

# Non-Equilibrium Phase Change in Metal Induced by Nanosecond Pulsed Laser Irradiation

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*Materials processing using high power pulsed lasers involves complex phenomena including rapid heating, superheating of the laser-melted material, rapid nucleation, and phase explosion. With a heating rate on the order of  $10^9$  K/s or higher, the surface layer melted by laser irradiation can reach a temperature higher than the normal boiling point. On the other hand, the vapor pressure does not build up as fast and thus falls below the saturation pressure at the surface temperature, resulting in a superheated, metastable state. As the temperature of the melt approaches the thermodynamic critical point, the liquid undergoes a phase explosion that turns the melt into a mixture of liquid and vapor. This article describes heat transfer and phase change phenomena during nanosecond pulsed laser ablation of a metal, with an emphasis on phase explosion and non-equilibrium phase change. The time required for nucleation in a superheated liquid, which determines the time needed for phase explosion to occur, is also investigated from both theoretical and experimental viewpoints. [DOI: 10.1115/1.1445792]*

**Keywords:** Ablation, Experimental, Heat Transfer, Laser, Phase Change

## 1 Introduction

High power lasers are being used in a variety of advanced engineering applications, including micromachining, pulsed laser deposition (PLD) of thin films, and fabrication of nanometer size particles and carbon nanotubes [1–4]. Most of these processes involve complex thermal phenomena, including rapid heating, non-equilibrium phase change, superheating, and rapid nucleation in a superheated liquid. Under intense radiation of a laser pulse, the surface of a target is heated with a heating rate of  $10^9$  K/s or higher. At laser fluences (energy per unit area) of about  $1 \text{ J/cm}^2$  or higher, melting and ablation (rapid removal of material) will occur.

There are several mechanisms of laser thermal ablation, namely normal evaporation at the surface, heterogeneous boiling, and homogeneous boiling. During high power pulsed laser ablation, homogeneous boiling, or phase explosion could be an important ablation mechanism [5–8]. The phase explosion phenomenon was first investigated in the earlier work of rapid heating of metal wires using a high current electric pulse [9,10]. It occurs when a liquid is rapidly heated and approaches the thermal dynamic critical temperature, and the instability in the liquid causes an explosive type of liquid-vapor phase change. Miotello and Kelly [5] pointed out that phase explosion was a likely mechanism in nanosecond pulsed laser ablation. Song and Xu [6] were the first to provide experimental evidence of phase explosion induced by a nanosecond pulsed laser. They also showed that surface temperature-pressure relation could depart from the equilibrium Clausius-Clapeyron relation [11,12]. It has also been suggested that phase explosion occurred during sub-picosecond laser ablation [13]. Using molecular dynamics simulations, Zhigeei et al. showed phase explosion occurred when the laser fluence was above a threshold value, while surface desorption occurred at lower laser fluences [14].

This paper is concerned with energy transport and phase change

in metal induced by a high power nanosecond pulsed laser, with an emphasis on phase change mechanisms and nonequilibrium phase change kinetics at the evaporating surface. Phase explosion induced by rapid heating will be described first. A brief review of the experimental evidence of phase explosion will then be given. The experiments were performed in the laser fluence range from  $2.5 \text{ J/cm}^2$  to  $9 \text{ J/cm}^2$ , which is commonly used for many applications including PLD and micromachining. The nucleation process in liquid leading to phase explosion is discussed in detail.

## 2 Thermal Mechanisms of Laser Ablation and Phase Explosion

The phase change process induced by pulsed laser heating can be best illustrated using the pressure-temperature diagram as shown in Fig. 1 [7]. The “normal heating” line indicates heating of a liquid metal when the temperature is below the boiling temperature. At the boiling temperature, the liquid and vapor phases are in equilibrium, which is shown in Fig. 1 as the intersection between the normal heating line and the binode line. The binode line represents the equilibrium relation between the surface temperature and the vapor saturation pressure, which is calculated from the Clausius-Clapeyron equation. Evaporation occurs at the liquid surface, which is a type of heterogeneous evaporation, or normal surface evaporation.

