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How to Crystallize Glass with a Femtosecond Laser

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Abstract: The crystallization of glass through conventional thermal annealing in a furnace is a well-understood process. However, crystallization by femtosecond (fs) laser brings another dimension to this process. The pulsed nature of the irradiation necessitates a reevaluation of the parameters for optimal crystallization and an understanding of the particularities of using fs laser. This includes adjusting the laser pulse energy, the repetition rate, and the writing speed to either initiate nucleation or achieve substantial crystal growth. Therefore, a key challenge of this work is to establish reliable calculations for understanding the link between the size of the crystallized region and an ongoing transition (e.g., solid-to-solid, liquid-to-solid), while accounting for the aforementioned laser parameters. In this context, and based on previous work, a temperature distribution (in space and time) is simulated to model the thermal treatment at any point in the glass. By setting the condition that the temperatures are between the glass transition and melting temperature, the simulated crystallized region size can be compared with experimental observations. For that purpose, knowledge of the beam width at the focal point and of the absorbed beam energy fraction are critical inputs that were extracted from experiments found in the literature. After that, the management of the crystallization process and the width of the crystallization line can be achieved according to pulse energy, e.g., crystallite size, and also the effect of the scanning speed can be understood. Among the main conclusions to highlight, we disclose the laser conditions that determine the extent of the crystallized area and deduce that it is never of interest to increase the pulse energy too much as opposed to the repetition rate for the uniform crystallized line.



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1. Introduction

Three dimensional localized crystallization in glasses brings interest as it introduces the possibility of precipitating crystalline phases that present optical non-linear, ferroelectric, or pyroelectric properties. For example, it leads to the formation of non-center-symmetric crystals in optically suitable glasses [1]. This approach underscores that crystallization, a thermo-kinetics process [2,3], is influenced by temperature (and time), occurring between the glass transition temperature (T_g) and the melting temperature (T_m) of the given precipitated phase(s), and dictating nucleation and growth rates. While spatially selective crystallization using a femtosecond laser has been extensively demonstrated in various glasses [1], this process appears more complex than using a continuous-wave (CW) laser, arising from the pulsed nature of the laser (up to several MHz), and its high peak intensity triggering non-linear processes. For example, in lithium niobium silicate glasses (LNS) [4], crystallization patterns of the LiNbO_3 phase strongly depend on pulse energy or laser polarization.

While some physical aspects of crystallization mechanisms have been understood, we aim to further explain and predict semi-quantitative aspects, particularly the correlation between laser parameters and specific optical or material properties. A goal is to minimize the number of experiments by performing calculations that facilitate a selection of relevant

parameters to induce crystallization. For this purpose, a simple analytical solution has been developed in a previous work [5] to physically describe the thermal dynamics induced by pulsed laser absorption and the subsequent transformations.

In this work, we first simulate the evolution of the temperature distribution induced by a pulsed fs laser. Once the temperature modulation is known, it can be combined with a time–temperature transformation (TTT) diagram for crystallization. The temperature calculation relies on modeling the energy source as spherical, and requires knowledge of several parameters:

(1) The ratio (labeled R_τ) between the pulse period ($\tau_{RR} = 1/RR$, with RR being the pulse repetition rate) and the heat diffusion time ($\tau_D = w^2/4D_{th}$, w being the light beam waist radius at $1/e$ at the focus, and D_{th} the heat diffusion coefficient or diffusivity). While R_τ depends thus on w , the latter is usually not reliably known due to the complexity of non-linear effects in the light–matter interaction. For this purpose, a compilation of values is extracted from the literature, allowing us to clarify its dependency on the incident pulsed laser energy (please refer to Appendix A).

(2) The fraction of the incident energy effectively absorbed by the material (labeled A). Absorption primarily occurs through non-linear absorption (multiphoton ionization). Plasma reflection or scattering is also expected, reducing the coefficient A . After the absorption of a small part of the pulse energy, the absorption becomes linear due to limitations of the electron plasma density [6] via a combination of multistep absorption, trapping, and electron–electron or electron–phonon collisions. Given the lack of precise information about all these processes, extracted values from the literature (reported in Appendix B) enable one to set A values. As one is not aware of that, A is a function of the incident pulse energy, the pulse duration, and the material composition.

Another problem more specific to crystallization is the location of the crystallization domain in the TTT diagram to the confined condition of the tightly focused fs pulsed laser. Indeed, the specificities of the process may change the limit of the crystallization domain compared to the classical one [7–9]. Due to these uncertainties, the approach is tested using LNS glasses for the laser conditions employed in [4,10], for which these aspects are relatively well known.

In this work, brief recall of the classical crystallization process (Section 2) is provided. Thus temperature calculation from a specific hypothesis (Section 3) is given, describing how crystallization process behaves first within a heat accumulation regime (later defined, see Section 4) and, secondly, without heat accumulation (see Section 5, large temperature oscillations). Finally, the results from the approach are compared with several experimental values according to pulse energy and scanning speed (Section 6) and we draw a conclusion (1) about the optimization of laser parameters, (2) that the width of the crystallization area can be understood, and (3) that the incident light energy fraction may change with the number of pulses.

2. Basic: Brief Recall of the Crystallization Process

The appearance of crystals in glass is a two-step process: nucleation and growth [2,9]. Crystallization is generally growth-limited at low temperatures and nucleation-limited at higher ones. Moreover, the domain of crystallization is defined from a TTT diagram [9]. It collects the time (called the incubation time) requested at a given temperature to observe a first seed. This diagram, generally established for isothermal treatment, takes the time origin ($t = 0$) when the sample is in the condition to crystallize for a given temperature. This temperature is incident between T_g and T_m , with crystallization occurring between these temperatures with only one transformation (otherwise, other temperatures have to be considered). A boundary can be plotted in this TTT diagram delimiting the appearance of 10^{-6} part crystallized in the glass volume (thick black line in Figure 1). The position of the crystallization domain in the TTT diagram is dependent on the treatment pathway. For example, its position will be shifted if the temperature is continuously decreasing (or not) from T_m [11]. In that case, the growth is delayed because the nucleation is slowed down.

But, for the purpose of this paper, this is ignored and we simply consider the thermal treatment curve experienced by the material at a given spatial position with the coordinates $\alpha_0, \beta_0, \gamma_0$. The time–temperature function is applied to this position ($T(\alpha_0, \beta_0, \gamma_0, t)$). This function of time is simply obtained by the displacement of the temperature distribution function (the variation of the temperature in space) in the static case. This approximation is valid for speeds smaller than the diffusion speed ($2D_{th}/w$, typ. a few cm/s). As recalled above, the thermal treatment should exhibit temperatures in the T_g to T_m range. However, heating a material using a pulsed laser, resulting in an oscillatory temperature in volume impacted by non-linear optical processes, is a complex problem that prevents one from easily drawing conclusions for managing the process. The important aspect of solving this issue is to take into account the effect of these parameters while preserving the main physics associated with the induced transformations. Consequently, in [5] we developed a simplified approach for understanding how $T(\alpha, \beta, \gamma, t)$ changes according to the laser parameters (pulse energy, pulse repetition rate, beam scanning speed, beam width, and material properties).

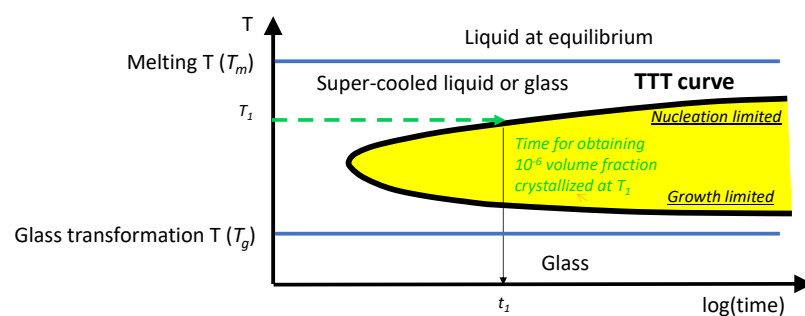


Figure 1. Crystallization domain in a Time-Temperature Transformation (TTT) diagram (in yellow). Its boundary is black. The glass transition and melting temperatures are lines shown in blue. T_1 is an example of isothermal treatment that leads to the incubation time t_1 required for crystallization to begin.

3. Temperature Distribution and Its Evolution during Laser Writing

For this purpose, a known fraction of the incident energy is assumed to be transformed completely into heat after a period of time that is much shorter than the diffusion time w^2/D_{th} , where w is the waist radius at $1/e$ and D_{th} the thermal diffusivity. For most of the inorganic glasses, the electron–phonon coupling time is around a few ps, and the diffusion time is smaller than μ s. This means that the pulse duration is assumed to be smaller than one hundred ns. So, it is largely the case that for the fs laser, the pulse duration is a fraction of a ps. Therefore, the heat diffusion starts after the electron relaxation and occurs only in the lattice phonons if there are no physical or chemical reactions. Consequently, the complicated events occurring at the ps level have no effect on the present calculation; otherwise, if the time averaged temperature, for instance, may change some non-negligible part of the pulse energy, it is not taken into account.

It is also assumed that no endothermic reaction is active in the dark that can use a significant part of the absorbed energy. The band structure of the material is assumed as not changing in the course of the irradiation, as is the non-linear absorption coefficient.

The 3D Fourier equation, with a spherical energy source at the focal volume, assuming a tightly focused laser beam and temperature-independent physico-chemical properties, is employed. Usually, for 3D direct laser writing, the NA of the focusing objective is above 0.5. This section is mostly drawn from what has been already published in [5]. The approximations taken into account are that the pulse durations considered are such that the thermal diffusion is not yet active, i.e., $\ll 0.1 \mu$ s and that the scanning speed (v) is much lower than the diffusion speed (typ. few cm/s). Consequently, the shape of the spatial temperature distribution is not time dependent; the only time dependence is introduced by the beam scanning taken in the α direction and appears as $\alpha + v \cdot t$. β and γ are fixed at the position β_0 and γ_0 , with γ direction corresponding to the beam propagation axis. The

scanning speed (v) defines the pulsed number deposited immediately as $N_p = 2w \cdot RR/v$. The laser pulse energy E_p defines the maximum temperature increment T_{00} , introduced by a single pulse above an initial temperature T_{init} : $T_{00} = \frac{A \cdot E_p}{\pi^2 \rho C_p w^3}$, with A the fraction of absorbed energy (previously defined); ρ and C_p are the glass density and heat capacity, respectively. Additionally, a normalized radius $r_w = r/w$ is defined, with r being a radial distance from the center of the beam focus.

