Voids in solid propellants

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1 Contents

2 Introduction

This study originally started as an investigation of the safety of firing solid propellant rockets with variations of the achieved propellant density.

In general, the concerns of trapped air in solid propellant may be eliminated by the use of vacuum mixing and casting, but within the scope of amateur rocketry, hand mixing and open air casting is common, and subsequently the propellants may contain some amount of trapped air. It is then of some importance to establish methods to predict the impact of the trapped air on the performance of the resulting propellant. Also, the aspect of safety comes in mind. There are numerous reports from fellow rocketry amateurs that hand mixed propellants in most cases will burn and behave more or less as expected even though the achieved density may be down to 90% of the theoretical. In some cases however, the motor explodes for apparently no reason, but this could very well be a result of voids in the propellant.

This report deals with the following topics:

- How to calculate the theoretical density of a propellant.
- What does a slice of propellant look like, when it contains trapped air.
- Simple theory - the behaviour of isolated bubbles.
- A numerical study of collided bubbles.
- A simulation of combustion of propellant with voids.

3 Effects of trapped air in composite propellants

Trapped air in composite propellants is normally considered unfavourable although it could be beneficial as burnrate modifier if the amount of trapped air could be controlled.

The main disadvantages of trapped air are decreased propellant density and risc of CATO. Decreased density means that the motorcasing has to be larger (heavier) to hold a specific amount of propellant, causing the total performance of the rocket as a system to drop. For amateur rocketry, this is usually of secondary importance. The primary concern is that trapped air influences on the burning surface of the grain, thus increasing the risc of a CATO. To reduce the amount of trapped air, it is common practice to degas the propellant during mixing. Using this technique, the resulting propellant density is usually very close to the theoretical, often better than 98%. Mixing without degassing may result in densities between 90 and 95% of the theoretical. In many cases however, the propellant may still turn out to work reliably. The natural question to ask is then: What is the critical propellant density? – The answer to this question depends on various things, including the burnrate exponent of the propellant in question.

Trapped air may be in three different forms: isolated air bubbles, air channels - “worm holes” and cracks.

Cracks are the results of bad propellant compositions, a poor manufacturing process, wrong storage conditions or plain handling errors. Cracks should not uccur under normal circumstances and will not be discussed further.

Isolated air bubbles is the most common type of trapped air and may be the result of poor degassing, viscosity problems or of “foaming” of certain types of binders. The effect of isolated air bubbles may be anything from neglegtable to catastrophic.

Wormholes are the result of either insufficient binder or foaming. Wormholes are usually microscopic, and may not be discovered by visual inspection. They do however form a network of channels throughout the grain, and when the grain is ignited an pressurised, the hot gases will penetrate the grain resulting in CATO.

Larger air bubbles or cracks may be discovered by inspection, visually or X-ray. Microscopic bubbles or wormholes may require inspection under microscope or dye-bathing. Still, the trapped air takes up volume, and estimation of actual propellant density is the most obvious way of non destructive determination of the amount of trapped air.

3.1Propellant density

The theoretical density of a propellant consisting of N ingredients may be written as:

$$\rho_{thery} = \frac{\sum_N m_i}{\sum_N \frac{m_i}{\rho_i}}$$

Where m_i is the mass of the i’th ingredient and r_i is the density of the i’th ingredient. The values of m_i is determined by weighing the ingredients during the process of manufacturing the propellant, while r_i may be determined from materials proporties tables or from experiments.

The actual density may be written as

$$\rho_{actual} = \frac{m}{V}$$

Where m and V is the mass and volume of the casted propellant, which may be determined by simply weighing and measuring the geometry of the propellant grain. Ideally, m should equal the sum of ingredient masses and V should equal the sum of ingredient volumes.

As an illustration on what the actual density means, consider a propellant segment for a coreburner, 100mm long, 54mm outer diameter and 24mm bore diameter. If the actual density is 95% of the theoretical, this means that the length of the grain increases by 5.26mm. Cutting such a grain into two parts and inspecting the surfaces roughly corresponds to counting the bubbles in a 2mm thick slice, which turns out to be: 5.5 bubbles of 4mm diameter or 44 bubbles of 2mm diameter or 351 bubbles of 1mm diameter.

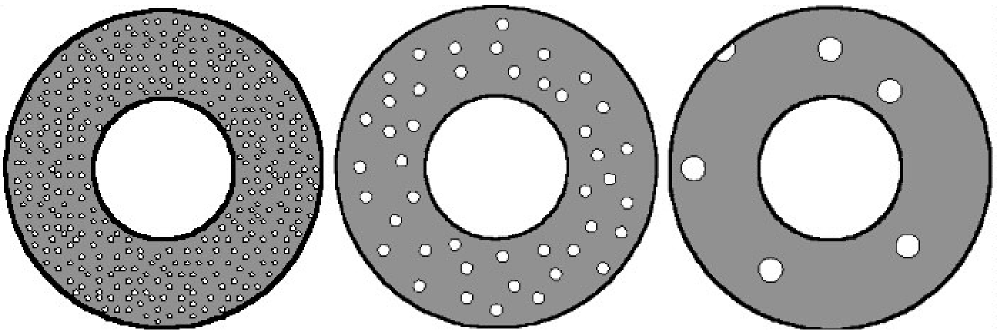


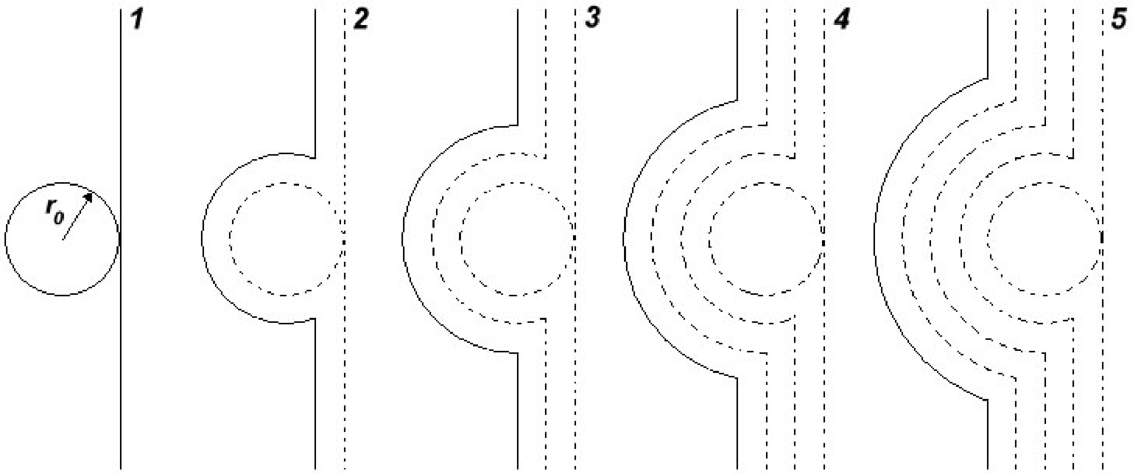
Illustration of 95% of theoretical density

For comparison: a cut through a real propellant segment (approximately natural size).

Cut through propellant segment

3.2Isolated air bubbles

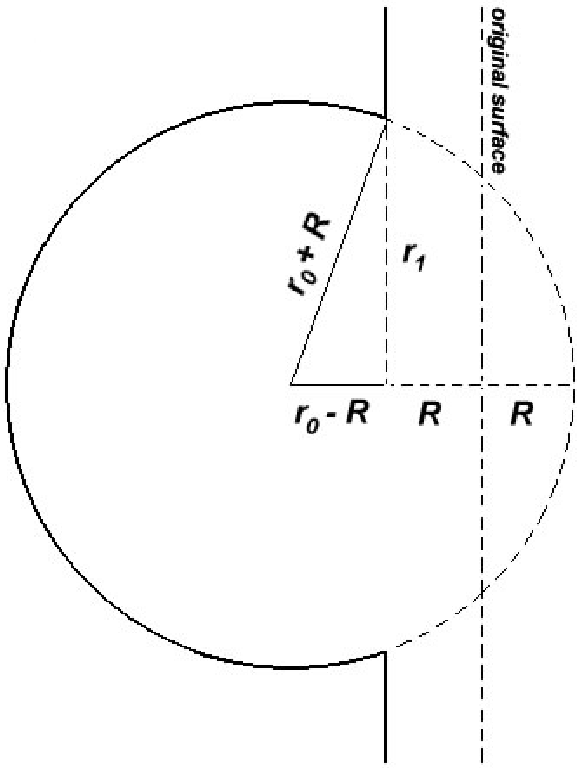
As an example, consider the case of a single spherical air bubble of radius r_0, just beneath the burning surface of solid propellant. A soon as the flame front reaches the bubble, the inside surface of the bubble ignites, and the bubble becomes part of the burning surface. The evolvement of the flame front may be illustrated as follows:



Propagation of flame front when an isolated air bubble is encountered

The evolving surface of the bubble will of course contribute to the total burning surface area. This additional (unwanted) surface area may be calculated from simple geometrical considerations as a function of the Regression length R.

