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The Fizzling Foam of Champagne

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yeast glycoprotein

> *"On le mérite en cas de victoire, en cas de défaite on en a besoin",*
> *"In victory, you deserve Champagne, in defeat, you need it"*
> Napoléon Bonaparte

Champagne is definitely associated to Dom Pérignon (1639–1715) who elaborated the "method champenoise".[1] By blending three wines (Pinot Noir, Pinot Meunier, and Chardonnay) in a barrel, he obtained a flat "base wine" that he bottled with added sugar and yeast in tightly closed bottles for a second alcoholic fermentation to produce more alcohol and carbon dioxide. This step of the process, called "prise de mousse", lasts about six weeks and is responsible for the fizzling foam of champagne. The subsequent long ageing on lees (the deposits of dead or residual yeast that sediments out) gives the flavor and bouquet to the champagne. After disgorging expels the lees, the wine is white, limpid (clear), and sparkling, and it is a universal symbol for happiness and success, highly prized for the celebration of very special events.

Actually, the process of making champagne has benefited from technological innovations. The quality of the glass bottles increased almost accidentally when, after the shortage of wood in England owing to the construction of warships, coal replaced wood in the glass furnaces. The result improved the glass annealing and made the bottle's mechanical strength much greater. Pilgrims of Saint Jalmes'way brought back stoppers from Galicia, these were made from the bark of cork oaks, and closed the bottles tightly during the second fermentation and ageing on lees. These strong and tightly closed bottles could withstand the high pressure of carbon dioxide generated. Tellier invented the frigorific machine used for the lees disgorging step.

Since then, champagne makers have researched the agronomical, oenological, and biochemical aspects, vines, yeast strains, and malolactic fermentation, to name a few. However, for the demanding consumer, the fizzling foam and the bubbling are definitely the most important organoleptic properties of champagne, even more than the flavor. Generous just after pouring the wine into the flute, the foam should collapse in a few seconds until it remains as a raft of bubbles at the surface of the wine (Figure 1 a,b). Then a hole appears at the center of the raft, which quickly expands until it remains solely as a bubble collar at the periphery of the wine surface, fed by trains of bubbles nucleated at some spots of the inner surface of the glass. For full enjoyment, the bubbling should last as long as the conversation about the celebrated event.

In this context, the Moët & Chandon Company decided to investigate the foam and bubbling appearance, and asked physicists to address the following issues:

- How can the champagne foaming properties be investigated systematically?
- Why does champagne from a same bottle bubble nicely in one glass and not in another?
- Why does the foam appearance of champagne differ from those of beer, gaseous water, or soda?
- Of all the chemical compounds in champagne, which ones are foam active?
- What is the origin of the "gushing", the dramatic formation of foam that may occur as champagne is being bottled on bottle-lines?

To answer these questions, academic scientists have investigated champagne as just another foaming liquid by performing experiments on the surface properties, the films, and bubbles, and the foam. The ultimate purpose was to relate the information gained at different scales. Experiments were performed with champagnes, base wines, and model solutions mimicking the base wines.

The wine of Champagne is an acidic hydro-alcoholic solution that contains a few $\mathrm{g\,L^{-1}}$ of glycerol, tartaric and malic or lactic acids, and amino acids, and at less than $\mathrm{g\,L^{-1}}$ concentrations, mineral ions, organic compounds, and, for example, proteins, glycoproteins, polysaccharides, polyphenols and volatile aromatic substances. The pH value is typically 3.0–3.2 and the ionic strength 0.02 M. It is supersaturated with carbon dioxide, whose partial pressure in the bottleneck is 7 atm at 20 °C in thermodynamic equilibrium with its concentration in the wine according to an empirical Henry-like law $P_{\mathrm{CO_2}} = K[\mathrm{CO_2}]$ where K depends on the temperature, the sugar and ethanol concentrations in the wine.[3]

Upon uncorking and pouring the champagne into the flute, the $\mathrm{CO_2}$ pressure in the wine abruptly decreases to 1 atm, and to restore the thermodynamic equilibrium, the champagne degases. The generous initial foam is due mostly to the $\mathrm{CO_2}$ molecules in the bottleneck. Degassing of the wine