All calculated temperatures are normalized with respect to T_{00} , as follows: $T_{norm} = (T - T_{init})/T_{00}$. T_{norm} is oscillating at periods of $1/RR$ at any distance from the focus center. This temperature oscillation is occurrent between a maximum (T_{max}) and a minimum (T_{min}), which varies according to the laser irradiation conditions. After a sufficient number of pulses, both T_{max} and T_{min} reach a steady state regime. Achieving this steady state regime is dictated by the ratio R_τ as previously defined and taking the form $R_\tau = 4D_{th}/RR w^2$. For instance, for large R_τ values (i.e., >16 for $T_{min} < 0.03T_{max}$) the pulse contributions are independent of each other, whereas for smaller R_τ values (<16), heat accumulation from pulse-to-pulse contribution begins to appear (and thus T_{min} overcomes $0.03T_{max}$).

N_{SS} corresponds to the minimum number of pulses necessary to reach the steady state regime. Its expression is given in Equations (A4) in Appendix D. This calculation can be performed either for T_{min} and T_{max} .

The temperature–spatial distributions of T_{max} and T_{min} (normalized in the form of T_{norm}) for various R_τ values are provided in Figure 2. When R_τ is small (large RR or small diffusivity), T_{min} and T_{max} have no large relative difference compared to their average values because the oscillation amplitude is always limited to $\exp[-(r_w)^2]$, whereas for T_{max} and T_{min} amplitude converges to $2/R_\tau$ at the beam center but converges to $\frac{\sqrt{\pi}}{R_\tau \cdot r_w} \text{erf}(r_w)$ elsewhere on heat accumulation. When this situation can be reached, the pulse energy can be adjusted to compensate for an RR increase. It is also worth noting that, when R_τ decreases, the shape of the curve converges to the $\text{erf}(r_w)/r_w$ curve (see Equation (A6) Appendix D). It is a consequence that the temperature distribution decreases much slower at large radius, compared to a gaussian one. This last shape is the shape of the energy source and of the temperature distribution for the case where R_τ is large. Note that in the case of heat accumulation, the overall maximum temperature (actually at the center of the beam) is defined by $A \cdot E_p \cdot RR$, i.e., roughly the average incident power.

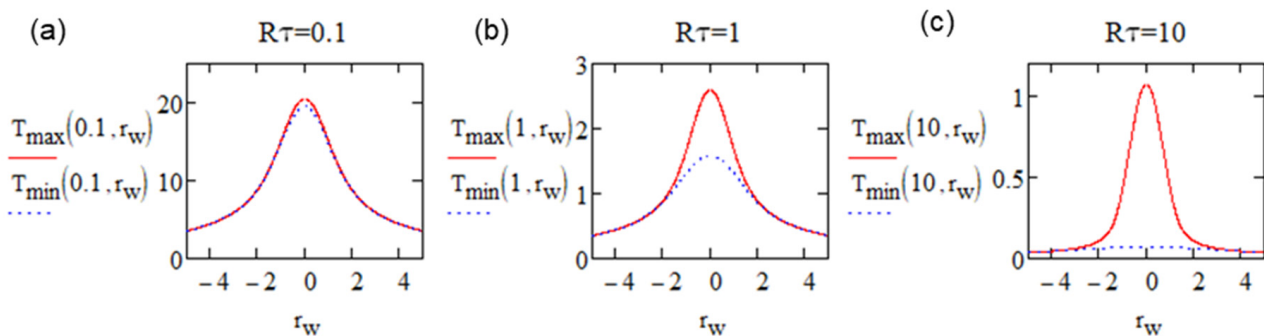


Figure 2. Spatial distribution of T_{min} (blue dash, by Equation (A3)) and T_{max} (red, by Equation (A1)) in the normalized form (see text) and as a function of the reduced radius r_w when (a) $R_\tau = 0.1$, (b) $R_\tau = 1$, and (c) $R_\tau = 10$.

For large R_τ values, corresponding to a small RR and/or large D_{th} , the oscillations are relatively large as pulse contributions are separated and thus T_{min} appears to have small values (See Figure 2c). If one considers negligible where T_{min} is smaller than 3% of T_{max} , then $R_\tau > 16$ (for values smaller than 6% of T_{max} , then $R_\tau > 7$; for $R_\tau > 10$, T_{min} is smaller than 4.4% of T_{max}). This defines the limit of the domain of heat accumulation. The increase in R_τ (Figure 2a–c) clearly shows that the shape of T_{max} is also converging with the increasing R_τ to the shape of the beam energy distribution (a gaussian beam, with an

envelope having a spatial distribution following $\exp[-(r_w)^2]$, therefore (and in the limited case) becoming independent of R_τ . The maximum absolute temperature at the center is T_{00} in this case. It is defined by E_p only (independent of R_τ and so especially of RR).

For intermediate R_τ values, exemplified in Figure 2b,c, the temperature oscillations are limited between T_{max} and T_{min} . This is shown in particular cases with the energy source volume appearing as a shoe box in [12] for $R_\tau = 2$ and 20 or in [13] for $R_\tau = 20$.

But, in this paper, it is specified that when $r_w > 2$, the difference between T_{min} and T_{max} vanishes, as seen in [14]. Therefore, the conditions of r_w and R_τ for neglecting the temperature oscillations are deduced and the use of an average temperature T_{mean} might be applicable (Appendix D Equations (A6)–(A8)).

Another important point for this current work is the dependence of the full width at half maximum (FWHM) of the temperature distribution with respect to R_τ . Its variation is less than a factor 2 in the relative radius scale (r_w). In fact, the largest change is at the base of the distribution.

4. Case of Low R_τ Values (High RR or Low D_{th}), i.e., within Heat Accumulation Regime

Here, R_τ is such that it is much smaller than 10, e.g., $R_\tau = 0.1$, due to the use of a large repetition rate or a weakly thermally diffusing material T_{min} is very close to T_{max} ($R_\tau = 10$ is the limit for $T_{min} = 4.4\% T_{max}$). In that case, a pulse contribution has no time to vanish significantly before the next pulse absorption induces another temperature increase. This is the case of heat accumulation, and the behavior is like that of Continuous Wave (CW) lasers.

In this section, we deal with conditions where the pulse number received at the same point (N_p as defined earlier) is above the number of pulses required to reach the steady state (N_{ss}). This situation yields two possibilities for which the temperature is higher than T_g : (i) the temperature remains lower than T_m , and (ii) the temperature overcomes T_m for some distance from the center of the beam focus during the thermal treatment. Each situation is described below.

(i) Moderate E_p leading to a temperature lower than T_m

To describe the temperature evolution and for illustration purposes, the laser parameters are set so that the temperature values fall within an acceptable temperature interval. In this section, we took as an example $T_g = 579$ °C coming from the physico-chemical properties of LNS glass and $T_m = 1257$ °C (T_m is the melting temperature of the formed LiNbO_3 crystals in LNS). Additional data requested for the calculation are provided in the Table A3 in Appendix C. Therefore, low absorption fraction (A) and pulse energy (E_p) values are used, as provided in the caption of Figure 3. The beam width at $1/e$ has been fixed to a “reasonable value” for such a small pulse energy, i.e., $w = 1$ μm. In this condition, similarly to Figure 2a, the oscillations (Equation (A2) in Appendix D) are small enough to be neglected. This can be observed in Figure 3, rendering T_{mean} a valid approximation if requested.

Then, the temperature distribution is transformed into the time domain to obtain thermal treatment curves (Figure 4b,c, T-t dependency), replacing the static normalized radius r_w by the coordinate of the place looked at in the moving material r_{wd} , taking the beam center as a reference (see Figure 4a). The relative position in the beam of this point is related to relative time from the following relation: $r_{wd}(t, v, d, \beta) = \sqrt{(v \cdot t / w + d)^2 + \beta^2}$. Then, the time origin of the treatment for crystallization is defined when T starts to overcome T_g . This occurs at a distance d from the center of the temperature distribution, i.e., at an abscissa d dependent on β (distance from the line axis), i.e., $d^2 = r_{wdg}^0{}^2 - \beta^2$. r_{wdg}^0 : the radius of the isotherm T_g is then obtained by solving $T_{mean}(r_{wdg}^0, R_\tau) = T_g/T_{00}$, where T_{mean} is an average temperature defined in Appendix D Equation (A6). r_{wdg}^0 is also the maximum width of the crystallized region.

Figure 4 displays a time–temperature thermal treatment. Therefore, provided that the crystallization domain is known (TTT diagram, see above), the scanning speed must be adjusted to ensure the thermal curve intersects with the crystallization domain, as in Figure 5, at a speed of v_1 or v_2 . For a speed higher than v_{lim} , the curve does not touch the domain anymore and crystallization is not possible. One can also see that for speed v_1 , crystallization starts from the bottom side of the domain and then crosses it and is thus not limited in growth. However, if T_{max} is not so large ($T_{max} < T_m$), the growth can be controlled. For v_2 , crystallization starts from the growth side and is sensitive to the pre-existence of nucleation seeds.