The surface evaporation process can be computed. The rate of atomic flux (atoms/m<sup>2</sup>s) leaving the surface during normal evaporation is given as [15]:

$$\dot{m} = \frac{p_s}{(2\pi mk_B T)^{1/2}}, \quad (1)$$

where  $\dot{m}$  is the mass of the evaporating molecule or atom,  $k_B$  is the Boltzmann constant, and  $p_s$  is the saturation pressure at the liquid surface temperature  $T$ , which are related by the Clausius-Clapeyron equation:

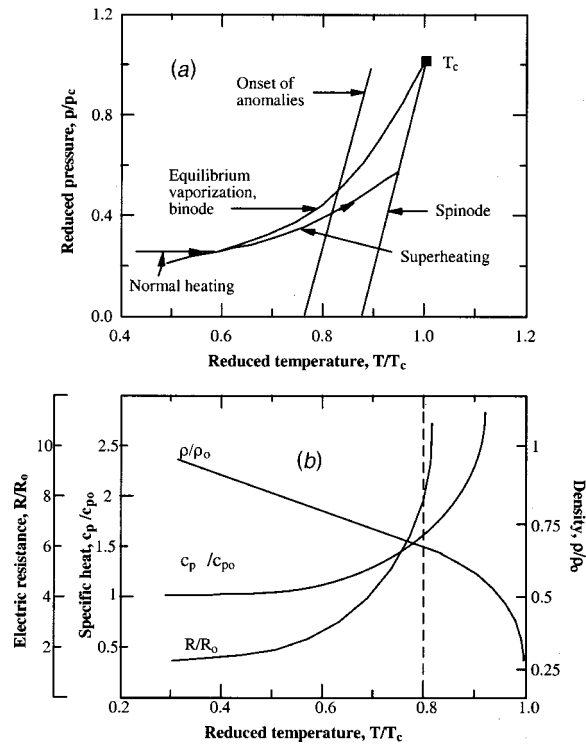
$$p_s = p_o \exp\left\{\frac{H_{lv}(T - T_b)}{RTT_b}\right\}. \quad (2)$$

In Eq. (2),  $p_o$  is the ambient pressure,  $H_{lv}$  is the enthalpy of vaporization, and  $T_b$  is the equilibrium boiling temperature at the ambient pressure (the normal boiling temperature).

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Contributed by the Heat Transfer Division for publication in the JOURNAL OF HEAT TRANSFER. Manuscript received by the Heat Transfer Division April 30, 2001; revision received November 16, 2001. Associate Editor: V. P. Carey.



**Fig. 1 (a)  $p$ - $T$  Diagram and (b) typical variations of physical properties of liquid metal near the critical point. The substrate “o” denotes properties at the normal boiling temperature.**

In a slow heating process, the surface temperature-pressure relation follows Eq. (2). On the other hand, when the heating rate is high enough such as what occurs during high power pulsed laser heating, it is possible to superheat a liquid metal to temperatures above the boiling point while the surface vapor pressure is not built up as rapidly. The liquid is then superheated, i.e., its temperature is higher than the vaporization temperature corresponding to its surface pressure. In this case, the heating process deviates from the binode, but follows a superheating line shown in Fig. 1, and the liquid is in a *metastable* state. The exact details of the superheating are not known, but should depend upon the heating rate. There is an upper limit for superheating of a liquid, the spinode [16–18], which is the boundary of thermodynamic phase stability and is determined by the second derivatives of the Gibbs’ thermodynamic potential [19]:

$$\left(\frac{\partial p}{\partial v}\right)_T = 0, \quad (3)$$

where  $v$  is the specific volume. Using Eq. (3), the spinode equation can be derived from empirical equations of state such as the van der Waals equation or the Berthelot Eq. [20]. As the temperature approaches the spinode, fluctuations of local density of a liquid metal increase rapidly, and  $(\partial p/\partial v)_T \rightarrow 0$ , resulting in a loss of thermodynamic stability. These fluctuations begin when the temperature approaches  $0.8 T_c$ , which drastically affect other physical properties. Figure 1(b) shows properties of a liquid metal near the critical point. Rapid changes of properties can be seen when the liquid temperature is above  $0.8 T_c$ . These drastic property changes are called anomalies, which are also indicated in Fig. 1(a). Usually, the onset of anomalies concurrently marks the onset of significant reduction or even disappearance of electrical conductivity of a liquid metal due to many isolated regions with few free electrons [21,22]. Thus, at the onset of anomalies, a liquid

metal is transferred from a conductor to a dielectric. Its transmission to optical radiation increases and surface reflectivity decreases.

A competing process that prevents superheating of a liquid is spontaneous nucleation. If the rate of spontaneous nucleation is high enough, homogeneous liquid-vapor phase change would occur. Therefore, the existence of the superheated state requires a low rate of spontaneous nucleation. The rate of spontaneous nucleation can be determined from the Döring and Volmer’s theory [23,24]. According to this theory, the frequency of spontaneous nucleation is calculated as

$$J = \eta \exp\left(\frac{-W_{cr}}{k_B T}\right), \quad (4)$$

where  $W_{cr}$  is the energy needed for vapor embryos to grow to nuclei at temperature  $T$ , or the work of formation of nuclei. (Embryos smaller than a critical size will collapse, while those larger than the critical radius, called nuclei, will favor growing in order to reduce free energy.)  $\eta$  is on the order of magnitude of the number of liquid molecules per unit volume, calculated as [23]:

$$\eta = N \left(\frac{3\sigma}{\pi m}\right)^{1/2}, \quad (5)$$

where  $N$  is the number of liquid molecules per unit volume, and  $\sigma$  is the surface tension. Note that the above results are derived based on the assumption that the heating rate is slow enough that an equilibrium distribution of embryos exists in the liquid.

According to Eqs. (4) and (5), the spontaneous nucleation rate increases exponentially with temperature. It has been calculated that the frequency of spontaneous nucleation is only about  $0.1 \text{ s}^{-1} \text{ cm}^{-3}$  at the temperature near  $0.89 T_c$ , but increases to  $10^{21} \text{ s}^{-1} \text{ cm}^{-3}$  at  $0.91 T_c$  [5]. For a slowly heated liquid, the number of nuclei generated by spontaneous nucleation will be high enough to cause homogeneous phase change at the normal boiling temperature. Therefore, a superheated state cannot be sustained. On the other hand, during high power pulsed laser heating considered in this work for which the time duration is on the order of tens of nanoseconds, the amount of nuclei generated by spontaneous nucleation is negligible at temperatures lower than  $0.9 T_c$ . Therefore, the liquid could possess considerable stability with respect to spontaneous nucleation. At a temperature of about  $0.9 T_c$ , a significant number of nuclei can be formed within a short period of time. Hence, homogeneous nucleation, or explosive phase change occurs, which turns the liquid into a mixture of liquid and vapor, leaving the surface like an explosion.

To analyze phase change induced by pulsed laser heating, it is also necessary to consider the time required for a vapor embryo to grow to a critical nucleus, which is called the time lag for nucleation. For most engineering applications, the time to form critical nuclei is too short to be considered. However, during pulsed laser heating when the heating time is on the order of nanoseconds or shorter, this time lag could be on the same order of the time period under consideration. Equation (4) can be modified to account for this time lag,  $\tau$ , which can be expressed as [24]:

$$J = \eta \exp\left(\frac{-W_{cr}}{k_B T}\right) \exp\left(\frac{-\tau}{t}\right), \quad (6)$$

where  $t$  is the time duration for which the liquid is superheated. The time lag  $\tau$  has been estimated to be [24]:

$$\tau = \left(\frac{2\pi M}{RT}\right)^{1/2} \frac{4\pi\sigma p_s}{(p_s - p_t)^2}, \quad (7)$$

where  $M$  is the molar weight of the substance. Skripov performed calculations based on Eq. (7) for metals and found the time lag to be approximately 1–10 ns [24].

