

Response to the Anonymous Referee #2, 25 Apr 2022 ('Comment on egusphere-2022-27')

The author proposes that a single mechanism is responsible for most sea spray aerosol, ranging from 5 nm to about 0.5 mm and due to bursting bubbles from 10µm through the jet drop process. I consider that this paper is of interest to the community as it presents a new vision of the problem. However, I have several comments that I believe need to be addressed before the paper can be published. It is also worth mentioning that the paper is relatively hard to read and follow.

I think the author needs to be clearer on what has been proven by experimental data at this point and which part of its theory remains hypothetical. This is not necessarily a problem but it needs to be made very clear that several statements are not backed up by data at this point (as far as I understand). If I followed correctly, the discussion on rarefaction remains highly hypothetical since no experimental data can back the claims from the author. I remain particularly impressed by the 2017's paper from the author on jet drop, but that theory was backed by many data. I am also unclear why the author did not consider any of the dry particles measurements by bursting from many other authors (e.g. Forestieri et al, Salter et al, Prather et al; Frossard et al, Sellegri et al etc). The literature is huge and I understand it is hard to keep track but it seems that the choice of data set might be at least discussed, so that the reader can understand why certain data are used and not others.

The issue of rarefaction is supported by just a series of numerical results, but they are sufficient to raise a central question on the collapse of the cavity at the bottom when no material (gas molecules) or just a few molecules are trapped in the collapsing final volume. According to the works of Eggers and coworkers on this subject, the collapsing cavity at its minimum acquires an increasing velocity that diverges as the cavity radius vanishes. Our results indicate that the collapsing geometry tends to a convergent funnel that opens at its narrower end engulfing a volume that decreases as the gas density decreases. For a vanishing density, that volume vanishes and the convergent funnel simply gets closed at its minimum cross section. In this case, at the point of collapse, the total momentum of the radially collapsing liquid gets entirely directed towards the outer side of the cavity with an enormous energy per unit volume. This would be compatible with the ejection of a very large number of high speed liquid molecule clusters and nanometric droplets.

On the other hand, I have included 7 additional data sets in the new version following the suggestions of the referee. In addition, the characteristics of each data set and their degree of verification of the theoretical distribution are discussed.

As a general point of discussion, I am not convinced that a single mechanism can explain all of the sea spray aerosols for two main reasons: a) there is plenty of chemical evidence of the importance of film drops, as it is expected to have more organic material in the film drops than the jet drops; and b) can the author clarify how the bubble population down to 10µm at the surface is justified? Again, this is not a show stopper but hypothesis and limitations should be discussed more openly.

I agree with the reviewer and this is why all mechanisms so far considered in the literature (jetting, film breakup and film flapping) have been incorporated in the general model. Please see figure 10 where the number of droplets supposedly produced by each mechanism as a function of the Laplace number is presented in a synthetic fashion. Moreover, for bubble sizes below 10 microns at the surface, the chemical composition of the resulting jet and film droplets would be indistinguishable.

Major comments:

1/ When discussing sizes, the author needs to specify if they mention the size at production, the size at 80% humidity or the dry aerosol size (all of which are being used in various parts of the literature). There are typically factor 2 to 4 variations for sea salt which make a big difference when arguing about "100nm" drops/particles. I do not recall jet drop data demonstrating 200nm drop size, as Brasz et al 2018 show a 1µm drop (which would be about 250 dry radius for a salt particle (so not a drop but a solid salt particle). This needs to be clarified throughout the text. Is the author talking about salt dry size? Liquid size? If considering salt, then field data suggest that particles below 10nm are essentially organic (see literature cited in the introduction).

The particle size measured under the conditions described in each publication has been carefully converted to droplet radius for each data set. I have considered the remaining humidity in the measured particle according to the method used (particle size drying above 100°C; particle size measured from 20% to 80% humidity, etc.). The water content of the particle is estimated based on an evaporative model with residues at the corresponding RH of the environment.

Besides, in Gañán-Calvo and López-Herrera 2021 (J. Fluid Mech. 929, A12) we report the ejection of droplets as small as 2 times the viscous-capillary length l_{μ} for $La=1000$ using numerical simulation. This corresponds to droplets with radii of 40 nm, or to 10 nm dry particle radius using seawater.

I propose that the ejected droplets can reach radii as small as 4 nm at the rarefied conditions in the bottom of the cavity collapse corresponding to $La=1000$ using seawater with air at atmospheric conditions, since the front radius of curvature of the ejected spout can reach sizes below 0.2 times l_{μ} (figure 2 in that work). Observe that the smallest experimentally reported particle radius is about 1.5 nm (O'Dowd et al 1997; Kremser et al 2021), corresponding to a 6 nm droplet radius. Based on these arguments, although obtaining direct evidence for the origin of these particles is impossible, the bubble jetting phenomenon is a well-justified candidate for pristine ocean aerosols in this range.