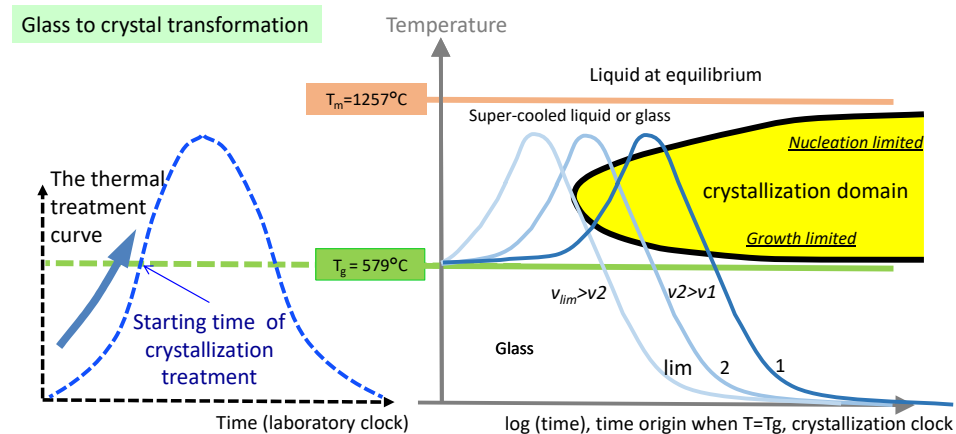


Figure 5. Display of the position of the treatment curve versus the crystallization domain in the case of solid glass to crystal transformation ($T_g < T < T_m$).

It is also important to note that r_{wdg}^0 is in principle larger than the half-width of the crystallized region. Indeed, r_{wdg}^0 is a circle where $t = 0$, but crystallization occurs eventually after some incubation time that could be longer than at the center, due to the decrease in T_{max} when going to the line's edge. This contributes to a narrowing of the line, but this effect is small, as shown in Figure 4 of [15]. In addition, at the speed limit, the width is not vanishing. The disappearance of the crystallization is thus arising from the process described in Figure 5. The width of the crystallization area is weakly sensitive to the scanning speed for a solid-to-solid transformation. This validates the crystallization criterion for T to be between T_g and T_m , used in our approach.

At the periphery of the line (e.g., for $\beta = 1.2$ in Figure 4), the temperature is smaller than that at the center, but the crystallization condition remains somewhat similar: the treatment curves cross the crystallization domain almost at the same incubation time. From this viewpoint, the results are rather intuitive. First, a lower scanning speed would lead to a larger crystal growth. Second, there is a minimum laser power ($P = E_p \cdot RR$) necessary to overcome T_g , with a maximum scanning speed necessary for the thermal treatment curve to cross the crystallization boundary. As the power increases, the speed limit increases until the maximum in space of the average temperature reaches T_m . Beyond this point, the crystallization process is different, and is the topic of the next section.

(ii) larger E_p leading to a temperature larger than T_m

A large E_p yields temperatures greater than T_m . In this case, if crystallization occurs, it starts from the liquid phase, with the system potentially crystallizing as the temperature decreases below T_m . Similar to the previous situation, $d(\beta)$ is defined by $d^2 = r_{wdm}^0{}^2 - \beta^2 \cdot r_{wdm}^0$, which is the radius of the isotherm T_m (i.e., a circle with a radius smaller than the one for T_g), and is then obtained by solving the following equation that includes T_m : $T_{mean}(r_{wdm}^0, R_T) = T_m / T_{00}$. r_{wdm}^0 is also the maximum size of the melted region. $\beta < r_{wdm}^0$ is represented by the dashed blue curve in Figure 6. When $r_{wdm}^0 < \beta < r_{wdg}^0$ (green curve), the results of section (i) apply. Then, the scanning speed should be adjusted to ensure the treatment curve reaches the crystallization domain. In this case, the entry

into the crystallization domain is necessarily from the top side (nucleation limited). It is sensitive to side stimulation because the side has crystallized before.

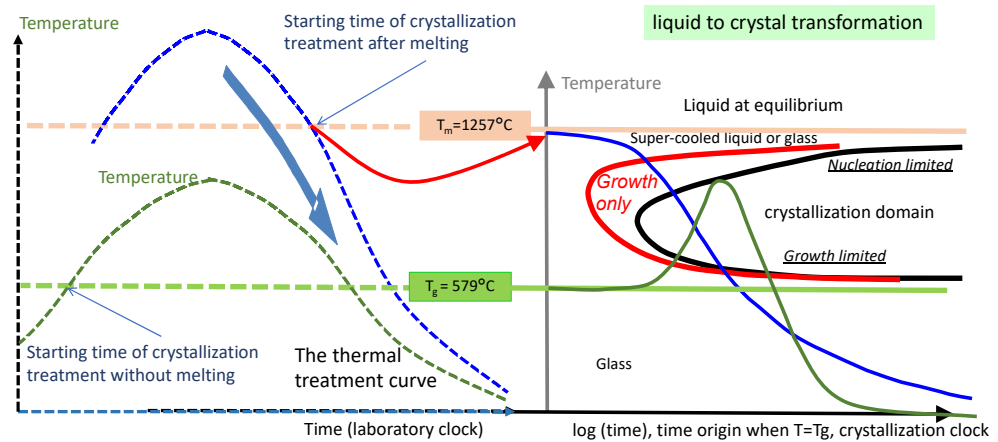


Figure 6. The position of the treatment curve versus the crystallization domain when a part of the trace is melting, i.e., a liquid-to-crystal transformation. The region delimited by the red one is for growth only.

5. Case of High R_τ Values (Low RR and Large D_{th}), i.e., out of Heat Accumulation Regime

Here, R_τ is such that it is larger than 10, due to the use of a small repetition rate or a strong thermally diffusing material. In that case, a pulse contribution has enough time to vanish significantly before the next pulse absorption arrival. There is no heat accumulation, but in Figure 2c this is true only for when r_w is smaller than a value of approximately 3. For the periphery of the heat-affected region, there is a smoothening of the temperature oscillations due to heat diffusion.

On the contrary, for a smaller reduced radius, T_{min} is close to zero, and the temperature oscillates between T_{min} and T_{max} during each period. Assuming that the pulse number received punctually (N_p) is above the pulse number required to reach the stationary state (N_{ss} formula Equation (A4) Appendix D), the temperature oscillations at the steady state can be simulated simply. Note that the oscillation at this stage is due to a series of pulse contributions collected in the function $T_{osc}'(r_w, x, R_\tau)$, where x (between 0 and 1) is the temporal position in the period and is thus the floating value of $t \cdot RR$. The simulation function of the temperature called *SimpulseT* is $SimpulseT(r_{wd}(t, v, d, \beta), R_\tau, E_p) / T_{00}(E_p) = T_{min}(r_{wd}(t, v, d, \beta), R_\tau) + T_{osc}'(r_{wd}(t, v, d, \beta), x(t, RR), R_\tau)$ (see Equation (A9) Appendix D) with r_{wd} defined as in the previous section and related to the time origin for crystallization according to one of the two cases for which the temperature is above or below the melting temperature T_m .

(i) Moderate E_p such that the temperature is not overcoming T_m

As it is seen in Figure 7, the punctual thermal treatment is beginning when $T_{max} \cdot T_{00}$ is overcoming the melting temperature for the first time during the scanning. The relative position in the beam is translated in relative time from the following relation:

$$r_{wd}(t, v, d, \beta) = \sqrt{(v \cdot t / w + d)^2 + \beta^2}; \quad d(\beta) \text{ defined by } d^2 = r_{wdg}^0{}^2 - \beta^2 \text{ with } r_{wdg}^0 \text{ the solution of } T_{max}(r_{wdg}^0, R_\tau) = T_g / T_{00}.$$

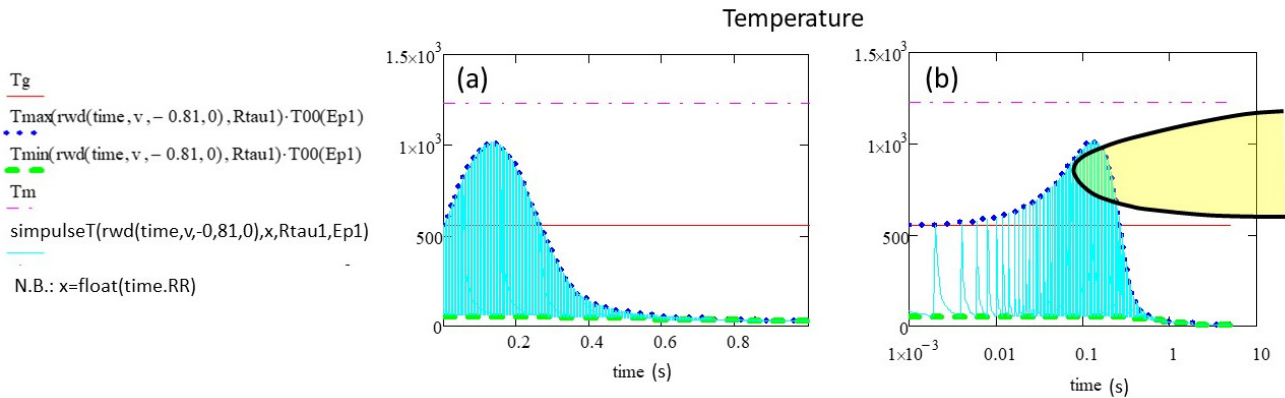


Figure 7. Thermal treatment curve (T_{max} , T_{min} , $SimpulseT$) for a point at the center (0,0,0) of the written line. $R_\tau = 13$, $A = 0.15$, $w = 1.65 \mu\text{m}$, $E_p = 0.5 \mu\text{J}$, 100 kHz, and $v = 10 \mu\text{m/s}$ (RR is fixed to 400 Hz just for illustrative purpose). Time is in (a) linear and (b) log scale.

However, the existence of oscillations between T_{min} and T_{max} is such that there are dead times, defined as the time for which the temperature decreases below T_g . Consequently, the efficiency, taken as the ratio between the active time (during which $T_g < T < T_m$) and the thermal treatment time, is much smaller than one. This is different from small R_τ values, again for which T_{max} is close to T_{min} , and T_{mean} can be employed.

The time for which crystallization is possible (as per the definition of efficiency before) is computed by solving the following equation: $SimpulseT(r_w, x, R_\tau) = T_g$. This gives the temporal interval $x1, x2$, graphically defined in Figure 8a during the pulse period and for which the temperature is above T_g according to r_w , i.e., the normalized distance to the beam center.

