

Why does the viscosity of mayonnaise increase when it is whipped energetically: a case for studying models linking volume fraction and viscosity of suspensions and emulsions

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Abstract

This supporting document is given in courses of food science and technology, when colloids are discussed. It is an introduction to the various models of viscosity that are often used for suspensions and emulsions such as mayonnaise sauce, focusing on the paradox of the increase in viscosity of the sauce when it is energetically whisked, but no oil is added, so that the volume fraction of emulsions does not change. Exercises are proposed, and references are provided to state-of-the-art articles regarding the various topics covered.

Keywords

colloidal systems, emulsions, models, viscosity, volume fraction.

This supporting document deals with models for calculating the viscosity of dispersed systems such as suspensions and emulsions, showing the limits of the various equations relating the proportions of the various phases of these systems and their viscosity.

It is for students at post graduate level following educational units in food science and technology, including molecular and physical gastronomy. They must have a bachelor's level knowledge of chemistry, physics, and mathematics. This includes, in particular, knowledge of the structure of proteins and lipids, and the basics of rheology. Elementary algebraic skills are required. The text is organized as explained in the Table of content (below), and it includes exercises (simple applications of the

discussed results rather than problems) that students are invited to make by themselves, as they are direct applications of the text given immediately before them.

Of course, in this introduction to rheological models, the state of the art is not given, but supplementary readings are proposed. The whole text is made in the context of exploring the phenomenon of viscosity increase in mayonnaise that is whisked vigorously without the addition of oil—and thus at a constant oil volume fraction.

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Table 1. IUPAC definitions for simple dispersed systems (IUPAC, 2025). Home-made mayonnaise sauces, whose largest oil droplets have diameters reaching 1 mm, do indeed fall under the IUPAC definition, because the distances between the droplets are of the order of magnitude described (this will be calculated later in this document).

Colloid:

A short synonym for colloidal system.

Colloidal system:

The term refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm , or that in a system discontinuities are found at distances of that order.

Emulsion:

A fluid colloidal system in which liquid droplets and/or liquid crystals are dispersed in a liquid. The droplets often exceed the usual limits for colloids in size. An emulsion is denoted by the symbol O/W if the continuous phase is an aqueous solution and by W/O if the continuous phase is an organic liquid (an 'oil'). More complicated emulsions such as O/W/O (i.e. oil droplets contained within aqueous droplets dispersed in a continuous oil phase) are also possible. Photographic emulsions, although colloidal systems, are not emulsions in the sense of this nomenclature.

Suspension:

A liquid in which solid particles are dispersed.

1. Learning objectives and assessment

Colloidal systems are ubiquitous in foods: they include gels (for example, jams, jellies, cooked eggs), suspensions (many sauces), foams (for example whipped egg whites) and emulsions (for example sauce mayonnaise) (Burke *et al.*, 2021). Their names are defined in the *Compendium of Chemical Terminology* of the International Union of Pure and Applied Chemistry (IUPAC, 2025), as shown in Table 1.

However, some physical and chemical systems whose properties are similar to those of the former systems have dimensions that do not correspond to colloids. For example, in some culinary dilute emulsions, the diameter of droplets often exceeds the usual limits for colloids in size and the distance between dispersed structures is larger than defined by IUPAC (1 nm – 1 mm) (IUPAC, 2006a). Such systems are rather “dispersed systems” (This vo Kientza, 2021a), and physicists speak of granular systems when gravity becomes important, acting on large solid structures.

In any case, both kinds of systems can include more than two phases, such as in whipped cream, in which there is a continuous water phase (phase 1) containing air bubbles (phase 2), as well as solid and liquid fat (phases 3 and 4), with proportions that depends on temperature (Bailey, 1950).

For all the dispersed systems, understanding how they are made and their properties calls for knowing:

- their physical structure at various scales (This vo Kientza, 2025),
- the chemical characteristics of the constituents that allow the preparation of the dispersed structures; in particular, “surfactants”, that is the compounds that reduce surface tension, play an important role;
- the main mechanisms by which the dispersed systems are formed (in qualitative and quantitative terms),
- the causes of their thermodynamic instability (in qualitative and quantitative terms).

In particular, one goal of food scientists and

technologists is to understand how the structure of dispersed systems, their key physical properties, including stability and rheological behaviour, are influenced by the overall ingredient composition and formulation conditions (Dickinson, 2015). This objective calls for an analysis of the interactions between the continuous phase (liquid) and the various dispersed entities, that is solid particles, liquid droplets, gas bubbles, dissolved macromolecules (including proteins and polysaccharides). One also need to understand how such interactions affects the behaviour of fluid phases, and which phenomena occur at solid-liquid interfaces. Viscosity is a key parameter for such studies.

Accordingly this supporting document discusses:

- algebraic or numerical equations relating viscosity to volume fraction (they are also called “models”),
- the importance of the interface.

Often in the text, students will be invited to calculate orders of magnitude using references that are given. Concerning these, they are not necessarily to be read: the course is self sufficient. But for good science and technology, any idea and any result is to be justified by a reference to the first authors who established the fact or introduced a new idea (Merton, 1942; Davidson *et al.*, 1997; Zigmond and Fischer, 2002; ICMJE, 2019). Moreover the students have to remember that any class does not end with the class itself; one is invited to study beyond it, and this is why some of the references given can guide them.

We wish to emphasize that this presentation is an introduction and does not reflect the state of the art. References to recent publications are provided at the end of several paragraphs.

After studying this supporting document, the students should be able to:

- express the viscosity of emulsions using the Einstein equation, the Taylor equation, the Kieger-Dougherty equation and the Yaron and Gal-Or equation,
- calculate the average distance between two

droplets of given diameter for an emulsion of given volume fraction,

- calculate the total area of droplets of given diameter in an emulsion of given volume fraction,
- calculate the viscosity of emulsions for which the viscosity of the dispersing (continuous) phase is given, in the limit of low volume fractions.

2. The question that will be studied

In this paragraph, we elaborate on the question that will be studied, considering a practical case of culinary preparation: making mayonnaise sauce. We describe a paradoxical phenomenon that occurs during this process.

Consider a dispersion of physical structures (solid particles, liquid droplets, gas bubbles) in a liquid. From a rheological point of view (the way the systems flow), this dispersed system is characterised to a first approximation by a set of parameters given below.

The first important parameter is the volume fraction ϕ of the dispersed phase, defined as the ratio between the total volume of dispersed phase (V_d), and the total volume of the emulsion (V):

$$\phi = \frac{V_d}{V}. \quad [1]$$

The volume fraction expresses how much the system is filled with the dispersed phase: it is certainly an important parameter, as this can be understood from obvious observations:

- a suspension which contains no solid particles (volume fraction equal to 0) flows as the liquid that it is (zero volume fraction, zero effect on viscosity);
- a suspension for which the volume fraction would be 1 would not flow at all, because it would be solid;
- for oil-in-water emulsions containing a large proportion ($> 90\%$) of oil, as droplets dispersed in an aqueous solution, the "resistance to flow" can be so high that a spoon stands in it (Lecocq, 1927);
- as well, a whipped egg white, that is a foam,

made mostly of air (in terms of volume, not masses), does not flow easily, and chefs consider it "firm" when a whole egg in its shell does not sink in it when it is deposited on the surface of the foam (personal communication).

[Exercise 1. If 100 g of an oil-in-water emulsion contains 75 g of oil, what is the volume fraction of oil.]

For characterizing the flow, the second important parameter is the viscosity of the continuous liquid phase. This can be understood, as, at the limit of no dispersed particles, the viscosity of the dispersed system is equal to the viscosity of the continuous liquid phase. We can therefore imagine a law of the viscosity η of the dispersion as the viscosity η_0 of the continuous liquid phase multiplied by a certain function of the volume fraction.

The "hardness" of the dispersed structures is also important: if air bubbles are dispersed in water, for example, the dispersion will flow more easily than if solid particles are dispersed, as the bubble can deform easily.

Finally the size distribution of the dispersed structures, as well as their shapes, contribute to the viscosity of the dispersed system: if the dispersion is sheared, the liquid will flow differently around spherical or elongated structures.