### 3 Experimental Investigation of Phase Explosion and Its Time Lag

This section describes studies on phase change mechanisms during laser ablation through a number of experimental investigations on laser-induced vapor. Although it is more desirable to measure the surface temperature and pressure for the study of phase change kinetics, direct measurement of the surface temperature is hampered by the strong radiation from the laser-induced vapor. On the other hand, properties of the vapor are strongly linked to the surface thermodynamic parameters. Therefore, knowing the properties of the laser-induced vapor could help to understand the phase change phenomenon occurring at the surface.

#### 3.1 Summary of Experimental Study on Phase Explosion.

The laser used for the experimental study is a KrF excimer laser with a wavelength of 248 nm and a pulse width of 25 ns (FWHM). The center, uniform portion of the excimer laser beam is passed through a rectangular aperture (10 mm by 5 mm) to produce a laser beam with a uniform intensity profile. A single 150 mm focal length CaF<sub>2</sub> lens is used to focus the laser beam on the target. Polished nickel (50 nm RMS roughness) is used as the target.

The following parameters are measured: transient transmissivity of laser beam through the laser-induced vapor plume, scattering of laser beam from the laser-induced vapor plume, transient location and velocity of the laser-induced vapor front, and ablation depth per laser pulse. Details of the experiments have been given elsewhere [7]. The experimental results are provided here for further discussions.

Figure 2(a) shows the transient location of the vapor front as a function of laser fluence. The measurement is based on an optical deflection technique, which is highly accurate (better than  $\pm 3$  percent) and repeatable. Figure 2(b) shows the averaged velocity of the laser-evaporated vapor. These are time-averaged vapor velocities from the vapor onset to 50 ns calculated from Fig. 2(a). It is seen that the vapor velocity increases with the laser fluence increase from about 2,000 m/s at the lowest fluence to about 7000 m/s at the highest fluence. However, the increase of velocity is not

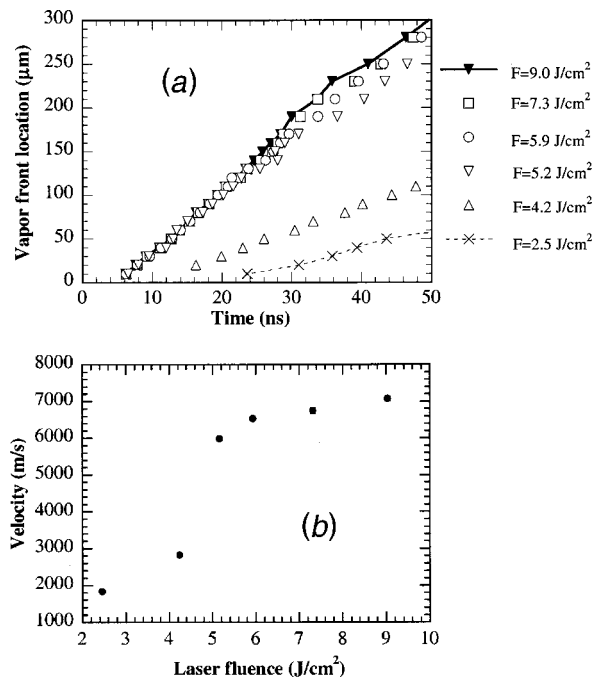


Fig. 2 (a) Transient locations of the vapor front as a function of laser fluence; and (b) vapor velocity as a function of laser fluence.