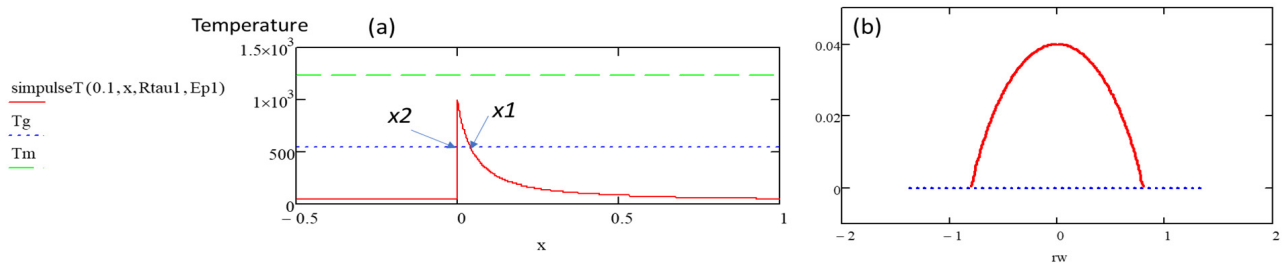


Figure 8. (a) Positions $x1, x2$ in the pulse period, between which the temperature is above T_g , (b) the efficiency (definition in the text) as a function of r_w , $x1$ red curve, $x2$ dashed blue curve. The same laser parameters as in Figure 7 are used.

At a given point in the material, the temperature is oscillating between $T_{max(r,t)}$ and $T_{min(r,t)}$ depending on R_τ and T_{00} . For contributing to the treatment of crystallization, the temperature must stay between T_g and T_m . Below T_g , the kinetics are too slow and above T_m the material is in the liquid state. When R_τ and T_{00} is such that $T_{(r,t)}$ is out of this interval, the treatment is inefficient. In this case, just a part of the T oscillation is active in contributing to crystallization treatment; this is defined in Figure 8b. As seen in Figure 8b, the efficiency of the thermal treatment (defined as $x1-x2$) is a function of the distance of the position away from the beam center (r_w). This reduction in efficiency means that to reach crystallization around the periphery of the beam, the scanning speed must significantly be decreased. In fact, in those conditions, the thermal treatment time is much smaller than the irradiation time. Furthermore, beyond some departure from the center (e.g., here $\beta > 0.7$, i.e., in the direction perpendicular to the scanning direction, with the parameters used in Figure 7), the crystallization is no more possible for kinetics reasons ($T < T_g$). r_{wdg}^0 defines the maximum width of the crystallization region.

(ii) **Large E_p such that the temperature is overcoming T_m**

In that case, a new treatment begins when a pulse oscillation is decreasing below T_m , assuming that the material melted before.

The use of the *SimpulseT* function is valid. Using this expression, the position in the period (x_3 in Figure 9a) for which the temperature has overcome T_m and returns below it is detected. This position is the starting time for thermal treatment that ends at position x_1 . But, if the next temperature pulse induces the temperature becoming greater than T_m , as the material is expected to melt and thus lose its memory, there will be a new time origin to compute from the next pulse. So, the last pulse defines the beginning of the treatment that goes on afterwards, i.e., when T_{max} is decreasing below T_m in the course of the scanning. This is obtained by solving $SimpulseT(r_w, x, R_\tau) = T_m$. This yields positions x_3 and x_4 in the period, as shown in Figure 9b.

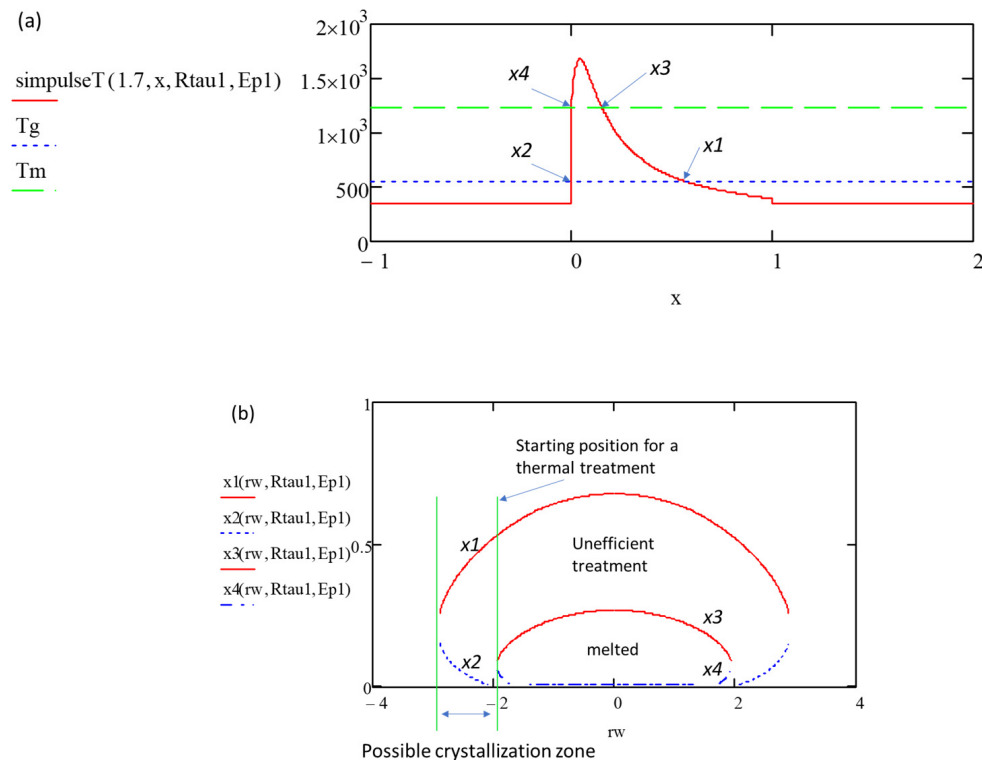


Figure 9. Values of x for the crossing points according to the distance from the beam center r_w . (a) Definition of the remarkable temporal locations in the period: x_1 and x_2 , where the temperature equals that of the glass one; x_3 , x_4 , where it equals that of the melting one. (b) Variation of the remarkable temporal locations according to the distance from the beam center. The part of the heat-affected region where crystallization is possible is also indicated. This computation has been achieved with $E_p = 5 \mu\text{J}$, $w = 1.65 \mu\text{m}$, $A = 0.2$, $RR = 60 \text{ kHz}$, and $R_\tau = 22$.

As seen in Figure 9, just a part of the pulse is “active” to induce crystallization ($x_2 - x_1 < 1$) and the involvement of just a part of the temperature distribution is also possible. Following the picture in Figure 9b, only the tail of the temperature distribution is used. When T is no longer overcoming T_m , and as shown in Figure 10 with $d = 1.92$ for $\beta = 0$, x_3 and x_4 do not exist anymore and, until x_1 and x_2 do, the temperature is larger than T_g .

From Figure 9a above, it can be noticed that the efficiency for crystallization is again smaller than 100% and that the writing speed must be decreased to trigger crystallization. Regarding the sides of the line ($\beta \neq 0$), the maximum of T_{max} decreases with y and the process described here will stop when T_{max} will no longer increase above T_m ($r_{wdg}^0 < \beta < r_{wdm}^0$). For these β , the situation is the same as the one described at the beginning of this section.

The transition is solid–solid and starts from the front of the T distribution, i.e., before the line center (in reference to the laboratory clock).

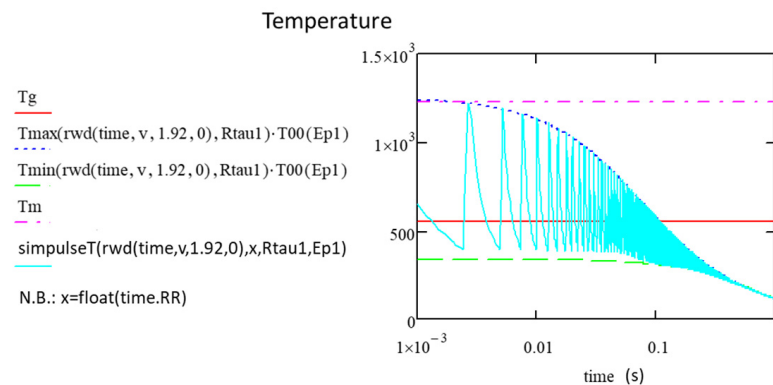


Figure 10. Temperature evolution over time when pulses have overcome T_m , corresponding to a liquid-to-solid transition. The last pulse contribution that does not overcome T_m defines the time origin. The computation is made with the parameters of Figure 9 with a scanning speed of $15 \mu\text{m/s}$.

6. Application to the Case of LNS Glass

The next section is dedicated to applying the above findings to an experimental case using LNS glasses. The objective of this section is to show how the width of the thermally transformed region is linked to laser parameters, especially to the pulse energy. It is based on a real case for which the beam waist and the fraction of absorbed pulse energy (A in T_{00} expression, Equation (A10) Appendix D) are crucial information, believed to be much smaller than shown in this paper. After data analysis from different authors, it is pointed out that the dependence on pulse energy of the beam waist w is not very sensitive to the material when comparing silica and the LNS family (Appendix A). On the contrary, the pulse energy dependence of A (Appendix B) is sensitive to the pulse duration and to the material. Therefore, the methodology in this section is to start with the pulse energy, the numerical aperture, and the pulse duration, to show that (1) the beam waist and the fraction of absorbed energy can be defined with enough accuracy for the purpose of this paper, and (2) then, with these quantities and their dependence on the laser parameters established reliably enough, to draw conclusions on the laser-induced crystallization process.

Let us start from a low pulse energy ($0.5\text{--}1 \mu\text{J}$). The experimental half-width of the crystallized area is measured to be $1.65 \mu\text{m}$ (using $0.7 \mu\text{J}$ in [4]) with the following laser parameters: wavelength 1030 nm , pulse duration 300 fs , $RR = 300 \text{ kHz}$, $NA = 0.6$, and $v = 5 \mu\text{m/s}$ [4]. With these values, solid–solid transformation (crystallization, ref. [16]) is shown to occur. On the other hand, the presence of nanogratings [17] indicates the size of the laser beam as these structures are only created by light. $w = 1.65 \mu\text{m}$ is deduced. However, A has to be adjusted. There are different processes that contribute to this fraction. The first one is the reflection of light (from Fresnel, or from the electron plasma mirror that is formed by the electron excitation in the conduction band or also from some light scattering). The second one is that, if a part is absorbed, a part is also transmitted as the absorption is never total in transparent materials with non-linear absorption. Since the modification is a solid–solid transformation, the temperature does not overcome T_m (as shown in the previous sections), and the value of A has to be smaller than 0.09 for $0.7 \mu\text{J}$. This value falls within the values found in the literature and presented in Appendix B Figure A2. Once all of these parameters are known, the simulation can be carried out similarly to its presentation in the previous sections.

