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MULTIPHASE TREATMENT OF ODTX IN HMX
SPHERES

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Introduction

In recent years considerable effort has been applied towards understanding the chemistry and transport involved in measuring and modeling the one-dimensional time to explosion (ODTX) in spheres of high explosives (HE) at Lawrence Livermore National Laboratory (LLNL).¹⁻⁵ In ODTX experiments, a constant boundary temperature is applied to a sphere of high explosive and the elapsed time required for the sample to explode is recorded. Because the symmetry of the system limits the time-dependent variations in temperature and chemical composition to the radial coordinate only, the time-to-explosion is referred to as the 'one-dimensional time-to-explosion', or ODTX. This type of experiment is an example of a system in which transport processes and chemical reactions are highly coupled. Thus any effort to model the performance of this system must include both chemical and transport processes.

The chemical model used by the researchers at LLNL is quite simple, and yet seems to capture the basic physical processes well enough to predict ODTX in HE spheres. Chemical TOPAZ was used to analyze the coupling of the chemistry and heat transport.⁵ In an earlier report, Dale Breshears at Los Alamos was able to predict ODTX using the same simple chemical model in an Microsoft Excel spreadsheet analysis which allowed the coupling to heat transport.⁶ In that report the question of whether such simple models can be more broadly applied to other experiments was raised, and an understanding of the LLNL experimental scenario and the details of the application of the model was gained.

Breshears concluded that the simple chemical reaction mechanism developed at LLNL by Tarver *et al.*⁴ clearly captured the basic features evident in ODTX experiments, and that he was able understand the LLNL model and reproduce the calculations using a different numerical approach. He pointed out that the most obvious shortcoming of the LLNL model is that all the species are considered to occupy each computational volume element completely. That is, the chemical constituents are modeled as being completely interpenetrating with uniform and constant density in a system without any phase distinction. It is believed that this limitation will adversely effect the LLNL model from successfully predicting the outcome of experiments other than ODTX in spheres.

What is needed to better assess the performance of the LLNL model in a more realistic physical sense is a multiphase treatment of both the transport and chemical processes. Gaseous species isolated in bubbles or other voids within a condensed phase matrix may lead to effects not captured by the single phase LLNL model. Prominent among these effects is a temperature deviation in which evolved gaseous species isolated in bubbles or voids experience limited heat transfer back to the condensed phase. In this case the chemistry within bubbles is carried out at a different temperature than that which occurs in the condensed phase, and the time to explosion may be altered. Another effect lost in a single phase treatment is chemistry which occurs only at a surface, or an interface between phases. Evaporation, sublimation, and autocatalyzed processes are important examples of such surface chemical interactions. Multiphase treatment also allows for the independent motion of the individual phases. Just as the phases can experience different temperature fields, they can experience different velocity fields as well. The well known memory effect in HE cook-off experiments may be related to the retention or loss of gaseous species evolved during heating cycles.

What will be discussed in this report represents a framework upon which multiphase and other real physical effects can be built. Chemical models of increasing complexity are envisioned and this methodology can provide a tool for evaluating new ideas against known experimental data. The recent work to be reported here addresses the multiphase issue of temperature deviation between phases undergoing chemical and heat transport processes. Modeling of the LLNL ODTX experiment will be performed with FLUENT, a commercially available computational fluid dynamics (CFD) code. FLUENT solves flows in 2D or 3D in Cartesian, cylindrical, or general curvilinear coordinates, with steady-state or fully time-dependent analysis. Multiphase flows in which two or more continuous phases are present can be solved with arbitrary volumetric sources of heat, mass, momentum, and chemical species applied through user-defined FORTRAN subroutines. FLUENT models these phenomena by solving the conservation equations for mass, momentum, energy, phase volume fraction, and chemical species for each phase using a control volume based finite difference method. The equations are solved using SIMPLE-like algorithms with an iterative line-by-line matrix solver and multigrid acceleration.

Before considering the temperature deviation issue and its dependence upon gaseous bubble diameter in a multiphase system, I will discuss the use of FLUENT for modeling the basic constant and uniform density LLNL ODTX problem. Following the discussion of the temperature deviation in the multiphase treatment, I will discuss possible extensions of this work to include more advanced multiphase effects such as surface reactions within bubbles and gas phase transport out of the HE sample.