For R < r_0 the geometrical quantities are as follows:



The surface contribution may be calculated as the surface of a sphere with radius R+r_0 minus the surface of the spherical cap lying to the right of the burning surface. Also the bubble "eats away" a circular area with radius r_1 of the original planar surface. In total, the surface may be determined from:

$A = A_{sphere} - A_{cap} - A_{plan}$

$A_{sphere} = 4\pi(R+r_0)^2$

$A_{cap} = 4\pi R(R+r_0)$

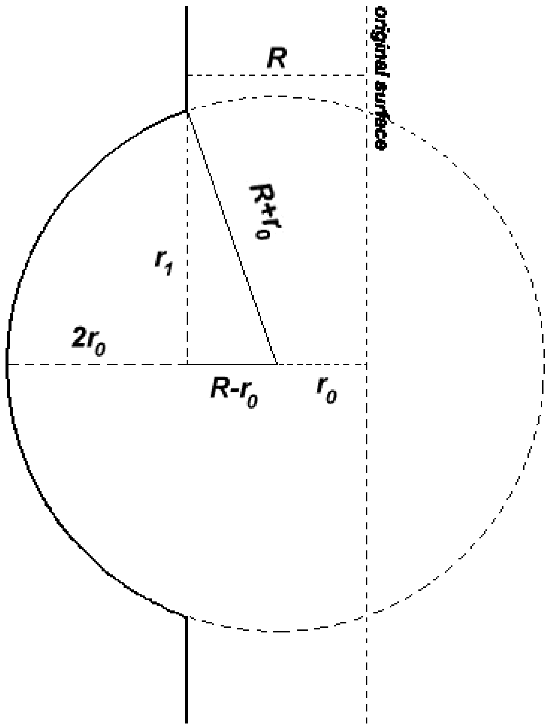
$A_{plan} = \pi r_1^2$

$r_1^2 = (R+r_0)^2 - (r_0-R)^2 = 4Rr_0$

Combining everything yields:

$\underline{A = 4\pi r_0^2}$

For $R > r_0$, the additional surface area may be determined in a similar fashion:



This time it is easier to calculate the area as the surface of the spherical cap to the left of the flame front minus the circular area in the planar surface:

$$A = A_{cap} - A_{plan}$$

$$A_{cap} = 4\pi r_0(R+r_0)$$

$$A_{plan} = \pi r_1^2$$

$$r_1^2 = (R+r_0)^2 - (R-r_0)^2 = 4Rr_0$$

Again, we end up with:

$$\underline{A = 4\pi r_0^2}$$

This result is somewhat surpricing, as $4pr_0^2$ is exactly the surface area of the original bubble. The evolvement of the flame front looks dramatic, but the net contribution to the burning surface area of a small bubble of air remains constant, regardless of the regression length.

In the case of isolated air bubbles, the total surface contribution is the sum of the surface of all bubbles in the grain. There is also the effect of bubble size: It is easily shown, that dividing the air from one large bubble into N smaller makes the total bubble surface area increase by a factor of $N^{1/3}$. Also the surface area is inversely proportional to the bubble radius, so at a fixed density, even while the total surface does not increase as fast as the number of bubbles, it is still prefereable with a few large bubbles instead of many small.

If the bubbles of trapped air can be considered as isolated, the total surface contribution from the trapped air is the sum of the surfaces of every bubble within the propellant. Is the bubble diameter small, the total surface may be alarmingly large, even at densities near the theoretical. In practice however, the bubbles are not really isolated. As the burning surface evolves, bubbles will collide tending to “eat” each other. Another effect is the final web thickness of the grain. When a bubble has grown to a sufficiently large diameter, it will hit the outer restriction of the grain. From that point it will evolve rather in a cylindrical fashion. Consider, for simplicity, that the air bubble is a cylinder of radius r_0 and length L. Such a cylinder will add $2pr_0L$ to the total surface, while at the same time it will reduce the original surface with its cross section area pr_0^2. The resulting net surface contribution is then: $pr_0(2L- r_0)$. When $r_0 > 2L$, the net area contribution is negative. As the combustion process actually increases r_0 and decreases L it can be seen, that an isolated bubble will start its “life” expanding spherically at a constant net surface contribution of $4pr_0^2$ until it at some point reaches the outer restriction of the grain and its net surface decreases – even getting negative.

3.3Collided voids

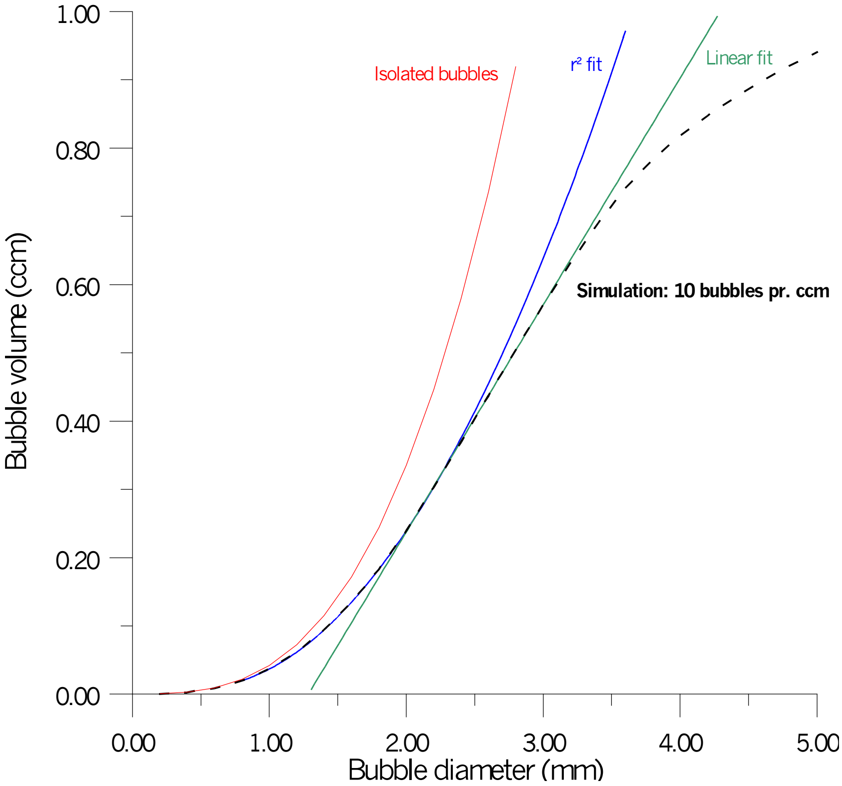
A general theoretical treatment of the case where the bubbles are allowed to collide is very difficult to do. Instead, the nature of collided voids is treated numerically the following way:

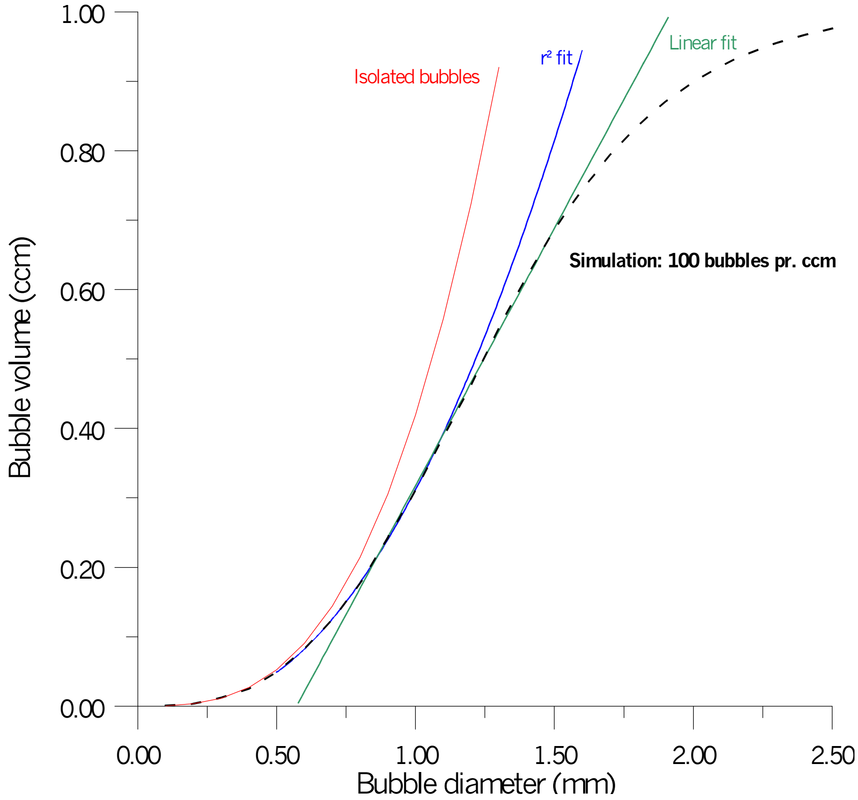
N voids are placed randomly within a cube, 1cm in each dimension. All voids are having the same diameter, initially set to zero. Furthermore, the voids are placed on grid points in a grid of spacing 0.1mm. The placemant of the voids ensures that all voids have individual center locations, but no further restriction is imposed on the placement of the voids. The actual volume of the (propellant) cube is the calculated for gradually increased values of the bubble radius. As the volume of the cube itself i known, the volume calculation makes it possible to extract the volume of the voids and the relative density of the propellant at any given bubble radius.

