Capillarity in Action

Hervé This vo Kientza
1 INRAE, AgroParisTech, UMR 0782 SayFood, 75005, Paris, France
2 Group of Molecular Gastronomy, INRAE-AgroParisTech International Centre for Molecular Gastronomy, F-75005, Paris, France

The phenomenon of capillarity can occur during culinary processes because the thermal treatment of animal or plant tissues weakens the material (whether collagenic tissue or plant cell walls) holding together the cells making up the tissues. This weakening is mainly the result of the hydrolysis of the polymers (collagen and pectin, respectively) that are responsible for coherence (Sila et al., 2006). When pores or cracks are created as a result of cell separation, a surrounding liquid (e.g., a sauce in which the plant or animal tissues are thermally treated) can enter the tissues by capillarity (De Gennes et al., 2004).

In this chapter, we discuss this mechanism of capillarity in the context of culinary processes, but we mainly observe that, whereas this mechanism certainly plays a role in exchanges of matter between food ingredients and their liquid environment, the question is not so much to admit the possible involvement of the mechanism as to assess its quantitative importance. We shall finish by proposing an easy way of introducing a flavour into a piece of plant or animal tissue.

Diffusion versus Capillarity

Before analysing particular phenomena that can be observed in the kitchen and investigated from a physical and chemical (i.e., molecular gastronomy) point of view, it is interesting to observe that, as we show here, capillarity was sometimes underestimated; Aguilera et al. (2004) discussed the fact that it occurs in chocolate, for which the mechanism is often said, incorrectly, to be “diffusion”. Such a confusion can be observed both in culinary and in scientific circles, as discussed in the chapter in this book about osmosis (“Osmosis in the Kitchen”).

For all the phenomena for which capillarity, diffusion, osmosis or “imbibition” is considered as the interpretation, the core question is the exchange of matter between food and its (often liquid) environment (This, 2019). For example, when roots of Daucus carota L. are heated in water with a view to producing a “carrot stock”, the aqueous environment is progressively enriched with many compounds, the most abundant being saccharides (D-glucose, D-fructose and sucrose) and amino acids (Cazor et al., 2006). The same holds for tomato sauces containing pieces of the bulb of Allium cepa L. (Tardieu et al., 2009), or when producing the beverage called “coffee” from ground, thermally processed seeds of Coffea (Febvay et al., 2019).

Water loss from the interior of foods during thermal treatments has sometimes been attributed solely to “diffusion”, and it is possible that some molecular diffusion occurs when the open channels of xylem and phloem of a cut plant tissue are in direct contact with an aqueous environment (Bauchard and This, 2015). However, other mechanisms can occur, such as the escape of water vapour when high temperature causes water to evaporate, either in the “crust” or inside the tissue if microwaves are used for heating (see chapter in this book on evaporation). Fu et al. (2003) studied moisture movement from the interior of a porous and moist food matrix (for example, bread dough) during microwave heating; the loss of water was due not only to moisture diffusion but also to bulk vapour flow (convection) caused by the positive pressure built up inside the product. Osmosis can also come into play when plant and animal tissues are in an aqueous environment, and the contraction of denaturated collagenic tissue can lead to “juice” release when animal tissues are thermally processed (Kopp et al., 1977).

It is not the purpose of this chapter to repeat why the word “diffusion” is sometimes overused in food science and technology, as this was very well explained by Aguilera et al. (2004), but it is useful to reiterate that the different velocities for material transfer obey different laws, even if diffusion and capillarity cannot always be readily distinguished after the solely kinetic determination of some compounds.

For molecular diffusion, the German physiologist Adolf Eugen Fick (1829–1901) stated that, in the presence of a concentration gradient, the net migration of molecules due to their random motion occurs from a region of high concentration to one of lower concentration; as seen in the chapter about osmosis, this can be expressed using the chemical potential. The second Fick’s law states that the rate at which this process proceeds at a point M(x,y,z) in space, for a diluted binary system, is proportional to the variation of the slope of the concentration gradient (Fick, 1855). The so-called diffusion equation reads:
\[
\frac{\partial c(x,y,z,t)}{\partial t} = D \Delta c(x,y,z,t)
\]

where \(c(x,y,z,t)\) is concentration at the point \(M\), at time \(t\), \(D\) is the diffusion coefficient, or diffusivity, and \(\Delta\) is the Laplacian operator.