As seen in Table 1, a colloidal system with a liquid continuous phase and liquid dispersed structures (droplets) is called an emulsion (IUPAC, 2006a). For example, the sauce called mayonnaise is one of the most popular of such food systems. It appeared at the beginning of the 19th century, under the name "magnonnaise" (Carême, 1801): the recipe involves dispersing oil in a mixture of egg yolk ($\sim 50\%$ water) and wine vinegar (more than 90% water) (USDA, 2026). Sometimes other definitions of the sauce are proposed (Culinaria Europe, 2015) allowing a wide variety of "optional ingredients", but they can be considered too lax, when the aim is protecting the consumers by mandating honest designations.

In the past, making this sauce was a very long process: a wooden spoon was to be used to rub the wall of the vessel for about 15 min (Carême, 1801). It was not known at that time, but the process divides the oil in droplets so small that they are visible to the naked eye. Today, using the right idea about the microstructure of this emulsion, less than 1 min is enough to make the sauce, using a simple fork for whisking (personal measurements).

Making the sauce, whatever the process, establishes that its viscosity increases when the proportion of oil (i.e., the volume fraction) increases. This phenomenon gives the opportunity to review here various “models” (this means: equations) used to describe the quantitative relationship between the viscosity of an emulsion and the volume fraction of the dispersed phase (Paragraph 3).

However, whatever the model chosen, experimental practice shows surprisingly that the same emulsion, when whisked more vigorously, without any change in the volume fraction of the two phases, exhibit an increase in viscosity; this will be explored here as well.

Indeed a mayonnaise sauce made with a fork and about 60 % oil (1 egg yolk, about 5 g vinegar, oil) has a low viscosity, but it becomes whiter and very firm when energetically mixed with a hand blender (without any more oil added), or when it is sheared using a wooden spoon that is repetitively rubbed for about 15 minutes against the edge of the container.

The change is paradoxical because, according to the simplest models, the viscosity of the emulsion should not change, once the emulsion has been prepared, for a constant volume fraction of the dispersed phase (in this case, the oil). This paradox is explored here: we will examine the effect of oil droplet fragmentation on the total water/oil interfacial area.

3. The various models linking viscosity and volume fraction

Let us first examine how the viscosity of an

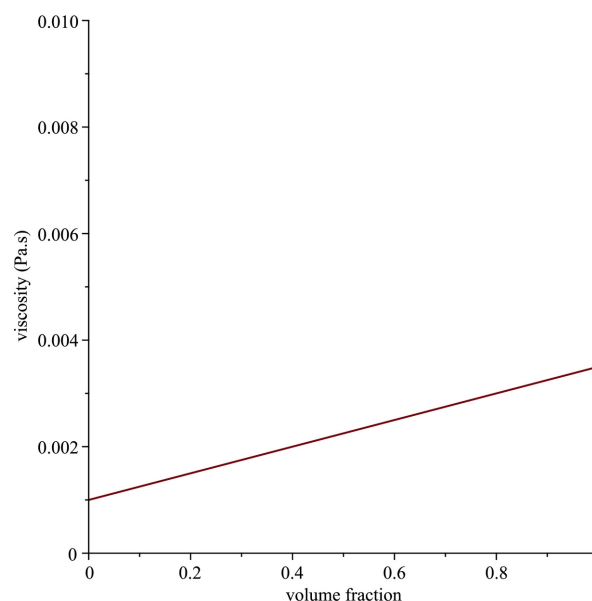


Figure 1. The Einstein equation, whose graphical representation is given here, describes the viscosity η of a dispersion as a function of the volume fraction ϕ of the dispersed phase. It was established for hard spherical spheres in the dilute regime. The fact that this model does not hold at high volume fraction is clearly shown in this picture: instead of describing an infinite viscosity when the volume fraction is high (the system is entirely solid, and it does not flow when the volume fraction of the dispersed phase is equal to 1), the equation predicts a finite value of the viscosity. In this picture, the viscosity value of the continuous phase is the one of water ($10^{-3} \text{ Pa} \cdot \text{s}$, or $1 \text{ mPa} \cdot \text{s}$).

emulsion depends on the volume fraction ϕ of the dispersed phase. Historically models were first developed for describing the dispersion of monodisperse solid spherical structures that do not interact with each other in a liquid (“hard spheres”). As said, in the limit case of a pure continuous liquid phase, that is a volume fraction ϕ equal to 0, the viscosity is of course the

viscosity of the liquid continuous phase of the emulsion:

$$\eta(\varphi)_{(\varphi=0)} = \eta_0. \quad [2]$$

Adding particles in the liquid, that is increasing the volume fraction φ of the dispersed phase, increases the viscosity of the emulsion, with an infinite value if the volume fraction of solid particles is equal to 1:

$$\lim_{\varphi \rightarrow 1} \eta(\varphi) = +\infty. \quad [3]$$

These two initial observations will help to interpret the various equations which were proposed for the viscosity of dispersions.

1. First of all, the Einstein equation expresses the viscosity η of a suspension of hard spheres in the dilute regime (Einstein, 1906; Hughes, 1949; This vo Kientza, 2022):

$$\eta = \eta_0 \left(1 + \frac{5}{2} \varphi \right), \quad [4]$$

where η_0 is the viscosity of the continuous liquid phase (dispersing medium) and φ is the volume fraction of the dispersed liquid phase (Figure 1).

Einstein derived this equation as a first-order expansion for the effective viscosity of a Stokes (viscous) fluid with a suspension of small rigid particles at low density (Einstein, 1905; 1906; 1956). His algebraic derivation relied on two important assumptions:

- (1) there is a scale separation between the size of the particles and the observation scale;
- (2) at first order, dilute particles do not interact with one another: this second assumption allowed Einstein to approximate this effective viscosity at low density by considering particles as being isolated.

In other words, the Einstein equation only applies to dispersions of hard spheres in the dilute regime (Bingham and Durham, 1922), that is suspensions rather than emulsions (IUPAC, 2006b). The volume fraction φ must be low, typically below 0.02 (Liu, 2019).

2. A similar equation can be found for deformable objects, such as oil droplets in emulsions. Taylor (1932) introduced it, based on the viscosity ratio

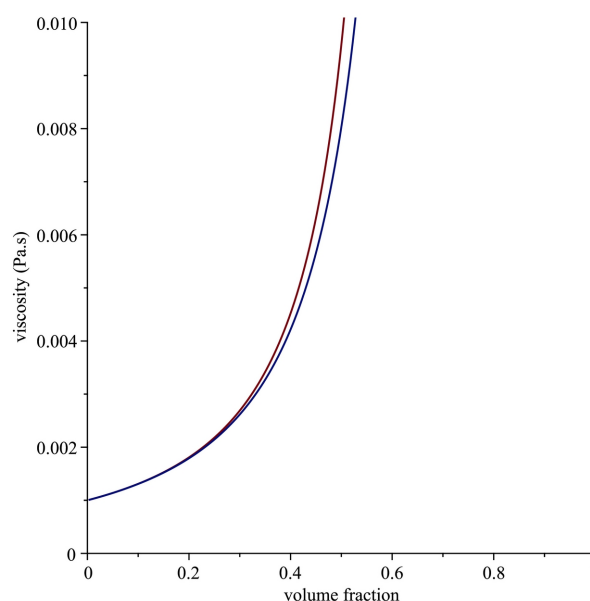


Figure 2. Graphical representation of the Krieger-Dougherty equations for two values (0.68 and 0.74) of the packing parameter.

$k = \frac{\eta_{dispersed}}{\eta_0}$ between the viscosity $\eta_{dispersed}$ of the dispersed liquid and the viscosity η_0 of the continuous phase:

$$\eta = \eta_0 \left(1 + \frac{5k+2}{2(k+1)} \varphi \right). \quad [5]$$

This equation only applies if the droplets are spherical, that is when the volume fraction of the dispersed phase is low ($\varphi \ll 1$), if the shear rate is low if any, and if droplet interactions are negligible (Kroy *et al.*, 1999; Pal, 2001). Again, the fact that the viscosity is a linear function of the volume fraction demonstrates that the equation cannot be right for higher volume fractions.

