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# Apollonian emulsions

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## Abstract

We have discovered the existence of extremely polydisperse High Internal-Phase-Ratio Emulsions (HIPE) in which the internal-phase droplets, present at 95% volume fraction, remain spherical and organize themselves in the available space according to Apollonian packing rules. Such Apollonian emulsions are obtained from dispersing oil dropwise in water in the presence of very little surfactant, and allowing them to evolve at rest for a week. The packing structure of the droplets were confirmed through size distribution measurements that evolved spontaneously towards power laws with the known Apollonian exponents, as well as comparison of the structure factors of aged HIPEs measured by Small-Angle X-ray Scattering with that of a numerically simulated Random Apollonian Packing. Thanks to the perfect sphericity of the droplets, Apollonian emulsions were found to display Newtonian flow even at such extremely high volume fraction. We argue that these fascinating, space-filling assemblies of spherical droplets are a result of coalescence and fragmentation processes obeying simple geometrical rules of conserving total volume and sphericity. We argue that these peculiar, space-filling assemblies are a result of coalescence and fragmentation processes obeying simple geometrical rules of conserving total volume and minimizing the elastic energy associated with interactions of neighboring droplets.

## 1 Historical introduction

In the third century B.C., in Hellenistic Alexandria, lived Apollonius of Perga who wrote ten famous books on geometry[1]. In his book “*Επαφαι*” (“Tangencies”), the last and most challenging problem was the construction of circles that

would be tangent to three given circles in the Euclidean plane. All copies of this book are now lost, but the question survived as an intellectual challenge, thanks to Pappus of Alexandria who reviewed the problem 500 years later and named it “Apollonius’ circle problem” [2]. From there, it became enriched through centuries of discussions amongst mathematicians: Viète (1600) reconstructed the plausible Apollonius solution using clues from ancient literature [3]; Descartes (1643) introduced the premise of three mutually tangent circles at the initial stage [4]; Leibniz (1706) [5] envisioned packing the plane with an infinity of non-overlapping circles [8, 7, 6]; Kasner et al. (1943) proved Leibniz conjecture, and Mandelbrot (1977) established the fractal nature of such a packing [9]. In parallel, Apollonius’ circle problem was extended to the three-dimensional space, with Soddy (1937) introducing close-packing in the context of an “infinitely infinite number of spheres that theoretically can be packed into [a hollow sphere]” [10]. About real applications of this problem to our world, Newton (1687) recognized its equivalence with triangulating a position from the differences of its distance with respect to three known points, giving us the ubiquitous Global Positioning System [11]. Medical imaging [12, 13] and pharmacology [14] have similarly benefited from Apollonius, both in experiment and simulation work. This non-exhaustive list demonstrates the problems timelessness and how it has occupied some of the most brilliant minds through the ages.

## 2 Outline of the present contribution

We consider here the three-dimensional variant of the Apollonian packing problem: by repeating the procedure ad infinitum, one could generate an infinite number of increasingly smaller non-overlapping spheres that would completely fill the spaces between the original ones. The final attainable volume fraction is thus 100%, contrarily to the case of monodisperse spheres where it is 74%. Since each constructed sphere must be selected precisely for its diameter, a constraint is set on the diameters of particles that will be used to fill the voids. If the original spheres are non-identical, the constructed spheres must possess a continuous power-law distribution of diameters [15]. The exponent of this power law is  $-(d_f + 1)$ , where  $d_f$  is the fractal dimension of the union of all sphere surfaces in the dense packing [6]. Advancements in numerical simulations have enabled accurate determination of the Apollonian packing exponent,  $d_f$ , usually found to be  $\simeq 2.47$  [16, 17, 18].

