Hydrocolloids between soft matter and taste: Culinary polymer physics

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Abstract

Hydrocolloids are well known for their wide use in for many products provided by many branches of the food industry. More and more they play an important role in many applications of the avant-garde cuisine, where according to many chefs their real strength is determined by their isolated use, rather than in combinations with other food thickeners and gelling agents. Indeed their thoughtful use in dishes and food systems allows developing sensible physical and more systematic "models for taste" in (molecular) gastronomy. The physical origin of taste development and taste release by structural changes in the mouth one of the subjects discussed in this paper. The general goal is the developments of models for structure–property–taste relationships on the basis of molecular material laws, which have their origin buried in the soft matter sciences. In this publication we are going to demonstrate, how simple ideas from polymer physics, including theory allow a deeper understanding of rheological properties and taste parameters. As an example we study mainly role of xanthan and develop a new type of model for its physical and gastronomic properties. These models can, however, provide a deeper understanding of molecular processes in food science beyond food technology.
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Introduction

Hydrocolloids are in most cases water-soluble large molecules, which enhance properties such as viscosity dramatically. This makes their application in food and cooking obvious. Well-defined changes of the flow properties yield significant effects in taste and mouth feeling (Handbook, 2000). Creams or with special flow properties stay longer in the mouth and release their taste slower, so that they match flow times for certain molecular processes match relevant time scales of the sensory experience. Such applications are well known in food industry. In most cases hydrocolloids are used to stabilise the mouthfeeling of a certain product under the natural and possible variation of physical parameters, such as acidity, salt or sugar content and basically the temperature, under which the product is eaten, e.g., directly out of the fridge or after some warming at room temperature. However, since their use in "molecular cooking" their special features became

available to new applications and the products are used on a practically basis by a broader public (Adria el Bulli, 2005; Vilgis, 2007).

In molecular gastronomy hydrocolloids are basically used as texturizers, which change the physical behaviour of liquid in a well-defined and systematic way, which allows a different unusual taste release that in low viscose liquids, whose taste does not stay too long in the mouth. Despite its simple and almost trivial nature of the statement a number of non-trivial physical facts come along. The most obvious one is the effect on the taste itself. Since the viscosity is enhanced, the flow properties are reduced and the liquid stays longer over the tongue. Alone this has to effects. The taste receptors those for sour, sweet, bitter, salty, umami and fatty taste are for quite some time longer under the influence of the molecules which trigger them, the taste becomes enhanced. A more secondary effect is more important. During the time the food stays in the mouth, the temperature of the liquid changes. During this process more of the volatile compounds responsible for the

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retronasal effects may escape from the liquid and evaporate. Hence the sensory effects are also enhanced.

These naïve thoughts suggest a number of physical requirements for a simple theory for the structure property taste relationship: (a) the description of the rheological flow properties, via the viscosity and the physical behaviour of the fluid, (b) a more detailed description of possible mechanisms of the taste release. Whereas point (a) is a physically well-defined question, which just relates physical quantities describing the fluid mechanical behaviour of the liquid with typical sensory quantities for the taste experience.

Already such statements yield a simple provides naïve ideas in the basic connections between food properties, likewise the viscosity η and typical taste experience $\tau*$. For the introduction a naïve dimensional analysis will be sufficient. Somehow it is obvious that the taste becomes optimised, when molecular and sensory time scales match each other. In the simplest version, the viscosity is the proportionality constant between the shear stress σ and the shear rate (Ferry, 1980)

$$\sigma = \eta\dot{\gamma}.$$

Shear stress σ and shear rate $\dot{\gamma}$ are controlled by the tongue, and the flow properties by the individual geometry between tongue and palatine. However, this naïve equation defines a time scale τ via the shear rate, which relates roughly the viscosity to the shear stress by

$$\tau \propto \eta/\sigma.$$

For a given shear stress the timescale is therefore controlled by the viscosity only and depending on the detection time $\tau*$ determined by physiological properties, such as receptor distance, an optimal taste sensation can be defined when $\tau*$ and τ are equal or of a very similar order. Therefore it is desirable to adjust the viscosity in such a way that these two times are similar.