3. Other equations are phenomenological (that is: adjusted from experimental data) or obtained through digital simulations, such as the Maron-Pierce equation (Marion and Pierce, 1956), or the Krieger-Dougherty equation (Krieger and

$$\eta = \eta_0 \left(1 + 5.5 \varphi \left(\frac{4\lambda^7 + 10 - \left(\frac{84}{11}\right)\lambda^2 + \left(\frac{4}{k}\right)(1 - \lambda^7)}{10(1 - \lambda^{10}) - 25\lambda^3(1 - \lambda^4) + \left(\frac{10}{k}\right)(1 - \lambda^3)(1 - \lambda^7)} \right) \right) \quad [7]$$

$$\eta = \eta_0 \left(1 + \varphi \left(\frac{2((5\lambda + 2) - 5(\lambda - 1)\varphi^{\frac{7}{3}})}{4(\lambda + 1) - 5(5\lambda + 2)\varphi + 42\lambda\varphi^{\frac{5}{3}} - 5(5\lambda - 2)\varphi^{\frac{7}{3}} + 4(\lambda - 1)\varphi^{\frac{10}{3}}} \right) \right) \quad [8]$$

Figure 3. The equations proposed by Yaron and Gal-Or [7] and by Choi and Scholwater [8].

Dougherty, 1959), which is a more frequently used equation for fitting to experimental data. The latter still expresses the viscosity η of the emulsion as a function of the viscosity η_0 of the continuous phase and of the volume fraction φ of the dispersed liquid, but it also involves the fraction of packing φ_m at which the viscosity becomes infinite (or close packing).

Often, φ_m is taken to be equal to 0.74, corresponding to perfectly ordered packing (Aste and Weaire, 2000), or to 0.64 for disordered or random closed packing:

$$\eta = \eta_0 \left(1 - \frac{\varphi}{\varphi_m} \right)^{-2.5\varphi_m} \quad [6]$$

Because the viscosity rises exponentially while approaching the random close packing limit, the calculation is usually not performed at very high volume fractions (Figure 2).

Later, Krieger (1972) determined that the value $\varphi_m = 0.68$ and an exponent equal to 1.82 provided a good fit to his experimental data up to a volume fraction of 0.5 (Figure 2) (Kroy *et al.*, 1999; Chevalier, 2006; Lemaire, 2024).

4. Another empirical equation that is one of the most realistic for emulsions is the equation of Yaron and Gal-Or, shown in figure 3, for which k has the expression of the Taylor equation, and which uses the parameter $\lambda = \varphi^{0.333}$ (Abbott, 2023).

However this equation does not converge toward the Taylor one, for low volume fraction, and the equation by Choi and Scholwater has been preferred (Pal, 2021) (Figure 3).

Of these equations, only the Einstein equation and the Taylor generalization are theoretically derived from the physical laws of physics. To date, for semi-diluted or concentrated suspensions and emulsions, there are only phenomenological models able to fit and predict the link between the viscosity and the volume fraction of dispersed elements.

Further reading:

Ayar *et al.*, 2026.

Ptáček *et al.*, 2026.

4. Calculations for monodisperse emulsions

Armed with these models, we now want to explore how the theoretical viscosity varies as a function of the size of the dispersed structures. About this question, there seems to be a paradox, because this size does not appear explicitly in the equations given above. We will carry out the calculations very gradually, giving full details, and we will constantly look for validations. We consider the simplest case of monodisperse emulsions (all the droplets have the same radius).

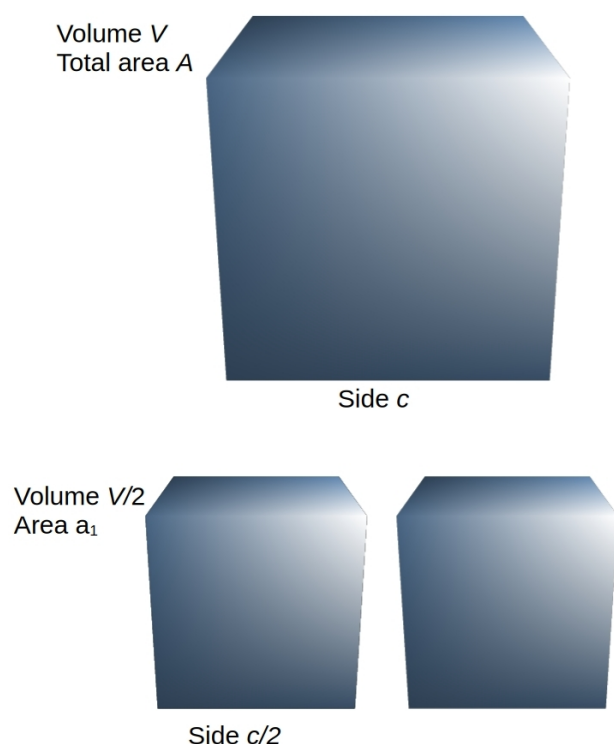


Figure 4. A cube of volume V (side c) is divided into two cubes of equal volumes. The total area increases from A to $2 a_1$.

4.1. Increasing the surface area

During the whipping of an already prepared oil-in-water (O/W) emulsion to which no more oil is added (This vo Kientza, 2021a), the volume of the dispersed phase and the volume fraction do not change, but the total area of the water-oil interface increases "considerably" during droplet splitting.

Here, "considerably" was put in quotation marks, because, in science, adjectives and adverbs must be, as much as possible, replaced by the answer to the question "How much?" (This vo Kientza, 2023a).

To estimate this increase, we propose to first explore a "cubic model", with:

(1) increasing the number of cubic droplets by

splitting all droplets into 2,
(2) increasing the number of cubic droplets by splitting all droplets into 8.
The same calculations will then be made for spherical structures.

4.1.1. The cubic model for a simple start

Initially, we consider a cube of dispersed phase of volume V . The length c of the side is equal to $V^{\frac{1}{3}}$, and the area A of the cube (6 faces) is equal to:

$$A = 6 c^2 = 6 \left(V^{\frac{1}{3}} \right)^2. \quad [9].$$

4.1.1.1. Dividing the volume by 2, for practice

Suppose we divide the volume V of the initial cube by 2 (Figure 4).

We obtain two equal volumes, of volume $V/2$, each with a side of length $\left(\frac{V}{2} \right)^{\frac{1}{3}}$ and a surface area a_1 :

$$a_1 = 6 \left(\left(\frac{V}{2} \right)^{\frac{1}{3}} \right)^2 = 6 \left(\frac{V}{2} \right)^{\frac{2}{3}}. \quad [10]$$

The total area A_1 for the two cubes is twice the area a_1 of one small cube, that is:

$$A_1 = 2 \cdot 6 \left(\frac{V}{2} \right)^{\frac{2}{3}}. \quad [11]$$

After division, the area increase is in the ratio:

$$\frac{2 \cdot 6 \left(\frac{V}{2} \right)^{\frac{2}{3}}}{6 V^{\frac{2}{3}}} = 2^{\frac{1}{3}}. \quad [12]$$

That is about 1.26, that is greater than 1: it means that the total area increases with such a division.

[Exercise 2. Above, the division of a volume was considered, but it is often a good calculation strategy to begin with a simple question (lower dimension), and to move by increasing order of

complexity (here: of increasing mathematical dimensions). The simplest case is proposed here as an exercise.

Consider a square having a side of length $c = 1$ (if it helps you, you can use units: $c = 10^{-6}$ m, for example).

1. Calculate first the perimeter.
2. Calculate the sum of the perimeters for two squares for which the sum of the areas is equal to the area of the initial square.
3. Calculate the increase in total perimeter.]

4.1.1.2. Dividing a cube by 8

The same calculation can now be performed, assuming that the side (rather than the volume) of the initial cube is divided by 2 (Figure 5).