Furthermore, the simulation also produces a "shadow image" of the voids in a 0.4mm thick slice of the propellant for each step in the simulation for visualisation.

Calculations are made for N ranging between 5 and 10000.

The variation of bubble volume with bubble diameter is shown below for the cases of 10 bubbles pr. cubic centimeter and for 100 bubbles pr. ccm. For comparison, the expected volumes according to the isolated bubble theory are also shown.





Both cases shows the same general behaviour:

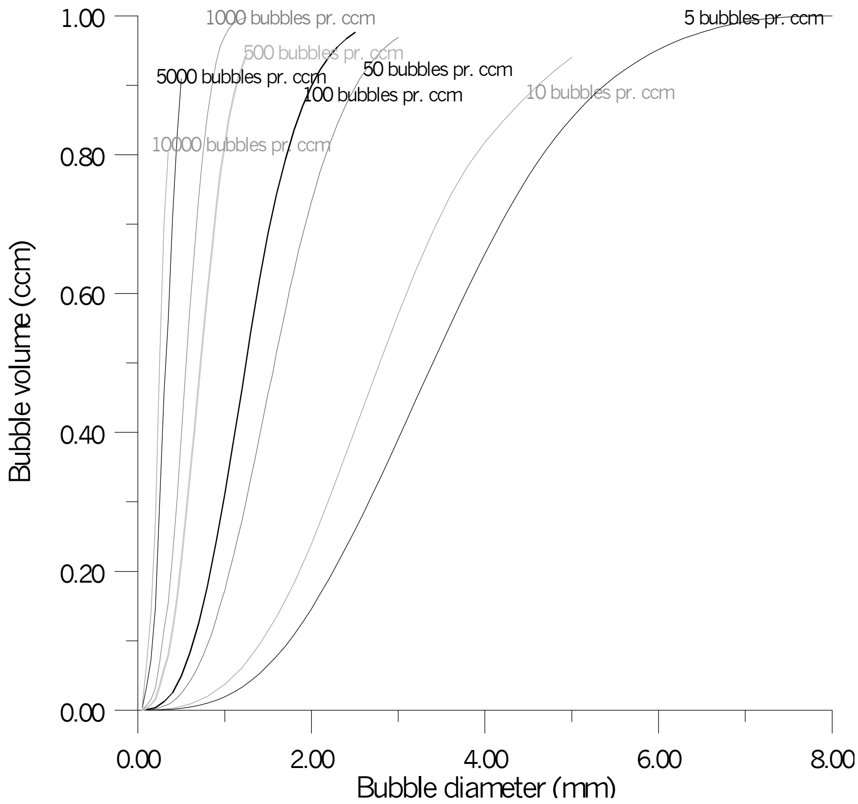
- At small values of the bubble radius, the bubble volume follows the isolated bubble theory.

- When the bubble radius increases, the bubbles starts to collide with their closest neighbours forming structures of cylindrical nature as the bubbles partly expands into volume already in use by its neighbours. Thus, the volume increases with r^2 and not with r^3.

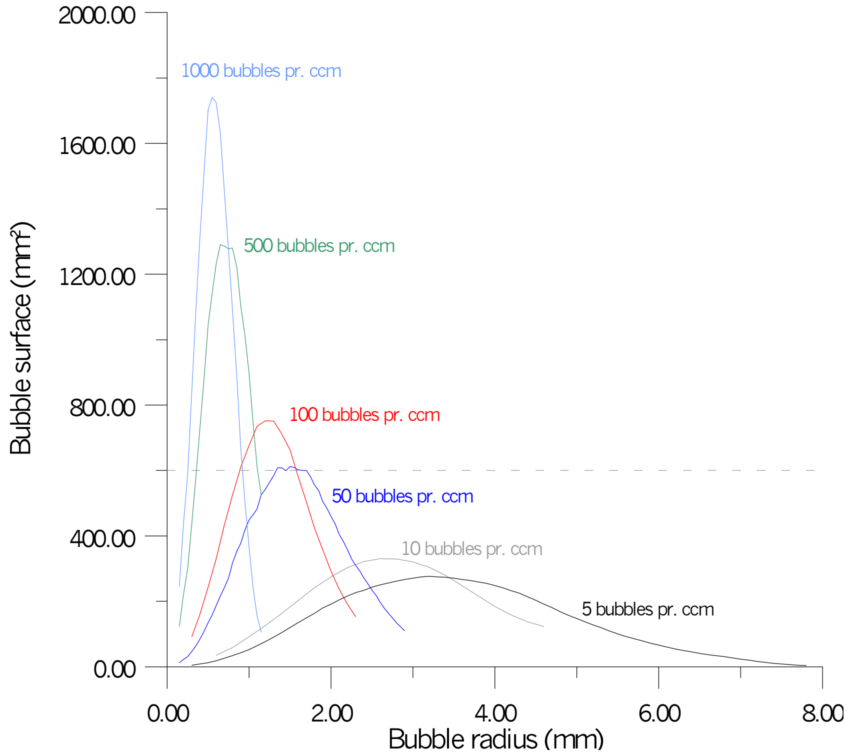
- This tendency continues as the cylindrical voids collides with more isolated bubbles and with other cylindrical voids. At some point, all voids will fuse into a network of connected channels - wormholes - that penetrates the entire propellant block. In this case, each bubble has collided with multiple neighbours, each sharing mostly the same volume, and only fractions of each bubble are allowed to expand with increasing radius. The total bubble volume now increases with r in a linear fashion.

- As the radius continues to increase, the volume expansion is further reduced as more bubbles collide with the surfaces of the cube, until ultimately all propellant volume is spent.

The volume-radius plots for the entire range of N is shown below.



Still, bubble volume is not the main point of interest. The main target of this investigation is the bubble surface. This is however quite difficult to calculate directly. Instead it may be calculated by differentiating the bubble volume: As the model assumes that all bubbles expands with the same rate, uniformly in all directions, the bubble surface may be represented by the volume increase at an infinitissimal increase of radius, i.e. dV/dr.

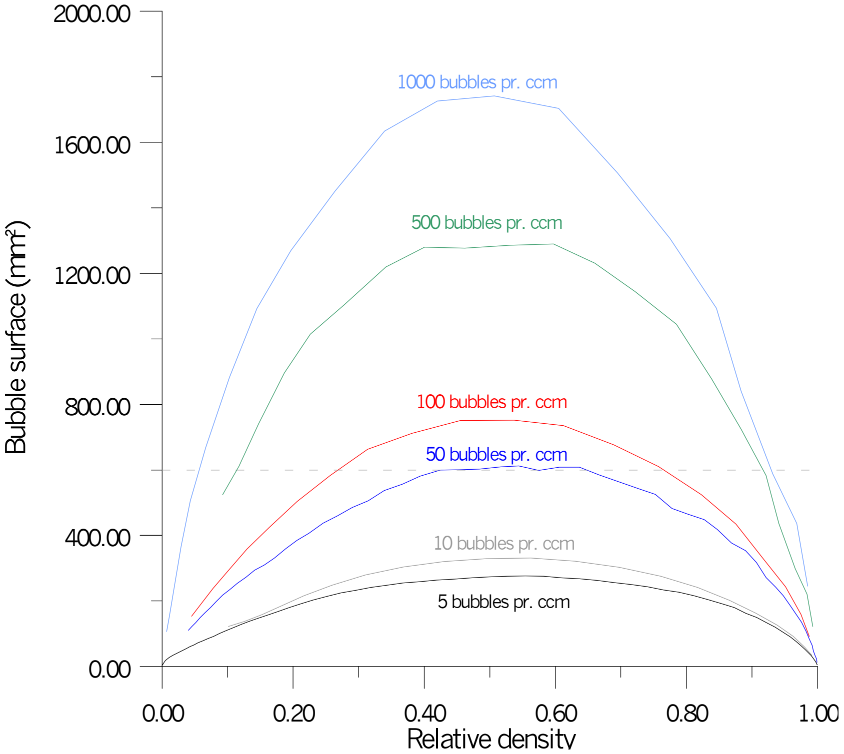


The total bubble surface as function of bubble radius is shown for different bubble densities. Numerical differentiation is very noise sensitive, so the surface plots has been smoothened. Also the plots for very high bubble densities has been discarded. For comparison, the total surface area of the cube is shown as a dotted line.