The results are summarized in Figure 11 and below:

- The possible crystallization would fall within a fraction of a second for $v = 5 \mu\text{m/s}$ provided that the efficiency was 100%, but this is obviously not the case. On the contrary, the maximum efficiency is 22% here (see Figure 11b). The real treatment time is thus $(x1\text{--}x2)$ multiplied by the time scale of Figure 11c. On the other hand,

as crystallization is actually observed in LNS for v up to $125 \mu\text{m/s}$ [15] in a $0.5\text{--}1 \mu\text{J}$ interval, with the following values: 1030 nm , $NA = 0.6$, $\tau_{RR} = 250 \text{ fs}$, $RR = 200 \text{ kHz}$, and $w = 1.6 \mu\text{m}$ (for which the steady state is reached). This leads to a position where the crystallization nose is in the time range of 10 ms , i.e., an order of magnitude lower than the isothermal treatments in a conventional furnace, in a large volume without a stress field [18].

- The calculated crystallized half-width is close to that of the beam waist, with the criterion that the temperature should be above T_g . It can be concluded that there is almost no line broadening originating from the thermal effect for this pulse energy as it is experimentally observed.

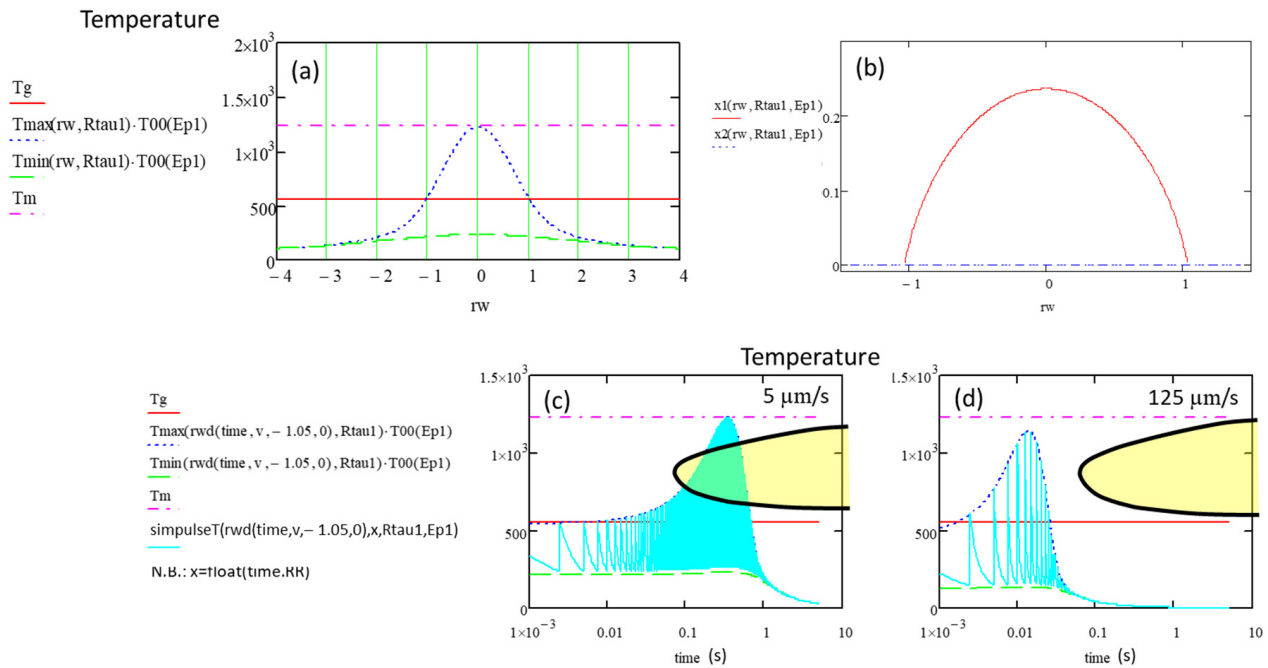


Figure 11. Temperature simulation in LNS glass for $E_p = 0.7 \mu\text{J}$, $A = 0.09$, $w = 1.65 \mu\text{m}$, $R_\tau = 4.4$, and scanning speed = $5 \mu\text{m/s}$ for (a–c): (a) T_{max} and T_{min} distribution, (b) the useful part of the T_{min} oscillations, (c) the corresponding treatment curve for $v = 5 \mu\text{m/s}$, and (d) the same with $v = 125 \mu\text{m/s}$.

Now, and based on the above discussion, one can wonder how width evolves when E_p is increased. To answer this aspect, two distinct examples are considered, at low and higher pulse energies.

First example: It is known that solid–solid transformation occurs until $1.0 \mu\text{J}$ and that for higher pulse energy, a part of the crystallized region originates from a liquid-to-solid transformation. For instance, let us consider the pulse energy $1.3 \mu\text{J}$. For this value, the half-width of the crystallized region is $3.73 \mu\text{m}$. The laser beam radius is collected from [4] and reported in Figure A1 at $2.6 \mu\text{m}$. R_τ thus decreases from 4.4 to 1.8 with the pulse energy increase. The indirect variation of R_τ with the pulse energy was not expected. It pushes the system to be in a heat accumulation regime even if RR is constant. Additionally, A increases itself to 0.15. Using these data, the computation is summarized in Figure 12.

The provided results indicate the following:

- The efficiency is close to 100% due to the effect of heat accumulation that increases T_{min} above T_g .
- The calculated crystallized radius is found to be $1.25 w$. There is thus a small broadening of 25% compared to the beam waist w . There is thus a crystallized part that is not submitted to the beam where there is no submicrostructuring induced by the laser light. There is also a melted region smaller than the beam waist (half-width = $0.48 w$).

It is also noted that there is no obvious correlation between the beam width and the melted region.

For completeness, another experimental result available for 1.8 μJ has been computed and reported in Table 1. It shows reasonable agreement with the experimental results.

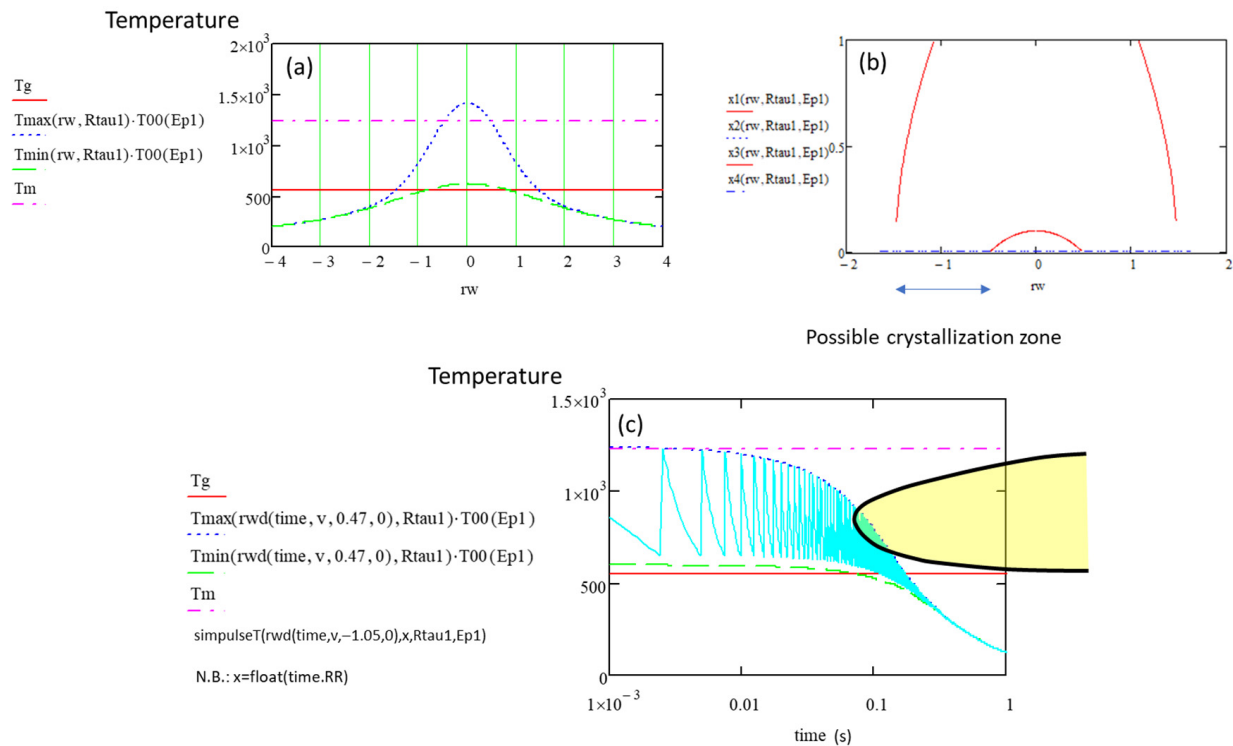


Figure 12. Temperature computation in LNS glass for $E_p = 1.3 \mu\text{J}$, $w = 2.6 \mu\text{m}$, $A = 0.15$, $R_\tau = 1.8$. Laser parameters: $\lambda = 1030 \text{ nm}$, $\tau_p = 300 \text{ fs}$, $RR = 300 \text{ kHz}$, $NA = 0.6$, and $v = 5 \mu\text{m/s}$. (a) T distribution, (b) efficiency, and (c) simulation on time.

Table 1. Summary of experimental and computed width according to the pulse energy.

