curves). b) Behavior of the same quantities in the case of a Gaussian pulse (chain curve) with a peak value $G_0 = 30$ MW/cm^2 (3) and 25 MW/cm^2 (4).

the laser interaction regime. When the radiation intensity is increased, an allowance must be made for the formation of a plasma in the flux of the evaporated matter. The kinetics of evaporation then needs to be considered separately.

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Translated by A. Tybulewicz