Point (b) is more delicate and requires more thoughts, since some of the taste compounds are water soluble whereas others are hydrophobic, but still bound in the fluid by special configurations of the water molecules forming cages around single hydrophobic volatile compounds. This suggests that a more detailed theory is needed, which describes the binding of the water in ionic or charged hydrocolloids.

Elementary theory of the viscosity enhancement by colloidal additives

The viscosity enhancement of fluids by adding uncharged colloidal particles goes already back to Einstein (1911) (de Gennes, 1976) and is described by a simple (first order) equation which can be derived by an effective medium theory

$$\eta = \eta_0(1 + 5/2\phi)mac_comma; \qquad (1)$$

here η_0 is the viscosity of the pure fluid, which becomes enhanced by the volume fraction ϕ of the added particles of a certain diameter (see Fig. 1). The geometric factor 5/2
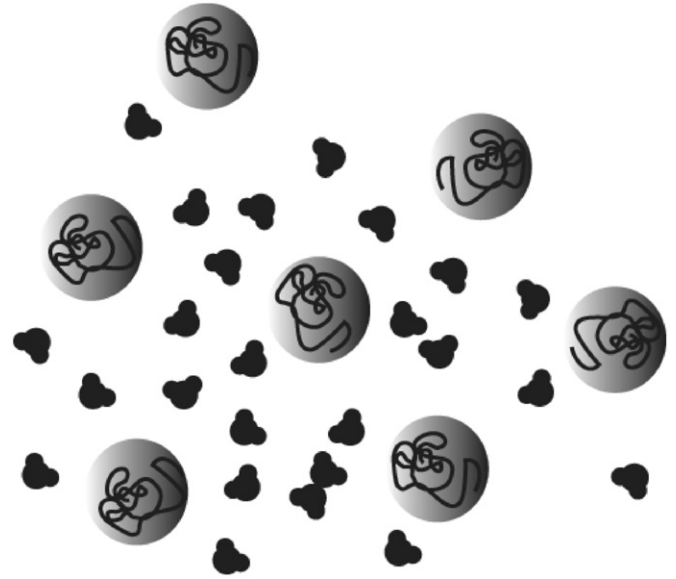

Fig. 1. The viscosity enhancement of a simple fluid by larger collodial particles. The colloidal additives slow don the motion by their presence. The resulting viscosity enhancement is to loewst order given by the volume fraction of the colloids. The spheres do not have to be spheres. They can be for example also flexible polymers with an effective (hydrodynamic) radius.

appears naturally since the particles are assumed to be spherical. The physical picture of this equation is quite simple. The smaller particles forming the pure fluid, e.g., water, move according to their thermodynamic timescale, which is basically determined, by the thermal energy k_{BT} and their interaction between them. The larger particles slow down this motion, since they are bigger and usually heavier. The net effect therefore is an enhancement of the viscosity.

This simple theory applies for any additives of basically spherical nature. It is also valid for neutral, on average isotropically shaped polymers whose radius of gyration is described by simple scaling relations of the form (de Gennes, 1976)

$$R \cong bN^v \qquad (2)$$

where b is the size of an elementary unit, called the monomer unit or repeat unit. N is the polymerisation degree, which corresponds to the total length of the chain molecule bN. The exponent v defines the shape of the polymers, i.e., for $v = 1$, the chains are described by rigid rods and $v = 1/2$ the chains are randomly coiled. Indeed the case of stretched chains will become important later, when we discuss in more detail the physical aspects of Xanthan, an important hydrocolloid in molecular gastronomy (Fig. 1).

Charged hydrocolloids: polyelectrolytes

Linear polymers, compared to highly branched systems have indeed the advantage, that they are much better soluble. Polar and charged polymers, so called polyelectrolytes are even better, since their shape and thus their effects on the