E_p (μJ)	Pulse Duration τ_p (fs)	w (μm)	A	R_τ	r_w (Crystal) Computed	r_w (Crystal) Experimental	r_w (Melt) Computed	r_w (Melt) Experimental	Ref.
0.5	300	1.23	0.035	7.9	1	uk	na	Na	This work
0.7	300	1.65	0.09	4.4	1.05	1.00	na	Na	[4]
1	300	2.23	0.12	2.4	1.18	uk	na	Na	This work
1.3	300	2.6	0.15	1.8	1.47	1.6	0.48	1.1	This work
1.8	300	3.0	0.2	1.3	2.29	1.86	1.02	Uk	[4]
4.2	175	4.5	0.32	0.9	3.79	3.50	1.71	Uk	[10]

N.B.: na means not applicable and uk means unknown.

Second example: there is a much higher pulse energy, let us say 4.2 μJ , as used by Veenhuizen et al. [10], with laser parameters as follows: 175 fs, 200 kHz, and a varied scanning speed v . The authors of the aforementioned reference observed a crystallization full width of 31.3 μm for 15 $\mu\text{m/s}$ and 9.82 μm for 75 $\mu\text{m/s}$, i.e., a significant variation. From Figure A1 in Appendix A, w seems to be around 4.5 μm and thus $R_\tau = 0.9$; A can be seen to be 0.32 from Figure A2 in Appendix B. The results are shown in Figure 13.

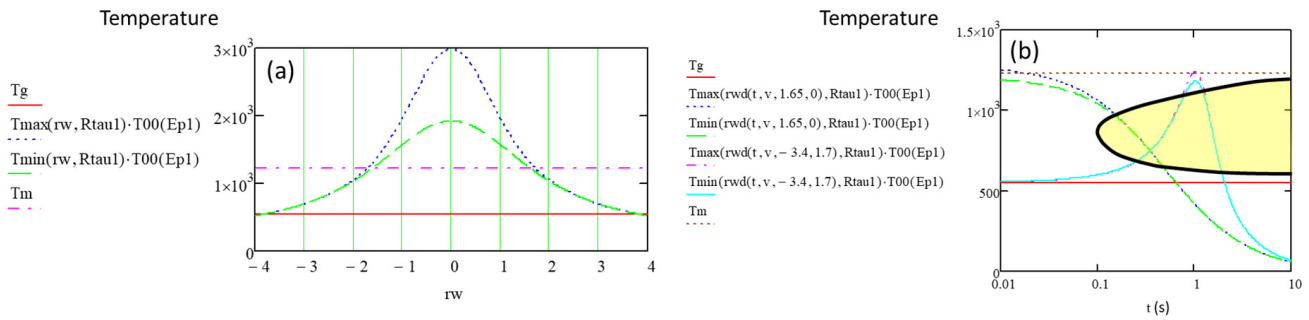


Figure 13. Temperature computation in LNS glass for $E_p = 4.2 \mu\text{J}$, $w = 4.5 \mu\text{m}$, $A = 0.32$, and $R_\tau = 0.9$. Laser parameters: $\lambda = 1030 \text{ nm}$, $\tau_p = 300 \text{ fs}$, $RR = 200 \text{ kHz}$, $NA = 0.6$, and $v = 5 \mu\text{m/s}$. (a) Temperature distribution, (b) simulation on time for two positions $\beta = 0$ (center of the line) and $\beta = 1.7$ (periphery).

Figure 13 allows a comparison of the treatment originating from the solid region and from the melted regions. The two curves penetrate the crystallization domain after a similar incubation time. However, in real time, the first one starts in front of the beam at a distance $3.4 w$ from its center, that is, before the temperature maximum, whereas the second starts $1.7 w$ after the temperature maximum. Consequently, the thermal treatment curve of the periphery is penetrating the crystallization domain before that of the center. The periphery is thus in a situation to stimulate the nucleation of the melted region. In addition, as both of the treatment curves have almost no oscillations, the efficiency is obviously 100%.

Let us now examine the effect of the scanning speed reported in [10]. A large variation in the width of the crystallization region was found (by a factor of three), whereas the speed varied by a factor of five. The origin of this variation is not primarily caused by the time shift of the treatment curves with the speed, as seen in Figure 5. The effect is quite small. Another possibility could be from the pulse number received punctually and that could be smaller than the quantity required for reaching the steady state. The steady state is reached after $N_{ss} = 7.6 \times 10^4$ pulses (from Equation (A4) Appendix A), whereas the number of pulses received punctually N_p is 1.2×10^4 pulses for $v = 15 \mu\text{m/s}$. However, for $v = 75 \mu\text{m/s}$, $N_p = 2400$, which is significantly lower than N_{ss} (>30 times less). Consequently, the steady state situation is not reached at those speeds. On the other hand, Figure 2 shows what the width at the beginning of the irradiation is like for a large R_τ , i.e., separated pulse contribution and increases in the course of irradiation due to heat accumulation. To compute the width in the transitory stage, it is assumed here that $T(r_{wdg}^0)$ crosses T_g for $r_{wdg}^0 > 2$. The use of T_{mean} is thus a good approximation. Therefore, the equation below has to be solved by deducing r_{wdg}^0 according to the number of pulses. It reads as follows (from Equation (A8) Appendix D):

$$\bar{T}(r_{wdg}^0, R\tau, N) = \frac{\sqrt{\pi}}{R\tau \cdot r_{wdg}^0} \cdot \left[\text{erf}(r_{wdg}^0) - \text{erf}\left(\frac{r_{wd}^0}{\sqrt{1 + N \cdot R\tau}}\right) \right] = \frac{T_g}{T_{00}} \text{ with } T_{00} = \frac{A \cdot E_p}{\pi^{3/2} \rho C_p w^3}$$

The increase in the width as a function of the pulse number is plotted in Figure 14. There is a broadening with the number of pulses that arises from heat accumulation as R_τ is around 1. $r_{wd}^0 = 3.5$ is found for the speed in consideration, i.e., a decrease from 3.8, the value at the steady state. This does not account for variation by a factor of three of the crystallization width. Even if the beginning of the irradiation is considered ($N_p = 1$), the possible variation would only be by a factor of two. On the contrary, the results reported in [15] and used in Figure 11 are in agreement with this explanation (the laser parameters are as follows: $\lambda = 1030 \text{ nm}$; $RR = 200 \text{ kHz}$; $NA = 0.6$; pulse duration = 250 fs). In that case, N_{ss} is around 50 whereas $N_p > 5280$ for a speed lower than $125 \mu\text{m/s}$. The steady state is always reached and the width is weakly varying as experimentally observed (this explanation is given for Figure 5).

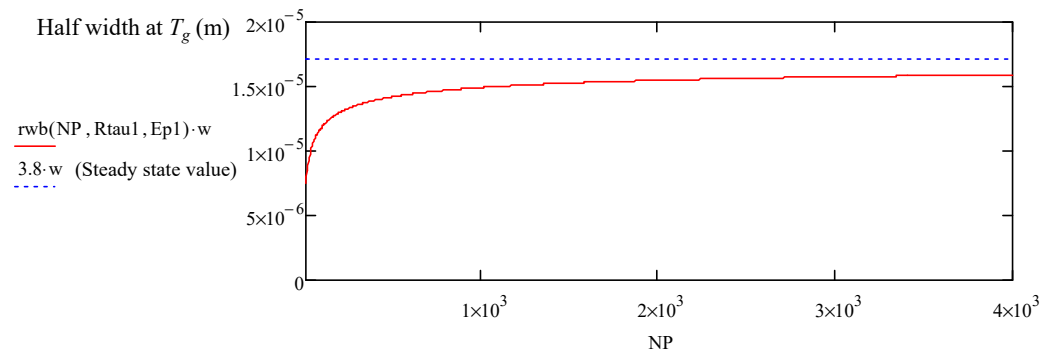


Figure 14. The half-width variation during the transitory stage ($N_p < N_{ss}$). The maximum width is $3.8 w$ ($w = 4.5 \mu\text{m}$) for $N_p > N_s$ (at steady state), for $E_p = 4.2 \mu\text{J}$, $R_\tau = 0.9$.

The question is thus: are there other reasons to change the crystallization width? The difference between the beginning and the steady state could be the change in absorption due to the creation of defects in addition to the non-linear one that plays the role of trapping centers of excited electrons produced by previous pulses. It is worth noticing that, only a variation of A from 0.135 to 0.32 may explain that r_{wdg}^0 changes from 1.6 to 3.8.

On the other hand, it is observed in [10] that for a given pulse energy above some speed, the crystallization which occurs is only solid-to-solid transformation. This means that, according to the calculation, T_{max} is no longer overcoming T_m . This is in agreement with lower absorption at a larger speed. Furthermore, the observation of the change in this turning point (here called v_t) with pulse energy leads one to consider that a particular dose D_0 is necessary for the absorption increase and for A to reach the value at the steady state. One would have, therefore, the following relation: $E_p \cdot 2w \cdot RR/v_t = D_0$. So, it would be possible to have an increase in temperature disconnected from the heat accumulation but arising from an increase in absorption related to defect creation.

Finally, Table 1 shows that the steady state width of the crystallized region varies with the pulse energy for two reasons: because the beam waist increases with E_p , and the temperature distribution expands relatively with the beam waist, R_τ decreases and the interaction is thus more and more sensitive to heat accumulation, and also because A increases with the pulse energy.

7. Discussion

Considering laser-induced crystallization, an analytical formula can be used to compute the temperature oscillations in time when the steady state is reached. These oscillations are limited between a maximum and minimum temperature, whatever the laser parameters and material properties, and established in the frame of a spherically symmetric energy source [5]. The broadening effect when increasing the pulse energy or the pulse density (inversely proportional to the beam scanning speed) was simulated.

Previously, it has been shown how the spatial distribution and specifically its FWHM is changing during the transition to a steady state depending on the ratio between the pulse period and the heat diffusion time (defined as R_τ). On the other hand, the temperature magnitude is defined by the beam waist and the fraction of absorbed incident energy (A). Thus, when applied to a real case and a reliable simulation is requested, it is necessary to consider 1) an increase in the beam waist (w) with the pulse energy, and 2) the increase in the A factor with the pulse energy and the pulse duration. Such constraints that originate from a non-linear effect in the solid can, for the most part, only currently be extracted from the experimental results available in the literature (see Appendices A and B) as mechanisms in the case of fs laser absorption are not clear enough for a robust simulation.