In general, these surface plot only tells that it is unfavourable to have high bubble densities. It is more intersting however, to plot the surface area against the relative propellant density. It is then clear that:

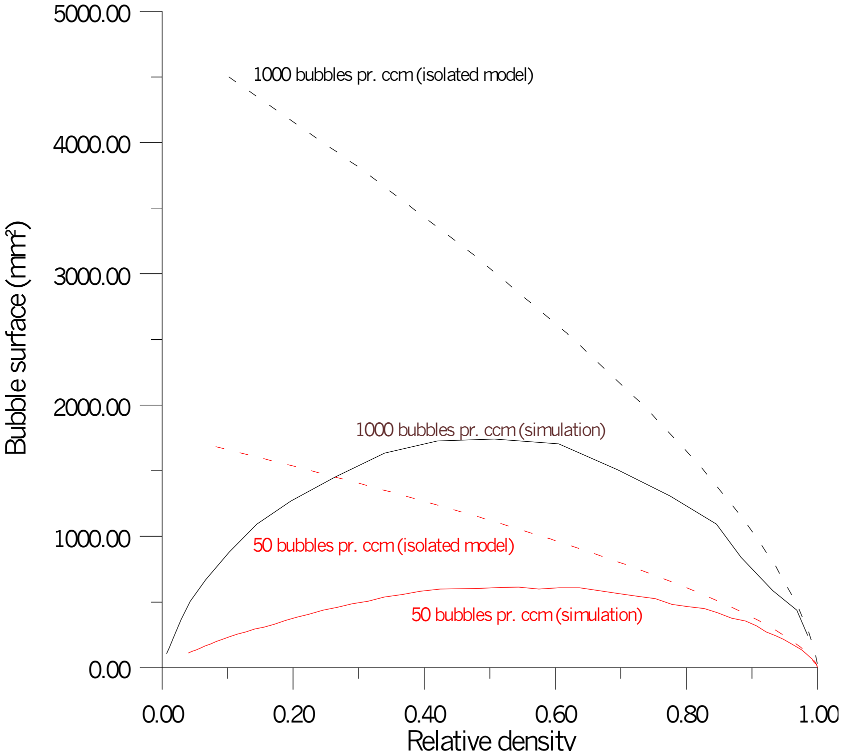
- It is preferable, at any given propellant density, to have a few large bubbles instead of many small - as was concluded also in the isolated bubble theory.

- Wormholes (bubble volume increases linearly with r - surface is invariant with r) occurs when the relative propellant density is below 0.8, almost independently of the bubble density (the smoothening of the graphs makes the limit look softer, but it may also be determined by inspection of the original volume data). For curiosity, it may also be noted that the surface limitations similarly domminates at relative densities below 0.35 almost independent of bubble density.



In general, the total bubble surface area is not really relevant as the bubbles are in general not lit all at once. The instant ignition of the entire bubble surface is only relevant in the case of wormholes. The simulation deals only with bubbles of uniform radius, but as the limit of wormholes lies at relative densities between 75 and 80 pecent for all simulations, it must be assumed that this holds also in the case of mixed bubble sizes. This is an important result: **Propellants of relative densities less than 0.8 are unsafe and may cause a CATO.**

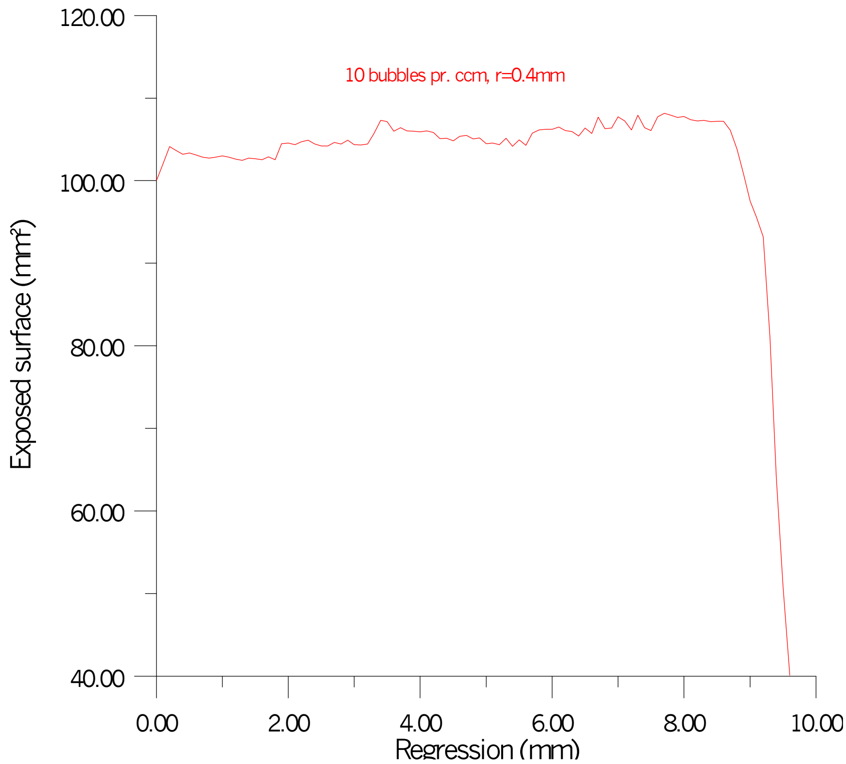
At last, the total surface area may be compared to the surface predicted by isolated bubble theory. It is seen that the isolated bubble theory predicts a somewhat larger surface area, but for relative propellant densities ranging between 0.9 and 1.0, the difference is not that big, and taking into account the complexity of the calculations, isolated bubble theory may be viewed as a simple and slightly conservative way of estimating the bubble surface - assuming that the bubble sizes are known.



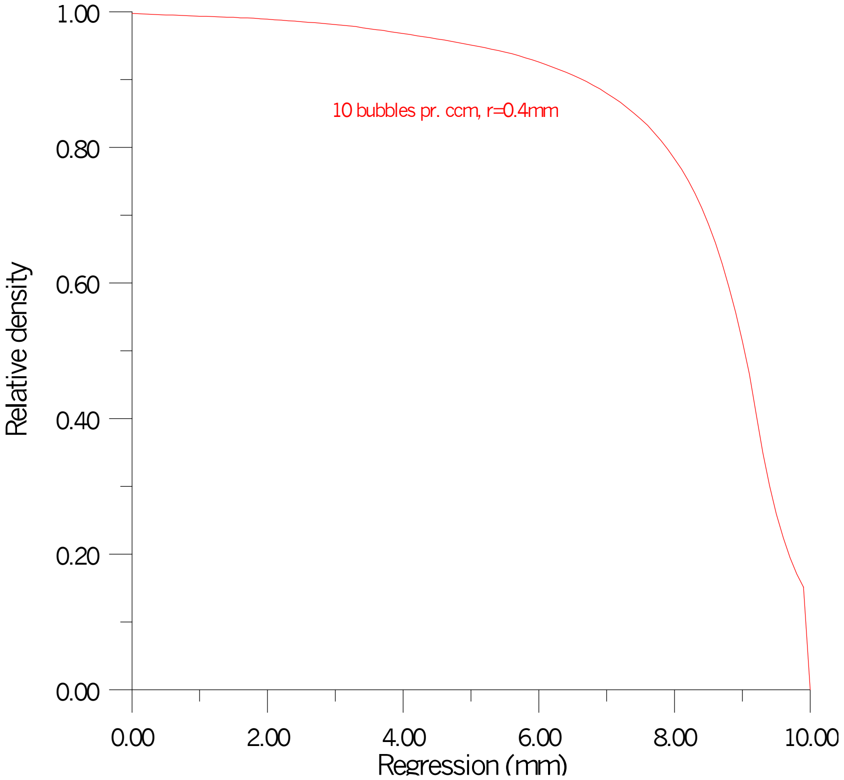
3.4Burning surface simulations

The maximum void surface calculations in the previous chapter are only of practical relevance if the entire suface ignites simultaneously, and that happens only in the case of wormholes. To get a more realistic view of the consequences of having voids in the propellant, the simulation is modified to reflect the progression of the flame front in a propellant block containing voids.

