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Technical Notes

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Microstructure of Composite Propellants Using Simulated Packings and X-Ray Tomography

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I. Introduction

COMPOSITE solid propellants are heterogeneous media in which particles are embedded in a rubber binder. For industrial applications, such particles are commonly ammonium perchlorate (AP) and aluminum (Al), the sizes of which are typically below 100μm.

As a general rule, simple mixture laws are often inappropriate for granular systems because they cannot capture the inherent microstructural features. This conclusion also stands for composite propellants, because various macroscale phenomena are strongly linked with the structure at microscale. They may be encountered in the field of detonation (e.g., hot-spot formation during deflagration–detonation transition), combustion (e.g., aluminum agglomeration and fine AP/binder premixed flames), mechanics (e.g., filler/binder adhesion), etc.

This obviously motivates an improved knowledge of propellant microstructure and also the ability to "build" representative numerical models of structures as input data for detailed multiphysics modeling (namely, computational fluid dynamics or finite element method codes). Those numerical microstructures are classically random packings of spheres, which have been studied for many years because they serve as useful models for a variety of physical systems (granular, porous, anamorphous materials, etc.). Yet, random packings should faithfully reflect the features of the actual propellant spatial structure, not only global properties (as volume fraction, for instance), but also second-order spatial statistics. This can only be checked with some in situ experimental characterization of the structure.

This work aims at comparing simulated random packings on a typical industrial AP/Al propellant together with experimental microstructure data to evaluate to which extent such simulated packing describe the actual microstructure. Experimental data are obtained through x-ray tomography of a propellant sample. This approach leads to genuine 3D statistical data in a nonintrusive way and allows a relative automatization of data sampling and processing.

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II. Random Packings

A. Packing Algorithm

A composite propellant is modeled as a random arrangement of hard spheres in a cube of fixed size L [so-called representative volume element (RVE)]. The simplest way consists of placing randomly, irreversibly, and sequentially nonoverlapping spheres, which is known as the random sequential addition (RSA) process [1]. In other words, the coordinates of the sphere center (x_i, y_i, z_i) and diameter D_i are randomized and the sphere is accepted if it does not overlap with previously accepted spheres. The procedure is then repeated until the actual volume fraction ξ reaches the prescribed volume fraction. Although this approach is appealing due to simplicity, it is not efficient in the sense that it is not possible to achieve high packing fraction (maximum for monomodal constant diameter sphere is about 0.38, known as the saturation limit [1]). This is clearly too low a value for composite propellant applications.

Some refined algorithms for packing that allow for higher volume fraction may be found in literature (e.g., [2–4]). We recall that the maximum packing fraction for random spheres of equal diameter D cannot exceed the so-called random close packing (RCP) fraction ξ_{RCP}, which is known to be around $\xi_{\mathrm{RCP}} \sim 0.64$ [5]. The algorithm we developed is roughly close to the Jodrey–Tory algorithm [3]. Basically, a set of random sphere centers C_i and diameters D_i are randomized. Then spheres grow and diameters are increased by an increment δD_i with possible overlapping. The algorithm proceeds then by iterative resumption of overlaps; if two spheres i and j overlap, then they are both spread apart symmetrically along vector $\mathbf{C}_i\mathbf{C}_j$ to a predetermined distance. The procedure is repeated until no overlap remains. Then sphere diameters are increased again and the global procedure is resumed till the desired packing fraction and diameters are reached.

Actually, the strategy used is a combination of both approaches presented: the latter algorithm is preferred for high-volume-fraction modes (here, coarse AP), whereas RSA is privileged (due to CPU performance) for ingredients in lesser quantity (aluminum and fine AP).

Spheres are packed in the volume bounded by the cubic RVE and are not allowed to extend beyond this domain (mimicking wall boundary conditions).

In our packing code, the number of modes is unlimited and the diameter for each mode may follow any distribution law.