In such a way, within the validity of the used approximation, the following is deduced:

(1) The crystallization management is facilitated in a heat accumulation regime ($R_\tau \ll 10$). This allows the temperature oscillations to be quite small compared to average temperature values; thus, the laser parameters (i.e., E_p , R) can be easily adjusted to be completely above T_g and below T_m during the thermal treatment time that is starting when the temperature is rising above T_g . Thermal treatment curves are computed. The scanning speed is also straightforward for the thermal curve to efficiently penetrate the crystallization domain. The crystallization process will originate from a solid–solid transition, and the width of the crystallized area is close to the beam waist. For the inorganic oxides, the thermal diffusivity is usually around $10^{-6} \text{ m}^2/\text{s}$ (within a factor of two) so the diffusion time from a source with a beam waist of $1 \text{ }\mu\text{m}$ is around $<0.5 \text{ }\mu\text{s}$. The above conditions apply when the repetition rate frequency is much larger than $0.4\text{--}0.2 \text{ MHz}$. However, if the focusing is not so tight, let us say $w = 2 \text{ }\mu\text{m}$, the heat diffusion time is four times larger and reaches $1\text{--}2 \text{ }\mu\text{s}$. So, the repetition rate has to be much larger than $5\text{--}10 \text{ MHz}$. However, in organic materials for which the diffusion time is $10\text{--}20$ times longer, the heat accumulation regime is more easily reached and the thermal width more easily predictable.

If the pulse energy is increased such that the temperature is becoming larger than the melting temperature around the center of the written line, the process changes; the starting time of the incubation is no longer when the temperature becomes larger than T_g but when T decreases below T_m , as the process is a liquid-to-solid transformation. The crystallization domain is penetrated from the growth side, which renders the process sensitive to external stimulation, in particular to crystallization induction from the periphery where the temperature does not overcome T_m . When departing from the center, the temperature maximum of the treatment curve decreases below T_m ; a solid-to-solid transformation is occurring again. There are two regions in the crystallized line. It is shown that the solid-to-solid transformation region crystallizes sooner than the melted one and thus is a source of nucleation for the melted one. The size of the crystallized region becomes larger than the beam waist in that case. The texture orientation of the line (if any) is thus defined by the peripheral region outside of the beam and so defined mainly by the temperature gradient orientation. The large broadening with the pulse energy is defined in this case mainly by the base of the temperature distribution (which follows a hyperbolic shape ($T \sim 1/r_w$)), although the beam waist and absorption fraction also give rise to a broadening contribution. We also pointed out an unexpected result: the stimulation of the heat accumulation regime on a pulse energy increase and not only on RR .

(2) On the other hand, when heat accumulation is small or negligible ($R_\tau > 10$, small RR , large diffusion time), the above processes are the same according to the pulse energy, but the temperature oscillates significantly. As a consequence, just a small part of the oscillation is efficient (a few or ten %). This contributes to a proportional decrease in the scanning speed in addition to a repetition rate that could here be smaller.

However, the weak efficiency of the growth rate and a moderate pulse energy allows for the penetration of the crystallization on the growth-limited side of the crystallization domain, and may allow for the production of independent nanocrystals that have been revealed to be orientable with laser polarization in the case of LNS glasses [19].

(3) An absorption increase may be observed in the course of the irradiation and produce a large increase in temperature, changing the crystallization process (from solid/solid to liquid/solid). This effect could be dose dependent ($D_0 = E_p \cdot 2w \cdot RR/v_t$) and leads to a transition speed v_t varying with the pulse energy. We suggest that this phenomenon arises from the formation of defects that are more easily ionized.

8. Conclusions

Using analytical formulae computed from very simplified approximations (spherical approximation), it is possible to simulate crystallization processes by irradiation with a fs laser. However, to obtain compatible results, the beam waist and the light absorption fraction have to be approximately known apart from the physico-chemical data of the glass. After that, the management of the crystallization process and the width of the crystallization line can be obtained according to the pulse energy, e.g., crystallite size, and also the effect of the scanning speed can be understood. For example, in particular that of LNS glass, the crystallization process may change with the scanning speed.

Lastly, the application of the temperature calculation can be extended to other processes depending on the temperature: the distribution of the fictive temperature, the viscoplastic effect (stress distribution), any chemical reaction that is thermally activated, chemical migration, the maximum energy for not erasing a type X or type II modification, the creation of luminescent defects, or the decomposition temperature of organic material. This management shall be even more accurate when the fs laser is applied to organic matter in order to avoid complete material decomposition.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A. The Beam Width from the Literature and from Our Experiments

For this, the width of modification lines achieved by a non-thermal effect is used. The most obvious one is a line width of type II nanogratings as their structure is produced only by the laser light, whatever the material's chemical composition.

Considering first the beam focused with a length with NA and the effect of self-focusing, the formula for the effective width at the focus in the material is given by Marburger et al. [20], Ashcom et al. [21], and Schaffer et al. [22], but their formula below does not take into account the defocusing effect due to electron excitation. The defocusing effect is dependent on the excited electron density during the pulse; thus, a too-short lifetime or a weak pulse energy in the excited state of the electron may lead to the absence of this effect. The effective beam waist radius is given below:

$$w_{eff} = \sqrt{\frac{\lambda^2/0.9\pi}{\frac{2\pi NA^2}{1-NA^2} + \frac{I\lambda^2}{P_{cr}}}} \text{ with } P_{cr} = \frac{3.77\lambda^2}{8\pi n_0 n_2} \text{ } n_2 \text{ being the non-linear refractive index}$$

$(3.2 \times 10^{-16} \text{ cm}^2/\text{W} \text{ [23,24]}), n_0 \text{ the relative one, } I \text{ the light intensity.}$

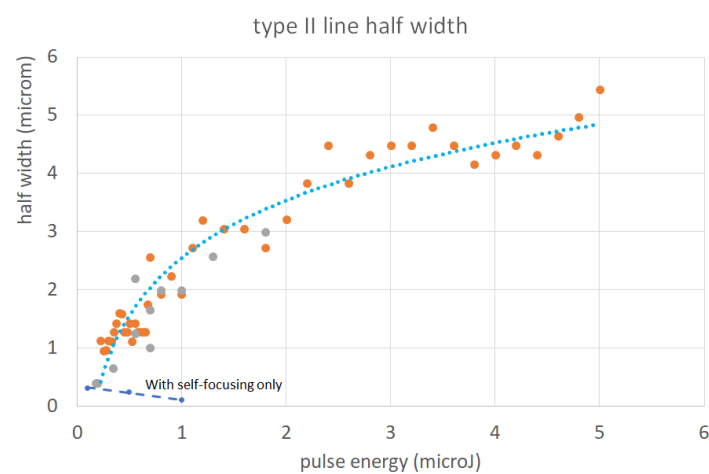
Increasing the pulse energy, the intensity increases and thus the width decreases due to non-linear effects. It is the contrary of what it is observed in the case of the laser leading to electron excitations [25].

In Lei et al. [26], the width increases with the energy above 0.2 μJ , although the electron density is of the order of 0.01 excited electrons. nm^{-3} . Even for 0.1 excited electrons. nm^{-3} , it is said that there is a weak defocusing effect and the half-width is 0.4 μm . However, without the defocusing effect, the width should decrease with a pulse energy increase.

These results and others are collected in Table A1 below.

Table A1. Some half-widths according to pulse energy, numerical aperture, and materials.

Wavelength (nm)	Pulse Energy (μJ)	NA	Half Width (μm)	Material	Ref.
1030	0.1	0.6	0.31	silica	Ashcom et al. [21]
1030	0.5	0.6	0.24	silica	idem
1030	1	0.6	0.1	silica	idem
1030	0.19	0.3	0.4	silica	Lei et al. Figure S2 of [27]
1030	0.55	0.3	1.25	silica	idem
1025	0.7	Not known	1.		Beresna et al. [28] (in air) Figure 4
1030	1	0.6	2	silica	Qiong et al. [29]
1030	0.5	0.6	1.3	G1?	idem
1030		0.6	0.7	B33	idem
1030		0.6	1.65	ULE	idem
1030	3	0.6	2.1	ULE	idem
1030	1	0.6	1.25	BGG-ZnO	idem
1030	2	0.6	2.25	BGG-ZnO	idem
1030	0.7	0.6	1.65	LNS	Cao et al. [4]
1030	1.3	0.6	2.6	LNS	idem
1030	0.5	0.6	1.6	LNSB	Muzi et al. [15]
1030	0.2	0.6	0.5	Suprasil	Our work
1030	5	0.6	5	Suprasil	Our work
1030	0.15	0.6	0.45	Suprasil	Our work
1030	2	0.6	1.75	Suprasil	Our work
800	0.18	1.35	0.4	glasses	Gamaly et al. [30] Figure 3
1030	0.8	0.6	2	Zn BGG	Yao et al. [31] Figure 2
1030	0.19	0.3	0.4	silica	Figure S2 of [27]
1030	0.34	0.23	0.65	silica	idem
1030	0.55	0.16	2.2	silica	idem

**Figure A1.** The half beam width according to the pulse energy from Table A1 for various compounds, $\lambda = \text{NIR}$, various NA, often at the steady state. The dots are experimental measurements, the line is just a guide for the eye.

Appendix B. Fraction of Absorbed Beam Energy

The incident beam intensity from the laser is a parameter that is dependent on the material properties as well as the beam propagation, and especially on the focusing strength. Indeed, for working in volume, materials do not absorb linearly but non-linearly with an exponent of the intensity light that depends on the materials and on the pulse duration because it depends on the excited electron density that occurs in the few 10 s fs [6]. The fraction of incident light absorbed is thus dependent on the intensity at the focus and around (before and after). In addition, the excited electron density may behave like a mirror and reflect a part of the incident intensity [32]. Moreover, for the largest incident power, the excited electron density may have a defocusing effect that decreases the intensity and thus the non-linear absorption [25]. All of these processes are intricate and complex and lead to difficult prediction without heavy computations. Needing an estimate of this quantity for our computation, various results are collected in the Table A2 below.