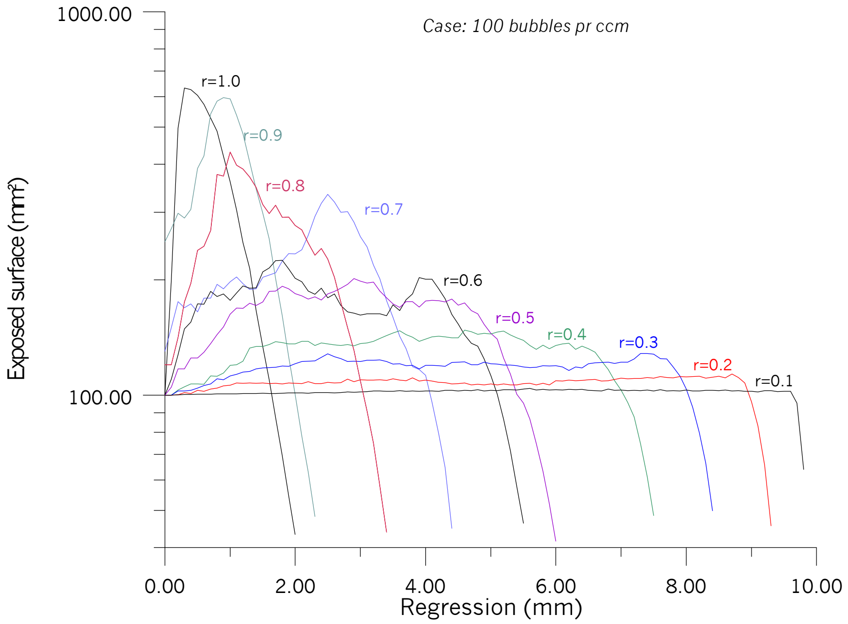
Once again, the simulation assumes that N voids are randomly dispersed within a cube of propellant, measuring one centimeter in each dimension. The voids are placed at individual locations and they intially all have the same radius. The simulation repeatedly calculates the volume of the propellant block, using the same method as previously. After each volume calculation, the propellant block is shrinked 0.1mm in one dimension to simulate that it burns on one side - the remaining 5 sides being inhibited. It is checked if any of the voids collides with the burning surface by checking if any point on the burning surface belongs within the perimeter of any void. Voids that collides with the burning surface are then marked as being "active". Then any active void is being checked for collision with any other void, to search for all the voids that may possibly be connected to the burning surface. The void-void collision test is repeated until the number of active voids is unchanged, as the sequence of the detection of the active voids may otherwise leave some connected voids undetected. Then, assuming that all surfaces connected to the burning surface ignites instantaneously and burns at the same rate in all directions on the entire connected surface, the radius is increased by 0.1mm for all active voids and the volume may be calculated once again. The total burning surface is then determined by differentiation of the volume-regression curve of the entire propellant block.



The simulation results shows that the burning surface increases as the flame front reaches the voids in the propellant. As long as the voids are isolated, the surface increases in steps. When the voids starts to collide, the surface area evolves more gradually. At large, the surface increases with the regression, but it can also decrease locally. As another consequence of the voids, the relative density of the propellant decreases during combustion.

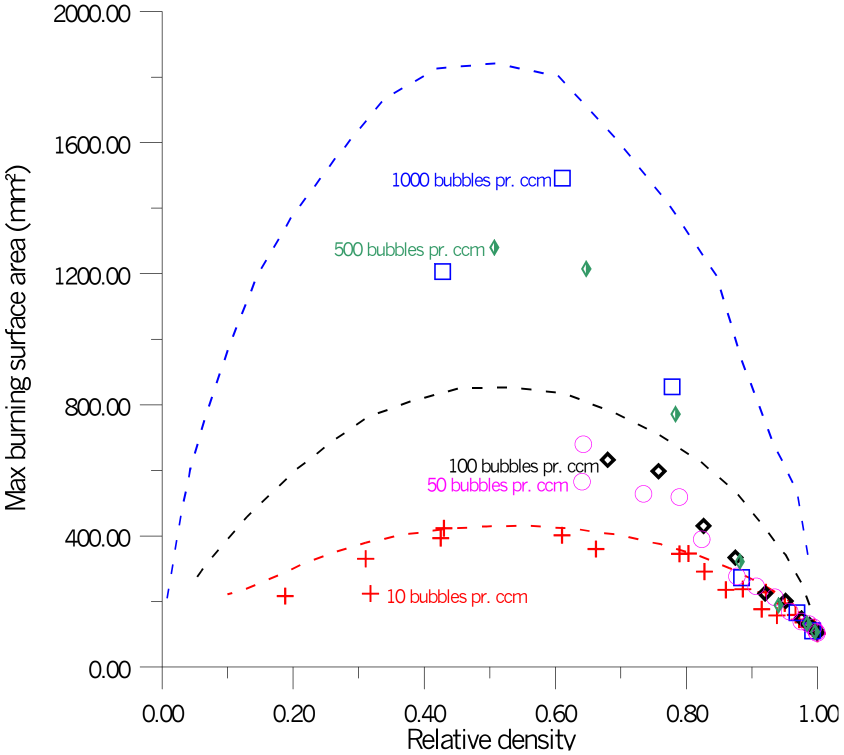


The simulated burning surface for 100 bubbles pr. ccm are shown below for variuos bubble sizes.



For small voids, the voids only increases the surface area slightly, but as the voids grow larger, the voids not only starts to contribute to the burning surface, but they also forces a faster consumption of the propellant, not unlike the effect of an increase of burn rate. For even larger voids, the combustion works itself into the wormhole condition, where the surface increases very fast until it limits - but even this case could be viewed as a burn rate increase.

The general tendency of the evolvement in burning surface is that the surface increases during combustion. Depending on the locations of the voids, the increase is not nescesarely strictly monotonic. The most important feature of the burning surface is its maximum. The maximum surface values may be estimated from the calculation of total void surface in the previous chapter, adding the 100mm^2 from the cube surface.



However, when the maximum values from the burning surface simulations are plotted on top of the total void surface + cube surface plots it turns out that the burning surface seems to be independent of bubble size. Instead - for all bubble densities - the burning surface maximum depends only of the relative density. For lower densities than 0.85, the burning surface approaches the predicted total void surface.

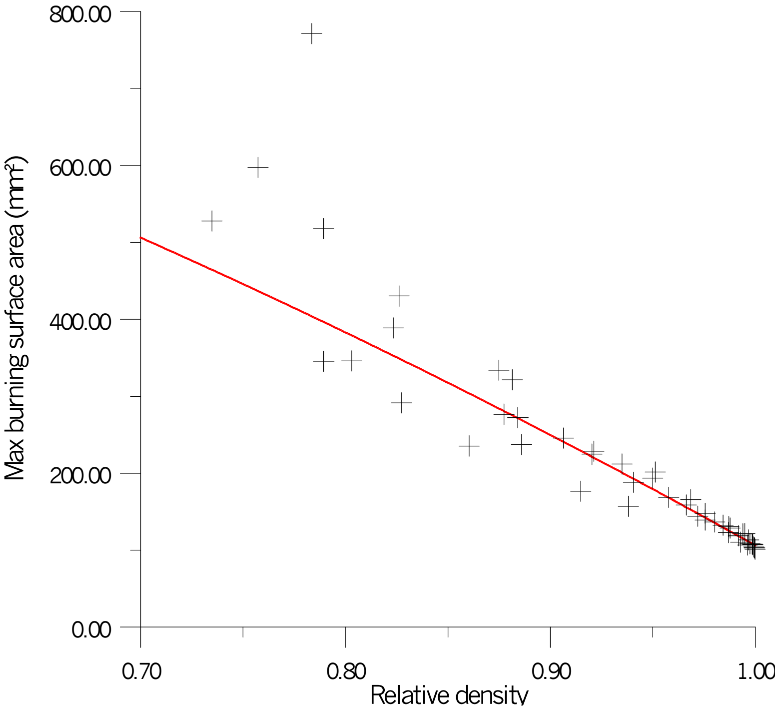
This is also a very important result, suggesting that the maximum burning surface may be written as:

$$A_{\text{burn, max}} = A_{\text{burn, nominal}} \cdot C_{\text{void}}$$

The "void coefficient" is written as:

$$C_{\text{void}} = -31.5 \cdot (\text{relative density})^2 + 45.0 \cdot (\text{relative density}) - 12.5$$

When the max surfaces for the entire range of data is plotted on top of the model, it is evident that the "law" is not valid when relative density is less than approximately 0.85, and that is only partially valid for relative densities below 0.9.