B. Example of Packing

The work will focus on a typical industrial AP/Al solid propellant that consists of 18% by weight aluminum, 68% by weight AP, and 14% by weight hydroxyl-terminated polybutadiene (HTPB) binder (in terms of volume fraction, this corresponds to 0.61 and 0.115 for AP and Al, respectively). The AP is bimodal with a mean-mass diameter of 10 μm for the fine AP and about 200 μm for the coarse AP, whereas aluminum has a mean-mass diameter of around 40 μm. Initial particle geometrical features are characterized by optical granulometry (Malvern MasterSizer) before propellant formulation so that density probabilities for diameter are known. For initial AP and Al particles, diameter distribution is fairly well correlated by log-normal laws. Figure 1 presents the cumulative size distribution for Al particles and a good agreement with a log-normal assumption for diameter is noticed. Because aluminum is the focus of the study, its size distribution is of major importance.

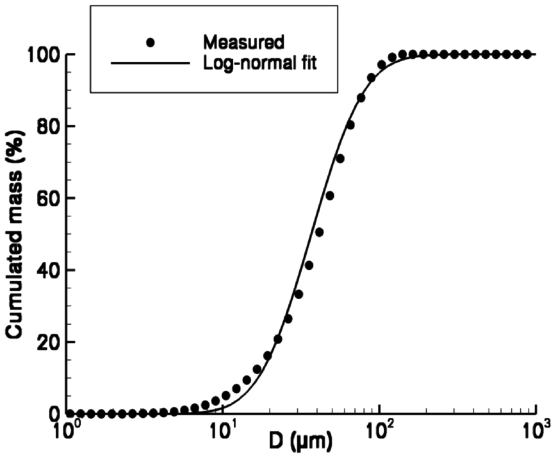

Fig. 1 Experimental and fitted size distribution for initial Al particles.

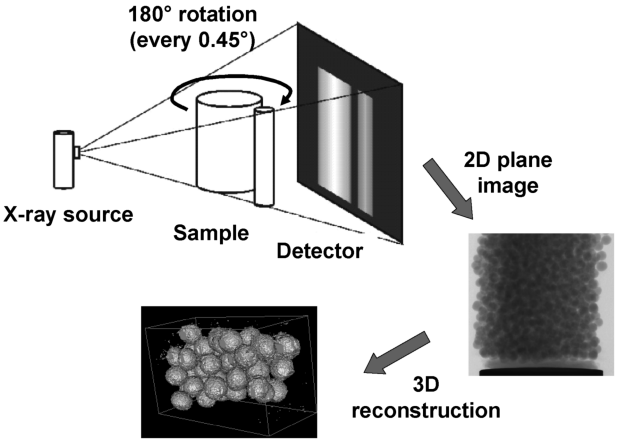

Fig. 3 X-ray microtomography analysis.

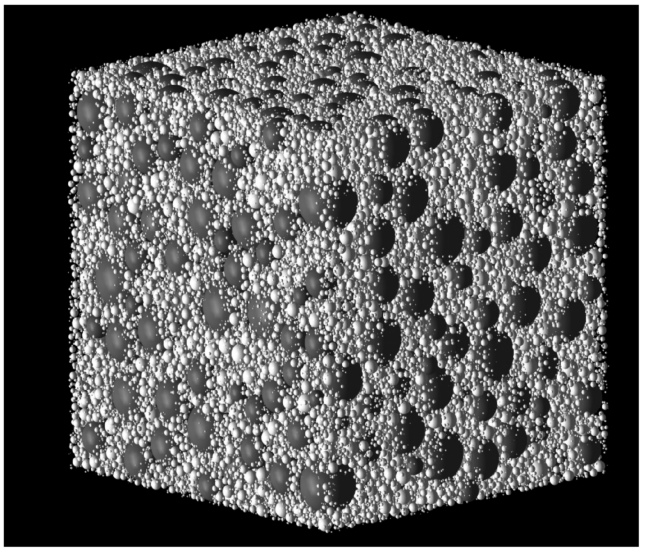

Fig. 2 Simulated packing for test propellant (fine AP is not shown).