Table A2. Fraction of absorbed energy according to pulse energy, pulse duration, numerical aperture of the focusing lens, and materials.

Wavelength (nm)	Pulse Energy (μ J)	Pulse Duration (fs)	NA	Fraction	Material	Ref.
800	0.1–0.7	50	0.5	0.2	silica	Couairon et al. [33]
800	1	90	Not mentioned	0.35	silica	Wu et al. [34]
800	2	90	Not mentioned	0.45	silica	idem
800	3	90	Not mentioned	0.54	silica	idem
800	0.06–0.12	100	Not mentioned	<0.12	metallic surface	Meng et al. [35] metal surface
800	0.25	100	Not mentioned	0.25	silica	Zhang et al. [36]
800	1/7.4	100	Not mentioned	<0.1	silica	idem
1026	4.2	175		0.58	silica	Computed from Veenhuisen et al. [10], see text
1030	0.6	190	0.16	0.25	silica	Wang et al. [37]
1030	1	190	0.16	0.36	silica	idem
1030	0.2	300	0.3	0.04 to 0.06	silica from 1 to 30 pulses	Wang et al. [37]
1030	0.6	300	0.16	0.05	silica	idem
1030	0.69	300	0.16	<0.15	silica	idem
1030	1	300	0.16	0.25	silica	idem]
1030	0.5	300	0.6	0.035	LNS	This work
1030	0.7	300	0.6	0.09	LNS	This work
1030	1.3	300	0.6	0.16	LNS	This work
1030	1.8	300	0.6	0.2	LNS	This work
1026	4.2	175	0.6	0.32	LNS	This work
1030	0.7	500	0.16	0.15	silica	Wang et al. [37]
1030	1	500	0.16	0.19	silica	idem
1030	1	700	0.16	0.1	silica	idem

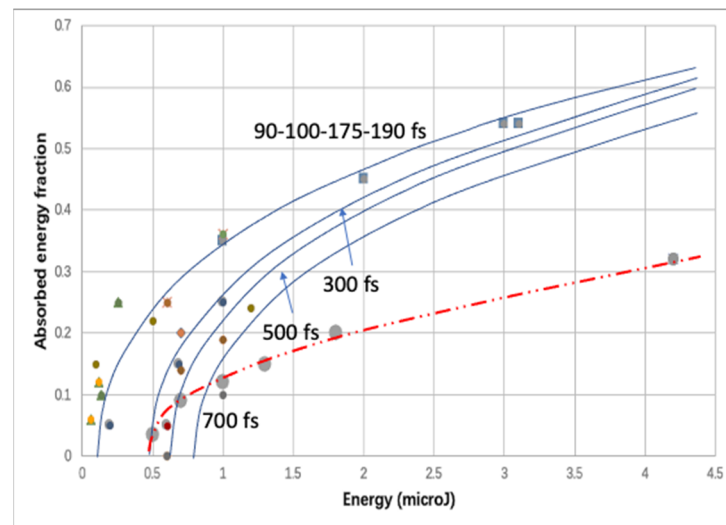


Figure A2. Plot of the absorbed energy fraction versus the pulse energy according to pulse duration (fs). The colors of the points make reference to Table A2: the blue curve is for silica and the red one is for LNS glasses. However, lines are just guides for the eyes.

The absorbed energy fraction is very sensitive to the pulse duration for <3.7 microJ but is less so for higher values (Zhang et al. [36]).

Appendix C

Table A3. Physico-chemical and laser parameters.

LNS Glass: 33Li2O-33Nb2O5-34SiO2 (mol %)		Ref.
Specific density (ρ , kg/m ³)	3830	Interpolated between SiO ₂ and NbLiO ₃ .
Heat capacity (C_p , J/kg.K)	787	idem
$K = D_{th} \cdot \rho \cdot C_p$ (J/K·m·s)	2.65	Computed from diffusivity
D_{th} (m ² /s)	9.1×10^{-7}	[38,39]
T_g (°C)	579	[40,41]
T_m (°C)	1257	[40,41]

Appendix D

After reaching the steady state (the number of pulses for that is given in Table A3 of [5]), the expressions of the temperature maximum, minimum and oscillations are as follows:

$$T_{max}(r_w, R_\tau) = \frac{\exp\left[-\frac{(r_w)^2}{1+x_m \cdot R_\tau}\right]}{[1+x_m \cdot R_\tau]^{\frac{3}{2}}} + \frac{\exp\left[-\frac{(r_w)^2}{1+(1+x_m) \cdot R_\tau}\right]}{2[1+(1+x_m) \cdot R_\tau]^{\frac{3}{2}}} + \frac{\sqrt{\pi}}{R_\tau \cdot r_w} \left\{ \operatorname{erf}\left[\frac{r_w}{\sqrt{[1+(1+x_m) \cdot R_\tau]}}\right] \right\} \quad (A1)$$

where $x_m = \frac{\sqrt{R_\tau} \sqrt{9R_\tau + 32(r_w)^2 - 3R_\tau - 8}}{8R_\tau}$ and where $r_w > \sqrt{\frac{3}{2} + \frac{2}{R_\tau}}$ (x_m limited to 1) or $x_m = 0$, when $r_w < \sqrt{\frac{3}{2} + \frac{2}{R_\tau}}$ for whatever value of R_τ or R_τ less than $\frac{2}{r_w^2 - 1.5}$ when $r_w^2 > 1.5$).

$$T_{osc}(r_w, R_\tau) \approx \frac{\exp\left[-\frac{(r_w)^2}{1+x_m \cdot R_\tau}\right]}{[1+x_m \cdot R_\tau]^{\frac{3}{2}}} + \frac{\sqrt{\pi}}{R_\tau \cdot r_w} \left\{ \operatorname{erf}\left[\frac{r_w}{\sqrt{[1+(1+x_m) \cdot R_\tau]}}\right] \right\} - \frac{\sqrt{\pi}}{R_\tau \cdot r_w} \operatorname{erf}\left(\frac{r_w}{\sqrt{1+R_\tau}}\right) \quad (A2)$$

$$T_{min}(r_w, R_\tau) = \frac{\exp\left[-\frac{(r_w)^2}{1+(1+x_m)\cdot R_\tau}\right]}{2[1+(1+x_m)\cdot R_\tau]^{\frac{3}{2}}} + \frac{\sqrt{\pi}}{R_\tau \cdot r_w} \left\{ \operatorname{erf}\left[\frac{r_w}{\sqrt{1+R_\tau}}\right] \right\} \quad (A3)$$

$$N_{ssmax}^r > \frac{1}{R_\tau} \left[\left(\frac{2}{R_\tau \cdot \varepsilon \cdot T_{max}(r_w, \infty)} \right)^2 - 1 \right] \quad N_{ssmin}^r > \frac{1}{R_\tau} \left[\left(\frac{2}{R_\tau \cdot \varepsilon \cdot T_{min}(r_w, \infty)} \right)^2 - 1 \right] \quad (A4)$$

$$T_{max}(r_w, R_\tau, N) \approx \frac{\exp\left[-\frac{(r_w)^2}{1+x_m\cdot R_\tau}\right]}{[1+x_m\cdot R_\tau]^{\frac{3}{2}}} + \frac{\exp\left[-\frac{(r_w)^2}{1+(1+x_m)\cdot R_\tau}\right]}{2[1+(1+x_m)\cdot R_\tau]^{\frac{3}{2}}} + \frac{\exp\left[-\frac{(r_w)^2}{1+(N-1+x_m)\cdot R_\tau}\right]}{2[1+(N-1+x_m)\cdot R_\tau]^{\frac{3}{2}}} + \frac{\sqrt{\pi}}{R_\tau \cdot r_w} \left\{ \operatorname{erf}\left[\frac{r_w}{\sqrt{1+(1+x_m)\cdot R_\tau}}\right] - \operatorname{erf}\left[\frac{r_w}{\sqrt{1+(N-1+x_m)\cdot R_\tau}}\right] \right\} \quad (A5)$$

When the mean T can be used, $\bar{T}(r, N) = \frac{1}{\tau_{RR}} \int_{\text{pulse period at } N} T(r, t) dt$; the formula is even simpler to use after reaching the steady state. τ_{RR} is the period = $1/RR$

$$\bar{T}(r_w, R_\tau, \infty) = \frac{\sqrt{\pi}}{R_\tau \cdot r_w} \operatorname{erf}(r_w) \quad (A6)$$

$$N_{ssm}^r(r_w) = \frac{1}{R_\tau} \left[\left(\frac{2 \cdot r_w}{\sqrt{\pi} \cdot \varepsilon \cdot \operatorname{erf}(r_w)} \right)^2 - 1 \right] \quad (A7)$$

$$\bar{T}(r_w, R_\tau, N) = \frac{\sqrt{\pi}}{R_\tau \cdot r_w} \cdot \left[\operatorname{erf}(r_w) - \operatorname{erf}\left(\frac{r_w}{\sqrt{1+N\cdot R_\tau}}\right) \right] \quad (A8)$$

The formula built for the simulation of the temperature oscillations at the steady state:

$$\operatorname{Simpulse}T(r_w, x, R_\tau, E_p) = [T_{min}(r_w, R_\tau) + T_{osc}'(r_w, x, R_\tau)] \cdot T_{00}(E_p) \quad (A9)$$

where $T_{osc}'(r_w, x, R_\tau)$ is just the function $T_{osc}(r_w, R_\tau)$ where x_m is replaced by x .

The maximum temperature induced by one pulse is $T_{00} = \frac{A \cdot E_p}{\pi^{\frac{3}{2}} \rho C_p w^3}$ with A the fraction of absorbed energy, ρ and C_p the glass density and heat capacity, w the beam waist at $1/e$, E_p the pulse energy. (A10)

Note that the time is introduced in the formula by r_{wd} which is a “moving” r_w (as the beam is scanning) and in x by rendering it periodic, i.e., in taking only the floating value of $t \cdot RR$.

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