Aguijera et al. (2004) showed that this model is widely used (and abused) by food engineers as a general model for mass transfer. The approach has the advantage that, by plotting experimental data in the form of log (unaccomplished ratio of mass transferred) against time, an apparent or effective diffusion coefficient, \(D_{eq}\), can be determined from the straight portion of the curve (Schwartzberg, 1987). The parameter \(D_{eq}\) is to be correctly redefined as a mass transfer coefficient, because it encompasses all possible forms of mass transfer involved in the process, not only diffusional ones.

A simple analysis used to adopt the Fickian diffusion model is to check whether the ratio of the mass \(m(t)\) transported as measured experimentally by the mass \(m(t=\infty)\) when the equilibrium is reached varies proportionally to \(\sqrt{t}\) (Geurtz and Oortwijn, 1975).

For capillarity, on the other hand, the most common expression for capillary rise is the so-called Lucas–Washburn equation, which assumes that the capillary pressure in a cylindrical capillary in contact with an infinite liquid reservoir is compensated by viscous drag and gravity (Krotov and Rusanov, 1999):

\[
\frac{2}{r} \frac{\gamma \cos(\theta)}{\mu} = \frac{8}{r^2} \frac{dh}{dt} + \rho gh
\]

where \(h\) is the distance the fluid is drawn into the capillary, \(\gamma\) the surface tension of the fluid, \(\theta\) the contact angle between the fluid and the capillary wall, \(r\) the radius of the capillary, \(\mu\) the density and viscosity of the liquid, respectively, and \(g\) the acceleration of gravity. The asymptotic solutions to this for short and long times were discussed by Quéré (1997) and by Zhmud et al. (2000). The short time limit (\(t \rightarrow 0\)) predicts that the liquid movement in a horizontal capillary should be proportional to the square root of time according to the expression:

\[
h = \sqrt{\frac{r \gamma \cos(\theta)}{2 \mu t}}
\]

A plot of \(h\) against \(\sqrt{t}\) is a straight line. Overall, curves for diffusion as well as for capillary flow show a square-root-of-time dependence for mass transport at short times.

### Sometimes, There Is No Entrance; Sometimes, There Is One

As stated earlier, the issue is generally not so much to know whether some capillarity can take place as how much of the matter transfer is due to capillarity at various times after the initial contact between food and its liquid (aqueous solution or oil) environment. Regarding marination of red meat (Aktas et al., 2003; Vlahova-Vangelova and Dragoev, 2014), one can observe that some publications discuss how the composition of wines determines the tenderizing of cubes of meat marinated in wines, but the mechanism is seldom discussed. Figure 15.1 shows the inner part of a muscle (longissimus dorsi) of Bos taurus that was thermally treated for 2 h in a solution of “fluorescein” (sodium;3-oxospiro[2-benzofuran-1,9'-xanthene]-3',6'-dilolate). Fluorescence spectroscopy was performed on ethanolic extracts of samples from this muscle, but the green fluoreseence is enough to assess that some fluorescein diffusion occurred in the gelatinized thick collagenic tissue and that some fluorescein also penetrated the meat by capillarity when the collagenic tissue was destroyed between muscular fibres. It is noteworthy that this entry of the marker, through diffusion and capillarity, occurred in spite of the strong meat contraction (by about one-third in mass).

The study of grilled meat (see chapter on salt and meat by This et al. in this handbook) corroborates this result; as shown by analysis of sodium chloride in meat being grilled, no salt was found inside the meat (processing times \(<10\) min), but, in other circumstances, salt can readily enter the meat (Figure 15.2) when salt crystals are deposited on the upper surface of meat being grilled; after “juices” appear at the upper surface, they dissolve the sodium chloride, and the salty solution moves inward if the collagenic tissue is weak and slits opens during cooking.

Capillarity occurs not only in muscular tissues but also in some dishes made of plant tissues. In particular, the French “gastronome” (actually a lawyer) Jean Anthelme Brillat-Savarin (1755–1826) told the story of a clergyman who would eat spinach (leaves of Spinacia oleracea) only if it had been cooked for several days with the regular addition of cream (Brillat-Savarin, 1825). Microscopic analysis of the spinach leaves did not show any absorption (swelling), but capillarity was important because the tissue disruption through pectin beta elimination created the...
Capillarity in Action

Possibility of much capillarity between softened fragments of spinach leaves. Of course, the phenomenon can also occur in many other plant tissues commonly consumed by humans, such as the stems of leeks (*Allium porrum*), bulbs of onions (*Allium cepa* L.) or shallots (*Allium ascalonicum*).

The Mathematics behind the Phenomenon

In order to control matter transfers through capillarity, a mathematical description of the phenomenon is useful. This begins by calculating the difference of pressure between the inside and the outside of a small structure dispersed in a medium.