Constant Density ODTX

This initial modeling investigation was performed in order to insure that a full understanding of the LLNL experiments and modeling approach was had, and to demonstrate the ability to predict the constant density ODTX results using FLUENT. To this end the rate constants and thermophysical data for the HMX decomposition reactions were taken directly from by Tarver *et al.*⁴ with the proper modification for molar densities applied to the third pre-exponential factor as discussed by Breshears.⁶ Thus the HMX decomposition model employed here goes as follows:

where HMX is the parent high explosive molecule, FRAGS represents the initial decomposition products, which can be thought of as 1/4 of the original HMX ring, and IGAS and FGAS are intermediate and final gaseous species. The following rate parameters are applied:

Reaction Number	(1)	(2)	(3)
ln frequency factor (1/s)	48.7	37.3	28.1
activation energy (kcal/mol)	52.7	44.1	34.1
order of reaction	1	1	2
heat of reaction at 298 K (cal/g)	+100	-300	-1200

with the following thermophysical properties:

property	HMX	FRAGS	IGAS	FGAS
density (g/cc)	1.865			
heat capacity (cal/g-K) at				
293 K	0.24	0.22	0.24	0.27
433 K	0.34	0.31	0.27	0.28
533 K	0.40	0.36	0.29	0.29
623 K	0.46	0.42	0.31	0.30
773 K	0.55	0.50	0.35	0.31
>1273 K	0.55	0.50	0.42	0.35
thermal conductivity (cal/cm-s-K) at				
293 K	1.23×10^{-3}	6.5×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
433 K	9.70×10^{-4}	5.0×10^{-4}	"	"
533 K	8.10×10^{-4}	4.0×10^{-4}	"	"
> 633 K	7.00×10^{-4}	3.0×10^{-4}	"	"
heat of formation at 298 K (cal/g)	+61	+161	-139	-1339

The geometry and grid for these calculations resembles a long slender 2D wedge. There is an axis of symmetry along the long base of the wedge to indicate that a solid 3D cone is being modeled. There are 30 computational cells in the radial direction. Four calculations were performed with various wall temperatures, and the results are shown in Figure 1 along with the by Tarver *et al.*⁴ experimental and numerical results. Some of the experimental data points have been left off of the figure for clarity. The wall temperatures evaluated are 540.5 K ($1/T = 1.85 \text{ e-}3$), 500 K ($1/T = 2.00 \text{ e-}3$), 482 K ($1/T = 2.075 \text{ e-}3$), and 470 K ($1/T = 2.13 \text{ e-}3$). The agreement with the data and the Tarver *et al.*⁴ calculations is excellent, which is not unexpected.

Figure 1 ODTX for LX-10 spheres of 0.5 inch diameter. Open diamonds are a sample of the experimental data, and the solid line are the numerical results of Tarver *et al.*⁴ The closed diamonds are the results of the current FLUENT calculations. Single phase treatment.

The radial profiles at the time of explosion for temperature and species mass fractions are shown in Figures 2a-2d for the four wall temperatures considered. As the boundary temperature decreases, an increasing amount of HMX in the LX-10 sample becomes involved in the final explosion. In the calculation with the highest wall temperature ($T = 540.5 \text{ K}$), significant chemical reaction has taken place only in the outermost radial locations. Exothermic reactions producing gaseous species are only seen in the outer 30 mils of explosive. A trend for increasing production of gaseous species is seen as the wall temperature is decreased. At a wall temperature of 470 K ($1/T = 2.13 \text{ e-}3$), gaseous species make up approximately half of the system mass, and are found throughout the sample. The HMX component is nearly completely

Figure 2a Radial profiles of temperature and species mass fractions for a wall temperature of 540.5 K - at the time of explosion. Single phase treatment.

Figure 2b Radial profiles of temperature and species mass fractions for a wall temperature of 500 K - at the time of explosion. Single phase treatment.

Figure 2c Radial profiles of temperature and species mass fractions for a wall temperature of 482 K - at the time of explosion. Single phase treatment.