This division creates 8 smaller cubes, each with a volume V_1 equal to:

$$V_1 = \frac{V}{2^3}. \quad [13]$$

And the side c_1 of the small cubes is (by definition of the division):

$$c_1 = \frac{c}{2}. \quad [14]$$

The area a_1 of one of these cubes is then:

$$a_1 = 6c_1^2 = 6\left(\frac{c}{2}\right)^2. \quad [15]$$

And the total area of the 8 cubes is:

$$A_1 = 8a_1 = 8 \cdot 6\left(\frac{c}{2}\right)^2. \quad [16]$$

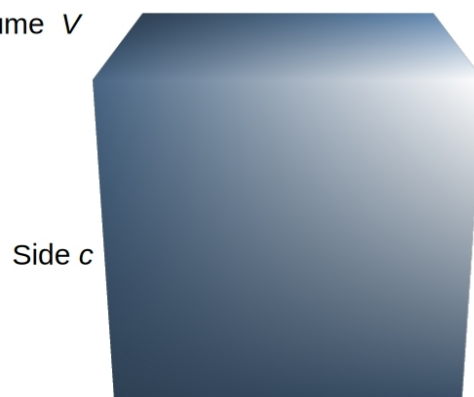
The increase in total area is now in the proportion:

$$\frac{A_1}{A} = \frac{8 \cdot 6\left(\frac{c}{2}\right)^2}{6c^2} = 2. \quad [17]$$

This ratio of 2 does not depend on the initial size of the cube, so if we divide it again, the area increases by the same proportion: after n successive divisions, the increase in area is 2^n .

Let us finish this section with a numerical application to fix our ideas: assume a cube with a side of 1 cm, which is divided 10 times into 8. The number of cubes formed is $8^{10} = 1\,073\,741\,824$,

Initial volume V
Area A



8 cubes of
volume $V/8$

Total area
 $8a_1$

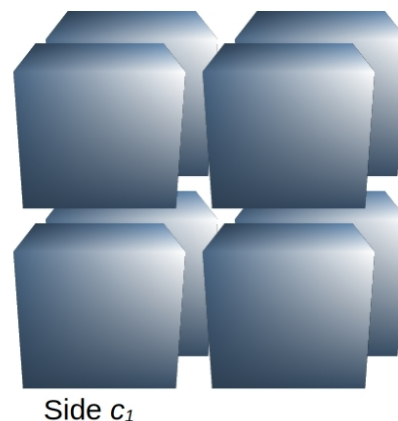


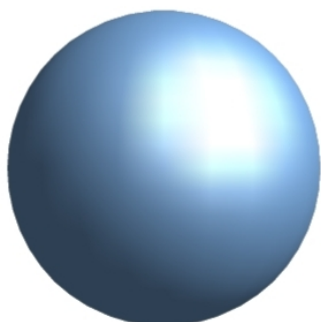
Figure 5. The division of a cube of side c (and area A) into 8 smaller cubes, each half the size (c_1) of the original cube, increases the total area. Each small cube has a surface area a_1 .

or around one billion. And the total area increases by a factor of $2^{10} = 1024$.

[Exercise 3. As for the exercise 2, a simplest case is proposed as an exercise. Consider a square of side $c = 1$.

1. Calculate first the perimeter and the area.
2. Calculate the sum of the perimeters for 4 squares having a side half the side of the initial square, and compare this sum with the initial perimeter.
3. Calculate the total area of the 4 squares and compare it to the area of the initial square.]

Initial volume
 V
Area A



Two spheres
of volume
 $V/2$,
Area a_1 for
each

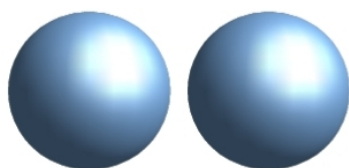


Figure 6. The division of a sphere into two identical spheres.

4.1.2. A spherical model

Above, we considered cubes, but the same tendencies apply to spheres, as we are now going to calculate (we can not stress enough that it is in our interest to practise simple calculations so as to become more capable, later on, step after step as shown here, of doing more complex calculations).

4.1.2.1. Dividing the volume of a sphere by 2

Consider an initial sphere of radius r . Its volume V is:

$$V = \frac{4}{3} \pi r^3. \quad [18]$$

The area A of its surface is equal to:

$$A = 4 \pi r^2. \quad [19]$$

If we divide the initial sphere into 2 smaller identical spheres (Figure 6), their volume becomes:

$$V_1 = \frac{V}{2}. \quad [20]$$

And their radius r_1 is given by the equation that expresses that the volume of each small sphere is equal to the half of the volume of the initial sphere:

$$\frac{4}{3} \pi r_1^3 = \frac{\frac{4}{3} \pi r^3}{2}. \quad [21]$$

After simplification:

$$r_1^3 = \frac{r^3}{2}. \quad [22]$$

Hence the radius r_1 as a function of r :

$$r_1 = \left(\frac{1}{2}\right)^{\frac{1}{3}} r. \quad [23]$$

An approximate value for $\left(\frac{1}{2}\right)^{\frac{1}{3}}$ is 0.79, smaller than 1.

The area a_1 of each half-sphere can be obtained from the radius r_1 :

$$a_1 = 4 \pi r_1^2. \quad [24]$$

Or:

$$a_1 = 4 \pi \left(\left(\frac{1}{2}\right)^{\frac{1}{3}} r\right)^2 = 4 \pi \left(\frac{1}{2}\right)^{\frac{2}{3}} r^2. \quad [25]$$

We are particularly interested in the increase in total area. Here, the ratio is:

$$\frac{2 a_1}{A} = \frac{4 \pi \left(\frac{1}{2}\right)^{\frac{2}{3}} r^2}{4 \pi r^2} = 2^{1/3}. \quad [26]$$

An approximate value of $2^{1/3}$ is 1.26, which is again greater than 1: the total area of the divided structures increases with the number of divisions. Let us observe also that it is the same value as for cubes (see above).

[Exercise 4. Just as the square is the two-dimensional object corresponding to the cube, the disk corresponds to the sphere. Consider a disk of radius $r = 1$.

1. Calculate first its perimeter.

2. Calculate the sum of the two perimeters for two disks for which the sum of the areas is equal to the area of the initial disk.

3. Calculate the increase in total perimeter.]

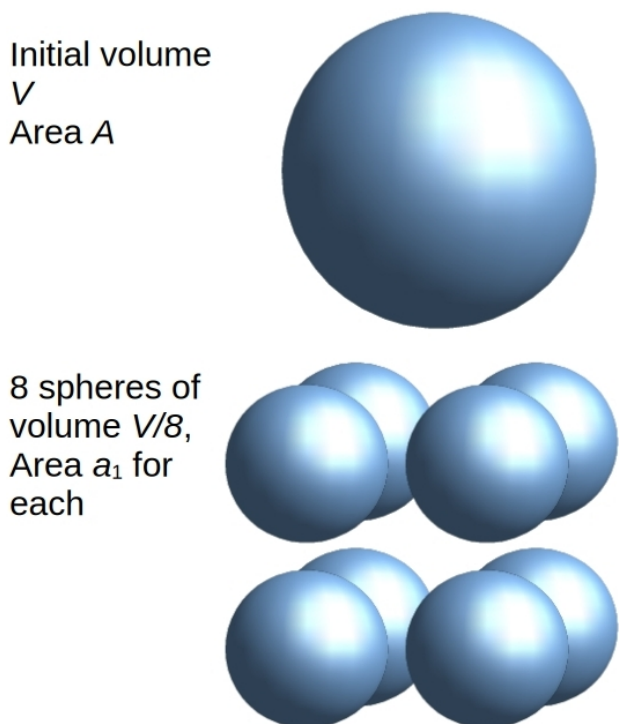


Figure 7. A sphere divided into 8 smaller spheres: their radius are half the size of the radius of the initial sphere.

4.1.2.2. A division of the volume by 8

At this stage, it is clear that the area increases with division, but we propose to do the calculation again, because we want to draw attention to the evolution of the radii.

Consider again an initial sphere of radius r and volume V given by:

$$V = \frac{4}{3} \pi r^3. \quad [27]$$

As said, the area A of its surface is equal to:

$$A = 4 \pi r^2. \quad [28]$$

If we divide the initial sphere into 8 smaller spheres (Figure 7), their volume becomes $v_1 = \frac{V}{8}$ and their radius r_1 is given by the following equation:

$$\frac{4}{3} \pi r_1^3 = \frac{1}{8} \frac{4}{3} \pi r^3. \quad [29]$$

Hence:

$$r_1 = \frac{r}{2}. \quad [30]$$

Here, as with the side of the cube, the radius is divided by 2, because the volume is divided by 8, that is 2^3 .