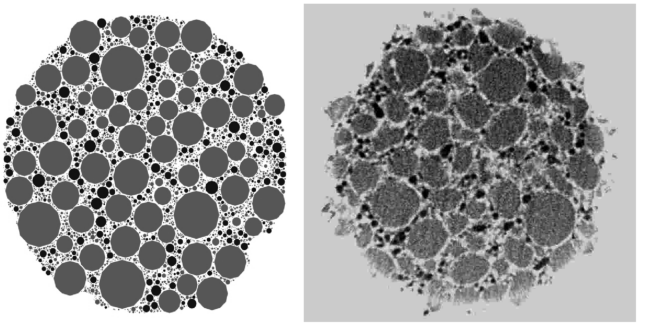

Fig. 4 Two-dimensional cut: packing (left) and tomography (right); Al is seen in black.

We will assume, moreover, that particle diameters are not affected during the propellant manufacturing process.

Figure 2 shows a packing that models the test propellant. The RVE is a cube of size $2 \times 2 \times 2$ mm^3. It consists of 750 coarse AP particles (dark gray), 119,000 Al particles (light gray), and roughly 2,700,000 fine AP particles, for a total compacity of about 0.73. However, for the sake of visibility, fine AP was removed in Fig. 2.

III. X-Ray Microtomography

A fully three-dimensional characterization of propellant microstructure morphology is obtained using an x-ray microtomograph (SkyScan 1072) available at SNPE Matériaux Energétiques. This technique consists of illuminating the propellant sample by a beam of x rays that are partially absorbed by the sample (see Fig. 3). This results in an absorption image, and from a series of images collected as the sample is rotated, a three-dimensional image is reconstructed. This method is particularly appealing due to its genuine 3D and nonintrusive character.

The image is then processed (through software Aphelion 3.2) especially to set the boundaries between binder and filler. Thresholding based on grayscale values easily separates AP, Al, and interstitial HTPB, due to different x-ray absorption. Finally, the image is corrected from edge effects by removing particles close to boundaries.

The propellant sample is typically a cylindrical core 5 mm high and 1 mm in diameter. Data were taken at a resolution of 1.8 μm/pixel. Hence, the smallest features resolvable are about a few pixels, or approximately 5 μm. A cutoff diameter of 5 μm is then imposed in any data processing so that grains too small are discarded. This prevents large quantification errors for the finest grains. Inherently, grains with a size smaller than the resolution will remain unresolved, being blended in the binder. On the other hand, reducing the sample size to improve the resolution would lead to a nonrepresentative structure, due to too low (or eventually zero) coarse AP fraction.

As an exception, the picture in Fig. 4 was taken on a slightly larger sample (diameter of 2 mm and resolution of $\sim$5 μm).

In the propellant sample tested, roughly 3300 aluminum particles were detected and considered for forthcoming statistics.

IV. Comparison and Discussion

A. First-Order Statistics

Figure 4 shows a 2D cut (arbitrary Z plane) for simulated packing and tomography. Tomography easily reveals coarse AP and aluminum particles (in black). Fine AP is not visible due to low size and is actually blended in the binder. Simulated packing and tomography qualitatively agree; in particular, it is seen that AP and Al are globally spherical and also that aluminum particles cluster between coarse AP particles. Note that in the packing, the fine AP is displayed this time.

The almost spherical shapes are typical of unground AP and coarse aluminum; however, the use of sphere packs probably becomes questionable for fine aluminum or ground AP.