It may be that this correlation only holds in the case of uniform bubble sizes. To investigate this, the simulation is repeated for the case of mixed bubble sizes. Two different strategies are used to generate the voids: Equal volume distribution and equal number distribution.

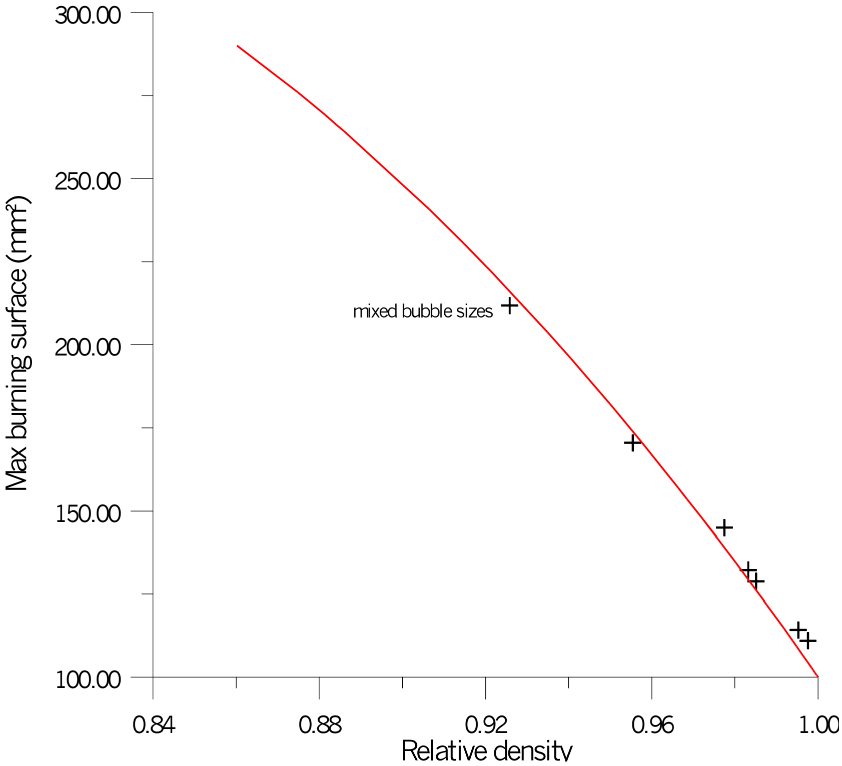
In case of the equal volume distribution, the voids have radius of 0.1mm, 0,2mm,... K*0.1mm. The number of bubbles of each size is determined, so that each size class of voids takes up the same volume. For practical reasons, K must be $\leq$ 15, but is otherwise determined as the highest integer number that generates at least one bubble of size K*0.1mm.

In case of the equal number distribution, the voids also have radius of 0.1mm, 0.2mm,...,1.5mm. The number of voids of each size is the same (and the total number of voids is a multiplum of 15).

The voids are placed randomly in the cube. It is checked that the bubbles do not collide during placement, as this would possibly distort the expected size distributiuon. In all other respects, the calculation is the same as in the case of uniform bubble size.

The maximally encountered burning surfaces in the mixed bubble size calculations turnes out to be in excellent agreement with the void coefficient model for both size distributions. It is therefore reasonable to assume that the void coefficient model holds in general for propellant geometries that may be considered as generalized cases of the cube burning form one side - this covers the most common core burning geometries.

It should be noted, that the void coefficient model is not excact as such. It is derivied as an average model that fits the results of a number of simulations. It may be used to predict the expected outcome of a motor firing, not to guarantee a successfull firing.



4 Conclusion

This study originally started as an investigation of the safety of firing solid propellant rockets with variations of the achieved propellant density.

The numerical study of voids in solid propellants has revealed a general relationship between the relative density of the propellant and the nature of the voids. An excact model of the idealised case of completely isolated voids has been created, but it turns out to be applicable only at relative densities close to 1.0. Generally one must take into account that the voids collide, thereby forming structures of more or less cylindrical nature. For relative densities less than 0.8, the voids forms long connected channel structures - wormholes - that penetrates the entire grain, and for relative densities below 0.35, the grain can no longer maintain its shape as a one piece structure.

Two conclusions may be drawn from the calculations of the calculations of the total surface of collided voids:

1) For a fixed value of the relative density, it is preferable to have a few large voids instead of many small voids. Surface defects may be viewed as a special case of this situation, and it may be concluded that even if a surface defect may look bad, it will in most cases have a minimal impact on the total exposed surface.

2) For a fixed number of voids, it is preferable to have the voids as small as possible. This may justify the method sometimes used by amateurs, to pressurize the grain during the casting process to shrink the diameters of the voids. In case the grain is casted in a vertical mould, the hydrostatic pressure of the propellant itself will actually shrink the voids in the lower part of the grain.

The most remarking result however, is that the surface of the voids in the unignited grain does not really correlate with the maximally exposed surface during burn. Instead, a close correlation has been revealed between the max burning surface and the relative density of the unignited grain - this correlation may be expressed by a simple "void coefficient", that does not depend on the number of voids or their sizes, but only on the resulting relative density of the unignited grain. The previous statements about surface defects and void shrinking still holds however. Shrinking the voids will increase the relative density, and a surface defect is a local phenomenom, that is not really covered by the void coefficient model.

The void coefficient model breaks down for relative densities below 0.85, where the max burning surface approaches the surface of the voids in the unignited grain. It is interesting to note, that if wormholes exists in the grain, the burning surface will remain constant during majority of the burn. In princible, this could be exploited to do high thrust, short duration motors operating at constant pressure, if the number and size of the voids could be controlled. The resulting density of such a grain would be quite comparable of the resulting density of a conventional star grain, however the effect of erosive burn will be harder to predict.

4.1Failure predictions based on the void coefficient model

One consequence of the void coefficient model is that it may be used to predict if a certain motor is likely to CATO or not.

In the following analysis, it is assumed that the burnrate of the solid propellant follows the St. Roberts burn rate law:

$$r = a \cdot P_c^{\,n}$$

where a and n are constants related to the propellant type (n is sometimes reffered to as the burn rate exponent). P_c is the combustion chamber pressure and r is the corresponding burn rate.

During steady state combustion, the mass flow through the nozzle throat equals (or at least approximates) the combustion mass flow at the exposed propellant surface. This may be expressed in the following relation:

$$P_c = b \cdot \left(\frac{A_b}{A_T} \right)^{1/1-n}$$

where A_b is the exposed burning surface and A_T is the nozzle throat cross section and b is a constant related to the solid propellant.

According to the void coefficient model, the exposed burning surface may be expressed as:

$$A_b = C_{void} \cdot A_{\text{burn, nominal}}$$

Thus it follows that:

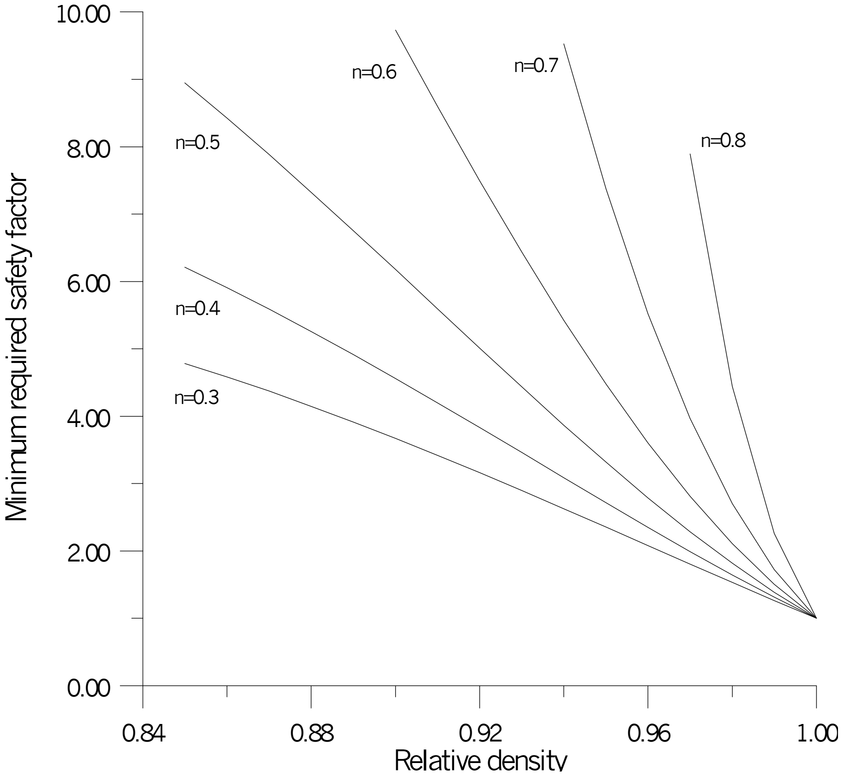
$$P_c = b \cdot \left(\frac{A_{\text{burn, nominal}}}{A_T} \right)^{1/1-n} \cdot (C_{void})^{1/1-n} = P_{\text{c,nominal}} \cdot (C_{void})^{1/1-n}$$