Consequently, this recursive packing protocol should be useful for assembling spherical particles into materials with infinitely small porosity. However, the practical use of this protocol in material manufacturing is severely limited, due to the necessity of mixing discrete populations of spherical particles and hoping that each particle would manage to find its preferred place in the network. Given that small grains (colloidal particles or emulsion droplets) have a tendency to segregate during processing [20], it seems highly unlikely that the desired self-positioning can occur on its own. It would obviously be much more attractive and convenient if we could generate materials which spontaneously evolved the

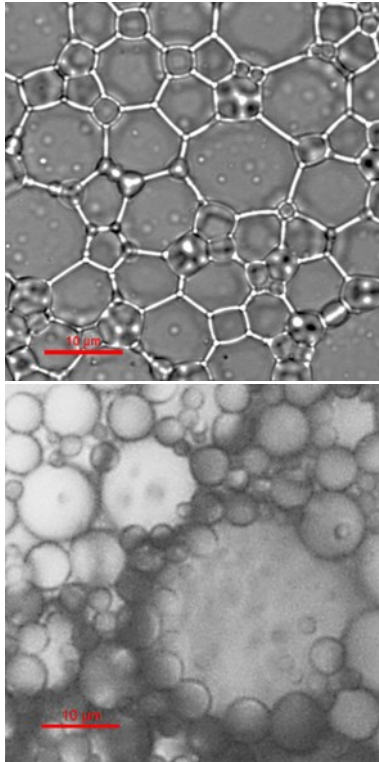


Figure 1: Optical microscope photo of oil-in-water HIPEs at  $\phi = 95\%$ . (top) surfactant-rich HIPE containing 20%wt non-ionic surfactant in the continuous phase. The droplets are distorted into polyhedral shapes. (bottom) surfactant-poor HIPE made with only 0.6% non-ionic surfactant in the continuous phase. The droplets remain perfectly spherical, with an extremely broad size distribution.

necessary size distributions and local placements.

Here, we report a first step towards this goal, namely: the fabrication of emulsions that evolve spontaneously to become materials with a random Apollonian packing structure.

### 3 The recipe for an Apollonian emulsion

We make these Apollonian emulsions by dispersing oil dropwise under constant stirring in an aqueous surfactant solution, much like making a mayonnaise. When oil volume fraction  $\phi$  exceeds the close-packing limit of spheres (64% for random[21] or 74% for ordered[21]), the emulsion is called a “High Internal-Phase-ratio Emulsion” (HIPE)[22]. In order to obtain space-filling structures, we continue the addition of oil until its volume fraction as the internal phase,

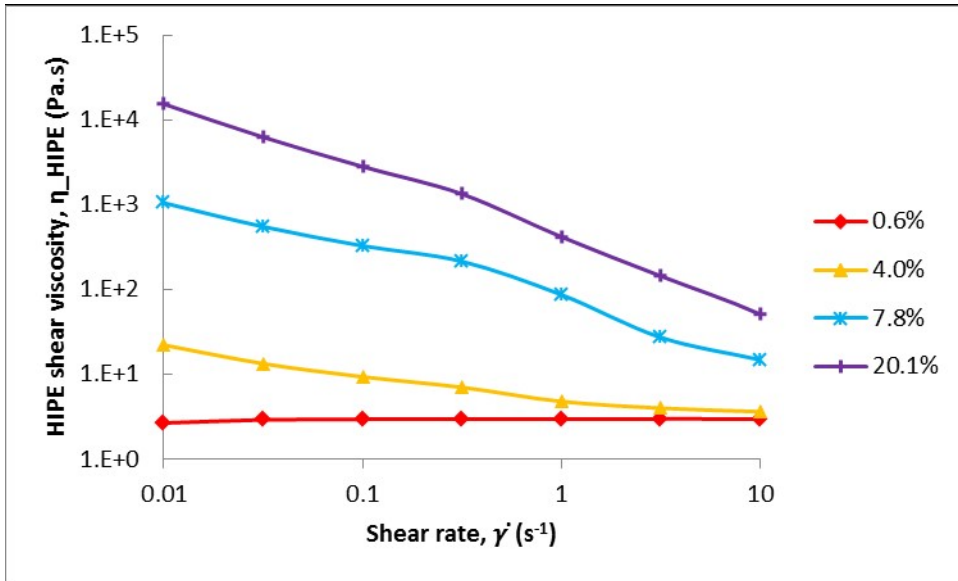


Figure 2: Flow curves of HIPEs with different amounts of surfactant in the continuous phase. The Apollonian HIPE containing 0.6% non-ionic surfactant in the continuous phase displays Newtonian flow behavior, as evidenced by the flat slope of the flow curve (red diamonds). As surfactant concentration increases, shear-thinning flow behavior is observed, which manifests as a negative slope. This is due to the progressive formation of faceted surfaces between the distorted droplets.