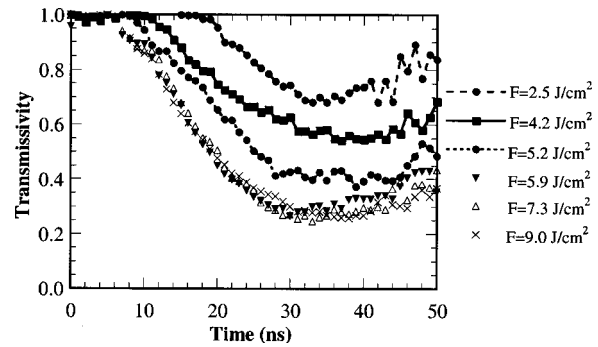


Fig. 3 Transient transmissivity of vapor as a function of laser fluence

monotonous. A sudden jump of the velocity is seen at the laser fluence of 4.2 J/cm<sup>2</sup>. In the laser fluence range between 5.2 and 9 J/cm<sup>2</sup>, the velocity is almost a constant.

The different relations between the vapor velocity and the laser fluence indicate different laser ablation mechanisms. The velocity of the vapor plume is determined by the pressure and the temperature at the target surface. The constant velocity at high laser fluences indicates that the surface temperature is not affected by the increase of the laser fluence. Such a constant surface temperature can be explained as a result of phase explosion. As discussed earlier, the surface temperature during phase explosion is about  $0.9 T_c$ , the spinodal temperature. Once the laser fluence is high enough to raise the surface temperature to the spinode, increasing the laser fluence would not raise the surface temperature further. On the other hand, when the laser fluence is below 4.2 J/cm<sup>2</sup>, the velocity increases over 50 percent. Therefore, the surface temperature increases with the laser fluence increase; normal vaporization occurs at the surface.

Figure 3 shows the transient transmissivity of the vapor at different laser fluences. The uncertainty of the measurement is less than a few percent in the time duration from a few nanoseconds to about 45 ns. Near the end of the laser pulse, the uncertainty of the measurement is larger ( $\sim 10$  percent), since the pulse intensity is weak. The data show that the transient transmissivity is almost identical for laser fluences higher than 5.2 J/cm<sup>2</sup>, which is exactly the same fluence region in which the velocity of the vapor changes little. This is also explained as a result of explosive phase change occurring at laser fluences above 5.2 J/cm<sup>2</sup>. Extinction of the laser beam is determined by the cross section of the energized atoms, which in turn is determined by the temperature of the vapor plume. The temperatures of vapor are about the same when the laser fluence is higher than 5.2 J/cm<sup>2</sup>, since the temperatures at the surface are all about  $0.9 T_c$ . Thus, transmission through vapor stays at a constant value.

Figure 4 shows the percentage of laser energy scattered from the vapor plume as a function of laser fluence. Scattering of laser energy is due to large size (on the order of sub-micron or larger) droplets in the vapor plume instead of (atomic) vapor. It is seen from Fig. 4 that there is almost no scattering (less than 0.5 percent, the measurement resolution) in the low laser fluence region. Therefore, there are no droplets in the vapor plume. When the laser fluence is higher than 5.2 J/cm<sup>2</sup>, the percentage of laser energy scattered by the plume is about 4 to 5 percent, indicating the existence of liquid droplets. This phenomenon again can be explained by the different ablation mechanisms. When explosive phase change occurs, the melted layer is turned into a liquid-vapor mixture. Therefore, the increase of scattering at the laser fluence of 5.2 J/cm<sup>2</sup> also indicates the transition from surface evaporation to phase explosion.

Figure 5 shows the ablation depth per laser pulse at different laser fluences. The ablation depth increases almost linearly from 14 to 20 nm with laser fluence when the laser fluence is less than

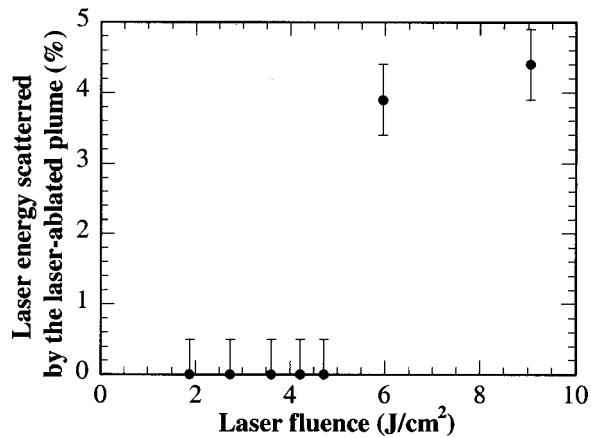


Fig. 4 Percent of laser energy scattered to the ambient as a function of laser fluence

