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Ultrafast thermal melting of laser-excited solids by homogeneous nucleation

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Homogeneous nucleation is considered as a mechanism for rapid *thermal* melting of solids irradiated with ultrashort laser pulses. Based on classical nucleation theory we show that for sufficient superheating of the solid phase the dynamics of melting is mainly determined by the electron-lattice equilibration rather than by nucleation kinetics. Therefore, complete melting of the excited material volume should occur within a few picoseconds. This time scale lies between the longer time scale for heterogeneous, surface-nucleated melting and the shorter time scale for possible nonthermal melting mechanisms.

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The nature of melting, i.e., the transition of a material from the solid to the liquid phase, is one of the fundamental questions of condensed matter physics. Usually, melting starts at the surface of a solid, since the barrier for heterogeneous nucleation of the liquid phase is zero at the solid-vapor interface.[1,2] However, if heterogeneous nucleation can be suppressed, a solid may be heated to temperatures considerably above its equilibrium melting temperature. Several theories have considered the fundamental stability limits of a superheated solid at which the material cannot survive in crystalline order.[3–8] These *static* approaches focused on the limit of *metastable* superheating[9] but did not take into account the kinetics of the phase transformation. Based on classical nucleation theory[2] a few attempts have been made to study the *kinetic* limits of the attainable solid phase superheating.[10,11]

In this work we extend these approaches to the rapid melting of solids that can be achieved by ultrashort pulsed laser irradiation. Laser pulses of femto- to picosecond duration provide a unique tool for preparing and studying extreme states of condensed matter. Initially, the solid is transformed into a highly nonequilibrium state as the optical energy is deposited in the electronic subsystem, while the lattice remains cold.[12,13] The time subsequently required to heat the phonon system depends on the particular material but lies typically in the range of picoseconds.[13,14] Consequently, by using short laser pulses of sufficient energy, very high heating rates of several tens or hundreds of kelvin per picosecond can easily be reached. Thus, it is expected that within a few picoseconds a solid may be heated to very high temperatures which, *transiently*, exceed well the melting temperature and also the *static* stability limits mentioned above. In fact, there are a few experimental indications of large superheating in laser-excited solids obtained by picosecond time-resolved electron diffraction[15,16] and time-of-flight mass spectroscopy.[17]

The dynamics of the solid-liquid phase transition induced by short laser pulses has been studied experimentally for more than two decades.[18] In accordance with the considerations on the electron-lattice equilibration[13,14] the experiments have shown that for pulse durations down to a few picoseconds[19] and also for femtosecond pulses close to the melting threshold[20–22] the phase transition can be described as a rapid thermal process. Up to now the available data seem to point towards a heterogenous melting process in which the liquid phase is nucleated at the surface and a melt front proceeds from the surface into the material with a velocity ultimately limited by the speed of sound. For example, in semiconductors like silicon, germanium, and gallium arsenide maximum melt-front velocities v_M up to 1000 m/s have been measured,[20,22–24] which also indirectly indicates large solid-phase superheating. These melt-front velocities result in total melting times $t_M = d/v_M \approx 100$ ps where $d \approx 100$ nm is a typical thickness of the heated layer.

Here we describe a different possibility for the laser-induced melting of solids due to fast *homogeneous* nucleation under strongly superheated conditions. By deriving an explicit expression for the melting time t_M we show that for sufficiently high superheatings a solid may melt completely within a few picoseconds, this time scale being mainly determined by the time needed for electron-lattice equilibration. Therefore this process can be significantly faster than heterogenous, surface-nucleated melting.

Based on Ref. 10 we consider the homogeneous nucleation of spherical nuclei in the bulk of a superheated crystal. Growth of lentil nuclei was investigated in Ref. 25. The elastic energy of lentil-shaped nuclei may be lower than that of spherical nuclei, so the nucleation will be even more rapid in this case. However, it was found that the formation of lentil-shaped nuclei is only preferable for small superheating.[10,26] Thus, the assumption of spherical nuclei is justified for the estimation presented here.

According to Ref. 10, the probability of the formation of one critical nucleus per time and volume at the temperature T is given by

$$\omega = 2\,A^{1/6} n_s^2 \sqrt{kT}\left(\frac{3k^4T_m^4}{16\pi q^4}\right)^{1/6} \eta \exp\left(-\frac{A/k^3}{T\,(T-T_m)^2}\right), \tag{1}$$

with

$$A=16\sigma_{sl}^3\pi k^2T_m^2/(3q^2), \tag{2}$$

where σ_{sl} is the surface tension between the solid and liquid phases, n_s is the density of the solid phase, T_m is the melting temperature, k is Boltzmann's constant, and q is the latent heat for melting. η is connected with the velocity of the phase boundary and given by $\eta = v_m c_p/(qk)$,[27] where v_m is an empirical constant determining the velocity of the growth of nuclei and being on the order of the speed of sound, and c_p is the heat capacity of the solid.