2/ Several papers have analyzed the composition of atmospheric aerosols. I am not a chemist but it seems that organic aerosol mostly originate from film drops (see recent work by Quinn, Prather, etc). How would the author reconcile its claim with the atmospheric chemistry literature? (some of it being cited in the manuscript). This is also related to my previous point as the link between organic aerosol and initial drop size is not obvious (at least to me).

As I commented previously, bubble sizes below 10 microns at the liquid surface would make the chemical composition of either their jet or film drops indistinguishable since both jet and film drops would drag liquid from the interfacial boundary layer whose thickness is larger than 10 microns (Hardy 1982). It is true that when the seawater surface relaxes (corresponding to the still conditions under which the composition has been measured with higher resolution), the chemical composition varies in scales as small as some nm from the surface (Hardy 1982, Fig. 4). However, as their rise time is too large, most of the bubbles of about 10 microns would only come out at the water surface if—and only if— they are turbulently drawn and forcedly exposed to the water surface via moving drops, liquid ligaments, films, etc. with scales in the millimetric and sub-millimetric range. Their surface conditions are obviously far from still and relaxed.

3/ Do we have observations of bursting bubbles of 10-1000 μ m at the surface of the ocean? Such small bubbles are observed down in the water column as they can be transported by turbulent processes. Simulations of bubble dynamics in upper ocean by JH. Liang and coauthors show significant transport of the small bubbles down in the mixed layer, leading to their full dissolution. There are discussions in papers on bubble gas exchange by Thorpe and Woolf which assume that bubbles below a certain size fully dissolve as their rise velocity would be too small to overcome turbulence fluctuations and those bubbles might never reach the surface. It seems that these questions deserve some discussion as they will be important to test the applicability of the proposed theory.

We usually reduce in our mind the average sea surface to a more or less planar surface. In reality, the dimension of the sea surface is not 2 at all: it is a fractal object whose actual surface value would stound us.

As I try to explain in my manuscript and noted in my previous response, large bubbles, dynamic voids, large films, ligaments of all scales, macroscopic drops of all scales... all those unsteady structures dynamically expose an immense volume of liquid to the air. These structures have a very special geometrical feature: the average distance from their bulk center to their surface is below the mm scale. On the other hand, micrometric sized bubbles are everywhere at the MBL since this is an air-supersaturated layer of water, and therefore they are especially present in surface drops, unsteady films, ligaments, etc. whose sizes are over one order of magnitude larger than the 5-30 micrometer bubbles producing the smallest jet droplets. Even unsteady films of large bubbles can be full of microbubbles.

In summary, those dynamic structures can very efficiently expose an immense number of microbubbles on their surface along their evolution, given that their hydrodynamic times are much larger than those of the collapse of the microbubbles. In this regard, it can not be ruled out that the experimental measurements of Jiang et al 2022 (PNAS) are completely contaminated with jetting droplets, which would make impossible to irrefutably attribute the mechanistic origin of their sub-micrometric measurements to either jet or film drops.

4/ I am not sure that the current literature “describes in great detail the chemical composition of ocean aerosols and their dependence on ambient (wind temperature)” There is a lot of uncertainties in the role of temperature, with some studies predicting an increase in ssa while other predict a decrease (see for example figure 1

in Forestieri et al 2018). Scatter in the role of wind spans two to three orders of magnitude (see review from deLeeuw et al 2011). This is a topic of intense scrutiny due to the difficulty of the field measurements.

I agree with the referee after assessing the statistical variability of data in the works mentioned. The complex and unclear influence of the temperature and the noise introduced by the wind variable is discussed in the revised manuscript under the correct view of the referee.

5/ When the author mentions “Two basic mechanisms are responsible of this droplet emission: bubble film breakup” (p Lhuissier and Villermaux (2012); Jiang et al. (2022)), “ I would encourage to cite previous work by Spiel, Blanchard, and others. The cited papers are not (by far) the first ones to describe film drops. The review of Lewis and Schwartz 2004 does an excellent job at summarizing the film drop evidence in the literature, in particular with respect to sub-micron aerosols. This part of the literature should not be overlooked as the Lhuissier and Villermaux (2012); Jiang et al. (2022) papers (while wonderful) present a specific vision of the problem (in the same way as the present paper presents the specific vision of the author). All of this is fine and part of the scientific process but the introduction should not focus on a specific subset of authors.

I take a careful note of the relevant suggestions of the referee in the revised version of my manuscript.