Figure 2d Radial profiles of temperature and species mass fractions for a wall temperature of 470 K - at the time of explosion. Single phase treatment.

gone. These results are consistent with the calculations of Breshears⁶ and the experimental observation that decreasing wall temperature leads to an overall more violent explosion.⁴

It is interesting to note that the explosion in these calculations never occurs right at the wall boundary. The wall is a perfect heat sink once the exothermicity of the process produces temperatures exceeding the wall temperature. This inhibits thermal runaway (explosion) in the near wall cells. The extent to which this effect may be observed experimentally depends upon factors such as the degree of contact resistance between the HE sample and the wall, and the thermal mass of the anvils which constitute the wall.

Figures 3a-3c contain time histories of the temperature and mass fractions at the radial point at which the explosion takes place. Results for the $T_w = 500$ K are unavailable. All the figures can be characterized by a temperature that rises quickly to a value approaching the wall temperature, remains nearly level for a long period of time, and then rapidly increases at the end of the calculation due to the explosion brought on by a high degree of exothermicity and thermal runaway. All of the figures also exhibit a sharp increase in the mass fractions of the gaseous species near the explosion time, both of the intermediate products, IGAS, and of the final products, FGAS. It is the production of these gaseous species through the exothermic reactions, expressions (2) and (3) above, that brings about the explosion of the HE sample.

It is interesting to examine which of these exothermic reactions, (2) or (3), is most responsible for the thermal runaway at the time of explosion. That is, which is exhibiting the greatest exothermicity at the different wall temperatures as the heating progresses and just before the explosion takes place. Figures 4a-4c show time histories of the heat release due to each of the exothermic reactions, and the ratio between these two rates. In all three figures, the heat release rate from reaction (2) far exceeds the rate from reaction (3) over most of the time history. For the calculations with the higher wall temperatures, Figure 4a and 4b, the rate from the second reaction is still two to ten times greater than the rate from the third reaction at the time of explosion. Only at the lowest wall temperature, Figure 4c, does the rate from the third reaction become equal to that from the second at the time of explosion. It would seem from this analysis that the heat release from reaction (2) has more influence on the time to explosion in these calculations than does that from reaction (3). This observation will help in the understanding of the multiphase ODTX calculations.

Figure 3a Time histories of temperature and species mass fractions for a wall temperature of 540.5 K - at the radial point of explosion. Single phase treatment.

Figure 3b Time histories of temperature and species mass fractions for a wall temperature of 482 K - at the radial point of explosion. Single phase treatment.

Figure 3c Time histories of temperature and species mass fractions for a wall temperature of 470 K - at the radial point of explosion. Single phase treatment.

Figure 4a Time histories for the heat release rate and heat release rate ratio for the two exothermic reactions in the LLNL model. $T_w = 540.5$ K. Single phase treatment.

Figure 4b Time histories for the heat release rate and heat release rate ratio for the two exothermic reactions in the LLNL model. $T_w = 482$ K. Single phase treatment.

Figure 4c Time histories for the heat release rate and heat release rate ratio for the two exothermic reactions in the LLNL model. $T_w = 470$ K. Single phase treatment.

Multiphase Treatment of ODTX

Here I will discuss the multiphase model in FLUENT and show the results of ODTX calculations performed assuming different characteristic bubble diameters for the gaseous phase. For the purpose of this calculation, all secondary phase mass is assumed to be contained in spheres dispersed uniformly in the primary phase. In these calculations, the HMX and FRAGS will make up the primary phase, and IGAS and FGAS will make up the secondary phase. Although in reality IGAS and FGAS are presumed to be collections of various gaseous species, for the purpose of comparing the results with the single phase treatment, I will assume that once again all constituent species in the calculation are at a constant and uniform density.

FLUENT solves a complete set of conservation equations for each phase. The enthalpy equations for each phase must therefore include a term that accounts for heat transfer between phases. In problems involving fluid flow, the momentum equations must also contain an interphase exchange term. For this ODTX problem it is assumed that the phases are stationary and that species do not diffuse, so I will not discuss the momentum exchange terms. I will concentrate the discussion on the interphase heat exchange term, and the interphase chemical species exchange terms.

So that a more direct comparison to the single phase implementation of the LLNL model can be made, it is assumed that all the chemical reactions are initiated within a particular phase. That is, they are not restricted to occur at surfaces of phase boundaries; although it is permitted for reactants to exist in one phase, while the products are accounted for in a different phase. This relatively simple interphase species exchange must be handled in a user-defined subroutine external to FLUENT, which generates the proper source terms for each specie in each phase. It should be noted, however, that surface reactions are perfectly acceptable with this methodology, and that more complex reactions sets that are expected to be developed will undoubtedly require that capability.