Given this, the area of one of these spheres is:

$$a_1 = 4 \pi r_1^2 = 4 \pi \left(\frac{r}{2}\right)^2. \quad [31]$$

And the total area of the spheres is:

$$A_1 = 8 a_1 = 8 \cdot 4 \pi \left(\frac{r}{2}\right)^2. \quad [32]$$

The increase in total area is in the proportion:

$$\frac{A_1}{A} = \frac{8 \cdot 4 \pi \left(\frac{r}{2}\right)^2}{4 \pi r^2} = 2. \quad [33]$$

The total area is multiplied by 2 each time the droplets are divided into 8 smaller droplets, so that for n successive divisions of this type, the total area increases as 2^n again as for cubes: do not you find this interesting? how would you explain it?).

So, if whisking more a mayonnaise results in a strong decrease of the droplets size, then one may hypothesize that the associated increase in surface area might be at the origin of the viscosity increase. If this would be the case, how could it be explained ?

[Exercise 5. As with square, it is now proposed to calculate the perimeters of disks after a division in 4. Consider a disk for which the radius is $r = 1$.

1. Calculate first the perimeter and the area of the initial disk.
2. Calculate the sum of the perimeters for the 4 disks having a radius half the size of the radius of the initial disk, and compare it (ratio) to the initial perimeter.
3. Calculate the total area of the 4 disks and compare it to the area of the initial disk.]

[Exercise 6. The golden ratio is a fascinating

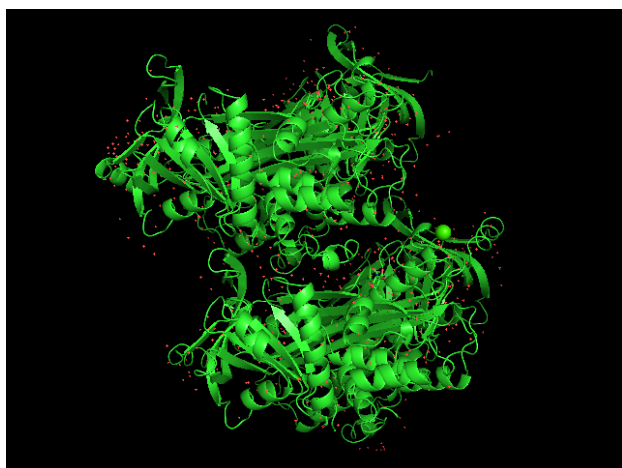


Figure 8. Proteins such as ovalbumin can contribute to the stability of emulsions. Many representations of proteins are possible (ribbons as here, solvent accessible, charge density, etc.), but for our calculation in this supporting document we only need to have an idea of them that will be useful for the calculation that we want to make. The size of ovalbumin molecules depends on pH and can be measured by light-scattering analysis: near the isoelectric point, it was found to be equal to 340 nm (Tomimatsu, 1965), that is it can cover an area of about 115,600 nm² (if we consider simply the square of the diameter, as we want an order of magnitude of the area) (credits: RCSC PDB).

number, appearing in a wide variety of geometry problems.

1. Consider a rectangle with a width of 1. Find the length such that, if a square with a side length equal to the rectangle's width is removed, the remaining part of the original rectangle is a smaller rectangle possessing the same properties as the large original rectangle.
2. Let Φ be the ratio of the length to the width. Calculate the perimeter of the golden rectangle.
3. Place four golden rectangles side-by-side to form a large rectangle. What is the ratio of its length to its width?
4. Calculate the perimeter of the large rectangle

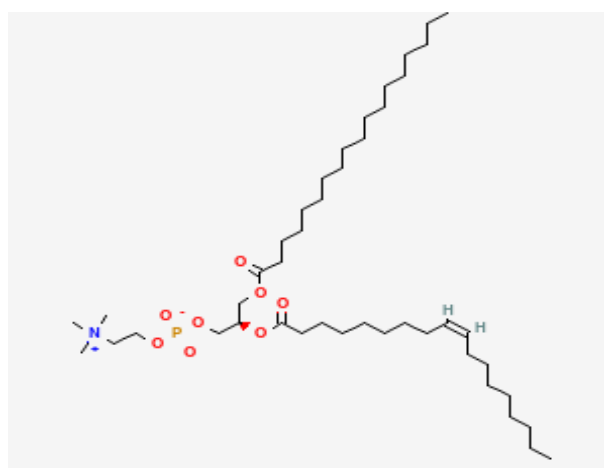


Figure 9. Phospholipids such as 1-stearoyl-2-oleoyl-sn-glycero-3-phosphocholine can contribute to the stability of food emulsions. For phospholipids, an order of magnitude of the area covered at the surface of an oil droplet is 0.65 nm² (Takamori et al., 2006). Here, the particular phospholipid shown is a “lecithin”, as it is a choline ester of a phosphatidic acid. The choline residue is on the left, including a nitrogen atom bound to three methyl groups and a small hydrocarbon moiety (CH₂-CH₂). The phosphatidic acid components include a phosphoric acid residue, a glycerol residue, and two fatty acid residues (here oleic and stearic acids) (IUPAC, 2006c) (credits: This vo Kientza).

thus formed, then determine the ratio of this perimeter to the perimeter of the golden rectangle.

5. Calculate the area of the golden rectangle and compare it to the area of the large rectangle formed by assembling the four golden rectangles.]

4.2. Taking a “skin” into account

So far, the dispersed structures (cubes or spheres) were considered as perfect geometric objects, the interface being assumed to be

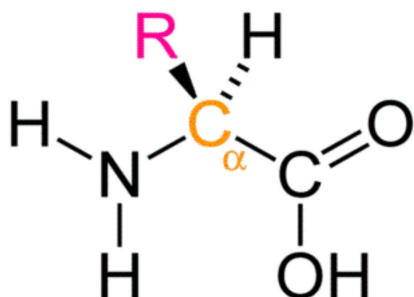


Figure 10. The general formula of the molecules of alpha amino acids includes an amino part (--NH_2) and a carboxylic acid part (--COOH). The letter R stands for remnant, or residue. It designates the characteristic side group of the various amino acids. Stricto sensu, what is shown here does not exist in aqueous solutions because the terminal groups are not both neutral: at low pH, the amino group is charged positively (--NH_3^+), but at high pH, the carboxylic acid group is deprotonated, and charged negatively (--COO^-). This does not generate any change in the calculation proposed here.

mathematically ideal, infinitely thin. However, for emulsions such as mayonnaise and other food systems, proteins and other compounds having smaller molecules (phospholipids, in particular) are essential for reducing the interfacial energy (This vo Kientza, 2021b). These molecules have non-zero volume, and some of their atoms have electric charge (which contributes to the extension of the molecule, due to the repulsion of charges of the same sign (Figures 8 and 9). Can their size really be considered infinitesimally small, compared with the size of droplets? In order to answer this question, we will now begin with the calculation of an order of magnitude of their size, and we will then compare it with the distance between dispersed structures.

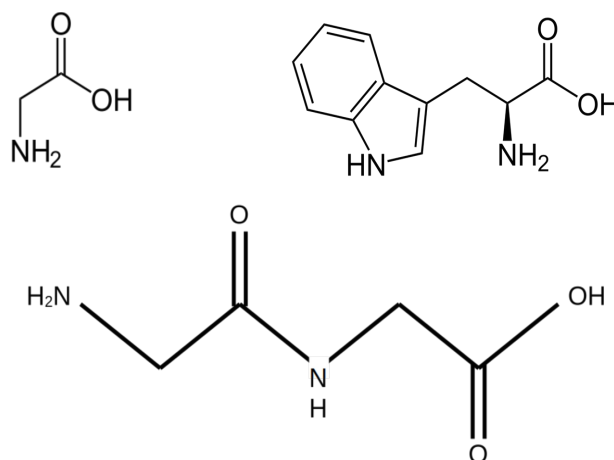


Figure 11. The structure of the molecules of L-glycine (top left), L-tryptophan (top right) and the dipeptide glycylglycine (bottom). As in figure 10, no electric charges are shown. The representations follow the usual conventions of chemistry, namely that carbon atoms are not indicated: they are present at each vertex of the representations. As for hydrogen atoms, they are most often omitted for the sake of clarity, and their presence is determined taking into account that carbon atoms are "tetravalent", meaning they have a total of four bonds with neighbouring or hydrogen atoms (not shown).