In Ref. 10, and similarly in Ref. 11, a *kinetic* limit of solid-phase superheating was defined by postulating a *nucleation catastrophe* at an arbitrarily chosen critical nucleation rate of $\omega_{cr}=1\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$. It is obvious that ω_{cr} is far too low to be of any importance for ultrashort pulse laser-induced melting on a picosecond time scale. In other words this nucleation catastrophe will not occur on such short time scales and *transient* superheating may be considerably higher in this case. Therefore, we give here an explicit expression for the melting time t_M due to homogeneous nucleation as a function of superheating by assuming that one critical nucleus exists per volume V_c of a critical nucleus. The volume of a spherical critical nucleus is $V_c=\frac{4}{3}\pi R_c^3$ with $R_c = 2\sigma_{sl}T_m/[q(T-T_m)]$ being its radius. With this, the melting time t_M can be expressed as $(\theta = T/T_m)$

$$t_M=(\omega V_c)^{-1}=\frac{3}{4\pi}\left(\frac{q(\theta-1)}{2\sigma_{sl}}\right)^3\frac{1}{\omega}. \tag{3}$$

By inserting Eq. (1) into Eq. (3) we obtain

$$t_M = N\times M\times f(\theta), \tag{4}$$

with

$$N=\frac{3}{64\pi}\left(\frac{16\pi}{3}\right)^{1/6}\frac{1}{k^{2/3}},$$

$$M=\frac{q^{14/3}}{n_s^2\,T_m^{5/3}\,c_p}\,\frac{1}{\sigma_{sl}^3\,v_m\,(A/k^3T_m^3)^{1/6}},$$

and

$$f(\theta)=\frac{(\theta-1)^3}{\sqrt{\theta}}\exp\left(\frac{A}{k^3T_m^3}\frac{1}{\theta(\theta-1)^2}\right).$$

The first factor N is a numerical factor of 4.15×10^{13} $(\mathrm{K/J})^{2/3}$, the second factor M is material dependent, and the third factor $f(\theta)$ is a function of superheating θ (and, through $A/k^3T_m^3$, material dependent as well).

Figure 1 shows the melting time calculated by Eq. (4) for different materials as a function of the superheating θ. In superheated solids with θ between ~1.3 and ~1.5, melting times of around 1 ps are easily reached for homogeneous nucleation.

It is important to note that this statement is generally valid, despite the fact that several material parameters entering Eq. (4) are not known precisely. For example, there is only limited knowledge of the surface tension between liquid and solid σ_{sl}. In Fig. 1 there are two curves for silver, based on two different values for σ_{sl}, given in Table I. We see that the value of σ_{sl} is crucial for calculating the melting time t_M. A difference of about 10% in σ_{sl} leads to a difference of about one order of magnitude in t_M. However, if one wants to calculate the superheating θ for a given t_M, exact knowledge of σ_{sl} is not important. The superheatings θ leading to a certain melting time differ only by about 5%.

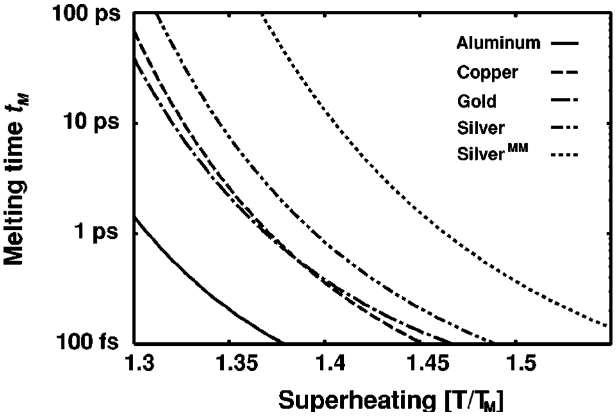

FIG. 1. Melting time for homogeneous nucleation calculated by Eq. (4) for different materials in dependence on the superheating T/T_m.

For our calculations we chose values for the surface tension between liquid and solid from Ref. 28; the values are given in Table I. The other material parameters entering Eq. (4) can be found in data books.[29] The empirical constant v_m was chosen to equal the mean sound velocity. In Ref. 28 a second set of values for σ_{sl} is listed, based on Ref. 30. These values are up to 30% lower than those in Table I, thus leading to a faster nucleation than shown in Fig. 1. For silver we consider a second value of surface tension, calculated from Ref. 10, where the parameter $A/k^3T_m^3$, Eq. (2), was found to equal 2.335. This set of parameters and the resulting curve in Fig. 1 are marked with the index "MM." The melting time t_M for silver is higher in this case than with the value for σ_{sl} from Ref. 28. However, the necessary superheatings θ for melting within a certain time do not differ very much.