The key chemical reaction for this multiphase treatment is the second step in the LLNL three-step model. This is the reaction that involves the decomposition of the condensed phase fragments (FRAGS) into intermediate gases (IGAS), and is thus responsible for taking mass from the primary phase into the secondary phase:

The expression for the interphase mass transfer is:

$$dm/dt [\text{kg/sm}^3] = k_2 \exp(-E_2/RT_\phi) Y_{\text{fr}\phi} \rho_\phi \alpha_\phi \quad (4)$$

where the subscript ϕ indicates a particular phase, in this case the primary (COND) phase, so that ρ_ϕ indicates the density of phase ϕ , $Y_{\text{fr}\phi}$ represent the mass fraction of the FRAGS (subscript 'fr') in phase ϕ , T_ϕ is the temperature of phase ϕ , and α_ϕ is the volume fraction of phase ϕ . The

transfer rate is described in terms of the total volume, not the phasic volume. It is obvious that as this reaction progresses the rate will eventually go to zero because the volume fraction, α_v , of the phase containing FRAGS is decreasing towards zero even as the mass fraction of FRAGS in the condensed phase approaches unity.

In the FORTRAN subroutine external to FLUENT, the mass transfer rate from (4) is written as a negative source in the FRAGS species conservation equation in the primary phase, and as a positive source in IGAS equation in the secondary (GAS) phase. It is assumed that the heat of this reaction is held initially by the products in the GAS phase. Chemical reactions that do not involve interphase mass transfer, that is LLNL model reactions (1) and (3), are handled within the standard homogeneous chemistry sub-model in FLUENT.

The multiphase effect that is the focus of this report involves the transfer of heat between phases, which implies that each phase is represented by its own temperature. Because the thermal conductivity of the primary phase (HMX and FRAGS) is an order of magnitude times greater than that of the secondary phase, heat is initially transported from the wall into the system through a path in the primary phase, and then transferred to the cooler secondary phase at locations which can be at some distance from the wall. At some point in time the reaction rate represented by equation (4) above becomes significant, and the temperature of the secondary phase exceeds that of the primary phase and the direction of heat transfer is reversed.

The extent to which the temperatures of the two phases are different depends upon the amount of heat being transferred, and the resistance to that heat transfer. I will assume that all of the secondary phase mass is contained in spheres of equal size, distributed evenly within the primary phase matrix. Because the mass in the ODTX system is assumed to be stationary, convective transfer between the spheres and the matrix is neglected. Radiative effects are also expected to be small, and are not actively modeled in this analysis. That leaves conduction of heat between the spheres and the primary phase matrix as the dominant transfer mechanism.

In the ODTX simulation, the times to explosion can be quite long, and so local heat transfer involving the secondary phase spheres can be approximated as proceeding in a quasi steady-state. The steady-state heat conduction rate in spherical coordinates can be expressed as,⁷:

$$q = -4 \pi r^2 (k dT/dr) \quad (5)$$

where q is in Watts [W], r is the radius, and k is the thermal conductivity. Integrating this equation from r_1 to r_2 (T_1 to T_2) I get:

$$q = 4 \pi k (T_1 - T_2) / (1/r_1 - 1/r_2) \quad (6)$$

The schematic in Figure 5 will help in understanding the following discussion. If I consider the spheres to be at a uniform temperature, which is a valid assumption given their small size (tens to

Figure 5 Schematic for spherical heat conduction.