4.2.1. Calculating orders of magnitude for the size and mass of proteins

In the caption of figure 8, the size of the ovalbumin molecule was given from the literature, but it is worth trying to find it calculating orders of magnitude, as a training. Regarding this question, it is useful to know that the egg white from hens (*Gallus gallus*) is made of 90 % water and 10 % proteins. There are more than 300 proteins (that is kinds of different molecules, with up to millions of billions of molecules for the main kinds) in egg white (Shi *et al.*, 2023), but the most abundant (54-58 %) is

ovalbumin (Huntington and Stein, 2001; PubChem, 2023).

Students know from biochemistry courses that protein molecules are made up of amino acid residues linked by peptide bonds. The molecules of amino acids (more precisely proteinogenic alpha amino acids) have the structure shown in Figure 10. Each molecule of amino acid includes a side group, the smallest of which is restricted to one hydrogen atom (for L-glycine) and the largest (in L-tryptophan) having two cyclic groups joined together, one pentagonal (with one nitrogen atom) and one hexagonal (Figure 11).

For L-glycine, we can estimate the molar mass. With about 1 g/mol for hydrogen, 12 g/mol for carbon, 14 g/mol for nitrogen and 16 g/mol for oxygen, one gets a mass $14 + 2$ for the amino part, a mass $12 + 16 + 16 + 1$ for the carboxylic group, plus a mass $12 + 2$ for the carbon atom and the two hydrogen atoms bonded to the central carbon atom, so that the total value of 75 g/mol is obtained (true value 75.067). For L-tryptophan, the same kind of calculation leads to a value of 202 g/mol, to compare with the true value of 204.225 g/mol (Lide, 2009).

An average molar mass of 110 g/mol is then calculated for amino acids, compared to the right value (137) given in the literature (as two hydrogen atoms and one oxygen atom are lost during the making of a peptidic bond, this value is reduced in peptides and in proteins) (Exercise 7).

[Exercise 7. Considering the chemical formula of the 20 proteinogenic amino acids, find the exact value of their molecular mass, and determine the average value for all the results. Compare it to the average value calculated above.]

How many amino acid residues are there in a protein molecule? Because we want to calculate an order of magnitude, the question becomes: is this number 1, or 10, or 100, or 1000, or 10,000, etc.?

We know that proteins are polypeptides, so that the number of their amino acid residues is greater than 10, according to the definition of the prefix "poly" by the IUPAC (2019). This is a lower bound,

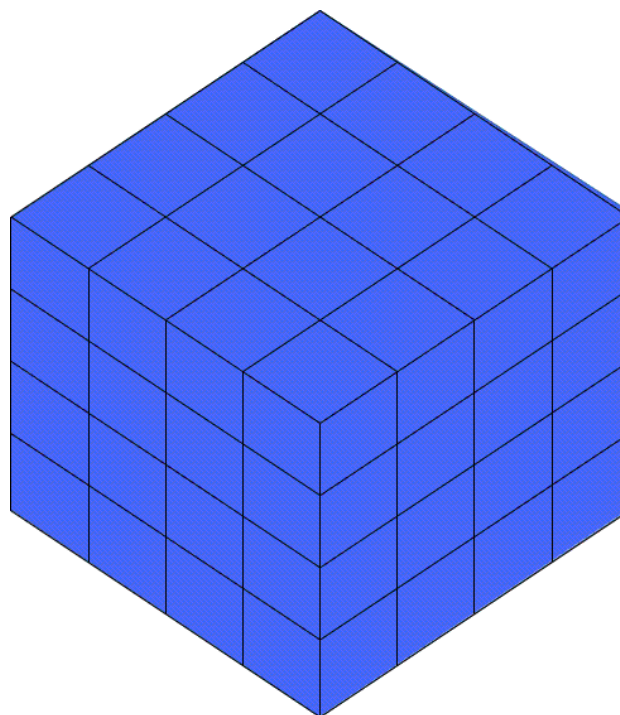


Figure 12. The folding of a protein "on a lattice": the amino acid residues are assumed to occupy the edges of all the elementary cubes of the large cube shown, and the question is to know the size of this large cube.

but for an upper bound, we can find that the largest protein in the human body, titin, has 35,000 amino acid residues (Callaway, 2024). As a conclusion, the number of amino acid residues in ovalbumin can be guessed to be between 100 and 1000. Indeed, for ovalbumin, the exact number is 385 (Huntington and Stein, 2001). Using this order-of-magnitude value and the average molar mass of an amino acid residue, we calculate a molar mass of $100 \cdot 110$, that is 11,000 g/mol. With the correct number of amino acids and the average molar mass of amino acids, we would obtain 52,745 g/mol, which is much closer to the exact value (45,000). In any case, we conclude that calculating orders of magnitude gives an idea of molecular characteristics to first order.

4.2.2. Another order of magnitude calculation: estimating the “size” of a protein

How large is a protein molecule? The notion of size deserves being discussed for complex objects (Pabst and Gregorova, 2007), but, as a first and very crude approximation, proteins can be approximated as parallelepipeds, with three characteristic dimensions. It is to be stressed that this calculation is very rough, as electrostatic attractions and repulsions are not taken into account, nor is the size of the side chains, which play a decisive role in the shape of protein molecules: protein folding is a very difficult problem, for which a Nobel prize was given in 2024 (Royal Swedish Academy of Sciences, 2024).

Considering, for example, the dipeptide glycylglycine (Figure 11), the length of the major axis corresponds to 6 covalent bonds. By estimating the length of one covalent carbon-carbon bond at 0.15 nm (Lide, 2009), we find that the approximate length of an amino acid residue is equal to $4 \cdot 0.15 = 0.6$ nm. How would this change if we took bond angles into account? This result would have to be multiplied by $\cos(\frac{\pi}{6}) = \frac{\sqrt{3}}{2}$, or a length of about 0.39 nm. In

what follows, for orders of magnitude calculation, a value of 0.4 nm will be used.

Anyway the size of a protein molecule depends on the folding of the polypeptide chain. Let us look at two extremes cases:

- the most compact folding,
- a full extension of the polypeptide chain.

For sure, they are unlikely, but they yield lower and upper values.

(1) For compact folding: Let us imagine that the amino acid residues (400) of a protein molecule occupy the edges of a regular stack of cubes, in the three directions of space (Figure 12). The question is: what is the size of the smallest meshed cube whose edges (external and internal) are all occupied by amino acid residues?

Each elementary cube has 12 edges, but any

of these edges is shared by 4 neighbouring elementary cubes, so that there are only 3 “full” edges per elementary cube ($12/4$) (admittedly, this is not strictly accurate for the elementary cubes, because some, on the outside edges, have different status, but we are looking for an order of magnitude). With 400 amino acid residues (that is edges of elementary cubes), there would therefore be $400/3 \approx 133$ elementary elementary cubes, that have to make a larger cube. To calculate the side (in units of elementary cubes) of the larger cube, we determine the cube root of 133: the number of elementary cubes per side is approximately 5. Ultimately a large cube having 5 elementary cubes on its side, with amino acid residues on all edges gives a rough representation of a fully coiled protein such as ovalbumin (remember that this is unrealistic, and calculated for setting a lower limit).

In order to determine the side of the larger cube in ordinary units, the size of an amino acid residue is needed: an order of magnitude of 0.4 nm was found above. Let us therefore count 5 elementary cubes per side, i.e. 2 nm (5×0.4) per side for a fully folded protein.

To validate this first calculation, another calculation involves multiplying the “volume of amino acid residue”, equal to the cube of the characteristic dimension of a residue, by the number of residues, then calculating the cube root of this volume. This calculation can be done in various ways, but here is one, as an example:

- for the volume of a residue (in nm), we begin by considering amino acid residues as parallelepipeds; assuming that amino acids have on average three covalent bonds in each spatial direction (Caillez, 2006), the volume is estimated equal to 0.4^3 nm^3 , i.e. 0.064 nm^3 ;
- for a perfectly compact polypeptide with 400 amino acid residues, the total volume would be about 25.6 nm^3 ;
- if it is a cube, the side (in nm) is equal to $25.6^{1/3}$, or 2.95, which is very close the value that was previously found.