6/ The fitting and reanalysis done in figure 2 needs to be clarified. I would encourage the author to first show the dimensional data and then the rescaling as the rescaling is not obvious/common in the aerosol literature. I would also encourage to provide a plot of the mean diameter/radius of the drops as a function of the bubble, as it seems to emerge from that rescaling and is not presented in the original paper (I think). The measurements from Jiang et al 2022 are presented in dry size so the scaling factors used in the reanalysis need to be mentioned.

Figure 2 has been modified and the account of steps taken to reach to the plot previously given are now explained in more detail as suggested by the referee.

7/ The discussion on the rarefaction effect is rather unclear to me. I would encourage the author to explain this better. Figure 7 is used as proof of the rarefaction effect but if I understand correctly comes from simulations. Does the author have any experimental evidence of this effect? I see this as a major issue with the claims of the author. They propose a theory leading to very strong claims but have no data to back it up. I would be more clear on some of the hypothesis that remain to be tested.

The rarefaction effect is indeed one of the more controversial and consequently –should it be correct- more innovative of the proposals given in present work. For consistency, I repeat the arguments given above:

The issue of rarefaction is supported by just a series of numerical results, but in my opinion should be sufficient to raise a central question on the collapse of the cavity at the bottom when no material (gas molecules) or just a few molecules are trapped in the collapsing final volume. According to the works of Eggers and coworkers on cavity collapse, the collapsing cavity at its minimum acquires an increasing velocity that diverges as the cavity radius vanishes. Our results indicate that the collapsing geometry tends to a convergent funnel that opens at its narrower end engulfing a volume that decreases as the gas density decreases. For a vanishing density, the convergent funnel gets closed at its minimum cross section. In this case, at the point of collapse, the ejection becomes completely directed towards the outer side of the cavity with an enormous energy per unit volume. This would lead to a jet reaching molecular scales with speeds overcoming that of sound in seawater (see Gañán-Calvo & López-Herrera 2021, Fig. 2).

Other comments:

8/ In 2.1.; “rd<0.5” is that micron?

Yes, it is. Corrected.

9/ I do not understand the statement: “The super-micron size range is comprised by wet aerosols and its presence is fundamentally reduced to marine and coastal regions

Boyce (1954)“

I try to be more explicit by saying this:

“Due to their inertia and relatively short settling time, aerosols in the supermicron range originating in the ocean would only be measured in marine and coastal regions.”

10/ I do not understand the statement “From this study and entirely attributing the fitted pdfs to micron- and submicron film droplets, one would conclude that (i) the droplet generation by film flapping will be distributed according to a lognormal for the nondimensional variable $\eta = \chi dLa^{-1/5}$, which reflects a reasonable dependency on the bubble size, while (ii) the more “classical” film rim fragmentation Lhuissier and Villermaux (2012) would yield droplets distributed according to a generalized inverse Gaussian as (1) independently of La .”

I try to be more explicit by saying this:

“One may conclude that droplets generated below 2 microns in Jiang’s experiments would be distributed according to a lognormal for the nondimensional variable $\eta = \chi dLa^{-1/5}$, which reflects a reasonable dependency on the bubble size for Laplace numbers below $10^{4.5}$ (bubble sizes below 0.65 mm). In addition, for millimeter-sized bubbles and above, the resulting droplets from Jiang’s experiments would be distributed according to a generalized inverse Gaussian as (1) independently of La . Jiang et al propose that the former side of the spectrum should be attributed to the film flapping mechanism, while the latter would be a consequence of the more classical film rim fragmentation (Lhuissier and Villermaux 2012). Although the jetting cannot be excluded in general conditions at least as an additional mechanism, in this work we will not challenge this proposal. Instead, we will keep it as part of the entire spectrum of potential mechanisms for those still seawater conditions consistent with Jiang’s experiments, i.e. in the cases where there are no surface turbulent waters generating millimeter sized droplets, ligaments and spumes.”

Could the author be more explicit?

11/ The discussion on enrichment for very small bubbles seems interesting but I am not sure I am fully following. It also seems to contrast with some other papers. I would encourage the author to discuss this in more details and clarify its hypothesis compared to other work in the literature (see the work from W.C. Keene, P. Quinn, A. Frossard, K. Prather, etc).

I hope my previous responses already address this relevant question. Turbulent sea surface waters would be saturated, or even super-saturated (depending on the statistical distance to the liquid-air interface) with air, which would convert the millimetric sized droplets, ligaments and spumes ejected as perfect moving platforms for the bursting of bubbles with sizes around $La \sim 1000$.

12/ I am not sure that the first sentence of the abstract is accurate. It is true in remote marine environment but probably wrong as a general statement.

That sentence has been tamed in the more general framework now discussed.