A well designed rocket motor casing is designed with a safety factor. This means that the motor casing will handle a chamber pressure that exceeds the MEOP of the motor. In terms of the void coefficient, the casing will (on average) handle the burn if:

$$S_f > (C_{void})^{1/1-n}$$

As C_{void} is directly related to the relative density of the propellant, one can easily determine the minimum required safety factor for the safe operation of specific propellant with a specific relative density.

The minimum required safety factor (assuming that except from the voids, the motor behaves nominally in any other respect!) is plotted below for different values of the burn rate exponent. For propellants based on ammonium perchlorate, the burn rate exponent will normally be in the range of 0.5. It may be seen from the plot, that in order to successfully fire a propellant with a relative density of 0.92, the chamber pressure may increase by a factor of 5. For potassium perchlorate propellants however, the burn rate exponent may be in the range of 0.8, and in this case, even a safety factor of 5, will not allow for a relative density of less than 0.98.



Theese figures may seem scaring, especially for those who regularly make hand mixed propellants of relative densities of 90-95%. One should remember however, that the simulations are based on the assumption that the voids are distributed evenly within the entire propellant volume. This is often not the case. Instead, the voids tend to be at the boundaries of the grain as the hydrostatic pressure in the mould will make the trapped air move towards the walls of the mould where there is a chance of a leak - or at least a chance to move towards a lower hydrostatic pressure. This means that the most parts of the propellant segment will have better than average relative density while the boundary zones may have very poor relative density - and as shown previously - if the relative density is as low as 35% or less, the void surface is regressive and may be tolerable.

5 Appendix

5.1Calculation of volume

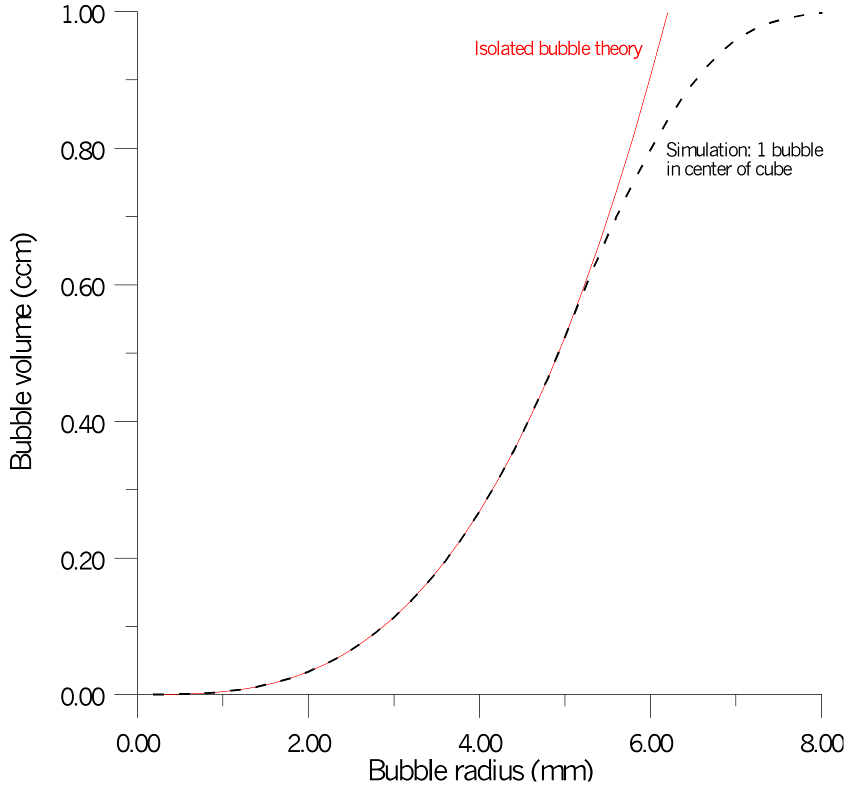
The calculation of actual (propellant) volume is performed in the following fashion:

The propellant cube is divided into subcubes, 0.1mm in each dimension. Each of the 8 cornerpoints and the centroid of the subcube are checked if they are belonging to the interior of any of the voids in the simulation. If the point under investigation does not belong to the interior of any void it contributes with 1/12 subcube volume in case of a cornerpoint and with 4/12 subcube volume in case of a centroid point.

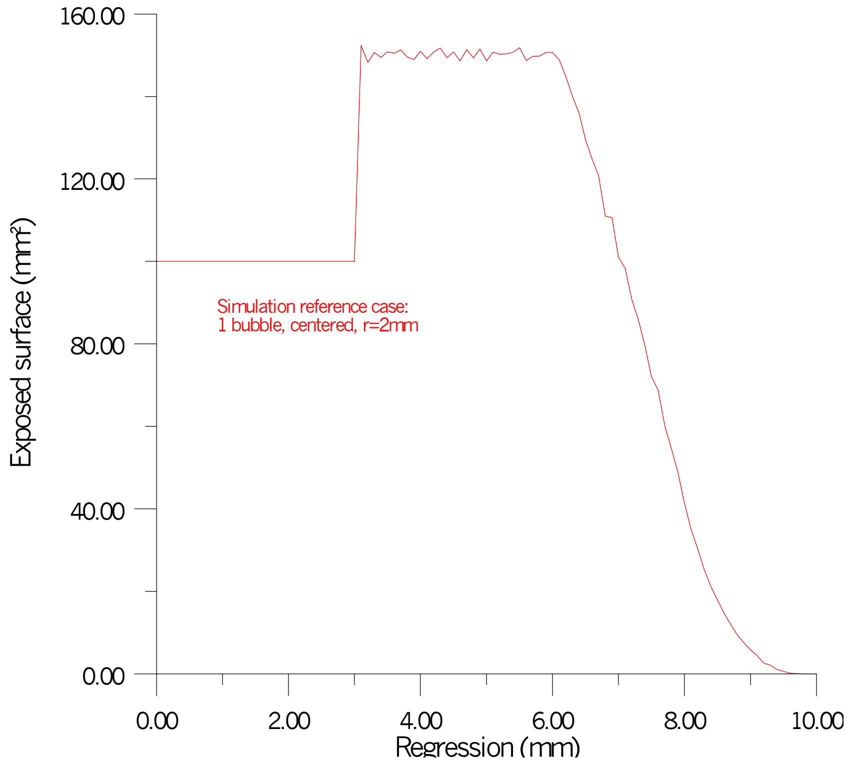
This calculation may be rearranged in a trapez method style to save significant calculation time, taking into account that the each of the corner points of a subcube also is a corner point in 7 other subcubes, except for the points on the surface of the entire propellant cube. This leads to the total algorithm:

- The 8 corners of the entire cube contributes with 1/12 subcube volume
- points on the edges (except the corners) of the entire cube contributes with 2/12 subcube volume.
- Points on the surfaces of the cube (except the corners and the edges) contributes with 4/12 subcube volume.
- All internal grid points within the entire cube contributes with 8/12 subcube volume.
- All subcube centroid points contributes with 4/12 subcube volume.

To prove the validity of the calculation, a reference case is made, placing one single bubble at the center of the propellant cube. In this case, the isolated bubble theory applies until the bubble radius exceeds 5mm and the bubble collides with the surfaces of the propellant cube. The result of this simulation beautifully agrees with the expectations.