4.0 J/cm<sup>2</sup>. When the laser fluence increases from 4.2 to 5.2 J/cm<sup>2</sup>, a jump increase in the ablation depth is observed, and stays relatively a constant at higher laser fluences. This again is explained as surface normal vaporization versus volumetric phase explosion. When phase explosion occurs, the liquid layer is ablated, therefore, the ablation depth is much greater than that of surface evaporation.

Since the surface temperature is maintained at a relatively constant value when phase explosion occurs, one question arises as to how the additional laser energy dissipates when the laser fluence is further increased. A possible explanation is that once the temperature reaches above 0.8  $T_c$ , the material is heated up less quickly, since it becomes less absorbing as seen in Fig. 1(b) allowing the laser energy to penetrate deeper into the material. Another reason is that when the temperature approaches the spinodal temperature, most of the additional incoming laser energy is consumed by nucleation instead of raising the temperature, and the nucleation rate increases exponentially around the spinode.

In a brief summary, these four independent experiments all show that surface evaporation occurs at laser fluences below 4.2 J/cm<sup>2</sup>, while an explosive phase change occurs when the laser fluence is higher than 5.2 J/cm<sup>2</sup>.

**3.2 Kinetics at the Evaporating Surface.** To understand the kinetics at the evaporating surface, the transient pressure of the evaporating surface is measured with the use of a PVDF transducer attached to the back of a thin nickel target. Details of the experiment have been given elsewhere [25]. The transient surface

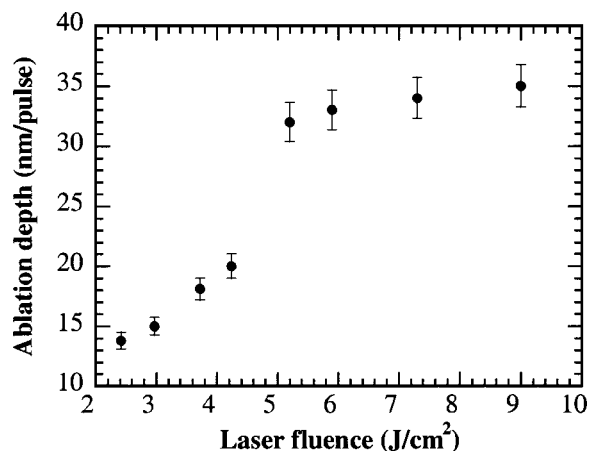


Fig. 5 Ablation depth as a function of laser fluence

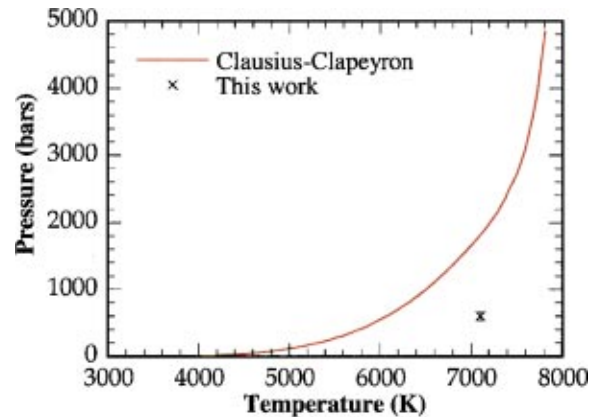


Fig. 6 Comparison between the Clausius-Clapeyron relation and the measured pressure at 0.9  $T_c$

pressure is obtained at various laser fluences. Of particular interest is the pressure when phase explosion occurs, which is determined to be about 600 bars ( $\pm 10$  percent) at 5.2 J/cm<sup>2</sup>. Figure 6 shows the Clausius-Clapeyron equation for Ni, together with the experimental data point at 5.2 J/cm<sup>2</sup>. It can be seen that the pressure obtained from the experiment is well below the equilibrium pressure, showing that the liquid is indeed superheated under pulsed laser irradiation.