Three-dimensional reconstruction via tomography data processing leads to a great amount of results. In particular, a good validation of the quality of the tomography data is by checking particle size distribution with initial known distribution. Figure 5 shows aluminum particle diameter distribution obtained both on packing and tomography. For reasons previously addressed, it is chosen to discard any particle for which the diameter is too low compared with

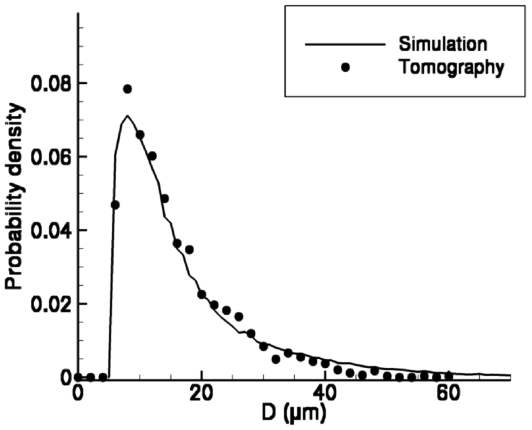

Fig. 5 Probability density for Al diameter.

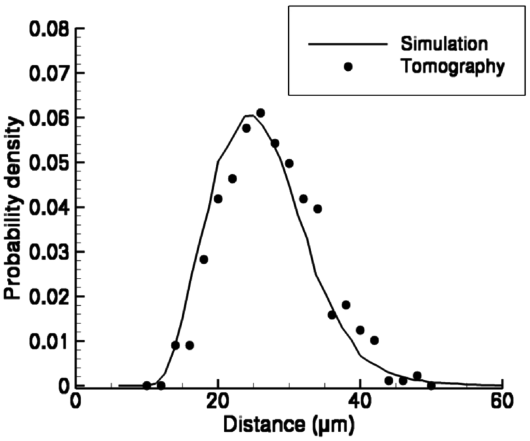

Fig. 6 Nearest-neighbor distribution for Al particles.

the resolution (1.8 μm), and a cutoff diameter of 5 μm is set. This cutoff value is also imposed for packing data processing to allow for comparison. This obviously explains zero probability density for $D < 5$ μm, noted in Fig. 5.

Evidently, results for packing reflects the real distribution because it was created with a log-normal law closely fitted to experimental Al initial distribution measured by granulometry (cf. Fig. 1). The fact that tomography results correlate fairly well with the packing data (and hence the actual data) means that this technique is able to correctly describe particle geometry at this resolution. Arithmetic mean diameter $D_{1,0}$ is computed to be 17 and 15 μm, respectively, for packing and tomography. As for $D_{4,3}$ diameters, tomography data give 35 μm, whereas a value of about 44 μm is expected from statistical distribution.

Aluminum volume fraction for tomography data is estimated to be 0.09, although a value of 0.115 is anticipated based on theoretical composition formulation. Those differences are due to the discarded part of particles (less than 5 μm) and also to data processing itself when separating Al particles from the surrounding binder (clipping effect). However, it is thought that clipping has the major effect, because it is deduced from size distribution (see Fig. 1) that Al particles smaller than 5 μm represent, at most, 1% of the total aluminum mass. Clipping may also explain the slight differences noted in diameters.

B. Second-Order Statistics

Volume fraction or particle size distribution are global first-order statistical data, but they cannot reveal the spatial pattern of the microstructure. As pointed out by Torquato [6], two microstructures with the same volume fraction and particle size may have dramatically different macroscopic properties. So-called second-order statistical properties are used in stochastic geometry to partially characterize the arrangement of the structure.

Let us now assume aluminum particle centers (obtained via packing or tomography) as a homogeneous and isotropic spatial point process. A first statistical descriptor is the nearest-neighbor distribution $G(r)$, which is the distribution of the distance from one typical point to the nearest other point. This gives information on local interactions that can be of great importance. As an example, the recent aluminum agglomeration model proposed by Jackson et al. [7] completely relies on these data.

Figure 6 shows the distribution of $G(r)$ for actual and simulated propellants. The peak by 25–30 μm indicates the most probable distance between two neighboring aluminum particle centers. It seems encouraging to note that the packing is fairly able to reveal this microstructural feature. However, it is feared that it may depend on the packing algorithm. In that particular case, the simple RSA algorithm was used for aluminum.