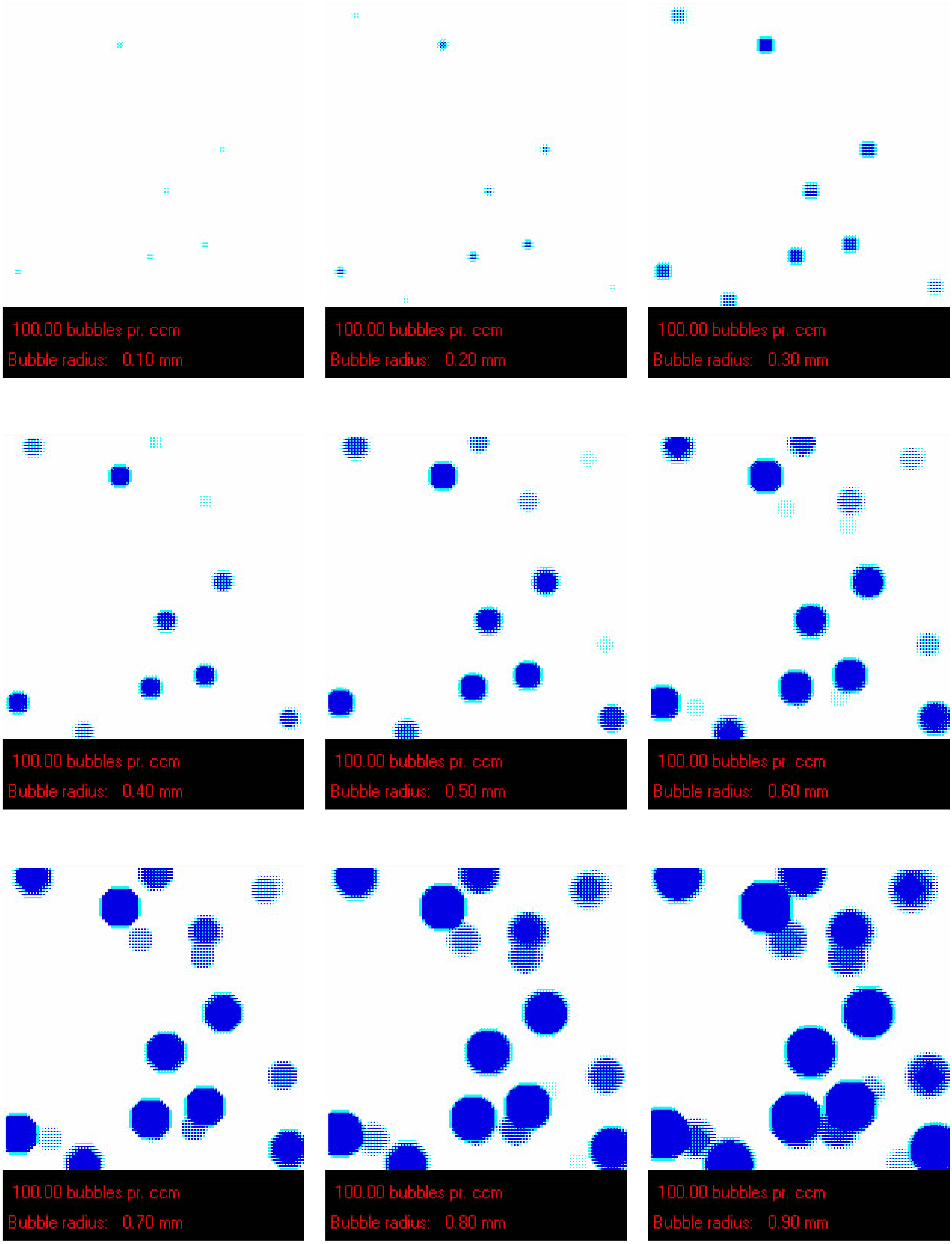


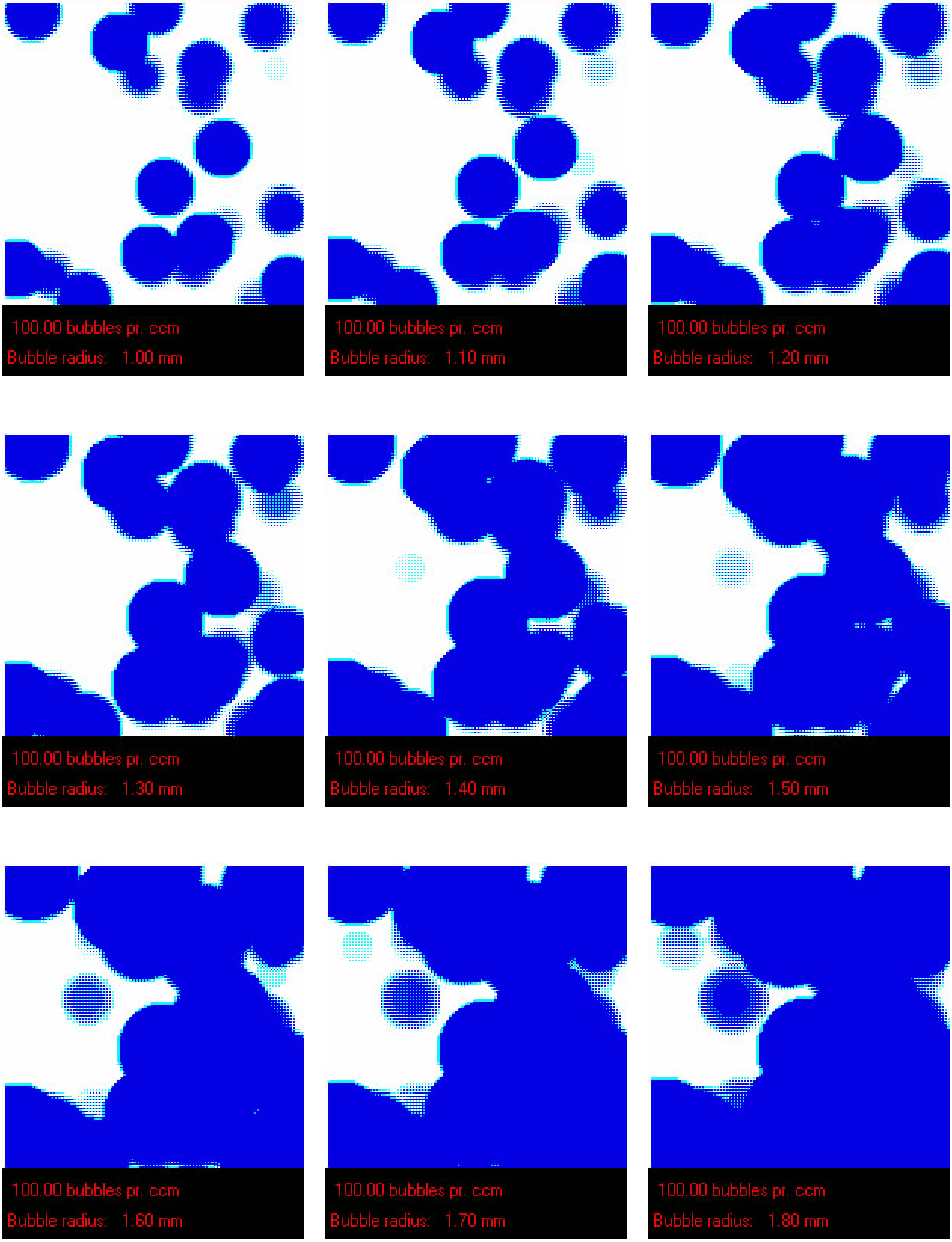
In the case of burning surface simulation, the calculation is verified by testing it with one centered bubble of radius 2mm. According to the isolated bubble theory, the burning surface should then be at 100mm^2 until the flame front hits the bubble. Then the surface should instantly increase to 150mm^2 and remain constant until the bubble intersects the surfaces of the propellant cube. The simulation is in full accordance with the theory!



5.2Shadow images

Shadow images are shown, illustrating the voids in a 0.4mm thick slice of propellant.




100.00 bubbles pr. ccm
Bubble radius: 1.00 mm
100.00 bubbles pr. ccm
Bubble radius: 1.10 mm
100.00 bubbles pr. ccm
Bubble radius: 1.20 mm
100.00 bubbles pr. ccm
Bubble radius: 1.30 mm
100.00 bubbles pr. ccm
Bubble radius: 1.40 mm
100.00 bubbles pr. ccm
Bubble radius: 1.50 mm
100.00 bubbles pr. ccm
Bubble radius: 1.60 mm
100.00 bubbles pr. ccm
Bubble radius: 1.70 mm
100.00 bubbles pr. ccm
Bubble radius: 1.80 mm