Let us begin by observing that, if a fluid can dissolve into another, energy is released, because bonds are created between molecules of the first fluid and molecules of the second fluid. On the other hand, if two fluids do not mix, it means that they need energy to be in contact. In particular, drops of one liquid dispersed in another organize so that their energy is minimized, i.e., the area $A$ of their contact surface is minimized. One can express this using the free energy, $F$ (here, for a simple treatment).

For example, we can write, at constant pressure:

$$dF = -PdV - SdT + \gamma dA$$

where $P$ is the pressure, $V$ the volume, $S$ the entropy, $T$ the absolute temperature, and $\gamma$ the “surface tension”, expressed in J/m² (but as 1 J = 1 N.m, it is often expressed in N/m).

Let us, for example, consider the gas inside a bubble in a liquid. The pressure inside the bubble is $P_{int}$ and the pressure outside is $P_{ext}$. Let the radius of the bubble (assumed spherical) be $r$.

If the radius of the sphere were increased from $r$ to $r+dr$, the change in the area $dA$ would be equal to:

$$dA = 4\pi(r + dr)^2 - 4\pi r^2 = 8\pi r dr$$

The work needed to increase the area by this value would be:

$$dF = -P_{int}dV_{int} - P_{ext}dV_{ext} - SdT + \gamma_{int/ext}dA$$

If we neglect the change in the entropic term, the equilibrium is reached for $dF = 0$. And because:

$$dV = 4\pi r^2 dr$$

At equilibrium, $dF = 0$, so that:

$$P_{ext} - P_{int} = -2\frac{\gamma}{r}$$

This is the Laplace equation (De Gennes et al., 2004).

Using this relationship, one can now calculate the “capillary rise”, i.e., the tendency of liquids to move upward in thin (this should be characterized using the “capillary length”) tubes (Daoud and Williams, 1999). If we consider a tube of which the lower part is in a liquid, this liquid moves upward by a distance $h$, and a meniscus is formed. $P$ being the atmospheric pressure, and $r$ the radius of the tube, the distance $h$ can be calculated (Figure 15.3).

The pressure inside the liquid, at the middle of the air–liquid interface $M$ can be calculated using the Laplace law.

If $P_{air}$ is the pressure (ambient) of the air, then:

$$P_M - P_{air} = -2\frac{\gamma}{r}$$

Because of the weight of the liquid, we can also express the hydrostatic pressure:

$$P_M - P_{air} = -2\rho gh$$

FIGURE 15.2 In the first example (a), a piece of beef meat (*Bos taurus, longissimus dorsi*, cut perpendicularly to fibres) was grilled. Because of the low content of collagenic tissue, the bundles of muscular fibres separated, creating crevices into which salted water could be attracted by capillarity. In the second picture (b), the sauce in which the meat was cooked entered deeply into the muscular tissue by capillarity, between the fibres, which separated due to the partial dissolution of the collagenic tissue.
Equating the two, we get:

\[ h = 2 \frac{\gamma}{\rho g r} \]

From this formula, we see the importance of not only the surface tension but also the density and the radius. In culinary processes, when the density cannot be changed, one can improve capillarity by increasing the surface tension or reducing the radius.

**The Example of “Shitao”**

Finally, let us observe that capillarity occurs generally for both aqueous solutions and oils in most plant and animal tissues, because culinary systems are full of both hydrophobic and hydrophilic compounds, establishing contacts by a diversity of intermolecular forces (Figure 15.4). However, the penetration of liquids inside such tissues does not always occur, and the problem of giving a specific flavour to the inside of three-dimensional ingredients does not always have a solution.

However, if a series of cuts are made on the sides of a plant or animal tissue, dipping this cut tissue into a sauce triggers the introduction of the sauce into the tissue by capillarity. In 2007, I proposed calling such systems “Shitao”, from the 17th-century Chinese painter having this name. A dish based on such principles was served at the gala dinner during which the first note by note dish was served, in the Mandarin Oriental Hong Kong, by the French chef Pierre Gagnaire (Figure 15.5).

**REFERENCES**


Bauchard E, This H. 2015. Investigating the performance of *in situ* quantitative nuclear magnetic resonance analysis and applying the method to determine the distribution of saccharides in various parts of carrot roots (Daucus carota L.), *Talanta*, 335–341.


This H. 2009. Cours de gastronomie moléculaire N°1, Belin/Quae, Paris.

This H. 2019. The science of molecular gastronomy and the art of innovative cooking, FEBS Letters, 411(9), 1677–1678.