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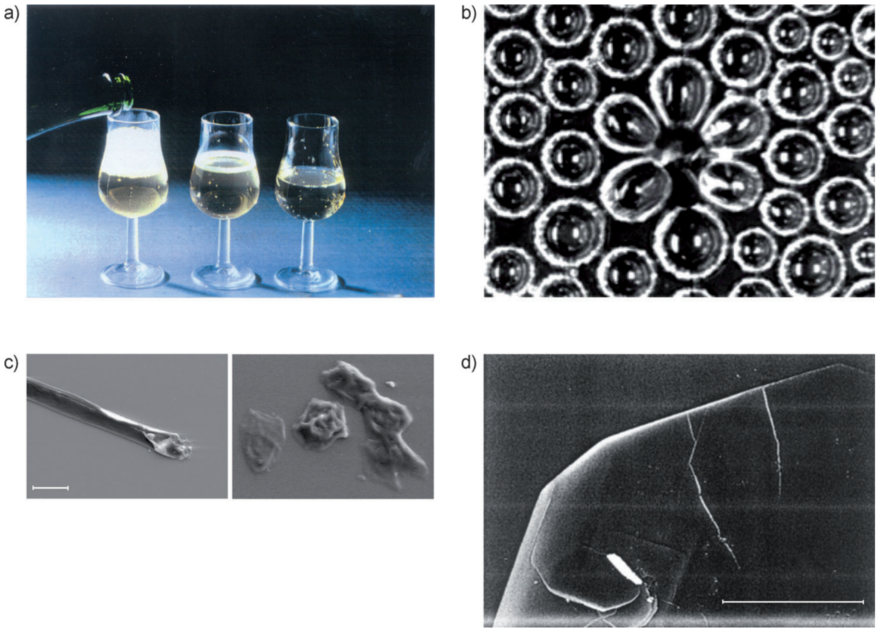

Figure 1. a) Filling of a flute (picture courtesy of Moët & Chandon). b) Upper view of a bubble raft showing a hole left by the bursting of a bubble.[2] c) TEM images of a fiber remaining attached at the inner surface after wiping the glass dry (left), and of a calcareous protuberance on a bottle wall, left by hard water (right). Scale bar: 20 μm. d) Cracks in a large crystal of calcium carbonate formed during bottle glass ageing. Scale bar: 20 μm.

occurs by diffusion of dissolved CO_2 molecules across the wine surface, while 20 % is due to bubbling.[4] Bubbling results from the nucleation of bubbles which have a radius larger than a critical value, which depends on the liquid surface tension and the gas supersaturation. Actually, champagne is only weakly supersaturated with CO_2 and neither homogeneous nor heterogeneous bubble nucleation occurs spontaneously; this would necessitate unrealistic supersaturation (1000 atm) to overcome the energy barrier.[5] A simple thermodynamic calculation shows that bubbles can only nucleate within the liquid at long and narrow pre-existing metastable gas cavities, with a radius of curvature larger than the nucleation value of 0.15 μm in champagne.[6] In 1996, Robillard and Lehuédé discovered that bubbling sites were either fibers or calcareous protuberances (Figure 1 c).[7] By chemical acidic cleaning in a dust-free laboratory white room, they very easily suppressed the bubbling. This explains why no bubbling is observed with some flutes, which presumably have molecularly smooth inner surface.

Two processes destabilize foams: 1) ripening, which occurs as smaller bubbles empty into larger neighboring ones, because of a larger capillary pressure (Laplace's law), 2) film rupturing, caused by a local excessive thinning and an insufficient quantity of adsorbed compounds to prevent it.

Ripening can be hindered by addition of a very small amount of insoluble gas. Silicone particles from lipstick and fatty particles from cream cakes are foam killers: they spread on the film surfaces and drag some adjacent film liquid with them, the film thins locally so that unbalanced attractive van der Waals intermolecular forces cause its rupture. Conversely, foam stability can be positively modified by surface-active macromolecules. Using a sparging method, Malvy et al.[8] measured foamability and foaminess, of mixtures of champagne and various proportions of its ultrafiltrate and ultraconcentrate, obtained by passing it through a molecular sieve (MWCO = 10 kDa). The more ultrafiltered wine in the mixture, the less surface-active compounds, and the lower the foaminess is and vice-versa. Moreover, Senée et al. also showed that the foam parameters of wines are vintage dependent.[9]