Although $G(r)$ is useful for determining local interactions between particles, its "shortsightedness" may not unfold spatial arrangement at larger scales. For that purpose, a good estimator (among many others) is the so-called pair-correlation function [8]

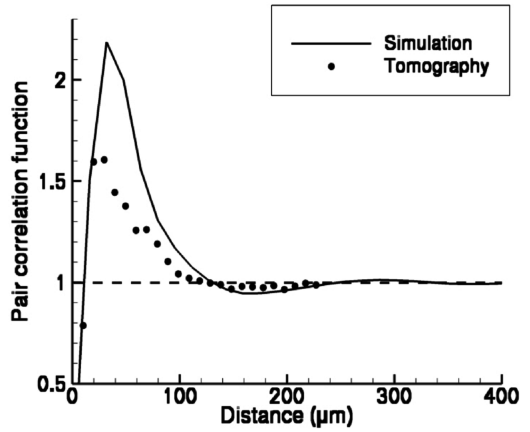

Fig. 7 Pair-correlation function for Al particles.

$g(r)$, which is related to the probability of finding one particle within a given distance from another particle. In particular, the shape of the $g(r)$ function provides useful information. For a homogeneous Poisson process (i.e., completely random), $g(r) = 1$ and values greater than one indicate aggregation.

Figure 7 shows the computed pair-correlation function for actual and simulated aluminum centers. The key feature is that they are globally coherent and exhibit several characteristic distances. Those characteristic distances are classically defined by local extrema of function $g(r)$ (see [8] for details).

The first distance is linked to the first maximum of g, globally around 30 μm: this peak is characteristic of the most frequent distance between neighboring points and roughly corresponds to the most probable nearest-neighbor distance (see Fig. 6).

For a small distance r (say, below 130 μm), values of g are greater than one, indicating that occurrences for those interpoint distances are frequent (that is, more frequent than for complete randomness). Such values greater than one thus mean that the pattern is locally aggregated, and in this case, this is obviously linked with clustering of Al particles between coarse AP, because they have to gather in the remaining space (see Fig. 4). Values of g lower than one (for r between 130 and 240 μm) are known to reveal an inhibition process, which basically means that there exists a regular pattern. A minimum of g is generally supposed to represent a typical length scale of the pattern, roughly 170 μm in the present case. Such a value is undoubtedly connected with an average coarse AP diameter, which is not surprising because we expect "bundles" of Al particles, each of them being separated by one coarse AP particle. As a conclusion, the shape of pair-correlation function g is coherent with a clustering of aluminum among coarse AP particles (commonly known as "pockets" [9]) and this is established for actual and simulated propellant.

V. Conclusions

The microstructure of a typical industrial AP/Al solid propellant was investigated by means of x-ray microtomography. Attention was especially focused on aluminum particle distribution because of its relevance for various applications (e.g., aluminum agglomeration, mechanics, propellant sensitivity, etc.). Data are experimentally obtained with a resolution down to 1.8 μm/pixel, which was shown sufficient for recovering initial diameter distribution for the aluminum used (mean-mass diameter of 40 μm). Processing tomography data also provides other statistical moments (e.g., volume fraction, nearest neighbor, etc.).

In parallel, a numerical simulation of the microstructure is obtained for the test propellant using classical packing algorithms. Special care is devoted to input data to stand as close as possible to actual propellant. Thus, all the particles are modeled (including fine AP) and exact distribution for grain diameter is used (by fitting optical granulometry data for initial ingredients).

The obtained packing showed surprisingly favorable correlation with experimental data for both first-order (i.e., global) statistics (volume fraction and aluminum diameter distribution) and also for second-order statistics: in particular, nearest neighbors and pair correlation. This ensures that the simulated packing properly models an actual propellant whether local interactions or large-scale structures are dealt with. Then simulated packings may be considered as a valuable tool when tackling detailed physics of composite propellants.

Acknowledgments

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