$\phi$ , is extremely high (95% – 99%).

The behaviors of a HIPE, like those of any emulsion, are determined by the properties of the surfactant monolayers that are available to keep oil droplets separated. In a surfactant-rich HIPE (typically 7 – 30%wt surfactant in the continuous phase for non-ionic surfactants), strong monolayers (or multilayers) keep oil droplets separated as soon as emulsification is completed. Consequently, high  $\phi$  can only be accommodated by deforming the oil droplets into polyhedral volumes separated by flat surfactant films[23, 28, 25] (Fig.1, top). The system then behaves like an elastic solid that withstands external stress by storing energy through further film distortion[26, 27]. Such surfactant-rich HIPE have been extensively studied, and the shapes of the polyhedral droplets have been determined. However, we took a seemingly unexplored path by severely reducing surfactant availability to only 0.6% in the continuous phase (water). We found that in surfactant-poor HIPEs, high  $\phi$  is accommodated by an Apollonian packing of extremely polydisperse droplets: indeed, spaces between large droplets are filled at all scales by smaller ones (Fig.1, bottom), indicating that the droplets are packed to minimize elastic energy preferentially.

## 4 Rheology of an Apollonian emulsion

Contrary to surfactant-rich HIPEs which exhibit plastic shear-thinning deformation beyond their yield stress[27, 28, 29], surfactant-poor HIPEs flow like Newtonian fluids (viscosity independent of shear rate, see Fig.2). Newtonian behaviour has never been documented in emulsions beyond  $\phi = 60\%$ [30, 31], making it all the more surprising that a HIPE at 95% displayed such behaviour.

## 5 Droplet size-distribution in Apollonian emulsion

Besides visual observation, another indication that our surfactant-poor HIPEs are Apollonian comes from measuring their droplet-size distributions through Dynamic Light Scattering. At short times, their number-weighted diameter distributions could be characterized by power-law decays, with exponents ranging between  $-3$  and  $-3.5$ . With time (about a week), these exponents consistently converged towards and remained between  $-3.48$  and  $-3.50$  regardless of the initial conditions. This range of values corresponds to  $d_f = 2.48 - 2.50$ , in good agreement with reported Apollonian  $d_f$ .

## 6 Structure factor of Apollonian emulsion

Finally, we measured the average correlation of oil droplet positions, using Small Angle X-ray Scattering. This average correlation was characterized by an experimental structure factor,  $S(q)$ , which is the ratio of the intensity  $I(q)$  scattered by the HIPE, to the intensity  $P(q)$  scattered by the same droplets in a diluted HIPE (dilution ratio 1/40)[32].

Structures factor,  $S(q)$ , of our surfactant-poor HIPEs are presented in Fig.4. Compared with the  $S(q)$  reported in the literature for nearly monodisperse colloidal systems, which have strong short-range order (main peak height  $S_{max} \simeq 2 - 3$ , and continue to oscillate at higher  $q$  values, they are strikingly different: in our HIPEs, the main peak had collapsed to  $S_{max} = 1.1$ , implying almost complete positional disorder among neighboring droplets.

We also compared the average structure factor  $\langle S(q) \rangle$  from these HIPEs with that of numerically simulated spheres packed at similar volume fraction according to a 3D Osculatory Random Apollonian Packing (ORAP) algorithm[33]. A 3D ORAP is built by sequentially adding the largest sphere compatible with the remaining voids, with the condition of gentle tangency with neighbouring spheres delimiting the void. An example of an ORAP system is shown in Fig.5. The excellent agreement between the experimental and numerical structure factors indicates convincingly that the droplets in surfactant-poor HIPEs are indeed organized like a Random Apollonian Packing.