Note that the surface tension between liquid and solid is related to the mechanical properties of the material and is thus expected to be temperature dependent itself. This is in-

TABLE I. Surface tension for different materials from Ref. 28 (Ag^{MM} from Ref. 10) and resulting parameters entering Eq. (4). Here $\theta(t_M=1\ \mathrm{ps})$ is the necessary superheating T/T_m for a melting time of 1 ps by homogeneous nucleation.

	$\sigma_{sl}[J/m^2]$	$A/k^3T_m^3$	$N\times M[\mathrm{fs}]$	$\theta(t_M=1\ \mathrm{ps})$
Al	0.093	0.956	17.24	1.31
Cu	0.177	1.49	8.62	1.37
Au	0.132	1.335	18.33	1.37
Ag	0.126	1.626	10.97	1.40
$\mathrm{Ag}^{\mathrm{MM}}$	0.142	2.335	7.2	1.46

dicated in Ref. 10, where the temperature dependence of the parameter $A/k^3T_m^3$, Eq. (2), was investigated. With increasing temperature the rigidity of the crystal decreases and thus the surface tension between liquid and solid will also decrease, leading to an even faster nucleation.

We would like to stress that the melting time t_M calculated through Eq. (4) represents only a rough estimate due to various assumptions and approximations. The actual nucleation rate may be different from Eq. (1) in the presence of a high density of critical nuclei as assumed here in the derivation of the melting time t_M. On the other hand, our expression for t_M is based on the assumption that a certain amount of nuclei of a certain size is statistically present in the solid. In reality, smaller nuclei also contribute to the melted volume. Moreover, critical nuclei built at times $t < t_M$ will continue growing and thus increase the fraction of melted volume at time t_M. There are also fundamental limits for t_M determined by microscopic kinetics. An atom at the phase boundary between solid and liquid changes to liquid phase not faster than $t \approx 100$ fs, estimated from the mean distance of atoms in the solid divided by the speed of sound. A similar lower limit is obtained when assuming that the minimum critical radius equals the mean atomic distance.

Therefore, Eq. (4) should not be expected to give accurate values for the melting time in a given situation. However, we believe that this equation is suitable for the intention of this work: namely, to demonstrate that the melting of superheated bulk material is generally possible in times comparable to the time needed for electron-lattice equilibration.

It is interesting to compare the *macroscopic* approach used in this work with recent molecular dynamics calculations.[31,32] These calculations, although not directly comparable to the highly transient situation considered in our work, provide detailed information on the *microscopic* processes determining the nucleation of the liquid phase in superheated solids. In particular in Ref. 32 it was shown that the predicted vibrational[3] and mechanical[5] instabilities of the lattice occur simultaneously but only locally, leading to the formation of destabilized clusters inside the superheated bulk. These local regions of disorder appear statistically and are interpreted as the sites where homogeneous nucleation of the liquid phase is initiated.

Finally, we should like to mention that the melting scenario described in this work competes with possible *nonthermal* mechanisms which can lead to phase changes on an even faster time scale. Recent experiments using femtosecond laser pulses of high fluences have demonstrated melting in less than 1 ps in a variety of covalently bonded materials.[20–22,33–38] This rapid phase transition is explained by a lattice instability due to the excitation of a high-density electron-hole plasma.[39,40] Since in this case the lattice becomes unstable prior to the heating of the phonon system, this process is often called *nonthermal* melting.

Therefore, in order to observe homogeneous thermal melting after short-pulse laser excitation it is important to choose the experimental parameters carefully. A material with a large penetration depth for the optical heating pulse, as well as a detection technique with a sufficient probing depth (for example time-resolved x-ray diffraction), is desirable. Moreover, a pulse duration of the order of the electron-lattice equilibration time (≈ 1 ps) should be chosen. Such a pulse still allows maximum heating rates but keeps the degree of electronic excitation as low as possible in order to suppress the above-mentioned nonthermal effects.

In conclusion, we considered rapid melting by homogeneous nucleation of the liquid phase in the bulk of a highly superheated solid. Our estimations show that for high superheatings of about $T \approx 1.5\,T_m$ different materials can melt within a few picoseconds. Such superheatings are readily attained after excitation with an ultrashort high-energy laser pulse. In this case the lattice is heated within a few picoseconds after irradiation, and the total melting time of the crystal by homogeneous nucleation is governed by the time needed for lattice heating. The process considered in our work requires more time than possible nonthermal mechanisms but it is significantly faster than the time needed for a melting front to proceed from the surface through the heated layer. It thus provides a third pathway for the laser-induced solid-to-liquid transformation in a bulk material with a time scale lying between the characteristic times of the melting processes investigated so far.

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