Some of the champagne compounds may show surface activity by themselves, for example, proteins, glycoproteins, and esters, or by association with other compounds (polysaccharides associated with proteins, for example). However, they are only present in small quantities, as demonstrated on a local scale by Liger-Belair et al. who measured the velocity of a bubble growing from the dissolved CO_2 molecules rising in glasses of champagne and in beer.[10] In champagne, the velocity follows a Hadamard–Rybczinski law, whereas it follows a Stokes law in beer. This result means that in champagne, the bubble behaves like a free bubble without adsorbed material; more exactly, the growth rate of the bubble surface is larger than the adsorption rate of the surface-active material on the bubble surface. Unlike the beer bubble, which behaves like a solid sphere, which indicates there are many adsorbed materials rigidifying the surface of the beer bubbles and enhancing the foam stability.

To analyze the action of the surface-active compounds, Senée et al. investigated by optical micro-interferometry the drainage of the film formed above a bubble attached to the surface of base wines in a container (Figure 2).[9] When the film thickness is about 100 nm, small aggregates appear progressively as small black spots in the film. The wine films continue to drain slowly but the mobility and growth aspects

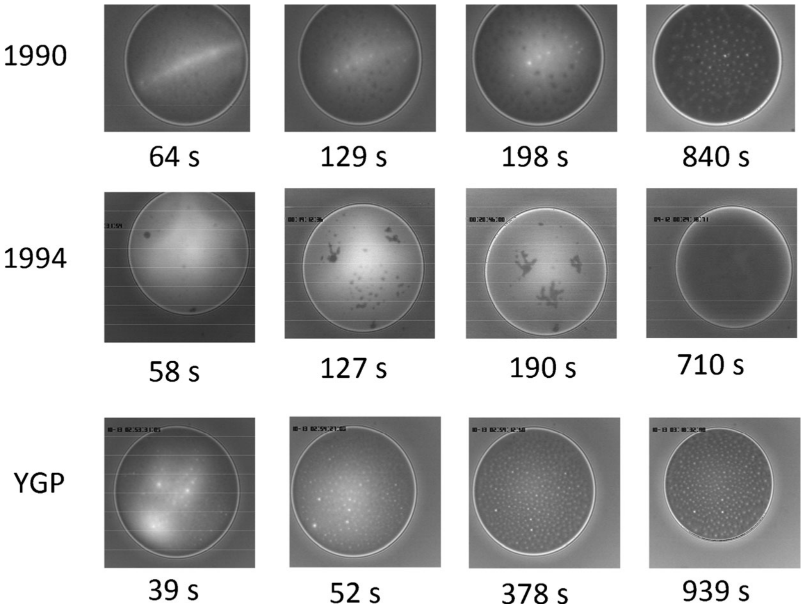

Figure 2. Top views of films formed from two base wines and a model yeast glycoprotein solution on top of a bubble attached to a wine surface (Experiments were performed in early 1996).

of the aggregates are drastically vintage dependent. With the 1990 base wine (Figure 2), the aggregates become organized in regular patterns, which gives a grainy aspect to the films. With the 1994 base wine, the aggregates move in the film forming dendritic patterns typical of the diffusion growth of bidimensional aggregates. In the closed container, the films do not rupture whereas similar films formed from simple hydro-alcoholic solutions rupture in less than 6 s. They rupture in 25 s and in 50 s for the 1990 and 1994 wines, respectively, if the container is open. The final film equilibrium thicknesses also change with the vintages, 16 nm for the 1990 wine and 35 nm for the 1994 one. Differences in the film equilibrium thickness are assigned to the different behavior of the aggregates in the film. It should be emphasized that no aggregates are present in the bulk liquids. Senée et al. repeated the experiments with model hydro-alcoholic solutions of yeast glycoproteins (YGP), which are the dominant macromolecules in the foam of champagne[11] with same alcohol content, pH value, and ionic strength as a typical base wine.[9] Remarkably, films from the model alcoholic solution of YGP at 3 $\mathrm{mg\,L^{-1}}$ concentration, drain like the 1990 wine, with aggregates organized in regular patterns. Their global foam parameters are also equal.