Another way to estimate the validity of the equilibrium evaporation kinetics is to compute the evaporation depth from the measured pressure using the Clausius-Clapeyron equation and compare the calculated results with the measured data. To do so, the transient surface temperature  $T$  is first calculated from the measured transient surface pressure  $p$  and the Clausius-Clapeyron equation, Eq. (2). Knowing the surface temperature and pressure, the evaporation velocity,  $V_{lv}$ , can be calculated from the atomic flux  $\dot{m}$  using Eq. 1, modified by a factor of  $m/\rho_l$ . The ablation depth per laser pulse is obtained by integrating the evaporation velocity over time. Note that this calculation can only be carried out for surface evaporation.

The calculated ablation depths at different laser fluences are shown in Fig. 7. It can be seen that the calculated ablation depths are greater than the measured values, by as much as a factor of seven to eight. This large discrepancy again indicates that the equilibrium interface kinetics and the Clausius-Clapeyron equa-

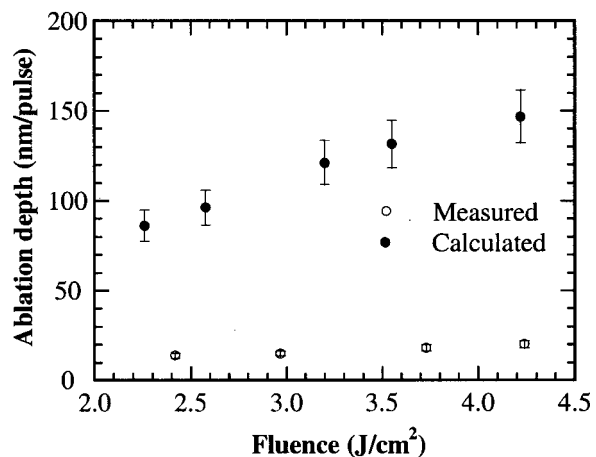


Fig. 7 Comparison between the measured ablation depth and the values calculated using transient pressure data and the equilibrium kinetic relation

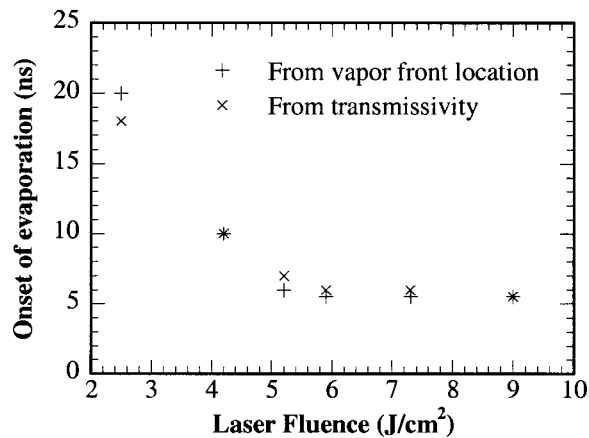


Fig. 8 Onset of evaporation as a function of laser fluence determined from the transient location of the vapor front and from the transient transmissivity through the vapor

tion do not correctly represent the actual surface temperature-pressure relation during pulsed laser evaporation.

**3.3 Time Lag in Phase Explosion.** Further examinations of Fig. 2(a) and Fig. 3 reveal another phenomenon: the onset of ablation, indicated as the time when the vapor front leaves the surface (Fig. 2(a)) and the time that transmission starts to decrease (Fig. 3), is about the same when the laser fluence is higher than 5.2 J/cm<sup>2</sup>. The onset of ablation is re-plotted in Fig. 8. It can be seen that, when the laser fluence is higher than 5.2 J/cm<sup>2</sup>, the onset of ablation does not change with the laser fluence, but remains at around 5.5 ns after the beginning of the laser pulse. The accuracy of this measurement depends on the time resolution of the measurement instrument, which is about 0.5 ns. The two independent measurements provide almost identical results.