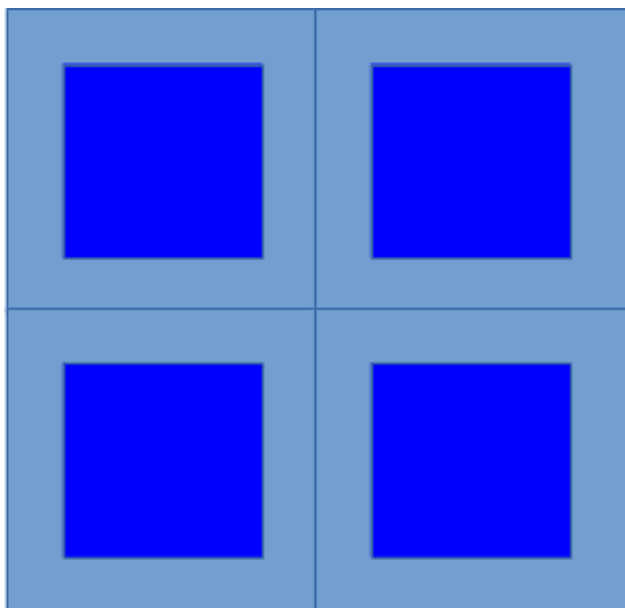


Figure 13. For a volume fraction of 0.5, half of the volume can be evenly distributed around the dispersed structures.

(2) For full extension: For the full extension of the protein molecules, it is simpler to estimate the full protein length, since we multiply the characteristic dimension of an amino acid residue by the number of amino acids, that is $400 \cdot 0.4 = 160$ nm.

Finally we conclude this paragraph by observing that the same protein can therefore be likened to a compact sphere nearly 3 nm in diameter, or to a long thread 0.3 nm in diameter (about 2 covalent bonds in the direction perpendicular to the chain of amino acid residues) and 160 nm long. Using the International System of Units, the ratio of protein size to droplet size of an emulsion is

therefore, at worst, between $\frac{160 \cdot 10^{-9}}{1 \cdot 10^{-3}} = 1.6 \cdot 10^{-4}$

m for large droplets (diameter 1 mm), covered with a layer of perfectly compact proteins, and $\frac{160 \cdot 10^{-9}}{1 \cdot 10^{-6}} = 1.6 \cdot 10^{-3}$ m for small droplets (in this case, 1 μ m in diameter), covered with a layer of

completely unfolded proteins, “bristling” on the droplets like the bristles of a hairbrush (This vo Kientza, 2023b).

As small as it is in the first case, it becomes all the more noticeable in the second case, and it is impossible to ignore the surface layer.

Further reading:

Protein folding is a very difficult problem, and in 2024, the Royal Swedish Academy of Sciences has decided to award David Baker, Demis Hassabis and John Jumper the Nobel Prize in Chemistry, for computational protein design and protein structure prediction (Royal Swedish Academy of Sciences, 2024).

Before, a useful book on the general question of polymers was published by Grosberg and Khoklov (1997).

More focused on protein folding, one can read: Bryngelson and Wolynes (1987; 1990), Onuchic et al. (1997), Wolynes (1997), Bastolla et al. (2000), Sharma et al. (2013).

About lattice calculation: Jiang and Zhu (2005).

Having completed these calculations, we can return to the question of determining the size of the “skin” covering the oil droplets, in order to compare this size to the distance between the droplets. On the one hand, this thickness of the skin increases the volume fraction, and on the

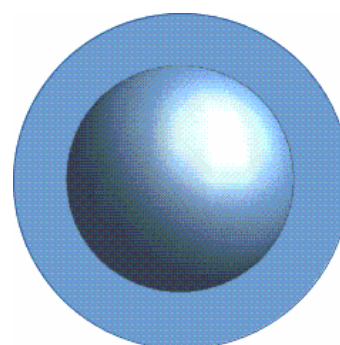


Figure 14. A sphere of oil and the volume occupied by molecules at the oil-water interface, or “skin”.

other hand, the molecules of the skin can contribute to interactions between covered droplets when the distance between oil droplets is small. Let us now calculate this.

4.2.3. How far apart are the droplets in an emulsion, assuming a volume fraction of 0.5?

Let us consider cubes of side c (modelling oil droplets) dispersed in a continuous phase, the total volume of the suspension being V , with a volume fraction of the dispersed phase $\varphi = 0.5$.

The total volume of the cubes is therefore $V/2$, and their number n is given by:

$$\frac{V}{2} = n c^3, \quad [34]$$

that is:

$$n = \frac{V}{2 c^3}. \quad [35]$$

The remaining volume, $V/2$, is distributed over the same number of cubes, so that, for each cube, the volume v of continuous phase (water) corresponding to that cube is:

$$v = \frac{(\frac{V}{2})}{n} = \frac{\frac{V}{2}}{\frac{V}{2 c^3}} = c^3 \quad [36]$$

(note that this last calculation is unnecessary: since the volume fraction is 0.5, the volume of liquid assigned to an elementary cube is obviously equal to that of the elementary cube itself).

If we assume that each cube has like a layer of continuous phase of thickness e around it (Figure 13), the volume of liquid around each cube is equal to the surface area of a cube ($6 c^2$) multiplied by the thickness of the skin (e), that is $6 c^2 e$. We can then calculate the thickness e , given by:

$$c^3 = 6 c^2 e. \quad [37]$$

That is:

$$e = \frac{c}{6}. \quad [38]$$

And the distance between two cubes is $2e$.

In other words, if we have cubes (modelling oil

droplets) of radius 0.1 mm, then the distances between two cubes are much greater than the thickness of the "skins". But the more numerous and smaller the "droplets", the smaller the distance between droplets, until interactions between droplets appear when skins overlap.

4.2.4. Back to the question of calculating the viscosity of an emulsion when the dispersed structures (droplets) are divided

Having a better idea of the systems we study, we now return to examining the viscosity of emulsions, taking into account the thickness of the interface. In order to calculate the viscosity, we need first to determine a modified volume fraction taking into account the skin (φ_s).

4.2.4.1. The algebraic derivation

We start with the a volume fraction of oil φ . For an emulsion of volume V , the volume V_o of oil is initially:

$$V_o = \varphi V. \quad [39]$$

If the oil droplets (without the skin) have a radius r_o , their individual volume v_d is equal to:

$$v_d = \frac{4}{3} \pi r_o^3. \quad [40]$$

To fully characterize the system, we need to determine the number of oil droplets, which appears in the expression stating that the total volume of oil in the emulsion is the sum of the volumes of all the droplets:

$$n_o \left(\frac{4}{3} \pi r_o^3 \right) = V_o. \quad [41]$$

The number n_o of droplets is then:

$$n_o = \frac{V_o}{\frac{4}{3} \pi r_o^3} = \frac{\varphi V}{\frac{4}{3} \pi r_o^3}. \quad [42]$$

In what follows, the increase in viscosity will be calculated using the various models considered in section 2. This involves calculating the increase in volume fraction of the dispersed

structures due to the skin, and then the increase in volume fraction.

If each drop is covered by a skin of thickness e_s (Figure 14), the total volume V_d of the dispersed phase is increased, because it includes the oil and the "skin":

$$V_d = n_0 \left(\frac{4}{3} \pi (r_0 + e_s)^3 \right) = \frac{\varphi V}{\left(\frac{4}{3} \pi r_0^3 \right)} \left(\frac{4}{3} \pi (r_0 + e_s)^3 \right) \quad [43]$$

To better understand the result, we rewrite it in a way that better shows the increase (the numerator is greater than the denominator):

$$V_d = \varphi V \frac{\frac{4}{3} \pi (r_0 + e_s)^3}{\frac{4}{3} \pi r_0^3}. \quad [44]$$

And the volume fraction with skin (φ_s) is equal to the ratio of the volume of the dispersed phase to the total volume:

$$\varphi_s = \frac{V_d}{V} = \varphi V \frac{\frac{4}{3} \pi (r_0 + e_s)^3}{\frac{4}{3} \pi r_0^3} = \varphi \frac{(r_0 + e_s)^3}{r_0^3}. \quad [45]$$

To better appreciate the result, we calculate the relative increase in volume fractions:

$$\frac{\varphi_s - \varphi}{\varphi} = \frac{\frac{\varphi (r_0 + e_s)^3}{r_0^3} - \varphi}{\varphi} = \frac{(r_0 + e_s)^3}{r_0^3} - 1. \quad [46]$$

Finally a result, such as this one, should be validated. Do you have any idea how?