hundreds of microns), then the GAS in Figure 5 can be assumed to be at temperature T_1 at a radius r_1 (and at all smaller radii). If the spheres are separated by distances large compared to r_1 , I can assume that T_2 persists in COND at a radius $r_2 = \infty$. If I also call $d_s = (2 \times r_1)$, the sphere diameter, then I can write:

$$q = 2 \pi k d_s (T_1 - T_2) \quad (7)$$

which is the steady heat transfer from a sphere to its surroundings via conduction only. Dividing by the volume of the sphere, V_s , I get:

$$q/V_s = 12 k (T_1 - T_2) / d_s^2 \quad (8)$$

which is the heat transfer per unit volume of GAS. Multiplying by the GAS volume fraction, α_g , and renaming T_1 to T_g , and T_2 to T_c , I get the heat transfer rate per unit total volume, Q :

$$Q = 12 k \alpha_g (T_g - T_c) / d_s^2 \quad (9)$$

This is the form of the expression which is used in FLUENT to account for interphase heat transfer. This heat transfer rate will be positive, that is to say flowing in the direction of increasing radius, when the GAS temperature is greater than the COND temperature, so the source term is $-Q$ for the secondary (GAS) phase, and $+Q$ for the primary (COND) phase.

It is instructive to note the circumstances under which the difference $T_g - T_c$ will be large. The most obvious circumstance is a high heat transfer rate Q . Another is a very low thermal conductivity in the primary phase matrix, although that will not be the case in these ODTX simulations. Two circumstances that we will face in these calculations are small values for α_g , and relatively large values for d_s .

In Figures 6a and 6b are shown the results of a two-phase ODTX calculation. The wall temperature is 540.5 K ($1/T = 1.85 \text{ e-}3$). The initial volume fraction of the secondary phase is 0.1 %, with a sphere diameter d_s of 200 microns. The most striking feature of these figures is the deviation in temperature between the two phases. Early in the calculation the COND temperature is nearly 20 K greater than the GAS temperature. The direction of the temperature deviation switches after less than one second, and the negative deviations are not shown in the time histories in Figure 6a. For most of the calculation the GAS temperature is greater than the COND temperature, and is nearly 10 K greater approximately 8 seconds into the heating process. The difference is at least 3 K for the rest of the calculation, with the deviation becoming very large, almost 100 K, near the explosion (not shown in Figure 6a).

The 10 K deviation near 8 seconds is due in part to the fact that the rate of interphase mass (and heat) transfer is becoming large at this point with the increase in COND temperature and FRAGS mass fraction. Another key factor is the relatively small GAS volume fraction, which is just beginning to rise with the increased interphase mass transfer. A small volume fraction means that all of the heat of reaction is being deposited into a relatively small mass, and thus the temperature of the GAS is driven upward. With this relatively large sphere diameter of 200 microns, the deviation in the phase temperatures is significant. The deviation decreases as the GAS volume fraction increases, until the large exothermicity associated with the approaching explosion drives the temperatures apart again at late times. Figure 6b contains a plot of the radial profiles of temperature and mass fractions. The large deviation in phasic temperature is quite evident in this figure. It should be noted that because the density is constant and uniform, mass and volume fractions mean the same thing.

Figure 7a and 7b contain the results of a similar multiphase calculation, except that the sphere diameter is 100 microns. Similar deviations between the COND and GAS temperatures are found, but the effect is not as pronounced as with 200 micron spheres. Examining Eqn. (9), and assuming that the heat rate Q and GAS volume fraction α_g are approximately the same in the calculations with differing d_s , we expect that the temperature deviation will go like the square of d_s . With a factor of two difference in d_s , we expect approximately a factor of four difference in temperature deviation. This is indeed the case, as the peak deviation near the 8 second point

Figure 6a Time histories of phasic temperatures and mass fractions for a wall temperature of 540.5 K and $d_s = 200$ microns. The GAS volume fraction is the same as the GAS mass fraction in this uniform density calculation, and is the sum of the IGAS and FGAS mass fractions.

Figure 6b Radial profiles of phasic temperatures and mass fractions for a wall temperature of 540.5 K and $d_s = 200$ microns. The GAS volume fraction is the same as the GAS mass fraction in this uniform density calculation, and is the sum of the IGAS and FGAS mass fractions.

Figure 7a Time histories of phasic temperatures and mass fractions for a wall temperature of 540.5 K and $d_s = 100$ microns. The GAS volume fraction is the same as the GAS mass fraction in this uniform density calculation, and is the sum of the IGAS and FGAS mass fractions.

Figure 7b Radial profiles of phasic temperatures and mass fractions for a wall temperature of 540.5 K and $d_s = 100$ microns. The GAS volume fraction is the same as the GAS mass fraction in this uniform density calculation, and is the sum of the IGAS and FGAS mass fractions.

in the 100 micron sphere calculation is approximately 2.5 K, which is four times less than the 10 K deviation noted above in the 200 micron sphere calculation.