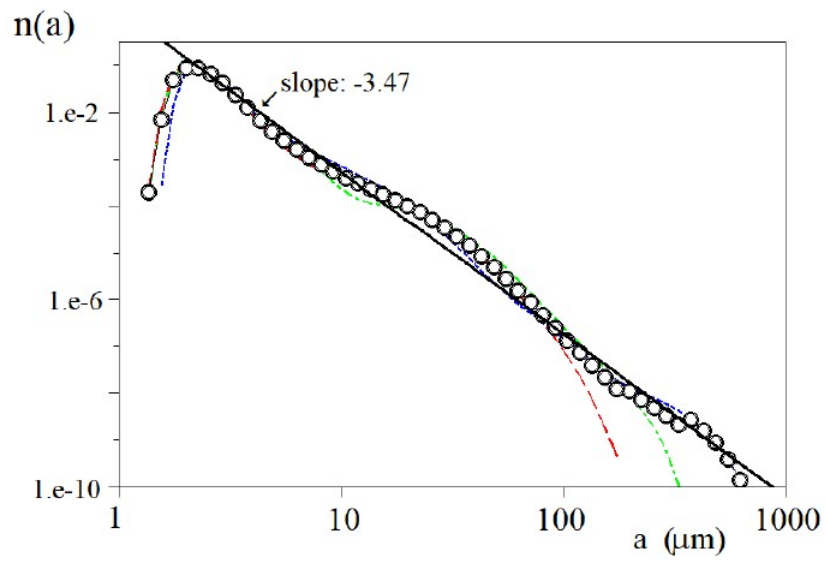


Figure 3: Droplet-diameter distribution of three surfactant-poor HIPES at  $\phi = 95\%$ , made at 200 rpm (blue dotted line), 500 rpm (green dot-dashed line) and 1000 rpm (red dashed line) measured by Dynamic Light Scattering. The open circles represent the averaged values of the three samples. The solid line representing a theoretical slope of  $-3.47$  (corresponding to the fractal dimension  $d_f = 2.47$ ) is drawn as a guide.

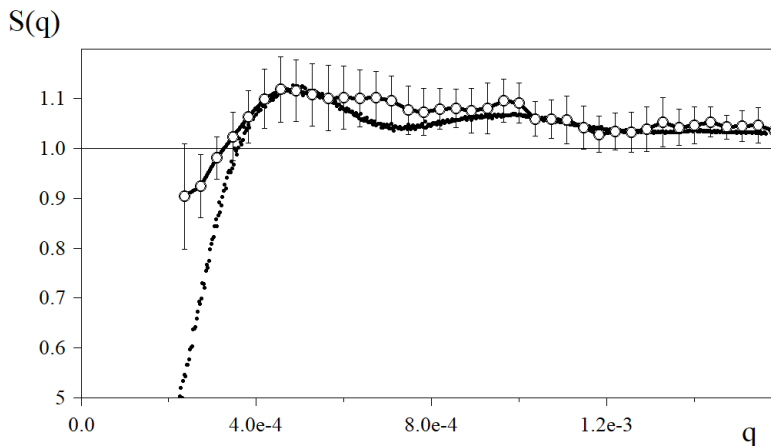


Figure 4: Averaged structure factor over three independent experimental surfactant-poor HIPEs,  $\phi \simeq 95\%$ , measured by SAXS (data are shown as circles ; the error bars are the standard-deviations for each value of  $q$ ). The black dots are the calculated  $S(q)$  of a numerical simulation of a 3D Osculatory Random Apollonian Packing system at the same volume fraction (part of the system is shown for illustration on the Fig.5).