[Exercise 8. In the equation [46], what happens if e_s goes to 0. How do you interpret the fact that the relative increase of the volume fraction of the dispersed phase with skin does not depend on the volume fraction of oil?]

4.2.4.2. A digital application to fix ideas

In scientific studies, it is generally recommended

to clearly separate algebraic and numerical calculations. However, it is also useful to determine the orders of magnitude of phenomena to guide reasoning. Here, we therefore propose to calculate the viscosity of emulsions using the various models initially presented. More precisely, we start from a given system; then we indicate numerical values for its relevant characteristics, in order to calculate the volume fraction and viscosity predicted by the various models.

The system considered is a mayonnaise-type emulsion, with a total volume of 1 L (10^{-3} m^3) and an initial volume fraction of 0.5, that is an oil volume of $0.5 \cdot 10^{-3} \text{ m}^3$. We first consider the emulsion loosely whipped, with oil droplets of a radius equal to 1 mm before calculating the viscosity for droplets 100, then 1000 times smaller. The viscosity values will be considered at 20 °C:

- for water: 1 mPa.s (White, 2008),
- for oil: 50 mPa.s (Interchimie, 2023).

Note that the viscosity of the continuous water phase of emulsions could be different from the viscosity of pure water, because it contains a wide variety of dissolved species, such as ions, protein molecules, molecular aggregates. Also, below, the number of decimal digits is chosen so that the differences between the various results appear more clearly.

First, for droplets of radius equal to 1 mm, the initial volume fraction (0.5) increases up to 0.500005 if a skin of compact proteins is taken into account, and to 0.50024 if the skin is made of unfolded proteins. How does this translate into terms of viscosity? This is what will be now calculated using the equations linking viscosity to the volume fraction.

1. Using the Einstein law:

- without skin, putting the data in the equation given in section 2, a viscosity equal to 2.25 mPa.s is calculated;
- with a skin of compact proteins, the viscosity becomes 2.25001 mPa.s (relative increase 0.0004 %);
- with skin of fully extended proteins, the viscosity

becomes 2.2506 mPa.s (relative increase 0.03 %). Here, the increase in volume fraction is small, and the increase in viscosity is small as well.

2. With the Taylor law:

- without skin, the viscosity predicted by this model is 2.235294 mPa.s;
- with a skin of compact proteins: 2.235305 mPa.s (relative increase: 0.0005 %);
- with a skin of fully extended proteins: 2.235887 mPa.s (relative increase: 0.03 %).

3. With the Krieger-Dougherty law:

Now, the packing coefficient $\varphi_m = 0.74$ is used:

- without skin, a viscosity equal to 9.57859 mPa.s is obtained: this model leads to a much higher viscosity than that given by Einstein and Taylor equations;
- with a skin of compact proteins, the viscosity is found to be 9.5790 mPa.s (relative increase 0.004 %);
- with a skin of fully extended proteins, the increase is larger: 9.6000 mPa.s (relative increase 0.2 %).

4. And finally with the Yaron and Gal-Or equation:

- without skin, the viscosity value, 11.7382 mPa.s, is much larger than with the Einstein and the Stokes equation, which is as expected: remember that they hold only for diluted systems; at high volume fractions, they underestimate the viscosity (Figure 1);
- with a skin of compact proteins, a small increase is found: 11.7386 mPa.s (relative increase 0.003 %);
- with a skin of fully extended proteins the viscosity reaches 11.7567 mPa.s (relative increase 0.2 %).

All this being done, we now want to better appreciate the effect of the division of the initial droplets from their initial radius r_0 to a final radius r_1 . From equation 45, we know that the volume fraction with skin φ_s is:

$$\varphi_s = \frac{\varphi(r_1 + e)^3}{(r_1)^3} \quad [47]$$

We saw earlier that for fairly large radii (previously, we used 1 mm), taking the skin into account made little difference in calculated viscosity, because the difference between the case without skin and the case with skin was small, due to the fact that the thickness of the skin was negligible compared to the radius of the drops. However, for droplets of radius 10^{-2} mm, the volume fraction is 0.50045 for a skin of compact proteins, but 0.524386 for a skin of extended proteins.

Let us use Krieger-Dougherty equation to appreciate the change in viscosity, as the Einstein equation and Taylor equations give much underestimated values as their range of validity is that of diluted systems. Without skin, we find the calculated viscosity is 9.5786 mPa.s, as seen before. With a skin of compact proteins, we calculate a viscosity 10.001 mPa.s, and the viscosity reaches 12.2683 mPa.s for a skin of extended proteins.

The conclusion is as follows: as soon as we consider a skin, even a division of the radii by 100 starts to produce an increase in viscosity. This is an interesting conclusion, because it means that even if we consider that the droplets are not interacting (no hydrodynamic effects or friction due to the droplets being close together), the volume increase effect linked to the interface is itself responsible for an increase in viscosity.

[Exercise 9. You are invited to have fun checking that, for the numerical hypotheses used, a division by 1000 leads to an impossible result for the case of a skin of extended proteins. Could you guess why?]

5. With skin, depletion... and polydispersity?

The previous sections have shown that when the size of the droplets is greatly reduced, as happens during the intense whisking of a mayonnaise with a blender or with an ultrasonic probe, then the volume of proteins or other biomolecules adsorbed at the interfaces is no

longer negligible. In this case, there is indeed an increase in the effective volume of the droplets, which could partly explain the observed increase in viscosity. But is this the only mechanism involved?

To be complete, we need to supplement this reasoning with three important elements:

(1) We must not forget that if biomolecules adsorb at the interfaces, it is because they were previously in the continuous phase. More molecules at the interfaces, and therefore more volume at the interfaces, means fewer molecules in the continuous phase.... and therefore lower viscosity of the continuous phase. As all the equations used give the viscosity of the suspension as a function of the viscosity of the continuous phase, this effect can be complex to assess, and will depend in particular on the conformation of the molecules in question, in the continuous phase or at the interface: do they occupy more or less volume there?

(2) Smaller droplets mean more droplet surface area and therefore, potentially, more interactions between the droplets. If these interactions are repulsive, then we can easily imagine a larger "effective" volume of droplets, simply because of these repulsions.

(3) The reasoning presented above applies to monodisperse systems, but in polydisperse systems, things are more complex. In fact, small drops can be arranged between large ones... and the maximum volume fraction that the droplets can occupy can thus be greatly increased. It follows that at the same volume fraction, a bi-disperse or polydisperse emulsion will have a much lower viscosity than a monodisperse emulsion. For more about bimodal distributions, see Patlazhan (1993), Wagner and Woutersen (1994), Spangenberg *et al.* (2014),

[Exercise 10. Using Open Alex, Google Scholar and the Web of Science, look for articles investigating the viscosity of emulsions with polydispersion.]

6. Conclusion

In this supporting document, it was shown how to use the various theoretical models for the viscosity of emulsions. The Einstein equation is historically important, but one should not forget that it was a first description, with strict limits. The example of mayonnaise, although a very simple sauce, defies theoretical interpretations, because many concomitant mechanisms are at play: when whisking, the size distribution of the droplets is modified, to become more monodisperse, which would result in an increase in viscosity; the increase in surface area associated with a reduction in size results in more repulsions in the system, and therefore a higher effective volume fraction; and the reduction in droplet size results in an increase in their effective volume, and therefore in the volume fraction occupied. As a whole, the assumption of a "skin" is credible, but one should remember that we did very crude calculation, because it is important for engineers to be able to calculate using orders of magnitude.

Further reading:

Rathee et al. (2017), Marenne and Morris (2017), Morris (2020), Zhang et al. (2022), Monti and Rosti (2023)

Aknowledgements:

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