In Figures 8a and 8b we show comparisons between the results of the 200 micron sphere multiphase calculation, and the single phase calculation with a wall temperature of 540.5 K. In Figure 8b it is shown that the time to explosion is slightly longer for the multiphase treatment than for the single phase treatment. The difference is approximately 1.7 seconds, which represents a 2.7% increase. An explanation for this increase can be found by examining Figure 8a. What we see is that the COND temperature lies close to, but below the single phase temperature for almost all of the heating process. The GAS temperature lies above the single phase temperature, as would be expected if approximately the same amount of energy is being deposited in each calculation. Because the COND temperature is being suppressed due to energy being bound up in the GAS phase, the rate of the second LLNL model reaction is being suppressed as well. In the section above discussing the single phase calculations, we found that this reaction was primarily responsible for the heat release resulting in the eventual explosion of the sample. Therefore suppressing this reaction rate results in a lengthening of the time to explosion in the multiphase treatment.

The lengthening of the time to explosion in these multiphase calculations is somewhat counterintuitive. One might expect that the increase in GAS temperature could be great enough to render the third LLNL model reaction more important than the second for determining the time to explosion. This would lead to a shortening of the time to explosion rather than the lengthening that is observed. In fact both effects are likely to be at work in these calculations, but it seems that the temperature suppression in the COND phase is more important. This makes some sense in that the reactions are sequential, and so a modification to the rate of an early step may serve to preempt an opposite modification in a later step.

Summary

The difference in the time to explosion due to the multiphase temperature deviation effect for the cases analyzed in this report was approximately 2.7%. Although this may not appear to be a significant difference, it leads one to conceive of scenarios in which the temperature deviation and other multiphase effects could make a much larger difference. For example, the three step sequential LLNL model includes high activation energy reactions for the first two steps, and a relatively low activation energy third step. Variations in temperature more dramatically effect the high activation energy steps early in the sequence. It is entirely conceivable that a more complex reaction set might include important high activation energy steps in the GAS phase, such as N-N bond breaking in HMX vapor (45 kcal/m),⁸ or additional high activation energy COND phase reactions, such as:

Any increasing complexity in the reaction set that involves high activation energy steps will require a multiphase treatment in order to properly capture the temperature at which this important chemistry is taking place.

The methodology for multiphase treatment presented in this report can be extended to include secondary phase bubbles that grow with time. One possibility is to prescribe an initial bubble density, with the initial diameter determined by the initial volume fraction. As interphase mass transfer takes place, bubbles could grow in diameter, rather than grow in number as in the current treatment.

Within any bubble, it is possible to include surface chemistry. In the current treatment the reaction rates are determined by the volume density of reactants in a particular phase. It would present no particular difficulty to modify those rates by the available surface area existing at phase interfaces.

In order to properly model an experiment such as Behrens¹⁰ in which the gaseous product concentrations are measured during a cook-off process, a multiphase method for modeling the transport of gases through a condensed matrix must be used. This is not a simple matter, although there are several methods for achieving that goal using FLUENT. Porous materials are currently not permitted in the multiphase models available to a FLUENT user. However, it is possible to model the effect of porosity by properly modifying the convective and diffusive coefficients of a non-porous material. The key is to capture the effect of permeability and momentum defect presented by a porous material through the altering of phenomenological coefficients and the introduction of source terms.

Another possible extension to the current work is to include a true liquid phase, and thus provide a full three phase treatment. This type of model would be necessary to investigate a burning type of event such as linear regression. In that scenario a solid matrix melts into a liquid which then evolves gases in a foam layer prior to burning to completion in the gas phase. Reaction mechanisms more complex than the LLNL three step mechanism are certainly required to model such an experiment. Such mechanisms exist for RDX explosive and modeling of that type has been pursued.¹¹ Advancement in this area for HMX modeling is certainly called for.

Figure 8a Time histories of COND and GAS multiphase temperatures, and the temperature from the single phase treatment. $T_w = 540.5$ K and $d_s = 200$ microns.

Figure 8b Time histories of HMX, FRAGS and mass fractions from both the multiphase and the single phase treatments. $T_w = 540.5$ K and $d_s = 200$ microns.

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