## 7 How is an Apollonian emulsion formed from a surfactant-poor HIPE?

Generally, the processes that occur during emulsion aging at rest are the fusion of droplets (coalescence), their fission (fragmentation), and the exchange of oil molecules between neighbours in contact[34]. In a common dilute emulsion, these processes take place spontaneously if they minimize the total free energy, of which the main contribution is the Helfrich curvature free energy integrated over the interface area of each droplet; coalescence and ripening contribute to the reduction of total interfacial area and lead eventually to macroscopic separation of oil and water. In a surfactant-poor HIPE, however, the main contribution to the total free energy is rather the elastic interaction energy in this overcrowded network. We have found two pieces of evidence that demonstrate this claim – firstly, all the droplets in a surfactant-poor HIPE are spherical in shape (Fig.1); secondly, we found an increase in the total interfacial area as the HIPE aged at rest, a direct inference from the asymptotic Porod’s limit of the HIPE’s measured SAXS intensity (Fig.6 bottom).

This increase is indicative of the creation of small droplets as the HIPE evolves. Accordingly, we argue that the processes causing two droplets to recombine in a surfactant-poor, highly crowded HIPE result in the formation of many spherical droplets, some larger, some smaller than the parent droplets. Repetitive evolution according to this coalescence-fragmentation mechanism then pro-



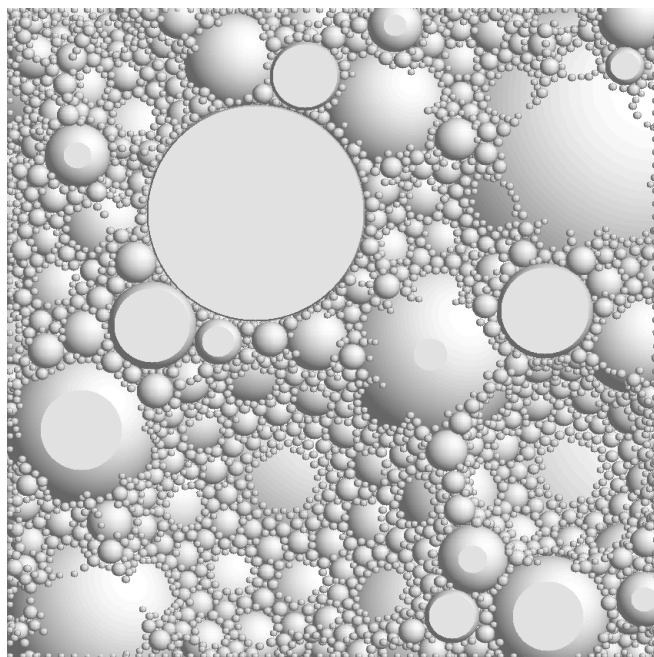


Figure 5: Cut through a simulated ORAP system of 30,000 spheres, at  $\phi = 92\%$ . The structure factor  $S(q)$  shown as the solid curve on the Fig.4 was obtained from this system.

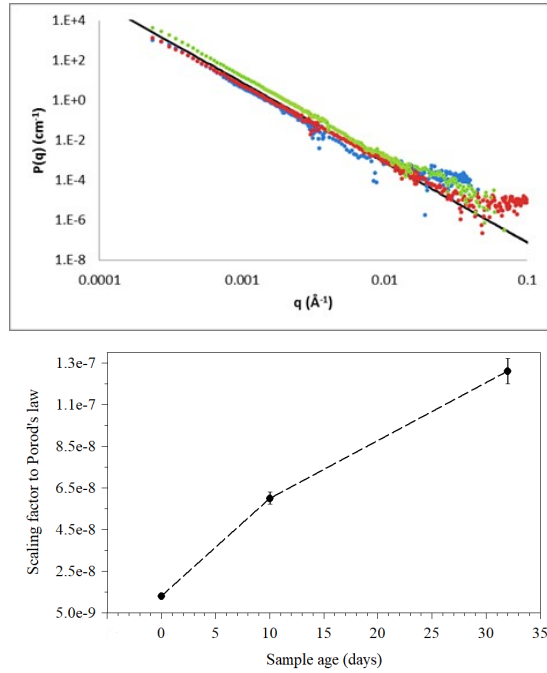


Figure 6: (top)  $P(q)$  of surfactant-poor HIPEs measured by SAXS at different ages: freshly made (blue), 1-week-old (red), 1 month-old (green). The solid black line represents Porod's law; (bottom) the scaling factor, found by fitting the experimental data to Porod's law, is directly proportional to the total surface area of the matter scattering the X rays. The major part of the error bars comes from background subtraction. The dashed line is a guide for eyes. This plot evidences the regular increase of the total surface area of a same system over a month of time.