The constant value of the onset of ablation can be explained as the time needed for phase explosion to occur, or the time lag for phase explosion. The experimental results discussed previously indicate that the phase explosion occurs when the laser fluence is higher than 5.2 J/cm<sup>2</sup>. At these laser fluences, the measured results of the vapor front location and the optical transmission are dictated by the mass removal due to phase explosion. Thus, the constant onset of ablation at laser fluences higher than 5.2 J/cm<sup>2</sup> indicates that the time lag prevents phase explosion to occur at an earlier time, and this time lag is about a few nanoseconds.

The experiments described in this paper are performed with the use of a 25 ns pulsed excimer laser on a nickel target. It is believed that the phase change phenomena discussed here should occur for other metals as well. On the other hand, if the laser fluence is *much* higher than the threshold fluence for phase explosion, it is possible that the surface temperature can be raised higher. In our experiments with a laser fluence above 10 J/cm<sup>2</sup>, it was indeed found that the velocity of vapor increases, and transmission and onset of evaporation reduces from the values of the constant region. Experiments with very high laser fluences should be conducted to investigate the possibility of heating the material above the limit of thermodynamic stability. A last note is on the phase change mechanisms induced by sub-nanosecond laser ablation. The threshold nature of ablation has been observed in many pico- and femtosecond laser ablation experiments [e.g., [8,26]]. Phase explosion is explained as the ablation mechanism induced by a femtosecond laser irradiation [13]. However, since the heating time is much less than the time lag of nucleation, much work is needed to gain a thorough understanding of ablation induced by a pico or femtosecond laser.

## 4 Conclusions

Heat transfer and non-equilibrium phase change during nano-second pulsed excimer laser ablation of nickel were investigated. Results of experiments showed surface evaporation occurred when the laser fluence was below 4 J/cm<sup>2</sup>. When the laser fluence was higher than 5 J/cm<sup>2</sup>, the liquid reached a metastable state during laser heating and its temperature approached the critical point, causing an explosive type of phase change. The kinetic relation between the surface temperature and pressure was found to deviate from the equilibrium Clausius-Clapeyron equation. With the given experimental conditions, the time lag of phase explosion was found to be around a few nanoseconds.

## Acknowledgments

Support of this work by the National Science Foundation and the Office of Naval Research is gratefully acknowledged.

## Nomenclature

$H_{lv}$	= latent heat of evaporation [J/kmole]
$J$	= frequency of spontaneous nucleation [ $m^{-3} s^{-1}$ ]
$k_B$	= Boltzmann's constant, $1.380 \times 10^{-23}$ J/K
$m$	= atomic mass [kg]
$\dot{m}$	= atomic flux, [ $s^{-1} m^{-2}$ ]
$M$	= molar weight, [kg/kmol]
$N$	= number density of atoms [ $m^{-3}$ ]
$p$	= pressure [ $N/m^2$ ]
$p_l$	= pressure in liquid [ $N/m^2$ ]
$p_s$	= saturation pressure [ $N/m^2$ ]
$R$	= universal gas constant, 8.314 kJ/kmol·K
$t$	= time [s]
$T$	= temperature [K]
$T_b$	= normal boiling temperature [K]
$T_c$	= critical temperature [K]
$v$	= specific volume [ $m^3/kg$ ]
$W_{cr}$	= energy required to form critical nuclei [J]

## Greek Symbols

$\eta$	= factor in Eqs. (4) and (5) [ $m^{-3} s^{-1}$ ]
$\rho_l$	= density of liquid [ $kg/m^3$ ]
$\sigma$	= surface tension [N/m]
$\tau$	= time lag of nucleation [s]

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