Now, surface tensions of base wines are only 2 $\mathrm{mN\,m^{-1}}$ lower than that of a hydro-alcoholic solution with the same alcohol content (ca. 48.5 $\mathrm{mN\,m^{-1}}$), which means that the wine values are due mainly to the alcohol. Interpretation of surface tensions of YGP solutions with and without alcohol strongly suggests that there is a competition between the ethanol molecules and YGP macromolecules in the adsorption process, with the alcohol hindering the YGP adsorption.

The origin of the aggregates could then be identified. It is unlikely that they are made of proteins. Proteins are highly denatured by ethanol, and particularly so at the protein isoelectric point when the ionic forces are weak. Ethanol acts primarily by weakening the hydrophobic bonds, and exposing the hydrophobic side chains to ethanol in the denatured state.[12] The protein adsorbability is significantly modified in the presence of ethanol. It is likely that proteins are precipitated in the bottle and are then expelled with the lees. The situation is very different for glycoproteins. YGP are essentially mixtures of mannoproteins and glucanes, the proportion of sugar is higher than 90 % and the molecular weight of each structure ranges from 40 kDa to more than 100 kDa. They are produced during the alcoholic fermentation and also by the autolysis of dead yeast cells as the champagne is aged on the lees.[13] The hydrophilic carbohydrates tend to protect proteinic moieties against denaturation by ethanol and to increase their solubility; the degree of the protection is, to a first approximation, a function of the number of hydroxy groups. Hence, it can be expected that the interactions between glycoproteins and the alcoholic solvent are intricately dependent on the quality and the sugar content of the glycoproteins, which changes with the vintage.

The aggregates are visible when the film thickness decreases to a value ranging between 50 nm and 100 nm. This value is comparable or smaller than the hydrodynamic diameter 120 nm of the YGP in the solution. A film is a confined system, which hinders Brownian motion in its reduced dimension, and which squeezes the polymeric sugar chains during its thinning. Solvent depletion and increase in the YGP volume concentration result. These processes occur as if the macromolecular concentration increases to a limiting value, corresponding to a supersaturation level where spontaneous precipitation occurs and flat-shaped microgels, with a diameter of approximately 6 μm and a thickness of approximately 15 nm, are formed. The presence of these microgels clearly prevents or slows down excessive thinning of the films, even when the container was open, which stabilizes the lifetime of the films and consequently of the bubble.

On bottling lines for magnum bottles, an excessive volume of foam larger than the 6–8 cm^3 volume of the bottleneck occasionally springs up from the bottom of the bottle. Just as for the bubbling in the flute, a pre-existing gas in a long and narrow cavity with low surface energy is necessary for bubble formation at the typical CO_2 saturation prevailing in champagnes. A few bubbles are unable to generate such a violent effect. Bottles are fabricated throughout whole year whereas they are only filled during a short period of the year. During storage, the bottle glass evolves and its inner surface attains a whitish color arising from the formation of crystals of sodium and calcium carbonates. Crystals of sodium carbonate are soluble in water whereas calcium carbonate crystals are only soluble in acidic solutions, such as champagne. Valant[14] observed that large crystals of calcium carbonate are cracked (Figure 1 d). The cracks can trap air bubbles with a 0.1 μm radius of curvature, which is smaller than the local critical radius of nucleation (0.5 μm). However, the dissolution of sodium carbonate and calcium carbonate close to the crack locally increases the CO_2 concentration, which locally increases the supersaturation and decreases the nucleation radius. The origin of gushing is thus to be found in chemically aided, non-classical heteronucleation.

The identification of the foam-active compounds in wine was a difficult task, mainly because wines are natural products whose resulting fine flavor and foam aspect depend upon many uncontrollable external factors, such as sunshine and precipitation during vine blossoming and ripening. Oenologists tend to hide these subtleties behind the "vintage" concept, and they only make taste assessments to appreciate wine quality. All base wines of champagne have essentially the same values of alcohol concentration, pH value, and ionic strength. The differences among the various vintages are related mostly to compounds existing in microscopic amounts, for example, organic volatile compounds, proteins and glycoproteins, and polyphenols. Their quality and concentration can vary significantly with the vintages. Laboratory experiments have already greatly enhanced the understanding of these differences by pointing out the role of the yeast glycoproteins, and explain why champagne foams can significantly change with the vintage.

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