duces an Apollonian structure as the smaller spherical droplets created occupy cavities in the vicinity of the coalescence event, minimizing the free energy of the HIPE by matching exactly the size of the of the cavity (condition of gentle tagency). We may then conclude that the main driving force of surfactant-poor HIPEs evolving towards an Apollonian state is the minimization of elastic energy in these crowded structures by preserving sphericity. This mechanism differs from droplet coalescence in dilute emulsions where the process is not spatially constrained, allowing for a change in droplet shape and concluding with a reduction in surface area and the subsequent expulsion of excess surfactant.

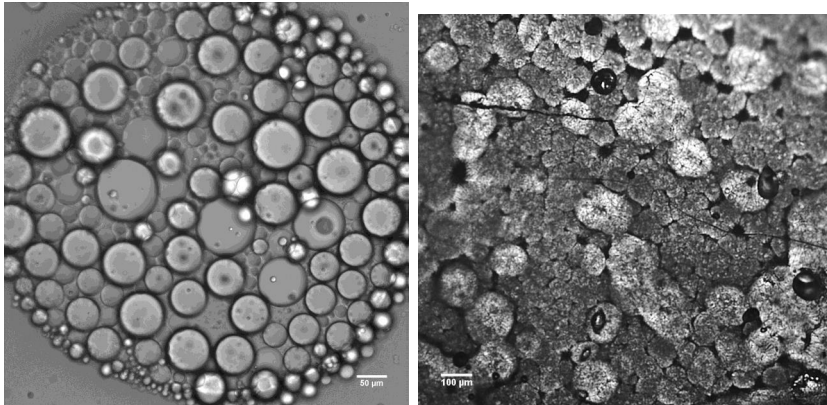


Figure 7: (left) an Apollonian emulsion at  $\phi = 92\%$  made from a polymer-solvent mixture as the internal phase, and 0.02% ionic surfactant as the continuous phase ; (right) as the solvent evaporated, the polymer solidified, preserving the space-filling Apollonian structure in the solid material obtained.

## 8 Possible extensions of the study

We made a cursory attempt to exploit the space-filling property of Apollonian emulsions by fabricating a solid material with little porosity and composed entirely with spheres. We used a polymer-solvent mixture of polycaprolactone and dichloromethane as the internal phase, and 0.02% ionic surfactant solution as the continuous phase. Applying our dropwise emulsification protocol, we attained  $\phi = 92\%$  and found an Apollonian packing of spherical liquid droplets (Fig.7, top). As the solvent evaporated, the polymer began to solidify[35]. We could therefore preserve the spherical geometry. However, non-uniform solvent evaporation from each Apollonian emulsion droplet resulted in somewhat imperfect sphericity in the final solidified material (Fig.7, bottom). Nonetheless, this demonstrates the first steps towards the use of Apollonian emulsions for optimal fabrication of extremely porous or extremely dense solid materials.

It is worth noting that solidification of the aqueous phase of an Apollonian emulsion would lead to an extremely porous material in the form of a solid structure of definite fractal dimension,  $d_f \simeq 2.47$ .

## 9 Conclusion

We have found a reproducible way to materialize an Apollonian packing of spheres by exploring surfactant-poor High Internal-Phase-Ratio Emulsions. It has remarkably taken over 2000 years since Apollonius of Perga defined the problem to discover a simple practicable condition that leads to such a fascinating structure in the real world. Our experimental observations show that droplets in such emulsions are spherical despite the very high internal-phase

volume fraction, and their size distributions follow a power law consistent with the Apollonian fractal dimension. The droplets in these special HIPEs yield structure factors matching that of a numerically simulated Osculatory Random Apollonian Packing. Such a kind of droplet organization has resulted in macroscopic behaviors differing from typical emulsions, for example, Newtonian flow, and the propensity to fill in the inner voids with tiny spherical droplets in spite of on-going coalescence.

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